TABLE VII

THE SOLID SOLUTION (K, NH₄)₂SO₄ IN AQUEOUS AMMONIA AT 25°

| | | Liquid solution | | | | | | | |
(NH₄)₂SO₄	NH₄Cl	Wt., per cent. K₂SO₄	KCl	NH₃	(NH₄)₂SO₄	Equiv. 1000 moles H₂O NH₄Cl	K₂SO₄	KCl	Solid phase. % (NH₄)₂SO₄
8.29	2.75	0.12		23.45	34.45	13.21	0.38		67.9
5.31	8.55	.24		22.77	22.93	45.56	.79		73.7
4.19	13.49	.25		21.79	18.95	75.32	.86		76.2
2.63	21.86	.42		19.75	12.96	132.9	1.57		67.4
2.33	22.47	.47		19.86	11.57	137.8	1.77		63.6
	23.04	.70	0.74	20.06		139.7	2.61	3.20	59.7
2.49	3.20	.46		21.42	9.38	14.88	1.32		16.0
2.03	9.00	.68		20.02	8.11	44.35	2.06		20.5
1.75	14.13	.84		18.96	7.42	73.94	2.70		23.6
	3.08	.07	3.83	21.29		14.44	0.20	12.89	0.5
	5.97	.09	3.70	20.66		28.85	.27	12.86	.8
	13.62	.21	3.43	18.82		71.70	.68	12.95	1.7
	3.10	.06	7.76	17.20		14.51	.17	26.07	0.3
	6.04	.08	7.55	19.64		30.47	.25	27.33	.7

tion I was investigated in equilibrium with the aqueous ammonia solutions: the results are given in Table VII.

A few of the contour lines, from the data of Table VII, are drawn in Fig. 2. It appears that the ammonium sulfate concentration of the solid solution drops off very rapidly in the direction from FB to D, and that solid phases of relatively small content in ammonium sulfate could be obtained from solutions varying considerably in composition.

Summary

The reciprocal salt-pair $(NH_4)_2SO_4 + 2KCl \rightleftarrows K_2SO_4 + 2NH_4Cl$ has been studied at 25° in water as solvent and in water saturated with ammonia at one atmosphere pressure. The solid phases existing are three solid solutions: (1) ammonium chloride containing potassium chloride up to a maximum of 2.5%, (2) potassium chloride containing ammonium chloride up to a maximum of 16.6% and (3) potassium sulfate–ammonium sulfate in all ratios. The potassium sulfate–ammonium sulfate phase was investigated as to variation of composition with variation in the liquid phase.

NEW YORK, N. Y.

Experimental Tests of Recent Theories Descriptive of the Salting-out Effect[1]

By PENROSE S. ALBRIGHT[2]

I. Introduction

In the Debye theory[3] of the "salting-out" effect the ions are considered as rigid spheres with the neutral molecules, solvent and solute, behaving as a continuous medium whose interaction with the ions is determined by the macroscopic dielectric constant. As a result of the electrical field existing about the ions the component of higher dielectric constant is pulled preferentially into the field and the one of lower dielectric constant is forced out. Thus, in the ternary system solvent–solute–electrolyte, there is a change of concentration of non-electrolyte solute with changing distance from the ion. In aqueous solution the solvent usually concentrates in the region of the ions because the dielectric constant of water is more frequently higher than those of other neutral molecules. In such cases there is an increase of the solute to water ratio in the portions of the solution removed from the field of the ions and there results a reduction of the solubility of the solute, referred to the total water present. If the dielectric constant of the water is lower than that of the solute, a "salting-in" will result.

The important quantity to be determined in an

experimental test of the theory is the characteristic or probability distance $\tilde{R}$ which makes it possible to give quantitative description to the change of concentration of non-electrolyte solute with distance r from the center of the ion. The concentration m_2 at any point is given by $m_2 = m_2^0$ exptl. $(-\tilde{R}^4/r^4)$, in which m_2^0 is the concentration at infinite distance from the ion and

$$\tilde{R}^4 = \frac{e^2 z_i^2}{8\pi RT} \times \frac{D_1 - D^0}{D_1 D^0} \times \frac{M_1 d_2 m_1^0 + M_2 d_1 m_2^0}{d_1 d_2 m_2^0}$$

The concentrations, m_2 and m_2^0, are expressed as mole fractions, z_i is the valence of the added ion, and D_1 and D^0 are the dielectric constants of the pure solvent and saturated solution, respectively. M_1, M_2, d_1 and d_2 are molecular weights and densities of the solvent and solute. This equation may be used for exact calculations if the solutions are very dilute both in ions and in non-electrolyte component.
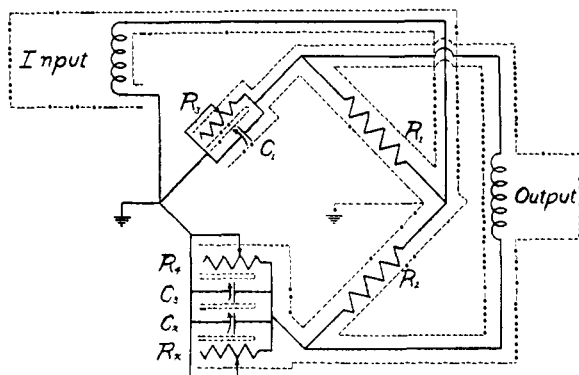

Fig. 1.—Radio-frequency bridge.

From these statements it is seen that to verify the theory observations must be made of the change of dielectric constant of the solution with concentration of non-electrolyte or of the dielectric constant of the saturated non-electrolyte solution. Such measurements have been carried out with aqueous solutions of aniline and ethyl ether at several temperatures and the data obtained have been utilized to calculate the change of solubility of the several non-electrolyte solutes as the amount of electrolyte added to the water is increased. These systems have been chosen because the results of reliable solubility determinations for them are available in the literature and a direct comparison with the requirements of the theory is made possible. In another article[4] a résumé was given of methods developed and used to evaluate the theoretical solubilities.

(4) Albright and Williams, *Trans. Faraday Soc.*, **33**, 247 (1937).

II. Experimental

A radio-frequency bridge was used for the measurement of the dielectric constants of the aqueous non-electrolyte solutions. The bridge elements were shielded carefully to prevent stray capacity effects between parts of the bridge and between operator and source of oscillations. Connections between the elements and positions of the shields are shown in Fig. 1. The inductance in all resistances and lead wires was kept as low as possible. Capacity measurements were made with a variable condenser. Dielectric constant values were obtained by dividing the difference in capacity between two fixed positions of the rotor when the plates of the condenser were immersed in the solution by the difference in capacity between the same positions when the cell was empty.[5]

The source of alternating current was a vacuum tube oscillator of the Hartley type with its radio-frequency output (0.57×10^6 cycles per second) modulated with a 1000-cycle microphone hummer. The detector for the adjustment of the capacitance and resistance balance in the bridge was a commercial radio receiver operated by direct current.

A special dielectric cell was designed and constructed to give adequate shielding, rapid heat exchange with water from the thermostat bath circulated about the container, low capacitative and inductive effects between leads, and exactness in operation. The dielectric cell is shown in the form of a diagram by Fig. 2.
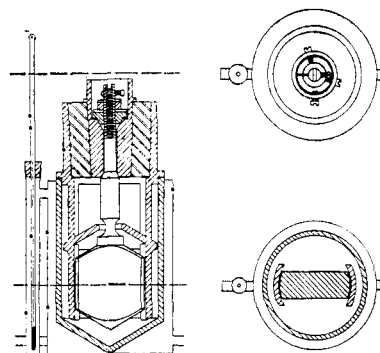

Fig. 2.—Dielectric cell.

The method of measurement was strictly one of substitution, with three arms of the bridge always remaining unaltered during a determination. Thus, for balance in the bridge the effective capacitance and resistance of the arm containing the dielectric cell were always constant. The exact amount of capacity and conductance introduced by moving the rotor from the low to the high position must be removed from the precision condenser and parallel constant capacity variable conductance in order that the bridge be in balance both before and after changing the position of the rotor. Thus, the capacity differences necessary for the calculations of dielectric constant are made available.

As a test of the purity of the liquids used, their boiling points at 760 mm. pressure and their densities were determined. The boiling points were corrected to 760 mm. pres-

(5) Daniels, Mathews and Williams, "Experimental Physical Chemistry," 2d ed., McGraw-Hill Book Co., Inc., New York, 1934.

Substance	Source	Purification	d^t_4	(B. p., °C. 760 mm.)
Acetone	Eastman	Bisulfite, anhyd. $CuSO_4$, Na_2SO_4, $CaCl_2$, fractionation	0.7846 (25°)	55.41–55.44
Aniline		Fractionation	.9958 (50°)	183.9–184.2
Ethyl ether	Mallinckrodt	Sodium, fractionation	.7024 (30°)	34.5–34.8
Glycine	Eastman	Ammonia free, dissolved cond. water, pptd. alcohol. Dried in vacuum		
Glycerol	Procter and Gamble	Fractionation, recrystallization	1.2585 (25°)	161 (11 mm.) 18.18° m. p.
Urea	Eastman	Recrystallization alcohol. Dried in vacuum		

sure by the use of Young's formula, $C = c(760 - P)$ $(273 + b. p.)$, where C is the correction to be added to the reading at pressure P, and c is Young's factor, depending upon the liquid. In order to determine the densities, a pycnometer of the Ostwald type was used. Data for purification and properties of the non-electrolyte solutes are presented in Table I.

Extreme care was taken with the purification of the water in order to keep its electrical conductivity as low as possible. All water used was purified by redistilling distilled water from a flask containing potassium permanganate and a little sulfuric acid, and condensing in a hard glass fractionating column. It was again distilled after the addition of sodium hydroxide.

III. Experimental Data

For the theoretical calculation of the per cent. of non-electrolyte salted out from aqueous solution it is necessary, first of all, to have dielectric

TABLE IIa
DIELECTRIC CONSTANT DATA FOR SATURATED SOLUTIONS OF NON-ELECTROLYTES IN WATER

Solute	Temp., °C.	D^0	Solubility, wt. %
Ethyl ether	18.00	75.60	7.25[a]
Ethyl ether	28.00	72.61	5.55[b]
Aniline	18.00	78.42	3.49[a]

[a] Euler, *Z. physik. Chem.*, **49**, 303 (1904). [b] Thorin, *ibid.*, **89**, 685 (1915).

difference in air for 62 consecutive steps averaged 1256.5 $\mu\mu$f, thus the air capacity difference between the two end positions was 20.27 $\mu\mu$f. With the plates covered with conductance water the average difference was 1590.4 $\mu\mu$f giving 78.48 for the dielectric constant of water at this temperature. Determinations at other temperatures gave the following results: at 18°, $D_1 = 81.13$; at 28°, $D_1 = 77.41$; and at 50°, $D_1 = 69.95$. Wyman[6] gives $D_1 = 78.54$ at 25° and $D_1 = 69.93$ at 50°.

The evaluation of the characteristic distance involves as well the determination either of the dielectric constant of the saturated non-electrolyte solution or of the change of dielectric constant of the solution with concentration of non-electrolyte. Tables IIa and IIb give such data for aqueous solutions of aniline and ethyl ether. Solubility data of the literature have been utilized in cases where saturated solutions are involved.

In addition there are presented dielectric constant and density data for aqueous solutions of urea and glycine (Table IIb) and of acetone and glycerol (Table III). The original intention in making these additional dielectric constant measurements was to provide convincing demonstration of the reliability of the apparatus; the experience with them has been that comparisons with data of Wyman[7] always gave excellent agree-

TABLE IIb
DIELECTRIC CONSTANT AND DENSITY DATA FOR SYSTEMS OF PARTIALLY SOLUBLE NON-ELECTROLYTES DISSOLVED IN WATER. CONCENTRATIONS EXPRESSED AS PER CENT., p, OR MOLES PER LITER OF SOLUTION, C

Non-Electrolyte	Temp., °C.	Dielectric constant (Air = 1)	Density d^{25}_4	Range of validity	Solubility, wt. %
Aniline	25.00	$D = 78.48 - 0.831p$	$d = 0.99707 + 0.000444p$	To saturation	3.67[a]
Aniline	50.00	$D = 69.95 - 0.765p$		To saturation	4.22[a]
Urea	25.00	$D = 78.48 + 2.66C$	$d = 0.9971 + 0.01725C - 0.0005C^2$	$C = 0$ to $C = 3$	..
Glycine	25.00	$D = 78.48 + 23.0C$	$d = 0.9971 + 0.0320C - 0.0010C^2$	$C = 0$ to $C = 2.5$	..

[a] Glasstone, Bridgman and Hodgson, *J. Chem. Soc.*, 635 (1927).

constant data for water at the several temperatures of the solubility determinations. The determination at 25° has been made by direct comparison of capacity differences between "high" and "low" positions of the cell rotor with the plates first in air and then in water. The total capacity

(6) Wyman, *Phys. Rev.*, **35**, 623 (1930).
(7) Wyman, THIS JOURNAL, **56**, 536 (1934).

ment. Unfortunately comparisons with figures of Åkerlöf[8] have not been so successful. Thus, this investigator gives 19.10 and 40.1 while the author finds 20.74 and 42.48 for the dielectric constants at 25°, of acetone and glycerol, respectively, and the data for the aqueous solutions relatively richer in the organic component sometimes show even larger differences. The acetone and glycerol figures presented here check closely with values listed in the "International Critical Tables."

TABLE III

DIELECTRIC CONSTANT DATA FOR SYSTEMS ACETONE–WATER AND GLYCEROL–WATER AT 25°

Densities of acetone–water solutions, expressed in weight per cent. of acetone, p, are given by the equation $d^{25}_4 = 0.9971 - 1.1487 \times 10^{-3} p - 7.975 \times 10^{-6} p^2 - 1.788 \times 10^{-8} p^3$ with maximum deviation ± 0.0009 from experimental values.

Acetone–Water		Glycerol–Water	
Wt., % acetone	D	Wt., % glycerol	D
0.00	78.48	0.00	78.48
10.01	73.08	9.88	75.98
19.96	67.62	20.33	73.86
29.98	61.90	30.19	71.44
39.93	55.74	39.67	68.93
50.24	49.34	50.23	65.72
60.06	43.39	60.15	62.38
70.07	37.33	70.00	58.52
80.03	31.50	79.86	54.08
91.23	25.41	90.42	48.66
100.00	20.74	100.00	42.48

IV. Calculations

Comparisons of calculated and experimentally observed solubilities of ethyl ether and aniline in aqueous electrolyte solutions at several temperatures are presented in Tables IV–VIII, inclusive. In Tables IV–VI, the theoretical values have been calculated by use of the limiting law, in Tables VII and VIII the theoretical values have been modified to meet the requirements of the Setschenow equation. Electrolyte solubilities C_s are expressed in moles per liter. The evaluation of theoretical solubility (limiting law) has been

TABLE IV

SALTING-OUT DATA FOR ETHYL ETHER IN AQUEOUS SALT SOLUTIONS AT 18°

Electrolyte	C_s	Per cent. salted out	
		Theory	Experiment[a]
KNO₃	1.0	25.8	31
LiCl	1.0	25.8	34
KCl	1.0	25.8	40
NaCl	1.0	25.8	42
Na₂SO₄	0.5	31.2	53

[a] Thorin, Z. physik. Chem., **89**, 685 (1915).

(8) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

accomplished by the use of equations similar to those given in the introduction. Ionic radius has been assumed constant and equal to 1.2×10^{-8} cm. Discussion of methods of obtaining the theoretical solubilities is given in another place.[2]

TABLE V

SALTING-OUT DATA FOR ETHYL ETHER IN AQUEOUS SALT SOLUTIONS AT 28°

Electrolyte	C_s	Per cent. salted out	
		Theory	Experiment[a]
NaI	0.5	14.7	2.6
NaBr	.5	14.7	20.0
NaCl	.5	14.7	23.4
NaF	.5	14.7	29.0
Na₂SO₄	.25	17.8	26.5
Na₂CrO₄	.25	17.8	27.9
Na₂MoO₄	.25	17.8	25.0
Na₂WO₄	.25	17.8	29.6
Na₃PO₄	.1667	20.1	28.7
Na₃AsO₄	.1667	20.1	28.2

[a] Euler, Z. physik. Chem., **49**, 303 (1904).

TABLE VI

SALTING-OUT DATA FOR ANILINE IN AQUEOUS SALT SOLUTIONS AT 18°

Electrolyte	C_s	Per cent. salted out	
		Theory	Experiment[a]
KCl	1.0	29.6	26
KCl	0.5	14.8	13
NaCl	1.0	29.6	29
LiCl	1.0	29.6	23
CaCl₂	0.5	35.8	17

[a] Euler, Z. physik. Chem., **49**, 303 (1904).

TABLE VII

SOLUBILITY DATA FOR ANILINE IN AQUEOUS SALT SOLUTIONS AT 25°

Solubility in water is 0.394 mole per liter

Electrolyte	C_s			
	0.25	0.5	1.0	2.0
Theoretical for 1-1 valence type	0.364	0.336	0.286	0.207
LiCl	.378	.365	.337	.275
NaCl	.358	.325	.275	.204
KCl	.363	.336	.295	.233
RbCl	.380	.367	.337	.275
CsCl	.405	.408	.405	.390
NH₄Cl	.385	.375	.362	.344
LiBr	.417	.430	.435	.420
NaBr	.380	.362	.330	.278
KBr	.375	.358	.336	.307
RbBr	.400	.400	.392	.370
CsBr	.424	.443	.472	.494
NH₄Br	.424	.436	.452	.462
LiI	.437	.455	.487	.570
NaI	.390	.391	.394	.405
KI	.393	.400	.405	.399
RbI	.432	.452	.488	.550
CsI	.455	.492	.549	.771
NH₄I	.425	.435	.492	.600
KNO₃	.383	.375	.350	.302

TABLE VII (Concluded)

Electrolyte	0.25	0.5	C_s 1.0	2.0
KClO$_3$	0.378	0.370	..	..
KAc	.360	.333	0.285	0.227
KOH	.350	.310	.238	.138
KF	.342	.292	.210	.120
NaNO$_3$	.371	.358	.333	.283
Theoretical for 1–2 valence				
type	0.325	0.267	0.181	0.083
BaCl$_2$	.348	.306	.236	..
K$_2$CO$_3$	.298	.215	.125	.032
K$_2$CrO$_4$	.307	.245	.164	.077
K$_2$SO$_4$	.293	.225	..	..
K$_2$C$_2$O$_4$	.303	.241	.150	..
Na$_2$SO$_4$	.288	.210	.100	..
(NH$_4$)$_2$C$_2$O$_4$	.328	.298	.295	..
Sr(NO$_3$)$_2$	.385	.374	.347	.300
Ba(NO$_3$)$_2$	.375	..	..	..
Theoretical for 2–2 valence				
type	0.314	0.250	0.158	0.064
MgSO$_4$	.314	.250	.158	..
Theoretical for 1–3 valence				
type	0.284	0.204	0.105	0.028
Na$_3$C$_6$H$_5$O$_7$	.258	.178	.090	..
Theoretical for 1–4 valence				
type	0.254	0.163	0.067	0.011
K$_4$Fe(CN)$_6$	.254	.170	..	..

Experimental solubility data for this table and the one to follow have been interpolated from figures given by Glasstone, Bridgman and Hodgson, *J. Chem. Soc.*, 635 (1927).

Further comparison of calculated and experimental solubilities is shown in graphical form by means of Fig. 3 in which the results of observations at 25° of the solubility of aniline in dilute
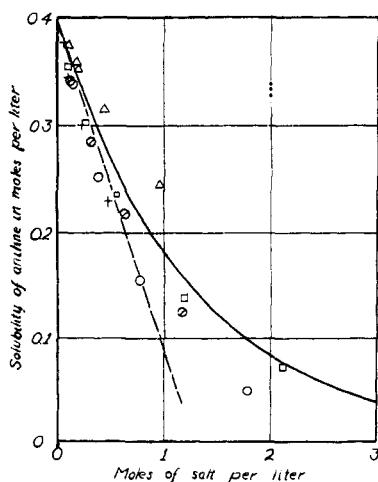

Fig. 3.—Observed (Glasstone, Bridgman, Hodgson) and calculated solubilities of aniline in dilute aqueous electrolyte solutions at 25°. △, BaCl$_2$; ○, K$_2$CO$_3$; ▢, K$_2$CrO$_4$; +, K$_2$SO$_4$; ⊕. K$_2$C$_2$O$_4$.

TABLE VIII

SOLUBILITY DATA FOR ANILINE IN AQUEOUS SALT SOLUTIONS AT 50°

Solubility in water is 0.448 mole per liter

Electrolyte	0.25	0.5	C_s 1.0	2.0
Theoretical for 1–1 valence				
type	0.411	0.378	0.318	0.225
LiCl	.427	.408	.370	.310
NaCl	.407	.365	.305	.225
KCl	.409	.373	.318	.248
RbCl	.428	.408	.367	.288
CsCl	.448	.438	.418	.392
NH$_4$Cl	.422	.402	.380	.363
LiBr	.462	.465	.465	.460
NaBr	.421	.401	.367	.313
KBr	.423	.400	.361	.324
RbBr	.452	.450	.430	.380
CsBr	.470	.493	.540	.590
NH$_4$Br	.476	.490	.505	.510
LiI	.485	.500	.538	.630
KI	.437	.440	.452	.480
RbI	.481	.497	.525	.575
CsI	.500	.540	.618	.783
NH$_4$I	.460	.480	.560	.730

electrolyte solutions by Glasstone, Bridgman and Hodgson[9] appear as points, the purely theoretical or limiting law solubility is given by a dotted line and the requirements of the familiar empirical equation of Setschenow with its constant evaluated so as to give the theoretical limiting slope are shown by the full line.

V. Discussion

There are available in the literature comparatively few complete systematic studies of the influence of a series of salts on the solubility of a given non-electrolyte. It is undoubtedly because of the limited number and kind of solutes investigated that the salting-out is widely believed to be only slightly, if at all, influenced by the character of the non-electrolyte. Thus, in the discussion of aqueous solutions one frequently finds the statement, direct or implied, that the primary factor in salting-out is a characteristic constancy of a binding of a part of the water by the ions. The water bound in this way thus becomes unavailable as solvent for the non-electrolyte and it becomes necessary to add more solvent in order to retain a given amount of non-electrolyte in molecular dispersion in the presence of the salt.

As indicated in the introduction, Debye ascribes the phenomenon to local changes in the average dielectric constant of the medium produced by the different attractions exerted upon the mole-

(9) Glasstone, Bridgman and Hodgson, *J. Chem. Soc.*, 635 (1927).

cules of the several types in the non-homogeneous electrical fields of the ions. In order to give quantitative character to the theory there is calculated the free energy of a mixture, the dielectric constant of which varies with distance from the ion, by balancing the gradient of osmotic pressure which is produced by the variable concentrations with the electrical forces produced by the ion. In the resulting law of distributions as a function of distance from the ion there appear the ionic charge and diameter, the dielectric constants of the components, and the absolute temperature. There is nowhere denied the existence of other forces or possible chemical combinations; the view is that the effect described plays the essential role, with individual actions exerting themselves as supplementary effects which become more and more pronounced as solute and electrolyte concentrations are increased.

In any discussion of the theory one must distinguish two problems. The first, and at present more important, concerns the general validity of the point of view, its development, and the method of evaluation; the second is whether certain of the assumptions made for the purpose of calculation can be used in all the kinds of cases met with in experiment, particularly in those in which a salting-in results. At present we are concerned with the first of these problems but we hope to return to the second one in another place.

Examination of the tables and figure reveals that the observed solubilities of ethyl ether and aniline in aqueous solutions containing electrolyte agree at least approximately with the requirements of the theory for salts of several valence types. As expected the differences between the requirements of the theory and the results of solubility measurements become smaller as the electrolyte concentration is reduced. A similar situation has been found to exist for the system water–ethyl acetate–electrolyte.[2] With the possible exception of the work with the most dilute solutions it appears as if the solubility measurements have been made in a concentration range too high for the limiting law of the theory and some degree of inaccuracy is introduced through the simplifying assumptions of the theory so that smaller differences ordinarily will occur.

Various equations have been proposed to describe the change in the solubility of non-electrolyte with electrolyte concentration. The most

familiar expression is that of Setschenow, as follows

$$\log (C^0_2/C_2) = kC_s$$

In this equation k is the salting-out constant. Since most of the solubility determinations have been made at salt concentrations too high to expect the limiting law of the theory to describe completely the results, the author has in some cases made use of this empirical equation with its constant adjusted so as to give to the curve the theoretical limiting slope. In this way another comparison is possible. In salt concentrations not greater than one molar the agreement between calculated and observed aniline and ethyl ether solubilities in water may be described as good for chloride salts and for all salts of the higher valence types, and as fair for bromide and nitrate salts and a number of miscellaneous uni-univalent electrolytes at temperatures 25 and 50°. Iodide salts give no agreement at all, as in a majority of the cases the non-electrolytes are actually salted-in, and even in dilute salt solution there is no unmistakable evidence of a tendency to approach the behavior required by the limiting law. It is an assignment of role to certain anions, such as the iodide ion, which has given the greatest difficulty because the experimental results appear to require the interpretation of an aggregation of non-electrolyte of lower dielectric constant in the field existing about the ions. The author cannot contribute further to explanations which have already been given for cases such as these.

The theory requires a regular change in salting-out as the ion radius increases, with the extent of the effect by a series of salts of the same valence type containing a common ion being in inverse order to the size of the ion. Experiments have long indicated a general regularity of this type in all salting-out data and in any successful theory this effect must be described. To be sure there appear many anomalies in the records of the experiments, but it must be remembered these solubility determinations have been made at rather high concentrations of salt and sometimes also of non-electrolyte, so that the limiting law at low concentrations with which the theory ought to be tested has been approached only in rare cases. In this connection recent work of Scatchard and Benedict[10] is particularly deserving of mention. Their freezing point data for aqueous solutions of dioxane and its mixtures with lithium, sodium,

(10) Scatchard and Benedict, THIS JOURNAL, **58**, 837 (1936).

and potassium chlorides are in accord with solubility determinations and, except for a minor discrepancy between the sodium and lithium ions, with the theory in question. Many additional experiments of this type in combination with precision dielectric constant determinations of the kind described here are required before a complete and searching examination can be made of the assumptions introduced for the purpose of quantitative calculations.

It is the intent of this report to show that in the more dilute aqueous salt solutions dielectric constant measurements of the kind described lead to calculated solubilities in good agreement with those actually observed, and to point out that in the case of most systems containing moderate to high concentrations of electrolyte the comparison shows the important effect in the salting-out to be a displacement of non-electrolyte from the electrical field about the ion. The data contribute to the establishment of the fundamental correctness of the point of view that the primary cause for the salting-out is the change of concentration of the non-electrolyte solute with changing distance from the ion caused by the preferential attraction of the medium of higher dielectric constant by the charged ion.

The author wishes to express his gratitude for the helpful advice of J. W. Williams throughout the course of this work.

Summary

Dielectric constant data have been obtained at several temperatures for aqueous solutions of acetone, aniline, ethyl ether, glycerol, glycine, and urea. Density determinations have been made at 25° for the solutions containing acetone, aniline, glycine, and urea.

These data and the Debye theory of the salting-out effect make possible calculations of the limiting slopes of the solubility curves for the non-electrolyte solutes as a function of salt concentration. In this report attention has been confined largely to systems containing aniline and ethyl ether. The dielectric constant measurements are found to lead to calculated solubilities in good agreement with those actually observed in the more dilute salt solutions and when larger differences appear they seem to be due in considerable measure to the fact that the solubility measurements have been made in a salt concentration range too high for the limiting law of the theory.

The data are most successful in that they contribute to the establishment of the essential correctness of the Debye theory which describes the primary salting-out in terms of the relative electrical susceptibility of the non-electrolyte components and the electrical fields of force in the neighborhood of the ions.

The Electron Affinity of Free Radicals. XII. ΔF of Addition of Sodium to Organic Compounds by the Potentiometric and Analytical Methods

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Two methods have been described for determining ΔF of addition of sodium to an organic compound. In the first the equilibrium constant of the reaction is obtained by a direct analysis of the equilibrium mixture[1] and in the second the e. m. f.[1] of the cell

$$\begin{array}{c|c|c} \text{Na} & \text{NaR} & \text{R}_2, \text{Pt} \\ \text{amalgam} & \text{solution} & \end{array}$$
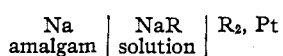
is measured, the two halves of the cell being separated by a sintered Pyrex glass disk.[2]

This paper reports further measurements with free radicals, ketones and unsaturated hydrocarbons, and the results obtained by the two methods are compared. Such data are useful in giving the quantitative effect of different groups on the reaction, thus aiding in the interpretation of structure, and in indicating the relative importance of steric hindrance and resonance energy in determining the properties of the molecule. Also, knowing the ionization potential of sodium, and combining this with suitable equations, the electron affinity of the free radical in the gaseous state may be obtained. This has been done for triphenylmethyl.[3]

(1) IX, Dorfman, THIS JOURNAL, **57**, 1455 (1935).
(2) Bent and Keevil, *ibid.*, **58**, 1228 (1936).
(3) Bent, *ibid.*, **52**, 1498 (1930).