

600. *The Effect of Solvent on the Ultra-violet Absorption Spectra of Aromatic Hydrocarbons with Special Reference to the Mechanism of Salting-out. Part I. Alcoholic Lithium Chloride Solutions.*

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The failure of the majority of published mechanisms of salting-out to account for all the experimental observations is discussed briefly. The possibility of obtaining some information on the environment of non-electrolytes in salt solutions from the study of ultra-violet spectra is considered.

The spectra of benzene, *m*-xylene, naphthalene, anthracene, and chrysene dissolved in alcoholic lithium chloride solutions are compared with the spectra of the same aromatic hydrocarbons in alcohol. Comparison is also made of the spectra of these aromatic hydrocarbons dissolved in alcohol with their spectra when dissolved in *cyclohexane*, and of the spectrum of benzene dissolved in *cyclohexane* with its spectrum in *n*-hexane. The effect of lithium chloride on the spectrum of benzyl alcohol in the absence of a diluent is recorded.

The observed changes in spectra are shown to be consistent with the salt's having caused a modification of the structure of the alcohol in the neighbourhood of the non-electrolyte. The spectra also indicate that the changes in the structure of the alcohol extend some distance from the ions: a conclusion which is in agreement with published entropy values for ions in alcoholic solutions. Any adequate theory of the mechanism of salting-out from alcoholic solutions must take cognisance of this structural factor.

THE simplest and oldest theory of the effect of a salt on the solubility of a weakly polar material in an ionising solvent assumes that the salt immobilizes a certain fraction of the solvent which is then no longer available for dissolution of the non-electrolyte. The unbound solvent is considered to be in the same state as when salt is absent. Solvation numbers can be calculated in this manner by measuring the reduction in solubility of a non-electrolyte produced by dissolving a salt. For example, Kosakewitsch (*Z. physikal. Chem.*, 1929, *A*, **143**, 216) derived a solvation number of 6.2 for lithium chloride in a *n*-lithium chloride alcoholic solution, using carbon dioxide as the non-electrolyte. This simple theory requires that the fraction of non-electrolyte salted out by a given concentration of a given electrolyte from a given solvent should be independent of the actual non-electrolyte employed, but because this is usually not found to be true additional postulates have to be made (see Bockris, *Quart. Reviews*, 1949, **3**, 177). For instance, Eucken and Hertzberg (*Z. physikal. Chem.*, 1950, **195**, 1) studied the salting-out effect of sodium, potassium, lithium, and magnesium chlorides on argon, krypton, xenon, oxygen, methane, and ethane from aqueous solutions, and calculated hydration numbers which were approximately independent of the non-electrolyte by allowing for the depolymerisation of the water by the salt and for the hydration of the non-electrolyte. However, this treatment requires additional justification because recent work on the self-diffusion of water indicates that no definite species of associated water molecules are present in liquid water (Wang, *J. Amer. Chem. Soc.*, 1951, **73**, 510, 4181).

Mathematical theories of salting-out from very dilute electrolyte solutions have been advanced by Debye and McAulay (*Physikal. Z.*, 1925, **26**, 22), Debye (*Z. physikal. Chem.*, 1927, **130**, 56), Butler (*J. Phys. Chem.*, 1929, **33**, 1015), Gross *et al.* (*Monatsh.*, 1929, **53**, 445; 1930, **55**, 287), and Altshuller and Everson (*J. Phys. Chem.*, 1951, **55**, 1368). These authors do not consider the molecular structure of the solvent but utilize bulk properties of the system such as the dielectric constant to calculate the changes in concentration resulting from the tendency of the more polarisable molecules to collect round the ions. Some general qualitative agreement is often found between these treatments and experiment (see Randall and Failey, *Chem. Reviews*, 1927, **4**, 271; Gross, *ibid.*, 1933, **13**, 91;

Heal, *Canadian J. Chem.*, 1951, **29**, 563), but these theories do not explain all the observations, and in particular they are inconsistent with the occurrence of "salting-in" and "salting-out" of one non-electrolyte in a given solvent by two different salts (see, e.g., Gross, *loc. cit.*; Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., 1950, p. 400). Factors other than the electrostatic forces must therefore also operate, as Debye himself pointed out (*loc. cit.*, 1927).

Recently, there have been attempts to explain salt effects as a structural phenomenon, and for this purpose the entropy change accompanying the transference of nitrous oxide (or oxygen) from an aqueous alkali halide solution to pure water has been computed (Frank and Evans, *J. Chem. Physics*, 1945, **13**, 507). This entropy change was found to be negative for nitrous oxide in lithium, potassium, and rubidium chloride solutions and in potassium bromide and iodide solutions. Such values can only be explained on Debye and McAulay's theory if additional *ad hoc* assumptions are made on the temperature-dependence of the dielectric constant and on the ionic salting-out radii. A tentative explanation of these observations was advanced in terms of the orientation of the solvent structure by the ions and by the non-electrolyte.

Clearly, any measurements which would give an indication of the conditions existing in the vicinity of the non-electrolyte molecules in a salt solution might contribute to a better understanding of the mechanism of salting-out. A number of studies of the effects of electrolytes on the spectra of coloured materials and on indicators has been published, but because the compounds employed were acids, bases, or substances with large complex molecules the interpretation of the results has been complicated by possible changes in dissociation and aggregation of the molecules containing the chromophore. To avoid these complications the effects of lithium chloride on the ultra-violet spectra of various aromatic hydrocarbons dissolved in ethyl alcohol have now been studied, and the results are reported in the present paper; in Part II (following paper) the effects of salts on the spectra of benzene and naphthalene dissolved in water are examined. For the present purpose ethyl alcohol was chosen as the solvent because it is transparent to ultra-violet light, and lithium chloride was chosen as the salt because it is a strong electrolyte in alcohol (Connell, Hamilton, and Butler, *Proc. Roy. Soc.*, 1934, *A*, **147**, 418). There is some evidence that hydrogen bonding takes place between alcohols and aromatic hydrocarbons in solution (Searles and Tamres, *J. Amer. Chem. Soc.*, 1951, **73**, 3704) but the occurrence of such interaction does not invalidate the conclusions of the present paper.

The changes produced by lithium chloride in the spectra of an alcoholic solution of an aromatic hydrocarbon were measured directly by the four-cell technique described below. The results for benzene, *m*-xylene, naphthalene, anthracene, and chrysene are shown in Fig. 1, where the differences ($\Delta\epsilon$) between the molar extinction coefficients of the solution under study and of the alcoholic solution are plotted against wave-length expressed in $m\mu$. In this paper all values of $\Delta\epsilon$ are measured with respect to the corresponding alcoholic solution. Table I summarises the maximum errors to be expected in $\Delta\epsilon$ for solutions of these compounds in *n*-lithium chloride and in *cyclohexane*. These maximum errors were assessed from comparisons of pairs of identical solutions.

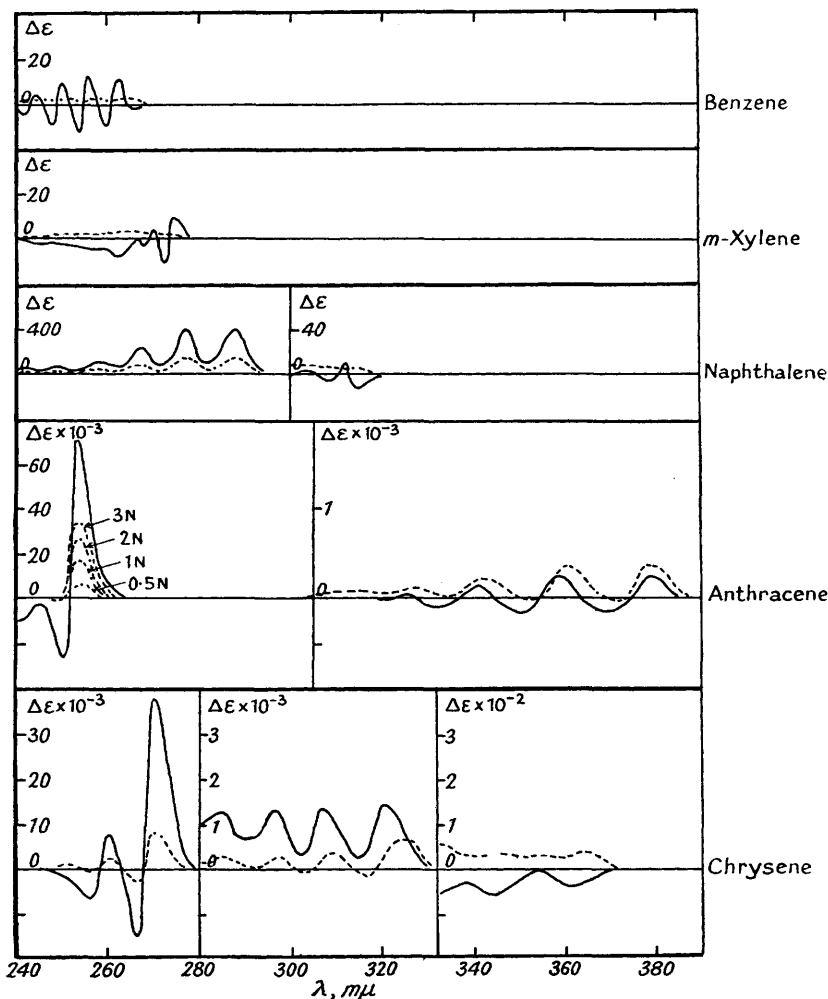
TABLE I. *Maximum error to be expected in $\Delta\epsilon$.*

Hydrocarbon	$\pm\Delta\epsilon$		Hydrocarbon	$\pm\Delta\epsilon$	
	<i>n</i> -Lithium chloride	<i>cyclo</i> -Hexane		<i>n</i> -Lithium chloride	<i>cyclo</i> -Hexane
Benzene	0.5	0.5	Anthracene {	1100	1100
<i>m</i> -Xylene	1	2		{ 240—260 $m\mu$	40
Naphthalene {	10	15	{ 300—390 $m\mu$	500	500
			{ 240—290 $m\mu$		
Naphthalene {	0.5	1	{ 250—280 $m\mu$	50	50
			{ 290—320 $m\mu$		
			{ 280—330 $m\mu$	10	10
			{ 330—370 $m\mu$		

The data in Fig. 1, taken in conjunction with the values in Table I, show that *n*-lithium chloride affects the spectra of all these aromatic hydrocarbons dissolved in alcohol to an extent exceeding the experimental error of measurement. This observation is not consistent with the simple hypothesis that the only action of salt is to immobilize a portion

of the solvent. Fig. 1 also shows the values of $\Delta\epsilon$ obtained with anthracene in the wavelength region 250—260 $m\mu$ for 0.5, 1.0, 2.0, and 3.0N-lithium chloride solutions. The values of $\Delta\epsilon$ increase numerically with increase in salt concentration, but there is no simple relationship between the numerical values of $\Delta\epsilon$ at any fixed wave-length and the concentration of the electrolyte.

FIG. 1.



— Difference in ϵ values ($\Delta\epsilon$) between cyclohexane and alcoholic solutions.
 - - - Difference in ϵ values ($\Delta\epsilon$) between 1N-LiCl and alcoholic solutions.

The observed changes in the spectra ($\Delta\epsilon$) produced by lithium chloride might be caused by direct electrostatic interaction of the ions with the chromophores or by a modification of the interaction of the solvent molecules with the absorbing aromatic nuclei. Both of these mechanisms may operate, but if the aromatic molecules tend to occupy regions of the solution far removed from the ions, as the Debye theory requires, then the hydrocarbon molecules will be shielded from direct electrical effects by alcohol molecules and the observed values of $\Delta\epsilon$ will probably arise mainly from changes in solvent-chromophore interaction. A 50-fold increase in the concentration of anthracene and a decrease in the path length in the same ratio for a 1N-lithium chloride solution gave a curve of $\Delta\epsilon$ in the region 240—260 $m\mu$ which was almost identical with that for the lower anthracene concentration

in a similar salt solution. This observation is compatible with the majority of the aromatic molecules in these solutions occupying parts of the solution remote from the ions. The following observations support the thesis that the observed values of $\Delta\epsilon$ for salt solutions arise mainly from a change in solvent-chromophore interaction.

If the alterations in the spectra caused by lithium chloride are a result of changes in the structure of the alcohol, then it might be expected that the observed $\Delta\epsilon$ values would be of similar magnitude to the $\Delta\epsilon$ values produced by changing to a completely different solvent. Fig. 1 shows that *N*-lithium chloride in alcohol results in smaller values of $\Delta\epsilon$ than does the change from alcohol to *cyclohexane* as solvent. Indeed, in the wave-length region 250—270 $m\mu$ the 1*N*-lithium chloride solution produces maxima in the $\Delta\epsilon$ curves which are numerically from one-fifth to one-third of those produced by *cyclohexane* for all the aromatic hydrocarbons shown in the figures. For naphthalene, anthracene, and chrysene in the higher wave-length regions the values of $\Delta\epsilon$ for the salt and for the *cyclohexane* solutions are of a similar numerical magnitude. The general parallelism between the magnitudes of the $\Delta\epsilon$ values for lithium chloride and for *cyclohexane* is compatible with a common origin for the effect of salt and of *cyclohexane* on the spectra. Additional evidence supporting this view is afforded by the spectra of benzene in alcohol-water mixtures shown in Fig. 3, Part II.

Although not immediately germane to the present argument, it may be noted that the $\Delta\epsilon$ curves for *cyclohexane* solutions of benzene, *m*-xylene, and anthracene show both positive

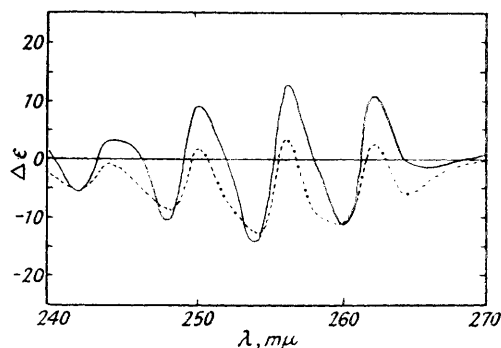


FIG. 2. Benzene.

— Difference in ϵ values between *cyclohexane* and alcoholic solutions.
 - - - Difference in ϵ values between *hexane* and alcoholic solutions.

and negative values throughout the wave-length region studied, but the curves for naphthalene and chrysene exhibit some interesting regularities. For instance, in the wave-length region 240—290 $m\mu$, the $\Delta\epsilon$ curve for naphthalene exhibits only positive values, while in the region 290—320 $m\mu$ both positive and negative values of $\Delta\epsilon$ occur. The chrysene curves exhibit three regions: from 250 to 270 $m\mu$ the $\Delta\epsilon$ curve has both positive and negative portions, from 280 to 330 $m\mu$ the $\Delta\epsilon$ values are all positive, and from 330 to 370 $m\mu$ they are all negative.

Fig. 2 allows the effect of *cyclohexane* and of *n*-hexane on the spectrum of benzene to be compared. This figure shows that the shape of the curve of $\Delta\epsilon$ plotted against wave-length is very sensitive to the structure of the solvent. This observation indicates that, although for some hydrocarbons the values of $\Delta\epsilon$ at a certain wave-length for the lithium chloride and for the *cyclohexane* solutions may be of opposite sign (*e.g.*, chrysene in region 330—370 $m\mu$), yet this behaviour is not incompatible with the effect of the salt being due to a modification in the structure of the solvent.

If the spectral differences produced by lithium chloride in ethyl-alcoholic solutions were due to a direct electrical interaction of the ions with the aromatic molecules, then it would be expected that solution of this salt in benzyl alcohol (with no additional solvent) would cause a spectral change in benzyl alcohol of the same type as is shown in Fig. 1 but of larger magnitude. Curves of $\Delta\epsilon$ plotted against wave-length could not be obtained directly for benzyl alcohol because of the difficulty of manipulating capillary-thickness absorption cells, but the optical densities of a solution of 1*N*-lithium chloride in benzyl alcohol and of benzyl alcohol alone were measured. These spectra are shown in Fig. 3, where the absorp-

tion peaks at $259\text{ m}\mu$ have been adjusted arbitrarily to equality by multiplying all the measured optical densities for one of the curves by a constant factor. A very small difference is found between the curves for benzene in 1*N*-alcoholic lithium chloride and for benzene in ethyl alcohol if these spectra are plotted in the same manner as in Fig. 3, although the salt curve does lie slightly above that for the ethyl-alcoholic solutions at the minima when these curves are adjusted to equality at $255\text{ m}\mu$. The effect of 1*N*-lithium chloride on the spectrum of benzyl alcohol is thus much greater than on benzene in ethyl alcohol, but is different in type, since the benzyl alcohol curve shows more structure in the presence of salt and lies below the benzyl alcohol curve, while the curve for benzene shows less structure in the presence of salt and lies above the curve for benzene in alcohol. The spectral changes produced by the salt and illustrated in Fig. 3 may be a result of the electrostatic field of the ions, but the spectral shifts recorded in Fig. 1 for the ethyl-alcoholic salt solutions probably have a different origin.

These observations on the spectra of ethyl-alcoholic lithium chloride solutions appear to afford direct experimental evidence of a modification in the structure of the alcohol by the ions even at some distance from the ion. This conclusion supports Eley and Pepper's

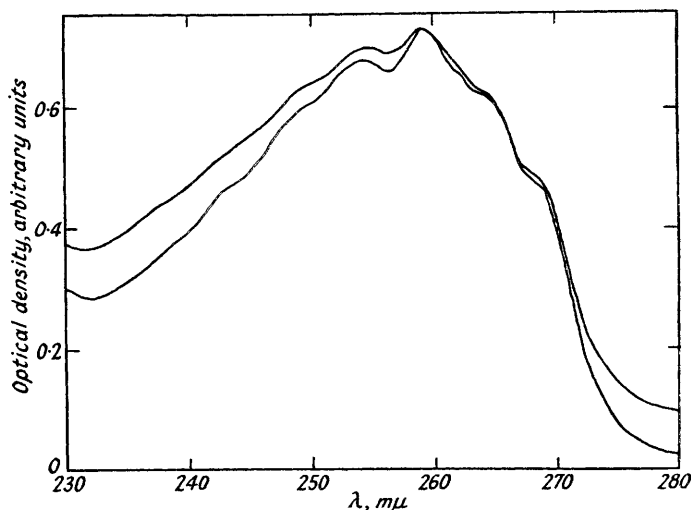


FIG. 3.

Upper curve : Benzyl alcohol.
Lower curve : Benzyl alcohol
+ LiCl.

tentative suggestion (*Trans. Faraday Soc.*, 1941, **37**, 581) that the shell of dipoles orientated by ions in methyl-alcoholic solutions causes the re-orientation of the solvent molecules in the bulk of the solution. Ions in ethyl alcohol would be expected to behave similarly. Obviously, any complete theory of salting-out from alcoholic solutions must take cognisance of the change in the structure of the solvent induced by the salt.

EXPERIMENTAL

Preparation of Compounds.—The benzene and *m*-xylene were standard specimens prepared at the Chemical Research Laboratory and were 99.99 ± 0.005 and 99.97 ± 0.02 mol. % pure, respectively, as established by freezing-point determinations. The naphthalene and anthracene were kindly supplied by the North Thames Gas Board: the former had a purity of greater than 99.99 mol. %, and the latter was a synthetic sample. The chrysene was a pure commercial sample which was recrystallised from alcohol. The benzyl alcohol was a redistilled commercial product.

The lithium chloride was purified and dried by Shaw and Butler's method (*Proc. Roy. Soc.*, 1930, *A*, **129**, 519). Their procedure was modified slightly in that the salt was washed with purified dry ether after crystallisation from alcohol and before drying in a stream of dry hydrogen chloride.

Commercial ethyl alcohol was used as a solvent without further treatment. Care was taken to use alcohol samples from the same bulk for each comparative measurement. *cyclo*Hexane

was purified by treatment with oleum followed by percolation through silica gel, and the *n*-hexane was prepared from a suitable fraction of Fischer-Tropsch product.

Preparation of Solutions.—The purely alcoholic solutions and those containing lithium chloride were made from a common stock solution of the aromatic hydrocarbon in alcohol and in this manner errors in the preparation of the solution were minimized.

The actual concentrations of the hydrocarbons used are summarized in Table 2.

TABLE 2

Hydrocarbon	G./l.	Hydrocarbon	G./l.		
Benzene	0.350	Anthracene {	240—260 m μ	0.0005	
<i>m</i> -Xylene	0.170		300—390 m μ	0.010	
Naphthalene {	240—290 m μ	0.025	Chrysene {	250—280 m μ	0.001
	290—320 m μ	0.500		280—330 m μ	0.010
				330—370 m μ	0.050

Spectrographic Measurements.—All measurements were carried out on a Unicam Quartz Spectrophotometer, a hydrogen lamp being used a light source. The wave-length scale was checked by using a mercury lamp, and the wave-lengths recorded are corrected for the small deviations found. No error in the percentage absorption scale was detected at a wave-length of 546.1 m μ by using a set of neutral filters kindly lent by the Light Division, National Physical Laboratory.

Four-cell Technique for measuring $\Delta\epsilon$.—The values of $\Delta\epsilon$ were obtained by a direct comparison of the spectra of the aromatic hydrocarbon in one solvent with that in another. The four quartz cells employed were of 1-cm. path length and were used in matched pairs A,B; C,D. The procedure used to measure $\Delta\epsilon$ for a lithium chloride solution was as follows. Cell A was filled with the required alcoholic lithium chloride solution containing the aromatic hydrocarbon, and cell C was filled with alcohol. Cell B was filled with an alcoholic solution of the aromatic hydrocarbon containing the same concentration of this material as in cell A. Cell D was filled with an alcoholic lithium chloride solution containing the same number of g. of salt per l. as the solution in cell A. Cells A and C were used together in the light beam, as were also cells B and D. Thus the light path contained the same components at the same concentration when cells B and D were used together as when cells A and C were employed. The cell contents were interchanged after one measurement in order to minimize any small residual differences in the transmission of cell A plus cell C as compared with cell B plus cell D, and in order to minimize any differences in the path lengths of cell A and cell C, and of cell B and cell D. Thus the optical density scale of the spectrometer was set equal to 0.050 with cell B plus cell D as standard, and the optical density, y_1 , of cell A plus cell C was measured. The solutions in cell A and cell B were interchanged, as also were the solutions in cell C and cell D, and a new difference reading, y_2 , was found by taking the cell A plus cell C as standard. The value of the function $[(y_1 + y_2)/2 - 0.050]$ was taken as the change produced by lithium chloride, and $\Delta\epsilon$ calculated. All the difference values ($\Delta\epsilon$) recorded in this paper are with respect to the alcoholic solutions as standards. The apparatus was not thermostatically controlled and the curves refer to a temperature of $20^\circ \pm 3^\circ$.

Capillary-thickness Cell.—The spectra of benzyl alcohol and of benzyl alcohol containing lithium chloride were obtained by means of a wedge cell. This was made from two thin quartz plates, gold leaf being used as a spacer at one end and with the other end of the wedge held together by a paper clip. Since the thickness of this cell could not be reproduced, the curves for benzyl alcohol and for 1*n*-lithium chloride in benzyl alcohol were plotted after arbitrarily adjusting the heights of the main peaks at 259 m μ to equality by multiplying all the values on one curve by a constant factor. No allowance was made for the small absorption produced by the salt itself at the small thickness employed.