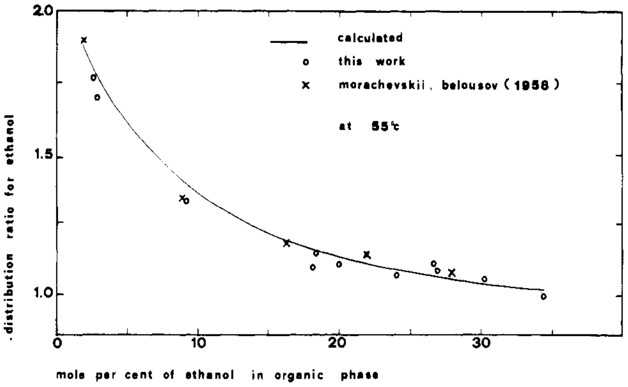

Figure 5. Distribution ratio for ethanol at 55 °C.

tions from Raoult's law. In other words, they cannot be used to predict vapor–liquid equilibrium as discussed by Yee et al. (*12*); they are only useful in describing liquid–liquid equilibrium. In Figure 5 our experimental values of the distribution ratio for ethanol at 55 °C are compared with those of Morachevskii and Belousov (*5*) at the same temperature; the two sets are in fair agreement.

Glossary

x_{EW}	liquid mole fraction of E in the W-rich phase
γ_i	activity coefficient of component i
θ_i	area fraction of component i
θ_i'	modified area fraction of component i
ϕ_i	segment fraction of component i

Subscripts

B	component (benzene)
E	component (ethanol)
W	component (water)

Registry No. Benzene, 71-43-2; ethanol, 64-17-5.

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Effect of Temperature on the Apparent Molal Volume of Ethylurea in Aqueous Solutions

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The densities of aqeous solutions of ethylurea in the concentration range 0.1–8 *m* have been measured at 15, 25, 35, and 50 °C. From densities the partial molal volumes of water, $\bar{V}_1$, and ethylurea, $\bar{V}_2$, and the apparent molal volumes of ethylurea, Φ_v, have been calculated. The latter have been fitted to two polynomials. The first gives the dependence of Φ_V on concentration, the second on temperature. Analysis of the dependence rests on the comparison with urea. The presence of the hydrophobic moiety in ethylurea is clearly reflected in concentration as well as temperature dependence. The implications for protein denaturation by ethylurea are briefly discussed.

For interpretation of conformational changes of globular proteins in aqueous solutions brought about by a denaturant, e.g., urea, it is useful to possess knowledge of the interaction between that denaturant and water. Urea has long been known as a strong denaturant for globular proteins since, depending on concentration, it produces partial or complete unfolding of protein molecules (*1*). Therefore, it is understandable that a large number of studies have dealt with the thermodynamic and other relevant properties of aqueous urea solutions. The main finding has been that urea is a statistical structure breaker. For details, the reader is referred to the review by Franks (*2*).

Introduction of an alkyl group into the urea molecule influences its denaturing activity. However, whereas methylurea does not differ much from urea in that respect, ethylurea differs distinctly from urea in denaturing activity (*3*, *4*). The difference should very likely also exist in the interaction between ethylurea, as compared to urea, and water. Among the thermodynamic properties the partial molal volume is a rather sensitive measure of that interaction. Additional information is obtained by determining the temperature coefficient of the apparent molal volume. Needless to say, the volume data are also interesting per se. The apparent molal volumes of ethylurea were determined at 15, 25, 35, and 50 °C.

Experimental Section

***Materials*.** Ethylurea (Merck, laboratory grade) was twice recrystallized from hot methanol. Before use, it was dried under vacuum over P_2O_5 at 60 °C for 24 h.

***Density Measurements*.** The densities were measured with a precision density meter DMA-02 (Anton Paar, Graz). The temperature of the cell compartment was controlled to ±0.01 °C with a Heto circulating thermostat. The temperature of the thermostat was set to ±0.005 °C with a platinum resistance thermometer. The instrument was calibrated with air and water. Since all solutions must be free of large particles, before measurement solutions were filtered through Millipore filters (type HA, pore size 0.45 μm). For each ethylurea concentration at least three measurements were performed. After each series of measurements, the cell was washed and dried and the calibration constant redetermined. Under the existing experimental conditions and the time lapse for 2 × 10^4 periods being

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Table I. Apparent Molal Volume, Φ_V, of Ethylurea and Partial Molal Volumes of Water, $\bar{V}_1$, and Ethylurea, $\bar{V}_2$, in Aqueous Solutions

d, g cm^{-3}	m, mol kg^{-1}	Φ_V	$\bar{V}_1$, cm^3 mol^{-1}	$\bar{V}_2$, cm^3 mol^{-1}
		T = 15 °C		
0.999 909	0.082 965	78.37	18.031	78.37
1.000 083	0.101 166	78.39	18.031	78.35
1.000 172	0.111 272	78.46	18.031	78.34
1.000 544	0.149 812	78.43	18.031	78.29
1.001 967	0.297 151	78.30	18.032	78.13
1.002 982	0.401 981	78.21	18.032	78.03
1.004 409	0.552 788	78.15	18.034	77.90
1.008 819	1.026 971	77.95	18.038	77.57
1.014 084	1.621 987	77.77	18.043	77.35
1.019 131	2.236 75	77.66	18.045	77.30
1.024 434	2.941 83	77.60	18.041	77.42
1.032 879	4.237 86	77.58	18.008	77.88
1.048 56	7.682 80	77.89	18.023	77.95
		T = 25 °C		
0.998 97	0.210 27	79.00	18.068	78.94
0.999 94	0.319 02	79.01	18.069	78.87
1.001 76	0.521 99	78.91	18.070	78.74
1.006 56	1.077 27	78.73	18.073	78.47
1.009 12	1.387 86	78.66	18.076	78.37
1.015 33	2.191 3	78.54	18.079	78.26
1.019 28	2.749 51	78.48	18.078	78.29
1.028 04	4.180 30	78.47	18.058	78.60
1.036 64	5.966 85	78.58	18.008	79.14
1.045 65	8.507 87	78.78	18.021	79.09
		T = 35.1 °C		
0.996 155	0.243 167	79.64	18.123	79.56
0.996 808	0.318 764	79.61	18.123	79.52
0.998 512	0.519 033	79.55	18.124	79.42
1.002 968	1.065 46	79.44	18.127	79.21
1.011 862	2.265 65	79.25	18.130	79.09
1.016 086	2.915 45	79.23	18.126	79.16
1.025 096	4.566 78	79.28	18.102	79.53
1.029 45	5.488 62	79.28	18.078	79.74
1.036 372	7.365 86	79.44	18.088	79.76
1.038 518	8.043 03	79.48	18.115	79.54
		T = 50 °C		
0.989 68	0.207 68	80.97	18.233	80.88
0.992 036	0.511 44	80.85	18.234	80.76
0.994 54	0.844 16	80.76	18.234	80.65
0.996 194	1.076 73	80.76	18.236	80.60
1.000 426	1.689 6	80.66	18.237	80.50
1.005 165	2.450 62	80.62	18.239	80.49
1.007 808	2.913 67	80.61	18.238	80.52
1.013 392	4.012 35	80.64	18.229	80.69
1.021 488	5.953 39	80.69	18.188	81.11
1.029 016	8.503 70	80.69	18.178	81.24

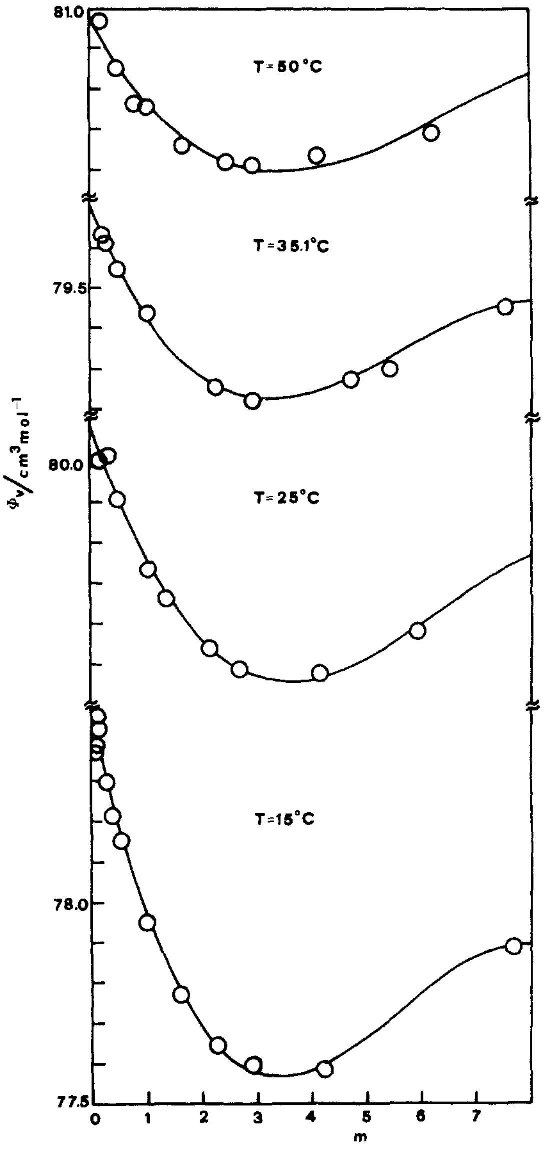

Figure 1. Apparent molal volumes of ethylurea in aqueous solutions at various temperatures as a function of concentration.

measured, the precision of the densities was about ±6 × 10^{-6} g cm^{-3}, which in turn corresponds to an uncertainty of about ±0.05 cm^3 mol^{-1} in partial molal volumes (*5*, *6*).

Results and Discussion

The densities of aqueous solutions of ethylurea have been measured at concentrations ranging from 0.1–8.5 *m*. The apparent molal volumes Φ_V have been determined from these densities (d) by using the equation

$$\Phi_V = 1000(d^0 - d)/(dd^0m) + M/d \quad (1)$$

where d^0 is the density of water, m is the molality of the solution, and M is the molecular weight of ethylurea. The values are given in Table I. From the densities, by the method of chords, the partial molal volumes of both components were obtained (cf. Table I).

By the method of least squares the apparent molal volumes in the concentration range measured were obtained as polynomial functions of concentration. The coefficients of polynomials at individual temperatures are listed in Table II and the functions are plotted in Figure 1. By using the same method, one can express the data at individual concentrations as polynomial functions of temperature. The coefficients of the resultant polynomial are given in Table III.

By differentiating the polynomial with respect to temperature we obtain the temperature coefficients of the partial molal volume Φ_E at individual concentrations

$$\Phi_E = (\partial\Phi_V/\partial T)_P \quad (2)$$

Table II. Concentration Coefficients of Polynomials of Apparent Molal Volume, Φ_V, of Ethylurea in Aqueous Solutions[a]

temp, °C	$\Phi_V{}^\circ$, cm^3 mol^{-1}	A_1, cm^3 mol^{-2} kg^1	10^2A_2, cm^3 mol^{-3} kg^2	10^3A_3, cm^3 mol^{-4} kg^3	10^3SD, cm^3 mol^{-1}
15	78.470	−0.621	13.060	−7.770	3
25	79.106	−0.415	7.997	−4.189	0.7
35.1	79.711	−0.339	7.223	−4.199	0.8
50	80.977	−0.249	4.857	−2.454	2

[a] $\Phi_V = \Phi_V{}^\circ + A_1m + A_2m^2 + A_3m^3$. Concentration range 0–8 *m*.

Table III. Temperature Coefficients of Polynomials of Apparent Molal Volume of Ethylurea, Φ_V, in Aqueous Solutions[a]

molality	B_0, cm^3 mol^{-1}	10^2B_1, cm^3 mol^{-1} °C^{-1}	10^4B_2, cm^3 mol^{-1} °C^{-2}	10^3SD, cm^3 mol^{-1}
0	77.831	3.561	5.425	2
1	77.043	5.873	3.130	4
2	76.594	7.169	1.848	4
3	76.409	7.691	1.339	3
4	76.412	7.680	1.358	2
5	76.523	7.374	1.664	1
6	76.682	7.017	2.012	0.8
7	76.798	6.850	2.161	1.4
8	76.800	7.107	1.867	4.0

[a] $\Phi_V = B_0 + B_1T + B_2T^2$. Temperature range 15–50 °C.

In connection with both polynomials it is interesting to note that the standard deviations of the fits are generally smaller than the errors observed in the determination.

We shall start the discussion by examination of the concentration dependence of Φ_V at the individual temperatures (Figure 1). The course of the curves is typical of solutes containing major hydrophobic moieties (*7–11*). It can therefore be concluded that the downward curvature of the apparent molal volume as a function of concentration reflects interactions between nonpolar groups and water, i.e., hydrophobic interactions. This conclusion is further corroborated by comparison with the Φ_V values for aqueous urea solutions (*12*). The concentration dependence is an upward curving function, and Φ_V increases with increasing urea concentration.

Considering the present state of our knowledge of aqueous solution, any interpretation of the peculiar form of the curves in Figure 1 can at best be qualitative. Therefore, we have chosen one of the simpler models of water structure, namely, that involving the equilibrium between a bulky and a dense state. The structural equilibrium between the two states can be written as

$$(H_2O)_b \rightleftarrows (H_2O)_d \qquad (3)$$

where b and d refer to the bulky and dense states, respectively. ΔV for the transition from left to right is negative. In the case of urea solutions where Φ_V of urea increases with increasing concentration (cf. above) it may be surmised that urea interferes predominantly with the dense state so that bulkier states are formed, which is reflected in increased values of Φ_V. Solute–solute association equilibria may be considered of minor importance (*13*). In ethylurea solutions, on the other hand, Φ_V is first decreasing with increasing solute concentration, reflecting the presence of the ethyl group. Interpretation in terms of the simple two-state model rests on the assumption that ethylurea at lower concentrations shifts the equilibrium in eq 3 from left to right; i.e., it acts as a structure promoter in contradistinction to urea, which is a structure breaker. When the minimum is reached, the structure-promoting activity appears to be lost. Not only this, the urea moiety becomes active, which is reflected in increasing Φ_V values. Further speculations on the details would be pointless.

Before proceeding to the discussion of the temperature coefficients Φ_E it is necessary to point out that in Figure 1 there is no indication of an inflection point at high dilution. A few measurements were made of 0.02 *m* ethylurea solution at 25 °C but no anomaly was observed. Moreover, at low concentrations, i.e., below 0.7 *m*, the dependence of Φ_V on *m* is nearly linear so that extrapolation to $m = 0$ may be considered objectionless.

The values of Φ_E at 25 °C calculated by using the equation given in Table II (cf. also Figure 2) range from 7.12 × 10^{-4} cm^3 g^{-1} °C^{-1} at $m = 0$ to 9.12 × 10^{-4} cm^3 g^{-1} °C^{-1} at $m = 8$; from $m = 2$ on there is little change with concentration. Comparison with the Φ_E values of urea solutions (*12*) shows that at low concentrations they are distinctly smaller. Thus, at $m = 0$ and 25 °C Φ_E for urea is 1.12 × 10^{-3} cm^3 g^{-1} °C^{-1}, at $m = 1$ it is 1.02 cm^3 g^{-1} °C^{-1}, and at $m = 2$ it is 1.05 cm^3 g^{-1} °C^{-1}. At higher concentrations of urea the values of Φ_E become smaller and comparable to those of ethylurea; thus at $m = 8$ and 25 °C Φ_E = 7.98 × 10^{-4} cm^3 g^{-1} °C^{-1}. On the basis of these findings it is possible to conclude that the values of Φ_E at low concentrations of ethylurea reflect the presence of the hydrophobic moiety; i.e., the solute apparently acts as a structure promoter. Similar behavior has been observed with other hydrophobic solutes (*14*). However, at higher concentrations the hydrophobic character is lost, and ethylurea behaves as a structure breaker, similar to urea. There are no firm grounds on which to found a trustworthy interpretation of this behavior. But the general situation is similar to that observed with the concentration dependence of Φ_V at fixed temperature. Thus, after examination of the concentration and temperature dependence of Φ_V of ethylurea in aqueous solutions, it is possible to claim that they characteristically reflect the interaction with water. The question of how the interaction between ethylurea and water differs from that between urea and water having been answered , it is appropriate to discuss the difference in denaturing activity of the two compounds. The data are available for human serum albumin and lactoglobulin (*3*, *4*). The first contains about 50% α-helix and the second about 50% β-sheets. In water at room temperature both proteins exist as stable compact molecules. The addition of urea or ethylurea to water changes the native structure. In the case of serum albumin both agents unfold the helical structure but on the concentration scale urea is far more effective. Interestingly, ethylurea becomes active at concentrations above 3 *m*. The situation is quite different with β-lactoglobulin. Whereas urea unfolds the β-sheets, ethylurea does not. On the contrary, the β-sheets are partly converted to α-helix. Again the activity appears at ethylurea concentrations above 3 *m*. At the moment there is no interpretation of the behavior since other thermodynamic data, especially Gibbs free energy, for the interactions involved are not available. It is known, however, that in mixed solvents preferential binding of the denaturant is necessary to bring about conformational changes (*15*). There is little doubt that to some extent it depends on the interaction between the denaturant and water.

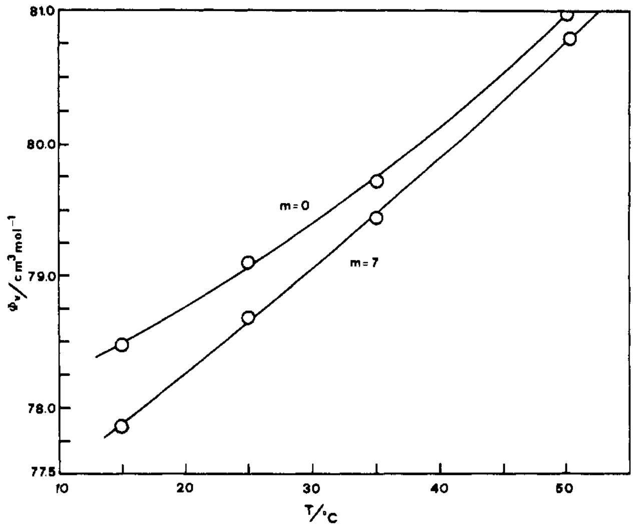

Figure 2. Temperature dependence of the apparent molal volume of ethylurea in aqueous solution at infinite dilution and at 7 *m*.

Registry No. Ethylurea, 625-52-5.

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Measurements of *PVTx* Properties for the R 22 + R 114 System

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The *PVTx* properties for the R 22 + R 114 system have been measured by the constant-volume method coupled with several isothermal expansion procedures. The results for five different compositions of 0, 20, 30, 50, and 75 wt % R 22 cover the range of temperatures 283–443 K and the range of pressures 0.13–9.11 MPa, which corresponds to the density variation from 94 to 1104 kg/m^3. The experimental uncertainties of the temperature, pressure, density, and mass fraction measurements were estimated to be no greater than 10 mK, 2.0 kPa, 0.09%, and 0.12%, respectively. The dew and bubble points and the interaction virial coefficients of the present system were determined. The critical locus is also illustrated.

As a part of our current research projects on the thermodynamic properties of refrigerant mixtures, we have measured the *PVTx* properties of the R 22 + R 114 system. The present R 22 + R 114 system is of particular interest as one of the promising working mediums for refrigeration and heat pump cycles. No experimental data, however, of the thermodynamic properties for this system have been available up to now. This paper reports the *PVTx* measurements for five different compositions of 0, 20, 30, 50, and 75 wt % R 22 in the range of temperatures 283–443 K and the range of pressures 0.13–9.11 MPa, which covers the density range 94–1104 kg/m^3. The dew and bubble points, critical locus, and interaction virial coefficients of this system are also reported. The purity of each component supplied was 99.99 wt % R 22 (chlorodifluoromethane, $CHClF_2$) and 99.94 wt % R 114 (dichlorotetrafluoroethane) being an isomeric blend of 95% $CClF_2CClF_2$ + 5% CCl_2FCF_3.

Experimental Section

The *PVTx* measurements of this work have been made by the constant-volume method coupled with several isothermal expansion procedures for a mixture of a certain fixed composition. The apparatus and experimental procedure used here are essentially the same as those used by Takaishi et al. (*1*, *2*) in similar measurements for the R 12 + R 22 system. The sample cell of 268.434 ± 0.006 cm^3 inner volume and the expansion cell of 55.583 ± 0.007 cm^3 were spherical in shape and made of 304 stainless steel. The prescribed quantity of each pure component was prepared by weighing the mass of the sample on a chemical balance with a sensitivity of 2 mg. The samples thus prepared were then supplied one by one into the sample cell immersed in liquefied nitrogen. The mass fraction of the sample mixture in the sample cell was determined to be the ratio of the mass of each component to that of the mixture with an uncertainty of no greater than 0.12%.

The sample cell assembled with the expansion cell and a differential pressure detector was then immersed into a thermostated fluid bath. The bath-fluid temperature was controlled within a fluctuation of ±5 mK by using a stirrer and electric heaters. After the thermal equilibrium between the sample and bath fluid was confirmed, the temperature of the bath fluid was measured with a 25-Ω platinum resistance thermometer (Chino: Model R800-1) with a precision of 5 mK on IPTS-68 by a Mueller-type bridge (Shimadzu: Model BD-100). The uncertainty of the sample temperature measurements was less than 10 mK. The pressure of the sample was transmitted to nitrogen gas. The pressure of the sample was balanced with that of nitrogen by means of the differential pressure detector with a sensitivity of 0.1 kPa. We measured the pressure of nitrogen gas thus transmitted with two different pressure gages: an air-piston pressure gage (Ruska: Model 2465) with an effective piston area of 0.083 917 1 ± 0.000 006 6 cm^2 for pressures below 4 MPa and an oil-operated dead-weight pressure gage (Futaba: Model TL-2) with 1.000 42 ± 0.000 20 cm^2 for those above 4 MPa. The uncertainty of the sample pressure measurements was less than 0.6 kPa for pressures below 4 MPa and less than 2.0 kPa for those above 4 MPa.

The density of the sample initially in the sample cell at a certain temperature and pressure was determined to be the ratio of the mass of the sample to the inner volume of the sample cell adjusted to account for the volume variation due to elevated temperature and pressure. After the *PVT* measurements along the initial isochore were completed for a prescribed temperature range, the sample within the sample cell was expanded into the preevacuated expansion cell under a homogeneous state. Throughout the expansion procedure, the bath-fluid temperature was controlled within a fluctuation of ±10 mK and both the sample cell and the expansion cell were rocked by a rocking device to ensure homogeneity of the sample density and composition within these two vessels. Then the *PVT* measurements were continued along the newly obtained isochore for a mixture of the same fixed composition. Repeating these procedures, we obtained a set of *PVT* data for the mixture of fixed composition along several isochores by a single charge of the sample. Because of the possible accumulation of uncertainty in the density measurements due to repeating the expansion procedures, we did not repeat the

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