Solution Properties of Urea–Alcohol–Water Mixtures

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Viscosities and densities of urea in alcohol or water–alcohol mixtures were measured for the temperature range from about 5° to 65°C. The viscosity of urea–alcohol mixtures was an exponential function of $1/T$, and the viscosity of urea–water–alcohol mixtures was an exponential function of $1/T^3$. A correlation for viscosity as a function of urea concentration and temperature for water–alcohol mixtures was found. The densities of urea–water–alcohol mixtures were linearly related to temperature, except for the case of pure water. A correlation for density as a function of urea concentration and temperature for water–alcohol mixtures was found. Activation energies of shear flow for urea–alcohol mixtures were estimated from the isobaric temperature coefficient of viscosity and compared reasonably with literature values. In addition, thermal expansion coefficients were calculated and compared with literature values.

Today, there are few sections of the chemical industry that do not, at some stage, utilize crystallization as a method of production, purification, or recovery of solid material. Many of the processes concerned with nucleation and crystallization of urea from solutions are not well understood. The present survey has revealed that the physical properties of urea solutions, which are closely related to the crystallization process, have not been systematically measured. No general correlation of viscosity–temperature or density–temperature for urea solutions has been reported.

The present work attempts to develop the empirical models for the viscosity and the density of urea solutions as a function of temperature and urea concentration and to estimate the activation energies of shear flow for urea solutions from the isobaric temperature coefficient of viscosity. It was also the objective of this study to determine the thermal expansion coefficients for this system.

Experimental

The Cannon-Fenske routine-type viscometers (size Numbers 25 and 75), manufactured by Cannon Instrument Co. were used for the experimental determination of viscosities of urea–water–alcohol mixtures at different concentrations and temperatures. The No. 25 viscometer was calibrated with the two-constant equation by Shah (*9*):

$$\eta = D\rho t' - E\rho/t' \qquad (1)$$

The No. 75 viscometer was calibrated by the manufacturer. A precision isothermal bath was used to control the temperature within ±0.01°C for all viscosity and density measurements. The time of flow of the solution in the viscometer was accurately determined by a timer to a tenth of a second. At each temperature a set of three time readings was taken. The maximum difference in the viscosity values determined from these readings at each temperature was less than 0.1%. From the time of flow and the density of the solution at the desired temperature, the viscosity was calculated. To minimize solvent evaporation, the top of the arm connected to the bigger bulb of the viscometer was covered by a piece of Scotch tape with a small hole in it to allow pressure equilibrium in the viscometer during the viscosity measurement. Under supersaturated conditions, special attention was given to ensure that there was no crystallization in the solution during the viscosity measurement, since even small amounts of crystals caused appreciable differences in flow time.

The densities of the solutions which were needed for determining the viscosities were measured by a densitometer together with a cathetometer. The densitometer was constructed from a 10-ml precision buret by connecting a 25-ml spherical glass bulb at the lower end and a glass stopper at the top, to prevent vapor loss during the measurement. Absolute ethanol was used to calibrate the volume of the densitometer. Knowing the weight and the densities of absolute alcohol at various temperatures, the volume of the densitometer was calibrated with the height of the cathetometer by changing the bath temperature from about 3° to 68°C.

To measure the density of the solution, 25 ml of the test solution was accurately measured by a pipet transferred to the densitometer and immediately covered by the glass stopper. The densitometer was then immersed in the constant temperature bath set at a predetermined temperature. Another portion of 25 ml of the test solution was accurately transferred to a weighing bottle by means of the same pipet. The weighing bottle was immediately sealed and weighed in an

Table I. Correlation Constants of Viscosity vs. Temperature in Urea—Alcohol Solutions
$\ln \eta = C_1 + C_2/T$

Solvents[a]	Urea concn[b] (7)	$-C_1$	$C_2 \times 10^{-3}$	Std % error
1	0.000	4.864	1.270	0.3
	16.827	5.165	1.491	0.4
	21.607	5.322	1.569	0.7
	27.743	5.214	1.573	0.7
2	0.000	5.074	1.423	0.6
	8.602	5.262	1.550	0.2
	10.935	5.296	1.580	0.1
	13.902	5.389	1.632	0.1
3	0.000	5.647	1.710	0.6
	3.971	5.563	1.714	1.6
	5.099	5.756	1.783	0.6
	6.547	5.843	1.827	0.1
4	0.000	5.487	1.613	0.5
	5.772	5.608	1.694	0.2
	7.486	5.692	1.739	0.0
	9.708	5.705	1.756	0.1
5	0.000	8.156	2.652	0.3
	2.177	8.021	2.626	0.6
	2.768	8.000	2.623	0.9
	3.518	7.859	2.584	0.5
6	0.000	6.575	2.074	0.5
	2.672	6.536	2.082	0.3
	3.466	6.592	2.104	0.3
	4.495	6.581	2.111	0.1

[a] 1. methanol; 2. 50% methanol and 50% ethanol; 3. ethanol; 4. 50% methanol and 50% 2-propanol; 5. 2-propanol; 6. 50% ethanol and 50% 2-propanol. [b] Grams of urea per 100 g of solvent.

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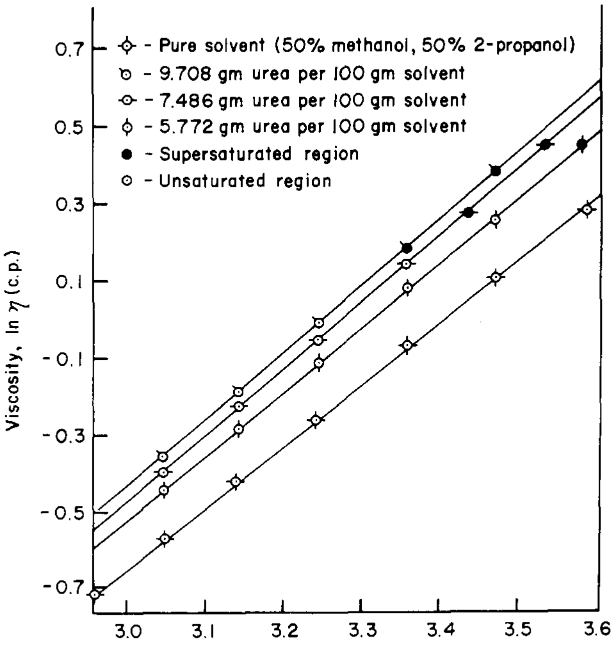

Figure 1. Viscosity of urea in 50% methanol-50% 2-propanol solution vs. temperature

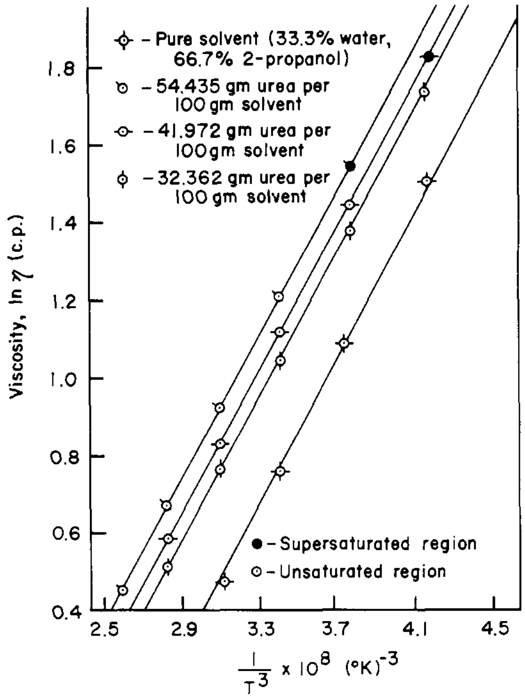

Figure 2. Viscosity of urea in solution of ⅓ water-⅔ 2-propanol vs. temperature

analytical balance reading to 10^{-4} g. The accuracy of measuring 25 ml of solution for each of the volume and weight portions was verified by determining the density of methanol at 15.28° ± 0.01°C. Five different measurements gave results of 0.7958, 0.7950, 0.7948, 0.7953, and 0.7951 g/ml, respectively. This compares with a literature value of 0.7957 from the data of Klason and Norline (*5*).

To determine the solvent lost during the solution transfer (average 30 sec), the weighing bottle was uncovered in the balance, and the weight lost in 30 sec was added to the original weight of the solution. This weight loss was actually very small, amounting to 0.0036 g for ethanol at 25°C, which corresponds to a density decrease of 0.0001 g/ml or 0.01%. The height of the solution in the densitometer tube was read with the cathetometer to the order of ±0.006 cm. The corresponding volume of the solution was obtained using a calibration curve as reported by Lee (*6*). From the weight and volume of the solution at the test temperature, the density was calculated. As with the viscosity measurements, three sets of density measurements were made at each temperature. Only the average value was reported as the maximum difference was less than 0.1%. For example, the measured values for ethanol at 15.15° ± 0.01°C were 0.7932, 0.7942, and 0.7939 g/ml for a maximum deviation from the average of 0.08%.

Materials

Certified ACS grade urea with a minimum purity of 99.978% from Matheson Coleman & Bell was used in all experiments. Recrystallized urea from doubly distilled water showed no significant effect in experimental results. Certified ACS grade methanol and 2-propanol from Fisher Chemical Co., absolute ethanol from Commercial Solvent Corp., and double distilled water were used as solvents.

Discussion

Viscosity. The viscosity data of urea in twelve different solvent mixtures were measured from about 5° to 65°C (*6*). The original experimental data are available from the ACS Microfilm Depository Service. As stated before, the average of three data points is reported to reduce the volume of data. Each solvent consisted of three different urea concentrations corresponding to the saturation concentrations at 10°, 20°, and 30°C, respectively, as reported by Lee and Lahti (*7*). The experimental viscosity data were fitted by means of least squares by using a digital computer. For urea in alcohol mixtures, the best correlation was of the form:

$$\ln \eta = C_1 + C_2/T \qquad (2)$$

This corresponds to Andrade's simple equation (*1*). The correlation constants as well as the standard deviations are summarized in Table I. Typical examples showing the correlation with experimental points are presented in Figures 1 and 2.

Table II. Comparison of Viscosity Data Between This Study and Literature Values

Liquids	Temp,°C	η_1,[a] cP	η_2,[b] cP	% error
Ethanol	10	1.466	1.479	0.9
	20	1.200	1.203	0.2
	30	1.003	0.993	−1.0
	40	0.834	0.829	−0.6
	50	0.702	0.700	−0.3
	60	0.592	0.598	1.0
Methanol	15	0.623	0.633	1.6
	20	0.597	0.587	−1.7
	25	0.547	0.546	−0.2
	30	0.510	0.509	−0.2
	40	0.456	0.445	−2.5
	50	0.403	0.393	−2.5

[a] Values were taken from "Handbook of Chemistry and Physics", 47th ed., Chemical Rubber Publ., Cleveland, Ohio, 1967. [b] Values were obtained from the viscosity curves of this study.

Viscosity data of pure ethanol and methanol measured in this study are compared favorably with literature values as

Alcohol Mixtures

Solvents	Urea concn[a] (7)	E_p, cal/g-mol
Methanol	0.000	2925
	16.827	3434
	21.607	3613
	27.743	3623
50% Methanol and 50% ethanol	0.000	3277
	8.602	3570
	10.935	3639
	13.902	3758
Ethanol	0.000	3938
	3.971	3947
	5.099	4106
	6.547	4208
50% Methanol and 50% 2-propanol	0.000	3715
	5.772	3901
	7.486	4005
	9.708	4044
2-Propanol	0.000	6108
	2.177	6048
	2.768	6041
	3.518	5951
50% Ethanol and 50% 2-propanol	0.000	4776
	2.672	4795
	3.466	4846
	4.495	4862

[a] Grams of urea per 100 g of solvent.

shown in Table II. The standard deviation is about 0.7% for ethanol and 1.7% for methanol.

Collins (*2*) found that the determination of the activation energy of the Eyring viscosity, from isobaric temperature coefficient of the transport property, was inconsistent with the assumed mechanism of the process. However, the following relation of isobaric temperature coefficient of viscosity is ordinarily used and is reasonably precise for calculating the activation energy of liquid fluid flow:

$$\left(\frac{\partial \ln \eta}{\partial T}\right)_p = -\frac{E_p}{RT^2} \qquad (3)$$

The calculated values are given in Table III. For pure methanol and ethanol, the calculated values of E_p compare favorably with literature values (*4*) with deviations of 7 and 3%, respectively. Therefore, estimated values of E_p for urea-alcohol solutions appear reasonable.

For solutions of urea in alcohol-water mixtures, viscosity and temperature relationships followed Litovitz's expression (*8*),

$$\ln \eta = C_3 + a/RT^3 \qquad (4)$$

probably due to the strong hydrogen bonding effect in the solution. The values of the above constants and standard deviations are presented in Table IV. The activation energy of fluid flow (E_p) which changes with temperature, can be evaluated by dividing "a" by the value of T^2. Viscosity data of water obtained from this study compared favorably with Gingham and White's values (*3*). This indicates that the experimental procedures used in this study were reliable for determining the viscosity of urea-water-alcohol mixtures.

A generalized correlation for viscosity as a function of urea concentration and temperature was developed as

$$\ln \eta = C_5' + C_6'S + (C_7' + C_8'S)/T \qquad (5)$$

Temperature in Urea—Alcohol—Water Solutions

$\ln \eta = C_3 + \dfrac{a}{RT^3}$

Solvents[a]	Urea concn[b] (7)	$-C_3$	$a \times 10^{-8}$	Std % error
1	0.000	2.383	1.931	0.8
	38.168	1.971	1.873	0.3
	49.009	1.894	1.881	0.3
	62.929	1.826	1.899	0.2
2	0.000	2.769	2.164	1.5
	65.628	1.857	1.687	0.6
	82.599	1.745	1.666	0.5
	103.959	1.654	1.666	0.1
3	0.000	2.334	1.706	0.7
	59.383	1.827	1.593	0.3
	75.490	1.723	1.589	0.3
	95.967	1.590	1.570	0.3
4	0.000	2.601	2.272	0.3
	32.362	2.097	2.126	0.4
	41.972	2.002	2.106	0.2
	54.435	1.914	2.109	0.1
5	0.000	2.959	2.407	3.7
	64.975	1.932	1.821	0.3
	81.777	1.778	1.759	0.9
	102.925	1.706	1.785	0.2
6	0.000	2.382	1.407	0.2
	85.884	1.673	1.321	0.5
	107.018	1.570	1.331	0.2
	133.353	1.501	1.378	0.2

[a] 1. 33.3% water and 66.7% ethanol; 2. 66.7% water and 33.3% ethanol; 3. 50% water and 50% methanol; 4. 33.3% water and 66.7% 2-propanol; 5. 66.7% water and 33.3% 2-propanol; 6. water. [b] Grams of urea per 100 g of solvent.

Table V. Generalized Viscosity Correlations for Urea—Alcohol Solutions

$\ln \eta = C_5' + C_6'S + (C_7' + C_8'S)/T^a$

Solvents[b]	C_5'	$C_6' \times 10^2$	$C_7' \times 10^{-3}$	$C_8' \times 10^{-1}$	Std % error
1	−4.857	−2.033	1.268	1.365	0.86
2	−5.045	−2.429	1.414	1.556	0.19
3	−5.167	−10.64	1.541	4.472	0.93
4	−5.487	−2.374	1.612	1.536	0.83
5	−8.309	+12.38	2.611	0.000	5.06
6	−6.488	−2.295	2.044	1.546	0.35

[a] S is the solubility of urea in solvent (g of urea per 100 g of solvent). [b] 1. methanol; 2. 50% methanol and 50% ethanol; 3. ethanol; 4. 50% methanol and 50% 2-propanol; 5. 2-propanol; 6. 50% ethanol and 50% 2-propanol.

Table VI. Generalized Viscosity Correlations for Urea—Alcohol—Water Solutions

$\ln \eta = C_9 + C_{10}S + C_{11}/T^{3a}$

Solvents[b]	C_9'	$C_{10}' \times 10^3$	$C_{11}' \times 10^{-7}$	Std % error
1	−1.971	3.583	5.833	3.00
2	−2.188	5.812	8.181	1.47
3	−2.358	8.232	9.178	0.90
4	−2.212	6.479	6.877	1.42
5	−2.194	5.253	7.265	1.31
6	−2.292	5.848	7.766	2.15

[a] S is the solubility of urea in solvent (g of urea per 100 g of solvent). [b] 1. water; 2. 33.3% water and 66.7% ethanol; 3. 33.3% water and 66.7% 2-propanol; 4. 50% water and 50% methanol; 5. 66.7% water and 33.3% ethanol; 6. 66.7% water and 33.3% 2-propanol.

for urea-alcohol solutions or

$$\ln \eta = C_9 + C_{10}S + C_{11}/T^3 \qquad (6)$$

for urea-alcohol-water solutions. The constants are tabulated in Tables V and VI for the various solvents. The viscosity of urea alcohol-water mixtures was predictable by using a linear combination of the solvent mole fractions times the urea-pure solvent viscosity of the form

$$\eta_{\text{mix}} = y_1\eta_1 + y_2\eta_2 \qquad (7)$$

Density. The densities of urea-water-alcohol mixtures were determined for temperatures from about 5° to 65°C by using the method mentioned earlier. A least-squares computer analysis of the experimental data indicated that the best correlation between density and temperature was of the form

$$\rho = A_1 + A_2t \qquad (8)$$

with an average 0.03% standard deviation, except for pure water which exhibited completely different behavior. This can probably be attributed to the strong hydrogen-bonding effect among the water molecules. To generalize the density and temperature relationship, attempts were made to find the correlation between the intersection constant (A_1) of the density curves and the concentrations of urea for the related solutions. The best correlation obtained was of the form

$$\rho = C_5 + C_6S + C_7S^2 + C_8t \qquad (9)$$

Table VII. Generalized Density Correlations for Urea–Water–Alcohol Mixtures
$\rho = C_5 + C_6S + C_7S^2 + C_8t$[a]

Solvents[b]	$C_5 \times 10^1$	$C_6 \times 10^3$	$C_7 \times 10^5$	$C_8 \times 10^4$	Std % error
1	0.064	3.988	−6.3	−8.465	0.04
2	8.090	3.955	−2.2	−8.925	0.06
3	8.013	3.536	−6.0	−8.548	0.05
4	8.977	2.903	−1.3	−8.143	0.07
5	9.664	2.281	−0.7	−6.935	0.12
6	9.042	2.771	−1.1	−8.016	0.09
7	9.687	2.378	−0.9	−6.618	0.07
8	9.410	2.409	−0.8	−6.981	0.06
9	8.036	3.325	−11.4	−8.493	0.08
10	8.038	3.932	−1.9	−8.655	0.05
11	8.079	4.150	−4.4	−8.749	0.04

[a] S is the solubility of urea in solvent (g of urea per 100 g of solvent), and t is temperature, °C. [b] 1. ethanol; 2. methanol; 3. 2-propanol; 4. 33.3% water and 66.7% 2-propanol; 5. 66.7% water and 33.3% 2-propanol; 6. 33.3% water and 66.7% ethanol; 7. 66.7% water and 33.3% ethanol; 8. 50% water and 50% methanol; 9. 50% ethanol and 50% 2-propanol; 10. 50% methanol and 50% 2-propanol; 11. 50% methanol and 50% ethanol.

The constants C_5, C_6, C_7, and C_8, as well as the standard deviation, are tabulated in Table VII. Typical examples are shown in Figures 3 and 4. The density data of urea-alcohol-water mixtures have not been reported in the literature, so that a comparison between the values obtained in this study and those reported in the literature can only be made for the pure solvents. As mentioned earlier, the densities of methanol are consistent with those of Klason and Norline (*5*). For any compositon of urea in alcohol-water mixtures, the density can also be estimated from the mole fraction linear combination of those of the pure components.

Thermal expansion coefficient. The thermal expansion coefficient of material at constant pressure has been defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial \ln V}{\partial T}\right)_P \qquad (10)$$

In the study of density, the liquid volumes of various urea-alcohol-water mixtures were measured at different temperatures under constant pressure by using the densitometer (*6*). For determining the thermal expansion coefficient, the logarithm of the volume data was plotted against the absolute temperatures, and the correlation was a linear function with little deviation. The values of the thermal expansion coeffi-

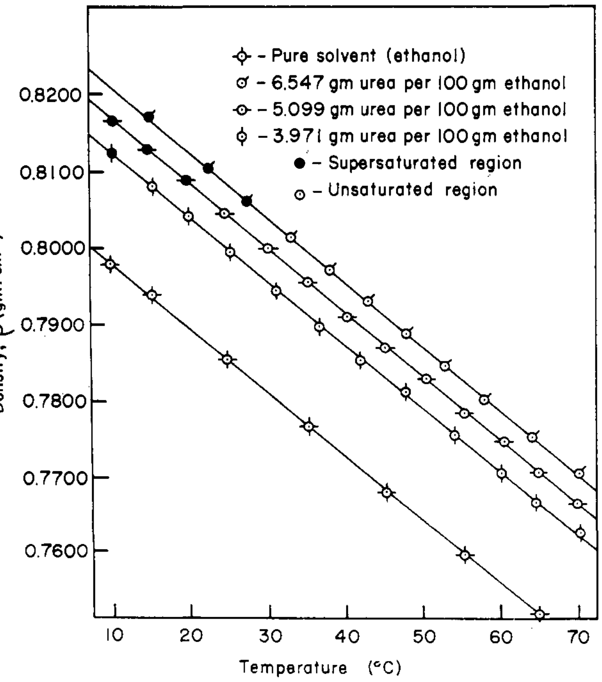

Figure 3. Density of urea–ethanol solutions vs. temperature

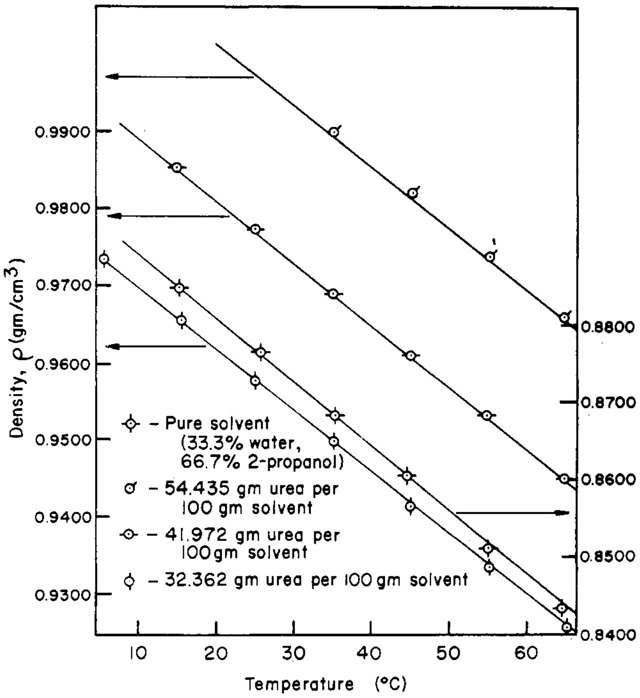

Figure 4. Density of urea in solution of ⅓ water–⅔ 2-propanol vs. temperature

Table VIII. Calculated Physical Properties of Urea—Water—Alcohol Mixtures

Solvents[a]	Urea concn[b] (7)	$\alpha \times 10^3$
1	0.000	1.127
	3.971	1.060
	5.099	1.066
	6.547	1.081
2	0.000	1.176
	16.827	1.070
	21.607	1.044
	27.743	1.024
3	0.000	1.100
	2.177	1.096
	2.768	1.092
	3.518	1.116
4	0.000	0.321
	85.884	0.552
	107.018	0.563
	133.353	0.570
5	0.000	0.967
	32.362	0.855
	41.972	0.835
	54.435	0.827
6	0.000	0.7515
	64.975	0.6456
	81.777	0.6401
	102.925	0.6407
7	0.000	0.9504
	38.168	0.8076
	49.009	0.8017
	62.929	0.7745
8	0.000	0.6736
	65.628	0.6218
	82.599	0.6234
	103.959	0.6178
9	0.000	0.7514
	59.383	0.6750
	75.490	0.6801
	95.967	0.6448
10	0.000	1.090
	2.672	1.074
	3.466	1.077
	4.495	1.116
11	0.000	1.121
	5.772	1.095
	7.486	1.088
	9.708	1.083
12	0.000	1.127
	8.602	1.089
	10.935	1.072
	13.902	1.060

[a] 1. ethanol; 2. methanol; 3. 2-propanol; 4. water; 5. 33.3% water and 66.7% 2-propanol; 6. 66.7% water and 33.3% 2-propanol; 7. 33.3% water and 66.7% ethanol; 8. 66.7% water and 33.3% ethanol; 9. 50% water and 50% methanol; 10. 50% ethanol and 50% 2-propanol; 11. 50% 2-propanol and 50% methanol; 12. 50% ethanol and 50% methanol. [b] Grams of urea per 100 g of solvent.

cient were calculated from the slopes of these curves by the computer least-squares analysis and are presented in Table VIII. The thermal expansion coefficient generally decreases with increasing concentration of urea in the same solvent mixture. This is probably because the urea molecules in the solution hinder the mobility of solvent molecules which otherwise would have higher collision rate among themselves and occupy a larger volume under the same increment of thermal agitation.

Nomenclature

a = activation energy constant (cal/g-mol) (K)^2
A_1, A_2 = constants in Equation 8
C_1, C_2 = constants in Equation 2
C_3 = constant in Equation 4
C_5, C_6, C_7, C_8 = constants in Equation 9
C_5', C_6', C_7', C_8' = constants in Equation 5
C_9, C_{10}, C_{11} = constants in Equation 6
D = constant in Equation 1
E = constant in Equation 1
E_p = activation energy of shear flow, cal/g-mol
p = pressure, atm
R = gas constant, 1.987 cal/(K) (g-mol)
S = concentration, g of urea/100 g of solvent
T = absolute temperature, K
t = temperature, °C
t' = time, sec
V = volume of solution, ml
y_1, y_2 = mole fractions in Equation 7

Greek Letters

η = viscosity, cP
η_{mix} = viscosity of solution mixture
η_1, η_2 = viscosities of urea-pure solvent in Equation 7, cP
ρ = density, g/ml
α = thermal expansion coefficient

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Supplementary material available: The original experimental data (33 pages). Ordering information is given on any current masthead page.