

**370.** *The Solvent Properties of Aqueous Solutions of Paraffin-chain Salts. Part I. The Solubility of trans-Azobenzene in Solutions of Cetylpyridinium Salts.*

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Aqueous solutions of paraffin-chain salts have considerable solvent powers for organic substances only slightly soluble in water alone. This is due to these salts forming, in solution, micelles of which the interior is composed of the paraffin chains in a liquid state of aggregation. Solutions of non-polar crystalline substances which are insufficiently soluble to modify considerably the properties of the micelle provide the simplest type of system. In this communication, measurements are reported of the solubility of *trans*-azobenzene in solutions of several cetylpyridinium salts. The ratio of azobenzene molecules to paraffin-chain ions is approximately constant over a wide range of concentrations and is of the same order as the molecular ratio in a saturated solution in paraffin in bulk. The constancy is not exact, and the ratio varies somewhat with the nature of the anion, indicating that the solvent power

of the micelle is slightly modified by its ionic environment. The transition in very dilute solutions from the ionically disperse to the aggregated condition is strikingly demonstrated by this solubility method. The method can be applied in the presence of high concentrations of simple salts, and the effect of these has been examined.

If an organic solvent, miscible with water, is saturated with a non-polar substance, it is a matter of common experience that the addition of a quite small amount of water will throw a large fraction of the substance out of solution. For example, from Christiansen's data (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1918, 4, No. 2) we find that the amounts of naphthalene dissolved by 100 g. of methyl, ethyl, and propyl alcohols after addition of 20 g. of water are respectively only 0.29, 0.41, and 0.53 of the amounts dissolved in the absence of water. After addition of 100 g. of water these fractions become 0.045, 0.094, and 0.24. The solvent power becomes much smaller still on further dilution. For example, acetone in 50, 20, and 10% mixtures with water has only 0.021, 0.0005, and 0.0002 of the solvent power of pure acetone for *trans*-azobenzene (present work).

This behaviour is entirely to be expected from considerations of statistical mechanics. It need only concern us now, however, to emphasise its very wide generality and to note an important further point which emerges from Christiansen's data and is supported by what other evidence is available on similar systems. The alcohols lose their solvent power on dilution by no means equally rapidly, but markedly less rapidly in the sequence methyl > ethyl > propyl. Comparison at corresponding mol.-fractions instead of weight fractions serves only to make the differences greater. This sequence is that of decreasing intimacy of mixture with water, as judged either by expectation from solution theory, by the ease with which the alcohol is salted out from water, or by the curvature of the vapour pressure-mol.-fraction plots. We may say that a solvent which mixes with water loses most of its solvent power for non-polar substances when it does so, and that the extent of this loss is a measure of the completeness with which the molecules are inter-dispersed.

Aqueous solutions of paraffin-chain salts, *i.e.*, salts in which the charge of one kind is carried by a group at the end of a long paraffin chain, have considerable solvent properties in addition to, and quite distinct from, their effectiveness as emulsifying agents (Pickering, J., 1917, 111, 86; Bailey, J., 1923, 123, 2579; Angelescu and Popescu, *Kolloid Z.*, 1930, 51, 247; Lester Smith, *J. Physical Chem.*, 1932, 36, 1401, 1672, 2455; Hartley, "Aqueous Solutions of Paraffin-chain Salts," Hermann, Paris, 1936, p. 41; McBain and Laing-McBain, *J. Amer. Chem. Soc.*, 1936, 58, 2610; Hartley, article in "Wetting and Detergency," Harvey, London, 1937, p. 153; Lawrence, *Trans. Faraday Soc.*, 1937, 33, 815; McBain and Woo, *J. Amer. Chem. Soc.*, 1938, 60, 223).

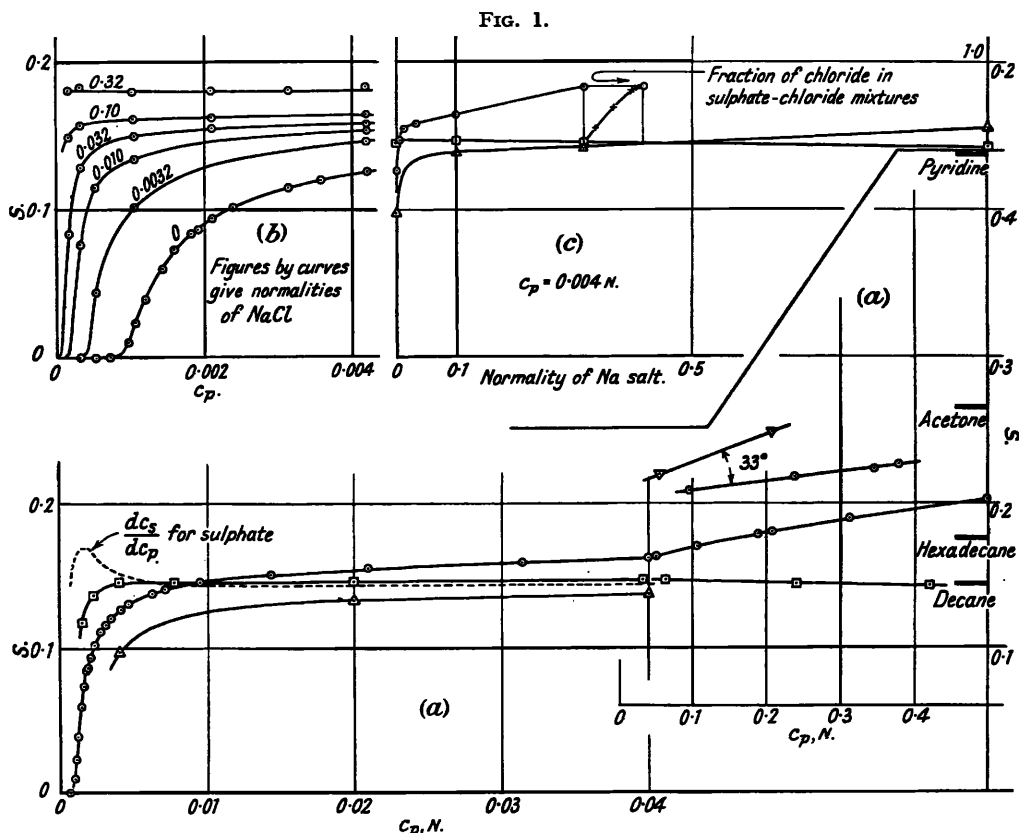
These salts, when in clear solution, greatly augment the solubility of many organic substances in water at dilutions where alcohol, acetone, etc., would produce only an immeasurably small effect. The molecular ratio of saturant (in excess of that which would be taken up by the water alone) to paraffin-chain salt is, by contrast with the corresponding ratio for a diluted ordinary organic solvent, only slightly dependent on manifold changes of dilution. When the saturant is a crystalline solid, this ratio, which we shall call the saturation ratio, is of the same order as the ratio of saturant to solvent in solution in an ordinary anhydrous organic solvent. The possibility that this behaviour might be due to the formation of very stable complexes between saturant and paraffin-chain ion is quite ruled out by the great variety of substances which can be dissolved, many of them very stable chemically, and of ionic groups to which the paraffin-chain may be attached. Furthermore, the saturation ratio is not quite constant and does not in general approximate to any simple integral ratio.

It must be concluded that the paraffin-chain salt, although it may be highly crystalline in the pure state, behaves as a *liquid* solvent on solution in water, and that that part of it which is responsible for the solvent action is *not diluted by the water* in the sense of being intimately dispersed as separate ions. This is exactly the conclusion to which other evidence on the properties of these solutions has led (Hartley, *loc. cit.*, 1936; Adam, *Ann. Reports*, 1936, 33, 103; Hartley and Runnicles, *Proc. Roy. Soc.*, 1938, A, 168, 420). The paraffin-chain ions aggregate into micelles with the ionic groups forming a hydrophilic

outer layer round a paraffin interior. The paraffin chains move freely in this interior, subject to the restrictions imposed by the limited size of the aggregate and the necessity of the ionic groups being "anchored" in the outer layer. The solution therefore in some ways resembles an amicroscopic emulsion of paraffin and will have the solvent properties of paraffin added on to those of water. For saturants which themselves have "amphiphatic" molecules (Hartley, *loc. cit.*, 1936, p. 44), *i.e.*, molecules having considerably separated groups of markedly different affinity, it is to be expected that orientation in the micelle will cause the solubility in a paraffin-chain salt solution to be more than additive for the paraffin and water contents. The various types of system encountered and to be expected have been discussed by Hartley (*loc. cit.*, 1937) and Lawrence (*loc. cit.*).

Fuller investigation of this solvent action should throw valuable light, not only on the constitution of the micelle, but also on more fundamental problems in solution and adsorption theory. This communication is concerned only with the simplest type of system—where the saturant is a non-polar crystalline substance, the solubility of which, although great enough to be easily measured, is not so great that the properties of the micelle will be considerably altered by its presence. Such a substance might be expected to dissolve entirely in the paraffin interior of the micelle, and so to give a saturation ratio independent of concentration and approximating to that obtaining in paraffin in bulk. Azobenzene was chosen as fulfilling the required conditions and being in addition easily purified and readily estimated in very dilute solutions by the photo-absorptiometric method.

In Fig. 1 (*a* and *b*) the saturation ratio is plotted against the concentration ( $c_p$ ) of paraffin-chain salt, and in Fig. 1*c* against the concentration of the corresponding sodium



Saturation ratios for cetylpyridinium salts in water ( $\odot$ , chloride;  $\triangle$ , acetate;  $\square$ , sulphate;  $\nabla$ , bromide) and for some undiluted solvents ( $-$ ). Values at 25° except where otherwise indicated.

salt for a constant value of  $c_p$ . Examination of the curve for cetylpyridinium chloride without added salt (Fig. 1a, with extension into high concentrations on a smaller scale on the right, and with the low concentrations on a larger scale in the lowest curve of Fig. 1b) shows that there is no detectable solvent action for  $c_p < 0.0009N$ . Above this concentration, the saturation ratio rises very rapidly, attaining a value more than half of that at 500 times this concentration within the first hundredth of this range. This is in line with other properties (Hartley, *loc. cit.*, 1936; Adam, *loc. cit.*). At just the same concentration, for example, the equivalent conductivity commences to fall very rapidly from the value characteristic of a normal electrolyte (Malsch and Hartley, *Z. physikal. Chem.*, 1934, A, 170, 321). It is due to there being a "critical" concentration for micelles, below which hardly any exist, and above which they contain most of any further paraffin-chain ions added. The abruptness of the transition is to be expected from mass-action considerations (Bury *et al.*, *Phil. Mag.*, 1927, 4, 841; J., 1929, 679; 1930, 2263. See also Murray and Hartley, *Trans. Faraday Soc.*, 1935, 31, 183).

The effect of addition of sodium chloride in lowering the critical concentration is illustrated in Fig. 1b. The lower parts of the curves are derived from direct plots of  $c_s$  (the saturation concentration of azobenzene) against  $c_p$ . In calculating the saturation ratio,  $S = (c_s - c_s^0)/c_p$ ,  $c_s^0$  is here the value of  $c_s$  in the appropriate solution of sodium chloride alone. Sodium chloride in 0.032N-concentration has already reduced the critical concentration for micelles from 0.0009N to less than 0.0001N. With higher concentrations of salt, the experimental accuracy is not sufficient to permit the still lower critical concentrations to be determined. These results are consistent with the low concentrations of paraffin-chain salt it was found possible to use in diffusion measurements in sodium chloride solutions without an increase of diffusion coefficient being apparent (Hartley and Runnicles, *loc. cit.*). The effect of salt found here in increasing the solubility of a non-polar substance in an apparently aqueous medium is a quite anomalous phenomenon unless it is looked upon as a secondary effect of a (partial) normal "salting out" of the active solvent. The very direct evidence that, at the critical concentration, the paraffin-chain ions aggregate into a virtually separate phase is conclusive against the alternative theory of Howell *et al.* (*Proc. Roy. Soc.*, 1936, A, 155, 386; 1937, A, 160, 440), put forward to explain the critical concentration for conductivity in pure solutions.

The broken curve in Fig. 1a represents the quantity  $dc_s/dc_p (= S + c_p \cdot dS/dc_p)$  for the sulphate. Its almost complete independence of concentration above *ca.* 0.006N (and of the concentration of sodium sulphate when added) shows that the solvent properties of the micelle are in this case almost uninfluenced by ionic environment. That it goes through a maximum (at  $c_p = ca.$  0.002N) can therefore only mean that, in this region, the micelle concentration (to which  $c_s$  is proportional) increases more rapidly than the total concentration, some of the already present single ions being incorporated into the micelles along with those added. This is the first direct experimental evidence of a prediction by Murray (*Trans. Faraday Soc.*, 1935, 31, 206; see also Hartley, *loc. cit.*, 1936, p. 25).

A similar maximum (not shown) is found in the case of the chloride, but is here hardly outside the experimental error and is obscured by the curve descending on to a slow upward slope which is maintained up to very high concentrations. Evidently, the solvent power of the micelles in the chloride solution increases with increase of concentration. It will be seen (Fig. 1c) to increase comparably with increase of sodium chloride concentration, after an initial much steeper increase of  $S$  due to completion of micelle formation. In the bromide solutions, the increase with  $c_p$  is greater. In the acetate solutions, it is less, and the effect of simple salt is also less.

The solvent powers of the micelles in the pure solutions increase in the same order as do their sizes as deduced from mobility measurements (Samis and Hartley, *Trans. Faraday Soc.*, 1938, 34, 1288). In the effect of addition of simple salt, however, there is no parallelism. Diffusion measurements indicate that, in excess of simple salt, the micelle size is hardly at all dependent on the nature of the anion or the concentration. The differences in size are thus reduced by addition of salt. The differences in solvent power are increased. It must be emphasised that the differences that we are here concerned with are all of a minor order

and do not indicate any fundamental changes in the structure of the micelles. Evidently only one of the factors controlling size is of significance in controlling solvent power. This is probably the extent of penetration of anions into the outer layer of the micelle. There is a greater fraction of halide ions incorporated in the micelle than of sulphate ions, a difference parallel to the solubility of the cetylpyridinium salts in organic solvents (cf. Samis and Hartley, *loc. cit.*). An outer layer extensively penetrated by halide ions (as ion pairs) will permit the inclusion also of the polarisable azobenzene molecules, whereas the outer layer of the micelle in the sulphate solutions, being more ionised and giving place more sharply to water, will permit this inclusion to a much smaller extent. In this connexion it is of significance that the solubility of azobenzene (as will be seen from the saturation ratios for pure solvents indicated on the right of Fig. 1a and recorded in Table II) is considerably less than ideal in paraffins and more nearly approaches the ideal in some polar solvents. The saturation ratio for cetylpyridinium sulphate is at all concentrations less than the value for hexadecane in bulk, as is to be expected on account of the restriction on the movement of the paraffin chains in the micelle and the pressure to which the micelle is subjected by the surrounding water (Hartley, *loc. cit.*, 1937). In the solutions of the chloride, however, and still more in those of the bromide, this ratio exceeds the value for hexadecane. The outer part of the micelle is presumably here coming into play. Could a crystalline paraffinic substance have been substituted for azobenzene, the behaviour would probably have been simpler.

Mobility measurements in mixtures of cetylpyridinium chloride and sulphate solutions indicated that the chloride ions, despite their lower charge, are preferred for attachment to the micelles. A corresponding experiment was made in this work, but the solutions with added sodium salts, in which the saturation ratios are more widely different, were chosen. An appreciable departure from a simple additive behaviour was evident in the sense of the solubility being more nearly that in the solution of chlorides only (see Table Ia and small inset in Fig. 1c). The departure is not apparently very great, but it must be remembered that the sulphate ions will be very much more concentrated relatively to the chloride at the surface of the micelle than in the bulk of the solution, so that the preference for incorporation of chloride ions in the micelle is in reality much greater than at first appears.

#### EXPERIMENTAL.

*Materials.*—*trans*-Azobenzene was purified as previously described (this vol., p. 633). It was obtained in small crystals, suitable for solubility work, by precipitating it from an acetone solution by slow addition of water with constant stirring. Before filtration, a small further amount of acetone was added to redissolve any very small nuclei, the presence of which was found to give rise to turbidity in dilute solutions of paraffin-chain salts. Freedom from superficial contamination with *cis*-form was confirmed by determining the solubility of the same sample in successive volumes of water, in which the *cis*-form is much more soluble.

Cetylpyridinium chloride was prepared as described by Hartley (*J. Amer. Chem. Soc.*, 1936, 58, 2347). The concentration of stock solutions was determined by electrometric titration with silver nitrate solution. The acetate was prepared in solution from a standard solution of bromide, as described by Samis and Hartley (*loc. cit.*); the solution, at first faintly cloudy, became perfectly clear after standing for some weeks, the residual colloidal silver bromide having precipitated in an adherent form on the walls of the glass vessel. A trace of acetic acid was added in the preparation to avoid development of a yellow colour which always takes place in alkaline solutions. The concentration was determined by titration with a cetane-sulphonate solution (Hartley and Runnicles, *loc. cit.*), and indicated that 0.5% of the cetylpyridinium had been lost during the conversion from the bromide. For some measurements, the preparation of sulphate solution described by Samis and Hartley was used, and for others a solution obtained by adding the equivalent amount of sulphuric acid to the acetate solution. The results were in good agreement, the free acetic acid in the concentrations used having apparently no effect.

Hexadecane (m. p. 17—19°) was a specimen (kindly supplied by Prof. N. K. Adam) prepared by decomposition of the magnesium compound of cetyl bromide with water. Decane (b. p. 172—175°) was prepared by the Wurtz method from *n*-amyl bromide. Other solvents used were commercial pure materials.

Since earlier measurements indicated a slow upward drift of solubility, traced to photochemical production of *cis*-azobenzene in solution (this vol., p. 633), all the measurements here reported were made in a dimly lit room and the thermostat water in which the solubility vessels were immersed was deeply stained with methyl-orange.

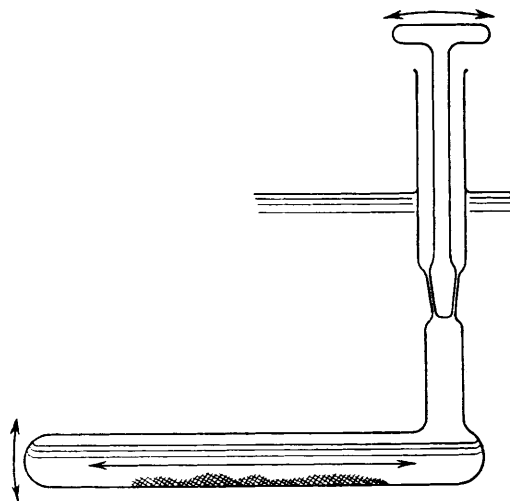
The vessels were of the shape shown in Fig. 2, of capacities from 5 to 100 c.c. according to the volume necessary for analysis. They were mounted in a frame, which was supported on bearings on the outside of the tank and subjected to a continuous rocking motion of about 15 cycles per minute. This gave to the vessels the motion indicated by the external arrows, and to their contents (which did not completely fill the "horizontal" tubes) that indicated by the internal arrows. The stoppers were recessed as shown below the water level to avoid condensation. This apparatus is very convenient, as a large number of vessels can be housed in one tank, and the mechanical parts are very simple and reliable.

Equilibrium was attained almost as rapidly in the paraffin-chain salt solutions as in water-acetone mixtures, 6 hours being usually sufficient. Confirmation of the equilibrium was obtained in typical cases by observation of the fall of the azobenzene concentration to its previous value after the vessels had been maintained at a higher temperature for some hours. To eliminate the possibility of decrease of concentration of paraffin-chain salt by adsorption on the solid saturant, each sample was treated with several successive samples of solvent when this was a dilute solution. No such effect was observed. Concentrated solutions of the chloride become appreciably more viscous on saturation with azobenzene. There is no noticeable effect on the sulphate or acetate, but a much greater effect on the bromide. At higher concentrations than 0.2N, this solution becomes much too viscous to filter, and even at this concentration the rocking of the vessel was quite ineffective in stirring the solution. The value recorded was obtained from a solution cooled after saturation at a higher temperature. The solution process is not to be confused with colloidal "peptisation." The solutions are perfectly clear, when the above-mentioned precaution is taken of avoiding excessively small crystals of the saturant, and even this is unnecessary with paraffin-chain salt concentrations above 0.005N.

Samples of the solutions were extracted for analysis through Jena micro-immersion filters, diluted with water or the appropriate sodium salt solution if necessary, and readings taken in a suitable cell on a photoelectric absorptiometer. Though the solutions were supersaturated at room temperature, they could be relied upon to remain so for the few minutes necessary for the measurements to be effected. Azobenzene separates from them in small scintillating plates whose presence is very easily detected.

The azobenzene concentrations were determined as follows. A larger volume than usual of one of the more concentrated solutions of each pure salt was saturated. A suitable volume of filtrate was made up to a standard volume with acetone, and the photometer reading taken. Standard solutions were then prepared from equal volumes of the original aqueous solution and various volumes of a more concentrated solution of azobenzene in acetone, made up to standard volume with acetone. A short interpolation of the photometer readings enabled the concentration of the saturated solution to be obtained. It was then used to make comparison solutions in water, with addition of further pure paraffin-chain salt solution and sodium salt solutions. Short interpolations could then give the azobenzene concentrations for solutions identical in composition, with respect to all components, with the filtrates or dilutions of them. At a given azobenzene concentration, the readings were but little influenced by the paraffin-chain salt concentration unless this was very low (*i.e.*, where a relatively large amount of the azobenzene is in solution in the water itself), but they were considerably influenced by the concentration of sodium chloride, less so by that of sodium acetate and very little by sodium

FIG. 2.



sulphate. It is noteworthy that the effect of these salts on the extinction of azobenzene is thus parallel to their effect on its solubility.

The accuracy of the analysis is 0.5—1% when the azobenzene concentration exceeds 0.0001N. At lower concentrations it is less, on account of the small fraction of light absorbed, and the absolute error may here be taken constant at about 0.000001N. The results, except

TABLE I.

$c_p$ ,  $c_{Na}$ , and  $c_s$  are the concentrations of cetylpyridinium salt, sodium salt, and azobenzene, respectively, in g.-equivs./l. (g.-mols. for azobenzene) at the temperature of measurement.

Chloride (not all values recorded); 25°.

$c_p \times 10^4$ .	$c_{Na} \times 10^2$ .	$c_s \times 10^4$ .	$c_p \times 10^4$ .	$c_{Na} \times 10^2$ .	$c_s \times 10^4$ .	$c_p \times 10^4$ .	$c_{Na} \times 10^2$ .	$c_s \times 10^4$ .
0.0	—	0.24	500	—	81.6	3.1	3.2	0.62
7.2	—	0.26	1045	—	178	10.4	3.2	1.78
9.5	—	0.35	2080	—	374	41.8	3.2	6.83
10.4	—	0.48	3120	—	586	0.0	10	0.20
11.9	—	0.70	4980	—	1000	3.1	10	0.69
18.0	—	1.75	3.1	0.32	0.24	10.4	10	1.89
23.8	—	2.68	10.4	0.32	1.30	41.8	10	7.10
41.8	—	5.54	41.8	0.32	6.42	0.0	32	0.18
71.4	—	10.3	3.1	1.0	0.47	3.1	32	0.75
143	—	21.9	10.4	1.0	1.63	10.4	32	2.06
209	—	32.6	41.8	1.0	6.71	41.8	32	7.88
314	—	50.2						
Chloride; 33°.								
960	—	200	3450	—	770	3800	—	860
2400	—	523						
Bromide; 33°.								
558	—	122	2070	—	510			
Sulphate; 25°.								
15.2	—	2.04	396	10	59.6	2480	—	356
22.5	—	3.31	0.0	32	0.17	4090	—	585
39.6	—	6.04	39.6	32	5.98	0.0	100	0.10
77.0	—	11.4	396	32	59.2	39.6	100	5.76
200.0	—	29.7	396	—	58.2	396	100	58.4
39.6	10	6.06	615	—	89.8			
Acetate; 25°.								
40.0	—	4.15	40.0	10	5.81	0.0	100	0.13
200	—	26.8	40.0	32	5.90	40.0	100	6.42
400	—	55.0						

TABLE Ia.

Mixtures of 0.00418N-cetylpyridinium chloride and 0.32N-NaCl with 0.00396N-cetylpyridinium sulphate and 0.32N-Na<sub>2</sub>SO<sub>4</sub>.

Chloride soln., %	0	20	50	80	90	100
$c_s \times 10^6$	598	646	714	769	784	788

TABLE II.

Solvent.	G. of azobenzene per 100 g. of soln.; 25°.	Saturation ratio.	Solvent.	G. of azobenzene per 100 g. of soln.; 25°.	Saturation ratio.
<i>n</i> -Decane	15.6	0.144	Pyridine	50.9	0.438
<i>n</i> -Hexadecane	12.2	0.176	Benzene	35.0	0.231*
Acetone	45.3	0.264	"Ideal"	—	0.50

\* Solid phase (C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>6</sub>.

TABLE III.

Weight % at 25°.			Saturation ratio.	Weight % at 25°.			Saturation ratio.
Acetone.	Water.	Azobenzene.		Acetone.	Water.	Azobenzene.	
54.7	—	45.3	0.264	20.4	79.6	0.0097	0.000145
67.8	17.5	14.7	0.0697	12.0	88.0	0.0026	0.000058
60.1	36.3	3.58	0.0189	—	100	0.00044	—
42.2	57.3	0.280	0.00211				

some of those for the chloride solutions, which have been omitted for the sake of brevity, are collected in Table I. The higher concentrations of paraffin-chain salt have been corrected for the appreciable expansion of the solution during saturation, the effective density of azobenzene being found to be 1.1.

Measurements in water-acetone mixtures, illustrating the behaviour of a normal solvent on dilution, are recorded in Table III. They were made similarly, except that samples were taken by weight. Comparison solutions were made by appropriate dilution of a standard acetone solution.

Solutions in pure organic solvents were cooled in the thermostat after preparation by addition of solvent to molten azobenzene. Samples were extracted in a hot, thick-walled pipette, weighed, and diluted with acetone. The necessary dilution was so great that comparison solutions in pure acetone were used. The solubility in benzene was so surprisingly low that an analysis of the solid phase, quickly dried between filter-papers, was made. One sample, dissolved in acetone and determined photometrically, contained only 71% of azobenzene. Another decreased in weight by 30% on exposure to air for some hours till constant weight was reached, a process accompanied by efflorescence, which was quite absent in similarly treated specimens from the other solvents. The solid phase in equilibrium with the benzene solution is thus presumably an equimolecular crystal *compound* ( $C_{12}H_{10}N_2, C_6H_6$  requires  $C_6H_6, 30.0\%$ ).

The author is greatly indebted to Miss E. K. Parsons, whose earlier measurements with a visual "colorimeter" demonstrated the value of the solubility method and the necessity of making the later improvements of technique.

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