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Volume Properties of the H_2O–DMF Mixture at the Pressure 0.101 MPa in the Temperature Range 278.15–323.15 K

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Abstract—The density of the water–*N*,*N*-dimethylformamide mixture throughout the entire range of compositions in the temperature range 278.15–323.15 K at atmospheric pressure (0.101 MPa) was measured. The coefficients of thermal dilatation α were calculated. The α value strongly depends on the composition of the mixture in the range $0 < X < 0.3$ (X is the molar fraction of dimethylformamide), which is associated with breakdown of water structure. An equation relating the molar volume of the water–dimethylformamide mixture to the composition of the mixture and to the temperature was proposed.

Previously the density of the water–*N*,*N*-dimethylformamide (DMF) system have been repeatedly measured [1–4], but systematic polythermic studies have scarcely been performed. Therefore, there is no way of calculating a reliable temperature dependence of the system volume because of both the insufficient accuracy of the available density data and the large errors that arise when one has to treat published data to reduce them to a common composition, etc.

In the present work we measured the densities of the H_2O–DMF system over the entire range of compositions (X = 0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9, 0.95, and 1.0 molar fractions) at atmospheric pressure (0.101 MPa) at 278.15, 288.15, 298.15, 308.15, and 323.15 K.

The resulting densities ρ of the water–DMF mixture are listed in the table. For the sake of comparison, we treated the data in [1–4] by the cubic splines procedure to fit them to our composition range.

To calculate the thermal dilatation coefficients α, the densities ρ of the H_2O–DMF mixture of each composition were related, via a second-order polynomial, to the temperature and then differentiated [Eq. (1)].

Density ρ (g/cm^3) of the H_2O–DMF mixture at the pressure p 0.101 MPa in the temperature range 278.15–323.15 K

X	278.15 K		288.15 K, present work	298.15 K		308.15 K		323.15 K, present work
	present work	[2]		present work	[3]	present work	[4]	
0.00	0.999964	0.999964	0.999098	0.997043	0.997300	0.994030	0.994032	0.988066
0.05	1.003441	1.003936	1.000241	0.996291	0.997260	0.991685	0.992606	0.981618
0.10	1.007680	1.007674	1.002554	0.996927	0.997421	0.990884	0.990916	0.981022
0.15	1.010384	1.010489	1.003852	0.996989	0.997715	0.989818	0.988403	0.978527
0.20	1.011225	1.011382	1.003743	0.996009	0.997193	0.988025	0.985480	0.975664
0.30	1.007808	1.008594	0.999253	0.990491	0.992311	0.981534	0.980044	0.967841
0.40	1.002197	1.002338	0.993264	0.984085	0.985875	0.974727	0.974070	0.960494
0.50	0.994471	0.994858	0.985364	0.976103	0.977557	0.966629	0.966541	0.952295
0.70	0.979923	0.980218	0.970626	0.961127	0.962305	0.951654	0.951744	0.937234
0.90	0.968002	0.968288	0.958566	0.949050	0.950268	0.939466	0.940189	0.925097
0.95	0.965494	0.965729	0.956023	0.946441	0.947355	0.936917	0.937821	0.922542
1.00	0.963138	0.963240	0.953664	0.944051	0.944500	0.934541	0.935581	0.920147

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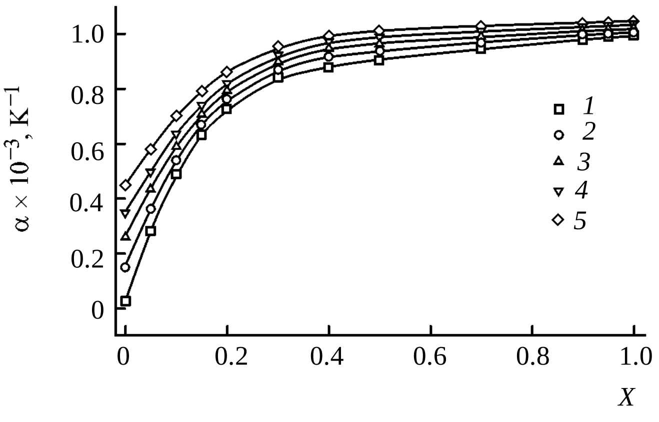
$$\alpha = -\rho\left(\frac{\partial\rho}{\partial T}\right)_{X,\,T} = -\left(\frac{\partial \ln\rho}{\partial T}\right)_{X,\,T} = \frac{1}{V_m}\left(\frac{\partial \ln V_m}{\partial T}\right)_{X,\,T} \quad (1)$$

Here ρ and V_m are the density and molar volume of the H_2O–DMF mixture of composition X. The resulting α values are shown in the figure.

The $\rho = f(X)$ dependences are peaked curves. The maximum at X ~0.2 gets lower until it almost disappears as the temperature is increased to 323 K. This maximum is formed by water–nonelectrolite association in the system and with changes in water structure produced by noneletrolyte molecules and by increasing temperature. It is known that the density of H_2O at 277.13 K is a maximum (the density of liquid water at this temperature is higher by about 10% that that of ice, and the number of nearest neighbors around each water molecule is 4.4 against 4 for ice [5]), which is explained both by a change in the fraction of linear hydrogen bonds and by partial "insertion" or "accomodation" in cavities of the tetrahedral water structure of free water molecules not incorporated into the ice-like frame [6, 7]. Correspondingly, at temperatures close to that of the water density maximum, an increase in the nonelectrolyte concentration gives rise to "insertion–accomodation" in these cavities of a part of nonelectrolyte molecules or their functional groups comparable in size with the cavities, and the resulting expulsion from them of water molecules. With increasing temperature, the number of water molecules in cavities of the tetrahedral water structure and the stability of the associates formed are decreased [8] by the enhanced molecular thermal motion, resulting in that at 323.15 K the density maximum of the H_2O–DMF mixture almost levels at X ~0.2.



Dependence of the thermal dilatation coefficient α on the composition of the H_2O–DMF mixture at p 0.101 MPa and T 278.15–323.15 K. Temperature, K: (*1*) 278.15, (*2*) 288.15, (*3*) 298.15, (*4*) 308.15, and (*5*) 323.15.

As seen from the figure, the $\alpha = f(X)$ dependences at various temperatures have an almost the same shape: the thermal dilatation coefficients of the H_2O–DMF mixture sharply increase at $0 < X < 0.4$, after which α changes monotonically and insignificantly. It is known that water, on account of its peculiar structure, has a low α value compared with other liquids. The sharp increase in α in the range $0 < X < 0.4$ relates to the build-up of the molar volume of the mixture at increasing temperature and constant pressure, associated with the expulsion of water molecules from cavities in the tetrahedral water structure and the increasing fraction of linear hydrogen bonds. As seen from the figure, increasing nonelectrolyte concentration and temperature cause unidirectional changes in α, and the increase of the molar fraction of DMF to 0.4 stronger affects α than the temperature increase from 278 to 323 K.

We propose Eq. (2) relating the molar volume of the H_2O–DMF system to the composition and temperature at atmospheric pressure at 278.15–323.15 K. This equation was obtained by a second-order polynomial fit of the composition and temperature dependences of V_m.

$$V_m = \sum_{k,l=0} A_{k,l} X^k T^l. \quad (2)$$

Coefficients of Eq. (2) are listed below.

	$k = 0$	$k = 1$	$k = 2$
$l = 0$	22.6443	–0.036027	6.89740×10^{-5}
$l = 1$	25.8864	0.106760	-0.30614×10^{-4}
$l = 2$	14.2644	0.049519	5.60161×10^{-5}

Equation (2) reproduces experimental V_m values for the H_2O–DMF mixture at p 0.101 MPa in the temperature range 278.15–323.15 K with a relative error of no more than 0.3%.

We used freshly twice-distilled water, chemical grade DMF purified by the procedure in [9] and stored over 4 Å molecular sieves. Aqueous solutions of DMF were prepared gravimetrically from degassed solvents with an accuracy of 1×10^{-3} mol%.

Density measurements were performed using an Anton–Paar DMA-60/602 densimeter with an accuracy of $\pm 1 \times 10^{-5}$ g/cm^3.

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