mett and Deyrup[4] covered approximately the same range. Both of these researches were put on an absolute basis by reference to the maximum freezing point. Gillespie calculated the data of both researches to this basis for comparison.

A wide investigation of the freezing point composition diagram has been made by several observers but, except near the melting point of anhydrous acid, their work is less accurate than that of Gable, Betz and Maron[2] who give references to most of the previous work.

In the immediate vicinity (99.95 to 100.05 wt. %) of absolute acid the present research is more accurate than those of H. and D. or G. Between 99.7 and 99.9 wt. % H_2SO_4 the present values of θ lie about midway between the two previous researches in this region. θ is smaller in the work of Gillespie and larger in the work of Hammett and Deyrup. Curves through the results of either observer lie just outside the estimated limit of error of the present results. There is essentially no error in the temperature measurement but the possible analytical error of ±0.005 wt. % at 99.8% is equivalent to 0.03°. The method used reduces error proportionally between the point of analysis and the maximum melting point so that at 99.9% the possible error was ±0.0025 wt. % corresponding to about 0.012°. The accuracy of the present work could have been improved by performing the analysis on a sample taken at a greater θ.

Gillespie gives 10.36° as the melting point of absolute acid. The value obtained in the present research is 10.371° (283.531°K.).

The present results differ considerably from those of Gable, Betz and Maron, especially at the lower temperatures between H_2SO_4 and $H_2SO_4 \cdot H_2O$. Their results are high, sometimes by as much as 2°. There is abundant evidence from melting and other fixed points in other concentrations, even at lower temperatures, to show that their temperature measurements are substantially correct. Some of the difference could be attributed to errors in sampling or analysis but it is not possible to explain the difference in that way. The results are high on both sides of the eutectic, whereas systematic analytical errors would be expected to raise the results on one side and lower them on the other side of the H_2SO_4–$H_2SO_4 \cdot H_2O$ eutectic. The only self consistent way of explaining the difference is in terms of unattained equilibrium in the boundary region about the melting crystals. The viscosity of sulfuric acid solutions is very high in this concentrated region which requires minimum heat leak, large crystal surface and thorough stirring to approach equilibrium.

The results of G., B. and M. on the dihydrate side of the monohydrate agree much better and in the more dilute regions, beyond the mono–dieutectic, it is expected that the results of G., B. and M. will suffice for the free energy calculations which will be presented in a later paper.

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[CONTRIBUTION FROM HARPUR COLLEGE, STATE UNIVERSITY OF NEW YORK]

The Solubilities of Naphthalene and Biphenyl in Aqueous Solutions of Electrolytes

BY MARTIN A. PAUL

RECEIVED MAY 13, 1952

The solubilities of naphthalene and biphenyl have been determined in aqueous solutions of several strong electrolytes at 25° by means of ultraviolet absorption. The data fit the Setchénow equation, in which the logarithm of the non-electrolyte's activity coefficient is expressed as a linear function of the concentration of the particular electrolyte. The effects of different electrolytes are generally similar to those reported for other non-polar solutes. Comparison with published data for benzene shows a progressive increase in the magnitude of the salting-out parameter for a given electrolyte from benzene to naphthalene to biphenyl, apparently accompanying the increase in the molal liquid volume of the non-polar solute. The results are discussed in terms of a theory proposed by McDevit and Long in connection with their data for benzene. Data are reported also for naphthalene at 0°.

The influence of various electrolytes on the solubility of benzene in aqueous solutions has recently been investigated by McDevit and Long[1] and by Saylor, Whitten, Claiborne and Gross.[2] McDevit and Long have proposed a theory according to which the non-polar solute has the effect of modifying the interaction between the solvent water molecules and the ions of the electrolyte to a first order of approximation merely by occupying volume. The salting-out parameter for a given electrolyte acting on a non-polar non-electrolyte should then be proportional in a first approximation to the non-electrolyte's own molal volume (in the liquid state), and for different electrolytes should depend on the relative extents of interaction between solvent and ions, as measured for example by the contraction in volume accompanying dissolution of the electrolyte. This theory has the merit of not only reproducing correctly the order of effectiveness of various electrolytes in salting out a particular non-polar solute but also accounting for the salting in observed with perchloric acid and certain other electrolytes having large anions or cations. It seemed desirable to obtain information for the larger non-polar molecules of naphthalene and biphenyl. For polar non-electrolytes, of course, interactions of a more specific nature may be expected between the neutral solute molecules and the ions on the one hand and the solvent molecules on the other, and this situation is indeed indicated by the nature of the experimental results for such substances when contrasted with certain

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(1) W. F. McDevit and F. A. Long, THIS JOURNAL, **74**, 1773 (1952).

(2) J. H. Saylor, A. I. Whitten, I. Claiborne and P. M. Gross, *ibid.*, **74**, 1778 (1952).

general regularities that appear in the behavior of non-polar solutes.

Experimental

The solubilities were measured by absorption of ultraviolet light, a Beckman Model DU spectrophotometer equipped with 1-cm. quartz cells being used for the purpose. Bohon and Claussen have shown that the solubilities of many aromatic hydrocarbons in water may be determined by this means, naphthalene having an absorption peak at 275 mμ and biphenyl at 246 mμ.[3] The method employed in general was to introduce about 30 ml. of the electrolyte solution into a 50-ml. glass-stoppered flask, together with a few tenths of a gram of the hydrocarbon. The flask after being heated in a hot water-bath until the hydrocarbon had melted was shaken vigorously during cooling until the excess hydrocarbon had recrystallized. It was then put into a water thermostat operating at 25.00 ± 0.05° and left there with occasional shaking for at least 48 hours. Samples were withdrawn by means of a 10-ml. transfer pipet whose tip was protected by a short length of rubber tubing plugged with cotton to filter out the excess crystalline hydrocarbon. This method gave solutions optically transparent in the visible range. A method was tested also in which the sample was displaced into the transfer pipet by means of air pumped into the flask, instead of in the ordinary way by suction; this procedure would reduce any loss of solute by evaporation during the transfer process, but no significant difference was observed between the results obtained by the two methods.

In the case of naphthalene, the 10-ml. samples were diluted with water to 25 ml., and in the case of biphenyl, to 20 ml., before introduction into the spectrophotometer cells. Blanks were run on the various electrolytes to test their contributions to the light absorption, and corrections were made accordingly where needed. At 275 mμ (for naphthalene) these corrections were practically insignificant, and at 246 mμ (for biphenyl), in no case did they amount to as much as 5% of the total optical density. Tests were also run which indicated that none of the electrolytes at the concentrations employed had any tendency to shift the wave lengths of the respective absorption maxima.

Some naphthalene solutions were run also at 0.1°. In these cases, the samples withdrawn from the equilibrium mixtures were introduced directly into the cells of the spectrophotometer and allowed to come to room temperature for analysis without further dilution.

The various salts were of reagent grade, dried at 120° before weighing. The acids were standardized volumetrically with ultimate reference to potassium hydrogen phthalate. Naphthalene and biphenyl were recrystallized from methanol. Redistilled water was used for all the solutions.

Results

TABLE I

ACTIVITY COEFFICIENT OF NAPHTHALENE IN AQUEOUS SOLUTIONS OF ELECTROLYTES AT 25°

Electrolyte	Electrolyte concn., C_s, g.-eq./liter	Optical density, $-\log (I/I_0)$, at 10:25 diln., 275 mμ	Activity coefficient, $\gamma'' = s_0/s$	$\log \gamma''$
None	0	0.475 ± 0.005	(1.000)	(0.000)
$^1/_2$ Na_2SO_4	0.258	0.380	1.250	0.097
	.399	.335	1.418	.152
	.399	.326	1.456	.163
	.644	.274	1.733	.239
	.766	.252	1.885	.275
	.798	.238	1.995	.300
	.798	.251	1.891	.277
	1.065	.200	2.373	.375
	1.065	.205	2.318	.365
NaCl	0.214	.420	1.131	.053
	.440	.355	1.339	.126
	.535	.359	1.324	.122
	.771	.298	1.594	.202
	1.101	.244	1.946	.289
KCl	0.568	.358	1.326	.123
	.838	.325	1.461	.165
	1.135	.278	1.709	.232
LiCl	0.211	.429	1.106	.044
	.356	.405	1.173	.069
	.528	.380	1.250	.097
	.761	.336	1.414	.150
	.968	.321	1.480	.170
	1.056	.312	1.521	.182
NaBr	0.292	.422	1.126	.051
	.512	.380	1.250	.097
	.731	.360	1.320	.120
	1.023	.321	1.480	.170
$NaClO_4$	0.434	.437	1.086	.036
	.868	.382	1.244	.094
	1.342	.357	1.330	.134
HCl	0.246	.457	1.040	.017
	.492	.442	1.075	.031
	.738	.441	1.077	.032
	.984	.431	1.101	.042
$HClO_4$	.259	.489	0.972	− .013
	.477	.531	.894	− .048
	.648	.529	.898	− .047
	.954	.558	.820	− .086
	.954	.579	.851	− .070

The data for naphthalene at 25° are presented in Table I and for biphenyl at 25° in Table II. In the fourth column of each table is given the molar concentration activity coefficient γ'' of the non-electrolyte, computed by dividing the optical density in the absence of added electrolyte by the optical density for the particular electrolytic concentration. This calculation is based on the assumptions that the hydrocarbons at the dilutions under consideration satisfy Beer's law and that their solutions in pure water up to their saturation points satisfy Henry's law so that their activity coefficients in the saturated solutions without added electrolytes may be set equal to 1. The actual solubilities in pure water at 25° are according to the data of Bohon and Claussen,[3] 0.000268 mole/liter for naphthalene and 0.0000485 mole/liter for biphenyl. The optical densities of the saturated solutions in pure water obtained in the present investigation ran consistently about 5% lower than those reported by Bohon and Claussen, but this small discrepancy is not considered to be significant in view of the relative way in which the data are employed. It may be noted that the relative value of the optical densities obtained for saturated naphthalene solutions in pure water at 0.1° and 25° in the present investigation is in perfect agreement with the corresponding relative value derived from the data of Bohon and Claussen.

From graphic plots of the data one can see that they fit the empirical Setchénow equation[4]

$$\log (s_0/s) = KC_s$$

where s_0 and s denote the solubilities of the non-electrolyte in pure water and in the salt solution,

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[3] R. L. Bohon and W. F. Claussen, THIS JOURNAL, **73**, 1571 (1951).

[4] See H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 397.

TABLE II

ACTIVITY COEFFICIENT OF BIPHENYL IN AQUEOUS SOLUTIONS OF ELECTROLYTES AT 25°

Electrolyte	Electrolyte concn., C_s, g.-eq./liter	Optical density, $-\log (I/I_0)$, at 10:20 diln., 246 mμ	Activity coefficient, $\gamma'' = s_0/s$	$\log \gamma''$
None	0	0.386 ± 0.010	(1.000)	(0.000)
$^1/_2$ Na_2SO_4	0.205	0.313	1.234	0.091
	.411	.258	1.495	.175
	.616	.218	1.770	.248
	.821	.173	2.230	.348
	1.027	.140	2.758	.440
NaCl	0.229	.317	1.218	.085
	.458	.287	1.345	.129
	.687	.245	1.575	.197
	.818	.222	1.738	.240
	.916	.221	1.745	.242
	1.145	.191	2.020	.305
	1.145	.186	2.075	.317
KCl	0.242	.322	1.198	.078
	.413	.301	1.281	.108
	.722	.256	1.506	.178
	1.032	.212	1.819	.260
LiCl	0.221	.329	1.173	.069
	.280	.350	1.103	.042
	.441	.309	1.249	.096
	.490	.294	1.312	.118
	.662	.283	1.364	.135
	.788	.271	1.424	.153
	.883	.247	1.561	.194
	.980	.228	1.691	.228
NaBr	.203	.356	1.084	.035
	.406	.323	1.195	.077
	.609	.306	1.261	.101
	.812	.256	1.506	.178
	1.014	.229	1.685	.226
$NaClO_4$	0.238	.372	1.038	.016
	.477	.336	1.149	.060
	.715	.317	1.217	.085
	.954	.303	1.274	.105
HCl	.197	.381	1.013	.005
	.394	.368	1.049	.021
	.590	.346	1.116	.048
	.787	.333	1.159	.064
	.984	.324	1.191	.076
	.984	.330	1.139	.056
$HClO_4$	.246	.419	0.921	− .036
	.492	.439	.879	− .056
	.737	.465	.830	− .081
	.983	.504	.766	− .116

respectively, their ratio being taken equal in the present instance to the ratio of the optical densities of the corresponding solutions and C_s denotes the concentration of the salt. The constant K depends upon the particular electrolyte, as well as upon the non-electrolyte whose solubility is involved and, in general, when the solubility is sufficiently high, may include an effect of self-interaction associated with change of the non-electrolyte's activity coefficient with significant change in its own concentration as the electrolyte is added. In the present instance, where in view of the low solubilities of the non-electrolytes, self-interaction terms may be regarded as negligible, the Setchénow constants K may be identified with true salting-out constants k_s of the various electrolytes,[5] and their values, derived from the data by the method of least squares, are summarized in Table III. Included for comparison are the corresponding values for benzene, taken from the work of McDevit and Long.[1] Except for possible inversion between lithium chloride and sodium bromide, whose effects are almost equal, the salting-out order for the various electrolytes considered is the same in all three cases. Furthermore, with certain minor exceptions (where the salt effects happen to be relatively small in magnitude and therefore subject to relatively large experimental error), the salting-out constant for a given electrolyte increases in magnitude from benzene to naphthalene, and again from naphthalene to biphenyl. It is interesting to note that this effect is observed also for salting-in with perchloric acid. In other words, the salt effects for the given set of electrolytes apparently fan out progressively as one goes from benzene to naphthalene to biphenyl.

TABLE III

SETCHÉNOW CONSTANTS AT 25°

Electrolyte	Benzene,[a] 89.4 ml./mole	Naphthalene, 125 ml./mole	Biphenyl, 149 ml./mole
$^1/_2$ Na_2SO_4	0.274	0.358	0.423
NaCl	.195	.260	.276
KCl	.166	.204	.255
LiCl	.141	.180	.218
NaBr	.155	.169	.209
$NaClO_4$	.106	.096	.113
HCl	.048	.046	.070
$HClO_4$	− .041	− .081	− .116

[a] W. F. McDevit and F. A. Long, reference 1.

At the head of Table III are listed the molal volumes of the non-electrolyte solutes. The values for naphthalene and biphenyl have been estimated for the liquid state by extrapolation from their densities at temperatures above their melting points. The value for naphthalene is 1.40 times and that for biphenyl 1.67 times as great as the value for benzene. Comparison with the relative values of the Setchénow constants indicates that for the first four electrolytes listed, the constants for naphthalene average 1.28 times as great as for benzene, while for biphenyl they average 1.51 times as great (the value for NaCl in this case pulling down the average somewhat). These results are quite consistent with the theory put forward by McDevit and Long, which suggests that the constants should increase somewhat less than in proportion to the molal volume of the non-electrolyte, the deviation from exact proportionality depending on the ratio of the ion radius to the sum of the ion and non-electrolyte molecule radii. For NaBr and $NaClO_4$, the values relative to benzene are much smaller, but for $HClO_4$, the salting-in effect is relatively considerably larger. It should be noted however that for $NaClO_4$,

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(5) See F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

TABLE IV

ACTIVITY COEFFICIENT OF NAPHTHALENE IN AQUEOUS SOLUTIONS OF ELECTROLYTES AT 0.1°

Electrolyte	Electrolyte concn., g.-eq./liter	Optical density, $-\log (I/I_0)$, undiluted, at 25°, 275 mμ	Activity coefficient, $\gamma'' = s_0/s$	$\log \gamma''$
None	0	0.475 ± 0.004	(1.000)	(0.000)
$^1/_2$ Na_2SO_4	0.215	0.397	1.196	0.078
	.400	.342	1.389	.142
	.646	.278	1.708	.232
	.803	.240	1.978	.296
	1.071	.185	2.566	.409
	1.078	.197	2.410	.382
NaCl	0.345	.395	1.201	.080
	.537	.348	1.364	.135
	.689	.338	1.405	.147
	.896	.290	1.636	.214
	1.149	.257	1.846	.266
LiCl	0.275	.422	1.125	.051
	.371	.403	1.179	.071
	.550	.362	1.311	.118
	.743	.348	1.365	.135
	.917	.317	1.497	.175
	1.060	.298	1.593	.202
NaBr	0.293	.422	1.125	.051
	.515	.399	1.190	.076
	.735	.364	1.305	.116
	1.030	.315	1.508	.178
HCl	0.247	.458	1.037	.016
	.494	.450	1.055	.023
	.741	.431	1.102	.042
	.988	.419	1.134	.054

HCl and $HClO_4$, the absolute magnitudes of the salt effects are comparatively small and therefore subject to large relative error, which is compounded when one makes comparisons among the different non-electrolytes.

Data for naphthalene at 0.1° are presented in Table IV. Comparison of the Setchénow constants at the two temperatures, given in Table V, suggests no significant trend. Such differences as are apparent hardly exceed experimental error, and one cannot establish a correlation with change in the water–electrolyte interaction, as suggested by the theory of McDevit and Long, though such a correlation apparently does exist for certain other non-polar non-electrolytes, and is not necessarily precluded by the present data.[5] An attempt was made to obtain data also for biphenyl at 0°, but the results were quite erratic; this is no doubt mainly due to the relatively large experimental error resulting from the low optical densities of the solutions, which were all below 0.300.

TABLE V

SETCHÉNOW CONSTANTS FOR NAPHTHALENE

Electrolyte	25°	0.1°
$^1/_2$ Na_2SO_4	0.358	0.366
NaCl	.260	.233
LiCl	.180	.191
NaBr	.169	.165
HCl	.046	.055

ENDICOTT, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Thermal Decomposition of $MeCl_4 \cdot 2C_6H_5COOR$ Type Compounds[1,2]

BY F. W. CHAPMAN, W. S. HUMMERS, S. Y. TYREE AND S. YOLLES

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Zirconium tetrachloride·2-methyl benzoate, zirconium tetrachloride·2-ethyl benzoate and the analogous ester addition compounds of hafnium tetrachloride undergo thermal decomposition to yield alkyl chloride and metal benzoate. Superimposed on this reaction, free metal chloride reacts with metal benzoate to form benzoyl chloride and oxygen-bridge polymers. Indications are that pure hafnium addition compounds decompose at a slower rate than the corresponding zirconium compounds. Residues from decompositions that are carried to completion are resin-like solids insoluble in all common solvents except concentrated sulfuric acid.

It has been reported that thorium tetrabromide[3] and rare earth bromides[4] react with ethyl benzoate at the ester reflux temperature to evolve ethyl bromide and leave normal metal benzoates as insoluble residues. For two rare earths[4] differences in reaction rates indicated a separation factor. The possibility of a zirconium–hafnium separation factor using the same reaction was indicated. Preliminary experiments in this Laboratory showed that zirconium tetrabromide (and chloride) reacts with ethyl benzoate to produce ethyl bromide (chloride), but not in theoretical yield. Furthermore, zirconium tetrabenzoate was not the other product. Dangyan[5] has reported that iron(III) chloride refluxed with ethyl benzoate liberates ethyl chloride in no more than 74% yield. Norris and Klemka[6] prepared a product of composition $AlCl_3 \cdot C_2H_5OOCC_6H_5$ which decomposed slowly at 165° to liberate ethyl chloride in 95% yield. The composition of the solid residue was postulated as $AlCl_2(OOCC_6H_5)$. In a previous paper[7] the authors reported the preparation of a series of addition compounds of the type $MeCl_4 \cdot 2C_6H_5COOR$, (where Me = Hf or Zr, and R = ethyl, methyl or phenyl) all crystalline substances, stable at room temperature in dry air.

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[1] From the doctoral dissertations of F. W. Chapman, W. S. Hummers and S. Yolles.

[2] Presented at the 119th Meeting of the A.C.S. at Cleveland, Ohio, April 11, 1951.

[3] R. C. Young, THIS JOURNAL, **56**, 29 (1934).

[4] R. C. Young, A. Arch and W. V. Shyne, *ibid.*, **63**, 957 (1941).

[5] M. T. Dangyan, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1780 (1938).

[6] J. F. Norris and A. J. Klemka, THIS JOURNAL, **62**, 1432 (1940).

[7] W. S. Hummers, S. Y. Tyree and S. Yolles, *ibid.*, **74**, 139 (1952).