causes a significant increase in basicity of alkoxide anions but appears to have little effect on the basicity of amines may also suggest that there is an opposing effect of "B-strain" which would be more important in the latter equilibrium between trivalent and tetravalent nitrogen than in the former, between univalent and divalent oxygen.

The Relative Effect of Various "R"'s on the Acidity of Different Functional Groups.—This effect was studied by plotting values of log K (in water)[29] for various RCO_2H compounds against the values of log K_e for the corresponding RCH_2OH, $RCHOHCH_3$, ROH, $RCONH_2$ and $RCONHC_6H_5$ compounds. The values of K_e have been suitably corrected. For example, they have been divided by two in the case of symmetrical glycols. In Fig. 2, the RCH_2OH plot, the data for the hydroxyl-containing R groups have been ignored in drawing the best line, since it seems likely that the anions of the glycols are stabilized by internal hydrogen bonding and hence that the equilibria measured here are really not of the same type as with the monohydroxy alcohols. It is seen that there is a close relation between the effect of an R group on the acidity of $-CO_2H$ and on $-CH_2OH$, but that it is not a perfect one. With the $-CHOHCH_3$, $-CONH_2$ and $-CONHC_6H_5$ compounds plotted in Fig. 3, the situation appears to be similar, but here the number of compounds studied is more limited. The ROH plot displayed very little correlation and is not shown.

Effect of Solvent Changes on Relative Acidity.—All values of K_e are, of course, larger in isopropyl alcohol than in ethanol, but it is interesting to relate the size of the change to the area over which the negative charge is spread in the anion derived from the various acids. From the data in Table V it is seen that this change is smallest with ethanol, where the negative charge is presumably almost entirely on one oxygen atom. It is somewhat larger with glycerol, perhaps indicating that the charge is somewhat dispersed by the hydrogen bonding of an unreacted hydroxyl group to the alkoxide oxygen atom. The largest changes are found with compounds in which the charge may be spread over several atoms by resonance. These data would be expected from the greater ability of ethanol to solvate the anions with more concentrated charges, which are susceptible to stronger solvation.

TABLE V

EFFECT OF SOLVENT ON RELATIVE ACIDITY

Compound	K_e in i-PrOH	EtOH	$\frac{K_e(i\text{-PrOH})}{K_e(\text{EtOH})}$
4,4'-Dinitrodiphenylamine	21600	43.4	500
2,4-Dinitrodiphenylamine	19600	26.68[a]	730
2,4-Dinitroaniline	2700	4.773[a]	570
Ethanol	0.95	0.058	16
Glycerol	175	5.5[a]	32
4-Nitrobenzamide	290	1.4[a]	210

[a] From the data of Stearns and Wheland.[11]

ATLANTA, GEORGIA

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[29] Better correlations may have been obtained by using the ionization constants in isopropyl alcohol solution, but these were not available.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Freezing Point Curves of Concentrated Aqueous Sulfuric Acid[1]

BY J. E. KUNZLER AND W. F. GIAUQUE

RECEIVED MAY 26, 1952

The freezing point composition curves for aqueous sulfuric acid have been investigated over the range $H_2SO_4{\cdot}2H_2O$–$H_2SO_4{\cdot}H_2O$ eutectic to somewhat on the SO_3 side of H_2SO_4. The regions near the melting points of H_2SO_4 and $H_2SO_4{\cdot}H_2O$ have been considered in detail so that the measurements can be used for calculating the change of free energy with composition. Evidence has been presented to show that maximum freezing sulfuric acid corresponds to absolute sulfuric acid within a few thousandths of a wt. %. On this basis we believe that maximum freezing sulfuric acid is a more accurate standard of acidimetry than can be prepared by any other known method. It has been shown that the relative compositions of maximum freezing anhydrous sulfuric acid and the maximum freezing monohydrate correspond to the theoretical H_2SO_4:$H_2SO_4{\cdot}H_2O$ ratio to within 0.01 wt. % H_2SO_4. Thus maximum freezing $H_2SO_4{\cdot}H_2O$ is a pure compound within 0.01 wt. % H_2SO_4. The melting points of H_2SO_4 and $H_2SO_4{\cdot}H_2O$ were found to be 10.371 and 8.489°, respectively.

Work in progress in this Laboratory on the thermodynamic properties of sulfuric acid requires the free energy of dilution. This can be determined from the freezing point curves of the several hydrates. Gable, Betz and Maron[2] have recently published an excellent phase equilibrium diagram of the sulfur trioxide–water system. However, these authors did not contemplate the use of their data for the determination of free energy from the freezing point lowering. A calculation of this type requires numerous precise values near to the melting points of the several pure phases. It was found desirable to supplement the data of G., B. and M. by very numerous measurements near the melting points of the anhydrous acid and the monohydrate. At the same time measurements of increased accuracy were obtained over the range from the $H_2SO_4{\cdot}2H_2O$–$H_2SO_4{\cdot}H_2O$ eutectic to somewhat on the SO_3 side of the anhydrous acid.

Apparatus.—The measurements were made in a one-liter dewar which had a long narrow neck. It was submerged, except for about 2 in. of the neck, in a one-gallon dewar of crushed ice. The sample dewar was equipped with a motor driven stirrer and the tops of both dewars were protected by Bakelite covers. Several small openings, with removable glass sleeves, were provided for the stirrer shaft, sampling, adding increments of the solution components, and for a ten-

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[2] C. M. Gable, H. F. Betz and S. H. Maron, THIS JOURNAL, **72**, 1445 (1950).

junction copper–constantan thermocouple. The acid was purified by distillation.[3] Samples were taken with a pipet which withdrew solution by means of an evacuated bulb which could be opened to the pipet by means of a stopcock. The pipet has been described by Kunzler.[3] Its special feature is an extension, in the form of a small chamber ending in a tip, attached to the pipet by means of a tapered ground glass joint. A sintered glass filter disk, with an average pore size of about 10 microns to exclude the fine acid slurry, is sealed across the middle of the chamber. During the period before equilibrium, a very small stream of nitrogen bubbles prevented entry of solution so that the sintered glass filter could not be contaminated by liquid. Non-equilibrium liquid can be produced by the melting of solid when a pipet at 25° is introduced, but any such liquid could not enter or be produced in the pipet as used here.

Method.—The determination of free energy from freezing point lowering measurements near the melting point of the acid, or that of one of its hydrates, requires a very accurate knowledge of the composition in this range. Withdrawing samples corresponding to each temperature observation is laborious and unnecessarily inaccurate. The method used is somewhat similar to those used by Hammett and Deyrup[4] and Gillespie,[5] in that the variation of composition was obtained by addition of weighed amounts of material.

A known weight of some 2300 g. of acid, a little on the SO_3 side of H_2SO_4, was placed in the dewar. The composition was known only approximately. About 20% of the acid was in the form of solid at the beginning but the amount was known only very roughly. Thus neither the over-all composition nor the composition of the liquid portion were known at the start.

Water was added in the form of small increments of aqueous acid, which was shown by analysis to have a composition of 96.20 ± 0.01%. This reduced heat introduction and gave increased accuracy with respect to the amount of water added. Near the melting point the temperature difference was read to 0.0001°, and was accurate to 0.0002°, after each addition. The laboratory in which the experiment was performed was thermostated at 25°. The increments of 96.20% acid were at 25° when added and thus at known heat content. The heat of stirring plus heat leak could be evaluated from the rate of change of melting point with time over long periods. This can be determined most accurately near the beginning and end of such a series where the rate of change of temperature with the amount of solid melted is greatest. The dewar vessel was treated as a calorimeter and an accurate record of its change in heat content was recorded from the beginning to the end of a series of observations. When the composition of the acid had reached about 99.79%, four samples of the equilibrium liquid were withdrawn and analyzed to within 0.005%.

The data were treated by plotting a curve of melting point against amount of 96.20% acid added. At the melting point maximum the composition corresponded to pure H_2SO_4 and this could be determined to 0.0002% acid. Since the amount of excess water between the melting point maximum and the end of the series was known to about 0.4%, the amount of solid at the end of the series could be calculated. The heat of mixing of 96.20% acid in the various solutions was available from the partial specific heat content measurements of Kunzler and Giauque,[6] although the calculations required one approximation before the final result was obtained. Since the heat content was known for each temperature measurement, the amount of solid and thus the composition of the liquid could be calculated. The heat of fusion of H_2SO_4, 2560 cal. mole^{-1}, was taken from the measurements of Rubin and Giauque.[7]

The heat quantities were known with sufficient accuracy so that the accuracy at each point was essentially not influenced by the calculation of the various amounts of solid during the experiment.

In regions farther removed from the melting points, the temperatures were observed, and samples removed for analysis to 0.005%.

The thermocouple was compared with a strain-free platinum resistance thermometer calibrated at the U. S. Bureau of Standards.

The observations are given in Table I in chronological order.

TABLE I

FREEZING POINT LOWERING IN AQUEOUS SULFURIC ACID

θ = freezing point lowering

Wt. % H_2SO_4	θ, °C.
Solid phase H_2SO_4 Series 1	
99.986	0.477
99.898	.472
99.897	.466
99.816	.986
99.557	2.57
Series 2	
99.276	4.20
99.017	5.78
98.707	7.67
98.378	9.77
Series 3	
93.806	44.04
93.835	43.75
94.010	42.20
94.260	39.93
94.513^a	37.70
H_2SO_4 crystals added	
95.062	33.29
95.311	31.25
95.591	29.08
95.801^a	27.26
96.065^a	25.20
H_2SO_4 crystals added	
96.222	24.32
96.622	21.47
97.090	18.19
97.490	15.50
97.847	13.16
Solid phase $H_2SO_4 \cdot H_2O$ Series 4	
93.382	39.96
93.256	38.56
$H_2SO_4 \cdot H_2O$ crystals added	
92.412	31.07
92.301	30.13
92.214	29.40
91.913	27.01
91.583	24.49
91.299	22.47
90.832	19.35
90.406	16.77
90.288	16.07
89.926	14.07
89.482	11.79
88.890	9.10
88.420	7.24
Series 5	
87.748	5.01
87.338	3.80
86.896	2.71
86.542	1.983
86.514	1.919
86.113	1.235
85.794	0.797
85.488	.461
85.189	.233
Series 5-a	
84.909	0.0874
84.895	.0821
84.880	.0762
84.828	.0562
84.775	.0408
84.723	.0277
84.672	.0168
84.620	.0087
84.570	.0035
84.518	.0004
84.469	.0002
84.419	.0020
84.371	.0059
84.323	.0117
84.276	.0204
Series 5 (cont.)	
84.006	0.1002
83.435	0.497
82.824	1.237
82.412	1.922
81.783	3.241
Series 6	
81.850	3.077
81.888	3.011
80.947	5.56
80.154	8.31
79.446	11.19
$H_2SO_4 \cdot H_2O$ crystals added Series 6 (cont.)	
78.921	13.63
78.329	16.52
77.745	19.77
$H_2SO_4 \cdot H_2O$ crystals added	
76.643	26.51
76.193	29.55
75.990	30.99
75.786	32.47
75.339	35.87
Series 7	
74.788	40.11
74.309	44.17
74.410	43.29
74.550	42.25
Solid phase H_2SO_4 Series 8	
100.096	0.288
100.086	.248
100.076	.214
100.057	.144
100.0386	.0784
100.0270	.0440
100.0193	.0249
100.0157	.0171
100.0121	.0105
100.0084	.0053
100.0047	.0018
100.0011	.0001
99.9974	.0005
99.9936	.0031
99.9902	.0084
99.9866	.0149
99.9830	.0234
99.9759	.0448
99.9689	.0720
99.9615	.1044
99.948	.1736
99.931	.268
99.914	.367
99.883	.565
99.850	.768
99.819	.964
99.787	1.155
99.791	
99.791	
99.787	

^{a} F.p. slightly high because amount of solid was low.

New material was used at the start of each numbered series in Table I. Some 30 to 10% of the sample was present as the equilibrium solid in the form of a slurry of fine crystals which were thoroughly and continuously stirred. Series 1 and 2 were measured in the order of descending temperatures by adding 96.20% sulfuric acid. Series 3, 4 and the first part of Series 5 were measured in order of ascending temperatures to take advantage of the heat capacity of the system. In Series 3, acid with about 30% excess SO_3 was used to increase the concentration, and finely divided crystals of H_2SO_4, cooled by means of solid carbon dioxide, were added where noted. In Series 4 and 5, except 5a, ice at 0° was used for dilution, and on the one occasion noted, crystals of $H_2SO_4 \cdot H_2O$ cooled by storing the container in solid carbon dioxide were added. In Series 6 and 7, dilution was with ice at 0° or at liquid nitrogen temperature as required. When it was necessary to add crystals of $H_2SO_4 \cdot H_2O$ or H_2SO_4 these were adjusted approximately to solution

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(3) J. E. Kunzler, work to be published.

(4) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(5) R. J. Gillespie, *J. Chem. Soc.*, 2493 (1950).

(6) J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 3472 (1952).

(7) T. R. Rubin and W. F. Giauque, *ibid.*, **74**, 800 (1952).

temperature before addition. The portion of Series 5 designated 5a and Series 8 covering the regions near the compounds $H_2SO_4 \cdot H_2O$ and H_2SO_4, respectively, utilized the calorimetric accounting method of determining concentrations as described above. The dilution in Series 5a was by means of water at 25° and in Series 8, 96.20% acid at 25° was used.

Equilibrium.—One of the sources of error in freezing point measurements depends on the extent to which equilibrium is attained between the solid phase and the bulk liquid which is analyzed. Even when heat leak is reduced to a minimum there will be a small amount of heat developed by the stirring which is essential to the attainment of uniform concentration. Thus prior to and during the period of observation there will be a small amount of crystal melting. In these circumstances one cannot escape the conclusion that the concentration in the immediate vicinity of the melting crystals will be rich with respect to the liquid resulting from the solid phase. In any two-component system this must raise the temperature above the value which would result from true equilibrium between the solid and the bulk liquid. The present measurements were made with a full appreciation of this difficulty and the conditions were such as to reduce it to a minimum. The finely ground crystals presented a very large surface. After additions of liquid, equilibrium was established within two minutes at the higher temperatures and within about 10 minutes at the lower temperatures. When cold solids, such as ice at liquid nitrogen temperatures, were added, a long period was necessary to bring them into equilibrium. Aside from this reason for slowness, equilibrium was reached rapidly even in the more concentrated regions and at lower temperatures where increased viscosity would reduce the rate of diffusion.

Comparison of Maximum Freezing Sulfuric Acid and Sulfuric Acid Monohydrate.—During the course of the present work the sulfuric acid content of maximum freezing sulfuric acid and its monohydrate were compared. The freezing point curve of the monohydrate is much flatter than that of the anhydrous acid but the maximum was located at 8.489° within a composition accuracy of 0.003 wt. %. The maximum at 10.371° for H_2SO_4 was determined to an accuracy of 0.0002 wt. %. The comparison showed that the two maxima were in agreement within 0.005% and it is conservative to assume that the total possible error is within 0.01%.

Evidence that H_2SO_4 Crystallizes as Absolute Acid to a High Degree of Accuracy.—Lichty[8] mixed equimolal amounts of sulfur trioxide and water and proved that the maximum melting point corresponded to absolute acid within 0.01 wt. %.

Rubin and Giauque[7] made a considerable number of unpublished determinations of the melting point of sulfuric acid as a function of the fraction melted. There was a small excess of $H_2S_2O_7$ in their sample. These measurements were made after waiting long periods, of about two hours, for equilibrium. They were not used by R. and G. to investigate the amount of impurity because it was not possible to estimate the freezing point lowering with sufficient accuracy, and also because related detailed measurements as a function of composition were unavailable. The needed observations were obtained during the present research.

In order to ensure uniformity in the temperature scales of the two researches, which is particularly important when the freezing point lowering, θ, is the objective, the melting point of sulfuric acid monohydrate, 281.649°K., was used as an intermediate temperature reference. This melting point is not very sensitive to composition and thus could be determined rather accurately. We have applied corrections to the melting point data of R. and G. to make them as accurate as possible for the present purpose. The results are given in Table II. The quantity $-A$, representing the moles deficiency of H_2O or the excess SO_3, per mole of H_2SO_4 is calculated provisionally on the assumption that the maximum melting point corresponds to pure sulfuric acid. It should perhaps be emphasized that ideal solution laws were not assumed in any of these calculations.

It will be seen that the total amount of $H_2S_2O_7$ present in the liquid does not change when the amount of the solid melted changes from 15 to 58%. It is evident that the solid does not have an appreciable amount of $H_2S_2O_7$ to contribute to the liquid produced by the melting. It is important to realize that the temperature composition data used as a basis for treating the data of R. and G. were obtained by a method in which the amount of the solid changed by only 1.6% during the investigation which has been mentioned above. It is also of interest to note that the activity of $H_2S_2O_7$ in the solution with 15% melted is about twice that when 58% is melted. This ratio is readily calculable from the freezing point curve. We believe that the above facts support the conclusion that $H_2S_2O_7$ is very insoluble in solid absolute sulfuric acid. There is no trend in the amount of $H_2S_2O_7$ shown in the last column of Table II.

TABLE II

MELTING POINT DATA ON H_2SO_4 CONTAINING A SMALL AMOUNT OF $H_2S_2O_7$

Freezing point lowering, °C.			$-A$, mole $H_2S_2O_7$ per mole H_2SO_4 in liquid	Fraction melted	Total $H_2S_2O_7$ present in liquid
Thermocouple	Res. therm.	Av.			
0.29	0.29	0.29	0.0052	0.15	0.0008
.155	.145	.15	.0032	.22	.0007
.127	.128	.128	.0029	.30	.0009
.081	.079	.080	.0021	.37	.0008
.058	.062	.060	.0017	.44	.0007
.046	.060	.053	.0016	.51	.0008
.050	.050	.050	.0016	.58	.0009
				Average	0.0008 ± 0.0001

Rubin and Giauque[7] made measurements of heat capacity below the melting point and evaluated the premelting heat calorimetrically. They give the result $A = -0.0006$ as compared to -0.0008 in Table II. They expressed the opinion that their results were low because insufficient time was allowed for equilibrium. Such a situation will result in a low concentration of impurity at the melting boundary and require a long time for equilibrium by diffusion and heat conduction. The results in Table II were based on the two-hour equilibrium period mentioned above and if a substantial part of this time had been used for equilibrium in the premelting heat measurements they would probably have given agreement.

Rubin and Giauque[7] also estimated the amount of $H_2S_2O_7$ impurity present in the liquid remaining at the H_2SO_4–$H_2S_2O_7$ eutectic point as 0.0010 mole of $H_2S_2O_7$ per mole of H_2SO_4 in the calorimeter. This estimate was based on a small amount of eutectic melting and is somewhat uncertain due to the fact that the heat of fusion of the $H_2S_2O_7$ phase is known only roughly. The value 0.0010 may be taken as comparable with the more reliable value of 0.0008 given in Table II. It may be shown that the activity of $H_2S_2O_7$ increases by a factor of about 150 between the melting point of H_2SO_4 and the eutectic and despite this large increase the results indicate that the H_2SO_4 eutectic solid phase does not contain any appreciable amount of $H_2S_2O_7$. In reaching this conclusion it is not assumed that the entire solid would continuously reconstitute itself along the freezing point curve. Even the assumption that a solid built up of layers deposited in equilibrium with the liquid during cooling should deplete the total available amount of 0.0008 mole $H_2S_2O_7$ by an appreciable amount if much solubility existed. We believe that the data as a whole indicate that maximum melting sulfuric acid corresponds to absolute H_2SO_4 within a few thousandths of a per cent. and that this procedure for preparing absolute acid is more accurate than any other known method. This is important in the present series of researches on sulfuric acid in this Laboratory since analytical procedures have been based on this standard. The details of these procedures will be published elsewhere.[3]

The fact that maximum melting sulfuric acid monohydrate and maximum melting sulfuric acid have relative compositions which agree with the ideal composition ratio for these compounds, taken with the fact that the latter is pure, also demonstrates that maximum melting $H_2SO_4 \cdot H_2O$ corresponds to the pure compound with high accuracy.

Comparison with Other Data.—Gillespie[5] covered the range 99.7% to 100.4% H_2SO_4 and Ham-

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[8] D. M. Lichty, THIS JOURNAL, 30, 1845 (1908).

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

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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).