XLV.—*Influence of Sucrose and Alkali Chlorides on the Solvent Power of Water.*

By JAMES CHARLES PHILIP and ARTHUR BRAMLEY.

In papers published some years ago (T., 1907, **91**, 711; *Trans. Faraday Soc.*, 1907, **3**, 140) one of the authors directed attention to the influence of various substances on the solubility of gases in water, and developed the suggestion, already thrown out in a general way by other workers, that this effect is connected with the hydration of these added substances. It was clearly shown that, contrary to the view held in some quarters, the solubility of a non-electrolyte in water may be affected to a notable extent by the presence of another non-electrolyte, and an attempt was made to calculate the average molecular hydration of sucrose in aqueous solution from the influence which this substance has in lowering the solubility of hydrogen in water. The influence of salts also was treated from the same point of view.

Whether the supposed hydration of the added substance is regarded as offering an adequate interpretation of the lowered solvent power of water for non-electrolytes or not, it is a matter of great interest to ascertain how the magnitude of the effect varies with the nature of the added substance, and to find how far it is independent of the particular non-electrolyte which is employed in measuring the solvent power of the water. It was with the object of throwing further light on this problem that the experiments described in this paper were carried out.

Since the publication of the earlier communications (*loc. cit.*) further experimental data bearing on the influence of non-electrolytes on the solubility of gases in water have become available (Usher, T., 1910, **97**, 66; Drucker and Moles, *Zeitsch. physikal. Chem.*, 1910, **75**, 405; Müller, *ibid.*, 1912, **81**, 483). The bearing of this work on the problem in question will be discussed in connexion with the results of the present investigation.

Gases are not the only non-electrolytes the solubility of which in water has been studied from the point of view developed in the foregoing paragraphs. Euler (*Zeitsch. physikal. Chem.*, 1899, **31**, 360) and Lundén (*Medd. K. Vetensk. Nobelinst.*, 1911, **2**, No. 15) have investigated the influence of salts on the solubility of ethyl acetate in water, the latter author regarding the phenomenon as a manifestation of neutral salt action. Rothmund (*Zeitsch. physikal. Chem.*, 1900, **33**, 401) and Biltz (*ibid.*, 1903, **43**, 41) have studied in a similar manner the effect of salts on the solubility of phenylthiocarbamide.

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Analogous experiments have been made by Euler (*Zeitsch. physikal. Chem.*, 1904, **49**, 303) with aniline and ethyl ether, and by McLauchlan (*ibid.*, 1903, **44**, 600) with iodine.

A compound, the solubility of which is to be taken as a measure of the solvent power of water in the presence of different added substances, must fulfil certain conditions. It should be indifferent, incapable of reacting with or being dissolved by, the added substance, sparingly soluble, and susceptible of accurate estimation. The number of non-electrolytes which satisfy these requirements, even approximately, is exceedingly small. Ethyl acetate, the compound employed by Euler and Lundén, whilst satisfactory in most respects, is open to the objection that its solubility is fairly high; its saturated solution, at the ordinary temperature, contains about 0.8 gram-molecule per litre. Phenylthiocarbamide is probably not quite indifferent to alkali salts, and the experiments of Bogdan (*Ann. Sci. Univ. Jassy*, 1903, **2**, 95) show that this substance is more soluble in solutions of non-electrolytes than in pure water, indicating that the solvent power of the non-electrolytes themselves for phenylthiocarbamide may be considerable. As regards aniline and ethyl ether, the difficulty of accurate estimation militates against their use, whilst iodine can scarcely be regarded as an indifferent substance.

In these circumstances it was thought advisable to employ the distribution method, and the work recorded in this communication is therefore a study of the variation in the partition coefficient of a suitable indifferent compound between an organic liquid (benzene or petroleum) and aqueous solutions of sucrose or alkali chlorides. The advantage of this method is that the concentration of the distributed compound can be kept as low as desirable, consistent with accuracy in its estimation. As distributed substance we have used ethyl acetate, phenol, and acetone. These compounds are all capable of accurate estimation in aqueous solutions even at low concentrations. As regards the other requisite conditions enumerated above, ethyl acetate is the most satisfactory of the three, since the available evidence indicates that the disturbance arising from the solvent power of the added substance (sucrose or alkali chloride) is probably least in this case. The significance of this factor will be discussed in connexion with the results obtained with the different distributed substances.

Dawson and McCrae (*T.*, 1901, **79**, 493) and Dawson (*Zeitsch. physikal. Chem.*, 1906, **56**, 605) have already employed the distribution method in the study of similar problems, but the distributed substances used, namely, ammonia and iodine, can scarcely be regarded as indifferent. A series of experiments, analogous

to those described in this paper, was made by Rothmund and Wilsmore (*Zeitsch. physikal. Chem.*, 1902, **40**, 624), who studied the influence of potassium sulphate on the partition of phenol between benzene and water.

EXPERIMENTAL.

As already stated, the distributed substances used were ethyl acetate, phenol, and acetone. The quantity of ethyl acetate present in aqueous solution was estimated by adding excess of standard sodium hydroxide solution, keeping for a sufficient time, and then titrating back with standard hydrochloric acid. The estimation of ethyl acetate in benzene or petroleum solution was carried out in the same way, except that a standard alcoholic solution of potassium hydroxide was employed for hydrolysis.

Phenol in aqueous solution was determined by conversion into tribromophenol, the actual procedure followed being that described by Redman, Weith, and Brock (*J. Ind. Eng. Chem.*, 1913, **5**, 389). Phenol in benzene solution was estimated by extracting three times with an equal volume of 2.5*N*-sodium hydroxide, acidifying the united extracts, and converting into tribromophenol as before. The accuracy of this procedure was tested and found to be satisfactory (compare Rothmund and Wilsmore, *loc. cit.*).

In the determination of acetone, whether in water or benzene solution, Messinger's method was employed (see Marriott, *J. Biol. Chem.*, 1913, **16**, 281). It was found that when an iodine solution is treated with alkali in large excess, and is then acidified, the quantity of iodine liberated, as estimated by standard thiosulphate, is slightly less than that originally taken. This discrepancy is being further studied, but for the purposes of the present investigation a suitable correction, based on blank experiments, was introduced.

In the experiments on the partition of ethyl acetate between benzene and water, pure commercial benzene was employed, but in those with phenol and acetone benzene specially purified by treatment with concentrated sulphuric acid and by redistillation was used, because of the complications that otherwise arose in the estimation of the distributed substances. Test experiments showed that the partition coefficient of ethyl acetate was the same whether pure commercial benzene or the specially purified product was used. The boiling point of the petroleum employed was 90—110°; the partition coefficient, however, for ethyl acetate varied slightly from one lot of petroleum to another, and care was therefore taken to use the same petroleum throughout each series of experi-

ments. The ethyl acetate, phenol, and acetone were all specially purified samples, boiling within 0.1° .

In the case of each of the three distributed substances, experiments were made to test the constancy of the partition coefficient over a considerable range of concentration. The data bearing on this point are reproduced in the following tables, in which C_w is the concentration (grams per litre) of the distributed substance in the aqueous layer, and P is the partition coefficient, that is, the ratio:

$$\frac{\text{concentration in benzene (petroleum) layer}}{\text{concentration in aqueous layer.}}$$

Ethyl Acetate between Benzene and Water at 20° .

C_w	2.480	1.629	1.590	1.472	1.199	0.805
P	12.23	12.19	12.16	12.19	12.21	12.24

Ethyl Acetate between Petroleum and Water at 25° .

C_w	3.339	3.098	2.943	2.674	2.561	2.335	2.122	1.924
P	3.442	3.435	3.453	3.450	3.430	3.454	3.453	3.457

Phenol between Benzene and Water at 20° .

C_w	0.945	0.888	0.711	0.594	0.475	0.356	0.238	0.119	0.0601
P	2.194	2.189	2.184	2.176	2.181	2.173	2.175	2.180	2.189

Acetone between Benzene and Water at 20° .

C_w	0.375	0.302	0.227	0.153
P	0.833	0.827	0.832	0.839

The mean values of the partition coefficient of ethyl acetate between benzene and water at different temperatures were found to be:

Temp.	11.9°	20.0°	25.0°	30.0°	40.0°
P	10.66	12.20	13.10	13.95	15.61

So far as we can find, the partition coefficient of ethyl acetate between benzene and water has not been determined previously, but data are already on record for the distribution of phenol and acetone between these two solvents. Rothmund and Wilshire (*Zeitsch. physikal. Chem.*, 1902, **40**, 611) determined the partition coefficient of phenol between benzene and water at 25° over a wide concentration range, and found values falling from 12.24 to 2.29, the corresponding concentrations of the aqueous layers being 49.8 and 2.56 grams of phenol per litre respectively. We find that the partition coefficient at 20° —mean value 2.182—is independent of the concentration, but it should be borne in mind

that our range of concentration—0.945 to 0.0601 gram of phenol per litre of the aqueous layer—is quite different from that covered by Rothmund and Wilsmore's experiments, and, further, even the figures given by these investigators show that the value of P is falling off much less rapidly at the lower concentrations. The temperatures also are different.

As regards the partition coefficient of acetone between benzene and water, Herz and Fischer find values of P at 25°, which range from 1.080 to 0.938, the corresponding concentrations of the aqueous layers being 128.6 and 12.76 grams of acetone per litre respectively. We find a practically constant figure for P at 20°—mean value 0.833—over a range of concentrations which are very much lower than those employed by Herz and Fischer.

The influence of sucrose on the distribution of ethyl acetate between benzene (or petroleum) and water is shown in the tables below. In these, N represents the concentration of the sucrose solution in gram-molecules per 1000 grams of water, and P is the partition coefficient, as defined already. S_w , calculated from the values of P , represents the *relative* quantities of ester present in 1 litre of the aqueous layers, the quantity present in 1 litre of water at the same temperature, and in equilibrium with the same benzene or petroleum solution, being taken as unity. S_w represents the relative quantities of ester present in those volumes of different solutions which contain 1000 grams of water, the quantity present in 1 litre of pure water at the same temperature and in equilibrium with the same benzene or petroleum solution being taken as unity. The fifth column, under the heading $(1-S_w)/N$, gives the values of what may be described as the "equivalent relative lowering of solvent power." The concentrations of ethyl acetate employed in these experiments were almost all within the range indicated in the tables on p. 383.

It is clear that in taking S_w as a measure of the solvent power of 1000 grams of water in the presence of different quantities of sucrose, the assumption is made that the sucrose itself does not dissolve any of the ethyl acetate. Since sucrose is insoluble in ethyl acetate, as we have found by experiment, there is a strong presumption that the solubility of ethyl acetate in sucrose is negligibly small. If the assumption were not valid, that is, if the sucrose were able to dissolve ethyl acetate, then the tabulated values of S_w , which are taken as measuring the solvent power of the water alone, are too high, and the values of $(1-S_w)/N$ are too low. In other words, the values of the equivalent relative lowering of the solvent power of water, calculated on the assumption that the added substance (sucrose) has no solvent power of its

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own, are minimum values (compare Philip, *Trans. Faraday Soc.*, 1907, **3**, 145; Caldwell, *ibid.*, 158). There are no doubt many cases where the assumption is not valid (compare Usher, T., 1910, **97**, 66), and that circumstance indicates the necessity of considering each case on its merits.

*Distribution of Ethyl Acetate between Petroleum and
Sucrose Solutions at 20°.*

<i>N.</i>	<i>P.</i>	<i>S_w</i>	<i>S_w</i>	$(1-S_w)/N.$
0.00	3.13	1.000	1.000	—
0.559	3.90	0.802	0.898	0.18
1.270	5.06	0.618	0.786	0.17
2.204	6.86	0.456	0.671	0.15
3.496	9.32	0.336	0.588	0.12

This table will serve to show in detail how the values of the equivalent relative lowering of solvent power have been ascertained, and the other results obtained for the influence of sucrose on the partition of ethyl acetate between petroleum (or benzene) and water may be communicated in a somewhat abbreviated form. It will be sufficient to indicate for each series the nature of the organic solvent used, and the temperature.

<i>N.</i>	Petroleum at 8.7°		Benzene at 11.9°		Petroleum at 16.5°	
	<i>P.</i>	$(1-S_w)/N.$	<i>P.</i>	$(1-S_w)/N.$	<i>P.</i>	$(1-S_w)/N.$
0.00	2.40	—	10.66	—	2.85	—
0.559	3.03	0.205	13.72	0.235	3.69	0.245
1.270	4.03	0.195	17.37	0.175	4.81	0.195
2.204	5.65	0.17	23.84	0.155	6.59	0.165
3.496	8.21	0.114	—	—	9.11	0.13

<i>N.</i>	Petroleum at 22.5°		Petroleum at 25°	
	<i>P.</i>	$(1-S_w)/N.$	<i>P.</i>	$(1-S_w)/N.$
0.00	3.24	—	3.45	—
0.559	4.07	0.195	—	—
1.270	5.25	0.17	5.52	0.16
2.204	7.00	0.145	7.24	0.135
3.496	9.60	0.115	—	—

<i>N.</i>	Benzene at 30°		Benzene at 40°	
	<i>P.</i>	$(1-S_w)/N.$	<i>P.</i>	$(1-S_w)/N.$
0.00	13.95	—	15.55	—
0.559	—	—	18.9	0.13
1.270	21.4	0.13	22.6	0.095
2.204	27.4	0.115	29.4	0.10
3.496	—	—	34.9	0.06

The influence of sodium, potassium, and lithium chlorides on the distribution of ethyl acetate, phenol, and acetone between benzene and water at 20° has also been investigated, and the results are communicated in the following tables. The significance of the

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symbols employed will be clear from the explanations already given in connexion with the experiments on sucrose solutions.

Sodium Chloride Solutions.

N.	Ethyl Acetate		Phenol		Acetone	
	P.	$(1-S_w)/N.$	P.	$(1-S_w)/N.$	P.	$(1-S_w)/N.$
0.00	12.20	—	2.182	—	0.833	—
0.506	14.75	0.32	2.615	0.305	0.938	0.20
1.02	17.72	0.29	3.16	0.29	1.056	0.19
1.55	21.4	0.265	3.84	0.265	1.193	0.18
2.08	25.7	0.245	4.66	0.245	1.342	0.17
3.196	36.9	0.20	6.77	0.205	1.705	0.15
4.37	51.6	0.17	10.04	0.175	2.13	0.13

Potassium Chloride Solutions.

N.	Ethyl Acetate		Phenol		Acetone	
	P.	$(1-S_w)/N.$	P.	$(1-S_w)/N.$	P.	$(1-S_w)/N.$
0.00	12.20	—	2.182	—	0.833	—
0.508	14.6	0.295	2.51	0.23	0.928	0.175
1.031	17.3	0.265	2.92	0.225	1.038	0.17
1.572	20.6	0.24	3.43	0.21	1.166	0.16
2.13	24.4	0.22	4.03	0.20	1.32	0.155
3.31	34.1	0.185	5.30	0.165	1.645	0.135
4.58	47.1	0.155	6.93	0.14	2.16	0.12

Lithium Chloride Solutions.

N.	Ethyl Acetate*		Phenol		Acetone	
	P.	$(1-S_w)/N.$	P.	$(1-S_w)/N.$	P.	$(1-S_w)/N.$
0.00	3.075	—	2.182	—	0.833	—
0.505	3.56	0.255	2.635	0.325	0.896	0.12
1.02	4.09	0.23	3.15	0.285	0.975	0.125
1.546	4.68	0.21	3.68	0.25	1.050	0.12
2.08	5.33	0.19	4.18	0.22	1.145	0.115

* These experiments were made with petroleum as the organic solvent instead of benzene.

A series of experiments made on the partition coefficient of ethyl acetate between petroleum and sodium chloride solutions at 20° is interesting, as showing that the values obtained for the equivalent relative lowering of solvent power are the same whether benzene or petroleum is used as the organic solvent. On comparing the following table with the corresponding one above the close agreement in the values of $(1-S_w)/N$ will be apparent.

Ethyl Acetate between Petroleum and Sodium Chloride Solutions at 20°.

<i>N.</i>	<i>P.</i>	$(1-S_w)/N.$
0.0	3.075	—
0.506	3.72	0.32
1.02	4.51	0.30
1.55	5.44	0.27
2.08	6.59	0.245

Discussion of Results.

The results recorded on p. 381, showing the influence of sucrose on the partition of ethyl acetate between benzene and water, emphasise the conclusion, already reached in the earlier communications, that the solvent power of water for a non-electrolyte may be affected to a notable extent by the presence of another non-electrolyte. This is quite opposed to Levin's view (*Zeitsch. physikal. Chem.*, 1906, **55**, 517) that solubility influences are appreciable only when ions are involved.

The values tabulated for $(1-S_w)/N$, the equivalent relative lowering of solvent power, exhibit a distinct increase with dilution in practically every case, whether the added substance is sucrose or an alkali chloride. This fact warrants the conclusion that whatever is the cause of the diminished solvent power of water in the presence of the added substance, it is some factor which becomes relatively more important as the proportion of water increases. In view of this, it does not seem to us permissible to calculate a *mean* value for the equivalent relative lowering of solvent power, as some authors have done under the impression that this quantity does not vary with the dilution of the added substance. Further, our results are opposed to Levin's contention (*loc. cit.*, p. 535) that solubility influences, such as those recorded above, are a phenomenon essentially of *concentrated* solutions.

It is instructive to compare our observations on the partition of ethyl acetate between benzene (or petroleum) and sucrose solutions with Müller's results (*Zeitsch. physikal. Chem.*, 1912, **81**, 483) for the influence of sucrose on the solubility of hydrogen, nitrogen, and oxygen in water at 15°. In order to facilitate the comparison, we have calculated from Müller's figures the equivalent relative lowering of solvent power in the way already described. The numbers under *N* represent gram-molecules of sucrose per 1000 grams of water:

Hydrogen.		Nitrogen.		Oxygen	
$N.$	$(1 - S_w)/N.$	$N.$	$(1 - S_w)/N.$	$N.$	$(1 - S_w)/N.$
0.504	0.23	0.376	0.16	0.403	0.13
0.743	0.14	0.731	0.175	0.943	0.165
1.245	0.13	1.25	0.17	1.16	0.17
1.36	0.14	1.26	0.15	2.20	0.14
1.92	0.12	2.69	0.10	2.84	0.125
2.20	0.125	2.76	0.125	2.92	0.12

These results are by no means regular, but, on the whole, the equivalent relative lowering of solvent power increases with the dilution of the sucrose. Further, the range covered by the values of $(1 - S_w)/N$ is very nearly the same whether the reference substance for the solvent power of water in presence of sucrose is hydrogen, nitrogen, oxygen (as in Müller's experiments), or ethyl acetate (as in ours). This shows that the effect is primarily determined by some factor involved in the relation of the sucrose and the water, and only secondarily, if at all, by the specific character of the reference substance.

It should be noted that the values of the equivalent relative lowering of solvent power deduced from Müller's measurements and from the work recorded in this paper are somewhat higher than the values calculated from Steiner's data for the influence of sucrose on the solubility of hydrogen in water. These data were used by one of us (*loc. cit.*) in an attempt to calculate the average molecular hydration of sucrose, and gave for this quantity figures between 5.4 and 6.5. The average molecular hydration can be obtained from $(1 - S_w)/N$ by multiplying by 1000/18, and if the range of values of $(1 - S_w)/N$ recorded above for sucrose solutions is taken as 0.20—0.12 at ordinary temperatures, this would correspond with an average molecular hydration ranging from 11 for the more dilute solutions to 6.5 for the more concentrated ones. These figures are distinctly higher than those hitherto regarded as most probable.

Of the results deduced for the influence of alkali chlorides on the solvent power of water, those obtained with sodium chloride appear to us to be the most trustworthy. This salt, of all those employed in this investigation, is the least soluble in any of the distributed substances, ethyl acetate, phenol, or acetone, and it may therefore be presumed that any disturbance arising from the solvent power of the salt itself is at a minimum in this case. Further, for the sodium chloride solutions, the values obtained for the equivalent relative lowering of solvent power are the same whether the distributed substance is ethyl acetate or phenol. This circumstance, although not furnishing absolute proof, is strong evidence in favour of the view that the values of $(1 - S_w)/N$ deduced

from the experiments with either of those distributed substances are a real measure of the extent to which the solvent power of the water has been affected by sodium chloride. Again, as pointed out on p. 381, the values deduced as above for the equivalent relative lowering of solvent power are minimum values, and hence the highest set of values obtained for $(1 - S_w)/N$ is to be regarded as in all probability the best measure of the lowered solvent power. These values lie between 0.17 for a $4N$ -solution of sodium chloride and 0.32 for a $0.5N$ -solution. Hence, on the assumption that the lowered solvent power of water in this case is due to the hydration of the molecules and ions of sodium chloride, the average molecular hydration would lie between 9.5 (for a $4N$ -solution) and 17.8 (for a $0.5N$ -solution).

In the case of the potassium chloride solutions the agreement between the values of $(1 - S_w)/N$ deduced from experiments (1) with ethyl acetate, (2) with phenol, is not quite so good, that is, the values of the equivalent relative lowering are not quite independent of the distributed substance. The figures resulting from the phenol experiments are somewhat lower than the corresponding ones based on the ethyl acetate experiments. We give the preference to the latter, on the general grounds already stated, and also on account of our observation that whilst both sodium and potassium chlorides are insoluble in ethyl acetate, phenol, in which sodium chloride is insoluble, dissolves a very small, but recognisable, quantity of potassium chloride. On the basis, then, of the ethyl acetate experiments, the value of the equivalent relative lowering of the solvent power of water in presence of potassium chloride rises from 0.155 for a $4N$ -solution to 0.295 for a $0.5N$ -solution. On the hydration hypothesis these figures indicate an average molecular hydration of 8.6 molecules and 16.4 molecules respectively, that is, somewhat below the corresponding numbers for sodium chloride. It should be noted also that the values deduced in this paper for the average molecular hydration are for both salts rather higher than those previously calculated from their influence on the solubility of hydrogen in water.

It will be observed that the values of $(1 - S_w)/N$ recorded for the partition of acetone between benzene and sodium or potassium chloride solutions are very much lower than those obtained with ethyl acetate or phenol as the distributed substance. We find that both chlorides are distinctly soluble in acetone, and the use of this compound as reference substance is therefore open to objection. In any case, the values of $(1 - S_w)/N$, based on the partition of acetone between benzene and sodium or potassium chloride

solutions, cannot be taken as a real measure of the lowering of the solvent power of water in the presence of these salts.

Consideration of the data obtained with lithium chloride solutions has convinced us that here also the values deduced for $(1 - S_w)/N$ are not to be regarded as giving a correct measure of the lowering of the solvent power of water. We find that all the three distributed substances, ethyl acetate, phenol, and acetone, especially the last-mentioned, are able to dissolve considerable quantities of lithium chloride, and this fact makes it probable that the solvent power of the salt itself for any of the three compounds is appreciable. If this is so, then the influence of lithium chloride on the solvent power of water cannot be estimated with any certainty by the method adopted in the case of sodium and potassium chlorides. The solvent power of lithium chloride itself being appreciable, it follows that the values of $(1 - S_w)/N$ in this case are too low, and understate the influence of the salt on the solvent power of water. Hence the calculated values of the average molecular hydration would also be too low. On the basis of the phenol experiments with lithium chloride solutions, the average molecular hydration of this salt would be nearly the same as for sodium chloride. It is certain, however, on the ground of other experimental data, that the lithium salt is more highly hydrated than the sodium salt (see Washburn, *Technology Quart.*, 1908, **21**, 386).

It is desirable to elucidate further the factors which determine the solvent power of water in presence of added substances, and it is our purpose to continue the inquiry on the lines described in this communication.

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[Received March 1st, 1915].