[CONTRIBUTION FROM THE PEARSON CHEMICAL LABORATORY OF TUFTS COLLEGE]

The Freezing Points of Concentrated Aqueous Solutions of Urea, Urethan, and Acetamide[1]

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The properties of aqueous solutions of nonelectrolytes are receiving more attention as the understanding of liquids and of solutions develops. Relatively few data for the freezing points of such solutions over a large concentration range and determined by the equilibrium method have been reported.[2] This paper describes an investigation of the freezing points of water solutions of three chemically related substances, urea, urethan, and acetamide to the eutectic points for the first two solutes, and to a 3 molal solution of acetamide.

Experimental Procedure

The equilibrium method of determining the freezing point of the solutions was used, employing a platinum resistance thermometer and apparatus already described.[3] The only changes in technique were the removal of the sample by suction and the saturation of the solutions with previously chilled air. The solutions were analyzed with a Zeiss portable interferometer, by the method of Adams[4] in which the unknown solution was compared with two known solutions of approximately the same concentration. This method resulted in an interpolation over a small range of concentration and minimized the chances of mistaking the proper interference band for comparison.

The urea and urethan,[5] obtained from the Eastman Kodak Company, were crystallized thrice with centrifuging from conductivity water. The crystals were dried in an oven at 55° for a day, and further dried by evacuating at room temperature with a Hy-Vac pump protected by a trap cooled with a solid carbon dioxide–acetone mixture. The material was stored in desiccators over solid sodium hydroxide. The acetamide was prepared from student preparations, twice distilled as recommended by Beilstein, and crystallized from alcohol and ether.[6] It was then crystallized twice from conductivity water, centrifuged with washing, and dried by means of the Hy-Vac pump. The ice and water were prepared in a manner already described.[3] Water obtained by melting a sample of the ice gave the same reading in the interferometer as conductivity water. All solutions of known concentration were prepared by weight, all weights being reduced to vacuum, and used within a few hours after their preparation.

Results

In Table I are given the number of the experiments in chronological order, the experimentally determined concentration expressed as molality (formula[7] weight of solute per 1000 g. solvent) m, the freezing point depression Θ, the quotient Θ/m, and the osmotic coefficient ϕ', for

TABLE I

FREEZING POINTS AND OSMOTIC COEFFICIENTS OF AQUEOUS SOLUTIONS OF UREA, URETHAN, AND ACETAMIDE

No.	m	Θ	Θ/m	$1 - \phi'$
		Urea		
3	0.324_{1}	0.595_{3}	1.837	0.011_{1}
11	$.431_{5}$	0.789_{3}	1.829	$.015_{1}$
4	$.645_{8}$	1.169_{8}	1.811	$.024_{6}$
10	1.521_{3}	2.673_{2}	1.757	$.053_{0}$
8	3.360_{1}	5.489_{7}	1.635	$.117_{5}$
2	3.369_{6}	5.594_{4}	1.660	$.104_{2}$
7	4.545_{3}	7.150_{6}	1.573	$.150_{0}$
6	5.284_{8}	8.082_{5}	1.529	$.173_{3}$
5	6.012_{6}	8.965_{9}	1.491	$.193_{6}$
1	8.082_{8}^{a}	11.414_{2}	1.412	$.235_{3}$
9	8.083_{3}^{a}	11.414_{6}	1.412	$.235_{4}$

[a] Eutectic point.

No.	m	Θ	Θ/m	$1 - \phi'$
		Urethan		
6	0.256_{8}	0.464_{2}	1.807	0.027_{1}
12	$.322_{3}$	$.577_{2}$	1.791	$.035_{8}$
5	$.384_{0}$	$.686_{3}$	1.787	$.037_{8}$
8	$.448_{2}$	$.791_{0}$	1.765	$.049_{9}$
4	$.476_{6}$	$.842_{6}$	1.768	$.048_{0}$
9	$.689_{5}$	1.188_{5}	1.724	$.071_{7}$
3	1.037_{7}	1.717_{6}	1.655	$.108_{4}$
10	1.132_{0}	1.812_{2}	1.643	$.115_{0}$
1	1.163_{3}	1.896_{8}	1.630	$.121_{6}$
2	1.193_{5}	1.944_{4}	1.629	$.122_{2}$
7	1.760_{9}^{a}	2.688_{7}	1.527	$.177_{0}$
13	1.762_{9}^{a}	2.688_{8}	1.525	$.178_{0}$
		Acetamide		
10	0.545_{3}	0.992_{0}	1.819	0.020_{3}
2	$.695_{2}$	1.255_{3}	1.805	$.028_{8}$
5	$.698_{7}$	1.268_{5}	1.815	$.022_{3}$
6	1.116_{3}	2.005_{8}	1.797	$.031_{9}$
7	1.876_{6}	3.308_{1}	1.763	$.049_{5}$
3	2.267_{8}	3.978_{1}	1.754	$.053_{9}$
11	2.397_{1}	4.209_{0}	1.756	$.052_{9}$
8	2.986_{6}	5.172_{9}	1.732	$.065_{2}$
4	3.067_{6}	5.336_{9}	1.740	$.061_{0}$
9	3.572_{0}	6.179_{4}	1.730	$.065_{9}$

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(1) The experimental portion of this paper is from a thesis submitted by F. W. Politi to the faculty of the Graduate School of Tufts College.

(2) (a) G. Scatchard and co-workers, THIS JOURNAL, **58**, 837 (1936), and preceding papers; (b) T. J. Webb and C. H. Lindsley, *ibid.*, **56**, 874 (1934); (c) Landolt-Bornstein-Roth-Scheel, "Tabellen," 5th ed., Vol. IIIb, 1935.

(3) H. M. Chadwell, THIS JOURNAL, **49**, 2795 (1927).

(4) L. H. Adams, *ibid.*, **37**, 481 (1915).

(5) H. M. Chadwell and B. Asnes, *ibid.*, **52**, 3507 (1930).

(6) E. C. Wagner, *J. Chem. Ed.*, **7**, 1135 (1930).

(7) Calculated from 1936 atomic weights. The new atomic weight of carbon of 12.01, accepted in 1937, would decrease the values of m for urea by 0.02%, for urethan and acetamide by 0.03%.

the chemical potential of the solvent at the freezing point of the solution, tabulated as $1 - \phi'$. The results for acetamide are the least consistent among themselves.

The values of the osmotic coefficient have been calculated from the equations[8]

$$\phi_f = \Theta/\lambda m \qquad (1)$$

$$\phi' = \phi_f(1 + 0.001\,\phi_f m) \qquad (2)$$

where $\lambda = 1.858$ and ϕ' differs from ϕ_f by a correction for the changing latent heat of fusion with temperature. The $1 - \phi'$ corresponds to the j-function of Lewis and Randall, except that the latter refers to the temperature of freezing of pure solvent. An equation of the form

$$\phi' = 1 - bm + cm^2$$

whose constants[9] were determined by the method of least squares describes the results over the whole range of concentration with a probable error of about 5×10^{-4}.

The values of Θ/m are 1–2% lower than those given in the "International Critical Tables."[10] This is to be expected because the latter are based on measurements made by the Beckmann method which tends to give high values for this ratio.

The only measurements of other colligative properties of these solutions which have been found, and with which these determinations can be compared, are the vapor pressure lowerings of urea solutions at 0° by Fricke[2c] (p. 2158). His values for the activity of the solvent are 0.4% higher than those calculated by interpolating our data. The comparison follows.

m	2.349	3.796
N_2	0.0405	0.0640
a_1/N_1 (F.)	1.006	1.010
a_1/N_1 (C. & P.)	1.003	1.006

Our values of a_1/N_1 are calculated from the formula[11]

$$\log a_1 = -0.004211\,\Theta - 0.0000022\,\Theta^2$$

Discussion

The values of $1-\phi'$ listed in Table I should be considered only as thermodynamic properties as defined by the equations given. They do not measure directly the deviations from the ideal solution, since $1 - \phi'$ for an ideal solution is not zero, but is defined[7] by

$$1 - \phi' = 1 - \frac{\ln(1 + x)}{x} = 0.00901\,m - 0.00011\,m^2 \qquad (3)$$

where $x = 0.018\,m$. By using equations (2) and (3) it can be shown that a molal ideal solution would freeze at −1.841°; if the molality was 7, the depression of the freezing point would be 7×1.739. The corresponding values of $(1-\phi')_{\text{Ideal}}$ are 0.009 and 0.058. Consequently, the deviations of these solutions of urea, urethan, and acetamide from ideal behavior are not as great as would be assumed from a cursory inspection of Table I.

These deviations from ideality can also be expressed in terms of activity coefficients. From the values of m and Θ/m given in Table I can be calculated the "preliminary" activity coefficient of the solute (γ') at the temperature of the freezing mixture by the graphical methods of Lewis and Randall.[12] The results of this calculation are given in Table II.

TABLE II

SMOOTHED VALUES OF THE ACTIVITY COEFFICIENTS

m	Urea γ'	Urethan γ'	Acetamide γ'
0.5	0.966	0.900	0.964
1.0	.933	.811	.938
1.5	.901	.734	.916
1.76[a]		.697	
2.0	.869		.896
3.0	.812		.864
5.0	.713		
7.0	.637		
8.08[a]	.604		

[a] Eutectic.

Figure 1 shows the change of the activity coefficient with concentration.

Gucker and Ayres[13] state that the apparent molal volume of urea solutions is a linear function of the first power of the molarity over a wide range of concentration, but that the heat capacity does not obey such a simple law. Their density measurements are not yet published. If their relationships between molality and molarity at 25° are used to calculate the molarity of our solutions, it is found that the activity coefficients do

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(8) G. Scatchard and M. A. Benedict, THIS JOURNAL, **58**, 837 (1936); G. Scatchard and S. S. Prentiss, *ibid.*, **56**, 1486, 2314 (1934).

(9) The values of the constants, together with the probable error (P) of ϕ' are as follows:

	b	c	P
Urea	0.03717	0.978×10^{-3}	5×10^{-4}
Urethan	.1067	3.38×10^{-3}	3×10^{-4}
Acetamide	.03437	4.52×10^{-3}	6×10^{-4}

(10) "International Critical Tables," Vol. IV, p. 262.

(11) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 284.

(12) Ref. 11, p. 287. The values of $1 - \phi'$ could be used for this calculation by omitting the second integral B.

(13) F. T. Gucker and F. D. Ayres, THIS JOURNAL, **59**, 2155 (1937).

not satisfy a linear function of the molarity,[14] but the curvature of the plot is much less than in the case of molality. The densities of these solutions at 0° are not available for more accurate calculations. The close connection between log γ and the volume change on solution has been reviewed by Hildebrand.[15]

In general, solutions composed of two polar constituents may show either positive or negative deviations from Raoult's law.[16] All of our solutions show positive deviations as is evidenced by the fact that a_1/N_1 is greater than 1, or that the osmotic coefficients are less than 1. Positive deviations are ascribed to weak intermolecular forces between solute and solvent.

The three solutes have a common $\mathrm{H_2{-}N{-}\overset{O}{\overset{\|}{C}}{-}}$ group, the rest of the molecule differing by a CH_3— in acetamide, a NH_2— in urea, and in urethan a C_2H_5—O—. As can be seen from Fig. 1, the magnitude of the deviation from ideal conditions increases in this same order, which is also the order of decreasing solubility. The solutes are more polar than water; the dipole moment ($\mu \times 10^{18}$ e. s. u.) of water is 1.85 and of acetamide[17] 3.7. The values for urea and urethan are not reported in the literature, but probably are of the order of 6–7 for urea and of 4 for urethan.[18] It is to be noted that the order of the deviations from Raoult's law is not the order of the dipole moments of the solutes. This might be expected from the complex nature of the intermolecular forces existing between very polar molecules.[19]

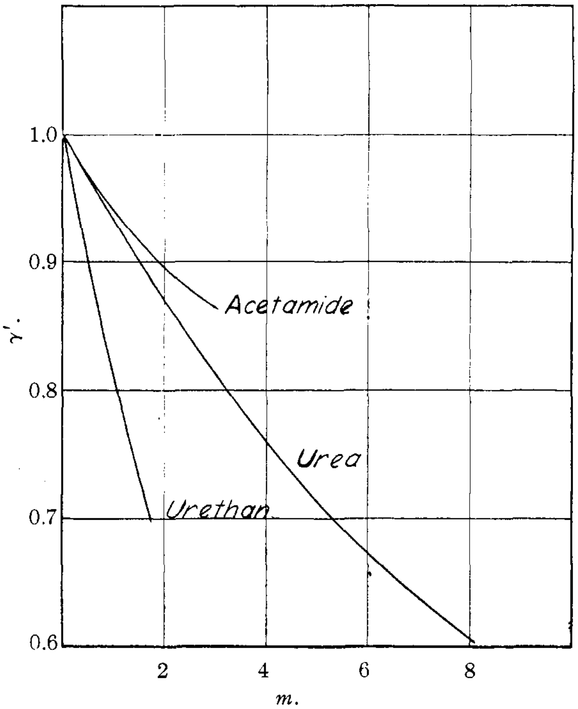

Fig. 1.—The change of the activity coefficient with molality.

We wish to express our indebtedness and gratitude to the Elizabeth Thompson Science Fund for providing us with the Zeiss interferometer used in the analyses.

Summary

This paper reports freezing points of aqueous solutions of urea and urethan over a concentration range to the eutective points, and of acetamide to 3 molal. The temperatures were measured with a platinum thermometer; the concentrations of solutions were determined by a Zeiss water-interferometer.

The "preliminary" activity coefficients have been calculated.

All of the solutions show positive deviations from Raoult's law. The magnitude of the deviation increases in the order acetamide, urea, urethan.

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[14] This is confirmed by unpublished vapor pressure measurements by Scatchard, Hamer, and Wood (private communication). In their forthcoming paper they plan to discuss the correlation between their data and the freezing point lowerings reported here.

[15] Hildebrand, "Solubility," second edition, Reinhold Publishing Corporation, New York City, 1936, p. 59 *et seq.*

[16] Ref. 15, p. 77; J. Kendall, *Trans. Faraday Soc.*, **33**, 1 (1937).

[17] W. D. Kumler and C. W. Porter, THIS JOURNAL, **56**, 2549 (1934).

[18] Very kindly predicted by C. P. Smyth, private communication, from the work of Devoto and co-workers, *Gazz. chim. ital.*, **63**, 495 (1933).

[19] Ref. 15, Chapts. IV and VI. The treatment of R. M. Fuoss, THIS JOURNAL, **58**, 982 (1936), of the interaction of polar molecules in determining thermodynamic properties applies to solvents of low dielectric constant.