at 15, 18, 20, 22, 25, 27 and 30°. In terms of Reynolds' criterion the velocities of flow varied between 25 and 63.

The resulting data were compared with previously determined viscosities of water in a manner to show any variations in *m*. It was found that any of the three viscometers reproduced the Bureau of Standards data for water on the assumption that *m* was zero. No evidence was found for believing that *m* changed in value due to the configuration of the capillary ends.

These results were discussed in relation to Dorsey's interpretation of *m*.

The viscosities of urethan solutions up to 4.5 moles/1000 g. of solution were determined at 20 and 25° for future use in standardizations. These data were given in reference to the Bureau of Standards data for water.

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[CONTRIBUTION FROM THE PEARSON CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE VISCOSITIES OF SEVERAL AQUEOUS SOLUTIONS OF ORGANIC SUBSTANCES. II

BY H. M. CHADWELL AND B. ASNES

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A study of the compressibilities and volume changes upon solution of several organic substances in water[1] has shown that with these properties, the effect of a change in the polymerization of the solvent is most apparent. The viscosities of these same solutions determined at 25°[2] showed no effect that could be ascribed to such a change in molecular state, for it was found that although the solutes had viscosities very much less than water, the aqueous solutions possessed a viscosity greater than water. If a depolymerization of the solvent was brought about by the presence of solute, the viscosity should be decreased, for the depolymerized water is supposed to possess a lower viscosity.[3] Determinations made at a lower temperature, where the water is supposedly richer in polymer, might show this effect more vividly. As a consequence, one of the viscometers (Viscometer I) whose standardization was described in the preceding paper, was used to measure this property at 10° of aqueous solutions of diethyl ether, methyl and ethyl acetates and urethan.

It has been reported[4] that aqueous solutions of urea show "negative viscosity," or viscosity less than water. Since this seems to be an exception to the general rule that aqueous solutions of non-electrolytes possess a viscosity greater than water, determinations were made at 5, 10,

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[1] Richards and Chadwell, THIS JOURNAL, **47**, 2283 (1925).

[2] Chadwell, *ibid.*, **48**, 1912 (1926).

[3] See, for instance, Tammann and Rabe, *Z. anorg. allgem. Chem.*, **168**, 73 (1927).

[4] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., **1922**, p. 179. The reference to Mutzel seems to be an error.

15, 20 and 25°. No evidence was found within the range of concentrations studied that this was an exceptional substance.

Purification of Materials

Water.—Thrice distilled water, similar to that described in the previous paper, was used for these experiments.

Methyl and Ethyl Acetates.—Samples of esters which had been purified for a previous investigation[2] were shaken with solid sodium carbonate, treated with phosphorus pentoxide, and distilled in an all glass apparatus consisting of a Richards–Barry flask and condenser. Practically all of the material boiled at the same temperature as in the first purification, 77.15° for the ethyl ester and 57.2° for the methyl acetate (760 mm.). Their densities ($d_4^{10}{}_{\text{vac.}}$) were 0.9127 and 0.9466, respectively.[5]

Urea.—Urea of the highest purity from a reliable commercial source was crystallized twice from water, the saturated solutions being prepared at 60° and the crystals separated and washed in a centrifuge. It was dried for several days in a desiccator over sodium hydroxide, dried in an oven at 50° and then kept in a desiccator over sodium hydroxide until used. The urea used in the 5, 10 and 15% solutions was purified in the same way from material of a different source.

The crystallizations were carried out rapidly and at comparatively low temperatures because of the possibility of changing urea into ammonium cyanate. Fawsitt[6] showed that such a change, caused by heating a solution at 100° for an hour, would increase the relative viscosity slightly.

Urethan.—The urethan was purified in a similar manner to urea, twice crystallized from water with centrifuging, washing and drying.

Apparatus and Technique

The apparatus used in these experiments has been described in the foregoing paper. (Viscometer I, having a capillary radius of 0.241 mm., was used throughout.) All of the precautions for accurate work were observed; for instance, the solution was moved from the lower to the higher bulb in the viscometer by an application of pressure of dry air rather than by suction.

The temperature of the thermostat was determined by a tenth degree thermometer that had been standardized by the Bureau of Standards. Variations of temperature were measured by a Beckmann thermometer. At 5° the thermostat remained constant to ±0.01°; at higher temperatures it was more constant, ±0.003°.

The solutions were made up by weight immediately preceding the experiment in all cases except the 5, 10 and 15% solutions of urea; in the latter cases a large amount of solution was prepared and used at the different temperatures.

The densities were determined in 10-cc. Ostwald pycnometers which were provided with a small bulb beyond the graduation scratch on the side arm. All densities were calculated to the vacuum standard.

Experimental Results

The experimental results are given in Tables I and II.

Table I contains the results for various solutions at approximately 10°, while Table II shows how urea solutions change with temperature. In

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[5] These values are in excellent agreement with those obtained by interpolation among the data of Young and Thomas, *J. Chem. Soc.*, **63**, 1191 (1893).

[6] Fawsitt, *Proc. Roy. Soc. Edinburgh*, **25**, 52 (1904). The equilibrium has been studied by Walker and Hambly, *J. Chem. Soc.*, **67**, 746 (1895).

Table I

The Relative Viscosities of Various Aqueous Solutions at 9.98°

%	m	t	$\rho_{\text{vac.}}$	η_r
		Methyl Acetate		
0	0	602.2	0.9997	1.000_0
3.857	.542	660.8	1.0016	1.099_4
5.768	.827	688.2	1.0025	1.146_0
9.048	1.344	731.2	1.0039	1.219_3
13.047	2.026	779.8	1.0055	1.302_4
14.417	2.275	792.6	1.0060	1.324_5
20.776	3.542	840.0	1.0080	1.406_5
23.117	4.061	849.4	1.0090	1.423_6
98.901		212.1	0.9485	0.334_1
100.000		207.4	.9466	$.326_1$
		Ethyl Acetate		
0.522	0.060	608.1	0.9998	1.009_9
2.613	.305	651.5	1.0001	1.082_3
2.845	.333	654.4	1.0002	1.087_2
3.206	.376	664.2	1.0002	1.103_5
4.804	.573	694.4	1.0005	1.154_0
6.683	.813	733.2	1.0008	1.218_9
98.216		267.6	0.9158	0.407_0
100.000		256.4	.9115	$.388_7$
		Diethyl Ether		
1.031	0.141	627.9	0.9979	1.040_8
1.408	.193	638.9	.9974	1.058_4
2.894	.402	680.8	.9951	1.125_3
5.751	.824	770.5	.9911	1.268_4
100.000		165.3	.7256	0.199_1
		Urea		
1.676	0.284	602.1	1.0044	1.004_5
4.116	.715	604.9	1.0111	1.016_0
4.162	.723	606.0	1.0113	1.018_0
8.078	1.464	614.1	1.0226	1.043_1
14.094	2.732	629.9	1.0399	1.088_1
19.488	4.031	652.8	1.0556	1.144_7
		Urethan		
2.213	0.266	630.1	1.0027	1.049_5
6.553	0.787	693.2	1.0086	1.161_4
8.812	1.085	724.5	1.0117	1.217_5
13.986	1.826	817.7	1.0187	1.383_7
25.643	3.872	996.7	1.0331	1.710_5

Table I the first column contains the percentage of solute by weight; the second, the number of moles per 1000 g. water (the molecular weights used were methyl acetate, 74.048; ethyl acetate, 88.064; ethyl ether, 74.077; urethan, 89.064; urea, 60.048); the third, the density in vacuum, and the

TABLE II

THE RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF UREA AT VARIOUS TEMPERATURES

Concentration of Solutions

Solution	A	B	C
% Urea by weight	5.00	10.00	15.00
Moles/1000 g. H_2O	0.876	1.850	2.939

	5.04°			9.98°		
No.	t	$\rho_{vac.}$	η_r	t	$\rho_{vac.}$	η_r
H_2O	698.7	1.0000	1.000_0	602.2	0.9997	1.000_0
A	701.3	1.0150	1.018_8	605.9	1.0140	1.020_6
B	709.7	1.0296	1.045_8	617.3	1.0283	1.054_4
C	726.7	1.0444	1.086_3	631.4	1.0428	1.093_8
	15.04°			20.01°		
H_2O	523.4	0.9991	1.000_0	462.3	0.9982	1.000_0
A	531.8	1.0132	1.030_4	471.0	1.0120	1.032_9
B	542.4	1.0273	1.065_6	482.0	1.0257	1.071_4
C	557.6	1.0415	1.110_6	496.4	1.0396	1.118_3

	25.07°		
	t	$\rho_{vac.}$	η_r
H_2O	410.6	0.9971	1.000_0
A	420.3	1.0106	1.037_6
B	430.4	1.0240	1.076_6
C	444.4	1.0376	1.126_4

fourth relative viscosity. The headings of the columns in Table II have the same meanings. The relative viscosity was calculated by the formula

$$\eta_r = \frac{t_s \rho_s}{t_o \rho_o}$$

Here the subscript *s* refers to the solution while *o* refers to water. The density (ρ) is that in air, obtained from the value of density in vacuum given in the table, by subtracting the weight of 1 ml. of air (0.0012).

The use of the simple formula for calculating viscosity is justified by the fact that in the preceding paper it was shown that this viscometer would reproduce the viscosities of water as accepted by the Bureau of Standards over the temperature range of 15 to 30° when the value of *m* (Formula 4, preceding paper) was taken as zero. From Dorsey's analysis of the flow of liquids through tubes, it is logical to assume that this same condition would be fulfilled for flows of smaller velocity.[7]

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[7] The absolute viscosities are not reported for the reason that the viscosities of water at 10 and 5° as calculated from the formula $\eta = 2.1851\, t \times 10^{-5}$ (obtained during the standardization of this viscometer and reported in the preceding paper) and the time of flow as given in Table II, are not in good agreement with the previously published values for water. The values are as follows, expressed in centipoises

	5.04°	9.98°
Calculated	1.524_9	1.313_9
Bingham and Jackson (B. of S.)	1.517_0	1.308_5
"International Critical Tables"	1.517_0	1.310_5

The times of flow for water are in agreement with those reported in the preceding

Discussion of Results

The relative viscosities of the urea solutions at different temperatures given in Tables I and II are plotted against moles per 1000 g. water in Fig. 1. The data are consistent except for the 5% solution at 25° which is slightly high (about 0.3%) and the 15% solution at 10° which is low (about 0.2%).

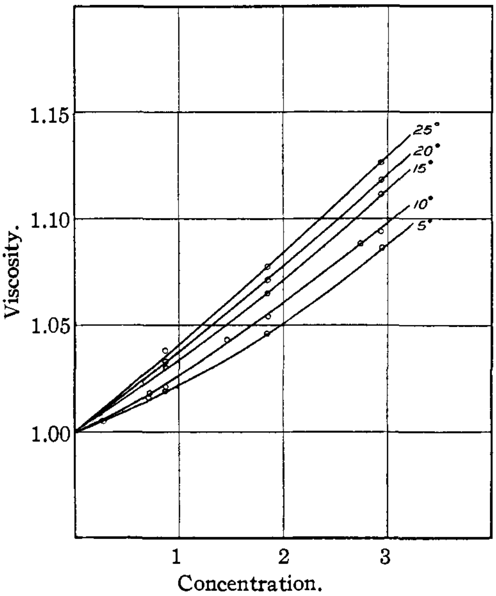

Fig. 1.—The viscosities of aqueous urea solutions at 5, 10, 15, 20 and 25°. The relative viscosities are plotted as ordinates, the concentrations expressed in moles per kg. of water as abscissa.

Rudolf[8] has reported determinations at 25° which show a minimum in the viscosity curve at a value less than that of water, but Fawsitt[9] could not verify his results using very pure urea. Ranken and Taylor[10] redetermined the viscosity of urea solutions at temperatures ranging from 8 to 45° and found that only in one solution was the viscosity less than that of water, namely, in the most dilute solution (0.03125 mole/liter) at 8°, the relative viscosity was 0.9985. This value was reported as reproducible.

paper with the exception of that for 20° (462.3 seconds instead of 461.3). Since this difference may have been caused by an accidental shifting of the viscometer in the holder, the time determined at the time of the experiments with the solutions was used in the calculations. An interval of approximately a year separated the two sets of experiments.

[8] Rudolf, *Z. physik. Chem.*, **43**, 257 (1903).

Moles/liter	0.937	0.469	0.234	0.117	0.058
η_r	1.010	1.002	.996	.993	.995

[9] Fawsitt, *Proc. Roy. Soc. Edinburgh*, **25**, 52 (1904).

Moles/liter	0.10	0.25	0.5	1.0	2.0
η_r	1.005	1.012	1.024	1.045	1.089

[10] Ranken and Taylor, *Trans. Roy. Soc. Edinburgh*, **45ii**, 397 (1906).

	Moles/liter...	0.03125	0.125	0.25	0.50	1.0
η_r	8°......	.09985	1.0012			
	15°.....			1.0085	1.0150	1.0325
	25°.....	1.0020	1.0050			
	30°.....			1.0113	1.0210	1.0443

Our results are slightly greater at 15° than those determined by Ranken and Taylor; at 20° they are in good agreement with those of Öholm;[11] at 25° they are considerably greater than those of Dunstan and Mussell,[12] up to a concentration of 2.5 moles/kg. of H_2O, and then they are smaller. The viscosities of supersaturated solutions of urea have been reported recently by Taimni.[13]

The curves in Fig. 1 include no evidence for concluding that urea solutions show "negative viscosity"[14]—viscosities lower than that of water. Certainly there is no such phenomenon as exhibited by certain salts. For example, the concentration of ammonium nitrate must be approximately 18% at 25° before the viscosity of the solution exceeds that of water. Bingham[15] has recommended the term "negative curvature" in referring to fluidity–concentration curves, to replace "negative viscosity." The terms are not synonymous, for it is evident that the fluidity curves for urea solutions would show negative curvature. The viscosities of very dilute solutions, preferably at low temperatures, were not investigated because of the necessity of a more refined method of measuring the time of flow.

The experimental results for all of the solutions are represented in Fig. 2, where the viscosity relative to water is plotted as ordinates and the moles of solute per 1000 g. of water as abscissa. There are also included the data for these solutions previously determined[16] at 25°. As would be expected, the relative positions of the curves for the various solutions are the same at 10° as at 25°, the ethyl ether solutions showing the greatest relative viscosity. The solutions of ethyl ether, ethyl and methyl acetates, and urethan have a greater relative viscosity at 10° than at 25°, while urea solutions are opposite, having a viscosity greater at 25° than at 10°. Furthermore, the viscosities of ether and ethyl acetate solutions are linear functions

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[11] Öholm, through "International Critical Tables," McGraw-Hill Book Co., Inc., 1929, Vol. V, p. 22.

Moles/liter.....	0.25	0.50	1.0	2.0	4.0	8.0
Moles/kg. H_2O..	.25	.52	1.08	2.33		
η_r..............	1.010	1.022	1.039	1.088	1.215	1.655

[12] Dunstan and Mussell, through "International Critical Tables," Ref. 11.

Wt. %..................	1.02	8.13	11.89	15.47	23.12
Moles/kg. H_2O............	0.18	1.46	2.24	3.08	
η_r........................	1.005	1.054	1.087	1.162	1.221

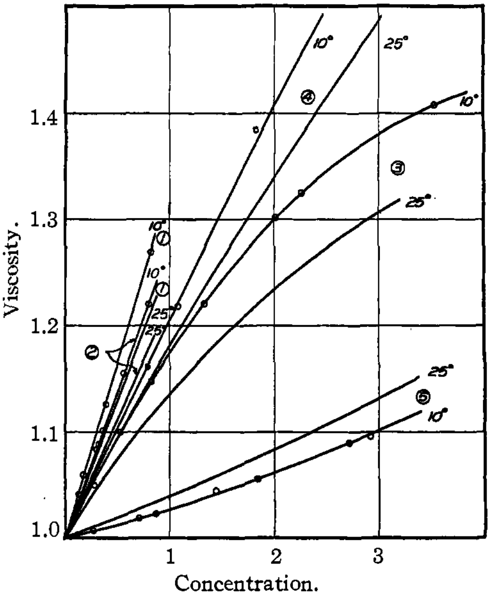
[13] Taimni, *J. Phys. Chem.*, **33**, 52 (1929).

[14] See Rabinovich, THIS JOURNAL, **44**, 954 (1922); Taylor and Moore, *Proc. Roy. Soc. Edinburgh*, **28**, 461 (1907); Taylor, *ibid.*, **25**, 227 (1904). Wagner and Mühlenbein, *Z. physik. Chem.*, **46**, 872 (1903), have shown that negative viscosity is exhibited by certain organic substances, for instance, cyanobenzene in alcohol.

[15] Bingham, Ref. 4, p. 178.

[16] Chadwell, Ref. 2. The values of relative viscosity were calculated from the value of η_1 given on p. 1918, for the viscometer was very similar to that used in the present investigation.

of the concentration expressed in the units chosen, while methyl acetate produces a convex curve and urea a concave. If the liquids were soluble in water in all proportions, the resulting curves would all show maxima, for the viscosities of the pure liquids are all very much smaller than that of water.[17] Urea, on the other hand, is a solid, and as the concentration increases, the viscosity of the solute has a more pronounced effect.



1, Ether; 2, ethyl acetate; 3, methyl acetate; 4, urethan; 5, urea.

Fig. 2.—The viscosities of aqueous solutions of ethyl ether, ethyl acetate, methyl acetate, urethan and urea at 10 and 25°. The relative viscosities are plotted as ordinates, the concentrations expressed in moles per kg. of water as abscissas.

In discussing the data determined at 25° it was shown that not only was there a connection between the volume of the dissolved molecules, but that there was a very close connection between the change in viscosity and the change in volume, calculated as the contraction in ml. which took place upon the formation of one liter of solution. When a large contraction took place, the viscosity of the solution would be comparatively great. A similar hypothesis has been developed more extensively by McLeod,[18] who postulated that the viscosity of a mixture as well as of a pure liquid is a function of the free space; that the increase in viscosity upon adding a solute is caused principally by the contraction, which has an effect similar to cooling the material. It is interesting, therefore, to see how this property of changing volume on solution changes with temperature. The necessary calculations could be made from the density data. Such data are summarized in Table III and shown graphically in Fig. 3.

The contractions given in the above table were calculated from the densities recorded in Table I for all of the liquids. Those for urea solutions

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[17] Solutions of dioxane and water, soluble in all proportions, produce a maximum. Herz and Lorentz, *Z. physik. Chem.*, **A140**, 408 (1929).

[18] McLeod, *Trans. Faraday Soc.*, **19**, 6 (1923); **19**, 17 (1923); **20**, 348 (1924); **21**, 151 (1925). A full discussion and several suggestions are made in Hatschek's "Viscosity of Liquids," D. Van Nostrand Company, New York, 1928.

TABLE III

CONTRACTIONS TAKING PLACE UPON SOLUTION. CHANGE IN VOLUME (ML.) UPON FORMATION OF ONE LITER OF SOLUTION

Moles/kg. H_2O	0.2	0.4	0.6	0.8	1.0	1.5	2.0	2.5
			Ethyl Ether in Water					
25°	3.0	6.5	10.1	14.0				
10°	3.0	6.3	9.4	12.5				
			Ethyl Acetate in Water					
25°	1.9	3.7	5.5	7.2				
10°	1.9	3.7	5.6	7.4				
			Methyl Acetate in Water					
25° 10°	1.6	3.1	4.5	6.8	7.1	10.2	13.1	15.5
			Urea in Water					
25°		(0.6)			1.3	1.8	2.1	2.5
20°		(.8)			1.7	2.2	2.8	3.2
15°		(.9)			2.0	2.8	3.4	4.0
10°		(1.0)			2.2	3.1	3.8	4.6
5°		(1.3)			3.0	4.0	4.9	5.6

are the volume changes for solid urea dissolved in water. The densities of solid urea were found by interpolation from the data of Dewar given in the "International Critical Tables."[19] The contraction for each of the solutions was calculated and plotted, and the above values found by interpolation.

The volume changes for urethan solutions were also calculated, for 10, 20 and 25°, making use of the data in the preceding paper, and Block's[20] data for both solid urethan and the supercooled liquid urethan. If the former (for the solid) are used, an expansion results; if the latter, a contraction which decreases with an increase in temperature.[21] The volume

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[19] "International Critical Tables," Vol. III, p. 45. The data used were

t, °C	5	10	15	20	25
d_4^t	1.3215	1.3204	1.3194	1.3184	1.3173

The slopes of the curves seem to show that the specific volumes accepted for the urea are too large, that the calculated contractions are consequently too large. No data are available for estimating the specific volume of liquid urea at these temperatures.

[20] Block, *Z. physik. Chem.*, **78**, 397 (1912).

[21] Contraction on formation of urethan solutions (interpolated data)

Moles/kg. H_2O	10°	20°	25°
1.0	4.1 (−0.1)	3.6 (−0.7)	3.3 (−1.1)
2.0	7.2 (− .5)	6.3 (−1.7)	5.9 (−2.3)
3.0	9.5 (−1.5)	8.3 (−3.0)	7.7 (−3.8)

The figures given in parentheses are expansions calculated from the densities of solid urethan; the others are contractions as calculated from supercooled liquid. The data used for the volume of 1 g. of urethan, either liquid or solid, are as follows (interpolated or extrapolated)

	10°	20°	25°
Liquid	0.9149	0.9230	0.9271
Solid	.8641	.8704	.8736

changes upon solution of urethan at 20° have been studied by Richards and Palitzsch.[22] They have pointed out that the expansion upon the solution of solid is probably caused by a large expansion due to the breaking up of the crystalline material counteracted by a contraction caused by the change in polymerized water. Our conclusion drawn from this interpolation is that the specific volume of molten urethan should be used to calculate the contraction, but its value is so uncertain, because of the large extrapolation, that little confidence can be placed in the results; consequently they are not plotted in Fig. 3.

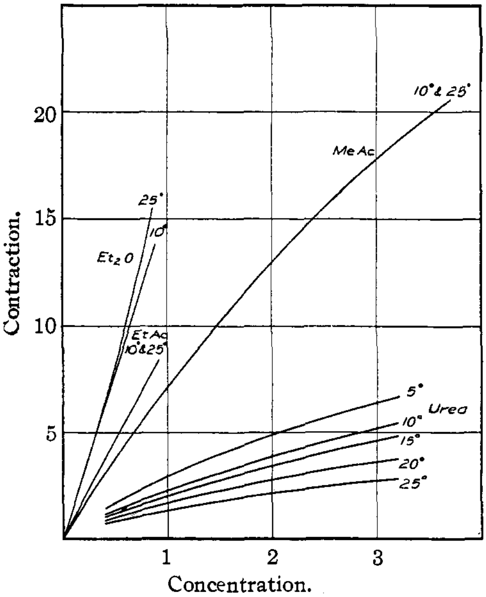

Fig. 3.—The contraction upon formation of aqueous solutions of ethyl ether, ethyl acetate and methyl acetate at 10 and 25°, and of urea at temperatures between 5 and 25°. The decreases in volume (ml.) upon formation of 1 liter of solution are plotted as ordinates, the concentrations expressed in moles per kg. of water as abscissas.

That the volume changes upon solution of the esters are the same at 10 and 25°, within the experimental error, is a surprise. One would expect a greater contraction at the lower temperature if it is assumed that the ester causes a depolymerization of the water, for water must be more highly polymerized at the lower temperature. More accurate density determinations probably would show slight differences.

The changes in volume on formation of solutions are interesting, irrespective of their bearing upon the question of viscosity. The method of representing concentration as moles of solute per 1000 g. of water is so chosen as to represent the effect of relative numbers of molecules of different solutes upon the same quantity (possibly different number of molecules) of water. The contraction is the greatest for ether, and successively less for ethyl acetate, methyl acetate and urea. This confirms the hypothesis that[1] the cohesive forces and internal pressures existing in the liquids play a large part in determining the volume of the systems. The forces under which the molecules of the various solutes exist in solutions of equivalent concentrations are probably about the same, and yet those forces are very different in

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[22] Richards and Palitzsch, THIS JOURNAL, 41, 60 (1919). Also Richards and Chadwell, *ibid.*, 47, 2283 (1925).

the pure liquids. When the molecular forces existing in a liquid are weak (small internal pressure), the liquid is light and volatile and possesses a large coefficient of compressibility. If such a liquid is distributed in a second liquid of greater internal forces, it would be exepcted that the volume would not be so large and that the extent to which a contraction took place would depend upon the difference in magnitude of the internal pressures. In the particular cases in question, the magnitudes of the contraction are in the same order as the coefficients of compressibility. The average compressibilities over the pressure range of 100–300 megabars at 20° are: ether 130, ethyl acetate 90 and methyl acetate 88.[1,23]

It is to be noticed that the viscosity and contraction curves in Figs. 2 and 3 for the different solutes are in the same relative positions for either 10 or 25°; but this correlation does not hold when a single solute is considered, showing that the change in volume is not the only determining factor of the viscosity. The urea solutions, for instance, show the greater relative viscosity at the higher temperature, while the contractions are greater at the lower temperature. This can be explained by postulating that the decrease in viscosity due to the depolymerization of the water, taking place to a greater extent at the lower temperatures, more than balances the tendency to increase the viscosity caused by the contraction. Such a counterbalancing of effects is not apparent in the positions of the curves for other solutes. In support of this hypothesis it should be pointed out that the aqueous urea solutions are more nearly ideal than the others: the internal pressures of the pure substances are very nearly alike, their mutual solubility is great, and the formation of solutions is accompanied by a small volume change.

Viscosity curves of binary liquid mixtures which show maxima have commonly been explained by assuming compound formation. If this is the real explanation, solvation is a very general phenomenon—more general than other properties of solutions would lead us to believe. The relative viscosity of all of these solutions (except urea) diminishes with an increase in temperature. In the case of aqueous solutions of salts[24] this is found to occur only in those solutions which contain highly hydrated materials, and is supposed to be due to the thermal decomposition of the hydrates.

In the cases of our particular solutes, freezing point measurements[25] have been made and the solutions found to be normal. Kendall and Harrison have interpreted the normal depressions caused by esters to mean that

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[23] Richards, Stull, Mathews and Speyers, THIS JOURNAL, **34**, 971 (1912).

[24] Rabinovich, *ibid.*, **44**, 956 (1922). Aqueous salt solutions show no correlation between negative viscosity and contraction.

[25] "International Critical Tables," Vol. IV, p. 262; Kendall and Harrison, *Trans. Faraday Soc.*, **24**, 588 (1928).

hydrates are formed which counterbalance negative deviations from Raoult's law arising from the fact that the solutions are not perfect.

The development of our knowledge of liquids from the electrical standpoint is only beginning, and yet enough progress has resulted to show that such a property as viscosity may well be considered from this point of view. Jones and Dole,[26] for instance, have shown that the viscosity of dilute salt solutions can best be represented by a formula which takes into account the effect of interionic forces. For binary mixtures of different liquids the shape of the viscosity–concentration curve depends upon the electrical nature of the molecules. If both of the components are non-polar, or one is dipolar (in the sense used by Debye) the curve is concave, but if both components are dipolar, the curve is convex.[27] Our liquid mixtures are composed of dipolar molecules, their electric moments[28] in the liquid state being: water 1.8, ether 1.24, methyl acetate 1.67 and ethyl acetate 1.74 (all $\times$ 10^{18}). These polar molecules in solution would be orientated[29] by the electrostatic field produced by other molecules into more or less orderly arrangements which might very well be manifested by an increase in the relative viscosity, as well as a contraction in volume. Furthermore, an increase in temperature reduces this orientation and the viscosity would become less, as is shown by the experimental data. A quantitative analysis of this contributing effect must await more extensive determinations of dielectric constants and the development of the theory of viscosity of liquids.

We wish to express our gratitude to the Elizabeth Thompson Science Fund for financial aid in this investigation.

Summary

The viscosities of aqueous solutions were determined at 10° of diethyl ether, methyl acetate, ethyl acetate, urethan and urea. In addition, measurements were made on urea solutions at 5, 15, 20 and 25°.

The contractions on solution of these substances were calculated from the densities, and the connection between these two properties was discussed.

Aqueous solutions of urea did not possess viscosities less than water at any of the concentrations studied, although the curvature of the viscosity–concentration curve was found to be positive. These solutions do not seem to be exceptions to the rule that aqueous solutions of non-electrolytes pos-

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[26] Jones and Dole, THIS JOURNAL, **51**, 2950 (1929); Falkenhagen and Dole, *Physik. Z.*, **30**, 611 (1929).

[27] Shown empirically by Errera, *Z. physik. Chem.*, **140A**, 273 (1929).

[28] Williams, *Chem. Rev.*, **6**, 595 (1929). The moments of urea and urethan have not been determined, so far as we know.

[29] See Langmuir, *ibid.*, **6**, 459 (1929), and Smyth, *ibid.*, **6**, 560 (1929).

sess a viscosity greater than that of water, irrespective of the viscosity of the solute.

The effect of depolymerization of water upon the property of viscosity was no more apparent at 10° than at 25°, except possibly in the case of the urea solutions.

The results were discussed from the point of view of compound formation and orientation of polar molecules.

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THE TITRATION CONSTANTS OF MULTIVALENT SUBSTANCES

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It has long been known that the titration curve of a multivalent acid resembles that of a mixture of monovalent acids. Based upon the apparent identity of these two classes of titration curves, as judged by experiment, H. S. Simms[1] has developed equations which correlate the apparent with the true dissociation constants of a multivalent acid. The equations are given for a divalent and trivalent acid, and the same considerations readily yield the equations for any number of valencies.

Apparently without knowledge of Simms' contribution, H. H. Weber[2] has recently treated this problem in a very similar manner. The equations which he obtains are more restricted and not as generally applicable as those developed by Simms, since he introduced the further assumption that the titration curve of the multivalent acid resembles that of a single monovalent acid. In discussing these two papers in our seminar, it became apparent that the assumption of resemblance is unnecessary, for the general equations of Simms may be obtained by a purely mathematical transformation of the classical dissociation equations given by the mass law.[3] This mathematical transformation yields no equations other than those developed by Simms, but in that the same relations are obtained without any assumption, the behavior of multivalent substances as described by the classical equations is vested with a slightly altered interpretation which rendered it desirable to communicate the calculations.

The classical dissociation constants for the n steps of dissociation of a multivalent acid may be written

[1] H. S. Simms, THIS JOURNAL, **48**, 1239 (1926).

[2] H. H. Weber, *Biochem. Z.*, **189**, 381 (1927).

[3] In a previous seminar Professor Scatchard was able to derive Weber's equations on the assumption that the probability of dissociation was the same for each group, and independent of the number of groups dissociated.