601. *The Effect of Solvent on the Ultra-violet Absorption Spectra of Aromatic Hydrocarbons with Special Reference to the Mechanism of Salting-out. Part II.* Aqueous Salt Solutions.*

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The spectra of solutions of benzene and naphthalene in alcohol and in water are compared, and a relation is indicated between the shapes of the absorption curves and the forces to which the aromatic hydrocarbons are subjected in solution.

The effects of lithium, sodium, and cæsium chloride on the spectra and solubility of benzene and of sodium chloride on the spectra of naphthalene in aqueous solutions have been studied. The spectra of saturated benzene solutions in water, 1N-sodium, 1N-lithium, and 1 or 2N-cæsium chloride are identical within the limits of experimental error. The spectra of the saturated benzene solution in 2N-sodium chloride exhibit smaller troughs, and the saturated solution in 2N-lithium chloride exhibits bigger troughs than the solution in pure water. The dependence of the form of the spectra on salt concentration for sodium chloride and for lithium chloride in water indicates that these salts produce more localised modifications in the structure of this solvent than does lithium chloride in alcohol. This conclusion is in agreement with evidence from the measurement of the entropy of the ions. The differences in the behaviour of these two salts are in harmony with published information on the structure of these solutions deduced from *P–V* data.

The changes produced in the spectra of benzene by sodium chloride and lithium chloride dissolved in various alcohol–water mixtures afford evidence of the preferential solvation of the ions by water. The effect of lithium chloride on the solubility of benzene and naphthalene and of sodium chloride on the solubility of benzene in alcohol–water mixtures is recorded.

THE solubility of many aromatic hydrocarbons in water is sufficiently high to enable the ultra-violet absorption spectra to be measured by means of a modern spectrometer with cells as short as 1 cm. For example, Fig. 1 gives the spectra of benzene determined in this way in water and alcoholic solutions. The saturated aqueous solution was used to obtain this curve because unsaturated solutions of known composition could not be manipulated without some loss of hydrocarbon. The peaks at approximately 254 mμ for benzene have been adjusted to equality in this figure by multiplying all the values for one curve by a constant factor, with the result that the ordinate of this graph carries a purely arbitrary scale. The spectrum of aqueous benzene solutions was studied by Henri (*J. Phys. Radium*, 1922, **3**, 181), who employed a photographic technique and recorded only the wave-length of the absorption maxima. The positions of the maxima do not bear any relation to the dielectric constant of the solvent. The changes produced in the positions of the maxima by different solvents are not very large, as was commented upon by Scheibe (*Ber.*, 1926, **59**, 2617).

The majority of published theoretical treatments of solvent effects on absorption spectra have sought to correlate the shifts in the wave-length of the maxima with such properties of the pure solvent as refractive index or dielectric constant (see, *e.g.*, Badger and Pearce, *Spectrochim. Acta*, 1951, **4**, 280 for a review; see also Bayliss, *J. Chem. Physics*, 1950, **18**, 292). Some experimental evidence that systems conforming to these treatments do in fact exist has been obtained from a study of the spectra of aromatic hydrocarbons in a limited series of solvents (*e.g.*, Coggeshall and Pozefsky, *ibid.*, 1951, **19**, 980) but more detailed investigations have revealed many exceptions (*e.g.*, Maddams and Schnurmann, *ibid.*, 1949, **17**, 108; 1950, **19**, 1430). Since such theoretical treatments are based solely on the properties of the pure solvents and all specific interactions between solvent and solute are neglected, it is not surprising that many exceptions are found in practice because the observed shifts are probably the result of the superposition of several effects (see Bayliss,

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* Part I, preceding paper.

loc. cit.). Thus, according to these theories the effect on the spectra of the forces which cause benzene and water to be only partly miscible and cause benzene and alcohol to be miscible in all proportions would be neglected. Further, these theories are usually concerned only with the position of the maxima and not with the general shape of the spectra. However, in Fig. 1 the shape of each curve is the striking feature and not the position of the maxima. There appears to be a general parallelism between the shape of the curve and the forces to which benzene molecules are subjected in solution. For instance, in alcohol, *cyclo*hexane, and *n*-hexane (see also Figs. 1 and 2, Part I), where the fugacity of the benzene is small, the spectra exhibit larger peaks and troughs than in water, where the fugacity is large. Naphthalene in water and in alcohol exhibits a similar behaviour qualitatively, but quantitatively the spectra show a smaller change in shape than does benzene in passing from a good solvent such as alcohol to a poor solvent such as water.

The spectra of saturated solutions of benzene in water, and in 1N-lithium, -sodium, and -cæsium chloride solutions were found to be indistinguishable when the peaks at 254 mμ were adjusted to equality by multiplying all the density values by the appropriate scale factor. Fig. 1 shows the curves for benzene in 2N-sodium and -lithium chlorides. The spectrum of saturated solutions of naphthalene in 1N-sodium chloride was found to be indistinguishable from that of the hydrocarbon in pure water when the peaks were adjusted to equality at 276 mμ, while the curve for this material in 2N-sodium chloride lies slightly above that for this hydrocarbon in water. Clearly, the change in the shape of the curves for both of these hydrocarbons is not proportional to the salt concentration. A similar dependence of the wave-length of the maxima of acetone in aqueous solutions on the concentration of calcium, lithium, and hydrogen chlorides has been reported by Schiebe (*Ber.*, 1925, **58**, 586). The present results, taken in conjunction with the data for anthracene (250—260 mμ) given in Fig. 1, Part I, show that the dependence of the spectra on salt concentration is very different for the aqueous and the alcoholic solutions. These differences are rendered even more noteworthy when it is remembered that the aqueous solutions are saturated with respect to the hydrocarbon, so that the aromatic molecules will be forced into fairly close proximity to the ions, while the alcoholic solutions are unsaturated and the hydrocarbon molecules can occupy regions remote from the ions. This factor would be expected to make the spectral changes for the aqueous solutions relatively more sensitive to small salt concentrations than those for the alcoholic solutions—a conclusion which is, however, contrary to observation. Therefore it must be concluded that the ions produce less disturbance in the structure of water than in the structure of alcohol; indeed, in 1N-aqueous salt solutions there appear to be regions remote from the

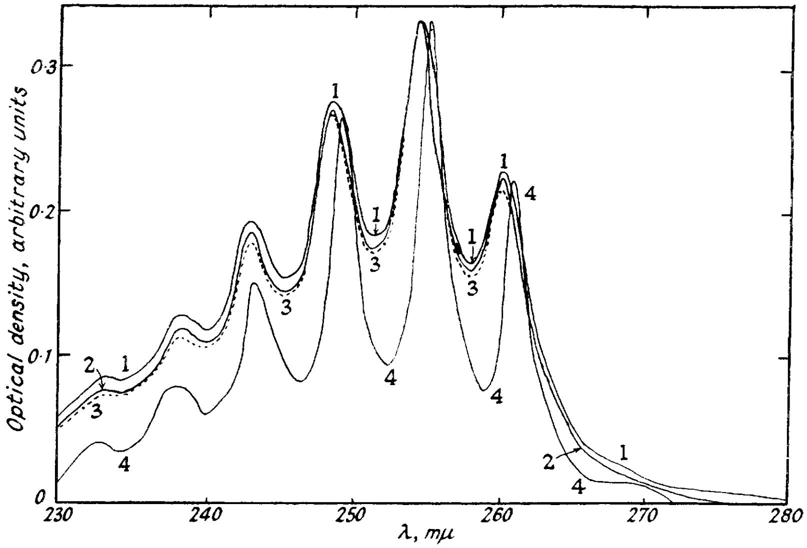

FIG. 1. *Benzene in various solvents.*

1, 2N-NaCl.
2, *Water.*
3, 2N-LiCl.
4, *Alcohol.*

ions where the solvent structure is little different from that in pure water. The conclusion that ions in water have a rather localised effect on solvent structure is in agreement with a tentative interpretation of the data on the hydration entropy of ions advanced by Eley and Pepper (*Trans. Faraday Soc.*, 1941, **37**, 581).

Cæsium chloride in 2N-aqueous solution is without measurable effect on the form of the spectra of benzene, and since the anions and cations in the alkali halide solutions probably act independently on the water structure, this observation indicates that the action of the chloride ion is much less than that of the lithium and sodium ions, a conclusion in agreement with the evidence obtained from transport-number measurements, etc. (*e.g.*, see Gross, *Chem. Reviews*, 1933, **13**, 91), on the behaviour of anions.

There is little information on the salting-out of aromatic hydrocarbons from aqueous solution. Gross (*loc. cit.*) has reported some unpublished work by Saylor which shows that 19·1% of the benzene is salted out by 0·5N-potassium chloride at 30° and some results by Saylor and Whitenfish which show that this hydrocarbon is salted out very little by cæsium chloride. The salting-out of benzene by sodium chloride at 20°±2° was found approximately to follow Setshenow's equation (*Ann. Chim. Phys.*, 1892, **25**, 226), *i.e.*, $\log (S_0/S) = kc$, where S_0 and S are the solubilities of benzene in weight units per unit volume of water and salt solution respectively, c is the salt concentration in moles/l., and k is a constant. This constant for benzene is 0·18 unit, which may be compared with the following recorded values for other substances in sodium chloride solutions: benzoic acid 0·18 (Larsson, *Z. physikal. Chem.*, 1931, **153**, 306); helium 0·053, argon 0·058, hydrogen 0·095, oxygen 0·132, nitrous oxide 0·101, ethylene 0·093, ethyl acetate 0·166, phenol 0·220 (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Table 12.10.5, Reinhold, 1950). The salting-out coefficient for benzene is therefore of approximately the same magnitude as for other substances of nearly the same molecular size (cf. benzoic acid and phenol).

The ratio (S/S_0) for benzene has been determined for 1N-solutions of lithium, sodium, and cæsium chloride as equal to 0·75, 0·68, and 0·84, respectively, and for the first pair of these salts the values for naphthalene were 0·60 and 0·70. These salting-out ratios for benzene do not follow the order of the reciprocal of the ionic radii as required by Debye's theory. From Fig. 1 it can be seen that the spectra of the 2N-solutions of lithium and sodium chlorides differ markedly, and if the sizes of the troughs in the curves be interpreted in terms of the forces on the benzene molecule as suggested earlier, it follows that benzene in sodium chloride is subjected to greater forces, and in lithium chloride to smaller forces, than in water. "Salting-out," however, occurs for the lithium chloride solutions because, although the benzene molecules are subjected to smaller forces in the salt solution than in water, yet the aromatic molecules only occupy regions remote from the ions. The order of the salting-out effect for these halides and the behaviour of the spectra appear to be explicable in terms of the effect of the ions on the structure of water as discussed by Gibson (*Science Monthly*, 1938, **46**, 103) in connection with the compressibilities of salt solutions. He has concluded that the lithium ions are sufficiently small to fit into the orderly arrangement of the water molecules and actually make the openwork structure more rigid, while sodium ions, which are larger, break down the open water structure. The spectra in Fig. 1 agree qualitatively with this conception. The differences between the effects of N-lithium and N-sodium chloride on the solubilities of benzene (0·75 and 0·68) and of naphthalene (0·60 and 0·70) are presumably to be ascribed to a difference in the dependence of the solubilities of these materials on the structure of the solvent.

There is much experimental evidence from thermodynamic, refractometric, partial molar volume, and conductimetric studies that water tends to collect preferentially around the ions in alcohol–water mixtures (see, *e.g.*, Butler and Robertson, *Proc. Roy. Soc.*, 1929, *A*, **125**, 694; Shaw and Butler, *ibid.*, 1930, *A*, **129**, 519; Butler and Lees, *ibid.*, 1931, *A*, **131**, 382; Connell, Hamilton, and Butler, *ibid.*, 1934, *A*, **137**, 418). According to the electrostatic theory of salting-out, benzene should occupy regions of the solution remote from the ions in salt–alcohol–water mixtures, and hence the spectra of benzene should be modified by addition of salt if these regions are partly depleted of water by the salt. In order to see whether this effect could be detected spectroscopically, curve 3 in Fig. 2

was obtained, where the optical density at 257·8 mμ of various alcohol–water mixtures (x is the mole-fraction of alcohol) containing 0·616 g. of benzene per l. is plotted against solution composition. In the same figure are plotted the corresponding quantities for benzene in 1N-sodium chloride solution for 0·00—0·30 mole-fraction of alcohol and for 1N-lithium chloride solution for the entire solvent range. The changes produced in the spectra of benzene by each of these salts for compositions 0—0·30 mole-fraction of alcohol are consistent with the supposition that benzene molecules in these salt solutions are surrounded by a solution richer in alcohol than the bulk composition. Sodium chloride produces a larger shift in the spectra than does lithium chloride for a given solvent composition, and this observation is probably to be ascribed to the greater affinity of lithium chloride for alcohol; *i.e.*, for a given initial solvent composition there are probably more alcohol molecules in the neighbourhood of a lithium than of a sodium ion.

The curve for the 1N-lithium chloride solution in Fig. 2 crosses that for the alcohol–water mixture alone at 0·50 mole-fraction of alcohol, which might be interpreted as indicating that the salt is preferentially solvated by alcohol in the alcohol-rich solutions; however, the optical density values for benzene in 1N-lithium chloride in 100% alcohol and for benzene in pure alcohol do not coincide (see values for x = 1·00 in Fig. 2), showing that this simple explanation is incorrect. The change in the spectra produced by the salt in 100% alcoholic solution is a result of a modification in the structure of the pure alcohol (see Part I), and a similar process probably complicates the interpretation of the spectral changes for alcohol–water mixtures of high alcohol content. This factor is probably not important for solutions of low alcohol content because, as Fig. 2 shows, all the curves coincide at x = 0. Hence, the curves in Fig. 2 for the composition range x = 0—0·30 can probably be interpreted solely in terms of the change in the water content of the " free " solvent, and the structure of the solvent in the neighbourhood of the aromatic molecules can be assumed to be the same as that of a solution of similar composition in the absence of salt.

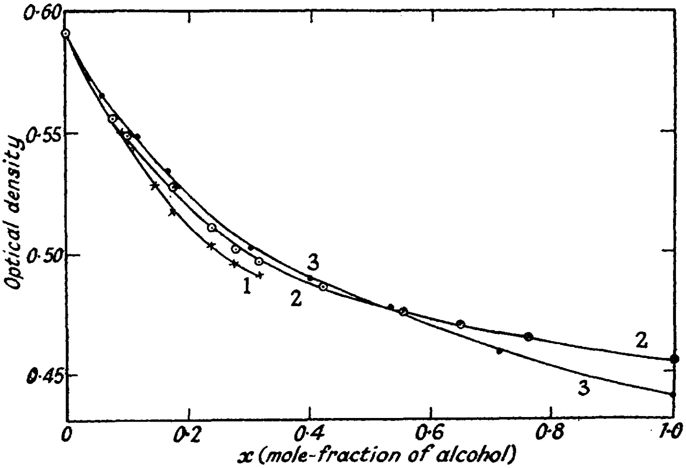

FIG. 2. *Benzene at* 257·8 mμ.

1, *Alcohol*–1N-NaCl.
2, *Alcohol*–1N-LiCl.
3, *Alcohol–water.*

Fig. 3 shows in more detail than Fig. 2 the effect of 1N-lithium chloride on the spectra of solutions containing 0·616 g. of benzene per l. dissolved in alcohol–water mixtures of 0·17, 0·27, and 1·00 mole-fraction of alcohol. Each $\Delta\varepsilon$ value was measured with respect to solvent of the same water–alcohol content. This figure strongly supports the conclusion reached in Part I that the effect of a salt on the spectrum of a dissolved aromatic hydrocarbon is due to a modification in the structure of the solvent, because if the effect had been due to direct electrical action of the ion on the hydrocarbon, all the curves in Fig. 3 would probably have been identical in form and the corresponding maxima and minima would have differed only in magnitude.

The preferential solvation of the ions by water should increase the concentration of alcohol in the free liquid of an alcohol–water mixture, and hence if a given quantity of alcohol is a better solvent for a non-electrolyte in the enriched solution than is the original mixture, the addition of salt should cause "salting-in" of the non-electrolyte. In this manner Wright (*J.*, 1926, 1203) explained the observation that if 1-c.c. portions of benzene were added to 100 c.c. of 50% alcohol until the solution was turbid, then the addition of solid sodium chloride would clear the solution again. Recently, Bockris and Egan (*Trans. Faraday Soc.*, 1948, **44**, 151) have advanced a similar explanation to account for the effect of sodium chloride on the solubility of benzoic acid in alcohol–water mixtures. The effect of 1N-lithium and 1N-sodium chloride on the solubility of benzene in alcohol–water mixtures in the range of solvent composition from 0·00 to 0·30 mole-fraction of alcohol, and also of 1N-lithium chloride on the solubility of naphthalene throughout the entire solvent range, has now been measured by a spectroscopic technique. The results of these measurements are summarised in Fig. 4, where the ratio (S/S_0) is plotted against x, where S is the solubility of the aromatic hydrocarbon per unit volume of the electrolyte solution, S_0 the solubility in the absence of salt, and x the mole-fraction of alcohol. Thus in this figure "salting-out" corresponds to $(S/S_0) < 1$, and "salting-in" is equivalent to $(S/S_0) > 1$. These curves show that sodium chloride "salts-in" benzene much more readily than does lithium chloride, and indeed the ratio (S/S_0) for lithium chloride only just exceeds 1 at $x = 0{\cdot}24$.

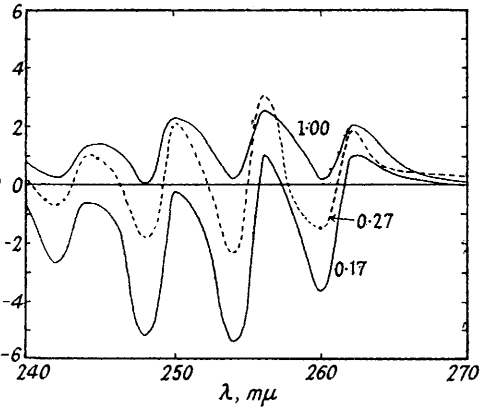

FIG. 3. *The effect of* 1N-*lithium chloride on the spectrum of benzene in various alcohol–water mixtures.*

(*The figures on each curve refer to mole-fraction of alcohol.*)

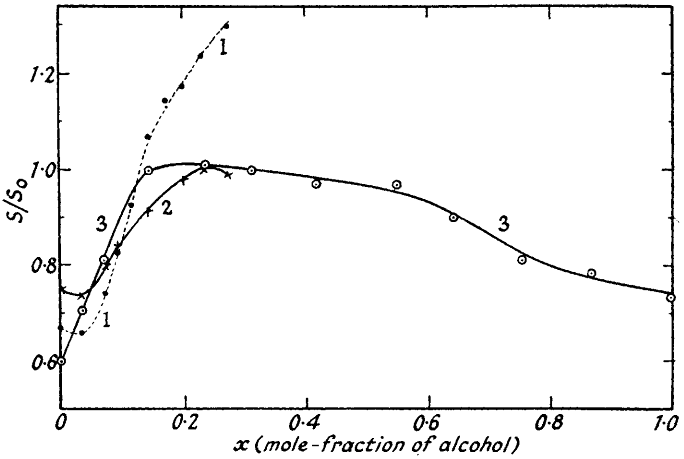

FIG. 4. *Relative solubilities of hydrocarbons in salt solutions.*

1, *Benzene in* 1N-NaCl.
2, *Benzene in* 1N-LiCl.
3, *Naphthalene in* 1N-LiCl.

The discussion of the curves in Fig. 4 in terms of the solubilities of the aromatic hydrocarbon in alcohol–water mixtures in the absence of salt can most readily be carried out if a simple model of the system is adopted. Suppose a salt is dissolved in a quantity of solution containing 1 g.-mol. of alcohol of composition x_1 mole-fraction of alcohol, and let both water and alcohol be bound to the salt by solvation. Let a fraction q of the alcohol present be bound in this way, and let the resulting " free liquid " contain a mole-fraction x_2 of alcohol. Then if it be assumed that the water and alcohol bound to the ions are incapable of dissolving non-electrolyte while the " free liquid " has the same power of dissolving the non-electrolyte as an alcohol–water mixture of the same composition in the absence of salt, the following expression is obtained if volume changes on mixing are neglected :

$$(S/S_0) = (1 - q)\phi(x_2)/\phi(x_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The function $\phi(x)$ is the number of g.-mols. of the non-electrolyte which dissolve in that quantity of an alcohol–water mixture which contains 1 g.-mol. of alcohol and has a composition of x mole-fraction of alcohol; $\phi(x_2)$ and $\phi(x_1)$ are the values of the function $\phi(x)$ at $x = x_2$ and at $x = x_1$, respectively.

The function $\phi(x)$ can readily be computed from solubility measurements of the non-electrolyte in a series of alcohol–water mixtures, and the resulting functions for benzene (range $x = 0{\cdot}00$—$0{\cdot}30$) and for naphthalene (range $x = 0{\cdot}00$—$1{\cdot}00$) are plotted in Fig. 5. This figure shows, *e.g.*, that 1 g.-mol. of 100% alcohol ($x = 1{\cdot}00$) dissolves 0·035 g.-mol. of naphthalene, while the same quantity of alcohol mixed with 3 g.-mols. of water (*i.e.*, $x = 0{\cdot}25$) dissolves 0·0022 g.-mol. of naphthalene. The function $\phi(x)$ tends to infinity as x tends to zero.

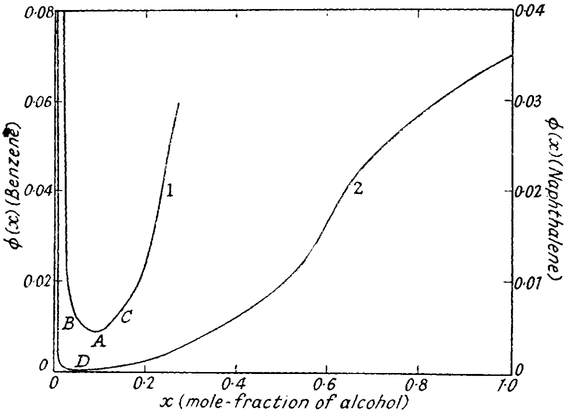

FIG. 5. *The function $\phi(x)$ plotted against x for :*

1, Benzene.

2, Naphthalene.

The curves in Fig. 4 can now be discussed in terms of equation (1) and Figs. 2 and 5. Since Fig. 2 shows that for x between 0·00 and 0·30 the relationship $x_2 > x_1$ is obeyed, it follows from Fig. 5 and equation (1) that if $q = 0$ then both salts will cause " salting-in " of benzene in solutions containing more than 0·10 mole-fraction of alcohol (*i.e.*, for points to the right of A, Fig. 5) because for these compositions $\phi(x_2)_1/\phi(x_1)$ will be greater than 1. Actually, if $q = 0$ " salting-in " might occur at lower alcohol concentrations, *e.g.*, at point B, Fig. 5, provided that composition x_2 corresponded with some point such as C, but on the present model when $q = 0$, " salting-in " *must occur* for alcohol concentrations greater than the composition at point A. However, Fig. 4 shows that lithium chloride does not produce " salting-in " until the mole-fraction of alcohol exceeds 0·22 and the corresponding value for sodium chloride is 0·13. These values therefore indicate that $q \neq 0$ for both of these salts and therefore some alcohol as well as water is immobilised by the ions. The difference between the solvent composition at which lithium ($x = 0{\cdot}22$) and sodium chloride ($x = 0{\cdot}13$) cause " salting-in " of benzene is to be ascribed to a higher value of q for lithium than for sodium chloride. This difference in the behaviour of the two salts is presumably a result of the same forces which cause lithium chloride to be appreciably soluble and sodium chloride to be slightly soluble in 100% alcohol. The naphthalene curves in Figs. 4 and 5 also lead to the conclusion that for lithium chloride $q \neq 0$, because if $q = 0$ then " salting-in " would be expected for alcohol concentrations greater than 0·05 (Fig. 5), while, as Fig. 4 shows, this does not in fact take place until a mole-fraction of 0·12 is attained. The lower alcohol concentration at which " salting-in " by lithium chloride commences with naphthalene compared with benzene is compatible with the solubilities of these hydrocarbons in the mixed solvents [*i.e.*, with the relative positions D and A, of the minima in the $\phi(x)$–x curves Fig. 5]. Therefore it may be concluded that lithium and sodium chlorides are preferentially solvated by water in alcohol–water mixture of 0 to 30% alcohol but the solvent sheaths contain some alcohol, and that of the lithium ion more than that of the sodium ion.

EXPERIMENTAL

Preparation of Compounds.—The history of the majority of the compounds used has been given in Part I. "AnalaR" Sodium chloride was employed, and the cæsium chloride was a purchased specimen used without further purification. The water used was doubly distilled.

Preparation of Solutions.—Allowance was made by means of subsidiary experiments for the volume change accompanying mixing in the preparation of alcohol–water and alcohol–water–salt mixtures. Saturated solutions of benzene were prepared by shaking a very slight excess of liquid benzene with the solvent and keeping it in contact with the solution for several days. Saturated aqueous solutions of naphthalene were prepared by melting the hydrocarbon in the solvent, vigorously shaking it, and allowing the solutions to stand for several days. A small quantity of undissolved hydrocarbon was always present in the cell when saturated solutions were measured.

Spectrographic Measurements.—The equipment used in Part I was employed, and quartz cells of 1 and 0·3 mm. were used as required. The four-cell technique described in Part I was used to obtain the data for Figs. 2, 3, and 4.

Salting-out Measurements.—These values were obtained from the ratios of the optical densities of the saturated salt solution and of the saturated solution without salt at convenient wave-lengths: each optical-density measurement was corrected for the absorption of the corresponding solvent mixture. The difference produced in the shape of the spectra of the aromatic hydrocarbon by the salt was neglected for this purpose. The error in (S/S_0) resulting from this approximation is probably less than 1% for the 1N-aqueous salt solutions and probably less than 5% for the 1N-alcoholic solutions. The actual temperatures used were not controlled and were 20° ± 3°, but the temperatures of any pair of saturated solutions of the same solvent composition, one with and one without salt, were the same.

Solubility Measurements.—These were obtained from the ratios of the optical densities, at a convenient wave-length, of the saturated solution to that of a synthetic mixture of approximately one-third of the concentration of the saturated solution. The values given in the following table were obtained in this manner for a temperature of 20° ± 3°.

The following solubilities are listed by Seidell ("Solubilities of Organic Compounds," Van Nostrand, New York, 1941, Vol. II): 100 g. of water dissolve 0·175 g. of benzene at 20°; 1 l. of water dissolves 0·022 g. of naphthalene at 15° and 0·030 g. at 20°; the solubility of naphthalene in alcohol is 10·2 g. per 100 g. of solvent at 20°. Andrew and Keefer (*J. Amer. Chem. Soc.*, 1949, **71**, 3644) have recorded that 1·74 g. of benzene and 0·0315 g. of naphthalene are dissolved in a litre of the saturated aqueous solutions at 20°. Recent measurements by Bohon and Claussen (*ibid.*, 1951, **73**, 1571) give a solubility of 1·79 g./l. for benzene and 0·028 g./l. for naphthalene at 20°. The figures in the above table are thus seen to be in satisfactory agreement with the published values.

Solubilities of benzene and naphthalene in alcohol–water mixtures.

Mole-fraction of EtOH in initial liquid	G./l. of satd. solution :		Mole-fraction of EtOH in initial liquid	G./l. of satd. solution :	
	C_6H_6	$C_{10}H_8$		C_6H_6	$C_{10}H_8$
0	1·78	0·025	0·271	42·1	—
0·034	2·03	0·039	0·312	—	4·74
0·072	2·61	0·078	0·415	—	9·60
0·094	3·14	—	0·548	—	20·2
0·117	3·56	—	0·642	—	37·1
0·142	6·00	0·30	0·754	—	47·5
0·169	9·08	—	0·867	—	58·3
0·200	15·1	—	1·000	—	70·3
0·234	24·5	2·10			

The work described in this and the preceding paper has been carried out as part of the research programme of the Chemistry Research Board and is published by permission of the Director, Chemical Research Laboratory, Teddington.

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