ION-ION AND ION-SOLVENT INTERACTIONS

by

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King Solomon said concerning Wisdom
and Knowledge ......

"A wise man will hear and will increase learning; and a man of understanding shall attain unto wise counsels: he will seek to understand a proverb, and the interpretation; the words of the wise, and their dark sayings. The fear of the Lord is the principal part of knowledge."

(Proverbs Ch. I, v.5-7. Margin)

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CHAPTER ONE

Charge Transfer Spectra

The term "charge transfer" in spectroscopy is generally used to describe an electronic transition, resulting in optical absorption, where there is partial gain or loss of a dipole as a result of transference of an electron from one energy level to another in either a molecule or some form of complex. The subject is reviewed by Rabinowitch[1] and Orgel[2].

Certain systems thought to absorb by a charge-transfer process will be summarised since they are of importance to the general discussion given later.

(a) Gaseous Alkali Metal Halides

On examining the absorption spectra of alkali halides in the gas phase Franck and co-workers[3] found that iodides and bromides have twin bands in the near ultraviolet and that chlorides give rise to a singlet band. They examined the spectral region from 200 to 400 mμ and established that the peak separations for iodides and bromides were almost equal to the energetic differences between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the free halogen atoms as obtained from atomic spectra. The theoretical splitting for chlorine from atomic spectra is only 880 cm^{-1} and hence it is not surprising that the chloride band is not resolved as a doublet. Franck[3] therefore interpreted the spectra as arising from a charge-transfer process and identified the first absorption band as

$$M^+X^- \xrightarrow{h\nu} MX \quad \text{(where X is in } {}^2P_{3/2} \text{ state)}$$

The energy of this process can be calculated.

$$\begin{tikzcd}
M^+X^- \arrow[r, "-\triangle a"] \arrow[d, "Nh\nu"] & M^+ & + & X^- \\
MX \arrow[r, "-\triangle s"] & M \arrow[u, "-Jm"] & & X \arrow[u, "Ex"]
\end{tikzcd}$$

$$Nh = Ex - Jm + \triangle s - \triangle a$$

$$= Ex - Jm + \triangle$$

$\triangle$ is thus the difference between the energy of formation of the normal ion-pair and that of excited alkali metal halide from normal atoms.

The energetic positions of the band maxima show that the ease of transference of an electron increases in the order $Cl < Br < I$. Surprisingly, changing the nature of the metal atom has no observable effect on the spectra of iodides. E.g. the iodides of sodium, rubidium and caesium all exhibit absorption bands with the maximum absorption of the first band occuring at 324 mμ. This has been interpreted in terms of two cancelling effects. Exchange of a light alkali metal M in MX for a heavier one causes a decrease in JM which would shift the band to higher energies but the simultaneous increase in radius of the cation would shift it to lower energies since the decrease in energy of formation of M^+X^- would decrease $\triangle$.

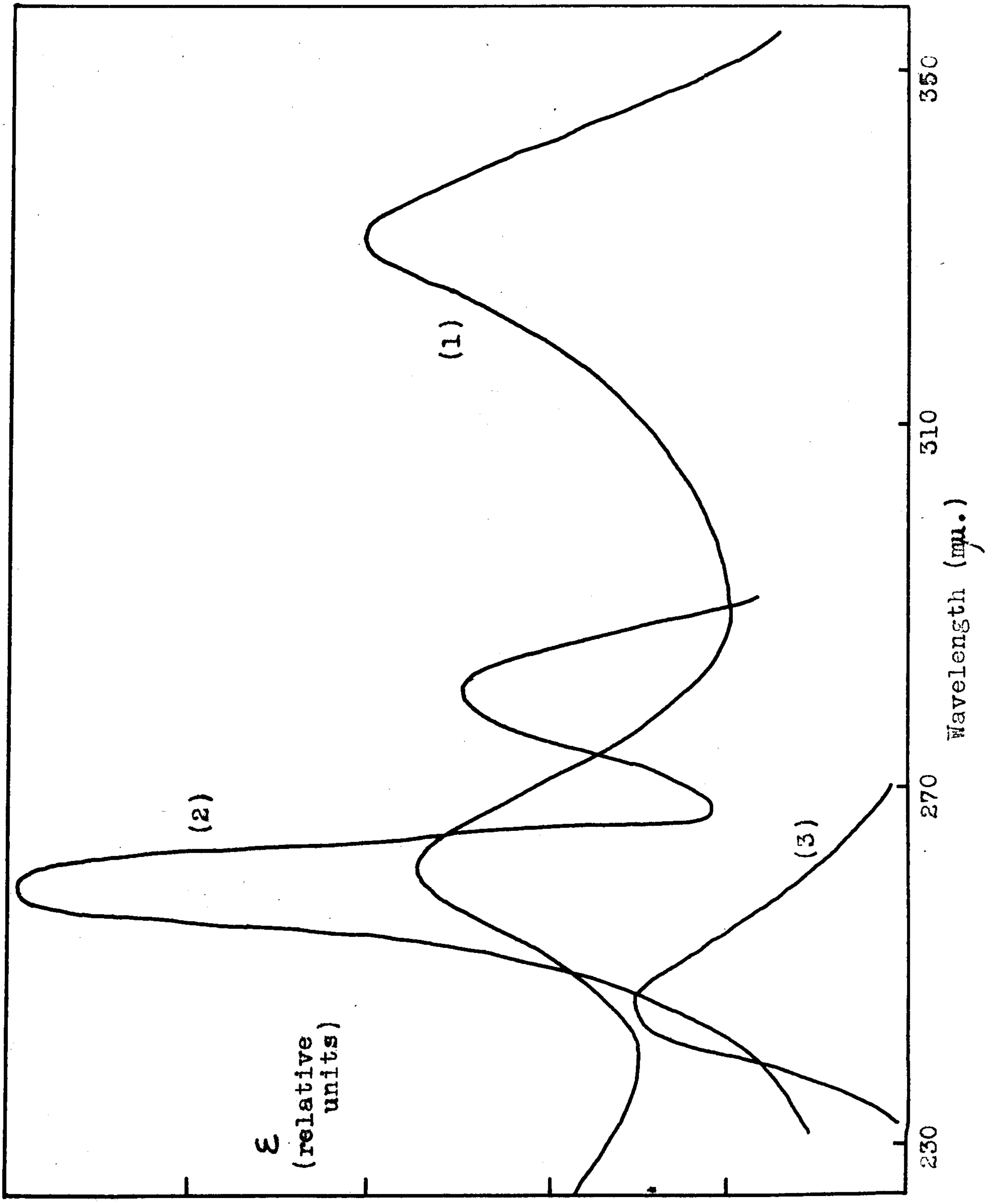


Fig.1.1. Absorption spectra of the sodium halides in the gas phase. (1),(2),(3), NaI,NaBr,NaCl, respectively.

(b) Crystalline Alkali Metal Halides.

The absorption spectra of many alkali halide crystals have been measured[4,5] and are found to consist of a series of bands with broad peaks and no resolvable fine structure. The extinction coefficients are greater than 10^4 and, as is in the case of the vapour, the low energy bands of bromides and iodides are doublets, the separation of which are again close to the $^2P_{3/2} \cdot {}^2P_{1/2}$ separation for the corresponding halogen atoms. The positions of the absorption maxima again demonstrate that iodide will release an electron more readily than bromide or chloride.

Mott[6] considers that bands found on the low wavelength edge of these spectra are caused by the movement of an electron into a conduction band and this is supported by the observation of photoconductance in this region[7]. The term "exciton band" is now used to describe all the absorption bands obtained in alkali halide crystals which are not attributable to the transference of an electron into a conduction band.

When the temperature is lowered the initial peak(s) sharpen and shift towards shorter wavelengths. Various workers have shown that there is a linear relationship between the energy of the peak maximum and temperature for NaI[8], KI[8,9], RbI[8], and CsI[10] (except close to 0°A).

(c) Gaseous Group II(b) Metal Halides.

Butkov[11,12] and also Wieland[13], have examined the spectra of the halides of many transition metals in the vapour phase. Bromides and iodides often give rise to doublets but frequently these doublets have peak separations which are not even approximately equal to that of the $^2P_{3/2}$, $^2P_{1/2}$ separation for the bromine and iodine atoms respectively. Katzin[14] has suggested, as a result of a survey of the literature, that the absorption spectra resulting from the movement of an electron to an excited orbital for all halides, whether in the gas phase or in solution, results in the formation of a halogen atom. The great scatter of his compilation does not, however, seem to bear out this contention. In the case of the dihalides of the transition metals zinc, cadmium, and mercury, it has long been established that in the vapour they are liner and also that in these molecules there is a considerable amount of covalent bonding.[15,16,17] It is just as feasible that the optical absorption bands are due to movement of charge from the halogen atoms towards the central metal atom, there thus being no change in the net dipole moment of the molecule.

The ease of the electronic transition for these molecules in the gas phase is of the order $Cl < Br < I$ and, in the case of the iodides, there is a small trend of the order $Zn < Cd < Hg$.

Absorption Spectra of Anions in Solution

(a) Halide Ions.

(i) In water

The absorption spectra exhibited by halide ions in aqueous solution all have the properties related above for crystals : the possibility of conduction bands, however, cannot be investigated since water, or indeed any other solvent, is not transparent to ultraviolet light in the 180 mμ region. The peak separation for the iodide maxima is again close to that for the $^2P_{3/2}$ and $^2P_{1/2}$ states of the iodine atom. The observed separation for bromide is only half that expected. This may well be due to the solution bands being somewhat broader than the crystal exciton bands and hence the two maxima are "pulled in" towards each other. This possibility will be considered in the Discussion. The absorption spectrum of chloride is again a singlet band. Theoretically it is possible to examine the chloride spectrum to see if it consists of two bands : practically, it would be very difficult.

The overlap of ground and excited states must be quite considerable since the bands again have molar extinction coefficients greater than 10^4.

The observed lack of effect upon the spectra of halide ions in solution on changing the nature of the positive ion is due to the ions being in a highly polar

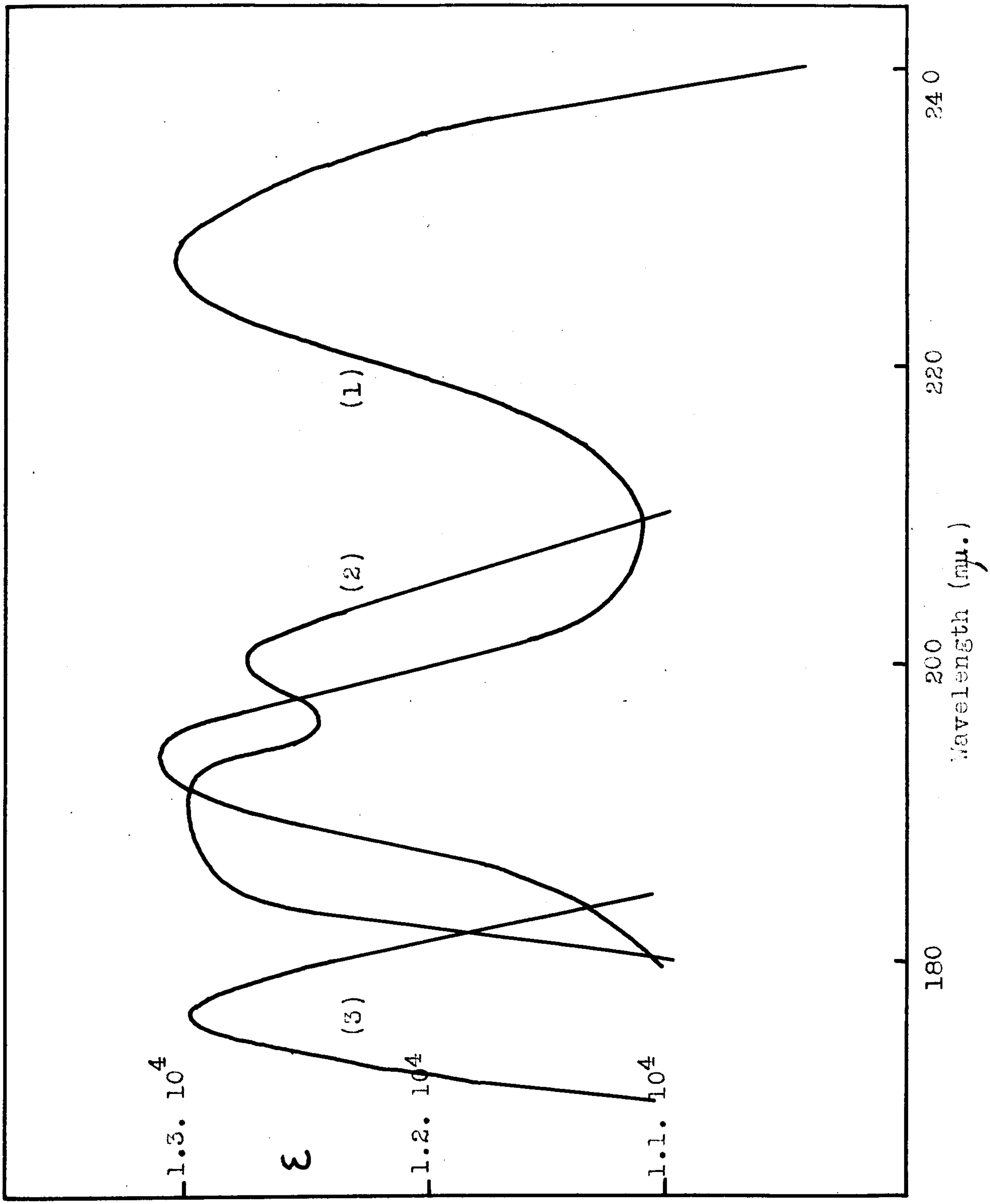


Fig.1.2. Absorption spectra of the halide ions in water. (1),(2),(3), I^-,Br^-,Cl^-, respectively.

medium and thus, being solvated, they can be considered as distinct entities at low concentrations.

(ii) Charge-Transfer to Solvent (C.T.T.S.)

Franck and Scheibe[13] interpreted these intense absorption bands as charge-transfer spectra and suggested that the act of light absorption by the hydrated anion ejected an electron from the anion to water and that the electron became a free "solution electron". They equated the energy of the maximum of the first absorption band of iodide to the following energy terms,

$$h\nu_{max} = E + H_{ion} + P - S - S',$$

where E is the ionisation potential of iodide, H_{ion} is its heat of hydration, P is the residual polarisation of the water dipoles, and S and S', are the heat of solution of the atom and the electron respectively.

The very low quantum yields of this reaction later led Franck and Haber[19] to suggest that the electron is transferred from the anion to a water molecule in the hydration sphere. This water molecule was assumed to dissociate immediately into OH^- and H thus

$$(X^-, H_2O) + h\nu \rightarrow X + H + OH^-$$

and

$$h\nu = E - E_{OH} + D_{H_2O} + \Delta$$

where D_{H_2O} is the energy of dissociation of water, E_{OH} is the electron affinity of the OH radical and Δ is the change in potential energy of the system caused by the electron transfer with unchanged positions of the atomic nuclei.

Farkas and Farkas[20] have pointed out that the dependence of the quantum yield of the decomposition of HI upon concentration, observed by Warburg and Rump[22], as well as that of pH observed by themselves[22], cannot be explained by this primary process and suggested that it consists of an electron transfer from the anion to a specific water molecule,

$$(X^-, H_2O) + h\nu \rightleftharpoons (X, H_2O^-).$$

If this transition is reversible it would account for the low quantum yields. However, a secondary reaction could take place, the electron further migrating as,

$$(X, H_2O^-) + H^+ \longrightarrow X + H_2O + H$$

thus accounting for the dependence upon $[H^+]$.

Farkas[20] derived the equation

$$h\nu = E + H_{ion} - E'_{H_2O}$$

E'_{H_2O} was described as the electron affinity of water. Calculations using this formula and the value of h at log = 0 gave roughly constant values of E'_{H_2O}, about 0.8 e.v. for Cl^-, Br^-, I^-, and OH^-. More recent data led Farkas and Klein[23] to revise this figure to 1.0 e.v. This treatment may be questioned on two grounds.

(i) The position of log ε = 0 is arbitrary and has no particular significance, especially since there is no explanation of the origin of the broadening of the absorption band in solution compared with the narrow band in the crystal.

(ii) E'_{H_2O} might well be expected to vary from one ion to another since it is not the true electron affinity of a water molecule but the resultant energy gained on conveying a free electron from infinity into liquid water, associating it with a water molecule, and creating around it the unstable system of orientated water dipoles identical to the system in existence prior to the removal of X^-.

A more recent approach has been made by Platzman and Franck[24] who postulated that the electron is not specifically attached to any one water molecule but that it moves in a 2s type orbital out in the bulk solvent, where the bulk dielectric constant can apply. The mean radius of this orbital is estimated as about 5.8Å

An alternative approach has been made by Smith and Symons[25]. The electron is considered to be confined within the solvent shell with its excited orbital described mainly by the hydrogen atoms of the surrounding orientated water dipoles. This type of approach, known as the "square well" technique, had been used previously to describe the F - centre bands found in alkali halide crystals. An F - centre is due to a crystal defect. If an anion is removed from its lattice site and an electron placed in the vacancy, then this will give rise to an

F - centre. The crude "square well" model is assumed to have walls of infinite height such that the electron will never be energetic enough to penetrate this energy barrier. The radius of the "square well", in solution, has been calculated by Smith and Symons[26] from the following equation.

$$E_{max} = I.P. + \frac{h^2}{8mr_o{}^2}$$

where E_{max} is energy of peak position of the first iodide absorption band, I.P. is the ionisation potential and r_o is the radius of the square well. For potassium iodide in water $r_o \triangleq 4\mathring{A}$.

The orbital described here is a 1*s* type orbital in contrast with the 2*s* type orbital of Platzman and Franck. The "square well" model and the "continuum" model of Platzman and Franck will be discussed in detail later.

(iii) Effect of change in environment.

It was recognised in the early 1930's by such workers as Scheibe,[27,28] Lederle,[29] and Fromherz,[30,31,32] that the position of the halide bands was dependent upon solvent and temperature. Jolly[33] measured the absorption band of iodide in liquid ammonia and obtained a peak at 254 mμ. Latimer and co-workers attempted to explain this result in terms of a photoionisatia model similar to that given by Pauling[34] for the iodide ion in water. The transition is supposed to lead to the formation of a solvated electron and an iodine atom surrounded by the solvent shell of the ion. Smith and Symons[25] have criticised Latimer's model on the grounds that, on the basis of the Franck-Condon principle, at the moment of light absorption the electron cannot move away from the iodide ion and also orientate ammonia molecules around itself at the same time.

The "square well" model also gives an explanation of the observed temperature and solvent effects. Since their r_o is linked with the orientated solvent molecules around the iodide cavity, an increase in temperature would increase the size of this cavity hence increasing r_o and, from their equation, decreasing E_{max}. This latter is found by experiment to occur[27]. E_{max} is found to vary linearly with temperature and hence a value for dE_{max}/dT is obtained. Since the various high dielectric solvents they used give, at a given temperature, different values for E_{max}, this has to be explained on their theory by a difference in cavity size, i.e. r_o varies from solvent to solvent. Further, since it was found that dE_{max}/dT increased as E_{max} decreased, this suggests that the fundamental difference between various solvents is not one of size but of the way in which the cavity expands with increase in temperature. Thus, at 0°K., the variation in E_{max} for different solvents would vanish since the effective radius of the cavity would be approximately equal to that of the ion plus the "radius"

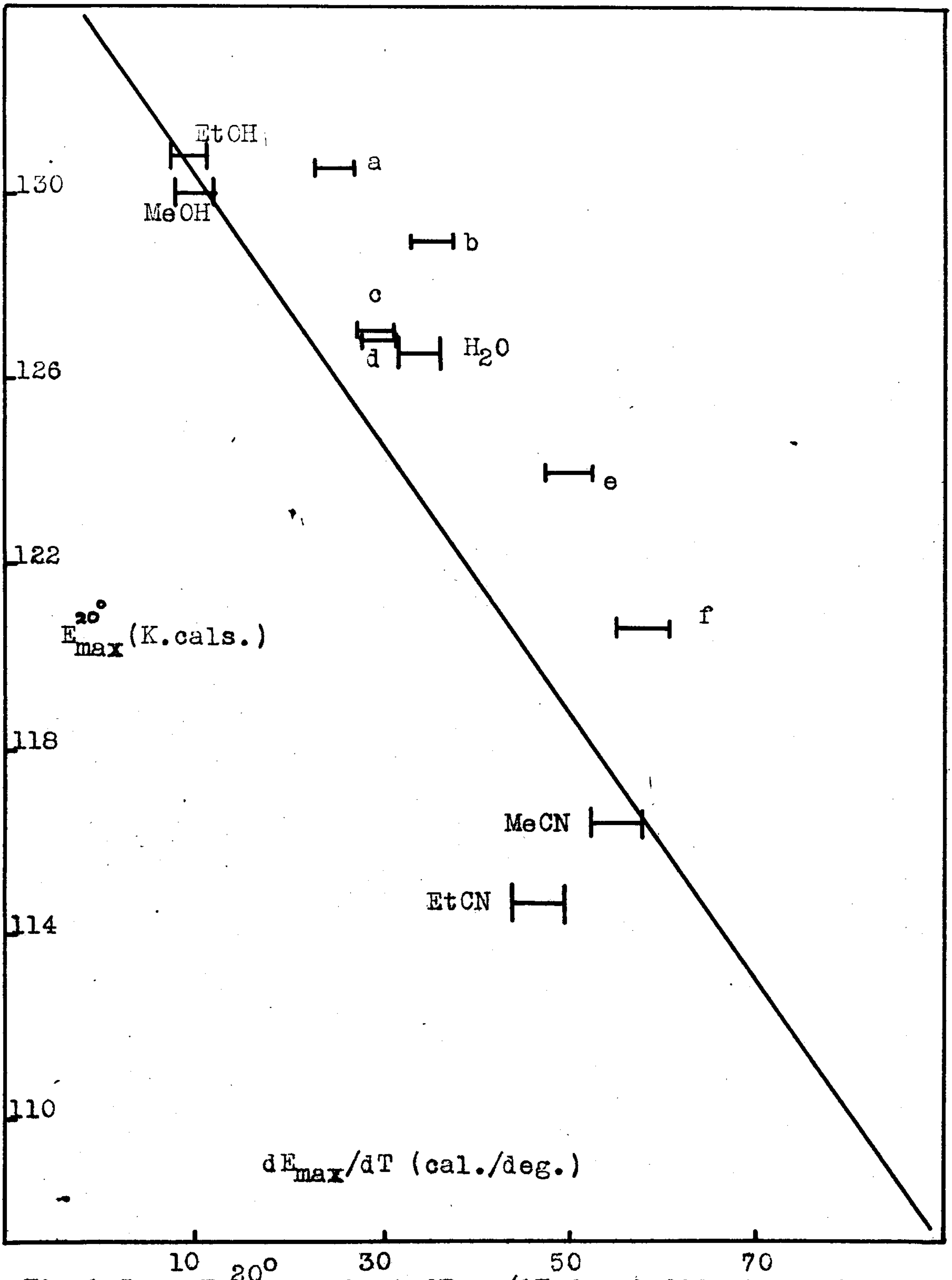


Fig.1.3. $E_{max}^{20^\circ}$ against dE_{max}/dT for iodide in various solvents. (a-f mixed solvents and salt solutions)

of the solvent.

Giving this a value $E_{max}(0)$ and letting $dE_{max}/dT = K$, then

$$E_{max} = KT + E_{max}(0)$$

for a given cavity.

For two solvents, A and B,

$$E_{max}(A) - E_{max}(B) = T(K_A - K_B)$$

Hence a plot of E_{max} against dE_{max}/dT for a given temperature should give a straight line of slope T. Fig. 1.3. shows the correlation Smith and Symons obtained.

More recently, however, Stein and Treinin[35] have modified the approach of Platzman and Franck and claim that the "continuum" model treatment is superior to that of Smith and Symons and can explain all the observed temperature and solvent effects. So far only their analysis of temperature effects has been published. The electron is still considered to move out into the bulk solvent but the effect of temperature on the band is attributed to changes in the ground state energy of the solvated ion.

They obtain the following equation from a thermodynamic cycle,

$$h\nu_{max} = E_x - L_x + (S_{ion} + E_p) - (S_e + E_e)$$

where E_x is the ionisation potential of the anion X^-, L_x is the heat of solvation of the atom, S_{ion} and S_e

are the electronic polarisation caused by the ion and electron respectively and E_p and E_e are the persistent (atomic and dipole) polarisation of the medium due to the ion and electron respectively. Introducing the numerical values for water at 25°C. they obtained, in eV,

$$h_{max} = E_x - L_x + 0.77\frac{e^2}{r_o} - 1.58.$$

They designated r_o as the "spectroscopically significant radius" of the ion in solution. (In future this term will always be written as r_o' to avoid confusion with the r_o of Smith and Symons) Laidler[36] has calculated the partial molar ionic volumes of various ions in solution at infinite dilution, $\overline{V}_i$, and has found, for ions of like charge, the following equation to hold,

$$\overline{V}_i = \frac{4}{3}\ (a r_c)^3 - BZ,$$

where r_c is the crystallographic radius, the factor $\alpha =$ 1.25, Z is the charge on the ion and B is a factor accounting for electrostriction, r_c is thus the apparent radius of the ion in solution. Improving the electrostriction term gave Hepler[37] a value of 1.23 for anions. Stein and Treinin evalulate r_o' for several anions and hence calculate values of α. The average of all their values is 1.27. Hence they claim that $h\nu_{max}$ may be calculated using only experimentally determinable quantities and that their treatment is valid. However, see Discussion.

(b) Simple Polyatomic Anions.

A large number of simple anions exhibit electronic bands of high intensity in the same region as the halide ions. Well known examples are OH^- and SH^-,[38] halogen oxyanions,[23, 39] nitrogen oxyanions,[39] and sulphur oxyanions.[40, 41, 42] Some of these are illustrated in figs. 1.4. and 1.5. Many of these absorption bands have been interpreted as occurring *via* a charge-transfer mechanism as for the halide ions. For example, the spectra of OH^-, XO_3^- and XO^-[23,39] (X = Cl, Br, I[6]), NO_3^-,[43,39] and $S_2O_3^{2-}$[2,44] have been interpreted in this way. However, unequivocal proof of this assignment on experimental grounds is often lacking. Smith and Symons[25] have tentatively suggested that observation of the effects of the constraints of temperature and change of solvent on these spectra may give the required evidence. Stein and Treinin[35] have examined the effect of temperature on the long wavelength edge of the bands of ClO_3^-, BrO_3^-, IO_3^- and OH^- at $\varepsilon = 5$ and claim that their results show that these bands are due to a C.T.T.S. mechanism. This may be challenged on two accounts.

(i) They do not allow for the broadening of the bands with increase in temperature, a factor that will be effectively zero at λ_{max} but will increase as ε decreases.

(ii) We have shown,[45] from examination of the spectrum of an iodate powder, that the solution band must contain

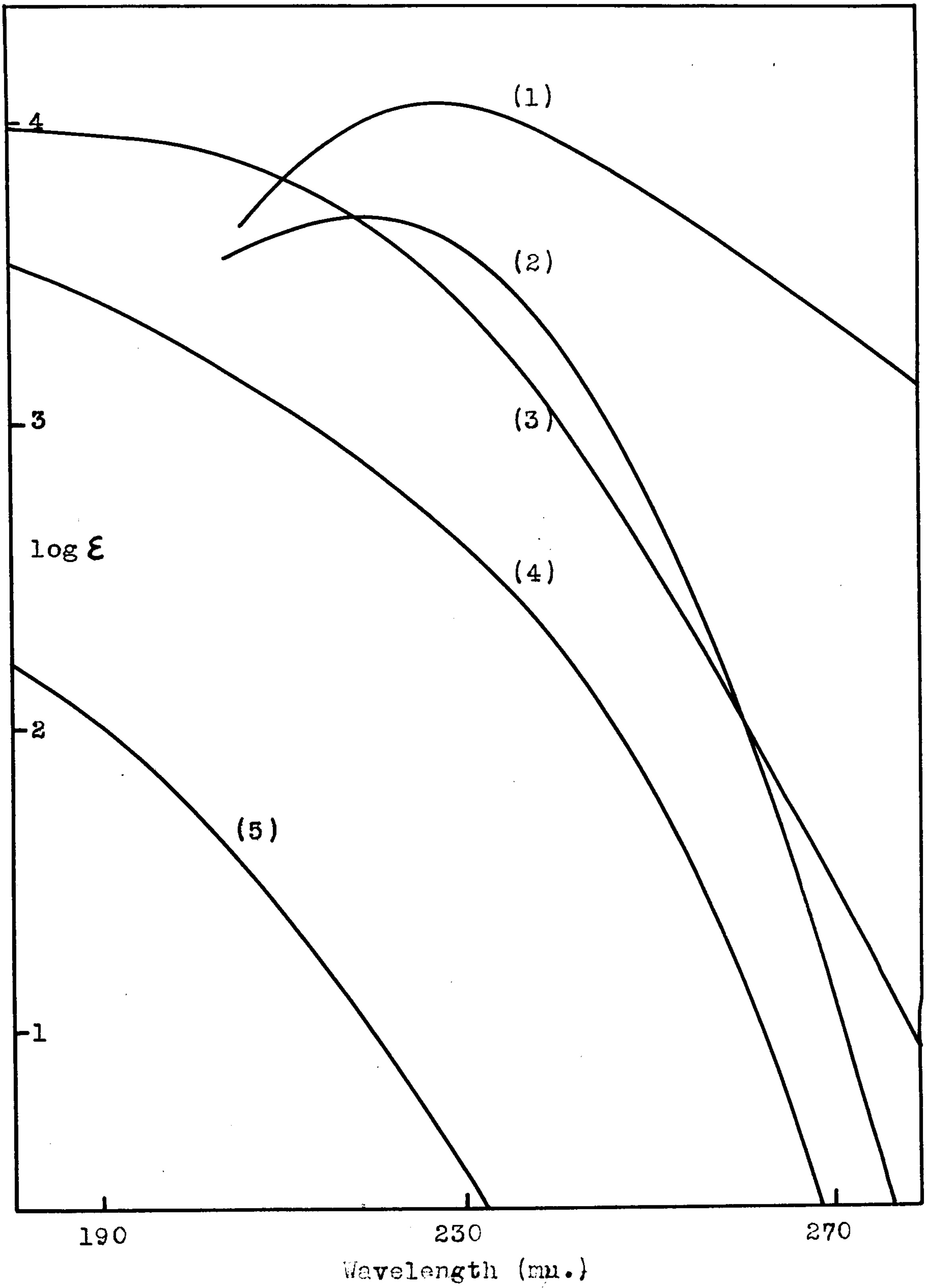


Fig.1.4. Spectra of (1) IO_4^- (2) $S_2O_3^{2-}$ (3) IO_3^- (4) BrO_3^- (5) ClO_3^-

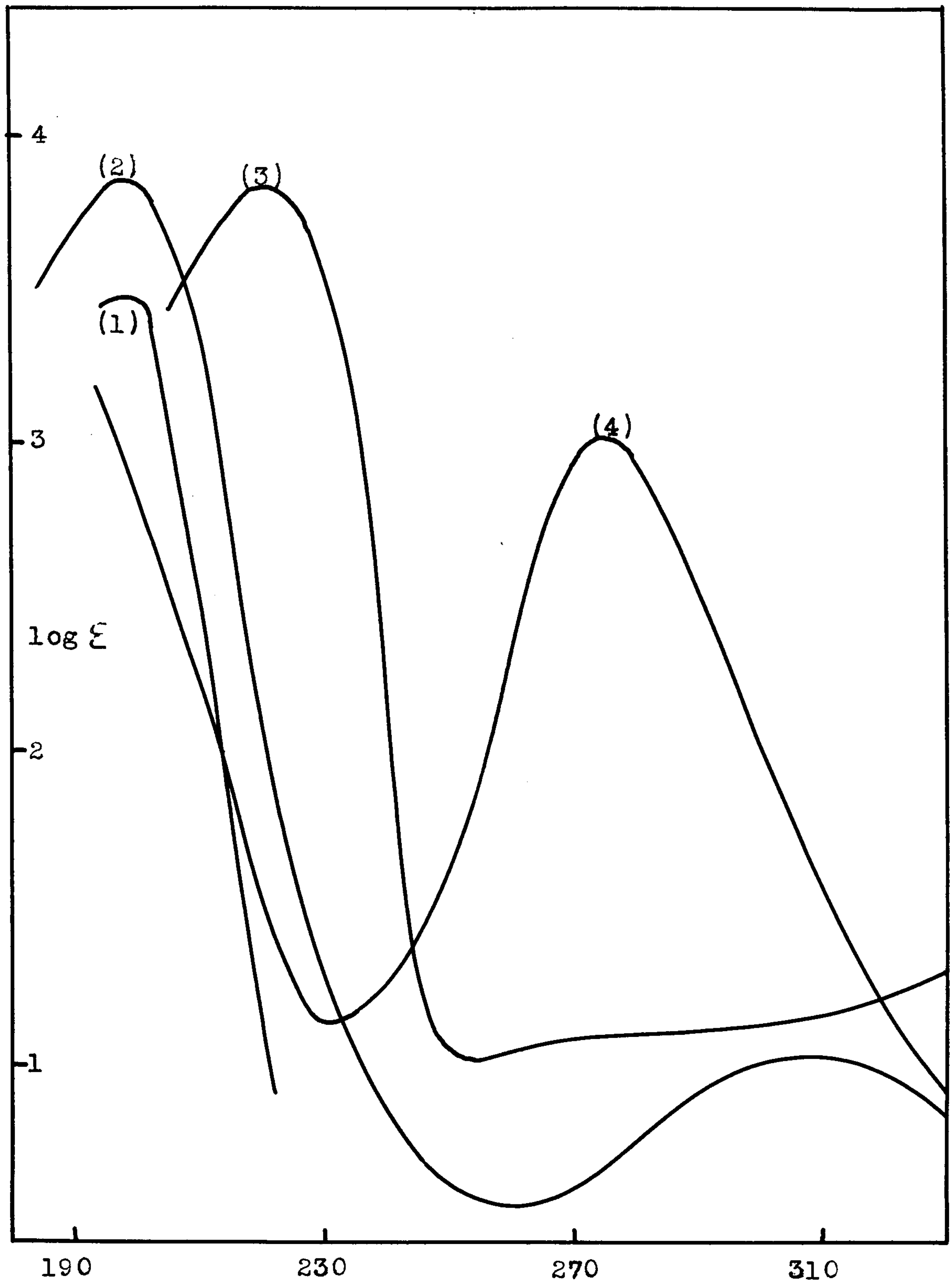


Fig.1.5. Spectra of (1) OH^- (2) NO_3^-
(3) NO_2^- (4) OCl^-

a hidden band, due to a forbidden transition, in the long wavelength edge of the spectrum, and, by analogy, chlorates and bromates probably also contain this hidden band. Thus they are observing, in the first three cases cited, the culminative effect of two bands.

Hence, for anions containing more than one atom, until the bands can be definitely assigned to C.T.T.S. spectra as against some form of intra-molecular charge transfer spectra, further investigation is needed.

Table 1.1.

λ_{max}(mµ) of zinc, cadmium, and mercury halides from the literature

		Salt	
Solution	ZnI_2	$CdBr_2$	CdI_2
Water	226.2,193 238.5[47] conc.soln	ca200	226.2,193 250[47] conc.soln
MeOH			239
EtOH	217,189;[27] 216[29]	211;[27] 213,192[29]	238,192;[27] 243,192[29]
n-PrOH			240-2[27]
MeCN			240-2[27]
Gas	238,224.5[12]		261,220[11]
	$HgCl_2$	$HgBr_2$	HgI_2
Water	200[32]	226;[32] ca.232[29]	265[32]
MeOH			267[48]
EtOH		234[32]	272;[32] 270, 213;[27] 274, 213;[29]

t-BuOH	218^{14}		275^{14}
$CHCl_3$			275^{14}
CCl_4			275^{14}
Gas		$227,210^{11}$	$266,224;^{13}$ $268,224^{11}$

(c) Complex Anions of Transition Metals.

(i) In general

Complex ions of the transition metals usually have at least one intense absorption band in the ultraviolet which has been interpreted as arising from an intramolecular transference of charge.[1,46] This study will be concerned only with those metals which have their inner d levels completely filled, in particular, the halides of zinc, cadmium and mercury. This avoids ambiguity which might come from the possibility of d - d transitions. Also, ions such as $PbCl_4^{--}$ and SnI_4^{--} have not been investigated since there is a lone pair of electrons on the central metal atom which affects the stereochemistry of the ions and the spectra in a complicated manner.

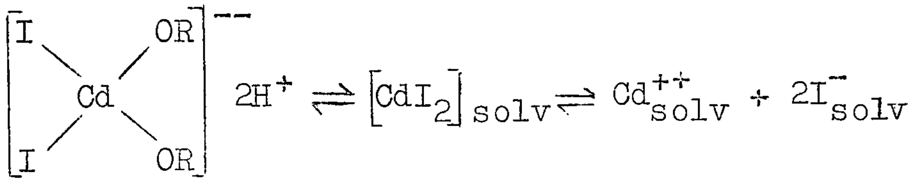
(ii) Halide Complexes of Cations with d^{10} configuration

Various workers[27,29,31,32,47,48] in the 1930's examined the spectra of the halides of zinc, cadmium, and mercury in solution. Table 1.1. summarises the results found. It may be seen that in many solvents the following dissociation does not always occur.

$$MX_2 \longrightarrow M^{++} + 2X^-$$

The absorbing species is then usually considered to be the undissociated dihalide. Delwaulle[49] has studied these halides in many solvents by Raman spectroscopy and her results are in accord with those of Woodward[50].

That such halides might have solvent molecules attached was suggested by Lederle[29], who postulated the following equilibria for cadmium iodide in alcoholic solution,



$$\left[\mathrm{CdI_2(OR)_2}\right]^{--} 2H^+ \rightleftharpoons [CdI_2]_{solv} \rightleftharpoons Cd^{++}_{solv} + 2I^-_{solv}$$

ROH being an alcohol. This suggestion does not appear to have received consideration : Delwaulle interprets her results in terms of linear molecules, in concentrated solutions. This problem will be further discussed later.

A fairly extensive spectral study of ion-ion interactions has been carried out by the early workers in this subject. The results obtained on addition of excess alkali halide to the dihalide solutions are summarised in Table 1.2. and fig. 1.6. These workers assumed that the spectral bands developed were due to the ion MX_4^{--}, and that MX_3^- could not be detected. Delwaulle[51] has stated that MX_3^- should exist; that it may have a solvent molecule co-ordinated and that she has not yet been able to obtain well resolved Raman spectra corresponding only to this complex.

Table 1.2.

λ_{max}(mμ) of zinc, cadmium and mercury halides in aqueous solution with excess common halide ion from the literature.

	Zinc
in aq. KI	238.5[47]
	Cadmium
in aq. KBr	217;[31] 215.5[47]
in aq. KI	256.6, 216;[47] 240[31]
	Mercury
in aq. KCl	228.5[32]
in aq. K,NaBr	249[32]
in EtoH + NaBr	251[32]
in aq.KI	323-4,267[32]
in EtoH + NaI	329,273[32]

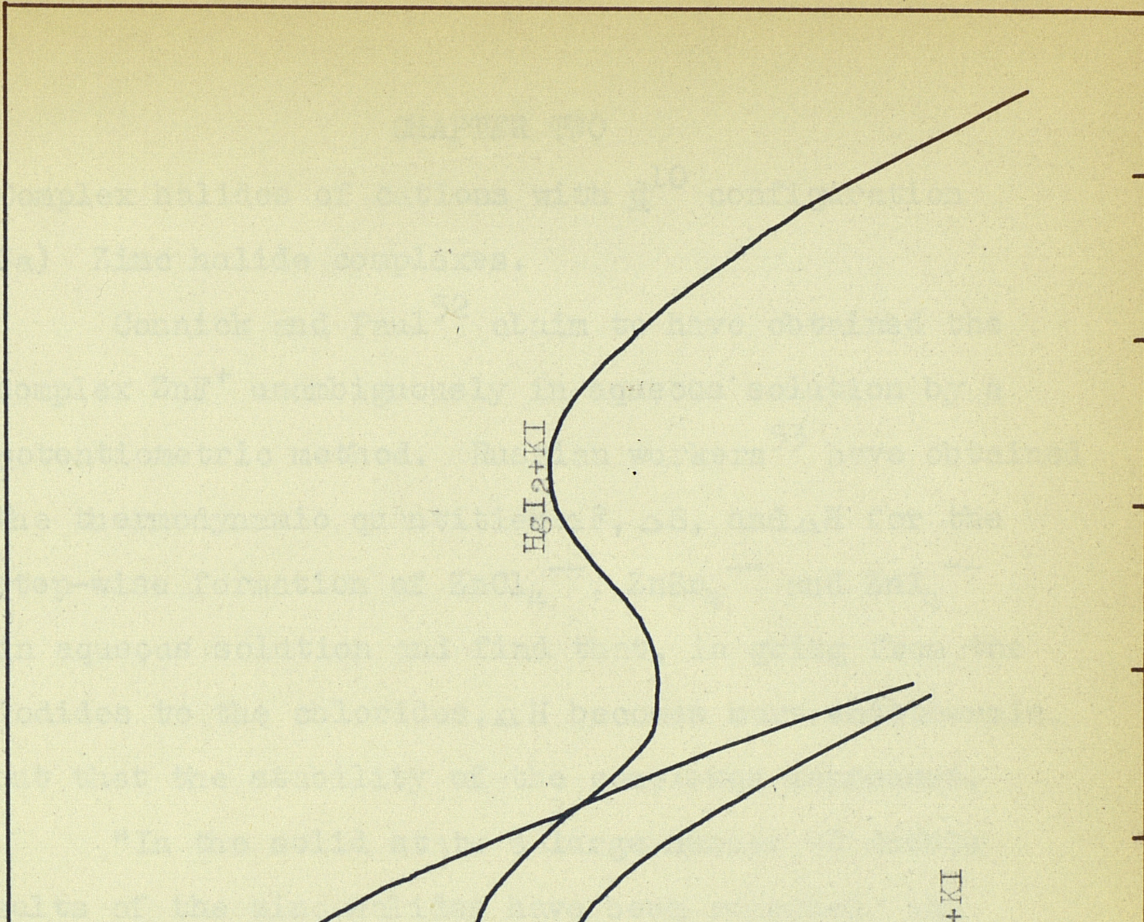


Fig.1.6. Representative spectra of Zn, Cd, and Hg iodide complexes in water.

CHAPTER TWO

Complex halides of cations with $\underline{d}^{10}$ configuration

(a) Zinc halide complexes.

Connick and Paul[52] claim to have obtained the complex ZnF^+ unambiguously in aqueous solution by a potentiometric method. Russian workers[53] have obtained the thermodynamic quantities ΔF, ΔS, and ΔH for the step-wise formation of $ZnCl_4^{--}$, $ZnBr_4^{--}$ and ZnI_4^{--} in aqueous solution and find that, in going from the iodides to the chlorides, ΔH becomes more endothermic, but that the stability of the complexes increases.

"In the solid state a large number of double salts of the zinc halides have been reported, and structural evidence indicates the considerable stability of the tectrahedral ion $ZnCl_4^{--}$ and a general preference for 4-coordinated structures." Bethel et al[54], after making the above statement, go on to suggest that their examination of the system $ZnCl_2$-HCl-CH_3CO_2H is interpretable by the following three equations.

$$ZnCl_2 + 2\ AcOH \rightleftharpoons H_2ZnCl_2\ (OAc)_2 \qquad (1)$$

$$2HCl + H_2ZnCl_2(OAc)_2 \rightleftharpoons H_2ZnCl_4 + 2AcOH \qquad (2)$$

$$H_2ZnCl_4 + H_2ZnCl_2(OAc)_2 \rightleftharpoons 2H_2ZnCl_3\ (OAc) \qquad (3)$$

Kolthoff and Coetzee[55] have found, by a polarographic study, that zinc ions form very stable complexes with halide ions in methyl cyanide and postulate a reversible reaction, similar to that in water, namely,

$$ZnCl_2 + aH_2O \rightleftharpoons Zn(H_2O)_b^{++} + 2Cl(H_2O)_c^-$$

and $$ZnCl_2 + dMeCN \rightleftharpoons Zn(MeCN)_e^{++} + 2Cl(MeCN)_f^-$$

Some doubt may be cast upon this latter equation since only 1:1 electrolytes appear to be ionised in methyl cyanide.

(b) Cadmium halide complexes.

Leden[56] has summarised the work on the chloride, bromide, and iodide complexes of cadmium up to 1940. The techniques used include cryoscopy, ebullioscopy, refractivity, conductivity, potentiometric titrations and E.M.F. measurements. The species which are claimed to be identified are CdX^+, CdX_2, CdX_3^-, CdX_4^{--} and CdX_5^{---}, where X = Cl, Br or I. The various association constants reported vary by factors of up to 10^4. The species CdX_5^{---} is only obtained from refractivity studies. Recently Ioffe[57] has challenged this method and has shown that the variation in refractive index obtained is within the experimental error of the method. Haldar[58] has claimed to have obtained CdI_5^{---} by a thermometric titration of CdI_2 and KI but Stromberg and Bykov,[59] by a polargraphic study and detailed calculations, have proved the non-existence of this complex.

Since 1940, other techniques which have been used to study the formation of CdX^+, CdX_2, CdX_3^- and CdX_4^{--}

include X-ray studies;[60] polarography;[59,61,62,63] anion-exchange resins;[64] examination of thermodynamic data;[65] the moving boundary technique;[66] solubility products;[67] E.M.F. measurements;[68] and an examination of molten salt systems. Within the last comprise such methods as examination of fusion diagrams;[69,70] voltaic cells in fused salts;[71] electrical conductivity, transport number, cryoscopy;[72,73] solubility;[74] and absorption spectroscopy.[75] Other evidence, of a more indirect nature, is that certain organic bases, in the presence of iodide ions form crystalline precipitates with cadmium iodide. For amino-alcohols and their esters[76] the general formula is quoted as $CdI_2 . 2(HI.B)$ where B is the organic base: for nitrogenous heterocyclic bases, mainly alkaloids, two complexes are found,[77] $AH\ CdI_3$ and $(AH)_2\ CdI_4$ where A is the alkaloid.

There are a few papers in the literature in which the complex ion $CdCl_6^{----}$ is stated to exist,[78] or that it might possibly exist.[72] Since the techniques used in these cases, e.g. conductivity and cryoscopy, cannot always categorically demonstrate which species is being examined, the $CdCl_6^{----}$ ion must at the moment be viewed with care.

The overall picture that emerges is that in solution the complex ions CdX^+, CdX_2, CdX_3^- and CdX_4^{--} are well established. In the cases where some workers cannot detect all these ions or, especially, where they cannot differentiate between, or identify, CdX_3^- and CdX_4^{--}, it may well be that the techniques used are not sensitive or specific enough rather than, as some would have it, that not all of the above four ions exist.

(c) Mercuric halide complexes.

A survey of the literature up to 1952 has been made by Ellendt and Cruse[79] in their paper on the formation constants of mercuric halide complexes. They show that there is a general acceptance of the complex anions HgX_3^- and HgX_4^{--} (where X = Cl,Br or I) for the alkali metal, ammonium, and tectra-alkylammonium cations. The techniques summarised are similar to those reported by Leden in his review of cadmium complexes. Ellendt and Cruse, by conductivity measurements in methyl cyanide and water, analyse their results in terms of three complex-forming reactions occuring according to the total reaction equation

$$4NR_4X + 4HgX_2 \rightleftharpoons NR_4Hg_2X_5 + NR_4HgX_3 + (NR_4)_2HgX_4$$

where NR_4 is the tectra-methyl or tectra-ethylammonium ion and X is a halogen. The considerable differences between the values for the equilibrium constants found in aqueous solution and in methyl cyanide as solvent are ascribed to the effect of solvation of the mercuric salts.

Sillen and co-workers[80] have undertaken an electrometric investigation of the equilibria between mercury and halogen ions and have tabulated equilibrium constants for reactions involving Hg^{++}, HgI^{+}, HgI_2, HgI_3^{-}, HgI_4^{--}, Hg_2^{++}, Hg_2I_2 and Hg.

Novel techniques, such as the use of radio-active tracers to determine the distribution of HgX_2 between water/benzene mixtures and the formation constants of HgI_3^{-} and HgI_4^{--} in the presence of iodide ions, have been used by Marcus[81] and also Moser and Voigt[82]: Scaife and Tyrrel[83] have determined the formation constants of $HgBr_3^{-}$ and $HgBr_4^{--}$ at different temperatures by a new method in which bromine and mercuric bromide compete for bromide ions. They claim that at low concentrations the absorption spectra of the solutions confirm their results.

The complex ion HgX_6^{----} does not appear to have been found; Scaife and Tyrrel have evidence for $HgBr_6^{--}$ and suggest that it is a weak donor-acceptor complex formed from $HgBr_4^{--}$ and bromine.

The picture is thus very much the same as for cadmium halide complexes, the main differences being twofold, (1) that mercury forms halide complexes more readily than cadmium and (2) that the tectrahedral ion HgX_4^{--} is more stable than CdX_4^{--} and appears to form in most cases almost to the exclusion of HgX_3^{-} (see Discussion). It is impossible to show the above two points unequivocally by a table containing formation constants as they vary so greatly : only an average of results from reliable methods and, say, the analysis of salts which can be easily isolated,[84] can demonstrate the validity of these statements.

CHAPTER THREE

Ionic Solvation

It has been shown in Chapter One that the nature of the excited state produced by a C.T.T.S. process is dependent primarily upon the nature of the solvent surrounding the ion : in the case of an intramolecular charge transfer process the role of the solvent was shown to be somewhat secondary.

The problem of ion-solvent interaction is as yet far from solved, despite the numerous experimental studies made. However, certain guiding principles have arisen from these studies and Ives,[85] and more recently Bell,[86] have summarised many of these. This section will therefore deal in detail only with those results pertinent to the qualitative discussion given later.

(a) The properties and structures of solvents.

Water is the only solvent whose properties and structure have been extensively investigated. However, there is a fairly wide opinion as to how the results obtained should be interpreted. Major contributions only to this subject will be mentioned here.

The high boiling point and freezing point suggest the presence of strong intermolecular forces in the liquid state. Density and X-ray measurements show that these forces produce an open structure in which the molecules are held apart, rather than packed together.

Bernal and Fowler[87] have suggested that in liquid water, as in ice, there is a quasi-crystalline structure built up in a tectrahedrally co-ordinated manner. Later X-ray scattering experiments[88] showed the "second shell peak" to be so diffuse as to suggest a very restricted continuity of order. Evidence from Raman spectra[89] suggests that any degree of crystallinity must be small since a given water molecule, at a given distance, appears to be bonded only to two or three neighbours. Pople's[90] re-examination of Bernal and Fowler's theory seems to have removed these discrepancies. The structure assumed for the water molecule has been developed from molecular orbital theory. The outer electrons in the water molecule are thought to occupy four tectrahedrally directed orbitals, two of which are associated with O-H bonds and the other two with lone pairs of electrons. Each molecule then tends to form four hydrogen bonds in tectrahedral directions, very much as proposed earlier.[91]

For solvents other than water very few unambiguous studies have been made concerning their structure especially since many of the mathematical expressions developed for water do not always appear to hold in non-polar solvents.

As the number of solvent molecules in the immediate vicinity of an ion must be governed by such factors as ion size, solvent size and packing, compressibility, and so on, it is to be expected that the problem of ion-solvent interaction will not be entirely or even primarily dependent upon properties of the bulk solvent.

(b) Studies of ion-solvent interaction.

The various methods which have been used to study the nature of ion-solvent interactions are summarised in Table 3.1.

Very few studies have been made with solvents other than water, hence, although it would possibly be better to treat the nature of ion-solvent interactions separately for each solvent, results that have been found will be mentioned under the appropriate subject headings.

Table 3.1. Methods to Study Ion-Solvent Interactions.

Thermodynamic	Dynamic	Physical
(i) Heats and Free Energies of Solution	(i) Ionic Mobilities	(i) Dielectric Constant
(ii) Entropy of Solution	(ii) Salting out of non-electrolytes	(ii) Nuclear Magnetic Resonance
(iii) Partial Molal Volumes	(iii) Stokes' Law	(iii) Infra-Red
		(iv) X-Ray scattering
		(v) Ultraviolet spectroscopy

(c) Thermodynamic Investigations

(i) Heats and Free Energies of Solvation.

According to electrostatic theory, when an electrically charged sphere of radius r is introduced into a continuous dielectric of value D, energy equal to $\frac{e^2}{2r}(1 - \frac{1}{D})$ is evolved, where e is the total charge on the sphere.[92] Many attempts have been made to apply this formula to the case of an ion dissolved in a solvent, despite our ignorance as to the value of r or of D.

Latimer[93] used this model in an attempt to obtain the individual heats of hydration of ions (H_{ion}) and found empirically that correlation could be obtained, taking D as ε_s for water, if the effective radius of the solvated ion was taken as $r_{ion} + 0.1\mathring{A}$ for anions and $r_{ion} + 0.85\mathring{A}$ for cations (where r_{ion} is the crystallographic ionic radius of Pauling). Verwey,[94] by a different empirical method, obtained almost identical values.

Bernal and Fowler,[87] Eley and Evans,[95] and Bockris,[96] on the other hand, assumed that if the Born equation holds, then ions of the same radius will have the same heat of hydration and obtained their individual values by an equal division of the heat of solution of KF.

These two approaches lead to very different values of the individual heats (H_{ion}), e.g., for I^-, Latimer finds 72 K. cals., but Eley and Evans find 45 K. cals. Each group of workers sought to obtain these values theoretically.

Eley and Evans, and Verwey, each made calculations of the ion-quadrupole interaction energies involved in the first layer of orientated water molecules and assumed that the Born equation holds at greater distances than the first hydration layer. Eley and Evans assumed four water molecules to be in this hydration layer, and Verwey six.

Verwey found (a) that 2/3 of the contribution to H_{ion} comes from the first layer, (b) that anions have larger values for H_{ion} because of the orientation in the first layer being anion....H – O – H, which allows these water molecules to participate in the water structure. However, both models are somewhat limited since there are alternative suggestions for the structure of the water molecules.[90] Further, the considerations of entropy, to be discussed later, suggest that any treatment in which it is assumed that the second and third layers of water molecules around an ion possess the same ordered structure as the bulk of the water must be a gross oversimplification.

Debye[97] and Webb[98] rejected this combination of continuum and ion-dipole approach and attempted to obtain values of H_{ion} by considering the dielectric saturation effects produced by the high field strengths of the ions. These treatments, however, took no account of the interactions between neighbouring water molecules and lead to values greater than are observed experimentally.

Passoth,[99] and recently Laidler,[100] have made fresh attempts to evaluate H_{ion} by this approach. According to Laidler, for ions of large radius and small charge, the Born equation values are not significantly far from the truth.

Eley[101] has made calculations of H_{ion} in methanol, employing an approach identical to that for the water model, i.e., by assuming (1) that the Born equation holds outside the first solvent layer and (2) that four methanol molecules are firmly oriented towards the ion in this layer.

(ii) Entropy of Solution.

Frank[102] and Frank and Evans[103] have interpreted solute-solvent interactions in terms of the free volume treatment of entropy.

The great loss in entropy to be expected when a gas molecule enters the confined state of solution in a liquid is normally offset by the loosening effect on the solvent due to intermolecular restraints. Thus, for simple non-polar gases in non-polar solvents, this entropy loss is in the range 10 - 15 cals. degree $^{-1}$ mole^{-1}. (Standard states one atmosphere for the gas and mole fraction unity in solution). For solution of such gases in water the entropy loss is much greater, being in the range 25 - 40 cal. degree^{-1} mole^{-1}. Further, while the entropy lost on solution in non-polar solvents is independent of temperature, the entropy lost in aqueous solutions decreases rapidly with increase in temperature.

To explain this, Frank and Evans suggested that each molecule on dissolution has an order producing effect upon the solvent: "the water builds a microscopic iceberg around the non-polar molecule".

In view of this, it might be expected that on dissolution of an ion in water, this order producing effect would be considerably enhanced, since besides the dispersion forces we are now imposing an electrostatic field from each ion of ca. 10^7 volts.cm.$^{-1}$ upon the solvent. In fact, the entropy loss upon solution of an ion is roughly the same as a non-polar solute of equal size:

e.g., KCl entropy loss per mole = 51.9 cal.degree.$^{-1}$

2 gm. atom of argon loss per mole = 60.4 " "

This effect appears despite the firmly bound layer of water molecules which must be present due to the electrostatic charge. The large increase in the

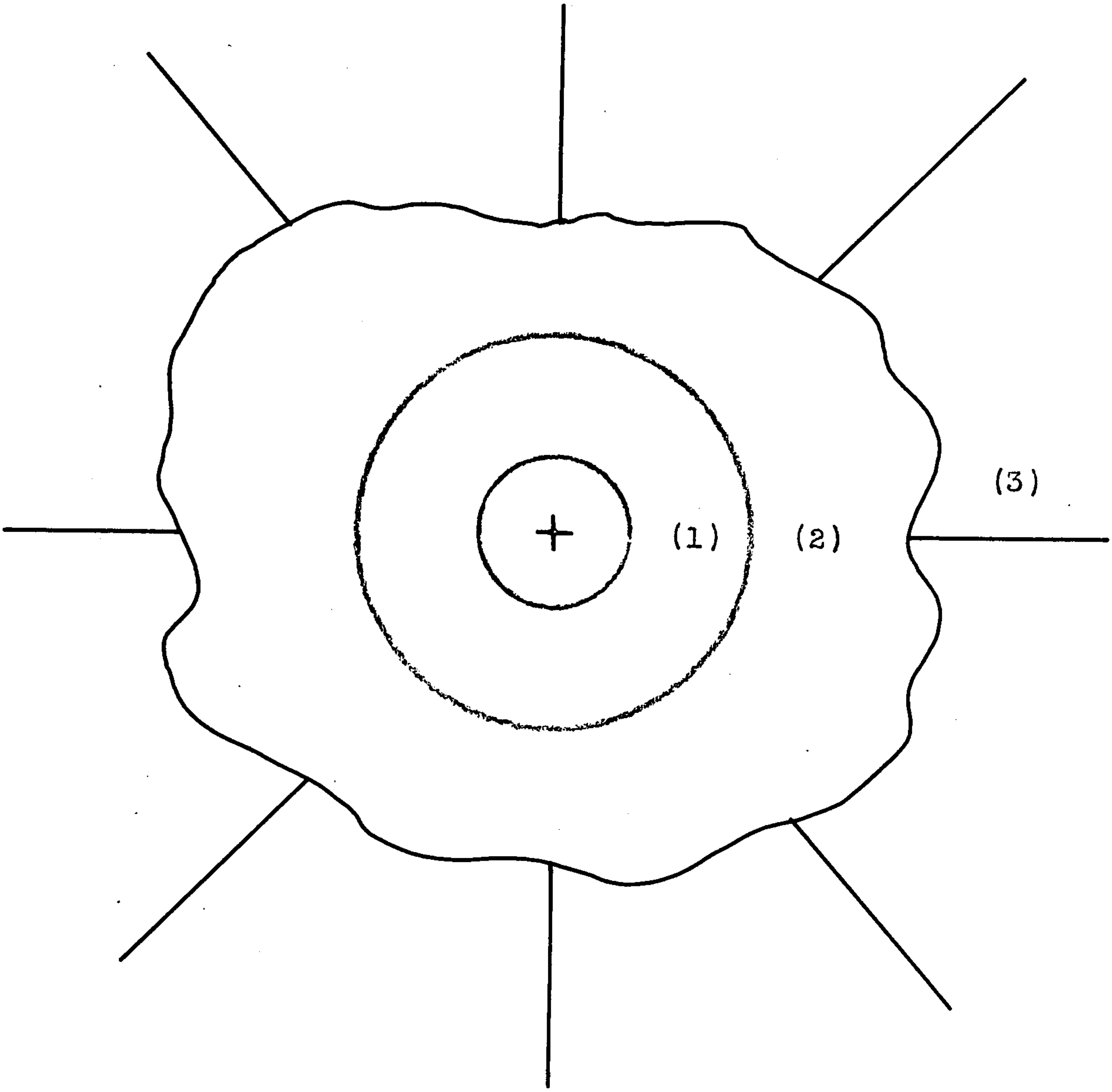


Fig.3.1. Simple model for the structure modifications produced by a small ion

(1) Region of immobilisation of water molecules
(2) Region of structure breaking
(3) Structurally "normal" water

Taken from Frank and Wen, Discuss. Faraday Soc., 1957, No. 24,134.

heat of solution shows that firm binding is present. The net effect of the ionic charge must, therefore, be to promote disorder in the water.

We must think accordingly of an ion in solution as having a firmly bound layer of water molecules, the number of these molecules being small because of steric interaction, followed by a region in which the water molecules are more disordered than in the bulk solvent. This area of disorder is roughly larger the larger the ion. (See fig.3.1.)

Only Li^+ and F^- among the univalent ions have a net order producing effect.

This behaviour is found only with water. The large entropy loss upon transferring an ion from water to methanol is due to the change from a net structure breaking influence to a completely order producing influence.

(iii) Partial Molal Volumes.

Laidler's treatment of ionic volumes[36] has been considered earlier (p.12.). The contraction of the solvent caused by the dissolution of ions is greater in methanol than in water, but this is probably due mainly to the greater compressibility of methanol.

(d) Dynamic Methods.

The results of these methods have been recently reviewed.[104] They have mainly been used to evaluate the number of water molecules which actually move with the ion, the so-called hydration number.

(i) Ionic Mobilities

It was pointed out as long ago as 1915[105] that the mobilities of the alkali cations (Li^+ = 38.7, Na^+ = 50.1, K^+ = 73.5, Rb^+ = 77.8) increase as the ionic radius increases, which is the opposite of what one would expect. This can be qualitatively accounted for by assuming that the hydration of the cation decreases along the series, but it is difficult to interpret this quantitatively in terms of a definite hydration number. This is because in order to obtain such a value the hydration number for one ion must be assumed.

(ii) Salting out of non-electrolytes.

The method of salting-out of non-electrolytes by added electrolytes always leads to an unequivocal order of hydration numbers for the monovalent cations but there is considerable disagreement over the actual values. This is again due to the fact that the hydration number for one ion must be assumed and that the basic assumption of the method, that the added non-electrolyte is inert, is invalid.[106] Consequently, the values obtained depend upon the particular non-electrolyte used.

(iii) Application of Stokes' Law.

Another method is based on the principle that if the size of the solvated ion could be determined, it should be possible to calculate the number of water molecules contained in it. By assuming that Stokes' Law is valid for the motion of ions, the radius of the hydrated ion can be obtained directly from values of the limiting equivalent conductivities.

For ions intrinsically large and of low surface charge (e.g., NEt_4^+) this assumption has been confirmed, as the product $\lambda^0 \eta^0$ (where λ^0 is the ionic mobility and η^0 the viscosity of water) is reasonably constant both over a range of temperatures and in a variety of solvents. Amis et al[107] have attempted to use this constancy of $\lambda^0 \eta^0$ to obtain information upon the solvation of halide ions in mixed solvents. By using a salt such as tectra-ethylammonium bromide any variation in the constancy of $\lambda^0 \eta^0$ can be ascribed to changes in the solvation of the halide ions. They concluded that bromide ions were highly solvated but appeared to lose some of their exterior solvent sheaths on raising the temperature. Strehlow and Koepp[108] have attempted to obtain a measure of preferential solvation of silver nitrate in water/methyl cyanide mixture by a method based on that of Hittorf.

Table 3.2. is a brief summary of the various hydration numbers that have been estimated by different methods.

Table 3.2. Estimated Hydration Numbers

Ion	Method			
	Mobilities	Diffusion	Activities	Compressibilities
Li^+	5	3	3	4
Na^+	4	1	2	5
K^+	4	1	1	5
Mg^{++}	12	-	5	12
Ca^{++}	10	-	4	10
La^{+++}	13	-	8	18[1]
F^-	-	-	2	4
Cl^-	4	0	1	2
Br^-	2	1	1	1
I^-	1	1	1	1

[1] Value for Pr^{+++}.

(e) Physical Methods.

These methods consist of comparing the properties of a given electrolytic solution with those of pure water under the same conditions. It might be expected that the presence of ions would cause a partial breakdown of the structure of water similar to the breakdown found on raising the temperature. That this is the case has been shown by X-ray scattering,[109] dielectric absorption,[110] infra-red absorption[111] and self-diffusion[112] studies.

(i) Dielectric constant measurements.

The static dielectric constant εs falls on the addition of electrolytes.[113] This decrease is linear up to a concentration of about 2N, above which the effect is less marked. A corresponding fall in the relaxation wavelength λs is observed. The depressions $\Delta\varepsilon s$ and $\Delta\lambda s$ are both influenced by temperature. e.g.

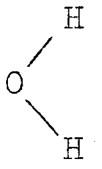
2.0 N NaCl solution

$\Delta\varepsilon_s$ increased by ca. 10% for 40°C rise

$\Delta\lambda_s$ decreased " " " " " "

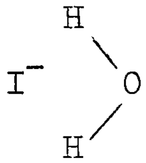
Since what is happening to the dipoles in these solutions is by no means clear-cut there can be no authorative explanation of these results. Hasted et al.[113] have put forward a qualitative interpretation in which it is assumed that the fall in dielectric constant is caused by a removal of water dipoles from the bulk of the solvent by the ion. These water dipoles surrounding the ion are supposed to be incapable of contributing to the measured $\Delta\varepsilon_s$ due to their firm orientation around the ion. It was assumed that this orientation was of the form:

cation



or anion H — O — H

the configuration being based on the work of Everett and Coulson.[114] The orientation around the anion still allows a certain degree of freedom so on this model $\Delta\varepsilon_s$ should be greater for cations than anions. Despite this assumption, and its use to obtain a division of the measured $\Delta\varepsilon_s$ of each salt, the value of $\Delta\varepsilon_s$ for the iodide ion is large. It was therefore tentatively proposed that the orientation around this anion might be:



They explained the % $\Delta\varepsilon_s$ increase with rise in temperature in terms of the increase of short range order around an ion as the water structure breaks down. A similar explanation is put forward for the decrease in relaxation wavelength with concentration and temperature.

These authors have calculated the dielectric constant of water as a function of distance from a point charge, using two different models, one proposed by Onsager and the other proposed by Kirkwood, and they find that for a cation the dielectric constant retains its bulk value up to 4Å from the ion and then falls sharply to a value of *ca.* 4 at 2Å. For an anion they find no such dielectric saturation and contend that the first shell of molecules around an anion have greater rotational freedom than the shell around a cation.

Robinson and Stokes[115] suggest that it seems equally likely that the difference in dielectric saturation round anions and cations is merely a matter of ionic size.

Similar experiments have been made using methanol as solvent,[116] an even more pronounced lowering of the dielectric constant being obtained, but no explanation has been made for this.

(ii) Nuclear Magnetic Resonance Studies

Nuclear magnetic resonance frequencies depend upon the electonic environment of the nucleus due to the magnetic shielding by the electron cloud. The electronic distribution around a given nucleus can be changed by external forces. The molecule is thus perturbed with the result that the resonance frequency is shifted. Electrolytic solutions can be studies by observing the shift of the resonance frequency of a certain cation or anion, e.g., ^{133}Cs or ^{19}F[117], or of the water protons,[118] with changing conditions.

The way ions shift the resonance frequencies of protons in water has been interpreted as the resultant of two effects, (a) breakdown of the H-bonded network of the water molecules causing increased shielding of the proton nucleus and (b) polarisations of the medium, such as orientation around an ion, causing a decrease in shielding. In terms of this very simple analysis experimental results show that:

(i) For uni-univalent salts (a) is predominent.

(ii) Concentration dependence of shift for these salts is linear up to about 4M, i.e., the influence of the ions cannot extend very far beyond the first solvent shell.

(iii) Negative ions always have the largest effect upon the proton resonance.

More recent observations upon the chemical shifts of the fluorine nuclear resonance for fluoride ion in a variety of environments have shown that the shift varies linearly with % of mole fraction of added organic solvent and is dependent upon the nature and concentration of added cations and anions. However, the caesium nuclear resonance frequency was found to be insensitive to solvent variations, and it was concluded that the large linear chemical shifts observed on addition of other electrolytes were almost completely due to the anions.

However, until the theory of nuclear magnetic resonance is more thoroughly understood, speculation must play a fair part in interpreting the observed results.

(iii) Infra-Red Spectra

Waldron[119] has recently studied the influence of metal halide salts upon the infra-red spectrum of water

Both the O-H stretching and bending frequencies are shifted strongly by anions but are unaffected by cations. The magnitudes of these shifts have been correlated with the heats of hydration of the ions. These results are interpreted in terms of the water molecule being orientated with its hydrogen atoms pointing towards the anion.

(iv) X-ray Studies

Brady and Krause[120] have recently measured the diffraction patterns of concentrated potassium hydroxide and potassium chloride solutions. They suggest that in potassium hydroxide solutions K^+, being approximately the size of a water molecule, enters substitutionally into the pseudostructure of water without apparently modifying it: they also estimate that it has a hydation number of 4. The chloride ion is interpreted as disrupting the water structure; a later paper by Brady[121] quotes a hydration number of 8 - 9 for it. The hydroxide ion is given a hydration number of 6.

(v) Ultraviolet Spectroscopy.

A large number of ions and reactions between ions and/or molecules have been investigated by ultraviolet spectroscopy. A fair proportion of the papers published include a tentative explanation of the sort of solvation that is thought to occur in the systems studied. Amongst the publications which appear to make a definite contribution to ionic solvation are those of Platzman and Franck[24] (and the extension of their "continuum" model by Stein and Treinin[35]) and those of Smith and Symons.[25,26] These papers have been discussed in Chapter One from the viewpoint of the migration of the electron in C.T.T.S. spectra. The implications of the "continuum" and "square well" models to ionic solvation can now be mentioned.

Both models assume that when an anion, the iodide ion being the one discussed in particular, absorbs a photon of energy h such that one of the six outer electrons moves to an excited orbital, that orbital is centro-symmetric around the iodine atom which, it is postulated, is then formed. Their basic difference is that whereas the "continuum" model requires the solvent to have the value of the bulk dielectric constant right up to the anion (even though the anion is supposed to have an order producing effect upon the surrounding solvent molecules), the "square well" model requires the adjacent water molecules to be orientated with their protons pointing towards the anion and the dielectric constant of the medium does not come into the calculations made.

In view of the earlier discussion, it would seem that the "square well" model has more to recommend it in that the maximum penetration of the excited electron is assumed to be ca $4\overset{\circ}{A}$ which thus indicates that it would spend much of its time on the orientated water protons, which would have a considerable $\delta +$ charge. In the "continuum" model, the excited electron is assumed to be bonded solely by an effective positive charge at the centre of the cavity, and no account is taken of the presence of orientated solvent molecules. The mean radius $\bar{R}_e$ of this orbital is calculated to be $5.8\overset{\circ}{A}$. This implies that the electron spends a not inconsiderable proportion of its life-time on the lone pair electrons of the orientated water molecules, a position of relatively high electron density. This is not a very acceptable physical concept. Although Stein and Treinin's modification of Platzman and Franck's model gives them a "spectroscopically significant radius" r_o^1, only about 1.27 the radius of the anion (which is then related to partial ionic molar volumes), the problem is still not overcome.

The extension of the "square well" model to other solvents leads Smith and Symons[26] to suggest that the orientation of alcohols around the anion would be such that the proton attached to the oxygen atom of the alcohol would be in the periphery of the cavity around the anion, and that the three protons in ammonia and methyl cyanide would all point towards the anion. They anticipate this on the grounds that they would expect lone pair orbitals, non-polar groups, and CN groups to orientate themselves away from the anion. They suggested that the slight deviations found with ethyl cyanide might arise because of steric interactions between bulky methyl groups. Thus as the number of "points of attachment" between the anion and solvent molecule increases, the radius of the cavity would be expected to increase. Their results, as interpreted on the simple "square well" model, are in accord with this view. (see Fig. 1.3.)

CHAPTER FOUR

Ionic Association.

When ions of opposite sign are close together, as undoubtedly will be the case in certain situations, there will be some association between the ions. The energy of their mutual electrical attraction may be considerably greater than their thermal energy and any ion-solvent interactions, so that they form a virtually new entity in the solution, of sufficient stability to persist through a number of collisions with solvent molecules. In the case of a symmetrical electrolyte, such ion-pairs will have no net charge, though they should have a large dipole moment. They will therefore make no contribution to the electrical conductivity, while their thermodynamic effects will be those of removing a certain number of ions from the solution and replacing them by half the number of dipolar "molecules". With unsymmetrical electrolytes the position will be more complicated, since the simplest and most probable type of ionic association, that of involving only two particles, will result in the appearance of a new ionic species of a charge type not previously present; this would contribute to the conductivity, though less than would its constituent ions in a free state. In such cases further association to form neutral species may also be reasonably expected.

(a) Definitions.

We are immediately confronted with the question: when can two neighbouring ions be termed an ion-pair? We shall proceed by describing briefly the various concepts of ionic association.

(i) As given by Bjerrum.

Bjerrum[122] evolved the idea that the average effects of ion-pair formation may be calculated on the basis that all oppositely charged ions within a certain distance of one another are "associated" into ion-pairs, though in reality a momentarily fast-moving ion might come within this distance of another and pass by without forming a pair. He proposed that this critical distance, usually denoted by , should be chosen as:

$$= \frac{|z_1 z_2| e^2}{2\varepsilon kT}$$

This is seen to be the distance at which the mutual electrical potential energy of the two ions:

$$|Z_1 Z_2| e^2/\varepsilon q$$

is equal to 2kT. It is possible to show the reason for this particular choice from a consideration of the Poisson-Boltzmann equation. If a graph is plotted for the number of ions in a shell 0.1Å thick at a distance <u>r</u> from a central ion (the calculation being made for the ions in the shell being of opposite charge to the ionic charge of the central ion) against the number of ions present in an aqueous solution of a 1 : 1 electrolyte at 25°, a curve is obtained with a minimum 3.57Å from the central ion. Thus for ions of opposite charge, if the distance of closest approach is $3.57|z_1 z_2|$Å or more, it is assumed that there will be no ion-pairs. If the ions can approach closer than this, Bjerrum would regard those within the sphere of radius $3.57|z_1 z_2|$Å as "undissociated" ion-pairs. It is to the ions outside that the Debye-Huckel theory is to be applied.

Since Bjerrum's first publication on this subject innumerable papers have appeared, many of them showing remarkable agreement with the theory, others criticising or seeking to extend or modify it. The basic theory is still in current use and the subject of much discussion. (For example, Guggenheim.[123]).

(ii) As given by Fuoss.

Recently Fuoss[124] has claimed to have shown that the theory of the conductance of symmetrical electrolytes is now substantially complete. In the past he has mathematically analysed various models and has now reached the conclusion that the following precepts should be observed:

(1) That the ions should be treated as hard spheres occupying space.

(2) Only when two ions of opposite charge are in

contact are they to be treated as ion-pairs.

(3) The length of time that the two ions remain in contact is entirely dependent upon their electrostatic and kinetic properties.

(4) During the time of contact neither ion can contribute to transport of charge, and neither ion is to be counted as a member of the atmosphere of other ions because the pair present only a dipole field to distant ions.

(5) All ions not in contact are counted as free ions.

(6) A continuum represents the solvent.

The recent book published on this theory by Fuoss and Accascina[125] has been criticised by Buckingham[126] who feels, in particular, that the authors have insufficiently emphasized the complexity of interacting ions and solvent molecules, in their approach.

(iii) As given by Winstein.

Winstein and co-workers[127] have recently studied solvolytic reactions of alkyl halides in the presence of added salts and have explained their results in terms of the following scheme.

$$RX \rightleftharpoons \overset{\delta+}{R}\text{ --- }\overset{\delta-}{X} \rightleftharpoons R^+X^- \rightleftharpoons R+X^- \rightleftharpoons R^+ + X^-$$

Alkyl Halide	transition state	"Intimate ion-pair"	solvent separated ion-pair	dissociated ions

From their results they calculated *Y* - values which are a measure of the "ion-solvating power of solvents."

Kosower[128], by an entirely different approach, has also obtained a measure of ion-solvating power, which he calls *Z*-values. He has shown that there is a linear relationship between Winstein's *Y* - values and his *Z* - values. The *Z* - values are obtained by measuring the optical absorption band that appears in concentrated solutions of 1-ethyl-4-carbomethoxypyridinium iodide in various solvents, the energy of the transition being the numerical *Z* - value. The transition must arise from the transference of charge from an iodide ion to a pyridinium ring with which it is in contact, thus forming a neutral molecule. By the Franck-Condon Principle this molecule can have no effect upon the surrounding orientated solvent molecules and hence the energy of the transition is a measure of the ability of the solvent to solvate the ion-pair.

(b) Spectrophotometric Investigations.

In principle, it should be possible, by a spectrophotometric study, to decide when an ion receives or donates electronic charge to one specific adjacent ion of opposite polarity by the appearance of a new band. There are, however, differences of opinion as to the worth of spectrophotometric methods in the study of ion-pair formation. These differences arise because, at times, insufficient attention is given to the nature of the electronic transitions involved. It has often been concluded that the spectra of ion-pairs are identical to those of the free ions.[129,130] This may well be true for certain intra-molecular transitions of either cations or anions,[131] but as a generalisation it is quite false.

On the other extreme, a change in optical density at an arbitrary wavelength with change in the ionic strength of a solution is sometimes attributed to ion-pair formation, even though no attempt has been made to decide whether this change is caused by the growth and decay of bands, or simply the shift or broadening of a band.[132,133] Since the location of absorption bands may be very sensitive to environmental changes[26,134] there can be little justification in such an arbitrary assignment. A further objection to this approach is that the electrolytes used are often known to form covalent complexes quite readily, and therefore the changes studied could equally well be due to complex formation.

CHAPTER FIVE

Scope of Present Work.

The scope of the present work has been, in the main, threefold:

(1) To test the crude "square well model" approach of Smith and Symons[25,26] under as many extreme conditions as possible.

(2) To attempt to find conditions such that solvated ions and ion-pairs could be identified together, spectroscopically, in solution by having one band rise as another band falls as the concentration of free ions and ion-pairs varies.

(3) To examine solutions of zinc, cadmium, and mercury halides alone, and in the presence of added electrolytes with a common ion, in an attempt to see whether or not all the complexes postulated in the literature can be identified by spectroscopy and possibly to investigate any ion-solvent interaction. An initial survey of the literature revealed that a considerable amount of the data required had already been obtained. However, their significance to the present problem appears to have been overlooked. These results will therefore be presented together with the experimental results obtained during this study.

CHAPTER SIX

Experimental Procedure.

(a) Spectrophotometric Measurements.

All measurements were made on a Unicam S.P.500 spectrophotometer, which had been specially selected by the makers because of its outstanding response in the 190-200 mμ region. The normal photocell, however, was replaced by a photomultiplier, which was the S.Z.G.500 Model manufactured by Prazisimsmessgeräte RSV, of Icking, Oberbayern, Germany, which incorporated a 1. P.28 photomultiplier tube. This resulted in a much greater sensitivity of the instrument than would normally be expected in the 200 mμ region. Also, slit-widths of around 0.1.mm. could be used and all results obtained in this region were reproducible to a high degree of accuracy.

The normal procedures for accuracy were observed:

(i) Care was taken to ensure that the hydrogen arc lamps were always in the optimum position and that they were replaced when their intensity in the 200 mμ region began to diminish.

(ii) Calibration of the wavelength drum was periodically checked by

(a) Using the visible lines of the lamp and (b) comparing the instrumental results for the peak position of potassium iodide, periodate and permanganate with the authentic values.

(iii) The transmission calibration was accepted as being correct in the region of optical density between 0.1 and 1.0 since Beer's law was obeyed in this range by solutions of potassium chromate in water.

1.0 cm., 0.5 cm. and 0.1 cm. fused silica cells were cleaned by washing thoroughly with water, rinsing in HF/teepol/HNO_3 mixture, rewashing with water, rinsing in pure ethanol and then steaming with purified water. For anhydrous solvents the cells were dried by rinsing in pure methanol and then warmed with a stream of hot air from a hair drier while passing a current of dry nitrogen through the cell. When a cell path length of 0.01 cm. was required 0.09 cm. quartz spacers were inserted into the 0.1 cm. cells.

The optical density of the solutions was kept in the range 0.2 to 0.6 and, if the blank had an appreciable absorption, the concentration of the species in solution and the cell path length were chosen so that the combined optical density of solvent and species was less than unity. However, the photomultiplier still appeared to be quite sensitive up to regions of total optical density 1.5 but any peaks observed in this region were not relied upon, and only the trend of the spectral curve was noted.

The following procedures were used:

(i) Solvent was placed in cells I and II (I and II being matched cells) and the optical density measured. If the optical density was greater than ±0.01 the cells were recleaned until this was not the case. The solution was then placed in cell II and the spectrum measured. Solution was then placed in cell I and the blank in cell II and the spectrum again measured. The mean of the measured optical densities was taken as the true optical density.

(ii) Solvent was placed in the cell and the spectrum of solvent and cell measured against air; the solvent was then replaced by solution and the spectrum again measured. The difference between the two values (at the same wavelength) was taken as the true optical density.

Readings were always made at sufficiently close intervals such that an accurate spectral curve could be drawn. The readings obtained were plotted against either wavelength or frequency ($cm.^{-1}$) and the position of maximum absorption was found from the graph by the method of rectilinear diameters. (see Fig. 7.1.)

(b) Temperature Control.

The Unicam S.P.570 Constant Temperature cell Housing was used for temperature studies. For low temperature work a new cell compartment was constructed, from the lid of which was suspended the cell thermostat.[135] This thermostat, which consisted of a perspex box into which the cells were clamped, was only for 1.0 cm. cells. The cells were thus actually immersed in the circulating fluid, which enabled rapid and stable thermal equilibrium to be attained.

Water was circulated through the thermostated cell housing by means of a small pump from either a thermostat maintained at the required termperature within ±0.1°C. or a large Dewar flask containing water and ice. For temperatures below 0°C. a Townson and Mercer Low Temperature Thermostat was utilised and pet. ether was circulated by the small pump via lagged tubing.

(c) Technique for Low Temperature Measurements.

The cell compartment was flushed out for at least one hour prior to measurement with thoroughly dry nitrogen (3 conc. H_2SO_4 traps and one liq. O_2 trap). If the solvent to be investigated was liquid at room temperatures, normal procedures were then followed, the filled cells being placed into position and the coolant passed through the cell housing. However, in the special case of liquid ammonia the following technique had to be adopted.

(i) After dry nitrogen had been passed through the cell compartment for one hour, a plastic bag with an elasticated top, which had previously been dried in a dessicator, was placed around the cell thermostat such that the stoppers of the cells were accessible. After replacing in the cell housing, dry nitrogen was again passed for half an hour.

(ii) Coolant was then passed through the cell housing until a temperature in the housing of -40°C. was reached.

(iii) The cell thermostat was then removed and rapidly filled with solvent and solution from pre-cooled pipettes.

(iv) The plastic bag was then rapidly removed and the cell thermostat quickly returned to the housing in order to prevent misting up of the cell windows.

(v) Temperature equilibrium was assumed to have been reached when the optical density remained steady at a certain wavelength.

(vi) The mean of the temperatures of the coolant before and after passing through the cell thermostat was taken as that of the thermostat : the difference was never more than 5°C.

(d) Purification of Solutes.

Inorganic salts used were of A.R. quality, when obtainable, and were usually recrystallised from purified water and dried at 110°C for 2 hours or under vacuum in a thermostatted drying-pistol. Lithium iodide was dissolved in A.R. acetone on a vacuum-line; anhydrous calcium sulphate was added and it was left to stand overnight. After filtration, the acetone was pumped off and the lithium iodide was then further dried in a drying pistol at 150°C, and stored over P_2O_5. Zinc perchlorate was prepared by addition of A.R. zinc oxide to A.R. 72% perchloric acid until there was a slight excess of the oxide. After filtration and heating until white fumes were evolved, white anhydrous zinc perchlorate was obtained. Cadmium perchlorate was obtained in a similar manner as colourless crystals which were not completely dehydrated since they decomposed on strong heating.

Tectra-n-butylammonium iodide was purified by recrystallising several times from acetone and drying under vacuum. Found m.p. 146.5° (lit.145°) Tectra-n-propyl and tectra-ethylammonium iodides were purified in a similar manner. Found m.p.271° and 180° respectively. (lit. — and 181°). Tectra-n-butylammonium perchlorate was prepared by mixing solutions in acetone of a slight excess of an equivalent of tectra-n-butylammonium iodide with an equivalent of silver perchlorate. The mixture was refluxed, filtered hot three times and the acetone removed under vacuum. The resulting salt was recrystallised four times from pure n-butanol and dried under high vacuum. Found m.p. 207-8° (lit. 203-4°).

(e) Purification of Solvents.

All water used was purified by double distillation from alkaline permanganate under oxygen-free nitrogen. Care was taken with all other solvents to ensure that they were anhydrous. However, if solvents were available in spectrograde quality, the results obtained on using them before and after drying with calcium sulphate or calcium hydride were compared and, if found to be identical, the solvent was assumed to be anhydrous and used as such. The following solvents were treated in this manner.

Methanol	(B.D.H. Special for Spectroscopy)
iso - Propanol	(" " " ")
Ethyl acetate	(" " " ")
Carbon Tectrachloride	(" " " ")
Chloroform	(" " " ")
Diethyl ether	(" " " ")
n - Hexane	(" " " ")
cyclo - Hexane	(" " " ")
n-Butanol	(" Specially purified for the determination of 17-ketosteroids.)
Methyl cyanide	(Eastman Kodak Co. Spectrograde)
Methyl formate	(" " " ")
iso - Octane	(" " " ")
Dichloromethane	(" " " ")
N-N-dimethylformamide	(" " " ")
cyclo-Hexanone	(H. & W. Purified, low in cyclo-hexanol.)

Other solvents were purified by the following techniques:

Benzene (B.D.H. 'M.A.R.' quality) was distilled from phosphorus pentoxide after standing for several weeks.

Dioxan (B.D.H. 'A.R.' quality) was refluxed with fused stannous chloride, fractionated, and then refluxed over sodium prior to final fractionation, a 50 cm. Vigreaux column being used. However, an equally effective method for removing peroxides was found to be that of refluxing for several hours over calcium hydride followed by direct distillation into a stoppered flask.

Anhydrous 1:3-dioxolane (kindly donated by Brotherton Ltd.) was freed from peroxides by fractionation alone.[136]

Acetone (B.D.H. 'A.R.' quality) was refluxed over and distilled from calcium sulphate[137] or distilled from and over phosphorus pentoxide, both methods always giving identical spectral results.

1:2-dimethoxyethane (Eastman Kodak Co.), dimethyl sulphoxide (B.D.H.) and tectrahydrofuran (B.D.H.) were dried with calcium sulphate or sodium wire and fractionated, when necessary, up a 50 cm. Vigreaux column.

0.880 ammonia solution (M & B 'A.R.' quality) was used as such.

Anhydrous ammonia was prepared from 'A.R.' aqueous ammonia by condensation under vacuum on to sodium hydroxide pellets, followed by condensation on to purified metallic sodium. Ammonia was distilled from the resulting blue solution as required.

The ultraviolet cut-off was determined for these solvents and is shown in Table 6.1.

Table 6.1.

Limits of transparency of solvents in mμ

Solvent	Cell length when optical density against air is 1.0.		
	1 cm.	0.1cm.	0.01 cm.
Methanol	210		
iso-propanol	210	190	
Ethyl acetate	254	249	
Carbon tectrachloride	265	248	245
Chloroform	245	235	223
Diethyl ether		200	
n-Hexane	210		
cyclo-Hexane	210		
n-Butanol	212		
Methyl cyanide	220		
Methyl formate	258		
iso- Octane	215		
Dichloromethane	231		212
cyclo-Hexanone			310 and 241-265
Benzene	282	280	278
Dioxan	240	215	210

N:N-dimethylformamide	268		
1:3-dioxolane		200	
Acetone	330		300 and 205-265
1:2-dimethoxyethane	215	205	
Dimethyl sulphoxide			242
Tectra-hydrofuran		208	
0.880 ammonia	222		
Liquid ammonia	*ca.*240		

(f) Preparation of Solutions

(i) Aqueous Solutions.

Aqueous solutions were prepared by dilution of a stock solution obtained from a known weight of the salt (micro- or semi-micro balance) made up to a known volume; occasionally solutions were made up such that dilution was not necessary.

(ii) Non-aqueous solutions.

The latter procedure mentioned above was generally used since most salts were sparingly soluble. In some instances, e.g., tectra-*n*-butylammonium iodide in carbon tectrachloride, the mixture had to be allowed to stand in the dark for several days with occasional shaking and the solution obtained by pipetting carefully from the surface of the liquid. At times, solute and solvent were refluxed together in the dark for 24 hours and pipetted hot into cells already heated to 40°C. in the cell housing in order to prevent loss of solute by recrystallisation. (E.g., tectra-n-butylammonium iodide in benzene.) In some solutions containing iodide, I_3^- was occasionally formed (detectable by its characteristic absorption spectrum). It was removed by adding small amounts of anhydrous ammonium thiosulphate and leaving for times varying from a few hours to a week until the spectrum of I_3^- was completely lost. Addition of calcium hydride was later found to be a somewhat quicker method for removing I_3^-.

(iii) Mixed Solutions.

Identical concentrations of iodide in solvents A and B were prepared by weighing. A known volume of A was added from a burette to a weighed graduated flask. After reweighing, solution B was run in from another burette up to the calibratijg mark. The solution was weighed again and the mole-fraction of solvent calculated from the recorded weights. Exactly the same volumes of pure solvents A and B were placed in another flask and the mixture used in the reference cell. By this method identical concentrations of iodide were obtained in all the various mixtures studied. In the case when iodide was insoluble in one of the solvents, a stock solution of the other solvent was diluted, prior to the addition of that solvent, such that, in the final solutions, the concentration of iodide was always approximately the same. Care was always taken to ensure that the solvent composition was the same in both cells, since slight differences can lead to an apparent shift of the peak if the solvent has a rising absorption in the wavelength region concerned.

(g) Diffuse Reflectance Spectra of Powdered Salts.[45]

(i) Theory.

The absorption spectra arise because multiple reflections of the incident light are accompanied by limited transmittance. They are measured by collecting monochromated light diffusely reflected from the powdered solid with a toroidal mirror which focuses the light on to the detector. This is compared with light reflected from a reference surface. The use of a photomultiplier as a detector is essential in the ultraviolet region in order to obtain good reproducibility coupled with high sensitivity.

(ii) Method.

Magnesium carbonate is generally used as a comparison surface. However, lithium fluoride was found to reflect between 10 and 20% more of the incident light, and this figure increased rapidly on going below 240 mμ. Experiments have been made with other reference surfaces, e.g., various filter-papers, but it has always been found that lithium fluoride is superior. Using lithium fluoride, readings have been obtained which appear to be reliable down to 210 mμ.

Specimens, together with lithium fluoride diluent, were ground with an agate pestle and mortar to a homogeneous fine powder. The relative amounts of lithium fluoride required depended upon the need to keep the final optical density below 0.6. When these precautions were not taken, spurious peaks and spurious broadening sometimes occured. After grinding, the powder was immediately spread on the metal dish of the attachment to give a flat compact surface comparable with that of the reference surface. (Small differences in optical density in regions where no bands occur were due to differences in spreading, which are unavoidable.)

For hygroscopic salts it was sometimes necessary to carry out the above operations in a dry-box. To avoid subsequent contact with water vapour the bottom of the specimen try was sometimes covered with silica gel.

When spectra of compounds with high extinction coefficients were measured in the ultraviolet region, even undiluted specimens did not appear to be optically black and it was sometimes possible to describe peaks which subsequently were found to be spurious. Such peaks had an optical density greater than 0.8 and did not decrease on initial dilution. The procedure, therefore, was to dilute until further dilution resulted in the expected decrease in optical density.

Peaks that could be reproduced with differing dilutions of the compound with lithium fluoride (normally between 1:5 and 1:15 by volume) were regarded as real and all others as spurious. However, when compounds with forbidden transitions were being studied, dilution was found to be undesirable.

A constant slit-width was used when each spectrum was being measured, the actual choice was made such that the instrument was as sensitive as possible in the wavelength region to be investigated. In the near ultraviolet and visible regions slit-widths as small as 0.1 mm. could be used and in the 220 mμ region slits of greater than 0.6 mm. were not necessary. The spectra were reproducible when plotted at different slit-widths.

(h) Mathematical Analysis of Spectra.

Since all the spectra observed had no fine structure it is reasonable to assume that the optical absorption in the ultraviolet region is due entirely to the movement of an electron from a ground into an excited state orbital which has no discrete vibrational quantum levels.

The spectra are thus a Gaussian distribution of energies and should approximate to a Gaussian Error curve of the general formula

$$y = Ae^{-\alpha(x-b)^2}$$

where A is the peak height, α is dependent on the width of the curve and b is the peak position. Accordingly, a Pegasus Digital Computor was very kindly programmed by Mr. R. Leonard of the Department of Civil Engineering to investigate this. Initial investigations showed that results of a high order of accuracy were required by the computor, especially in the case of spectra where it was impossible to observe peak positions, e.g., aqueous bromide solutions. The following procedure was thus adopted for bromide solutions:

(i) An approximately 0.1 M solution of KBr was prepared and its spectrum taken, at various temperatures, in the wavelength range such that the optical density readings were between 0.5 and 0.2 and at wavelength intervals of 0.2 mμ.

(ii) This solution was then diluted 1 : 1 and the above procedure repeated.

(iii) The diluted solution was further diluted 1 : 1, the above procedure repeated, and so on until readings were being obtained at around 205 mμ.

(iv) Over one hundred accurate readings were thus obtained and were then scaled according to their dilution.

(v) These were then submitted to the computor, with their corresponding frequency, in the order of highest optical densities first. The computor then obtained the best Gaussian curve through the submitted points. It then automatically proceeded to leave out the last (lowest) point submitted and to fit a Gaussian curve to the remainder and so on until there were about thirty points left. (In future, this procedure will be referred to as "tailing".)

(vi) The experimental points were then submitted in the reverse order (highest optical density last) and procedure (v) repeated. (Known as "topping".)

(vii) Finally the points were submitted in the order: highest optical density obtained; lowest obtained; next highest; next lowest and so on. (Known as "alternate topping and tailing.")

(viii) The results obtained from the computor were the three constants of the curve, A, α, and b and, when required, points on the computed curve at selected intervals in order to plot it on the experimental curve.

(ix) The peak position of the band (b) was then calculated from an average of all the reasonable results obtained. A "reasonable" result was obtained by inspection: it was possible to eliminate certain results because, at times, the values for A, α, and b were far from the average and expected values. This is because either the last or first of the series of points being examined by the computor at any one time is inaccurate and consequently, in order to accommodate this point, the Gaussian curve found by the Computor has different constants to those found previously. When this inaccurate point is not at or near the end of the submitted experimental points but near the middle, its effect upon the computed curve is negligible. The above comment only applies when the long wavelength edge of a band is being investigated and the experimental points are some way from the peak position.

(x) Procedure (ix) can only be followed when the spectrum does not contain a hidden band. When it does, and the band is suspected to be the short wavelength side of the observed spectrum, the experimental points are submitted and only the procedure of "topping" is performed. The curve constants obtained begin by varying greatly and then settle down to a steady value. The spectrum can thus be split into two or more bands and the position at which the hidden band ceases to contribute to the observed spectrum ascertained.

CHAPTER SEVEN

Experimental Results.

(a) Iodide Ion.

The examination of the literature in Chapter One has shown that the spectra of solvated iodide ions are markedly dependent upon medium and temperature. Fig. 7.1. shows iodide in water at two different temperatures. To examine this dependence more fully four main constraints have been placed, when possible, on the environment of iodide ions in solution and their effect upon the iodide spectrum noted. The constraints are:

(1) using a variety of pure solvents

(2) changing the temperature of these solutions

(3) using mixed solvents

(4) adding salts which do not absorb strongly in the 220 mμ region.

(i) Aqueous Solutions.

Much of the information that might be required concerning the effect of the above constraints that can be used on aqueous iodide solutions has already been documented. Recently Stein and Treinin[35] have repeated the work of Smith and Symons[25,26] and report a value for the shift with temperature of the first absorption band of aqueous iodide as 33.7 cals/deg., the previously recorded figure being 32 cals./deg. As yet the second iodide band has not been examined for

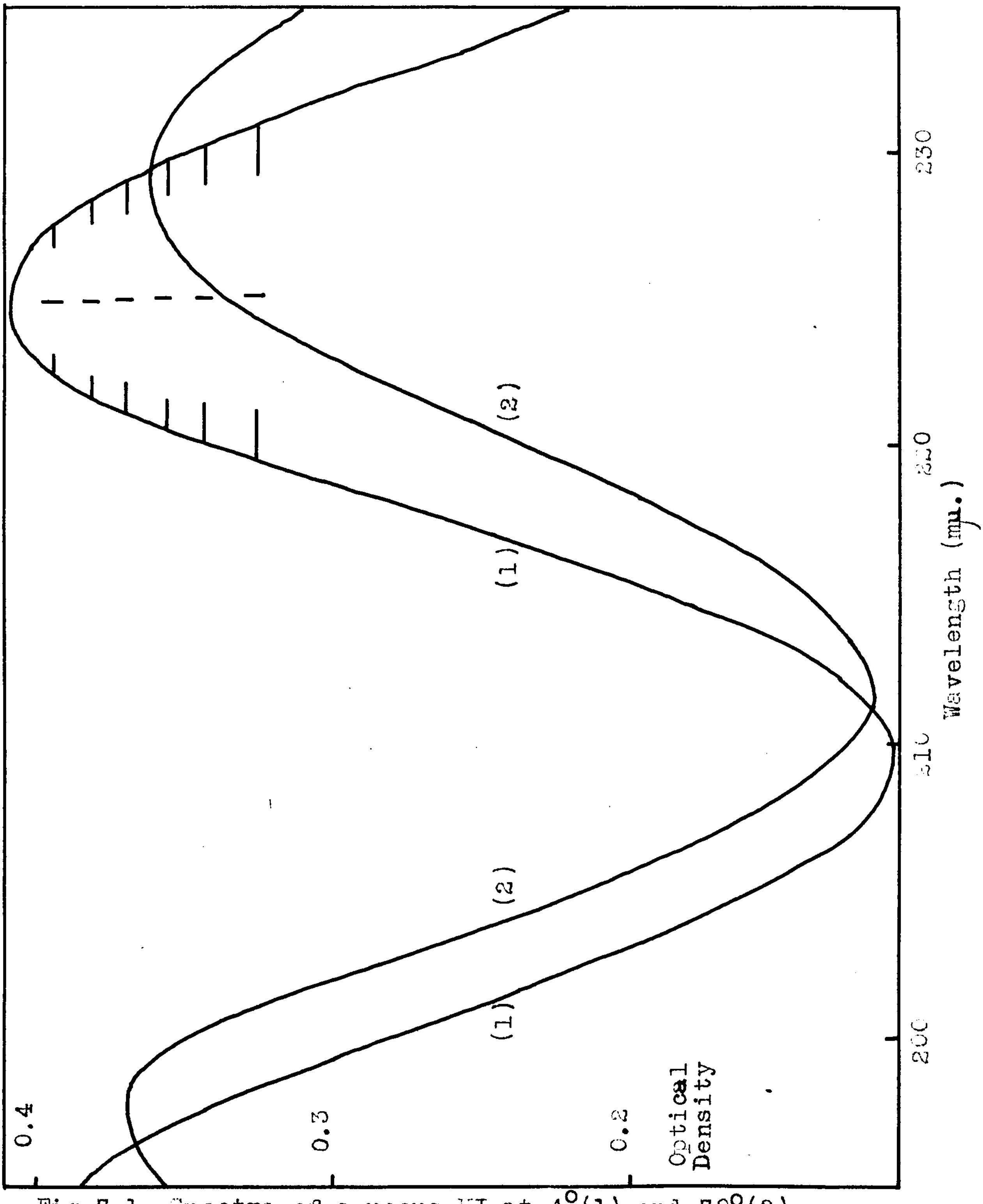


Fig.7.1. Spectra of aqueous KI at 4°(1) and 70°(2), and showing method of "rectilinear diameters".

temperature dependence since its peak position (ca. 194 mμ) cannot be accurately located unless special precautions are observed.

Smith and Symons have reported that the effect of adding the electrolytes NaCl, KCl and KF appears to produce equal shifts of the iodide spectrum at equal concentrations. Private communication with Stein and Treinin has led to a re-examination of this work since they had found a small but definite dependence upon the nature of the cation for equal concentrations. The results found are listed in Table 7.1. and compared graphically with those of Smith and Symons in Fig. 7.2. It may be seen that the shift of the iodide spectrum to the ultraviolet increases approximately with increasing cationic size. Although Diamond and Fromhertz[138] have reported that the iodide spectrum is independent of the corresponding cation (Li, Na, K, Ca, Sr, Ba, Cs) and concentration up to 6.0M, Doucet,[139] on the other hand observed that the spectrum was dependent upon concentration, the whole band being shifted towards the ultraviolet with increase in concentration, but that the effect was comparatively small and may be considered negligible at concentrations below 0.01M. Since these workers had to use extremely thin films at these high concentrations their results may be subject to some error. The spectrum of an iodide solution containing

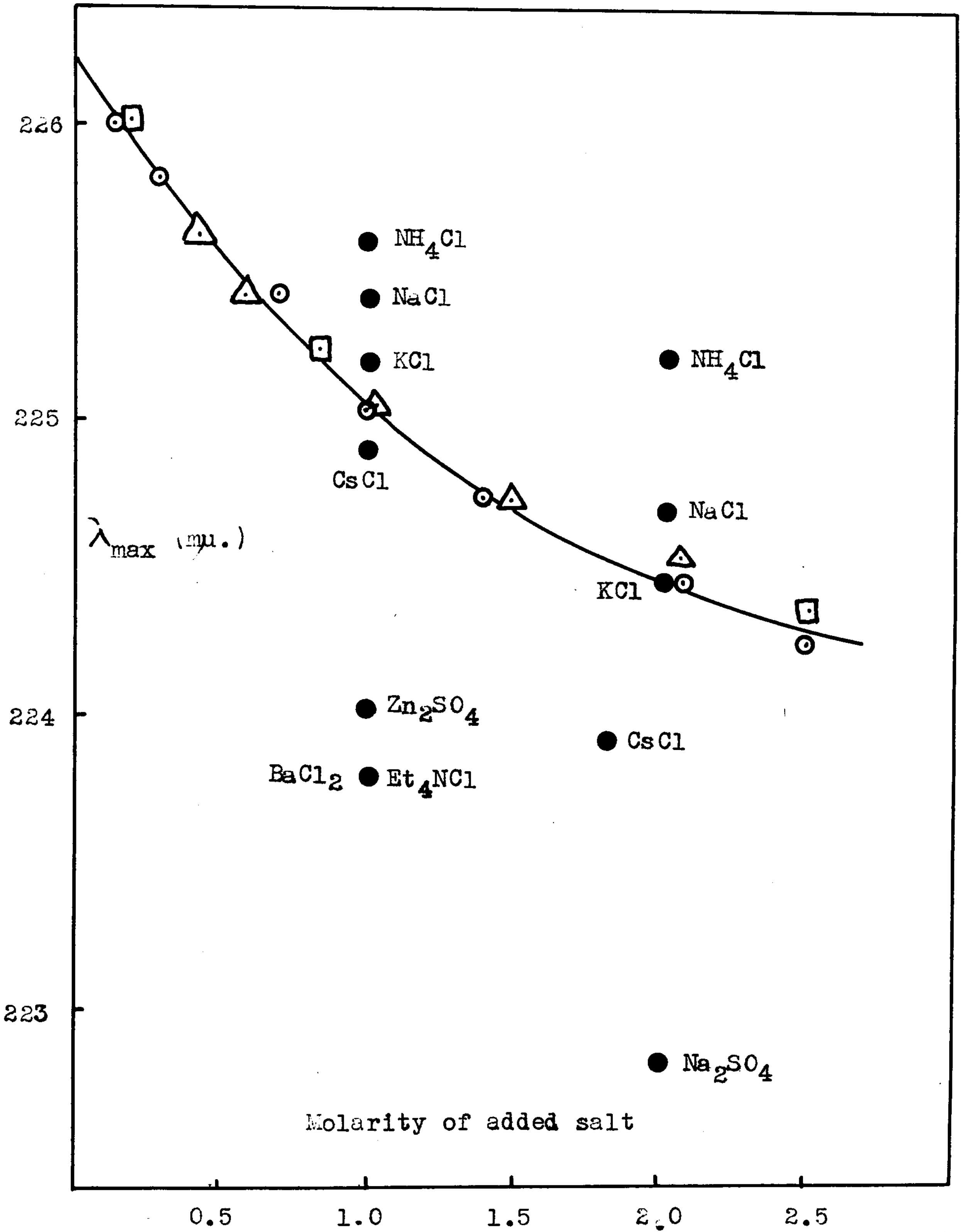


Fig.7.2. Effect of added salts upon the iodide spectrum (20°)
○ KCl □ NaCl △ KF results of Smith (ref. 135)
● Present work

a large positive ion, $(n\text{-Bu})_4N^+$, at a concentration of 7.33×10^{-2}M and between two quartz plates giving an effective cell length of 0.001 cm., has been measured and the peak was shifted down to 225.6 mμ, a shift of 0.6 mμ., which is outside the limits of experimental error.

Table 7.1.

Comparison of $\lambda_{max}^{20^\circ}$ (mμ) for iodide in aqueous salt solutions of electrolytes with crystallographic cation radius (r^+)

Salt	Concentration		r^+(Å)
	1M	2M	
NH_4Cl	225.6	225.2	1.03
NaCl	225.4	224.7	0.98
KCl	225.2	224.5	1.33
CsCl	224.9	223.9[a]	1.65
Et_4NCl	223.8		2.28[b]
Na_2SO_4		222.8	
$ZnSO_4$	224.0		
$BaCl_2$	223.8		

[a] 1.8M. [b] Estimated from a model.

In all cases, only negligible changes in band height and shape are produced by the addition of salts.

(ii) Non-aqueous Solutions

The results of this study have shown that certain solvents were comparable with water on changing environment and temperature, and fitted the empiral correlation of Smith and Symons[25,26]. These solvents are reported in Section (ii) I: the remaining solvents investigated, which generally had low dielectric constants, are reported in Section (ii) II.

(I) Good Solvating Solvents

The position of maximum absorption of iodide in these solvents is listed in Table 7.2. The results of other workers are given in Table 7.3.

Table 7.2.

Position of maximum absorption for iodide in various solvents.

Solvent	Salt	Temp	λ_{max}(mμ)
MeOH	KI,($\underline{n}$-Bu)$_4$NI	20	219.8
iso-PrOH	KI,($\underline{n}$-Bu)$_4$NI	20	219.0
n-BuOH	KI,($\underline{n}$-Bu)$_4$NI	20	218.0
MeCN	KI,($\underline{n}$-Bu)$_4$NI	20	245.8
Acetone	KI,($\underline{n}$-Bu)$_4$NI	4	254.0
cyclo-Hexanone	($\underline{n}$-Bu)$_4$NI	15	259.5
Dimethyl sulphoxide	KI,($\underline{n}$-Bu)$_4$NI	26	242.3[a]
1:3-dioxolane	($\underline{n}$-Bu)$_4$NI	26	236.5
0.880 ammonia	KI,($\underline{n}$-Bu)$_4$NI	20	232.3
Liquid ammonia	KI	-46	254.5

[a] see text.

Table 7.3.

Results of other workers for the position of maximum absorption of iodide in various solvents.

Solvent	Salt	λ_{max}(mμ)	Reference
MeOH	K, Na, Li, NH_4, NEt_4 Iodide	219.1	29
MeOH	KI	221.0	140
n-BuOH	KI	218.0	140
MeCN	K, Na, NH_4 Iodide	244.4	29
MeCN	KI	246.1	140
Acetone	KI	248.0	128
Dimethyl sulphoxide	KI	241.7	128
Liquid ammonia	K, Na, NH_4 Iodide	254.0	33

It may be observed that the results obtained compare well with those in the literature. One reason for any slight discrepances is that much of the published work was performed before the temperature dependence of the spectra was realised and hence the temperature at which these spectra were measured is not always reported. Two more points require mention: (i) Kosowers' value of 251.7 mμ for iodide in acetone[128] is lower than our value. This may well be due to traces of water in his acetone (cf. Fig.7.9.) He also reports a value of ε_{max} = 9,300; we find ε_{max} = 14,300.

(ii) The ultraviolet cut-off for dimethyl sulphoxide is 241-3 mµ, depending upon temperature, and hence any peak reported in this region may well be spurious, if this limit is ignored, and due to stray light effects. It is felt that the value obtained here of 242.3 mu is spurious, especially since $\mathcal{E}_{max}$ = 10,500 (Kosower[128] obtained $\mathcal{E}_{max}$ = 11,000), the usual value obtained for iodide ion in solution being 14,000; the peak was also not symmetrical.

(1) Effect of Temperature.

It is well established that when a graph of the peak position of iodide in energy units is plotted against temperature[8,9,10,25,26,35] a straight line relationship is found. It was therefore considered that for the solvents investigated, five points were sufficient to obtain accurately the slope of the line, dE_{max}/dT. Fig. 7.3. shows the results obtained. Fig. 7.4. shows how these and other solvents compare with the correlation of Smith & Symons. dE_{max}/dT was not obtained for iodide in <u>cyclo</u>-hexanone because of the difficulty of locating the band maximum accurately (*cf* Table 6.1.), nor for dimethyl sulphoxide since the true absorption maximum could not be measured.

(2) Effect of added salts.

The low solubility of salts in several of these solvents made measurement of spectra in the presence

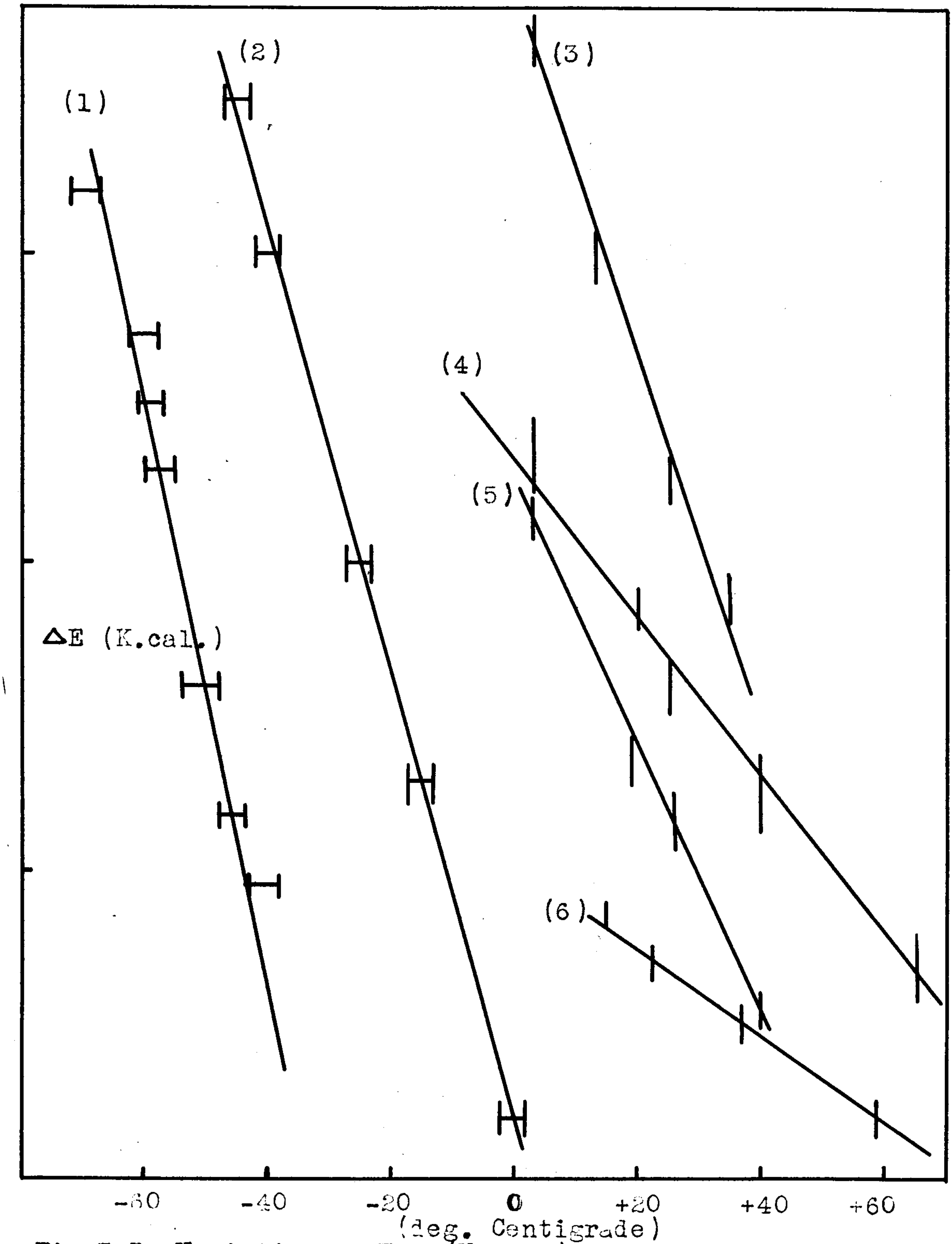


Fig.7.3. Variation of E_{max} (K.cal.) for the first band of iodide with temperature.
(1) Ammonia (2) Acetone (3) 1:2-dimethoxyethane
(4) n-BuOH (5) 1:3-dioxolane (6) Dioxan

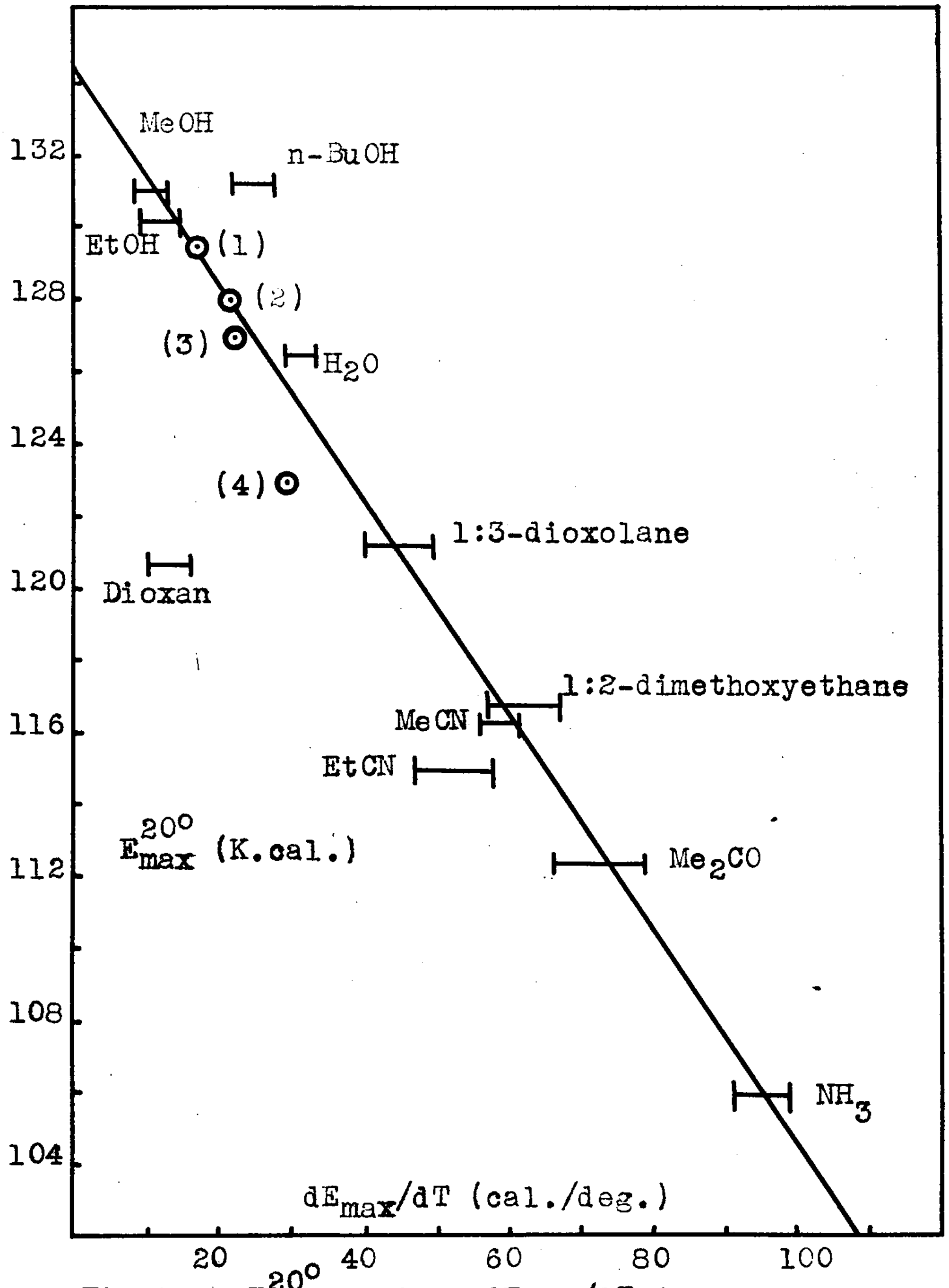


Fig.7.4. $E_{max}^{20^\circ}$ against dE_{max}/dT for iodide in all the solvents investigated.
(1) KI crystals[9] (2) CsI crystals[10]
(3) RbI crystals[8] (4) NaI crystals[8]

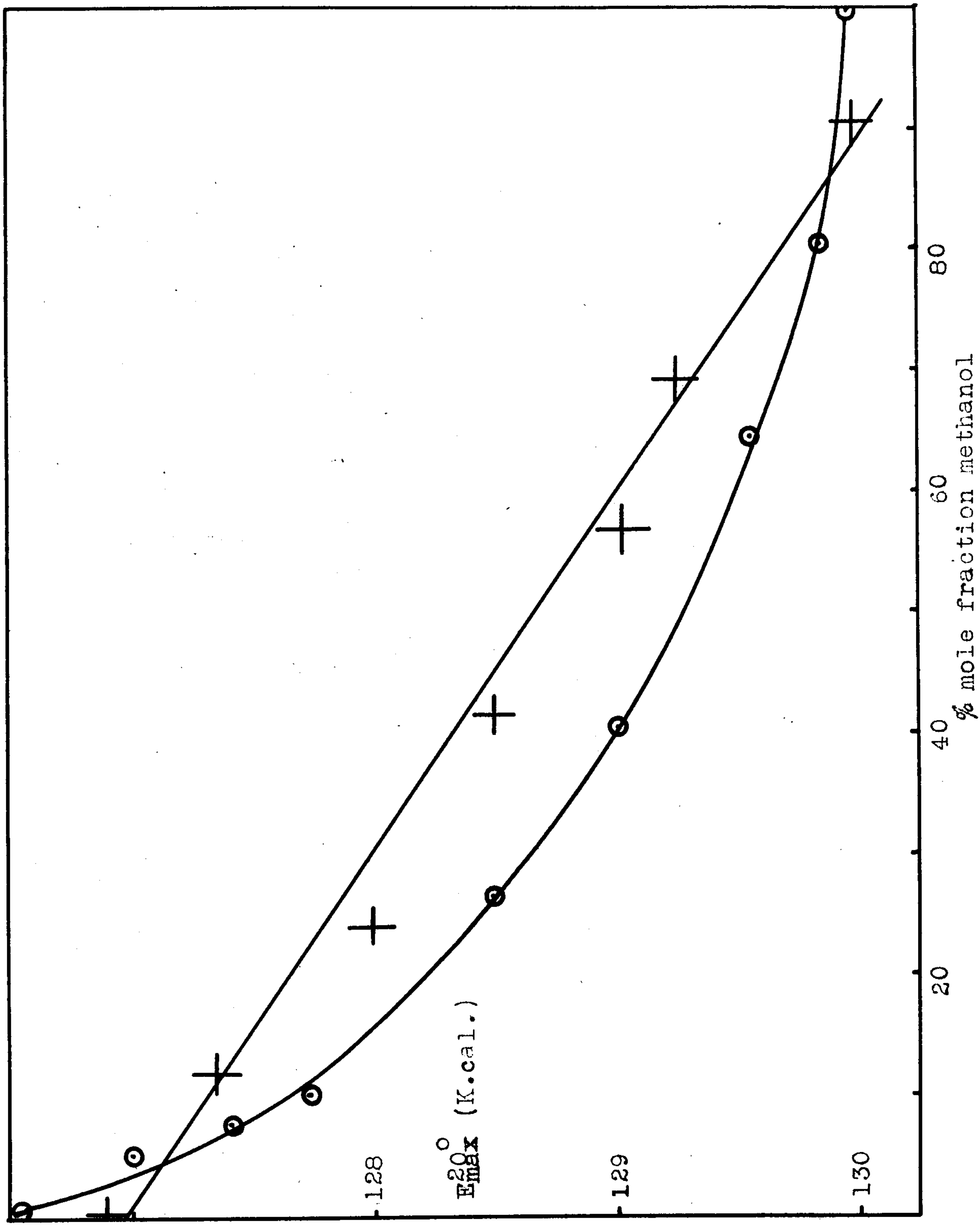


Fig.7.5. E_{max} (K.cal.,20°) for the first band of iodide in $MeOH/H_2O$ solutions against % mole fraction MeOH.

⊙ results of Fig. 2 in ref.25. (Part I)

+ solutions containing 1M KF.

of added electrolyte difficult. ($\underline{n}$-Bu)$_4$NI in 1:3-dioxolane was investigated in the presence of a large excess of ($\underline{n}$-Bu)$_4$NClO$_4$ and the band was shifted the expected amount down to 234 mµ.

A study was undertaken of the variation of λ_{max} of iodide in methanol/water mixtures containing 1M potassium fluoride. Fig.7.5. shows a plot of E_{max} against mole fraction methanol. The results of Smith and Symons[25] are included for methanol/water mixtures. It may be seen that the addition of potassium fluoride straightens the curve previously obtained.

(II) Poor Solvating Solvents.

(1) Pure solvents.

Values of $\lambda^{20°}_{max}$ for ($\underline{n}$-Bu)$_4$NI in various solvents are included in Table 7.4. Identical values were obtained using ($\underline{n}$-Pr)$_4$NI and Et$_4$NI in chloroform. However, in carbon tectrachloride, ($\underline{n}$-Pr)$_4$NI gave a band at 268 mµ and Et$_4$NI, after refluxing in the dark for a week, gave evidence of a band below 267 mµ. (cf Table 6.1.) In general alkali metal iodides were insoluble in these solvents; however, after prolonged shaking in the dark with dioxan, caesium iodide gave a band at 235 mµ : so also did rubidium iodide after refluxing in the dark for a week. These bands were identical with those obtained from ($\underline{n}$-Bu)$_4$NI and ($\underline{n}$-Pr)$_4$NI in this solvent.

The solubility of (*n*-Bu)$_4$NI in hexane, *cyclo*-hexane and *iso*-octane, even after prolonged refluxing, was found to be vanishingly small. The spectra of hot solvents all showed a very weak band in the 290 mμ region together with a rising absorption at lower wavelengths comparable with that found for mono-ethers. (cf Fig.7.6.) However, optical densities were less than 0.1 in 1.0 cm. cells.

The diffuse reflectance spectra of (*n*-Bu)$_4$NI and Et$_4$NI are given in Fig.7.7.

Table 7.4.

Band maxima of, and effect of temperature on, the spectrum of tectra-*n*-butylammonium iodide in various solvents.

Solvent	$\lambda^{20^\circ}_{max}$ (mμ)	dE_{max}/dT (cal./deg.)	"theoretical" dE_{max}/dT (cal./deg.)
CCl_4	293	0	124
C_6H_6	290 [a]	-	124
Et_2O	290	-	124
Tetra-hydrofuran	290 [a]	-	124
Dioxan	237	14 ± 3	45
1:2-dimethoxyethane	245	62 ± 5	59
$CHCl_3$	240-245 [b]	-	50-60
CH_2Cl_2	246	-	60

[a] Shoulder; hence dE_{max}/dT unobtainable but probably zero.

[b] A positive shift occurs, but owing to the breadth of this band dE_{max}/dT was not accurately obtainable.

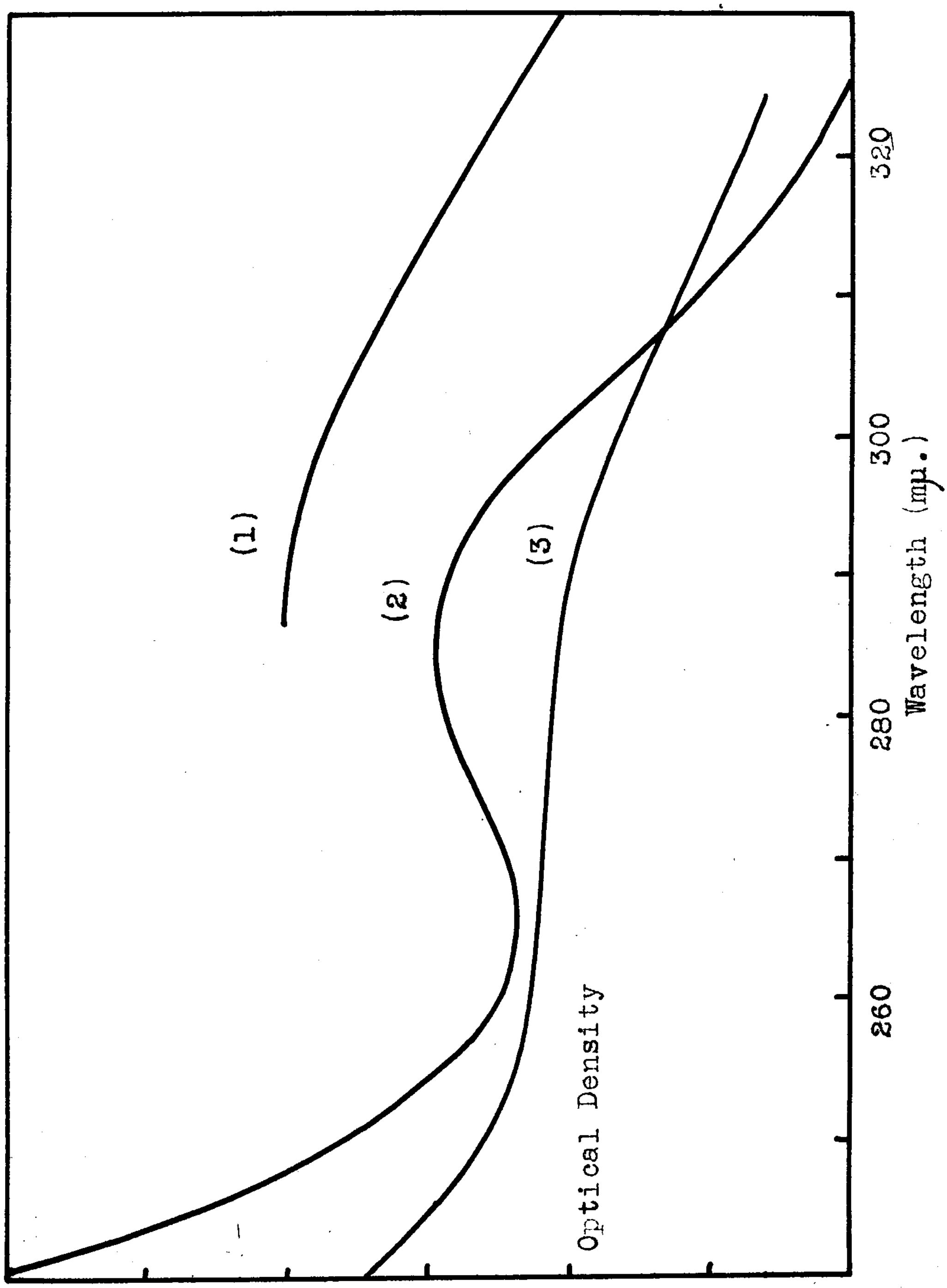


Fig.7.6. Spectra of $(n\text{-}Bu)_4NI$ in some poor solvating solvents. (1) Benzene (2) Diethyl ether (3) Tetrahydrofuran

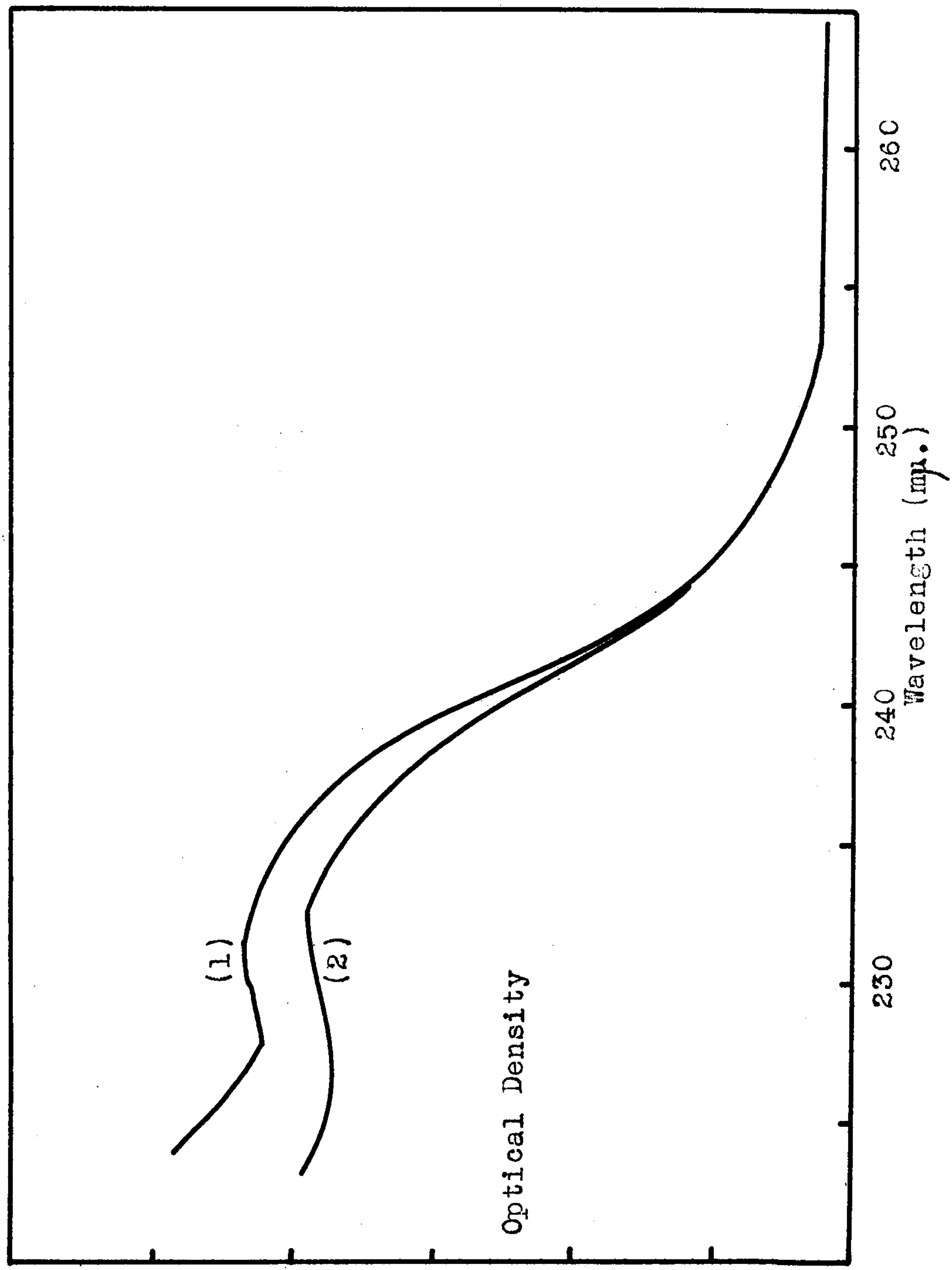


Fig.7.7. Diffuse Reflectance Spectra
(1) $(n\text{-}Bu)_4NI$ (2) Et_4NI

(2) Effects of Temperature.

The results found for the dependence upon temperature for the spectra of iodide in these solutions are summarised in Table 7.4, and the values for dE_{max}/dT are compared with those that would be predicted from the correlation of Smith and Symons. (cf Fig.1.3.)

(3) Mixed Solvents.

Detailed spectroscopic studies have been made on ($\underline{n}$-Bu)$_4$NI in the following mixed solvents: carbon tectrachloride/chloroform; carbon tectrachloride/methanol; cyclo-hexane/iso-propanal; acetone/dioxan; and acetone/water. Of these mixtures only carbon tectrachloride/chloroform and carbon tectrachloride/methanol gave any evidence for the rise of one band with the diminution of another with change in solvent composition (Fig.7.8.) For other mixed solvents, a progressive shift of the iodide band was observed (Fig.7.9.) quite comparable with the shifts for water/solvent mixtures.[25] The results of variation of E_{max} with % mole fraction composition are shown in Fig.7.10. Constructed curves have been drawn for mixtures containing dioxan, e.g., the spectrum resulting from the addition of the iodide bands in pure dioxan and pure acetone in no way resembles any of the spectra obtained from any of the dioxan/acetone mixtures. (Fig.7.11.) It was established that the bands for all

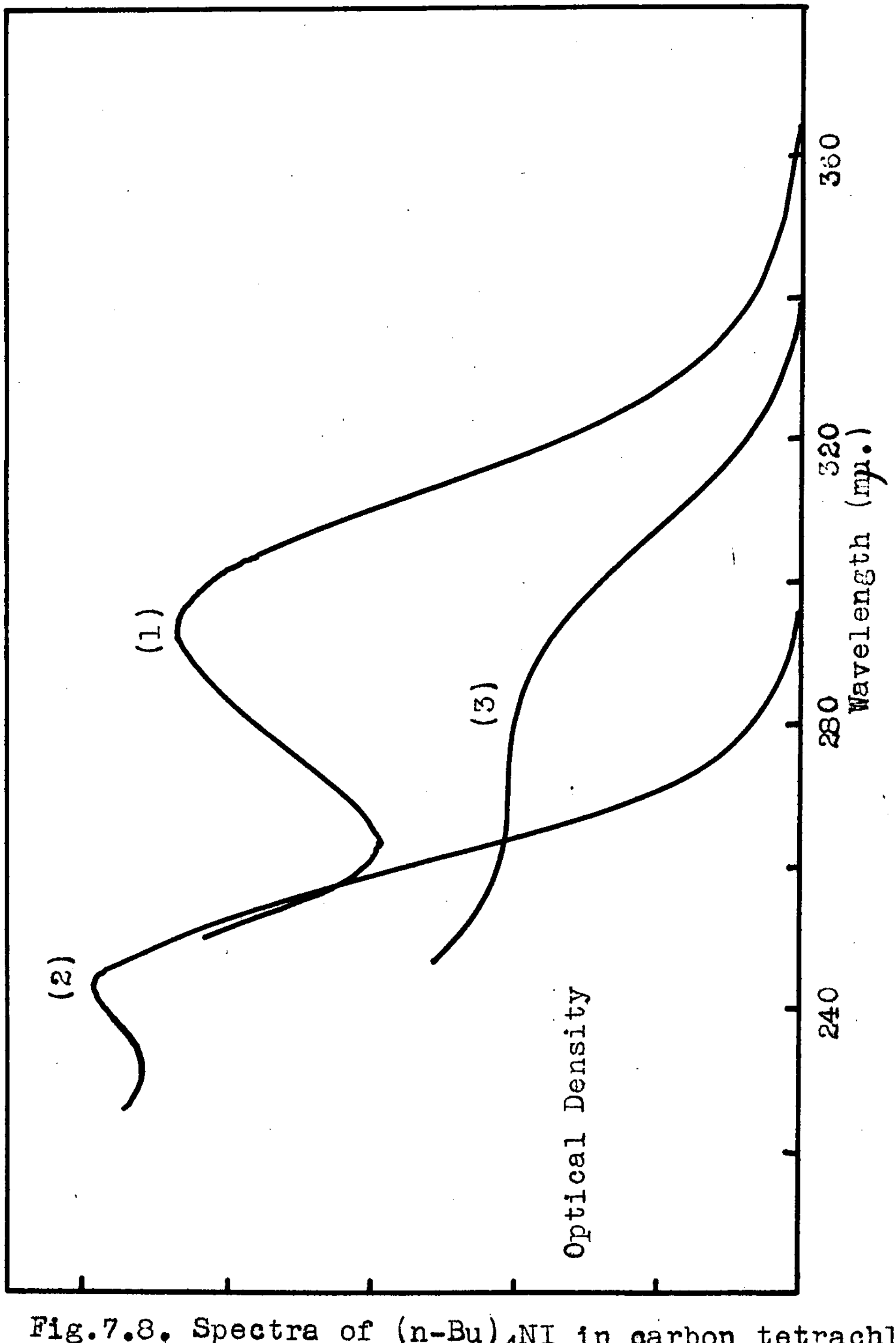


Fig.7.8. Spectra of (n-Bu)$_4$NI in carbon tetrachloride, chloroform, and carbon tetrachloride/chloroform mixture.
(1) Carbon tetrachloride (2) Chloroform
(3) Carbon tetrachloride/chloroform containing 90% by volume chloroform.

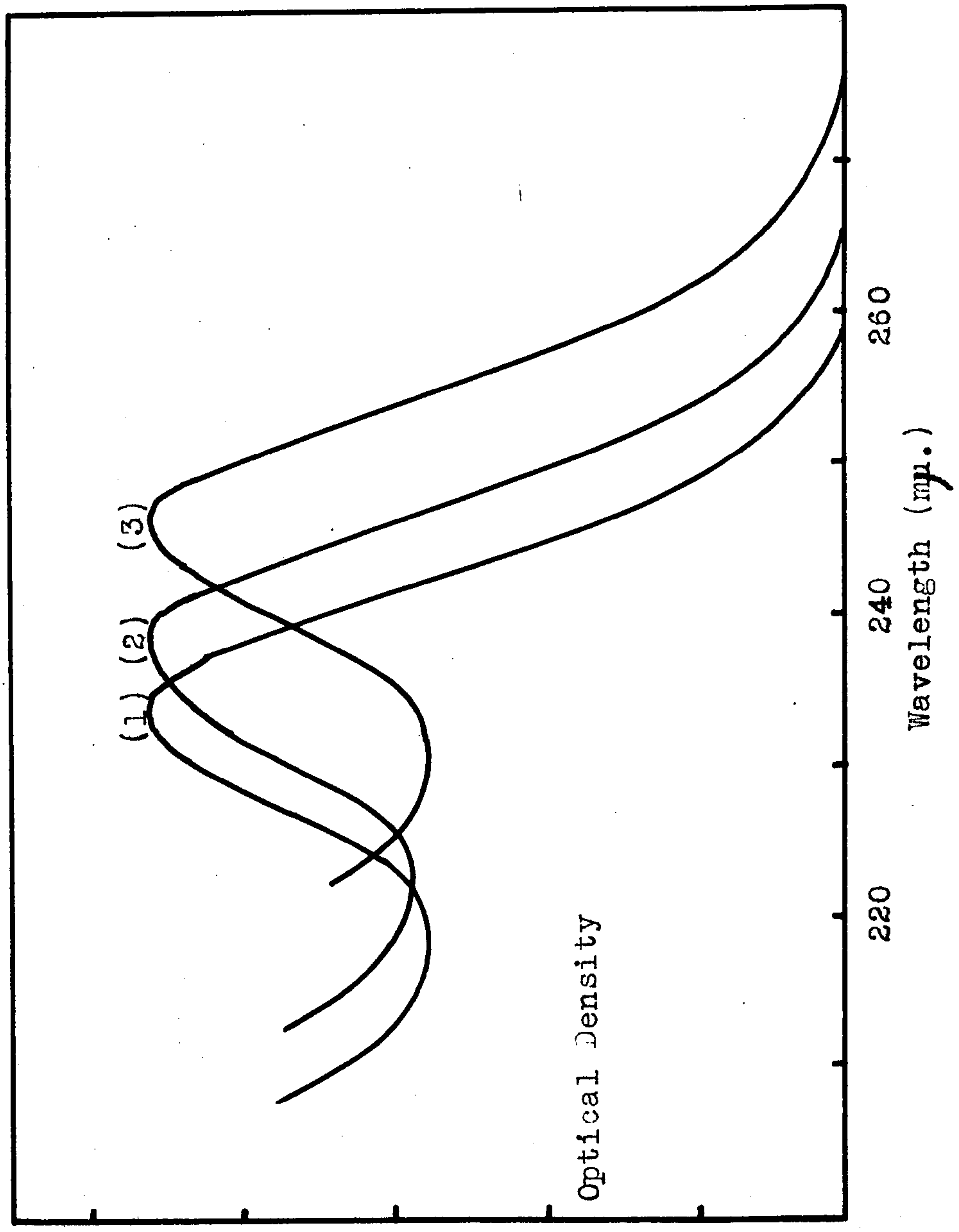


Fig.7.9. Spectra of $(n\text{-Bu})_4$NI in dioxan, acetone,
and dioxan/acetone mixture.
(1) Dioxan (2) <u>ca</u>. 50% Dioxan/acetone
(3) Acetone

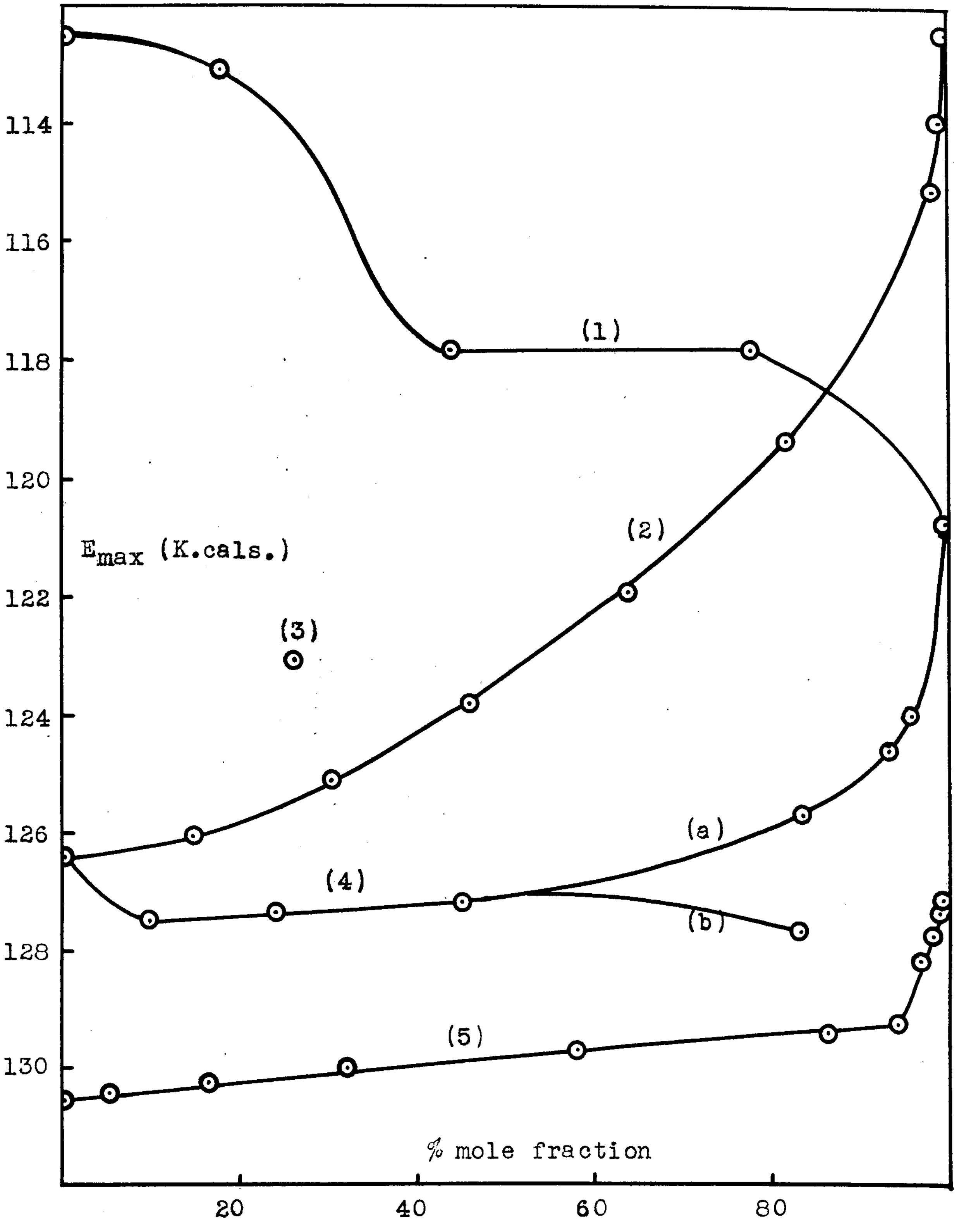


Fig.7.10. E_{max}(K.cal.,20°) for the first band of iodide against % mole fraction.
(1) acetone→dioxan (2) water→acetone
(3) 0.880 ammonia (4) water→dioxan (a) R_4NI
(b) alkali metal iodides
(5) iso-PrOH→cyclohexane

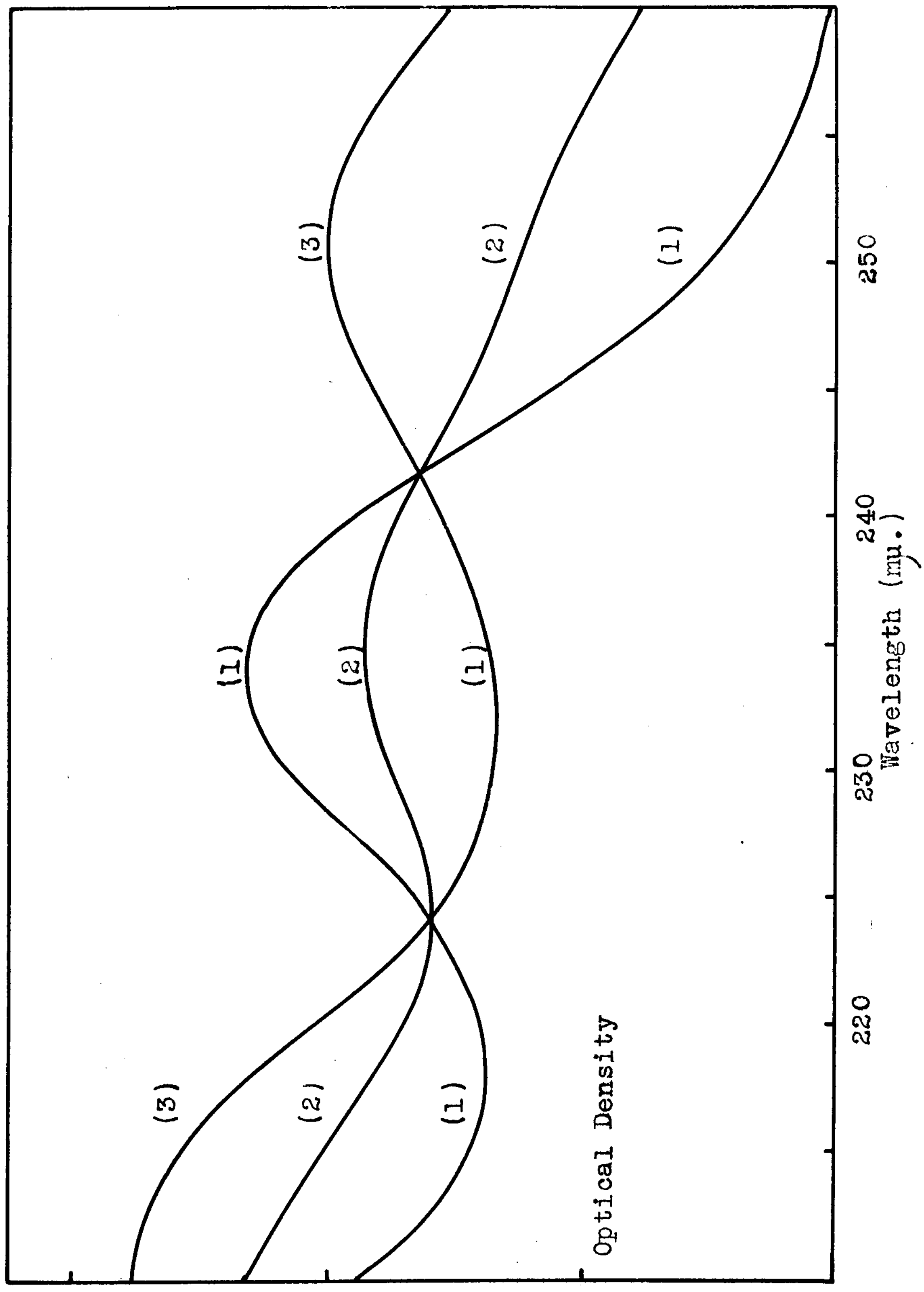


Fig.7.11. **Constructed Curves**
(1) Iodide in dioxan
(2) Iodide in acetone
(3) Curve resulting from addition of 50% (1) to 50% (2)

mixtures except those containing carbon tectrachloride and cyclo-hexane could not be reproduced by the addition, in various proportions, of the bands obtained from iodide in the two components. Preliminary investigations into dioxan/iso-propanol and dioxan/methyl cyanide mixtures also agreed with these conclusions.

With dioxan/water mixtures results were obtained somewhat different to the above in that the band in pure dioxan is very broad relative to that in water, and there is a steady increase in the band width in the 90% mole fraction dioxan region. (cyclo-hexane/iso-propanol mixtures also showed somewhat similar broadening in the 95-99% mole fraction cyclo-hexane region.) Pronounced differences were also observed in this region for the shifts for $(\underline{n}\text{-Bu})_4NI$ and $(\underline{n}\text{-Pr})_4NI$ on the one hand and certain alkali metal iodides on the other (Fig.7.10.) Sparing solubility made these observations somewhat unreliable except in the case of lithium iodide where the trend was ultimately reversed, the band shifting to shorter wavelengths in pure dioxan.

(4) Addition of tectra-n-butylammonium perchlorate.

When $(\underline{n}\text{-Bu})_4NClO_4$ was added to dioxan the 237 mμ band was shifted to the ultraviolet in the normal way (cf Table 7.1.) and a shoulder appeared in the 280 mμ

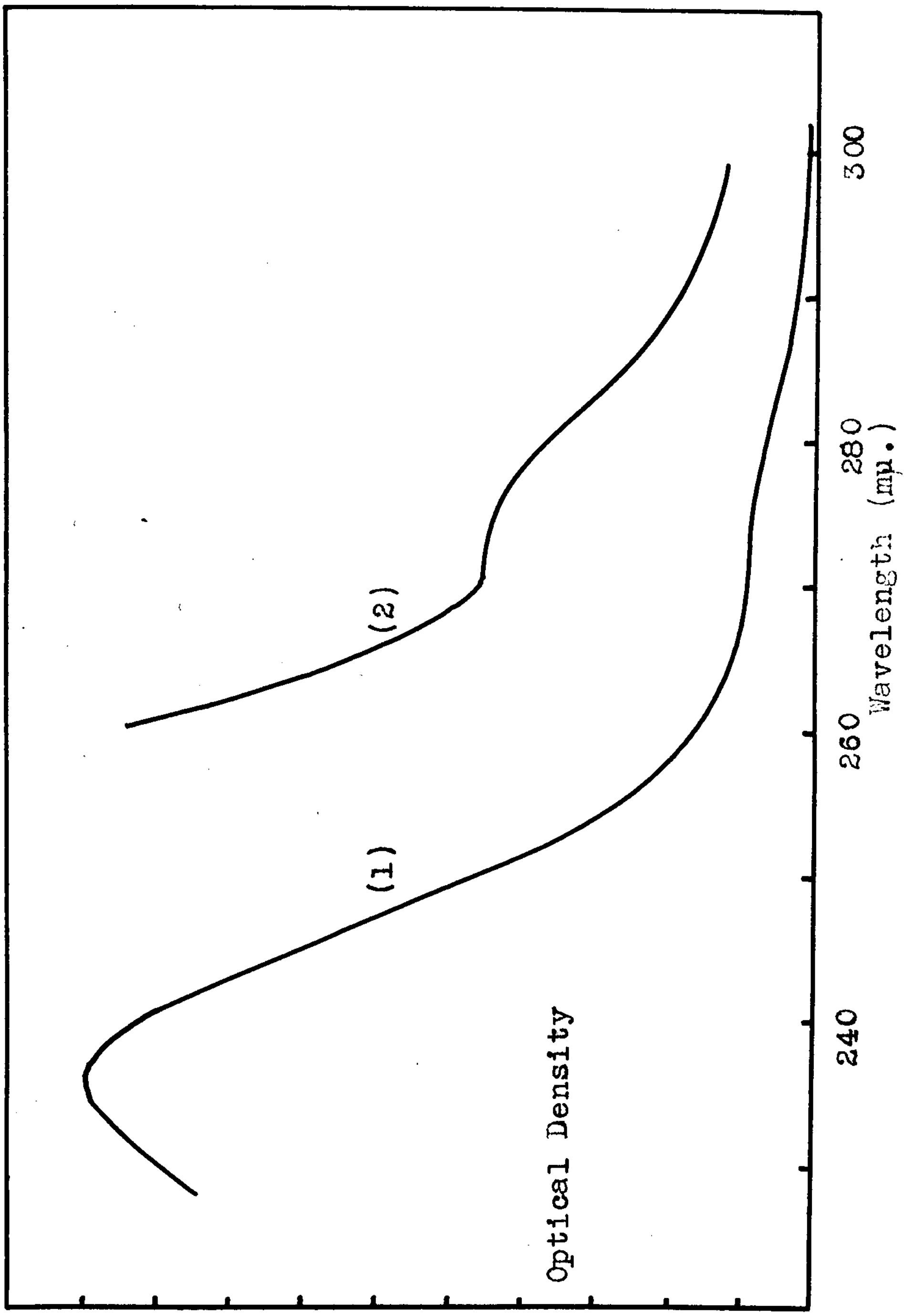


Fig.7.12. Spectra of $(n\text{-}Bu)_4NI$ in dioxan with excess $(n\text{-}Bu)_4ClO_4$
(1) 0.1 cm. cells (2) 1.0 cm. cells

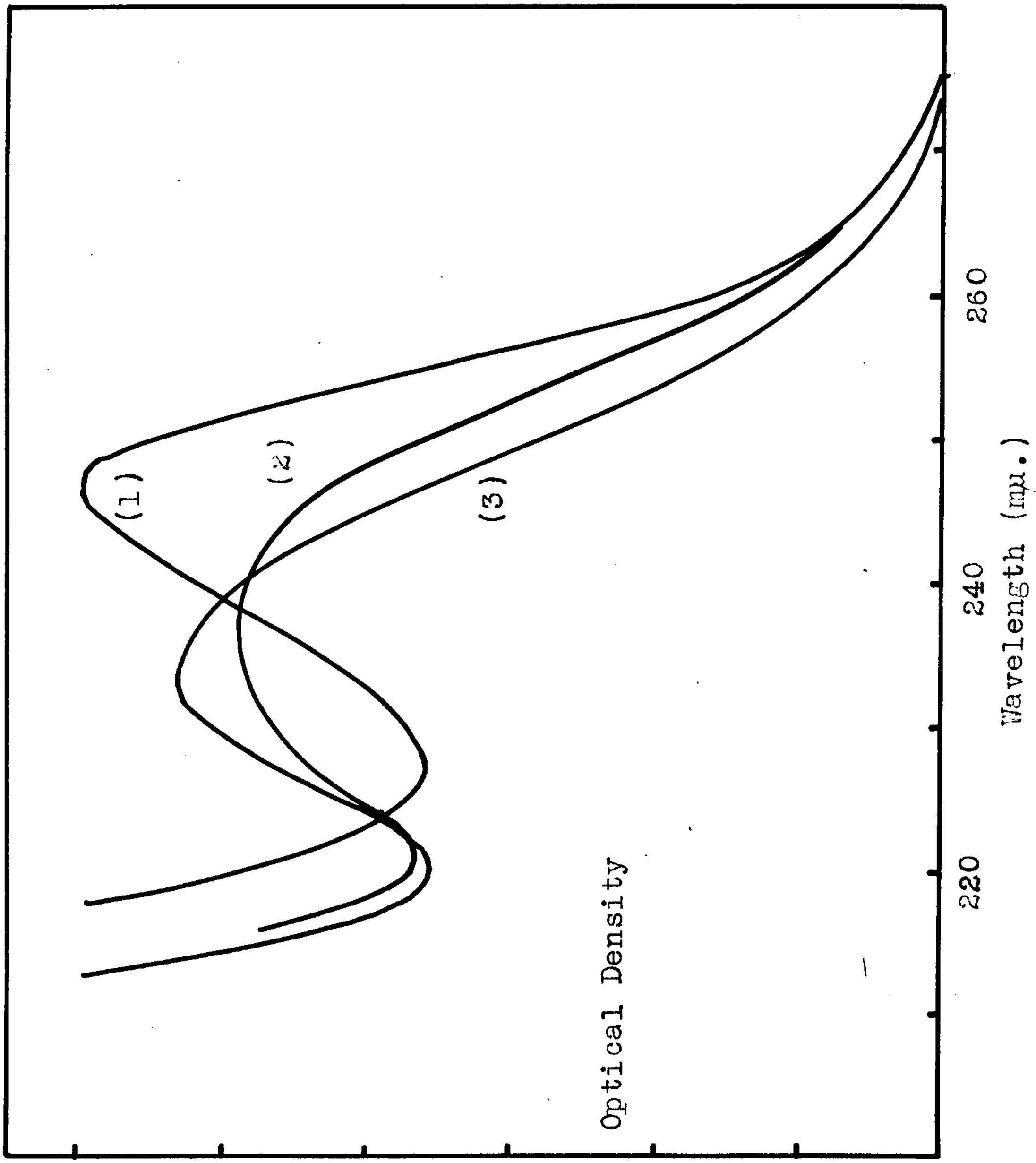


Fig.7.13. Spectra of $(n\text{-}Bu)_4NI$ in 1:2-dimethoxyethane

(1) in pure solvent
(2) with some $(n\text{-}Bu)_4NClO_4$
(3) with excess $(n\text{-}Bu)_4NClO_4$

region (Fig.7.12). With 1:2-dimethoxyethane the 245 mμ band broadens and then sharpens to a band at 235 mμ as progressive amounts of the perchlorate are added. An examination of the band width at half-height, and the shape and relative heights of the bands at comparable concentrations, suggests very strongly that the 245 mμ band falls as the 235 mμ band rises (Fig.7.13). A large shift to high energy, together with a marked broadening, was also found when the perchlorate was added to a solution of iodide in chloroform. However the resolution of the bands was poor and precise measurements impossible.

Addition of the perchlorate to benzene or diethyl ether produced no effect upon the shoulder at 290 mμ. (fig.7.6.).

(b) Bromide Ion

So far only preliminary investigations have been made on the effect of temperature and environment upon the bromide ion. Typical spectra obtained for potassium bromide in water and in methyl cyanide are shown in Fig.7.14. It may be seen, in the case of methyl cyanide, where the absorption band is shifted somewhat to the visible compared with the water band, that the spectrum appears to result from the strong overlap of two bands, thus inhibiting direct observation of λ_{max}. These bands are thought to be those of the

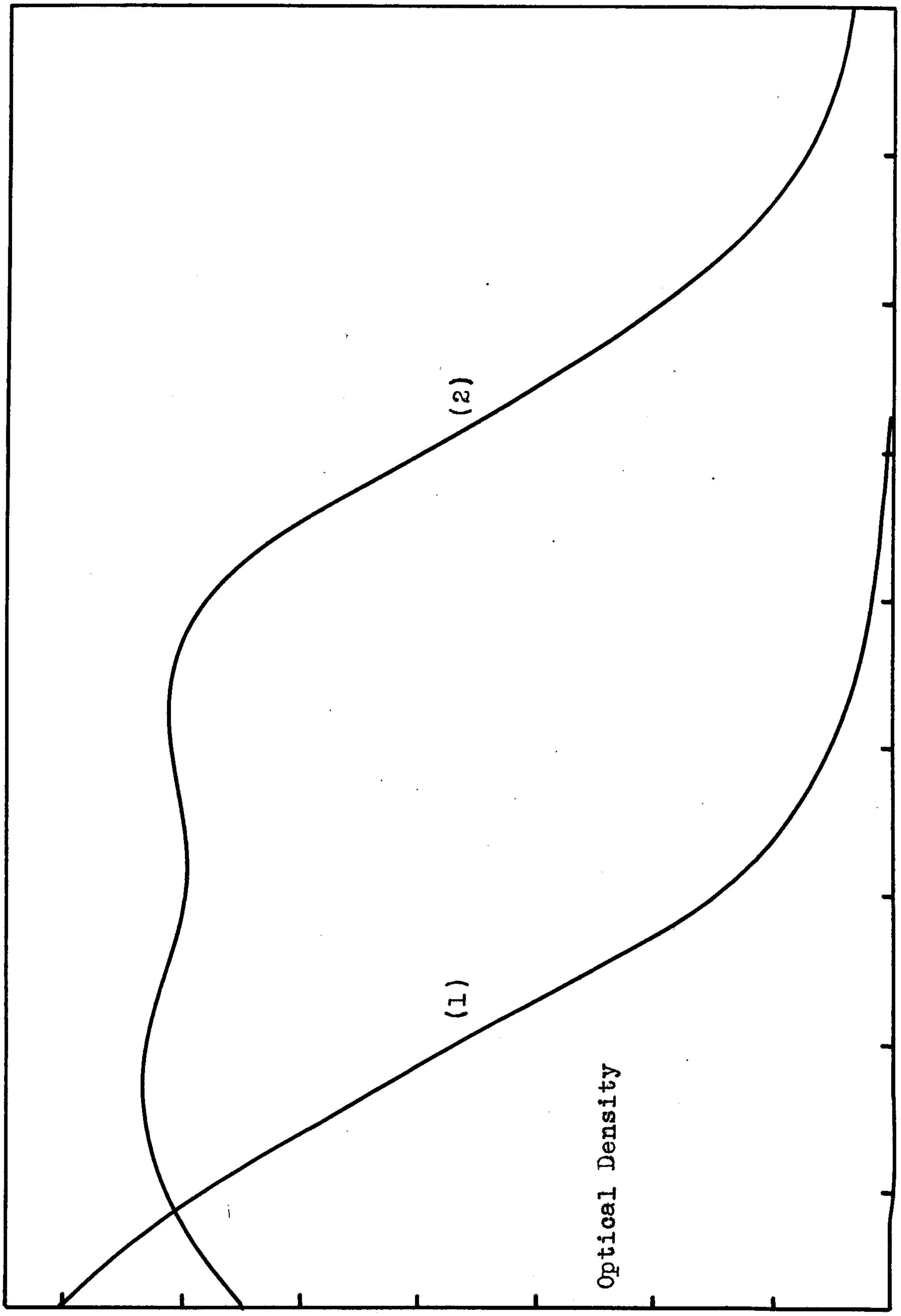


Fig.7.14. Spectra of KBr in (1) water (2) methyl cyanide

$^2P_{3/2}$. $^2P_{1/2}$ states of the bromine atom,[1,2] the theoretical splitting being 3,500 $cm.^{-1}$ This study has therefore been mainly concentrated on attempts to analyse the spectral results obtained in order to locate the peak position of the first absorption band of bromide.

(i) Gaussian Analysis

The procedure for submitting the experimental points obtained to Gaussian analysis by a Digital Computor has been described in Chapter Six. Three sets of over one hundred points obtained from a careful study of the bromide ion in water, at 3°, 25°, and 53°, were submitted. It was found that the computed results from bromide at 3° were so varied after "topping", "tailing", and "alternate topping and tailing," that they were untrustworthy. It was concluded that the points submitted probably contained several that were sufficiently inaccurate to invalidate the majority of the computed constants of the Gaussian curves: slight variations in temperature during spectral measurements may well have been the cause.

The average of all the results for bromide at 25° and 53° that were obviously allowable values gave the positions for the first absorption band as 196.5 and 198.1 mμ respectively. Assuming that the band shifted linearly with temperature dE_{max}/dT was calculated as 36 cals/deg., a value which compares most favourably with that for iodide in water, 33 cals/deg.

Analysis of the spectra of potassium bromide in methyl cyanide by computor showed that the number of points submitted (around 15) was insufficient for accurate results.

(ii) Analysis of effect of temperature.

The long wavelength edge of the spectrum obtained from potassium bromide in methyl cyanide was plotted, in the 240 mµ region, at five different temperatures. Graphs of transition energy (k.cals) against temperature were then plotted for eleven different optical densities and values for dE/dT calculated. These were then plotted against E^{20°, obtained from the graphs, and a straight line drawn through them. Thus, if it is assumed that on raising the temperature the band shifts and broadens; that the broadening increment is linearly proportional to the transition energy; and that dE_{max}/dT is the same as for iodide (55 cals./deg.), then the straight line can be extrapolated to this value and hence a measure of $E^{20^\circ}_{max}$ obtained. $E^{20^\circ}_{max}$ was found to be 219±3 mµ., depending upon the slope of the line chosen. Thus the spectra have to be measured with an accuracy greater than which is experimentally possible at the moment before more than a qualitative result is obtained.

(iii) Construction to obtain λ_{max}.

Fig.7.15. shows an analysis of bromide in methyl cyanide. This type of analysis can only be performed on spectra in which it is estimated that the effect of more than 50% of the second bromide band is being observed. The procedure is:

(1) Find the mid-point of the spectrum by the method of rectilinear diameters, as far as possible, and by observation of the mid-point of the shallow trough between the two peaks, the latter procedure probably being the more reliable.

(2) It is assumed that the two hidden bands are of equal height and shape, thus the mid-point of the observed spectrum results from a 50% contribution of each band. The half-height of this mid-point is then plotted.

(3) The lower half of the long wavelength edge of the observed spectrum is then plotted commencing from this point in the directions of higher and lower energies.

(4) These curves are then subtracted from the experimental one thus completing the analysis.

(5) The method of rectilinear diameters on the first (analysed) bromide band shows the accuracy of the original assignment of the mid-point of the spectrum. For bromide in methyl cyanide at 25° λ_{max} for the first absorption band was obtained as 217.6 mμ. Subtracting

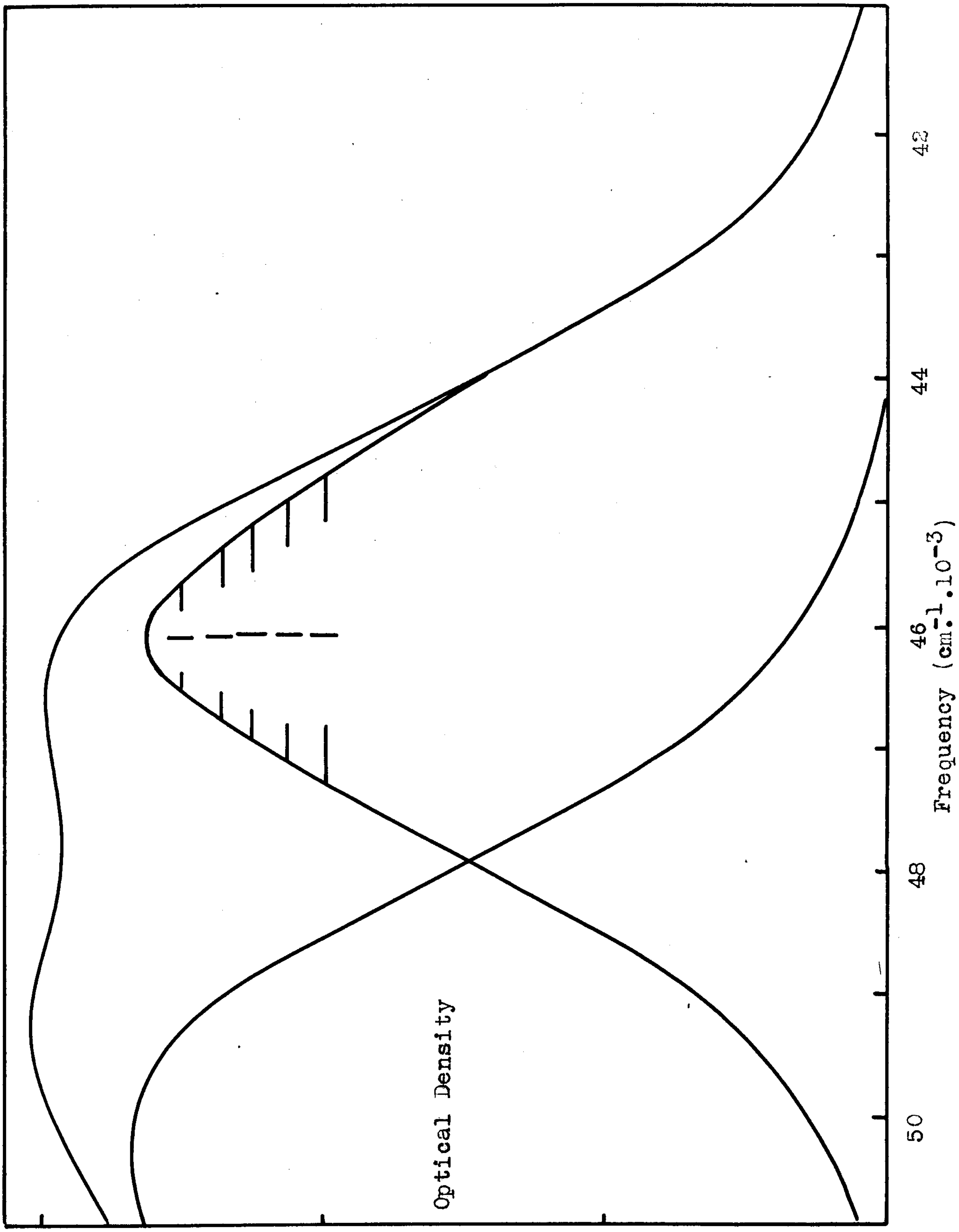


Fig.7.15. Analysed spectra of KBr in methyl cyanide

from this the value for the theoretical splitting of of the $^2P_{3/2}$. $^2P_{1/2}$ states of bromine (3,500 cm.$^{-1}$), a value of 201 mu was obtained for λ_{max} of the second band. This is feasible from the spectral results. However, it may be observed that the general shape of the spectrum of bromide in methyl cyanide is very similar to that of bromide in water, as reported by Scheibe (Fig.1.2.). The reason for the pronounced broadening of the second band is not known: it may be due to experimental error or the appearance of another band.

When this analysis was applied to a similar spectrum at 40° it was then possible to calculate a value of $dE_{max}/dT = 55$ cals./deg. Although this is numerically the same as iodide in methyl cyanide, it must be subject to somewhat greater limits or experimental error.

The energy difference for the calculated values of $E^{20^\circ}_{max}$ in water and methyl cyanide for bromide compares well with the corresponding energy difference for iodide in these solvents.

(c) Zinc and Cadmium Iodide Complexes.

(1) Pure Solvents.

The iodides of zinc and cadmium have been examined by ultraviolet spectroscopy in the following solvents: <u>iso</u>-propanol, <u>n</u>-butanol, and methyl cyanide. No systematic solvent dependence was observed. Values for

λ_{max} are recorded in Table 7.5., the results of other workers have been given in Table 1.1. Values for λ_{max} were found to agree with the accepted literature values of 9,000.

Doehlemann and Fromherz[47] have shown that in concentrated aqueous solutions of zinc and cadmium iodides they found bands at 238.5 and 250 mμ respectively. Using the thinnest cells available, and the corresponding maximum concentration allowable, we were unable to obtain these bands. However, the cells used by Doehlemann and Fromherz were far thinner.

(2) Effect of Temperature.

The bands were found to be slightly affected by change in temperature. The values of λ_{max} found at 3°, 25°, and 40° are recorded in Tables 7.6. and 7.7., together with the calculated values of dE_{max}/dT.

(3) Effect of added salts.

When anhydrous zinc perchlorate was added to zinc iodide in the above three solvents (equal amounts being added to the blank) a new band, of lower molar extinction coefficient, appeared at higher energies. As progressive amounts of the perchlorate were added the observed effect was that the original band appeared to broaden and shift and then narrow when it reached a steady value (Fig.7.16 and Table 7.8.).

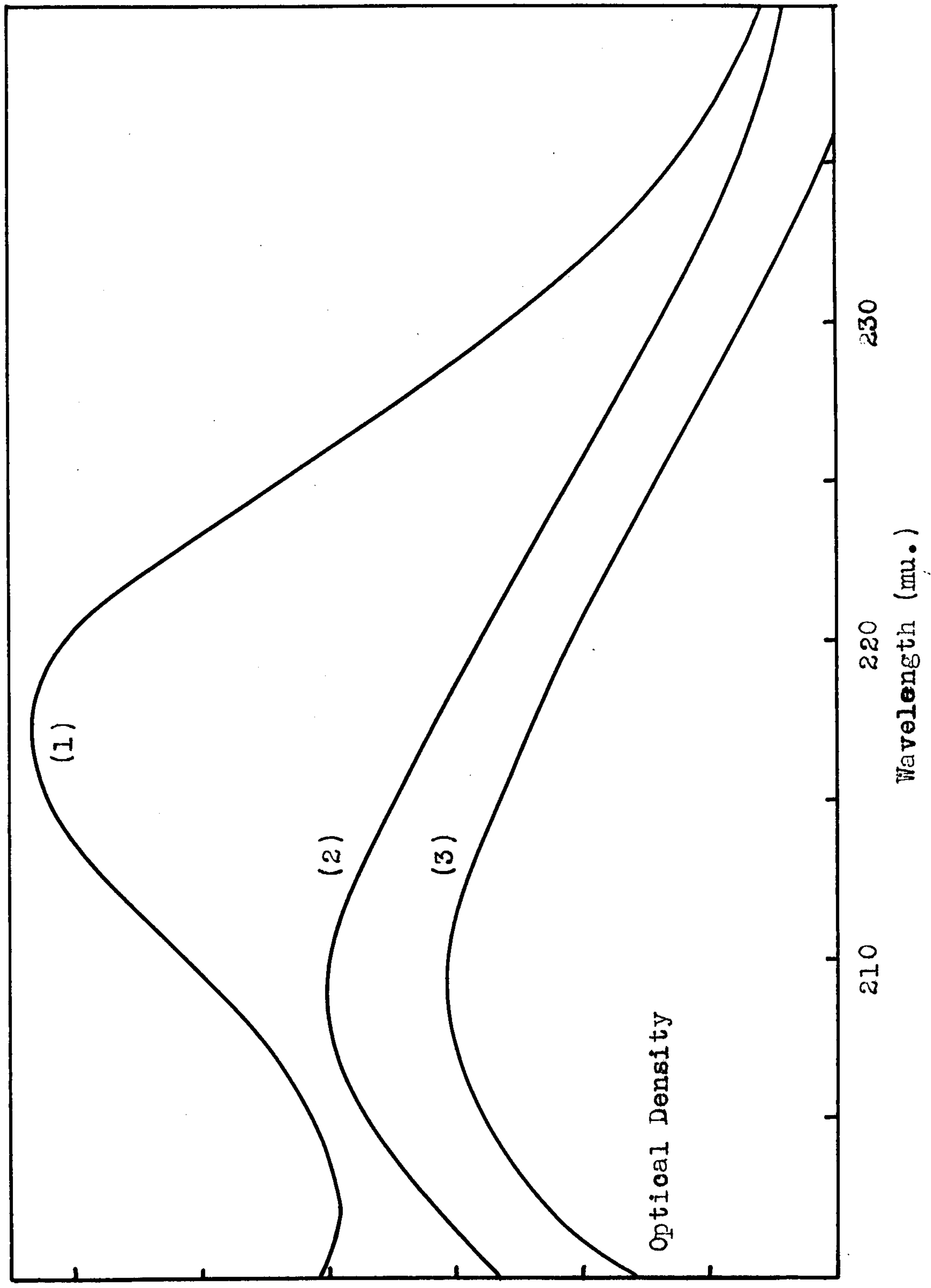


Fig.7.16. Spectra of ZnI_2 in <u>iso</u>-PrOH

(1) in pure solvent
(2) with some $Zn(ClO_4)_2$
(3) with excess $Zn(ClO_4)_2$

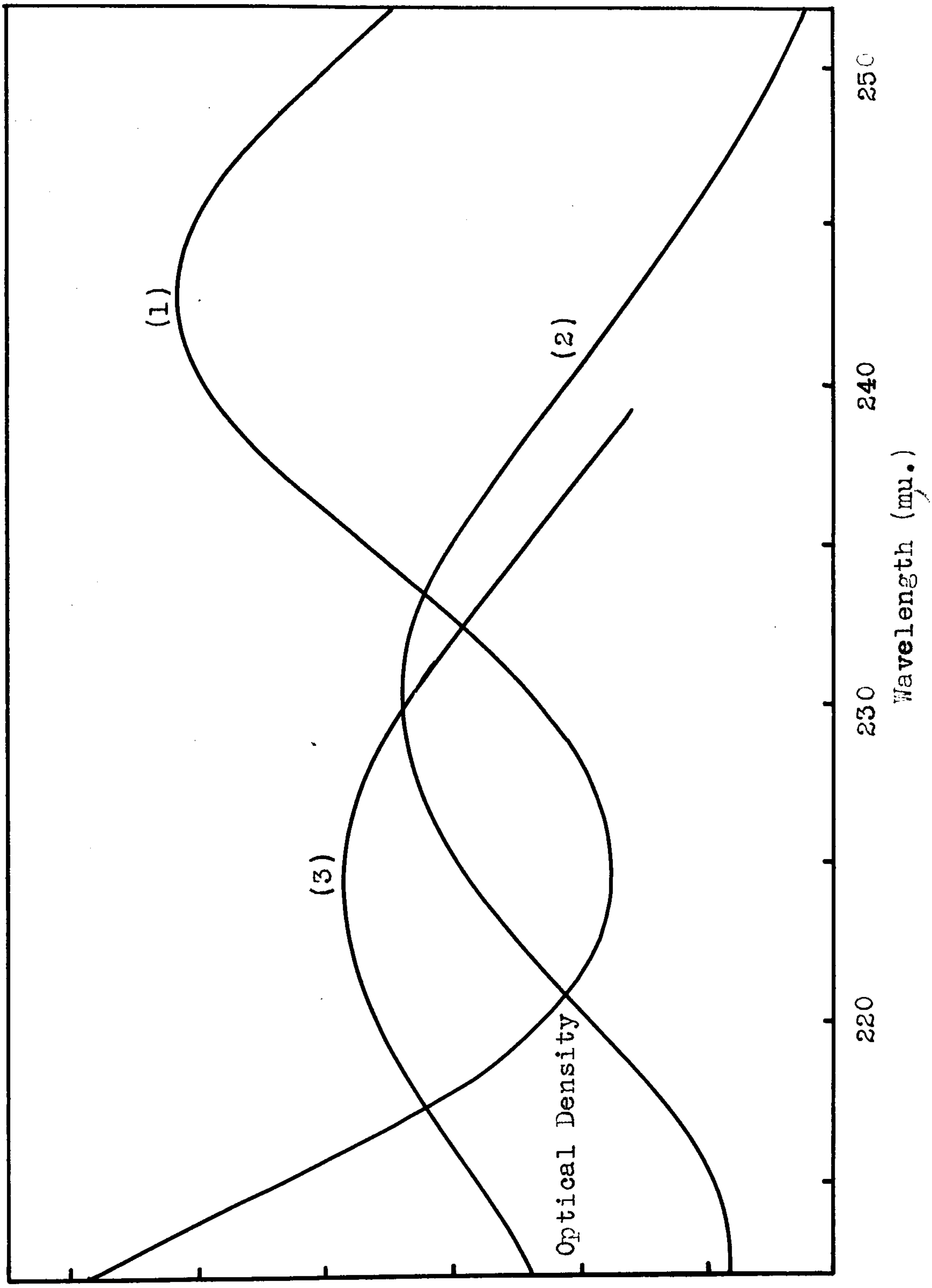


Fig.7.17. Spectra of CdI_2 in iso-PrOH
(1) in pure solvent
(2) with some $Cd(ClO_4)_2$
(3) with excess $Cd(ClO_4)_2$

Table 7.5.

Values of $E^{20^\circ}_{max}$ for ZnI_2 and CdI_2 in various solvents

Solvent	ZnI_2	CdI_2
iso-PrOH	131.08	118.23
n-BuOH	131.71	117.73
MeCN	131.83	117.69

Table 7.6.

Values of λ_{max} at various temperatures and dE_{max}/dT for ZnI_2

	Temperature			dE_{max}/dT
Solvent	3°	26°	40°	(cals./deg.)
iso-PrOH	217.55±0.05	218.25±0.25	218.95±0.05	22.6
n-BuOH	216.9±0.1	217.1±0.015	217.8±0.05	16→22
MeCN	216.55±0.05	217.05±0.05	217.6±0.01	15

Table 7.7.

Values of λ_{max} at various temperatures and dE_{max}/dT for CdI_2

	Temperature			dE_{max}/dT
Solvent	3°	26°	40°	(cals./deg.)
iso-PrOH	241.9±0.1	241.9±0.05	241.9±0.05	- 3 ⟶ + 3
n-BuOH	242.3±0.2	243.1±0.025	243.45±0.01	14
MeCN	242.9±0.1	243.05±0.05	243.35±0.05	7

Corresponding results were obtained on addition of cadmium perchlorate to cadmium iodide solutions. Although the cadmium perchlorate was not completely anhydrous (See Chapter Six) this fact did not appear to affect the results (Fig.7.17. and Table 7.8.).

Since iodide ions absorb strongly in this region the effect of the addition of excess potassium iodide could only be observed in the case of cadmium iodide in alcohols. Evidence was obtained for a band at lower energies, at ca. 248 mμ. The molar extinction coefficient of this band could not be accurately determined. (Fig.7.18.)

Table 7.8.

Values for $_{max}$ for solutions of ZnI_2 and CdI_2 containing excess $Zn(ClO_4)_2$ and $Cd(ClO_4)_2$ respectively.

Solvent	ZnI_2	CdI_2
iso-PrOH	209.2 ± 0.3	227.9 ± 0.1
n-BuOH	210.2 ± 0.3	225.55 ± 0.25
MeCN	211.8 ± 0.3	225.1 ± 0.1

(4) Diffuse Reflectance Spectra.

Diffuse reflectance spectra were measured for diluted zinc and cadmium iodide powders and are shown in Fig.7.19. The procedure for hygroscopic salts had to be used in the case of zinc iodide and it was not found possible to resolve any bands in zinc iodide powders.

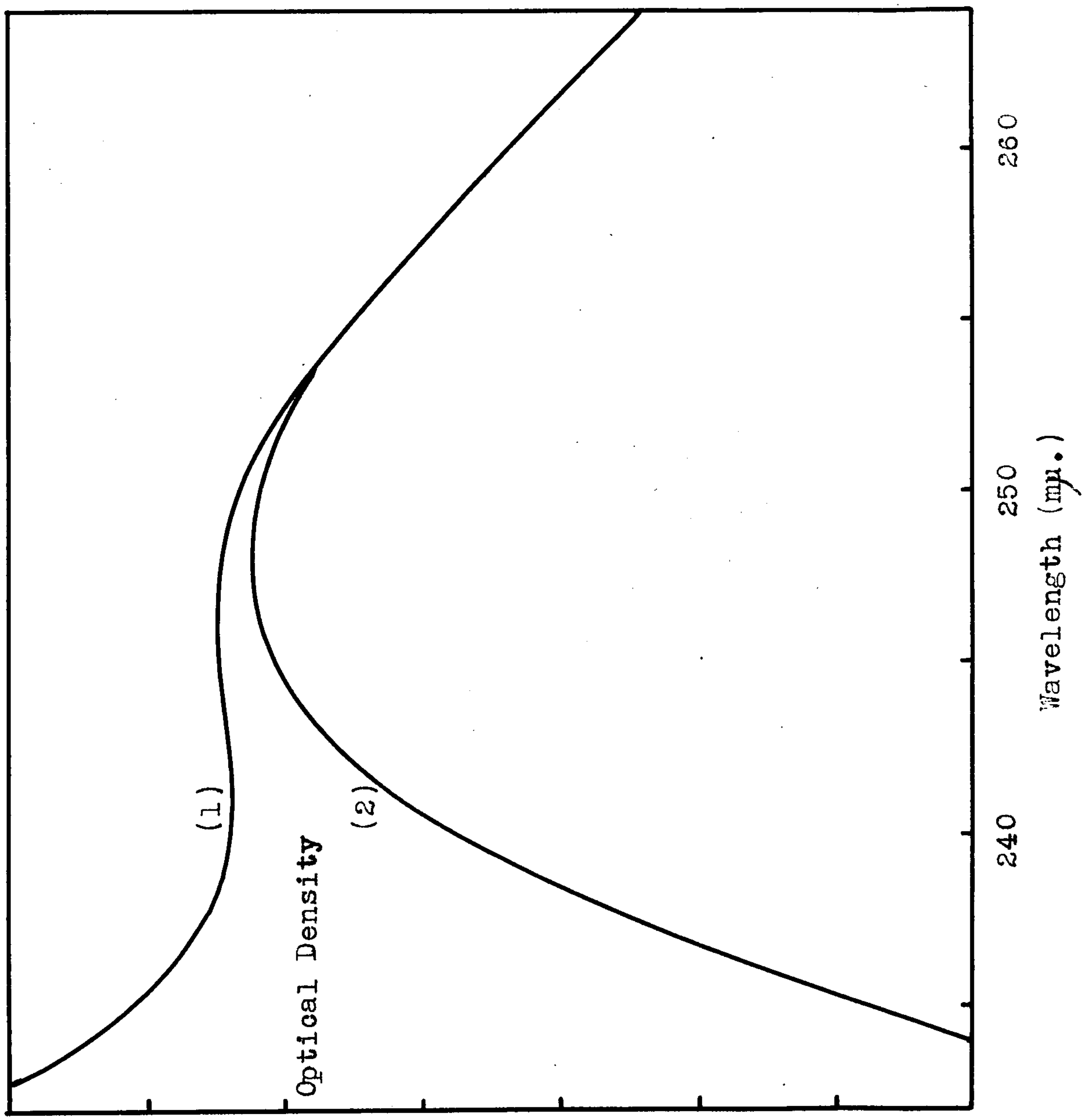


Fig.7.18. Spectra of CdI_2 + excess KI in n-BuOH
(1) using n-BuOH blank
(2) with same concentration KI in n-BuOH blank

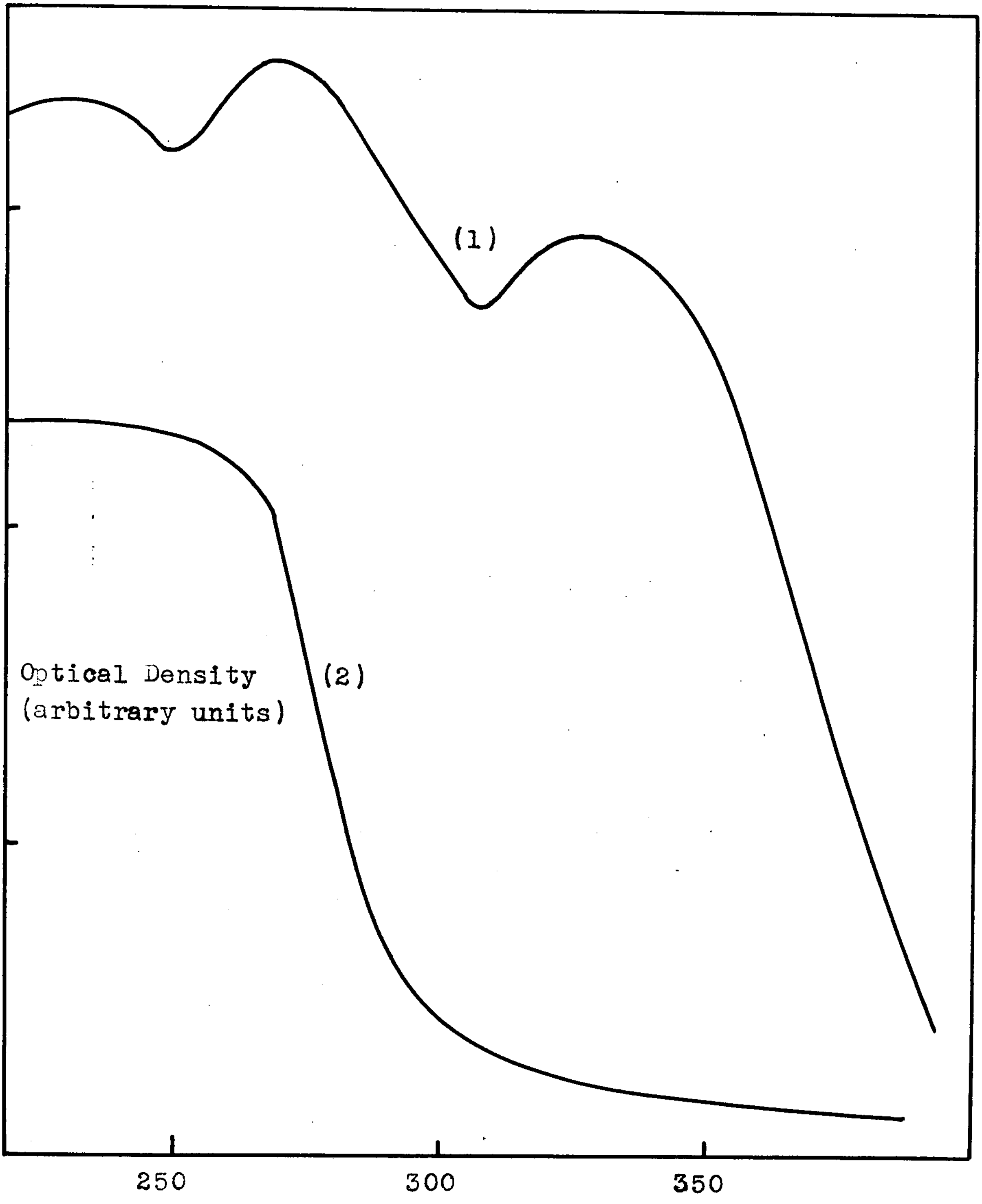


Fig.7.19. Diffuse Reflectance Spectra
(1) CdI_2 (diluted) (2) ZnI_2 (diluted)

(d) Mercury Iodide Complexes.

Preliminary investigations have been made on the effect of solvent, temperature, and added salt on the ultraviolet spectrum of mercuric iodide.

(1) Pure Solvents

Spectra have been measured for mercuric iodide in a variety of solvents; Table 7.9. lists these solvents and the values found for $\lambda_{max}^{20^\circ}$ (mμ) (See also Fig.7.20.). Mercuric iodide was found to be readily soluble in all solvents except water and iso-octane. Fromherz and Lih[32] state that the solubility of mercuric iodide in water does not exceed 0.00013 M. It was found to be even less soluble in iso-octane; however a band at 275 mμ. could be established. In methyl cyanide mercuric iodide appeared to dissociate to some extent since in this solvent a shoulder appeared in the 290 mμ region: Beer's Law was also not accurately obeyed. The molar extinction coefficient appeared to be around 6,000, the value quoted in the literature. In N-N-dimethylformamide mercuric iodide appeared to dissociate even further, a distinct band appearing at 301 mμ as well as the 273 mμ band.

(2) Effect of Temperature.

In water, methyl cyanide and methylene chloride the band position of mercuric iodide appeared to be completely insensitive to temperature over a 40° range:

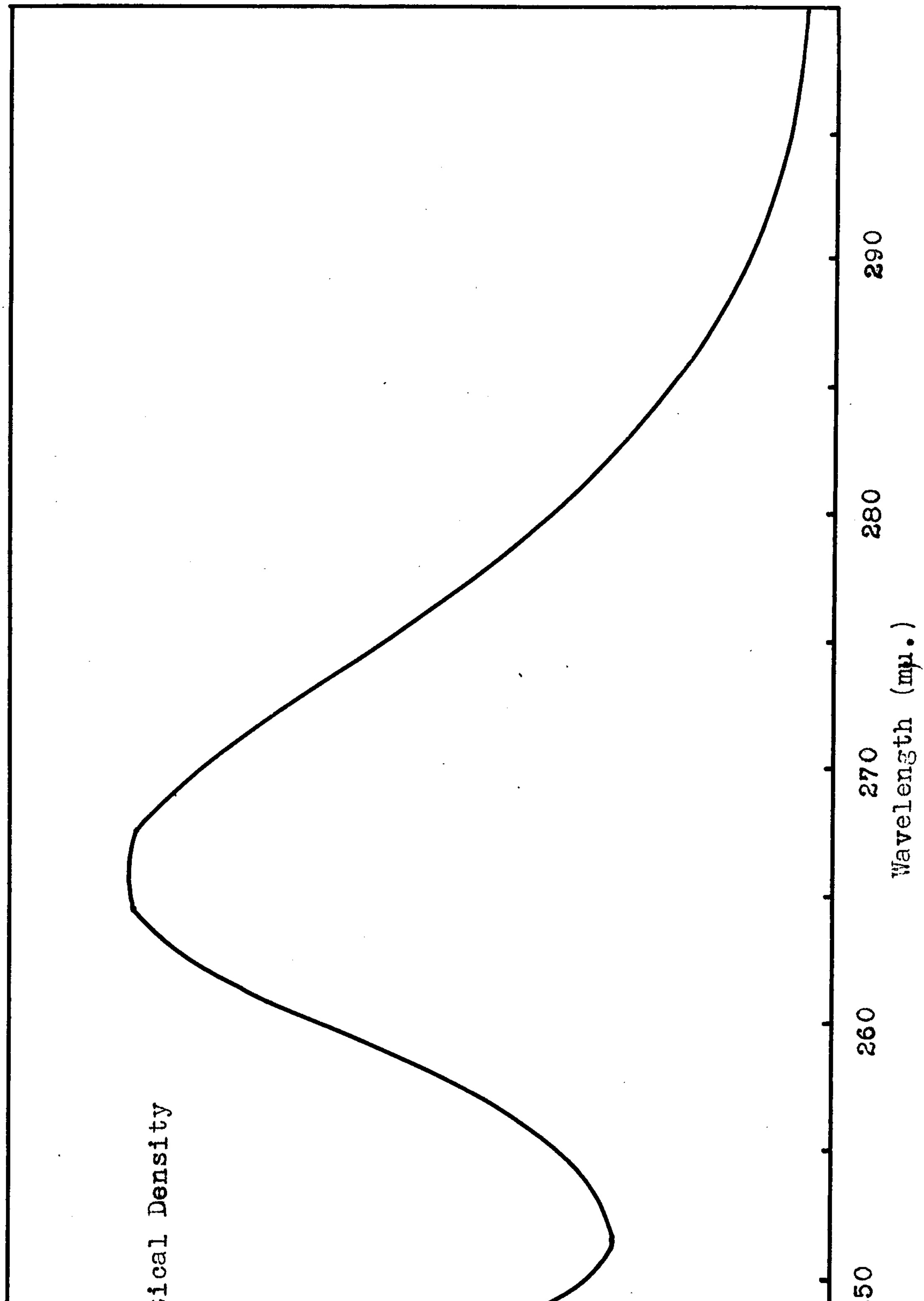


Fig.7.20. Spectra of HgI_2 in methylene chloride

all that was observed was a slight decrease in bandwidth with a corresponding increase in band height on decreasing temperature.

(3) Addition of tectra-n-butylammonium iodide.

The effect of added iodides on the spectra of mercuric halides in water and ethanol have been investigated by Fromherz and Lih[32] and are summarised in Table 1.2. The effects of the addition $(\underline{n}\text{-Bu})_4NI$ to mercuric iodide spectra have been investigated and are summarised in Table 7.9. In all cases the spectra were found to be different to those found for mercuric iodide with excess iodide in water and ethanol.[32] A typical example is shown in Fig.7.21. and this may be compared with Fig.1.6. It can be seen that whereas in water two bands are reported at 324 and 265 mμ., this study shows that on addition of iodide the original band shifts slightly to higher energies and a new band developes in the 305 mμ region, a shoulder also appearing in its long wavelength edge in the 340 mμ region. On increasing the amount of iodide added the shoulder was not resolved; indeed the ratio of the relative heights of the 305 mμ band and the shoulder appeared to remain constant at around 2:1.

However, the above results were not found in the case of the high dielectric solvent N-N-dimethylformamide. Addition of increasing amounts of $(\underline{n}\text{-Bu})_4NI$ caused the

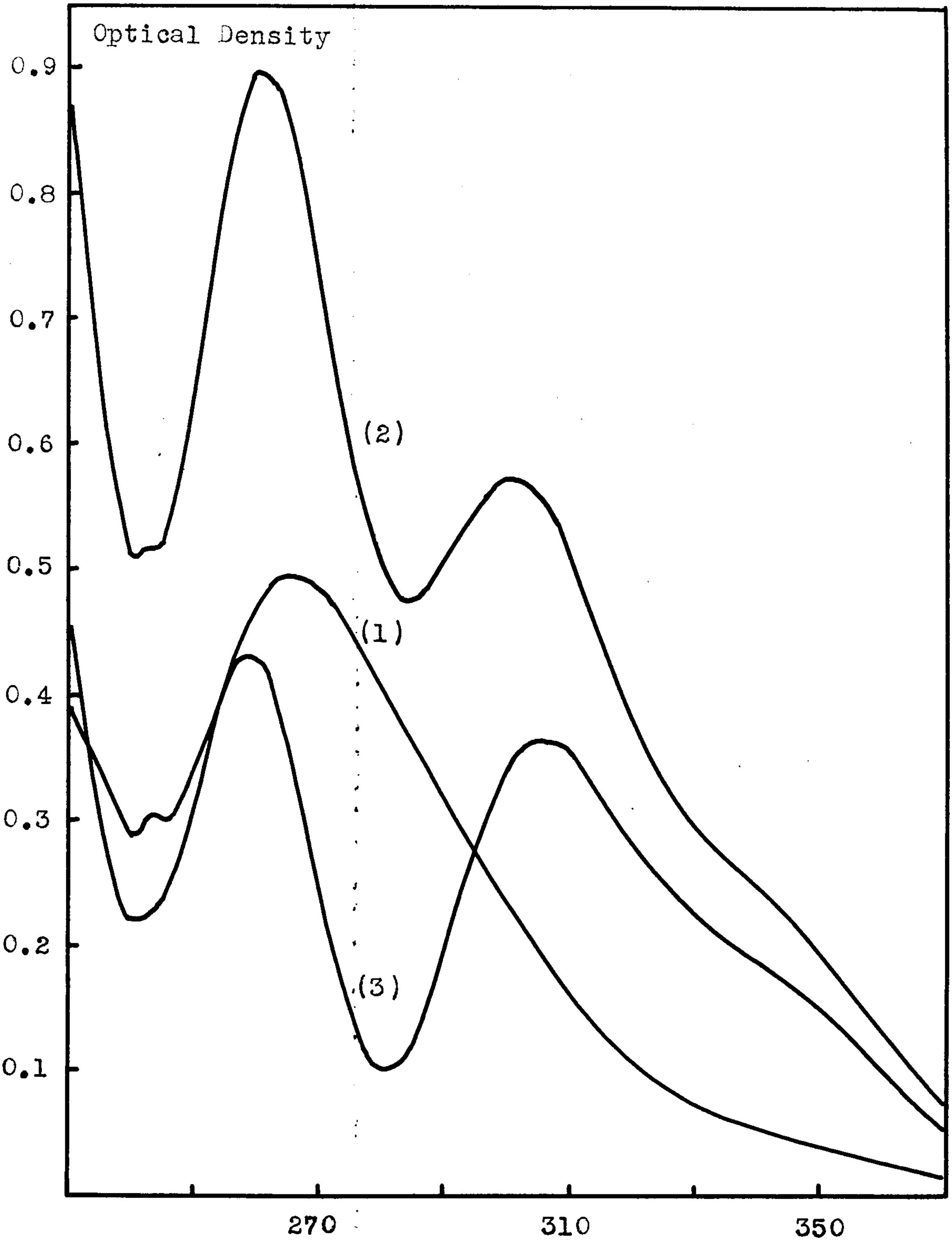


Fig.7.21. Spectra of HgI_2 in methyl cyanide
(1) in pure solvent
(2) with some $(n\text{-}Bu)_4NI$
(3) (1) subtracted from (2)

301 mμ band to shift to 305 mμ. A shoulder then began to appear in the 330 mμ region and on further addition of $(\underline{n}\text{-Bu})_4$NI the 305 mμ band began to decrease in height as another band was located at around 333 mμ. This band was finally resolved at 335.5 mμ on addition of more iodide, the 305 mμ band then being completely lost. Although the addition of $(\underline{n}\text{-Bu})_4$NI caused the 273 mμ band to shift to higher energies where it could not be resolved due to the intense absorption of N-N-dimethylformamide below 263 mμ (Table 6.1.), a rising absorption into the ultraviolet was always observed at all concentrations of $(\underline{n}\text{-Bu})_4$NI. Pertinent spectra are shown in Fig.7.22 and 7.23.

Table 7.9.

Values of $\lambda^{20^\circ}_{max}$ for HgI_2 in various pure solvents, and in the presence of added $(\underline{n}\text{-Bu})_4$NI.

		With $(\underline{n}\text{-Bu})_4$NI	
Solvent	$\lambda^{20^\circ}_{max}$(mμ)	$\lambda^{20^\circ}_{max}$(mμ)	
Water	265	-	-
Methyl cyanide	265	260.5	<u>ca</u>.301
Methyl formate	264	259	<u>ca</u>.303
Methylene chloride	272	259.5	<u>ca</u>.307
Ethyl acetate	269	261	<u>ca</u>.306
<u>iso</u>-octane	275	-	-
N-N-dimethylformamide	273	- [a]	<u>ca</u>.305

[a] Compare Table 6.1.

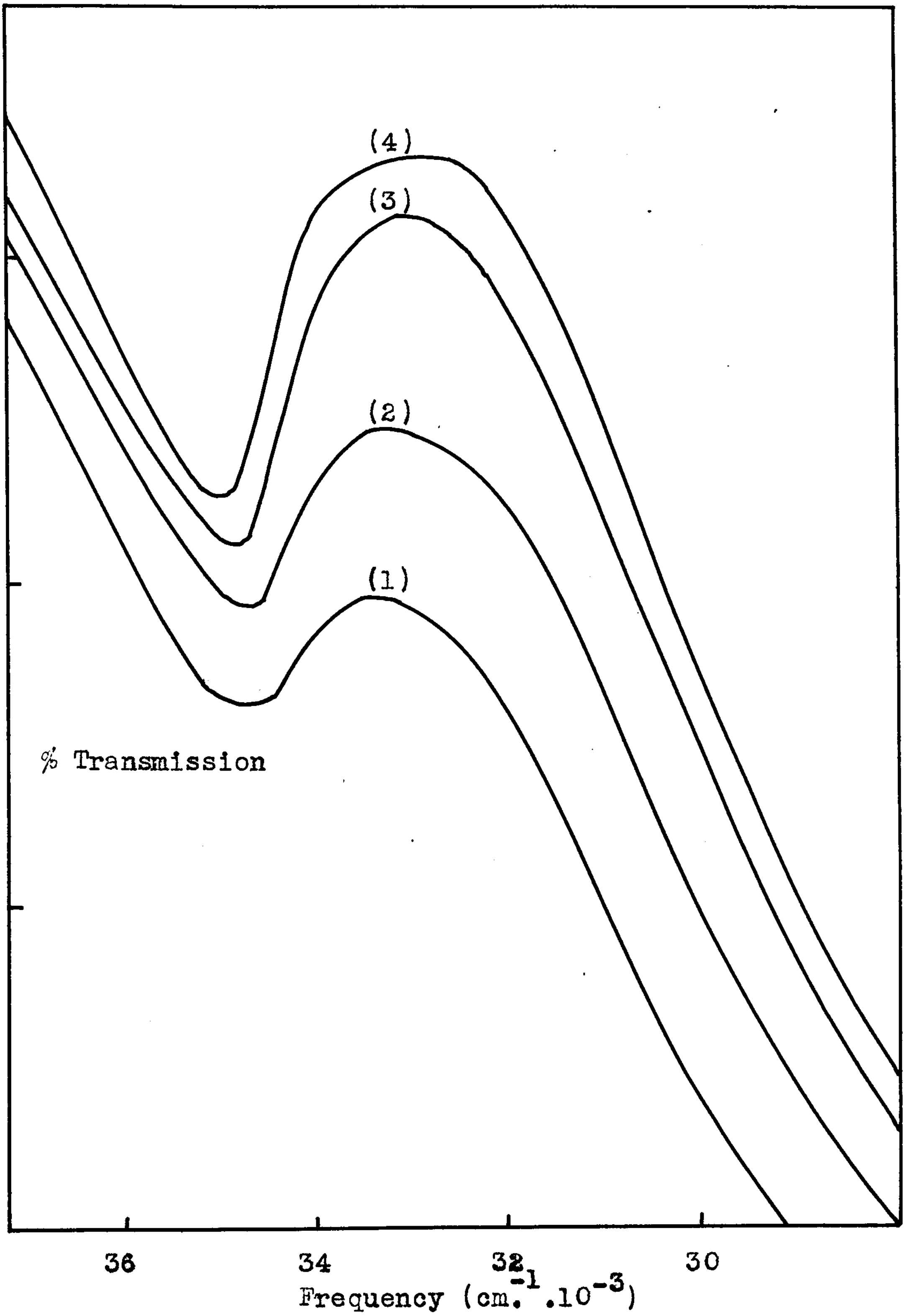


Fig.7.22. Spectra of HgI$_2$ in N-N-dimethylformamide

(1) in pure solvent
(2)→(4) effect as increasing amounts of
(n-Bu)$_4$NI are added

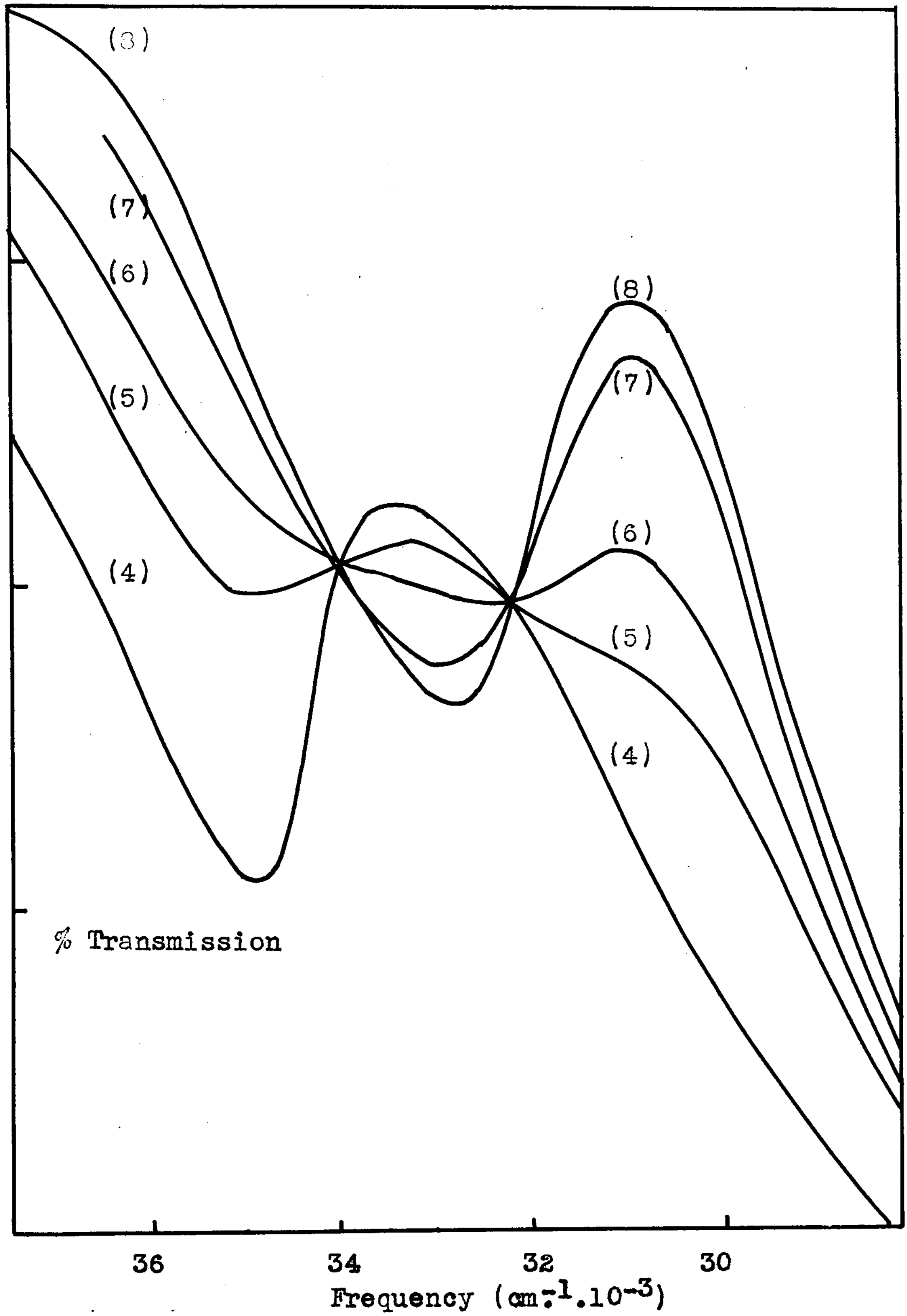


Fig.7.23. Spectra of HgI_2 in N-N-dimethylformamide Continued from Fig.7.22. showing effect of still further addition of $(n\text{-}Bu)_4NI$

CHAPTER EIGHT

Discussion

(a) C.T.T.S. Spectra and Ionic Solvation.

In order to interpret the spectral results in terms of ion-solvent interactions it is necessary to have a reasonable idea concerning the nature of the orbital of the excited electron. It has been shown in Chapter One that the suggestions that the electron is ejected to bulk solvent as a solvated electron or that it is associated with a specific solvent molecule are not consistent with experimental results.

The present day concept of C.T.T.S. spectra is that of an electron moving in a discrete, centrosymmetric orbital which is largely described by the potential field of the polarised solvent molecules and electronic repulsion effects. We have seen in Chapter Three that it is impossible to obtain, at present, more than a qualitative picture of the structures of solvents and the arrangements of their molecules around ions. Thus any mathematical treatment of C.T.T.S. spectra is at once hampered by this limitation, and it is therefore necessary to make certain postulates concerning the structures of solutions: the suitability of the postulates being upheld, or otherwise, by the final results of the treatment.

There are two extreme views which require consideration: the electron may move in a diffuse orbital embracing a considerable proportion of the surrounding solvent[24,35] or it may be closely confined to the first layer of solvent molecules.[25,26] It would therefore be well to examine comparable systems which have been thoroughly investigated mathematically.

(i) F-centres and Ionic Crystals.

Comparison of the excited state for aqueous iodide with bands originating in a crystal lattice will only prove fruitful if the "confined" approach is correct. This is because the first shell of orientated solvent molecules around iodide will closely resemble the crystalline environment, but beyond this region no comparison is possible.

The most recent studies upon F-centre electrons indicate that they are closely confined within the anion vacancy. These electron spin resonance[141] and electron nuclear double resonance studies[142] show conclusively that on the six cations defining the vacancy the unpaired electron density is quite high, and on the next shell of cations, extremely low. In a recent review by Gourary and Adrian[143] various theoretical treatments are considered. These authors have concluded that to postulate that the crystal may be considered a polarisable continuum is to be internally inconsistent since the resulting wave functions are far too compact for the continuum model to be even approximately true. They have been able to accommodate the electron spin resonance and electron nuclear double resonance results in their theoretical analysis.

It would seem reasonable to suppose that the orbital for the first exciton band for iodide in an ionic lattice may be subdivided into two component orbitals, one close to the central iodine atom and the other on the periphery of the vacancy. The former will be an orbital very similar to the 6s atomic orbital of iodine, and the latter, being close to the first shell of cations, will be similar to the outermost part of the ground state orbital of an F-centre. Thus it follows that since the "confined" model is most suitable for the F-centre, it will also be most suitable for the first excited state of iodide in an ionic crystal.

(ii) Molten Salts

Although the arrangements of cations and anions around each other in molten salts will not be quite so specific as in a crystal lattice it is still reasonable to assume that it is much the same as in a crystal. Recently Rhodes and Ubbelohde have studied crystal structure by ultraviolet absorption spectra before and after melting.[144] These authors use the "confined" model approach[26] as describing the situation and show that there is a proportionality between dE_{max}/dT and the coefficient of linear expansion of the crystal. However their measured peak positions must be viewed with some suspicion since they are not in the expected region of the spectrum. Their extinction coefficients are only a quarter of the usual value obtained. Further, in many cases, in the far ultraviolet region, extinction coefficients of zero are recorded. Such results are not recorded for the compounds investigated in other systems in this region: indeed, the very sharp decrease in extinction coefficient is very indicative of stray light effects.

Greenberg and Sundheim[145] have measured the ultraviolet absorption spectra of potassium bromide and iodide in molten KCl/LiCl and KBr/LiBr eutectics. Unfortunately, their results must be disregarded on similar grounds to those of Rhodes and Ubbelohde since they measure peaks in the optical density regions 2 - 3: Boston and Smith (private communication) have calculated that Greenberg and Sundheim's bands can all be accounted for in terms of stray light effects and are therefore spurious.

(iii) The "expanded" model.

The foregoing results show that the "expanded" model must be rejected in favour of the "confined" model. However, other aspects of the "expanded" model will now be considered. In attempting to describe the iodide ion in solution Platzman and Franck[24] treat the solvent as a continuum and ignore the molecular nature of the primary solvation layer. The wave function that results from their calculations is that for a hydrogen atom with an effective charge of 0.55. They reject the 1s level in favour of a 2s level which then turns out to be quite diffuse, and since they do not consider the central iodine atom this surely implies that the lowest energy state should be a 1s state. This state is found to be closely confined and thus it would appear that their model is not self consistent. Further, as has been discussed previously, if the electron were in a 2s type orbital this would place it close to the lone pair electrons of the first layer of water molecules which would exert a repelling force upon the electron, and the evidence obtained from other solvation studies suggests that there is no orientation of water molecules outside the first layer.[102,103]

Since the treatment of Stein and Treinin[35] still uses the basic assumptions of Platzman and Franck,[24] not much weight can be placed upon their "spectroscopically significant radius", r_0^*. Further, their method of calculating E_{max} for aqueous iodide depends largely upon the value of H_{ion}, a value which is by no means known to the degree of accuracy required by their equation.

(iv) The "confined" model

When the ultraviolet absorption spectra of iodide in ionic crystals and in solution are compared a marked similarity may be noticed. The energetic separation between the first and second bands in both cases is close to the theoretical value for the $^2P_{3/2}$, $^2P_{1/2}$ states of an iodine atom. They also fit a Gaussian error curve remarkably well. Lowering the temperature causes the bands to shift to higher energies and sharpen. Graphs of E_{max} against temperature show a linear relationship except close to 0^oK. The literature results for various alkali iodide crystals are included on Fig.7.4. and can be seen to fit quite closely to the correlation of Smith and Symons.

The spectra of iodide in a foreign lattice has not been thoroughly investigated. However, it has been found that the spectrum of iodide in potassium bromide crystal as host is shifted markedly towards the far ultraviolet.[146] This result may be compared with the similar shift obtained for iodide in aqueous salt solutions.[25,26] Since the lattice vacancy available to iodide in potassium bromide must be smaller than that occupied by iodide in potassium iodide, the ground state of iodide will be somewhat compressed. Consequently in order to accommodate the observed shift it is necessary to postulate that the excited state is de-stabilised to a far greater extent than the ground state. Since the "expanded" model[24,35] requires all environmental changes to be related to the ground state, the excited orbital being so diffuse as to be essentially unaffected, this shift is not in accord with this model: on the other hand, it is entirely consistent with the "confined" model.[25,26]

(v) Oscillator Strengths.

The oscillator strength (f) of a band is a measure of the probability of the transition causing optical obsorption and, since the band of iodide is a Gaussian distribution of energies, it is obtained by finding the area under the spectral curve. This may be carried out by one of three main methods:

(1) By direct measurement of the area under the absorption curve.

(2) By applying the formula for a transition from a ground to an excited state,

$$f = 4.31 \times 10^{-9} \int \varepsilon_\nu \, d_\nu$$

This can be written approximately as

$$f = 4.31 \times 10^{-9} \, \varepsilon_{max} . \Delta\nu$$

where ε_{max} is the molar extinction coefficient of the band and $\Delta\nu$ the band width at half-height in cm.$^{-1}$

(3) From the constants of the Gaussian equation that fits the curve. These constants can be obtained by submitting the experimental points outlining the curve to a Computor as described in Chapter Six. From the

Gaussian equation

$$y = Ae^{-\alpha(x-b)^2}$$

the oscillator strength is calculated by

$$f = 4.31 \times 10^{-9} A \sqrt{\frac{\pi}{\alpha}}$$

Since there are six p electrons on the iodide ion anyone of which can move into the excited orbital, the maximum value of oscillator strength for iodide is six. The oscillator strength for iodide in solution as estimated by methods (2) and (3) is about 0.25 for the first absorption band: the same value was also found for the second band of iodide in water.

Values for pure crystalline iodides are not very precise since the effective thickness of the crystals is difficult to measure but approximate values that have been calculated from the literature are listed in Table 8.1. It may be seen that the results approximate to those for iodide in various solvents. Comparison with iodide in molten alkali chlorides is more satisfactory. Boston and Smith (private communication) have measured the long wavelength edge of iodide in molten chlorides and, after fitting the band to a Gaussian curve, obtained an oscillator strength of 0.24, a result which is remarkably close to that for solvated iodide.

Thus comparison of oscillator strengths is a further means whereby the "confined" model is supported: since it is found to be the best procedure for describing the situation in ionic crystals, comparable oscillator strengths are not to be expected if the "expanded" model is the best analysis of C.T.T.S. spectra.

(vi) The "square well" approximation.

A very simple model has been used in an attempt to interpret environmental constraints on the spectrum of solvated iodide ions. Smith and Symons[25,26] have suggested that if polarisation changes were ignored it is possible to evaluate the kinetic energy of the electron in its excited state from the equation for an electron in a square-well of radius $\underline{r}_0$ and with infinitely steep walls. Other factors that have been ignored are (1) the presence of the iodine atom in the centre of the well, (2) the electron affinity of the surrounding solvent molecules, (3) the possible existence of other excited states, (4) that in the ground state of the well, and almost certainly in the case of other excited states, the electron may be able to "see" the top of the well, and (5) no estimation is made of the situation outside the well and the possible influence of exterior forces upon the well. Despite all this, they obtained reasonable qualitative agreement with experiment.

Because, at the moment, it is not possible to make allowances for all the ignored facets of the "square-well", oscillator strengths cannot be calculated on this model. Further, since the transition probability depends upon overlap between the 5p level of the iodide ion and the orbital of the excited electron, this will only be important near the iodide ion. The simple approach of an electron in a 1s orbital in the "square-well" is completely inadequate in this region.

Table 8.1.

Oscillator strengths for the first band of iodide ions in various media

Medium	Water	molten alkali chlorides	CsI[a]	KI[b]
Oscillator strength	0.25	0.24	0.23	0.28

[a] Philipp and Taft, J. Phys. Chem. Solids, 1956, 1, 159.

[b] Pick, Landolt-Bornstein, Vol.6, Part 4, p.872.

However, appreciation of why the experimental oscillator strength for the first transition (0.5) is much less than the theoretical maximum of 6, may be helped since both the 5p and 6s functions of iodide change sign often, and at different regions in space, thus greatly reducing the overall transition probability.

The results of this study have shown that for solvents which are good ionic solvators the "square-well" model is still compatible with the experimental observations. However, two points raised by Smith and Symons require further consideration.

(1) The "points of attachment" postulate

Their suggestion[26] that the size of the cavity around iodide ions in solution may be dependent on the number of hydrogen atoms orientated towards iodide and the stereochemistry of the solvent has been mentioned on p.41. The present studies appear to uphold this postulate. For example, ammonia and acetone can have three "points of attachment" and have values of dE_{max}/dT greater than that for methyl cyanide (see Fig.7.4.). (cyclo-hexanone has a structure very similar to that of acetone and if it could be investigated might thus be close to the acetone value.) It might be reasonable to expect that the hydrogen atoms orientated towards iodide in the case of 1:3-dioxolane would be the two which are situated between the two oxygen atoms and not the other four. Electronic repulsion effects between neighbouring oxygen atoms, for stereochemical reasons, may well explain why the cavity, and hence dE_{max}/dT, is bigger for this solvent than for water, but still less than the value for methyl cyanide. The reason why the value for n-butanol is somewhat to the right of the theoretical line may mean that increasing temperature affects the long hydrocarbon chain in a manner that causes the rate of expansion of the cavity to be somewhat greater than that which would be expected. A systematic study of alcohols with increasing length and size of the hydrocarbon chain might prove interesting.

(2) Mixed Solvents

(a) Preferential solvation

In their work on iodide in mixed solvents Smith and Symons found that a plot of E_{max} against % mole fraction of added solvent was not linear (see Fig.7.5.) and that values obtained for dE_{max}/dT were greater than they would predict (cf. Fig. 1.3.) They attributed this to preferential solvation by the more polar component, usually water. They found that for mixtures of water and the lower alcohols, however, the curve obtained tended towards linearity with increase in temperature. A linear relationship has been observed for plots of mole % alcohol against the shift of the fluoride nuclear resonance band in concentrated potassium fluoride solutions and this linearity has been interpreted in terms of the composition of the first layer of solvent molecules around the anions being effectively that of the bulk solvent.[117] The concentration of potassium fluoride in the solutions studied was greater than that of the iodide solutions investigated by a factor of 10^3 and we felt that competition for the available solvent molecules in concentrated solutions might over-ride any preferential solvation effects. The spectrum of iodide in various water/methanol solutions containing 1.0 M potassium fluoride was therefore measured (Fig.7.5.) and it may be seen that deviations from linearity have been greatly reduced, just as was found at elevated temperatures.

(b) Specific complexing with solvent

Kosower[128] has suggested that the C.T.T.S. band for solvated iodide should correlate linearly with the Z-value of the solvent (cf. Chapter Four), and he found a correlation for aqueous ethanolic solutions (Fig.8.1.) Since he found that the solvents methyl cyanide, acetone, and dimethyl sulphoxide did not fall on this line he stated that iodide would form specific 1:1 complexes in these solvents, the bands observed being similar to a charge-transfer of the type postulated for pyridinium-iodide complexes. However, in these pyridinium complexes there must be a loss of a dipole on the formation of the neutral species. If the postulate that the excited orbital in C.T.T.S. spectra is centrosymmetric around the anion is correct, then there can be no loss or gain of a dipole during the movement of an electron into the excited state. The fact that methyl cyanide and acetone have high molar extinction coefficients and fit the correlation of Smith and Symons (Fig.7.4.) seems further evidence of no specific complexing in these solvents.

We think it unlikely that iodide and ammonia should form a 1:1 complex and have evaluated the *Z*-value of 0.880 ammonia from the intense absorption band in the 260 mμ region of pyridine N-oxide. Using our value of iodide in this solvent (Table 7.2.) we have included this result on Fig.8.1., together with values for iodide in aqueous dioxan, chloroform, methylene chloride, and *iso*-propanol. It may be seen that there is now no correlation, only a great scatter.

One further test was applied. If it is possible that iodide and acetone form a 1:1 complex, then in aqueous acetone one might expect to be able to measure two bands, one being due to purely solvated iodide ions (C.T.T.S.) and the other characteristic of the 1:1 complex. In all the mixtures studied a steady shift of the band was all that was observed (Fig.7.10.) and the appearance of a new band was never detected. Further, the spectrum of iodide in aqueous solution containing 45% mole fraction acetone (Fig.8.2.) was subjected to Gaussian analysis by a computor, and the computed curve was found to fit extremely closely to the experimental curve and showed no evidence of a hidden band. When the computed curve was subtracted from the experimental curve the long wavelength edge of a band was revealed. The peak position calculated for this band by the computor was close to that expected for a doublet of separation 7,600 $cm.^{-1}$, the separation of the $^{2}P_{3/2}$. $^{2}P_{1/2}$

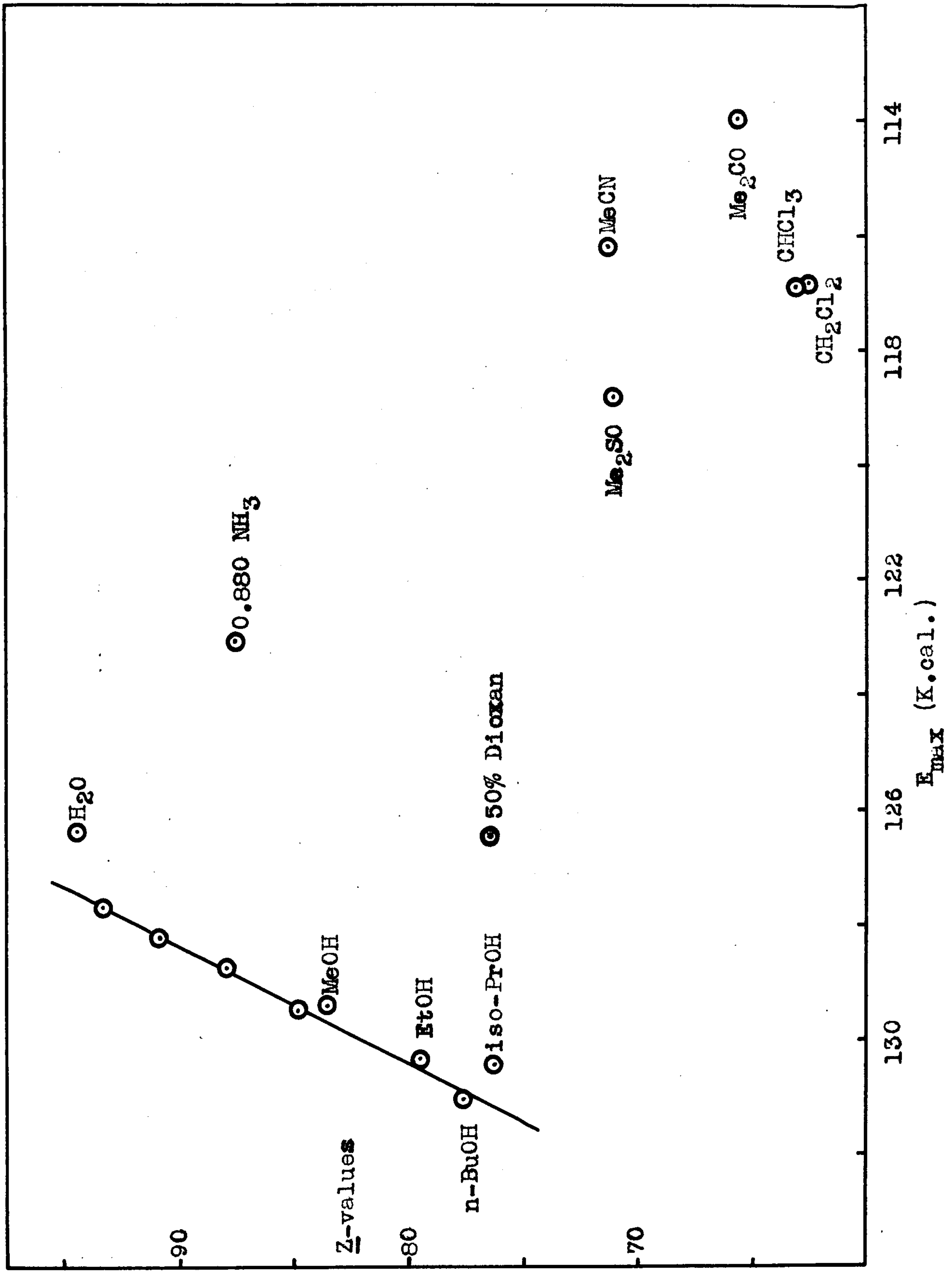


Fig.8.1. Z-values for various solvents against the values of E_{max}(K.cal.20^o) for iodide in these solvents.
The line is taken from Fig.1. of ref. 140. (Part II).
The unlabelled points refer to various water/ethanol mixtures.

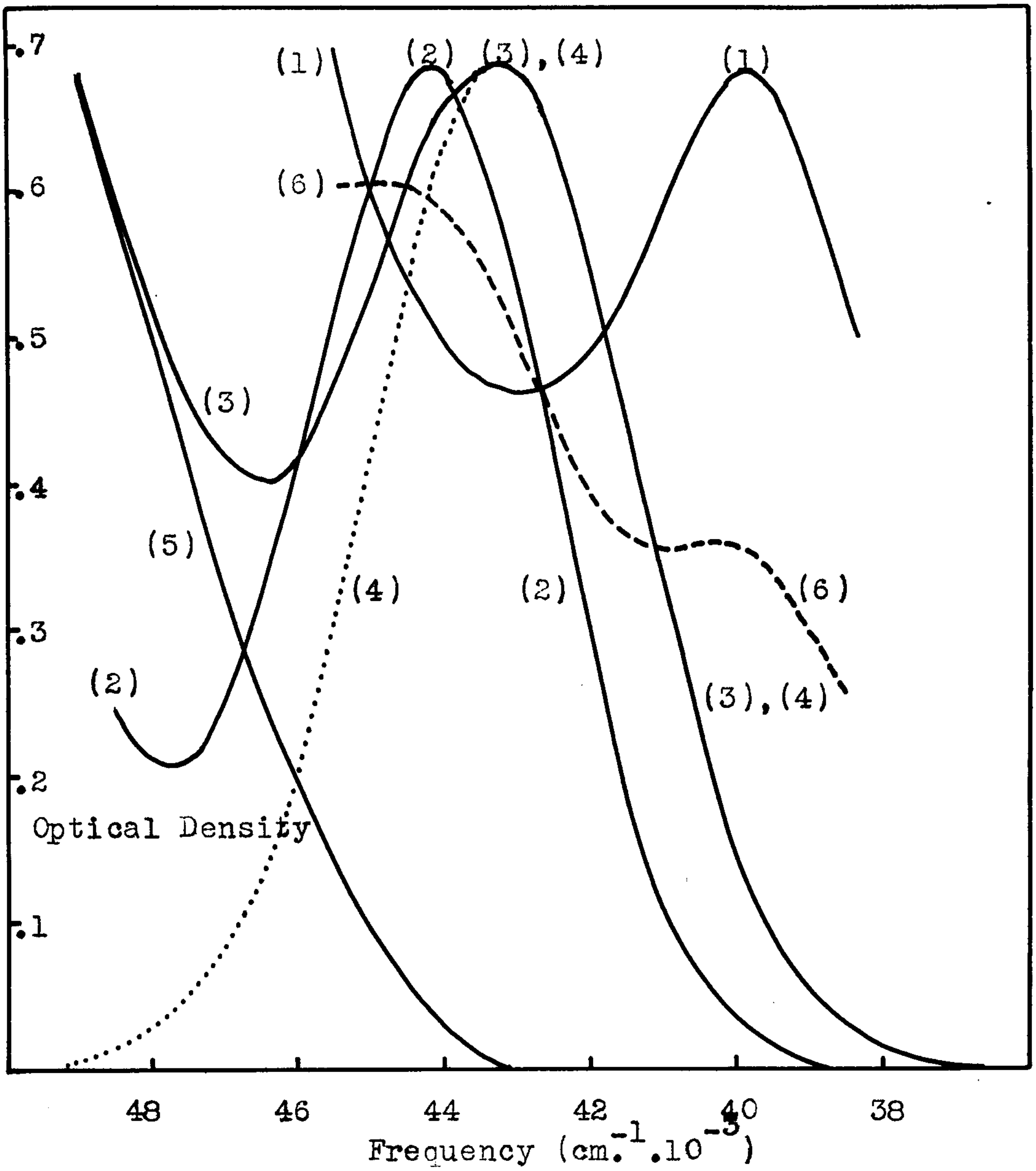


Fig.8.2. Example of the analysis of spectra of iodide in mixed solvents.

(1) Iodide in acetone (2) Iodide in water
(3) Iodide in 46% mole fraction acetone
(4) Gaussian Error Curve (5) Second iodide band obtained by subtraction of (4) from experimental band (3)
(6) Curve resulting from addition of 50%(1) to 50%(2)

states of the iodine atom. The broken curve in this figure was constructed from the addition of the two outer curves (iodide in water (a) and iodide in acetone (b)) to show the spectrum that would be expected if two distinct species were both present in equilibrium in equal concentration in the mixed solvent.

Thus it may be concluded that specific complex formation between iodide and solvent molecules in these solutions cannot be detected by spectroscopy.

(c) Concentrated aqueous electrolytes

The effect of added electrolytes on the spectra of aqueous solutions of iodide has now been found not to be completely independent of cation with constant anion. The iodide absorption bands appear to be steadily moved towards higher energies on addition of electrolytes, there being no evidence of the appearance of a new band even in almost saturated solutions. If λ_{max} for iodide is measured in, say, 1.0 M solutions of various alkali metal chlorides (Table 7.1.) it may be seen that the greater the cationic size, the greater the shift from the position of aqueous iodide. However, one must not argue that the effect of cations increases with ionic radius. One could equally well suppose a hypothetical "ideal" solution containing electrolyte which does not interact with iodide in any specific manner and assume that this reference band lies on the lower wavelength side of all the bands measured in real solutions. In this case increasing divergence from ideality would be attributed to decreasing size of the cation. Thus no definite conclusions are possible.

The actual behaviour of the iodide band in concentrated aqueous electrolytes is thought to be due to a combination of various effects including dehydration, fortuitous contacts and general polarisation. Very marked shifts have been found for the ^{133}Cs nuclear resonance line of aqueous caesium ions and the ^{19}F line of aqueous fluoride ions on the addition of other electrolytes.[117] It was found that the ^{133}Cs line shift was dependent only upon the added anion but that the ^{19}F line shift was dependent upon both added anions and cations.

Spectroscopic investigations on solutions of hexammino cobaltic iodide and related compounds containing added iodide have revealed a new band in the 270 mu region,[147,148] probably due to a charge transfer between $Co(NH_3)_6^{+++}$ and I^- when in contact. The small values estimated for the extinction coefficients of these bands suggest that the overlap between ground and excited states is not very great, the acceptor orbital being somewhat localised on the central metal atom thereby reducing the transition probability: however, it is also possible that the extinction coefficients reported are too small.[149] It was established that the new band was not due to an intramolecular transition of the ion $Co(NH_3)_5I^{++}$.[147]

(b) Ionic Interactions[150]

Various spectrophotometric studies (in the visible and ultraviolet region)[44,129,131,132,133] have been made recently by different workers on ionic interactions in solutions of electrolytes. A certain amount of ambiguity has arisen, however, since the concept of ion-pair formation is ill-defined and environmental changes can sometimes affect different types of electronic transitions in a variety of ways.[25,26,131]

(i) Ion-pair formation

An ion-pair, as visualised by Fuoss,[151] is a pair of ions in physical contact, all other ions not in this condition being designated free ions. The thermodynamic calculations of Denison and Ramsey[152] are the basis of this simple model which has, however, been criticised.[126] For example Prue and Otter[153] hold to the original theory of Bjerrum as extended by Guggenheim,[123] in which is introduced a distance of closest approach of free ions (d), in addition to the contact distance (a). Ion-pairs are then defined as ions which are closer than d and they are treated as neutral molecules: for ions with separations greater than d, Debye-Hückel theory is applied since they are considered free. Eigen's results of relaxation spectrophotometry[154] appear to have been ignored by these authors. He has obtained well resolved results interpretable in terms of specific interations at close distances in which one or more solvent molecules separate the ions, and a general interaction at larger distances.

(ii) Definitions

For clarity, we define the following terms relating to interactions between cations and anions:-

(1) Complexes -

Two or more ions, in contact, held together by covalent bonds.

(2) Contact ion-pairs -

Ions, in contact, but with no covalent bonding between them.

(3) Solvent shared ion-pairs -

Pairs of ions, linked electrostatically by a single (orientated) solvent molecule.

(4) Solvent separated ion-pairs -

Pairs of ions, linked electrostatically but separated by more than one solvent molecule.

(5) Ion-pairs -

This term includes classes (2), (3), and (4) and will be used when distinction between them cannot be made.

Classes (1) and (2) are extremes, and in certain cases classification may be arbitrary. For example, the substituted pyridinium iodide examined in various concentrated solutions by Kosower[128] to evaluate his Z-values is a case in point. The iodide ion and the pyridinium ring are assumed to be in contact but since various partially covalent structures can then be visualised, it is impossible to be certain that the absorpting entity is a contact ion-pair and not a complex. When transference of charge between ions in contact occurs some weak "covalent" forces must be present. Although we have endeavoured to eliminate the occurence of complex formation by studying tetra-alkylammonium salts there must be a small amount of covalent bonding in the contact ion-pairs discussed below. (For alkali halide ion-pairs in the gas phase this must still be true.) In the ground state, however, this contribution to bonding must be small, and it is ignored in the ensuing sections.

Classes (3) and (4) must be distinguished from the symmetrical interactions which occur in any solution. Solvent separated and solvent shared ion-pairs have axial symmetry and should be well separated from like units in dilute solutions.

(iii) Contact ion-pairs

The main feature of the results obtained in solvents of very low ion-solvating power, such as carbon tetrachloride, is that a band is found in the 290 mμ region having the following characteristics.

(1) The band is not strongly solvent-dependent (as opposed to the spectrum of solvated iodide ions[25,26]). In fact, the spectrum in certain mixed solvents (Fig.7.8.) is composed of two superimposed bands suggesting that two distinct species are present. As reported in Chapter Seven this behavious is not found in solvent mixtures containing only solvated iodide ions (Fig.7.10.)

(2) The peak position of the band is independent of temperature, a feature not found with iodide in good solvating solvents. If the electronic transition giving rise to optical absorption was of the type depicted for an electron in a "square-well" defined by orientated solvent molecules,[25,26] then from the correlation in Fig.1.3. a shift of 20 mμ would be predicted for a 50° change in temperature.

(3) A band in this region can be developed on addition of an excess of tetra-n-butylammonium perchlorate to a solution of tetra-n-butylammonium iodide in dioxan (Fig.7.12.).

(4) The band maximum is found at progressively shorter wavelengths as the alkyl group (R) in R_4N^+ is reduced in size. Such dependence upon the nature of the cation is not detected in dilute solutions of iodides in good

solvating solvents (cf. Tables 7.2. and 7.3.).

We therefore conclude that the new band in the 290 mμ region is diagnostic of the contact ion-pair ($\underline{n}$-Bu)$_4$NI (and the 268 mμ band of the contact ion-pair ($\underline{n}$-Pr)$_4$NI). The implications of this conclusion, if it be correct, is that the predominance of contact ion-pairs in solutions of electrolytes in solvents of low dielectric constant is much less than is commonly supposed. Since it is generally agreed that there is extensive ionic association in many of the solvents in which contact ion-pairs are not detected by this spectroscopic method it would seem that, as against recent conclusions,[151,152] solvent shared and solvent separated ion-pairs are distinct entities in these solutions.

Further, the solvents in which tetra-alkylammonium iodides exist, in small concentrations, as contact ion-pairs (CCl_4 and C_6H_6) have small or zero permanent dipole-moments, and one would expect them to be very poor ionic solvators. However, being fairly polarisable, they are then likely to retain contact ion-pairs in solution.

(iv) Solvent shared ion-pairs

Two interesting phenomena were observed on addition of excess tetra-$\underline{n}$-butylammonium perchlorate to iodide in diethers. In 1:2-dimethoxyethane the usual salt shift is not observed but, instead, the formation of a new band at 235 mμ (Fig. 7.13.): in dioxan there is a small shift of the main band to higher energies, together with the development of a new band in the 280 mμ region, characteristic of contact ion-pairs.

We tentatively conclude that the new band in 1:2-dimethoxyethane is due to solvent shared ion-pairs, since our previous discussion rules out contact ion-pairs and since by far the most probable alternative unit with sufficient specificity to give rise to a distinct band is the solvent shared ion-pair.

There is further evidence that ion-pairs, other than contact ion-pairs, can give rise to unique absorption spectra. Since dioxan solutions give contact ion-pairs in the presence of excess tetra-n-butylammonium ions, it may be supposed that the iodide band at 237 mμ is, at least in part, due to solvent shared ion-pairs. This band is far less sensitive to changes in temperature than would be expected for freely solvated iodide,[25,26] in contrast with the band for iodide in 1:2-dimethoxyethane (see Table 7.4. and Fig. 7.4.).

We are thus able to distinguish four classes of solvent:

(1) Solvents in which ion-pairs predominate.

(2) Solvents in which solvent shared ion-pairs

predominate but in which contact ion-pairs can form.

(3) Solvents in which solvent separated ion-pairs predominate but in which solvent shared ion-pairs can form.

(4) Solvents in which neither contact nor solvent shared ion-pairs can be detected under our conditions.

(v) Solvent separated ion-pairs

Various techniques, in particular conductimetric experiments, suggest that some unspecified form of ion-pairing occurs in some solvents of class (4). Our results would suggest that these ion-pairs are separated by more than one solvent molecule and, indeed, that ionic association of this type is probably more common than any other. It is probably worth recording that although the solvents of class (4) in which ionic association is thought to be important have low bulk dielectric constants, they have relatively large dipole moments.

(vi) Nature of the electronic transition in ion-pairs

(1) Contact ion-pairs

The essential feature of C.T.T.S., crystalline alkali halides, and F-centre bands has been discussed in terms of the accepted centrosymmetric orbital for the excited electron. For alkali halide contact ion-pairs in the gase phase such symmetry cannot be the case and the transition, which almost certainly involves electron-transfer from the halide to the alkali metal ion, is found in quite a different region of the spectrum.[2] For such an ion-pair to exist in solution one could predict a shift of this band to shorter wavelengths since solvation should stabilise the ground state more than the excited state. It is most unlikely that this effect would be large enough to shift the band into the 215-245 mμ region where most bands attributable to solvated iodide ions occur.

We therefore propose that in the case of tetra-alkylammonium iodide contact ion-pairs the transition is not C.T.T.S. but electron-transfer from iodide to the cation, the electron being held in an expanded orbital possibly similar to that described by Becker et al.[155] for the electron in metal-ammonia solutions. Since the molar extinction coefficients of these transitions were greater than 10^4, there must be considerable overlap between the postulated orbital of the cation and the iodide ion. Thus it follows that the cation orbital must be very diffuse.

In this way we can have some qualitative understanding of the dependence upon the nature of the cation; we are unable at the moment to offer a quantative explanation.

(2) Solvent shared ion-pairs

The appearance of this band is less readily understood. We suggest that the transition is C.T.T.S. for the following reasons (a) the movement of an electron on to the cation is unlikely since the overlap of ground and excited states would surely be small and λ_{max} is found to be greater than 10^4, (b) on the "square-well" model of C.T.T.S. spectra the electron does not penetrate the first layer of solvent molecules, (c) this band has a slight dependence upon temperature (Fig. 7.4.), which might be expected for iodide ion in a cavity distorted, and probably reduced in size from the value expected for purely solvated iodide in this solvent, by the close proximity of the positive ion. Distortions such as these, from spherical to axial symmetry, are known to shift the first exciton band of crystalline alkali iodides.[156]

If this transition is considered in terms of the "expanded" model it would be necessary to postulate that the excited electron spent a fair proportion of its time on the adjacent positive ion. One would then expect (a) this band to be cation dependent, which it is not, and (b) that it would appear in the same region as, and have the same properties as, the band ascribed to contact ion-pairs. Further, it is difficult to see how the addition of excess tetra-<u>n</u>-butylammonium ions can be explained on this model, since they can be considered pictorially as competing for solvent molecules and, when in large excess, removing some of the orientated solvent molecules in the solvent shared ion-pairs thereby creating contact ion-pairs.

(3) Solvent separated ion-pairs

The transition in this case is considered to be C.T.T.S. since the iodide bands in solvents of classes (3) and (4) have values of dE_{max}/dT that would be predicted from the correlation of Smith and Symons, and the cations are sufficiently far removed to have negligible influence.

The points made above for an explanation on the "expanded" model treatment still, in general, hold. The addition of excess tetra-n-butylammonium ions to form solvent shared ion-pairs can again be considered in terms of competition for the available solvent molecules. It was not found possible to observe a band in the 290 mμ region after the solvent shared ion-pair band was obtained, for the solution became saturated soon afterwards.

(vii) Relation to other work

Ingold and co-workers[157] have extensively investigated ion-pair formation from studies of organic reaction mechanisms, in particular kinetic studies of the reactions of triarylmethyl compounds in benzene. An essential aspect of this work is that electrolytes are present as contact ion-pairs. Our work confirms this postulate, in the particular case of tetra-alkylammonium halides. Contact ion-pairs are likely to be still more favoured when triarylmethyl carbonium ions are one constituent, since the high acceptor power of these cations should make charge-transfer forces of considerable importance. These forces probably contribute to the stability of the carbonium ion ion-pairs shown to occur in solutions of low dielectric constant by Evans and co-workers.[158]

In these studies only contact ion-pairs are considered as specific entities. However, as has been mentioned in Chapter Four, Winstein and co-workers[127] have found evidence for both contact and solvent separated ion-pairs as a result of studying salt effects upon the rates of solvolysis and racemisation of various organic compounds.

Sadek and Fuoss[159] have recently re-examined earlier conductance data on tetra-n-butylammonium bromide in various binary mixtures, including carbon tectrachloride/methanol. They now obtain a linear relationship when the logarithum of the association constant of the ion-pair is plotted against the reciprocal of the bulk dielectric constant, for a constant value of <u>a</u> in the three systems studies. Their results are shown in Fig.8.3. Since, at a given dielectric constant, different values of K_A are obtained they interpret them in terms of an additional effect which is specific for a given ion-solvent system, and suggest that it may be interaction between ions and solvent dipoles. However, examination of their figure suggests that they may not be justified in drawing the three lines all with the same slope: if one point is omitted in their results for CCl_4/MeOH and CCl_4/EtOH mixtures, better straight lines could be drawn not parallel to the line for CCl_4/$PhNO_2$ mixtures. Nevertheless, it was considered that if tetra-n-butylammonium iodide was used in place of the bromide no significant difference would be made to the results of Sadek and Fuoss. By monitoring the reaction spectroscopically the concentration of contact ion-pairs in various mixtures could be accurately calculated and hence a value of the association constant derived. Although these authors did not carry out investigations close to pure carbon tetrachloride, preliminary studies by us in this region have shown that the association constant, as calculated from spectroscopy, in no way follows the bulk dielectric constant of the medium as required by Sadek and Fuoss. It was found that, for equal concentrations of iodide, the concentration of contact ion-pairs was reduced by a factor of 2 in a solution of carbon tetrachloride

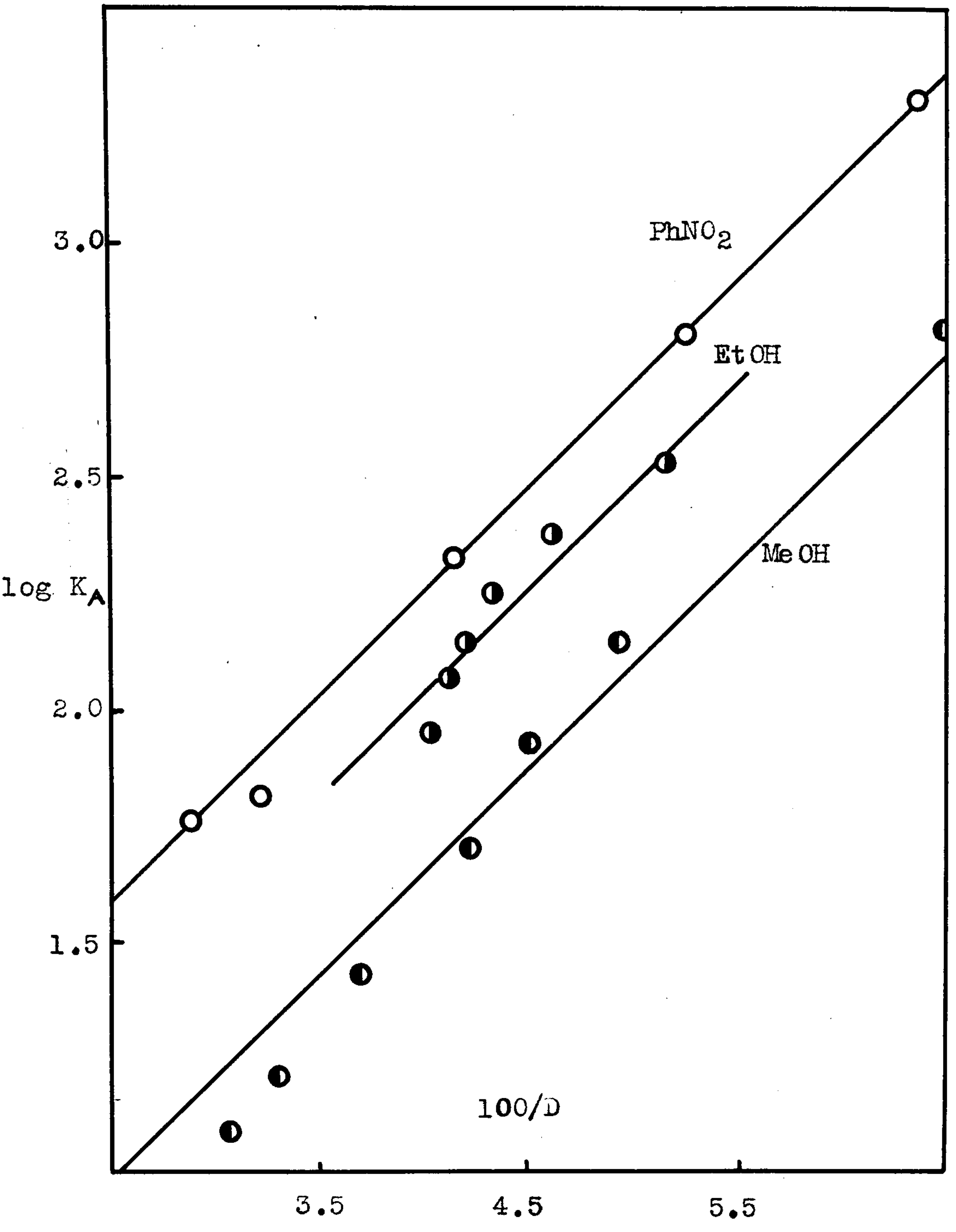


Fig.8.3. Dependence of association constant K_A upon dielectric constant (taken from Fig.4. of ref. 159.)

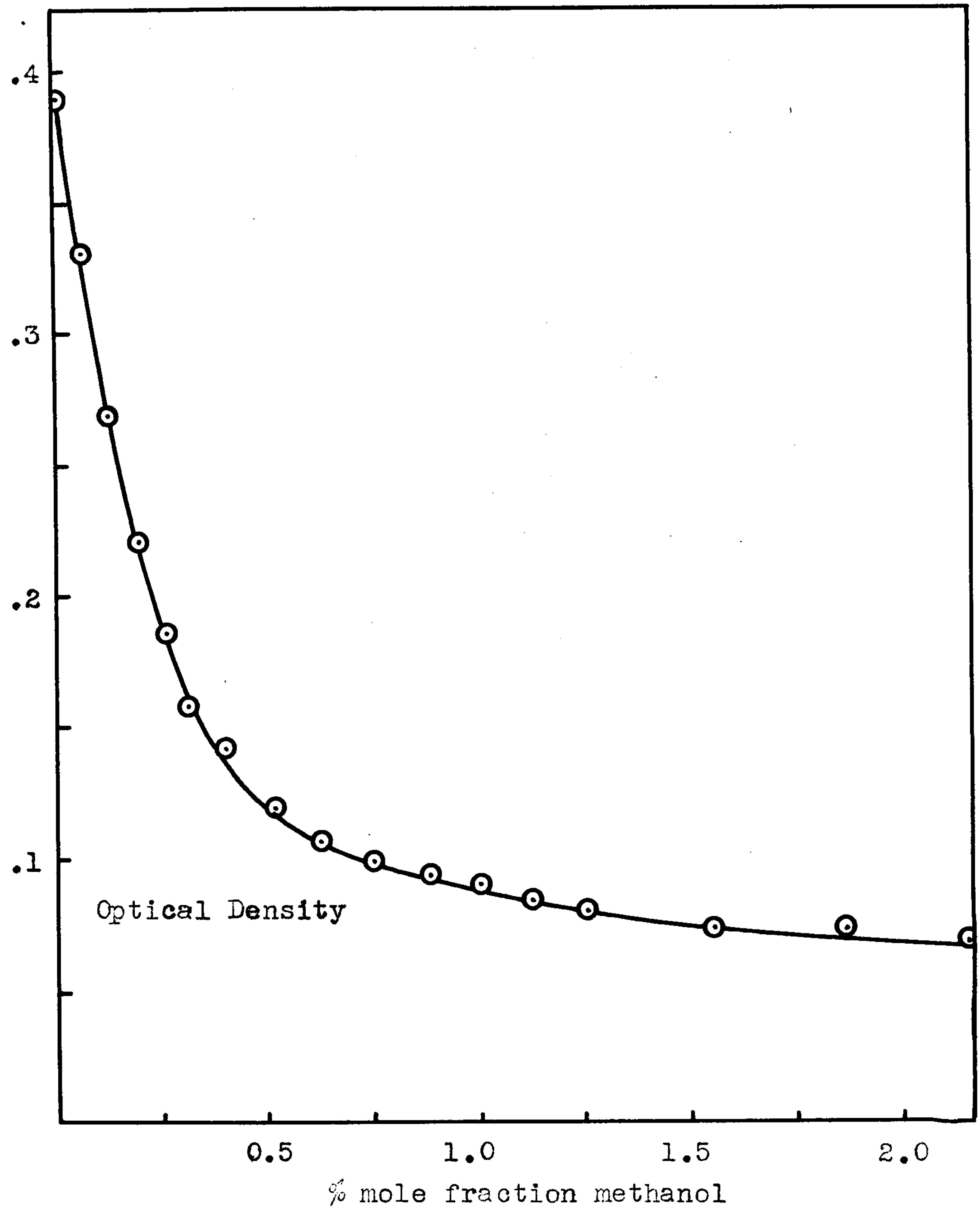


Fig.8.4. Plot of % mole fraction methanol in carbon tetrachloride/methanol mixtures containing the same concentration of $(n\text{-}Bu)_4NI$ against the measured optical density at 293 mu.

containing 0.25% mole fraction methanol, compared with the pure solution. The results are summarised in Fig. 8.4. It was concluded that in the solutions studied by Sadek and Fuoss there are no spectroscopically detectable contact ion-pairs. It was hoped that solvent shared ion-pairs would be detectable in these mixtures by, perhaps, a hesitation in the curve of Fig. 8.4., but no definite evidence was obtained in this respect and it was not possible to examine the spectra of these solutions much below 260 mμ. due to the absorbance of carbon tetrachloride. However, the effect of addition of cyclo-hexane on the spectra of tetra-n-butylammonium iodide in iso-propanol was investigated throughout the whole range up to 99.3% mole fraction cyclo-hexane (Fig. 7.10.). Above 95% mole fraction cyclo-hexane λ_{max} shifted rapidly with change in solvent composition and the band became broader. These results may be interpreted as meaning that one or more specific units are at least partially formed under these conditions, but that they are sufficiently varied or affected by change in environment to render the method of curve-analysis outlined earlier unsuitable.

(c) Complex Iodides of Cations with d^{10} Configuration

(i) Detection of iodide in a complex

It has been suggested above that the characteristic and large changes in the band maximum of iodide when under various constraints can be used to distinguish between purely solvated iodide ions and iodide either in contact with, or under the electrostatic attraction of, cations. From the results reported in Chapter Seven a clear distinction between solvated iodide and iodide associated with zinc, cadmium, or mercury cations can be made. For example, zinc iodide in iso-propanol has a band at 218 mμ which is very close to that for potassium iodide. However, potassium iodide in methyl cyanide absorbs at 246 mμ whereas the band for zinc iodide in methyl cyanide remains in the 218 mμ region. Simple electrostatic contact ion-pairs such as those described earlier are not important constituents in the solvents used and hence we conclude that the new species formed are best described as complexes with some covalent bonding between iodide and the cation.

We shall proceed by considering the number of iodide ions bonded to each cation in the solutions studied as a prelude to a discussion of the structure of the complexes and the nature of the electronic transitions.

(ii) Anion-cation ratios

When zinc and cadmium iodides are dissolved in water at concentrations less than 0.01 M, only the band for aqueous iodide is observed, with the accepted value for λ_{max}. We therefore conclude that the following dissociation is essentially complete,

$MI_2 \rightarrow M^{++} + 2I^-$ (where M is Zn, or Cd.)

However, for similar concentrations of the salts in methyl cyanide, iso-propanol and n-butanol, bands are found which are relatively independent of the nature of the solvent being at around 218 and 243 mμ for zinc and cadmium iodides respectively. Thus if disproportionation was now occuring it would have to be of the form:

$MI_2 \rightleftharpoons MI^+ + MI_3^-$ etc.

Considering for the moment the case of cadmium iodide (zinc iodide following by analogy), addition of excess Cd^{++} ions results in the loss of the 243 mμ band and the appearance of a new band at 225 mμ. The possibility that the 243 mμ band is due to CdI^+ is therefore eliminated and we can safely allocate the bands at 243 and 225 mμ to iodine attached to cadmium in the ratios 2:1 and 1:1 respectively.

Further, addition of excess iodide ions gives new bands either at 248 or 258 mμ, depending upon the solvent. These bands are reasonably assigned to CdI_3^- and CdI_4^{--} respectively. Raman spectroscopic studies[49] clearly establish the presence of CdI_4^{--} in concentrated aqueous solutions containing excess iodide in exactly the same conditions required for the development of the 258 mμ band. However, in concentrated aqueous solutions there are found Raman lines which correspond to the complex MI_4^{--} as well as to a tri-atomic molecule and an unidentified species.[51] This is not inconsistent with spectral results since Doehlemann and Fromherz[47] have examined concentrated solutions of zinc and cadmium iodides in water and they have found bands at 238 and 256.5 mμ respectively, band positions which are close to those attributed to the MI_4^{--} complexes. Further, in the case of cadmium iodide, before the 256.5 mμ band was resolved a band was obtained at 250 mμ., the position of the CdI_3^- complex. This latter band was found to be more predominant in solvents known not to be good solvators for doubly charged ions.

Raman spectra of these di-iodides in ethanol and methanol give rise to lines corresponding to tri-atomic molecules and the unidentified species.[51] Spectral studies have found that in these solvents the spectra are dependent upon concentration and that the tetrahedral complex is not formed.[27]

The assignment of the bands arising from the dissolution of mercuric iodide in various solvents is somewhat simplified. The first absorption band for mercuric iodide in the gas phase has been found to be at 268 mμ: the band positions for this compound in solution, including aqueous solution, have been found, by other workers[29,32] and in this study, to be in this region. It is therefore reasonable to assume that the species giving rise to these bands are mercuric iodide molecules, the anion-cation ratio thus being 2.

It has been found, however, that in certain solvents mercuric iodide begins to dissociate. E.g., HgI_2 in methyl cyanide gives rise to a shoulder in the 290 mμ region in addition to the HgI_2 band, and in dimethylformamide the shoulder is now resolved at 301 mμ. Addition of iodide to these has shown that, in the former case, and indeed in most of the other solvents investigated, a band appears at around 305 mμ together with a shoulder in the 340 mμ region which is not resolved: in the latter case, progressive addition of iodide results in the diminution of the 301 mμ band as another is resolved at 335 mμ. We may therefore assume that we are observing the step-wise formation of HgI_4^{--} from HgI_2, HgI_3^- predominanting in the less polar solvents.

Fromherz and Lih[32] were of the opinion that only the highly co-ordinated ions MX_4^{--} and the simple ions MX_2 were present in the aqueous solutions they studied, solutions which contained high concentrations of halide ion. We do not dispute this conclusion for aqueous solutions but suggest that our results essentially substantiate the proposal of Orgel[2] that "it might be expected to find all the intermediate species", under the correct conditions.

Further, Figs.7.22 and 7.23 show that as progressive amounts of iodide are added to mercuric iodide in N-N-dimethylformamide, after a certain concentration of iodide is reached two isobestic points are obtained, thus providing extra evidence that there is an equilibrium between two complexes in this solution. These figures also show that until HgI_3^- is the predominant species in solution HgI_4^{--} is not formed.

It may be noted that addition of small amounts of iodide to mercuric iodide in other solvents resulted in a shift of the band to higher energies (Table 7.9.). We suggest that the magnitude of this shift is not entirely due to the rise of the 300 mμ band and thus if the di-iodide bands of zinc and cadmium are similarly dependent upon the concentration of added electrolyte, this would explain the observed lack of good isobestic points (Figs. 7.16 and 7.17.).

We thus feel that, in principle, it is possible to obtain in solution the four major complexes postulated as a result of other experimental work, namely MI^+, MI_2, MI_3^-, and MI_4^{--}, where M is zinc, cadmium, or mercury. However, the solvent seems to play a large part in determining the appropriate conditions for their appearance and will therefore affect association constants. It is hoped to undertake a further study of this aspect. Table 8.2. summarises the average values of λ_{max} for the various complexes.

These are our main conclusions, but other facets require mention.

Table 8.2.

Average values of λ_{max} for the various iodide complexes

	MI^+	MI_2	MI_3^-	MI_4^{--}
Zinc	210	218		238
Cadmium	225	243	248	258
Mercury		268	305	335

(iii) The structure of the complexes and solvent co-ordination.

We have seen that mercuric iodide dissolves, for the most part, undissociated and since in the gas phase mercuric iodide is linear, it is a reasonable assumption that the molecules are linear in solution with no solvent co-ordination, any solvent effects being secondary. Since the molecule is linear there is no gain or loss of dipole during the transition: however there is a redistribution of charge which should be at least weakly influenced by solvent. Although the total variation in λ_{max} is only about 10 mμ., there does appear to be a very rough correlation with Kosower's Z-values[123] for solutions in solvents whose Z-value is recorded. Raman spectroscopic studies have shown that mercuric halides, including mixed halides, are linear in solution.[51]

However, the observed spectral bands for solutions of zinc and cadmium iodides cannot be so simply explained. The major difficulty is that the bands are considerably shifted towards higher energies compared with the gas phase bands, from 238 to 218 mμ. and from 260 to 243 mμ. for zinc and cadmium iodides respectively in non-aqueous solvents. Raman studies have shown that in these solvents we are still dealing with a linear tri-atomic species.[51]

To explain these observations we can make two postulates,

(1) that the molecule is bent with two solvent molecules attached to give an approximately tetrahedral structure, or

(2) that it is linear with four solvent molecules fairly loosely co-ordinated to form an approximately octahedral unit.

Suggestion (1) appears to be already negated by Raman spectroscopic evidence: (2) will be discussed in detail in the following section.

There is no evidence relating to the co-ordination of solvent in the complex MI^+, but it seems likely that an iodide ion is displaced by one solvent molecule in the solutions studied rather than by perchlorate ion, which has very weak co-ordination properties.

The complex MX_3^- may be either planar with no solvent molecules attached, or tetrahedral with one attached. In principle it is possible to elucidate the structure by Raman spectroscopic investigations: in practise, the lines observed so far are too weak for positive identification.[51]

The complex MX_4^{--} can have no solvent molecules attached since the Raman spectroscopic evidence obtained can only be interpreted in terms of the molecule being a pure tetrahedron.[50]

(iv) The nature of the electronic transition

The gas phase spectrum of mercuric iodide, with two bands at 210 and 266 mμ., has been interpreted by Walsh[160] in terms of the transition $(\Pi g)^4 \rightarrow (\Pi g)^3 \tilde{\Pi} u$, i.e., largely an $\underline{n} \rightarrow \pi$ transition, non-bonding iodide electrons moving into a largely non-bonding $\underline{p}-\pi$ level on mercury. In effect, this is a charge-transfer from iodide inwards. However, he ignores the possible use of mercury $\underline{d}$-levels and the possibility of the formation of iodine atoms. This latter, which would be favoured by Katzin[14], would appear to be unlikely since,

(1) mercuric chloride also gives rise to two bands,

(2) the first band is very much weaker than the second band,

(3) the band separations are not compatible with the $^2P_{3/2}$, $^2P_{1/2}$ states of the iodine atom, and

(4) the transition must involve both iodine atoms.

The more intense 210 $m\mu$ continuum is interpreted in terms of an allowed transition, the excited state being a fairly linear $^1\Sigma_u^+$ excited state with stretching frequencies very much less than those of the ground state. The 266 $m\mu$ continuum is represented as transitions to strongly bent $^1B_2$ upper states, correlating with $^1\Delta_u$, a forbidden transition.

Thus since the spectra of mercuric iodide in the gas phase and in solution are essentially identical, the electronic transitions can be considered to be the same.

By analogy, the same type of transition should be occuring in the iodides of zinc and cadmium but experiment has shown that the band maxima are shifted to higher energies in solution. It is well known that the chemical properties of these elements are not very similar. For example, if we consider aqueous solutions of zinc and mercuric iodides, we find that Zn^{++} "binds" to water preferentially and a large excess of iodide ions, or a concentrated solution,[47] is required to alter this, whereas mercuric iodide dissolves unchanged and is very sparingly soluble. In a recent review Ahrland, Chatt, and Davies[161] have divided the Periodic Table into two main classes, (a) and (b). Their division is based, in general, on the stability of complexes formed with the halogens. In class (a) are those elements which form more stable complexes with fluorine than with the other halogens, and class (b) contains those elements which form less stable complexes with fluorine than with the other halogens. On their classification zinc falls into class (a), mercury into class (b) and cadmium is a border-line case between the two. The results of Sillen and his associates[80] indicate that cadmium is more in class (b) than in (a) since their investigations into the equilibrium constants for cation-halide ion interactions suggest that for mercury and cadmium, the iodide complexes are the most stable and the chlorides the least stable: for zinc the reverse is the case. They also found that the mercuric complexes are much more stable than those of zinc and cadmium: this is compatible with the spectral results of Fromherz and Lih[32]. They found that, in water, a band attributable to HgI_4^{--} was formed on addition of stoichiometric amounts of iodide, whereas a large excess was required in the case of zinc and cadmium.[47]

Thus if we now consider the earlier suggestion of an octahedral unit with four co-ordinated solvent molecules for zinc and cadmium iodides in the media studied, we would expect a shift to higher energies relative to the gas phase transition since the co-ordinated solvent molecules would decrease the ease of the transition. That is, if the co-ordinated solvent molecules are orientated with the negative ends of their dipoles towards the central metal atom (and the molecules of the bulk solvent that are in the proximity of the iodine atoms being probably orientated with their positive dipolar ends towards iodine) then we would expect the ground state to be stabilised and the excited state destabilised with respect to the vapour phase band. Hence this is an explanation of the observed shift to higher energies. We would expect the peak position to be dependent upon the co-ordinating power of the solvent. However, the solvents we have used all have somewhat similar co-ordinating powers and in any case, there is the competing effect of the solvating powers of the solvents in the vicinity of the iodine atoms.

Orgel[162] has shown that the tendency for Hg^{++}, in contrast with Zn^{++} and Cd^{++}, to form linear XY_2 complexes rather than symmetrical octahedral complexes, can be rationalised in terms of suitable promotion of $\underline{d}^{10}$ electrons.

The observed temperature effects on the di-iodide complexes can be interpreted in terms of the preceding postulates. The lack of the dependence of the position of λ_{max} for mercuric iodide in solution is indicative of no complexing with solvent molecules while the small shift to the visible in the case of zinc and cadmium iodides may be explained on the grounds of the increased kinetic and vibrational energies of the co-ordinated solvent molecules increasing the ease of the transition: however, it is possible that slight disproportionation occurs in these solutions and that the equilibrium changes with temperature. Under some circumstances this could give rise to an apparent shift.

SUMMARY

Previous investigations have shown that many simple anions, in aqueous solution, exhibit one, or occasionally two, intense absorption bands in the 200 $m\mu$ region. These spectra have been interpreted as Charge-Transfer To Solvent bands and in the particular case of iodide, environmental changes, such as temperature, solvent, and ionic strength, have been interpreted in terms of the postulate that the excited electron is held in a potential well defined by the orientated solvent molecules. The energy required to excite the electron has been evaluated by a "square-well" approximation and, on this basis, the position of maximum absorption was found to be governed primarily by the radius of the cavity formed by the orientated solvent molecules. The present work has shown that, despite adverse criticism, this model still accomodates the observed results on iodide ion in a wide range of solvents: preliminary studies, including Gaussian analysis with the Pegasus Digital Computor, on the bromide ion show that it, too, appears to obey the correlation for iodide.

Anomalous results were obtained for iodide in certain solvents of low dielectric constant which have been interpreted in terms of the formation of contact ion-pairs and pairs of ions separated by one

or more solvent molecules.

It has been found that although iodide ions do not appear to complex specifically with solvent molecules, they will form the range of complexes MI^{+}, MI_2, MI_3^{-}, and MI_4^{--}, where M is zinc, cadmium, or mercury, under the appropriate conditions.

REFERENCES

1. RABINOWITCH Rev. Mod. Phys., 1942, 14, 112.

2. ORGEL Quart. Rev., 1954, 8, 422.

3. FRANCK, KUHN & ROLLEFSON Z. Physik, 1927, 43, 155.

4. HILSCH & POHL Z. Physik, 1929, 59, 812.

5. SCHNEIDER & O'BRYAN Phys. Rev., 1937, 51, 293.

6. MOTT Trans. Faraday Soc., 1938, 34, 500.

7. FERGUSSON Phys. Rev., 1944, 66, 220.

8. TEEGARDEN Phys. Rev., 1957, 108, 660.

9. FESEFELDT Z. Physik, 1930, 64, 623.

10. PHILIPP & TAFT J. Phys. and Chem. Solids, 1956, 1, 159.

11, BUTKOV Z. Physik, 1931, 71, 678.

12. BUTKOV Physik Z. Sowjetunion, 1933, 4, 577.

13. WIELAND Z. Physik, 1932, 76, 801.

14. KATZIN J. Chem. Phys., 1955, 23, 2055.

15. AKISHIN & SPIRIDONOV Krystallografiya, 1957, 2, 475.

16. BRAUNE & LINKE Z. phys. Chem. B, 1935, 31, 12.

17. WIELAND & HERCZOG Helv. Chim. Acta., 1949, 32, 889.

18. FRANCK & SCHEIBE Z. phys. Chem. B, 1929, 5, 355.

19. FRANCK & HABER S.B. preuss. Akad. Wiss (Phys. Math.), 1931, p.250.

20. FARKAS & FARKAS Trans. Faraday Soc., 1938, 34, 1113.

21. WARBURG & RUMP Z. Physik, 1928, 47, 305.

22. FARKAS & FARKAS Trans. Faraday Soc., 1938, 34, 1120.

23. FARKAS & KLEIN J. Chem. Phys., 1948, 16, 886.

24. PLATZMAN & FRANCK Farkas Memorial Volume (Jerusalem, 1952), p.21; Z. Physik, 1954, 138, 411.

25. SMITH & SYMONS Trans. Faraday Soc., 1958, 54, 338, 346.

26. SMITH & SYMONS Discuss. Faraday Soc., 1957, No.24, 206.

27. SCHEIBE Z. Electrochem., 1928, 34, 497.

28. FRANCK & SCHEIBE Z. phys. Chem. A, 1928, 139, 22.

29. LEDERLE Z. phys. Chem. B, 1930, 10, 121.

30. FROMHERZ & MENSCHICK Z. phys. Chem. B, 1929, 3, 1.

31. FROMHERZ & LIH Z. phys. Chem. A, 1931, 153, 321.

32. FROMHERZ & LIH Z. phys. Chem. A. 1933, 167, 103.

33. JOLLY U. C. R. L., 1952, 2008.

34. PAULING Phys. Rev., 1929, 34, 956.

35. STEIN & TREININ Trans. Faraday Soc., 1959, 55, 1086, 1091.

36. COUTURE & LAIDLER Canad. J. Chem., 1956, 34, 1209.
LAIDLER & PEGIS Proc. Roy. Soc. A, 1957, 241, 80.

37. HEPLER J. Phys. Chem. 1957, 61, 1426.

38. LEY & ARENDS Z. phys. Chem. B. 1929, 6, 240.

39. FRIEDMAN J. Chem. Phys., 1953, 21, 319.

40. LEY & ARENDS Z. phys. Chem. B, 1932, 15, 311.

41. LEY & KÖNIG Z. phys. Chem. B, 1938, 41, 365.

42. AWTREY & CONNICK J. Amer. Chem. Soc., 1951, 73, 1842.

43. HEGEDUS Acta. Univ. Szeged. Chem. Mineral Phys., 1939. 7, 7.

44. AMES & WILLARD J. Amer. Chem. Soc., 1953, 75, 3267.

45. GRIFFITHS, LOTT, & SYMONS Analyt. Chem., 1959, 31, 1338.

46. RABINOWITCH & STOCKMEYER J. Amer. Chem. Soc., 1942, 64, 335.

47. DOEHLEMANN & FROMHERZ Z. phys. Chem. A, 1934, 171, 353.

48. LEY Angew. Chem., 1928, 41, 845.

49, DELWAULLE Compt. rend. Congr. Soc. Savantes Paris et Dept., Sect. sci., 1955, 41.

50. ROLFE, SHEPPARD, & WOODWARD Trans. Faraday Soc., 1954, 50, 1275.

51. DELWAULLE Bull. Soc. chim. France, 1955, 1294.

52. CONNICK & PAUL J. Amer. Chem. Soc., 1958, 80, 2069.

53. SHCHUKAREV, LILICH, & LATYSHEVA Zhur. neorg. Khim., 1956, 1, 225.

54. BETHEL, GOLD, & & SATCHELL J. Chem. Soc., 1958, 1918.

55. KOLTHOFF & COETZEE J. Amer. Chem. Soc., 1957, 79, 370.

56. LEDEN Z. phys. Chem. A, 1941, 188, 160.

57. IOFFE J. Gen. Chem. (U.S.S.R.) 1956, 26, 3627.

58. HALDAR J. Indian Chem. Soc., 1946, 23, 205.

59. STROMBERG & BYKOV J. Gen. Chem. (U.S.S.R.), 1949, 19, 245.

60. NATTA & PASSERINI Gazzetta, 1928, 58, 472.

61. KORSHUNOV, MALYUGINA, & BALABANOVA J. Gen. Chem. (U.S.S.R.), 1951, 21, 685.

62. MARKHAM & TUR'YAN J. Gen. Chem. (U.S.S.R.) 1952, 22, 1973.

63. TUR'YAN & SEROVA Zhur. neorg. Khim., 1957, 2, 336.

64. LEDEN Svensk Kem. Tidskr., 1952, 64, 145.

65. KING J. Amer. Chem. Soc., 1949, 71, 319.

66. ALBERTY & KING J. Amer. Chem. Soc., 1951, 73, 517.

67. KORENMAN J. Gen. Chem. (U.S.S.R.), 1948, 18, 1233.

68. TREUMANN & FERRIS J. Amer. Chem. Soc., 1958, 80, 5048.

69. BERGMAN & IL'YASOV Zhur. neorg. Khim., 1957, 2, 395.

70. IL'YASOV & BERGMAN J. Gen. Chem. (U.S.S.R.), 1956, 26, 1457.

71. FLENGAS & INGRAHAM Canad. J. Chem., 1958, 36, 780.

72. JANZ, SOLOMONS & GARDNER Chem. Rev., 1958, 58, 461.

73. ARTSDALEN J. Phys. Chem., 1956, 60, 172.

74. IVERSON Diss. Abs., 1958, 18, 829.

75. DUKE & IVERSON J. Phys. Chem., 1958, 62, 417.

76. BOUILLOUX Bull. Soc. chim. France, 1957, 547.

77. DUQUENOIS Analyt. Chim. Acta., 1947, 1, 50.

78. AGGARWAL Z. anorg. Chem., 1957, 291, 134.

79. ELLENDT & CRUSE Z. phys. Chem., 1952, 201, 130.

80. QVARFORT & SILLEN Acta. Chem. Scand., 1949, 3, 505, and related papers

81. MARCUS Acta. Chem. Scand., 1957, 11, 329.

82. MOSER & VOIGT J. Inorg. Nuclear Chem., 1957, 4, 354.

83. SCAIFE & TYRREL J. Chem. Soc., 1958, 392.

84. MEYER J. Chem. Educ., 1953, 20, 145.

85. FEATES & IVES J. Chem. Soc., 1956, 2798.

86. BELL Endeavour, 1958, 17, 31.

87. BERNAL & FOWLER J. Chem. Phys., 1933, 1, 515.

88. MORGAN & WARREN J. Chem. Phys., 1938, 6, 670.

89. CROSS, BURHAM & LEIGHTON J. Amer. Chem. Soc., 1937, 59, 1134.

90. POPLE Proc. Roy. Soc. A, 1951, 205, 163.

91. VERWEY Rec. Trav. chim., 1941, 60, 887.

92. BORN Z. Physik, 1920, 1, 45.

93. LATIMER, PITZER & STANSKY J. Chem. Phys., 1939, 7, 108.

94. VERWEY Rev. Trav. chim., 1942, 61, 127.

95. ELEY & EVANS Trans. Faraday Soc., 1938, 34, 1093.

96. KORTUM & BOCKRIS Textbook of Electrochemistry, (Elsevier), 1951, p.122.

97. DEBYE Z. Physik, 1933, 36, 100.

98. WEBB J. Amer. Chem. Soc., 1926, 48, 2589.

99. PASSOTH Z. phys. Chem., 1954, 203, 275.

100. LAIDLER Seminar. University of Rome, Oct. 1956.

101. ELEY & PEPPER Trans. Faraday Soc., 1941, 37, 581,

102. FRANK J. Chem, Phys., 1945, 13, 478, 493.

103. FRANK & EVANS J. Chem. Phys. 1945, 13, 507.

104. BOCKRIS Quart. Rev., 1949, 3, 173.

105. REMY Z. phys. Chem., 1915, 89, 469.

106. DEBYE & McAULAY Z. Physik, 1925, 26, 23.

107. AMIS Z. phys. Chem. N.F., 1956, 7, 360. and earlier papers.

108. STREHLOW & KOEPP Z. Electrochem., 1958, 62, 373.

109. STEWART J. Chem. Phys., 1939, 7, 689.

110. DAVIES Quart. Rev., 1954, 8, 250.

111. GANZ Ann. Phys. 1937, 28, 445.

112. WANG J. Phys. Chem., 1954, 58, 686.

113. HASTED, RITSON & COLLIE J. Chem. Phys., 1948, 16, 1.

114. EVERETT & COULSON Trans. Faraday Soc., 1940, 36, 633.

115. ROBINSON & STOKES Electrolyte Solutions (Butterworths), p.21.

116. LANE & SAXTON Proc. Roy. Soc. A, 1952, 214, 531.

117. CARRINGTON, DRAVNIEKS & SYMONS Mol. Phys. 1960, in press.

118. SCHOOLERY & ALDER J. Chem. Phys., 1955, 23, 805.

119. WALDRON J. Chem. Phys., 1957, 26, 809.

120. BRADY & KRAUSE J. Chem. Phys., 1957, 27, 304.

121. BRADY J. Chem. Phys., 1958, 28, 464.

122. BJERRUM K. danske vidensk. Selsk., 1949, 7, No.9.

123. GUGGENHEIM Discuss. Faraday Soc., 1957, No.24, 53.

124. FUOSS J. Amer. Chem. Soc., 1959, 81, 2659.

125. FUOSS & ACCASCINA Electrolytic Conductance 'Interscience) 1959.

126. BUCKINGHAM J. Roy. Inst. Chem., 1960, 84, 17.

127. WINSTEIN Experientia Supplementum, II, 152, and earlier papers.

128. KOSOWER J. Amer. Chem. Soc., 1958, 80, 3253, 3261.

129. POPOV & HUMPHREY J. Amer. Chem. Soc., 1959, 81, 2043.

130. KOLTHOFF, STOCESOCA & LEE J. Amer. Chem. Soc., 1953, 75, 183[illegible].

131. SMITHSON & WILLIAMS J. Chem. Soc., 1958, 457.

132. GIMBLETT & MONK Trans. Faraday Soc., 1955, 51, 793.

133. DAVIES, OTTER & PRUE Discuss. Faraday Soc., 1957, No.24, 103.

134. KOSOWER J. Amer. Chem. Soc., 1956, 78, 5700.

135. SMITH Ph.D. Thesis, Southampton University.

136. LEGAULT & LEWIS J. Amer. Chem. Soc., 1942, 64, 1354.

137. PULLIN & POLLOCK Trans. Faraday Soc., 1958, 54, 11.

138. DIAMOND & FROMHERZ Z. phys. Chem. B, 1930, 9, 299.

139. DOUCET Compt. rend., 1943, 216, 198.

140. KOSOWER, MARTIN, & MELOCHE J. Chem. Phys., 1957, 26, 1353.

141. LORD Phys. Rev. Letters, 1958, 1, 170.

142. FEHER Phys. Rev., 1957, 105, 1122.

143. GOURARY & ADRIAN Solid State Physics, 1960, Feb. issue.

144. RHODES & UBBELOHDE Proc. Roy. Soc., A, 1959, 251, 156.

145. GREENBERG & SUNDHEIM J. Chem. Phys., 1958, 29, 1029.

146. DELBECQ, ROBINSON & YUSTER Phys. Rev., 1954, 93, 262.

147. LINHARD & WEIGEL Z. anorg. Chem., 1951, 266, 49.

148. EVANS & NANCOLLAS Trans. Faraday Soc., 1953, 49, 363.

149. KING, ESPENSON, & VISCO J. Phys. Chem., 1959, 63, 755.

150. GRIFFITHS & SYMONS Mol. Phys., 1960, 3, 90.

151. FUOSS J. Amer. Chem. Soc., 1958, 80, 5059.

152. DENISON & RAMSEY J. Amer. Chem. Soc., 1955, 77, 2615.

153. PRUE & OTTER Discuss. Faraday Soc., 1957, No.24, 123.

154. EIGEN Discuss Faraday Soc., 1957, No.24, 25, 119.

155. BECKER, LINDQUIST, & ALDER. J. Chem. Phys., 1956, 25, 971.

156. MARTIENSSEN J. Phys. Chem. Solids, 1957, 2, 257.

157. HUGHES, INGOLD, PATAI, & POCKER J. Chem. Soc., 1957, 1206.

158. BAYLES, EVANS & JONES J. Chem. Soc., 1955, 206.

159. SADEK & FUOSS J. Amer. Chem. Soc., 1959, 81, 4507.

160. WALSH J. Chem. Soc., 1953, 2280.

161. ARHLAND, CHATT & DAVIES Quart. Rev., 1958, 12, 265.

162. ORGEL J. Chem. Soc., 1958, 4186.