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p–V_m–x Properties of Water–Dimethylformamide System at 288.15 K over the Pressure Range 0.1–100 MPa

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Abstract — The compressibility factors k $(\nu_{(p_0)} - \nu_{(p)})/\nu_{(p_0)})$ of water–dimethylformamide (DMF) binary mixtures are measured over the entire concentration range at 288.15 K and pressures of up to 100 MPa with a constant-volume piezometer. The specific and molar volumes in the water–DMF system are estimated as well as the isothermal compressibility coefficient s and excess and partial molar volumes of the system components. The composition dependence of the specific volume in the water–DMF system has extrema, its shape being pressure-dependent; such a dependence of the compressibility factor passes through a minimum; and the partial coefficient of the isothermal compressibility of water has an inversion point.

In the previous work [1] we reported on the compressibility factor k in the water–DMF system at 278.15 K and a pressure of up to 100 MPa. This work is a continuation of study of the volume properties of the indicated system, and here we report on the compressibility of the water–DMF binary mixtures over the entire concentration range at 288.15 K over the pressure range from 0.101 (atmospheric pressure) to 100 MPa.

The volume properties of the water–DMF system at 288.15 K were studied previously but only at atmospheric pressure [2], and we found no data in the literature on aqueous DMF solutions at this temperature and high pressures, except for the only work [3] in which the compressibility coefficient k of DMF is given at a pressure of up to 280 MPa.

Using data from [4] on the density at 0.101 MPa (Table 1) and k, in this work we estimated the specific (ν) and molar (V_m) volumes in the water–DMF system at a pressure of up to 100 MPa, and also the isothermal compressibility coefficients (β_T), partial coefficients for water ($\overline{\beta}_1$) and DMF ($\overline{\beta}_2$), excess volumes V_m^E, and partial molar volumes of water ($\overline{V}_1$) and DMF ($\overline{V}_2$) in the system water–DMF.

The compressibility coefficient k is written as

$$k = (\nu_{(p_0)} - \nu_{(p)})/\nu_{(p_0)}, \quad (1)$$

where $\nu_{(p_0)}$ and $\nu_{(p)}$ are the specific volumes in the H_2O–DMF system at atmospheric and experimental pressures, respectively. The k values obtained for every composition were then described by polynomial (2) (Table 2).

$$k = a_0 + a_1 p + a_2 p^2. \quad (2)$$

The $\overline{V}_1$ and $\overline{V}_2$ values (Table 3) were calculated by Eqs. (3) and (4), respectively.

$$\overline{V}_1 = V_m - x(\partial V_m/\partial x)_{p,T}, \quad (3)$$

$$\overline{V}_2 = V_m - (1 - x)(\partial V_m/\partial x)_{p,T}. \quad (4)$$

To obtain the derivatives $\partial V_m/\partial x$, the concentration dependences of the molar volumes of the mixtures were described by a cubic polynomial and then differentiated.

The partial molar volumes of DMF in water at infinite dilution $\overline{V}_2^{\infty}$ were estimated from the apparent molar volumes Φ_{V_2} using Eq. (5).

$$\Phi_{V_2} = \frac{(\rho_1 - \rho_{mix})(1 - x)M_1}{x\rho_{mix}\rho_1} + \frac{M_2}{\rho_{mix}}, \quad (5)$$

where ρ_1 and ρ_{mix} are the densities of water and water–DMF mixtures, respectively; x is the DMF

Table 1. Density ρ (g cm^{-3}) of water–DMF mixtures (0.101 MPa, 288.15 K)[a]

x	ρ	x	ρ
0.00	0.99910	0.40	0.99326
0.05	1.00024	0.50	0.98536
0.10	1.00255	0.70	0.97063
0.15	1.00385	0.90	0.95857
0.20	1.00374	0.95	0.95602
0.30	0.99925	1.00	0.95366

[a] (x) Mole fraction of DMF; the same in Tables 2–5.

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Table 2. Coefficients of Eq. (2) and standard deviation s (k) for water–DMF system (288.15 K, 0.1–100 MPa)

x	$a_0 \times 10^4$	$a_1 \times 10^5$, MPa^{-1}	$-a_2 \times 10^6$, MPa^{-2}	s ($k \times 10^2$)
0.00	–0.33070	46.303	0.5826	0.0019
0.05	0.95966	39.319	0.4003	0.0001
0.10	0.42681	37.229	0.3980	0.0007
0.15	0.03626	37.227	0.4376	0.0005
0.20	1.4822	37.237	0.4321	0.0026
0.30	2.3160	39.322	0.4942	0.0013
0.40	1.1626	42.727	0.6357	0.0024
0.50	1.7395	45.539	0.7210	0.0049
0.70	2.5859	50.563	0.8559	0.0068
0.90	3.3243	55.238	0.9959	0.0077
0.95	3.3436	56.496	1.043	0.0091
1.00	3.2188	57.807	1.095	0.0099

mole fraction in the mixture; and M_1 and M_2, molecular weights of water and DMF, respectively. In calculations, the apparent molar volumes of DMF at all pressures in mixtures with $x \le 0.2$ was expressed in the form of Eq. (6).

$$\Phi_{V_2} = \Phi_{V_2}^{\infty} + b_V m, \quad (6)$$

where m is the reduced molal concentration of DMF in water, $\Phi_{V_2}^{\infty}$, limiting apparent molar volume at $m \to 0$, and b_V, the constant of proportionality (at infinite dilution, $\Phi_{V_2}^{\infty} \equiv \overline{V}_2^{\infty}$ [5]).

Basing on the results obtained, we also estimated the isothermal compressibility coefficients β_T (Table 4) and partial coefficients of the isothermal compressibility of water ($\bar{\beta}_1$) and DMF ($\bar{\beta}_2$) using Eqs. (7)–(9).

$$\beta_T = -1/v(\partial V/\partial p)_{x,T} = -1/V_m(\partial V_m/\partial p)_{x,T}, \quad (7)$$

$$\bar{\beta}_1 = -1/\overline{V}_1(\partial \overline{V}_1/\partial p)_{x,T}, \quad (8)$$

$$\bar{\beta}_2 = -1/\overline{V}_2(\partial \overline{V}_2/\partial p)_{x,T}. \quad (9)$$

Table 3. Partial molar volumes of water ($\overline{V}_1$, cm^3 mol^{-1}) and DMF ($\overline{V}_2$, cm^3 mol^{-1}) in water–DMF system (288.15 K, 0.1–100 MPa)

x	Parameter	p, MPa						
		0.101	10.0	20.0	40.0	60.0	80.0	100.0
0.00	$\overline{V}_1$	18.03	17.95	17.87	17.71	17.57	17.43	17.30
0.00	$\overline{V}_2$	73.11	71.33	73.06	73.05	72.96	72.84	72.68
0.05	$\overline{V}_1$	18.09	18.02	17.94	17.80	17.66	17.53	17.41
0.05	$\overline{V}_2$	71.51	72.07	71.14	70.80	70.48	70.19	69.95
0.10	$\overline{V}_1$	18.04	17.97	17.90	17.76	17.63	17.50	17.39
0.10	$\overline{V}_2$	72.29	72.70	71.85	71.43	71.04	70.70	70.43
0.15	$\overline{V}_1$	17.92	17.85	17.79	17.66	17.54	17.42	17.31
0.15	$\overline{V}_2$	72.97	73.26	72.45	71.97	71.52	71.12	70.83
0.20	$\overline{V}_1$	17.76	17.70	17.64	17.53	17.41	17.30	17.20
0.20	$\overline{V}_2$	73.56	74.21	72.97	72.43	71.94	71.49	71.17
0.30	$\overline{V}_1$	17.42	17.37	17.33	17.24	17.15	17.06	16.97
0.30	$\overline{V}_2$	74.57	74.92	73.88	73.24	72.67	72.14	71.77
0.40	$\overline{V}_1$	16.99	16.96	16.94	16.88	16.82	16.76	16.69
0.40	$\overline{V}_2$	75.32	75.47	74.54	73.85	73.21	72.64	72.22
0.50	$\overline{V}_1$	16.57	16.57	16.56	16.54	16.51	16.48	16.43
0.50	$\overline{V}_2$	75.89	76.07	75.07	74.33	73.65	73.04	72.59
0.70	$\overline{V}_1$	15.74	15.78	15.81	15.85	15.87	15.89	15.88
0.70	$\overline{V}_2$	76.52	76.21	75.65	74.87	74.17	73.53	73.02
0.90	$\overline{V}_1$	15.15	15.19	15.24	15.30	15.33	15.34	15.34
0.90	$\overline{V}_2$	76.66	76.21	75.79	75.00	74.30	73.65	73.09
0.95	$\overline{V}_1$	15.08	15.12	15.16	15.21	15.23	15.23	15.21
0.95	$\overline{V}_2$	76.65	76.20	75.78	74.99	74.29	73.64	73.06
1.00	$\overline{V}_1$	15.04	15.07	15.11	15.14	15.14	15.13	15.10
1.00	$\overline{V}_2$	76.66	76.20	75.77	74.98	74.27	73.62	73.02

Table 4. Isothermal compressibility coefficient ($\beta_T \times 10^{10}$, Pa^{-1}) in water–DMF system (288.15 K, 0.1–100 MPa)

x	p, MPa						
	0.101	10.0	20.0	40.0	60.0	80.0	100.0
0.00	4.666	4.554	4.444	4.231	4.026	3.830	3.656
0.05	4.008	3.917	3.829	3.666	3.520	3.389	3.274
0.10	3.757	3.681	3.605	3.456	3.311	3.171	3.033
0.15	3.756	3.665	3.576	3.408	3.252	3.109	2.979
0.20	3.865	3.737	3.620	3.417	3.252	3.119	2.994
0.30	4.128	3.971	3.828	3.584	3.390	3.238	3.096
0.40	4.413	4.246	4.090	3.814	3.579	3.384	3.235
0.50	4.747	4.547	4.360	4.027	3.749	3.528	3.371
0.70	5.329	5.075	4.840	4.429	4.096	3.836	3.650
0.90	5.854	5.555	5.278	4.796	4.405	4.103	3.885
0.95	6.001	5.684	5.391	4.883	4.475	4.161	3.940
1.00	6.149	5.814	5.505	4.971	4.544	4.218	3.991

Table 5. Excess molar volume ($-V_m^E$, $cm^3\,mol^{-1}$) in water–DMF system (288.15 K, 0.1–100 MPa)

x	p, MPa						
	0.101	10.0	20.0	40.0	60.0	80.0	100.0
0.05	0.198	0.181	0.162	0.129	0.102	0.079	0.059
0.10	0.430	0.399	0.367	0.313	0.267	0.228	0.191
0.15	0.647	0.607	0.568	0.499	0.440	0.389	0.343
0.20	0.832	0.785	0.740	0.660	0.591	0.531	0.479
0.30	1.051	0.997	0.945	0.853	0.775	0.709	0.649
0.40	1.159	1.102	1.049	0.954	0.876	0.796	0.747
0.50	1.107	1.054	1.003	0.913	0.837	0.770	0.713
0.70	0.779	0.740	0.700	0.632	0.578	0.532	0.490
0.90	0.277	0.262	0.244	0.216	0.196	0.179	0.163
0.95	0.139	0.132	0.123	0.107	0.097	0.089	0.080

The derivatives $\partial\overline{V}_1/\partial p$ and $\partial\overline{V}_2/\partial p$ were obtained by differentiation of the square polynomials describing the composition dependences of the partial molar volumes of the system components.

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

$$V_m^E = V'_m - V'^{\mathrm{id}}_m. \quad (10)$$

Here the ideal molar volume V'_m was calculated from the molar volumes of water (V_{1m}) and DMF (V_{2m}) by Eq. (11).

$$V'^{\mathrm{id}}_m = V_{1m} - x(V_{1m} - V_{2m}). \quad (11)$$

The composition dependences of the specific volume in the water–DMF system at 288.15 K (Fig. 1) and various pressures have extrema, as at 278.15 K [1], despite the fact that at 288.15 K the structure of water is more distorted because of thermal motion of molecules [6, 7]. The minimum at $x \sim 0.2$ is due to both the formation of water–DMF associates [8] and the distortion of the structure of water itself with increasing DMF concentration.

As DMF is added to water, the CH_3 groups of DMF are arranged in the cavities of the tetrahedral network of the structure of water. In this case, on the one hand, the water structure becomes distorted, and on the other hand, the structure of the H_2O–DMF binary mixture is somewhat stabilized. The extremum at $x \sim 0.05$ in the composition dependences of the specific volume reflects the resultant of these competing processes.

Increasing external pressure results in distortion of the hydrogen bonds in the water structure, with the deformation of the cavity network being stronger at higher pressures, resulting in decreased tetrahedral ordering. Therefore, at low DMF concentrations in water, the stabilizing effect due to insertion of the methyl groups of DMF into the cavities of the tetrahedral network of the water structure is weaker than at lower pressures. At increased pressure, as seen from Fig. 1, after addition of the first DMF molecules to water, the system forms a less compact structure, i.e., the specific volume increases. However, with increasing DMF concentration, the stabilizing effect of DMF contributes more and more significantly, which, in turn, provides compaction of the water structure, decreasing the specific volume. Figure 1 shows that this mechanism is dominant up to x ~0.2, after which the effect caused by distortion of the network of hydrogen bonds starts to prevail.

Table 4 shows that the dependence β_T–x at constant pressure passes through a minimum at x ~0.15–0.2. As known, the compressibility of aqueous solutions reflects the relative contributions of various interparticle interactions [9]. The β_T can be expressed as a sum of the vibrational and configuration terms: $\beta_T = \beta_{vib} + \beta_{conf}$, where β_{vib} is the term associated with thermal vibrations of molecules in the mixture and β_{conf} is the configuration term caused by the distortion of the equilibrium between the structure of the solution and a more compact structure formed through breakdown and (or) deformation of the H bonds under the action of various factors. Increasing pressure decreases the free volume as well as the average interparticle dstance in both the loose and more compact structures realized in the water–DMF system, thus decreasing the vibrational contribution to the compressibility. Furthermore, increasing pressure shifts the structure equilibrium in the solution toward more compact structure, i.e., decreases the configuration contribution also. Therefore, the compressibility of the solutions should decrease with increasing pressure, which is consistent with the experiment.

Data on the partial coefficients of the isothermal compressibility of the components in the binary system (Fig. 2) show that $\overline{\beta}_2$ gives a monotonically changing contribution to β_T over the entire composition range, whereas the behavior of $\overline{\beta}_1$ is more complicated, demonstrating an inversion point at x ~0.3 ($\overline{\beta}_1$ is pressure-independent) and also the range of compositions where $\overline{\beta}_1 < 0$. Finally, the results reveal a complex nature of the effect of the water structure on the compression resistance in the water–DMF system.

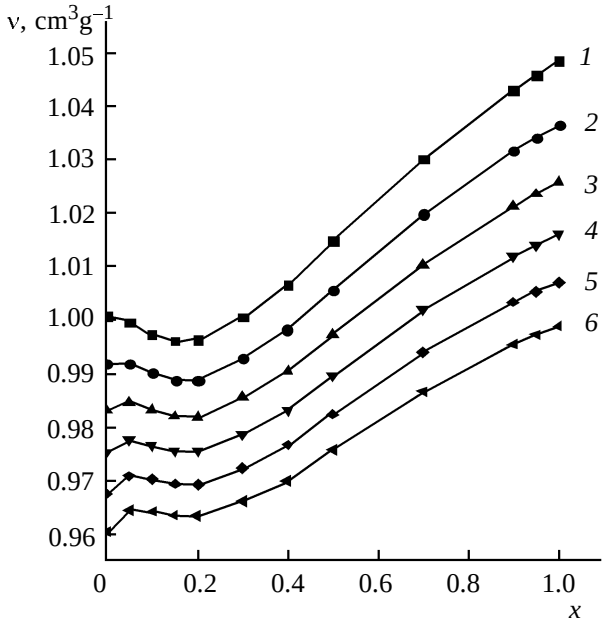

Fig. 1. Specific volume ν in water–DMF system as a function of the DMF mole fraction x at 288.15 K and various pressures. p (MPa): (*1*) 0.1, (*2*) 20, (*3*) 40, (*4*) 60, (*5*) 80, and (*6*) 100.

Table 3 shows that the composition dependence of $\overline{V}_1$ has a maximum. At small DMF concentrations (up to x ~0.05), $\overline{V}_1$ increases and then decreases with further increasing x. The position of the maximum at x ~0.05 remains unchanged with increasing pressure over the entire experimental range. At $x > 0.5$, the $\overline{V}_1$–x curve passes through an inversion point ($\overline{V}_1$ does not depend on the pressure). Table 3 shows that $\overline{V}_1^{\infty}$ is practically independent of the pressure. Such a behavior of the dependence $\overline{V}_1^{\infty}$–p can be attributed to the compensating effect of the pressure on the electrostriction component of $\overline{V}_1$ [10]. The $\overline{V}_2$ in the system water–DMF monotonically decreases with increasing pressure at constant composition (except for $\overline{V}_2^{\infty}$). With increasing DMF concentration at constant p, $\overline{V}_2$ initially increases at x ~0–0.05, then passes through a minimum at x ~0 .05, and, finally, monotonically increases.

Table 5 shows that mixing water with DMF is accompanied by compaction ($V_m^E < 0$), and the dependence V_m^E–x at constant pressure passes through a minimum at x ~0.35–0.4. Increase in the pressure does not change the position of the minimum, but only increases the excess molar volume of the mixture, characterizing the system H_2O–DMF at higher pressures as a system having a lower deviation from ideality.

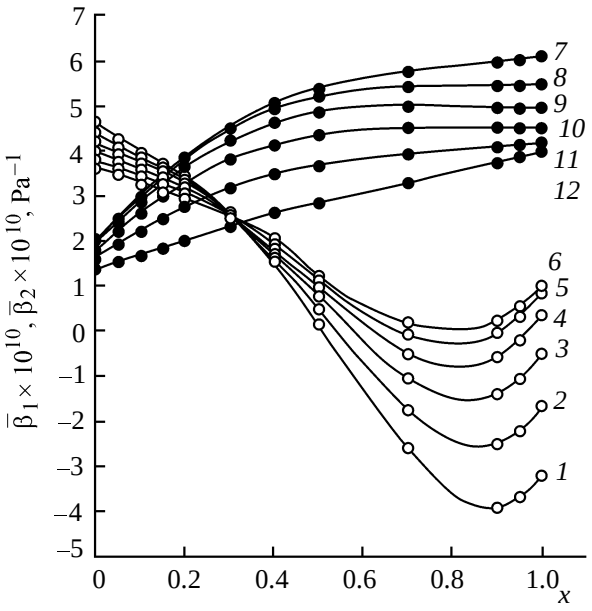

Fig. 2. Partial coefficients of isothermal compressibility of (*1*–*6*) water ($\bar{\beta}_1$) and (*7*–*12*) DMF ($\bar{\beta}_2$) in water–DMF system as functions of the DMF mole fraction x at 288.15 K and various pressures. p (MPa): (*1*, *7*) 0.1, (*2*, *8*) 20, (*3*, *9*) 40, (*4*, *10*) 60, (*5*, *11*) 80, and (*6*, *12*) 100.

EXPERIMENTAL

In the work we used freshly double-distilled water. DMF (chemically pure grade) was vacuum-distilled twice and stored over molecular sieves (4 Å). The residual moisture content in DMF was determined by Fischer titration to be no more than 10^{-2} wt%.

Aqueous DMF solutions were prepared gravimetrically to within 10^{-3} wt% using degassed solvents. In the work we studied 12 compositions with x 0.0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9, 0.95, and 1.0 (x is the DMF mole fraction).

The densities of water–DMF binary mixtures were measured at the atmospheric pressure on an Anton Paar DMA-60/602 vibration densimeter to within 10^{-5} g cm^{-3}.

The compressibility coefficients k were measured on an experimental setup described in [11, 12] using a constant-volume piezometer not relieved of pressure. The volume of the piezometer at 288.15 K was 487.5 cm^3. The temperature was controlled to within 0.01 K, and the pressure was measured to within 0.05%.

REFERENCES

1. Egorov, G.I., Syrbu, A.A., and Kolker, A.M., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 7, p. 1386.
2. Afanas'ev, Yu.N., *Candidate Sci. (Chem.) Dissertation*, Ivanovo, 1982.
3. Easteal, A.J. and Woolf, L.A., *J. Chem. Soc., Faraday Trans. 1*, 1985, vol. 81, no. 11, p. 2821.
4. Egorov, G.I., Syrbu, A.A., and Kolker, A.M., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 5, p. 744.
5. Belousov, V.P. and Panov, M.Yu., *Termodinamika vodnykh rastvorov neelektrolitov* (Thermodynamics of Aqueous Nonelectrolyte Solutions), Moscow: Khimiya, 1983.
6. Samoilov, O.Ya., *Struktura vodnykh rastvorov elektrolitov i gidtratatsiya ionov* (Structure of Aqueous Electrolyte Solutions and Hydration of Ions), Moscow: Akad. Nauk SSSR, 1957.
7. Zatsepina, N,G., *Fizicheskie svoistva i struktura vody* (Physical Properties and Structure of Water), Moscow: Mosk. Gos. Univ., 1987.
8. Bushuev, Yu.G. and Korolev, V.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 4, p. 592.
9. Eisenberg, D.S. and Kauzmann, W., *The Structure and Properties of Water*, Oxford: Clarendon, 1969.
10. Hamann, S.D., *High-Temp.–High. Press.*, 1992, vol. 24, no. 3, p. 489.
11. Egorov, G.I., Syrbu, A.A., and Kolker, A.M., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1998, vol. 41, no. 2, p. 59.
12. Egorov, G.I., Gruznov, E.L., Kolker, A.M., and Krestov, G.A., *Razvitie tekhnologii promyshlennykh sinteticheskikh sverkhtverdykh materialov i sozdanie oborudovaniya* (Advances in Technology of Industrial Synthetic Extra-Hard Materials and Development of Equipment), Minsk: Beloruss. Gos. Univ., 1990, p. 61.