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P–V_m–x Properties of Water–Dimethylformamide Mixtures at 278.15 K and Pressures of up to 100 MPa

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Abstract—The compressibility coefficients $k = (v_0 - v)/v_0$ of water–dimethylformamide (DMF) binary mixtures in the entire composition range at 278.15 K and pressures of up to 100 MPa were measured with a constant-volume piesometer. From the measured densities at atmospheric pressure and the coefficients k, the following quantities were calculated: specific and molar volumes of water–DMF mixtures at the examined parameters of state, excess molar volumes, partial molar volumes of the components, and variation with external pressure of the excess Gibbs energy of the water–DMF system. At all the pressures, the dependence $k = f(x)$ (where x is the mole fraction of DMF in the mixture) passes through a minimum at x ~0.2. The composition dependence of the specific volume of water–DMF mixtures also shows extrema, and its shape depends on the pressure. The partial molar volume of water at infinite dilution in DMF slightly depends on pressure.

Data on volume properties of binary systems are very important for describing interactions in systems of molecules with different functional groups at various parameters of state. Furthermore, for aqueous solutions of nonelectrolytes, the temperatures close to that of the water density maximum are of particular interest. In this case, data on the effect exerted by high pressures on the volume properties of mixtures reveal more clearly the structural features of H_2O as influenced by the nonelectrolyte.

Here we report data on the compressibility k of water–dimethylformamide (DMF) binary mixtures in the entire composition range at 278.15 K and pressures from 0.101 (atmospheric) to 100 MPa.

$$k = (v_0 - v)/v_0, \qquad (1)$$

where v_0 and v are the specific volumes of the H_2O–DMF system at P_0 0.101 MPa and at a given pressure P, respectively.

From our experimental data on the density of H_2O–DMF mixtures, obtained at atmospheric pressure with a vibration densimeter, and from the coefficients k of the system, we calculated the specific (v) and molar (V_m) volumes of the mixture, excess (V_m^E) and partial molar volumes of water ($\overline{V}_1$) and DMF ($\overline{V}_2$), and variation with external pressure of the excess Gibbs energy $\Delta_{P_0-P}G_m^E$ in the water–DMF system.

The volume properties of water–DMF mixtures at 278.15 K were studied previously at atmospheric pressure [1, 2]. We found no published data on the volume properties of aqueous DMF solutions at this temperature and high pressures.

We used double-distilled water and chemically pure grade DMF, which was distilled two times in a vacuum and stored over 4 Å molecular sieves. The residual content of water in DMF, determined by Fischer titration, did not exceed 1×10^{-2}%.

Aqueous solutions of DMF were prepared gravimetrically with an accuracy of 1×10^{-3} mol % from degassed solvents. In this work, we studied 12 compositions (x = 0.0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9, 0.95, 1.0), where x is the mole fraction of the nonaqueous component in the mixture.

The densities of water–DMF mixtures were measured at atmospheric pressure with an Anton Paar DMA-60/602 device accurate to 1×10^{-5} g cm^{-3}. The results are listed in Table 1.

Table 1. Density (ρ, g cm^{-3}) of water–DMF mixtures at atmospheric pressure and 278.15 K (x is the mole fraction of DMF)

x	ρ	x	ρ	x	ρ
0.00	0.99996	0.20	1.01123	0.70	0.97922
0.05	1.00344	0.30	1.00781	0.90	0.96800
0.10	1.00768	0.40	1.00220	0.95	0.96549
0.15	1.01038	0.50	0.99447	1.00	0.96314

The compressibility coefficients k were measured on a device designed by us [3] for measuring the compressibilities of nonelectrolyte solutions in the temperature range 240–500 K and pressures of up to 150 MPa, using a constant-volume piesometer under pressure. The piesometer was a thick-walled stainless steel vessel with a volume of 487.5 cm^3 at 278.15 K. The piesometer was calibrated with water, methanol, and *n*-hexane [4–6] whose compressibilities are known with a fairly high accuracy. The temperature in a 90-l thermostat was maintained to within 0.01 K. The pressure was measured with 0.05% accuracy with a system consisting of commercial MP-2500 load-piston manometer and D-100 tensoconverter [7].

The experiment consisted of adding a known volume of a mixture ΔV to a piesometer of volume V_0 filled with this mixture and compressing the resulting volume $\Delta V + V_0$ to V_0. Then, after thermostating to dissipate the evolved heat, the pressure in the piesometer was measured.

The compressibility coefficient $k = (v_0 - v)/v_0$ was calculated as follows:

$$k = (\Delta V - \upsilon)/(\Delta V + V_0), \qquad (2)$$

where υ is the correction for baric expansion of the piesometer, which was determined by preliminary calibration. The resulting values of k for each composition were described by second-degree polynomials (3) with respect to pressure (Table 2):

$$k = a_0 + a_1 P + a_2 P^2. \qquad (3)$$

The specific volumes v and molar volumes V_m at various parameters of state were calculated from the experimental compressibility coefficients k using the densities of the mixtures, ρ, measured at atmospheric pressure.

The partial molar volumes of water $\overline{V}_1$ (Table 3) and DMF $\overline{V}_2$ (Table 4) were calculated by Eqs. (4) and (5):

Table 2. Coefficients of Eq. (3) and rms deviation ($\Delta k/k$) for water–DMF mixtures at 278.15 K and pressures of up to 100 MPa (x is the mole fraction of DMF)

x	$a_0 \times 10^4$	$a_1 \times 10^4$	$-a_2 \times 10^6$	$(\Delta k/k) \times 10^2$	x	$a_0 \times 10^4$	$a_1 \times 10^4$	$-a_2 \times 10^6$	$(\Delta k/k) \times 10^2$
0.00	0.266823	4.85251	0.63252	0.03	0.40	1.07351	4.01391	0.55805	0.18
0.05	0.87677	3.91983	0.38705	0.03	0.50	0.977235	4.28697	0.64846	0.12
0.10	0.996341	3.67256	0.39659	0.12	0.70	1.94147	4.81770	0.81970	0.22
0.15	–0.98646	3.62207	0.41796	0.11	0.90	3.03642	5.26709	0.94806	0.21
0.20	–0.18419	3.61835	0.42597	0.03	0.95	2.93232	5.36433	0.97316	0.19
0.30	1.02337	3.76255	0.47425	0.27	1.00	2.74873	5.45605	0.99409	0.24

Table 3. Partial molar volumes of water ($\overline{V}_1$) in water–DMF mixtures at 278.15 K and pressures of up to 100 MPa (x is the mole fraction of DMF)

x	$\overline{V}_1$, $cm^3\ mol^{-1}$, at indicated pressure, MPa										
	0.101	10	20	30	40	50	60	70	80	90	100
0.00	18.02	17.93	17.84	17.76	17.68	17.61	17.53	17.46	17.39	17.32	17.25
0.05	18.08	18.00	17.92	17.85	17.78	17.71	17.64	17.57	17.50	17.44	17.38
0.10	18.02	17.94	17.87	17.80	17.73	17.66	17.59	17.53	17.47	17.41	17.35
0.15	17.89	17.82	17.75	17.68	17.62	17.55	17.49	17.43	17.37	17.31	17.25
0.20	17.72	17.66	17.60	17.54	17.47	17.41	17.36	17.30	17.25	17.19	17.14
0.30	17.35	17.31	17.26	17.21	17.17	17.13	17.08	17.03	16.99	16.94	16.90
0.40	16.90	16.88	16.86	16.83	16.80	16.77	16.74	16.71	16.68	16.64	16.61
0.50	16.46	16.47	16.47	16.46	16.45	16.44	16.42	16.41	16.39	16.37	16.35
0.70	15.62	15.66	15.69	15.72	15.74	15.75	15.76	15.77	15.77	15.78	15.78
0.90	15.10	15.14	15.16	15.19	15.21	15.23	15.23	15.24	15.24	15.24	15.25
0.95	15.07	15.09	15.10	15.13	15.15	15.15	15.15	15.15	15.14	15.14	15.15
1.00	15.08	15.09	15.08	15.10	15.11	15.10	15.09	15.08	15.06	15.05	15.05

$$\overline{V}_1 = V_m - x(\partial V_m/\partial x)_{P,\, T = 278.15\,\mathrm{K}}, \qquad (4)$$

$$\overline{V}_2 = V_m - (1 - x)(\partial V_m/\partial x)_{P,\, T = 278.15\,\mathrm{K}}, \qquad (5)$$

To determine the derivatives $\partial V_m/\partial x$, the composition dependences of the molar volumes of mixtures were approximated by third-degree polynomials and then differentiated.

The partial molar volumes of DMF in water at infinite dilution, $\overline{V}_1^{\infty}$, were found from the apparent molar volumes determined as follows:

$$\Phi_{V_2} = \frac{(\rho_1 - \rho_{\mathrm{mix}})(1 - x)M_1}{x\,\rho_{\mathrm{mix}}\,\rho_1} + \frac{M_2}{\rho_{\mathrm{mix}}}, \qquad (6)$$

where ρ_1 and ρ_{mix} are the densities of water and water–DMF mixture, respectively; x, the mole fraction of DMF in the mixture; and M_1 and M_2, the molecular weights of water and DMF, respectively. For this purpose, the concentration dependence of the apparent molar volumes of DMF for the compositions $x \le 0.2$ at all the pressures was presented in the form

$$\Phi_{V_2} = \Phi_{V_2}^{\infty} + b_V m, \qquad (7)$$

where m is the reduced molal concentration of DMF in water. It is known [8] that, in the extrapolation $m \to 0$, $\Phi_{V_2}^{\infty} \to \overline{V}_1^{\infty}$.

From the data obtained, we also calculated the partial compressibility coefficients of water, $\overline{k}_1$, and dimethylformamide, $\overline{k}_2$:

$$\overline{k}_1 = (\overline{V}_1^0 - \overline{V}_1)/\overline{V}_1^0, \qquad (8)$$

$$\overline{k}_2 = (\overline{V}_2^0 - \overline{V}_2)/\overline{V}_2^0. \qquad (9)$$

The excess molar volumes V_m^E (Table 5) were calculated by Eq. (10):

$$V_m^E = V_m' - V_m^{',\mathrm{id}}. \qquad (10)$$

The molar volume of the ideal system $V_m^{',\mathrm{id}}$ was determined from the molar volumes of water, V_{1m}, and DMF, V_{2m}:

Table 4. Partial molar volumes of DMF ($\overline{V}_2$) in water–DMF mixtures at 278.15 K and pressures of up to 100 MPa (x is the mole fraction of DMF)

x	$\overline{V}_2$, cm^3 mol^{-1}, at indicated pressure, MPa										
	0.101	10	20	30	40	50	60	70	80	90	100
0.00	72.11	72.17	72.31	72.41	72.49	72.55	72.60	72.62	72.61	72.57	72.54
0.05	70.45	70.33	70.20	70.06	69.93	69.80	69.67	69.54	69.42	69.29	69.16
0.10	71.30	71.12	70.94	70.77	70.60	70.43	70.27	70.11	69.96	69.81	69.65
0.15	72.02	71.81	71.58	71.37	71.16	70.97	70.78	70.59	70.41	70.23	70.05
0.20	72.66	72.40	72.14	71.90	71.66	71.44	71.22	71.01	70.80	70.60	70.41
0.30	73.75	73.43	73.11	72.81	72.53	72.26	71.99	71.74	71.50	71.26	71.04
0.40	74.55	74.18	73.82	73.49	73.17	72.86	72.57	72.29	72.03	71.76	71.51
0.50	75.15	74.76	74.37	74.02	73.68	73.35	73.04	72.75	72.46	72.19	71.92
0.70	75.78	75.36	74.96	74.58	74.22	73.89	73.56	73.25	72.95	72.67	72.38
0.90	75.90	75.48	75.08	74.70	74.34	74.00	73.68	73.37	73.07	72.78	72.50
0.95	75.90	75.48	75.08	74.70	74.34	74.00	73.67	73.36	73.06	72.78	72.49
1.00	75.89	75.47	75.07	74.69	74.33	73.99	73.66	73.35	73.05	72.76	72.47

Table 5. Excess molar volume V_m^E of water–DMF mixtures at 278.15 K and pressures of up to 100 MPa (x is the mole fraction of DMF in the mixture)

x	$-V_m^E$, cm^3 mol^{-1}, at indicated pressure, MPa						x	$-V_m^E$, cm^3 mol^{-1}, at indicated pressure, MPa					
	0.101	20	40	60	80	100		0.101	20	40	60	80	100
0.00	0	0	0	0	0	0	0.40	1.207	1.093	0.994	0.910	0.837	0.771
0.05	0.212	0.169	0.132	0.100	0.073	0.051	0.50	1.146	1.037	0.943	0.863	0.794	0.731
0.10	0.460	0.392	0.333	0.282	0.237	0.199	0.70	0.799	0.725	0.656	0.600	0.551	0.505
0.15	0.690	0.603	0.532	0.468	0.411	0.364	0.90	0.284	0.260	0.234	0.213	0.194	0.177
0.20	0.882	0.784	0.701	0.628	0.563	0.508	0.95	0.144	0.131	0.118	0.107	0.097	0.087
0.30	1.107	0.996	0.899	0.817	0.748	0.679	1.00	0	0	0	0	0	0

$$V_m^{\prime,\mathrm{id}} = V_{1m} - x(V_{1m} - V_{2m}). \qquad (11)$$

From the calculated V_m^E, we determined the variation with external pressure of the excess Gibbs energy in the water–DMF system:

$$\Delta_{P_0-P} G_m^E = G_{m(P)}^E - G_{m(P_0)}^E = \int_{P_0}^{P} V_m^E \, dP. \qquad (12)$$

The composition dependences of the specific volume of water–DMF mixtures, measured at various pressures, pass through extrema (Fig. 1). A minimum at x ~0.2 is attributable both to formation of water–nonelectrolyte associates in the mixture [9] and to changes in the water structure due to its break by the nonelectrolyte molecules. It is known that the density of H_2O at 277.13 K has a maximum (at this temperature the water density is almost 10% higher than that of ice I), and the number of nearest neighbors around each water molecule increases from 4, characteristic of ice, to 4.4, which is due to a change in the relative content of linear hydrogen bonds [10] and to partial accommodation of free H_2O molecules, not incorporated in the icelike framework, in voids of the tetrahedral water structure [11]. Correspondingly, at temperatures close to that of the density maximum, with increasing nonelectrolyte concentration its molecules or functional groups whose size is comparable to that of voids in the water structure become partially accommodated in these voids, displacing from them H_2O molecules. Since, at 278.15 K, the water structure is an icelike (ice I) framework disturbed by thermal motion, with the voids partially filled with water molecules [11], on adding DMF the CH_3 groups of DMF molecules become accommodated in the voids of the tetrahedral water framework. On the one hand, such a process, involving displacement of free H_2O molecules from voids of the water structure by hydrophobic CH_3 groups, breaks the water structure; on the other hand, the structure is somewhat stabilized, becoming more "crystalline" and "ordered." In the process, the vibrational motion of water molecules in the tetrahedral framework becomes braked, and this framework can be considered as a "subcryoscopic iceberg." Competition of all these effects is just responsible for appearance, with increasing pressure, of an extremum at x ~0.05 in the composition dependences of the specific volume. As the external pressure grows, hydrogen bonds in the water structure are deformed; at high pressures, the deformation of voids in the framework is stronger, decreasing the tetrahedral ordering. Therefore, on adding small amounts of DMF, the effect of stabilization of the water structure due to incorporation of CH_3 radicals of DMF molecules in the voids of the tetrahedral framework will be less pronounced than at lower pressures. As a result, at high pressures, as seen from Fig. 1, the system becomes less compact on adding the first DMF molecules, i.e., the specific volume increases. However, as the DMF concentration grows, the stabilizing contribution from incorporation of CH_3 radicals into voids of the water structure increases, which makes the water structure denser and decreases the specific volume. As seen from Fig. 1, this trend keeps up to x ~0.2, after which the contribution from the break of the hydrogen bond framework becomes prevailing.

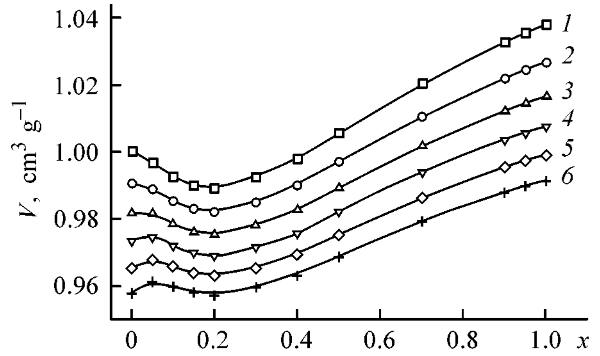

Fig. 1. Specific volume of water–DMF mixtures at 278.15 K as a function of composition. Pressure, MPa: (*1*) 0.1, (*2*) 20, (*3*) 40, (*4*) 60, (*5*) 80, and (*6*) 100.

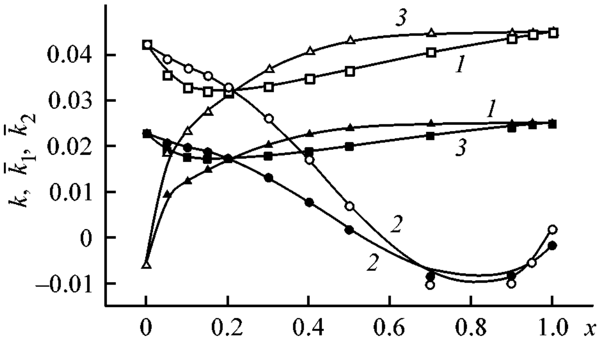

Fig. 2. Composition dependences of the (*1*) compressibility coefficient of water–DMF mixtures and (*2*, *3*) partial compressibility coefficients of H_2O and DMF, respectively, at 278.15 K and pressures of (*light figures*) 100 and (*filled figures*) 50 MPa.

As seen from Fig. 2, the dependence $k = f(x)$ at 278.15 K and a constant pressure passes through a minimum at x ~0.2. Changes in the intermolecular interactions in the system with increasing DMF concentration in the pressure range 0.1–100 MPa result in that, up to x ~0.9, for water–DMF mixtures k is lower than for water. With addition of DMF, k sharply decreases in the composition range up to x ~0.1. At a minimum (e.g., for 100 MPa), k of the mixture amounts to only 88% of k of water. Since, with increasing pressure, the free volume and mean interparticle distance should decrease, both in less compact and more compact structures of the mixed solvent, an increase in pressure shifts the structural equilibrium toward the more closely packed structure of the mixed solvent. The composition dependences of the partial compressibility coefficient of water, $\bar{k}_1$ (Fig. 2), pass through a minimum at x ~0.7–0.9 (with $\bar{k}_1$ at $x > 0.5$ being negative), which indicates that the contribution of the water compressibility to k at this composition is at a minimum. It should also be noted that, in the composition range x ~0.9–1.0, $\bar{k}_1$ grows with increasing DMF concentration, suggesting a quite different mechanism of the water effect in the H_2O–DMF system at these compositions. As the DMF concentration is increased, $\bar{k}_2$ grows up to x ~0.5, after which, in the range $0.5 < x < 1$, $\bar{k}_2$ remains virtually constant.

As seen from Table 3, the composition dependence of the partial molar volume of water $\bar{V}_0 = f(x)$ passes through a maximum. On adding small (up to x ~0.05) amounts of DMF, the partial volume of water $\bar{V}_0$ increases, and on further addition of DMF it decreases. The position of the maximum at x ~0.05 is virtually independent of pressure in the examined range. At $x > 0.5$, the curve of $\bar{V}_0 = f(x)$ passes through an inversion point (the partial volume of water is independent of pressure). It was found previously that, in aqueous solutions, the partial molar volumes of organic components $\bar{V}_2^\infty$ in water at infinite dilution always decrease with increasing pressure, and the partial molar volumes of water $\bar{V}_1^\infty$ at infinite dilution in organic solvents either increase [12–15] or decrease [16, 17] with increasing pressure, although the decrease is always insignificant. As seen from Table 3, the partial molar volume of water $\bar{V}_1^\infty$ is virtually independent of pressure. Such a trend is attributable to the compensating effect of pressure on the electrostriction component of $\bar{V}_1$ [18]. The partial molar volumes of DMF, $\bar{V}_2$ (Table 4), monotonically decrease with increasing pressure at a constant composition (except $\bar{V}_2^\infty$). As for the concentration dependence of $\bar{V}_2$ at constant pressure, at x ~0–0.05 it decreases by ~3 cm^3 mol^{-1}, passes through a minimum at x ~0.05, and then monotonically increases.

As seen from Table 5, $V_m^E < 0$, and its concentration dependence at a constant pressure passes through a minimum in the range x ~0.35–0.4, i.e., in the examined range of parameters at 278.15 K formation of water–DMF mixtures is accompanied by contraction. An increase in pressure does not affect the position of the minimum and only decreases the absolute value of the excess molar volume of the mixture, i.e., at high pressures, the deviations of the H_2O–DMF system from ideality are smaller.

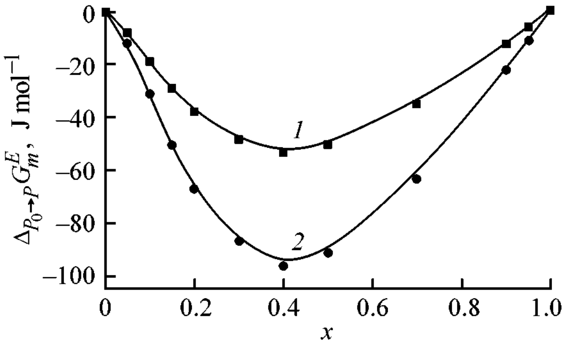

Fig. 3. Composition dependences of the excess molar Gibbs energy of water–DMF mixtures at 278.15 K and pressures of (*1*) 50 and (*2*) 100 MPa.

The $\Delta_{P_0-P} G_m^E$ values are also negative and, at a constant pressure, pass through a minimum at x ~0.35–0.45 (Fig. 3). As the pressure is increased, $\Delta_{P_0-P} G_m^E$ decreases, i.e., the pressure exerts a stabilizing effect on the water–DMF system.

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