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Densities and Volumetric Properties of Ethylene Glycol + Dimethylsulfoxide Mixtures at Temperatures of (278.15 to 323.15) K and Pressures of (0.1 to 100) MPa

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Densities, ρ, and compressibility coefficients, $k = (v_o - v)/v_o$, of ethylene glycol (1) + dimethylsulfoxide (2) mixtures were measured over the whole concentration range at pressures of (0.1 to 100) MPa and temperatures of (278.15 to 323.15) K. Excess molar volumes, isothermal compressibility, and thermal isobaric expansivity coefficients as well as thermal pressure coefficients were calculated. It was revealed that concentration dependences of specific volumes, v, at some state parameters passed a minimum. The shift of minimum position to molar fraction $x_2 = 0.5$ was observed with increasing pressure and decreasing temperature. The negative excess molar volumes, V_m^E, indicated a compression of EG (1) + DMSO (2) systems when mixing. Composition dependences of isothermal compressibility, κ_T, and thermal isobaric expansivity coefficients, α, as well as thermal pressure coefficients, β, were near-linear. Both increasing and decreasing of κ_T and β values were observed with x_2 increase depending on temperature and pressure magnitudes within the range of state parameters investigated.

Introduction

The solvents such as amphiprotic ethylene glycol (EG) and aprotic dimethylsulfoxide (DMSO) were chosen because of their wide use in applied chemistry and participation in biological processes. Both of these solvents are widely used for cryopreservation of living organisms as they are endocellular cryoprotectors; i.e., they are able to penetrate inside the cell. Such cryoprotectors prevent ice crystal generation due to H-bond formation with water molecules.

Ethylene glycol ($\varepsilon = 34.57$, $\mu = 2.28$ D at 293 K, and freezing temperature of 260.55 K[1,2]) is able to form the water-like H-bond network. Unlike water, these bonds can be both inter- and intramolecular thus giving a more homogeneous and therefore less mobile network.[3−7] An intramolecular H-bond in an EG molecule is weaker than an intermolecular H-bond because of the small distance between oxygen atoms and significant tension of such molecule conformation. The formation of intramolecular H-bonds in EG results in the decrease of the number of intermolecular H-bonds per one molecule as compared with water.[6,7] In contrast to vapor in liquid EG at normal conditions, a finite fraction of trans-conformers stabilized by two intermolecular H-bonds is in equilibrium with gauche-conformers.[6−8]

Dimethylsulfoxide ($\mu = 4.30$ D, $\varepsilon = 48.9$ at 293 K, and freezing temperature of 291.60 K[1,2,9]) is a highly polar solvent not forming the space H-bonds network and tends toward self-association.[10−12] The molecular dynamics (MD) simulations[13,14] demonstrated that in liquid DMSO the weak H-bonds C−H···O=S are formed. With a pressure increase,[15] in DMSO the strong bounded molecular aggregates are formed resulting in more structural order of the liquid. Such molecular aggregate formation was due to both the intermolecular distances shortening and larger coincidence of vibrational motions of neighboring molecules. It was supposed that liquid DMSO structure was similar to the solid one.[16] Moreover, the DMSO molecule is able to reveal the solvophobic effects in systems with a H-bond network.[17−19]

In EG−DMSO liquid mixtures, the formation of two structures is possible.[20] The first one is when the EG gauche-conformer is stabilized by one, relatively weak, intramolecular H-bond and one intermolecular hydrogen bond with DMSO. The second structure is realized when the trans-conformer is free to form two, stronger, intermolecular hydrogen bonds with DMSO. This may account for the apparent preference of EG molecules to assume a trans-conformation in DMSO.[20] MD simulation in the gas phase[21] has shown the formation of complexes with structure of EG:DMSO = 1:1 stabilized by three H-bonds including two bonds formed by CH_3 groups.

Densities at 298.15 K[22] and 308.15 K[23] were previously measured at atmospheric pressure for EG−DMSO systems. The values of excess molar volumes V_m^E were negative, and $V_m^E = f(x)$ function passed the minimum at $x_2 = 0.5$. Moreover, the mixing enthalpies, H_m^E, of the EG−DMSO system were measured at the same pressure and temperature.[24] It was shown that H_m^E values were negative, and the minimum position corresponded to $x_2 = 0.3$.

Unfortunately, we have not found any data on EG−DMSO system studies under high pressure though the influence of the latter on the individual solvents has been investigated.[15,25−31]

The present work is a part of our in-process investigation of volumetric properties of binary systems as a function of composition, temperature, and pressure.[32−36]

Experimental Section

Reagents. For the solvent purification, we used procedures developed on the basis of recommendations given in refs 37 and 38.

Ethylene glycol (99.8 % purity) was purified by vacuum distillation (boiling temperature was 349 K), collecting the

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Table 1. Experimental and Literature Data on the Density Values of Pure EG and DMSO at Atmospheric Pressure

	T	$\rho/(\text{g}\cdot\text{cm}^{-3})$	
solvent	K	experimental	literature
ethylene glycol	278.15	1.12377	1.12371;[45] 1.1222;[46] 1.124265;[47] 1.123664;[48]
	288.15	1.11683	1.11676;[45] 1.1156;[46] 1.117244;[47] 1.116906;[48] 1.11710;[49] 1.11674;[50]
	298.15	1.10983	1.10980;[22] 1.10977;[45] 1.1086;[46] 1.110212;[47] 1.109913;[48] 1.11006;[50] 1.1094;[51] 1.10988;[52] 1.10999;[53] 1.1085;[54] 1.10950;[55] 1.1099 (298.2 K);[56] 1.10991;[57]
	308.15	1.10281	1.10307;[23] 1.10272;[45] 1.1019;[46] 1.103164;[47] 1.103089;[48] 1.10268;[49] 1.10288;[50] 1.10289;[52] 1.10294;[53] 1.10250;[55] 1.10282;[58]
	323.15	1.09212	1.09202;[45] 1.092946;[48] 1.0923 (323.2 K);[56] 1.09105;[58]
dimethylsulfoxide	298.15	1.09536	1.09530;[22] 1.0960;[59] 1.09629;[60] 1.09543;[61] 1.0956;[62] 1.09533;[63] 1.09539;[64] 1.09637;[67] 1.0954;[68] 1.09560[69]
	308.15	1.08536	1.08548;[23] 1.08641;[60] 1.0856;[62] 1.08560;[65] 1.0847;[66] 1.08647;[67] 1.0870;[68]
	323.15	1.07028	1.0698;[66] 1.07159;[67] 1.07075;[70] 1.07030;[71]

Table 2. Comparison of Literature and Our Experimental Data on Compressibility Coefficients for Individual Solvents

	T	k^a	
solvent	K	experimental	literature
ethylene glycol	298.15	1.679 (50 MPa); 3.115 (100 MPa)	1.692 (50 MPa);[29] 3.13 (100 MPa);[29] 3.135 (101.3 MPa);[30] 3.03 (98.1 MPa)[31]
	303.15		2.93 (101.3 MPa)[25]
	318.15		1.810 (50 MPa);[29] 3.331 (100 MPa)[29]
	323.15	1.854 (50 MPa); 3.409 (100 MPa)	
dimethylsulfoxide	298.15	2.449 (50 MPa)	2.404 (50 MPa);[26]
	308.15	2.670 (50 MPa); 4.522 (100 MPa)	2.51 (50 MPa);[26] 5.00 (100 MPa);[26] 2.65 (50 MPa);[27] 5.31 (100 MPa)[27]
	323.15	2.917 (50 MPa); 4.716 (100 MPa)	2.38 (50 MPa);[15] 4.30 (100 MPa);[15] 2.63 (50 MPa);[26] 5.27(100 MPa);[26] 2.75 (50 MPa);[27] 5.46 (100 MPa);[27]

[a] k values from refs 15, 26, and 27 for DMSO were determined by the Tait equation.

medium fraction. This fraction was dried with sodium sulfate calcinated and after decantation was repeatedly distilled at $T \approx$ 349 K.

Dimethylsulfoxide (99.95 % purity) after chilling at 288 K was dehydrated with NaOH for 24 h and repeatedly doubly vacuum distilled at 315 K collecting the medium fraction.

The purified and dried solvents were stored in a vacuum with molecular sieves (4 Å). The water mass fraction in the solvents was determined by the K. Fisher method and did not exceed 0.02 %, which was equal to $x(\text{H}_2\text{O}) = 6\cdot10^{-5}$ in EG and $x(\text{H}_2\text{O}) = 5\cdot10^{-5}$ in DMSO. The comparison of densities and compressibility coefficients of purified solvents used in the work with literature data is presented in Tables 1 and 2, accordingly. A reasonable agreement of our experimental results with literature data[22,23,45−71] was found. However, the densities from ref 46 are lower and the data from ref 60 are higher in all temperature ranges.

The mixtures under investigation were prepared by the gravimetric method, with balance error of $\pm\, 5\cdot10^{-5}$ g, from degassed solvents avoiding the contact with atmospheric air. Uncertainty of mole fraction values was less than $2\cdot10^{-5}$.

Density Measurements. The densities of pure solvents and their mixtures at atmospheric pressure ($p = 0.101$ MPa) were measured by a vibration densimeter ("Anton Paar" DMA-4500). Each density measurement was preceded by the densimeter calibration with dry air and doubly distilled water. For density determination, only freshly made solutions were used. The temperature was kept within 0.01 K, and density values repeatability was of $1\cdot10^{-5}$ g$\cdot$cm^{-3}. The uncertainty of density measurements did not exceed $5\cdot10^{-5}$ g$\cdot$cm^{-3}. The filling of the densimeter with solution under study was realized by self-flowing without contact with air. Every solution was preheated above the measurement temperature to prevent bubbling. In total, the densities of 26 mixtures at temperatures of (278.15, 288.15, 298.15, 308.15, and 323.15) K were measured. The average values of five density measurements for each solution were calculated, and results were presented in Table 3.

Compressibility Measurements. Compressibility coefficients were measured with a device described earlier[39−41] using constant volume piezometers unloaded from external pressure. A schematic presentation of this device is given in Figure 1. The empty modified piezometer[35,41] was put into the hermetical loading container which was vacuumized, and the solvent was sucked in the piezometer thus avoiding the solvent contact with air. Then this loading vessel with piezometer filled, the empty high-pressure vessel with mercury, and the vessel with water were placed in a liquid thermostat. After thermostatting of all items, the piezometer was quickly pulled from the loading vessel and placed into the high-pressure vessel, and then water was added as a hydraulic fluid. Thus, the same temperatures of all components of the high-pressure vessel were realized preventing the untimely ingress of mercury in the piezometer. Moreover, the contact of water in the high-pressure vessel with the solvent under investigation in the piezometer became impossible because the piezometer capillary was immersed in the mercury before water addition. Pressurization of the high-pressure vessel was realized without removing it from the thermostat to prevent temperature disturbance. Then pressure was built up with press. The system was kept under required pressure for 5 min, and the pressure release was started. The rate of pressure buildup and release was rather low to ensure the isothermality of the process. After depressurization of the high-pressure vessel, the mercury locked in the piezometer was withdrawn and weighted with an uncertainty of $5\cdot10^{-5}$ g.

The temperature in the thermostat was kept with an accuracy of 0.01 K. The pressure was produced and measured with a pressure gauge with a maximum uncertainty of $\pm$ 0.02 MPa. At 298.15 K, the piezometer and capillarity volumes were 39.9686 cm^3 and 0.0019 cm^3, accordingly. The repeatability of k values in a set of four measurements was within the limit of

Table 3. Densities, ρ, for Ethylene Glycol (1) + Dimethylsulfoxide (2) Mixtures at Atmospheric Pressure and at Different Temperatures

	$\rho/(\text{g}\cdot\text{cm}^{-3})$				
x_2	T/K = 278.15	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 323.15
0.00000	1.12377	1.11683	1.10983	1.10281	1.09212
0.00452	1.12378	1.11683	1.10983	1.10278	1.09205
0.00721	1.12381	1.11684	1.10982	1.10276	1.09203
0.01811	1.12389	1.11688	1.10982	1.10273	1.09195
0.03033	1.12398	1.11691	1.10981	1.10269	1.09183
0.04027	1.12405	1.11694	1.10981	1.10263	1.09172
0.07007	1.12418	1.11698	1.10974	1.10245	1.09139
0.10969	1.12431	1.11695	1.10955	1.10212	1.09085
0.14083	1.12441	1.11693	1.10942	1.10188	1.09044
0.19339	1.12441	1.11674	1.10906	1.10133	1.08961
0.23396	1.12434	1.11655	1.10872	1.10086	1.08896
0.32442	1.12405	1.11595	1.10782	1.09965	1.08733
0.37635	1.12376	1.11549	1.10721	1.09889	1.08633
0.44291	1.12328	1.11480	1.10629	1.09776	1.08493
0.48917	1.12288	1.11425	1.10560	1.09694	1.08392
0.56538	1.12214	1.11329	1.10444	1.09556	1.08223
0.62977	1.12126	1.11227	1.10324	1.09418	1.08061
0.69463	1.12052	1.11132	1.10213	1.09291	1.07907
0.81422	–	1.10913	1.09960	1.09007	1.07574
0.86700	–	–	1.09837	1.08868	1.07415
0.92660	–	–	1.09709	1.08725	1.07250
0.95768	–	–	1.09636	1.08643	1.07155
0.98362	–	–	1.09574	1.08576	1.07076
0.99199	–	–	1.09554	1.08553	1.07050
0.99681	–	–	1.09542	1.08539	1.07035
1.00000	–	–	1.09536	1.08536	1.07028

$5\cdot10^{-5}$, and the maximum total error for k values determination did not exceed $1\cdot10^{-4}$.

The compressibility coefficient is defined by

$$k = (v_o - v)/v_o = (\rho - \rho_o)/\rho \tag{1}$$

where v_o, ρ_o and v, ρ are specific volumes and densities at atmospheric pressure ($p_o = 0.101$ MPa) and pressure p.

The values of k were calculated by the equation

$$k = 1 - \frac{(V_{\text{piez}} - V_{\text{cap}})(1 - k_{\text{glass}}) - m_{\text{Hg}}(1 - k_{\text{Hg}})/\rho_{\text{Hg}}}{V_{\text{piez}}} \tag{2}$$

where V_{piez} is the piezometer volume; V_{cap} is the capillary volume; m_{Hg} is the mass of mercury locked in the piezometer; ρ_{Hg} is the density of mercury at a temperature of experiment and atmospheric pressure; and k_{glass} and k_{Hg} are the compressibility coefficients of silica glass and mercury at pressure and temperature under question. The V_{piez} and k_{glass} values were calculated with state equations for mercury and water[42−44] for every p,T-parameter of experiment.

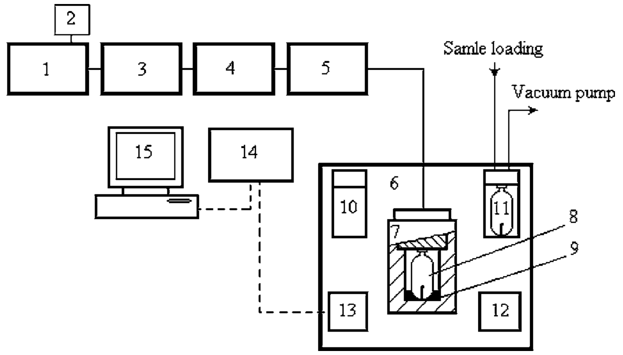

Figure 1. Schematic presentation of a device for measurement of compressibility coefficients: 1, oil pump; 2, digitized Bourdon gauge; 3, high-pressure screw pump; 4, pressure dead weight gauge; 5, liquid separator with Teflon diaphragm; 6, liquid thermostat; 7, high-pressure vessel; 8, modified Adams piezometer; 9, mercury; 10, vessel with water; 11, container with piezometer; 12, reference mercury thermometer with graduation scale of 0.01 K; 13, platinum resistance thermometer; 14, control unit; 15, computer. The continuous lines represent hydraulic connections, and the dashed lines represent electrical connections.

The measured compressibility coefficients of ethylene glycol + dimethylsulfoxide mixtures are listed in the Table 4.

Results and Discussion

Excess molar volumes, V_{m}^{E}, were calculated using experimental data by the equation

$$V_{\text{m}}^{\text{E}} = V_{\text{m}} - (1 - x_2)V_1^{\text{o}} - x_2V_2^{\text{o}} = (1 - x_2)M_1(1/\rho - 1/\rho_1) + x_2M_2(1/\rho - 1/\rho_2) \tag{3}$$

where V_{m} is a mixture molar volume; M_1, V_1^{o}, ρ_1 and M_2, V_2^{o}, ρ_2 are molar masses, molar volumes, and densities of ethylene glycol and dimethylsulfoxide, accordingly; ρ is the mixture density; and x_2 is DMSO molar fraction. The uncertainty of excess molar volumes determination was $\pm$ 0.02 $\text{cm}^3\cdot\text{mol}^{-1}$.

Isothermal compressibility coefficients, κ_{T}

$$\kappa_{\text{T}} = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,x} = \left(\frac{\partial \ln \rho}{\partial p}\right)_{T,x} \tag{4}$$

were calculated from the pressure dependences of mixture densities over the whole range of compositions and temperatures studied. Every such dependence was presented as a polynomial of the second order and differentiated. The results obtained are presented in the Supporting Information (Table S1).

Thermal isobaric expansivities coefficients, α

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_{p,x} = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{p,x} \tag{5}$$

were calculated from the temperature dependences of mixture densities over the whole range of compositions and pressures

Table 4. Compressibility Coefficients, *k*, for the Ethylene Glycol (1) + Dimethylsulfoxide (2) Mixture at Temperatures of (278.15 to 323.15) K and Pressure of (0.1 to 100) MPa

		$k \cdot 10^2$ at p/MPa				
x_2	T/K	10.0	25.0	50.0	75.0	100.0
0.0000	278.15	0.344	0.832	1.571	2.243	2.892
	288.15	0.360	0.859	1.623	2.345	3.015
	298.15	0.372	0.889	1.679	2.425	3.115
	308.15	0.383	0.913	1.735	2.528	3.226
	323.15	0.399	0.962	1.854	2.711	3.409
0.0181	278.15	0.346	0.835	1.576	2.259	2.911
	288.15	0.359	0.868	1.642	2.352	3.027
	298.15	0.375	0.896	1.692	2.444	3.136
	308.15	0.388	0.924	1.753	2.551	3.251
	323.15	0.402	0.970	1.871	2.732	3.433
0.0403	278.15	0.348	0.840	1.590	2.278	2.933
	288.15	0.362	0.874	1.651	2.365	3.046
	298.15	0.377	0.903	1.710	2.471	3.152
	308.15	0.390	0.930	1.767	2.570	3.267
	323.15	0.405	0.981	1.894	2.761	3.462
0.0701	278.15	0.350	0.843	1.598	2.303	2.961
	288.15	0.364	0.879	1.667	2.396	3.075
	298.15	0.383	0.912	1.728	2.510	3.184
	308.15	0.382	0.931	1.784	2.598	3.301
	323.15	0.410	0.996	1.926	2.801	3.499
0.1097	278.15	0.354	0.849	1.612	2.333	2.996
	288.15	0.369	0.889	1.686	2.430	3.120
	298.15	0.370	0.922	1.748	2.544	3.226
	308.15	0.367	0.937	1.817	2.654	3.343
	323.15	0.415	1.016	1.965	2.852	3.550
0.1408	278.15	0.356	0.856	1.625	2.355	3.022
	288.15	0.371	0.895	1.703	2.456	3.155
	298.15	0.361	0.919	1.773	2.574	3.262
	308.15	0.361	0.943	1.834	2.689	3.390
	323.15	0.416	1.030	1.995	2.892	3.591
0.1934	278.15	0.357	0.862	1.647	2.389	3.066
	288.15	0.380	0.912	1.726	2.493	3.213
	298.15	0.342	0.924	1.808	2.627	3.332
	308.15	0.358	0.957	1.870	2.741	3.455
	323.15	0.424	1.057	2.049	2.960	3.659
0.2340	278.15	0.359	0.871	1.667	2.413	3.102
	288.15	0.385	0.929	1.756	2.519	3.248
	298.15	0.333	0.921	1.820	2.675	3.376
	308.15	0.351	0.969	1.904	2.784	3.508
	323.15	0.429	1.076	2.092	3.011	3.712
0.3244	278.15	0.362	0.892	1.715	2.467	3.174
	288.15	0.399	0.957	1.802	2.590	3.348
	298.15	0.335	0.945	1.872	2.770	3.481
	308.15	0.352	1.000	1.979	2.896	3.619
	323.15	0.442	1.124	2.184	3.128	3.830
0.3764	278.15	0.363	0.904	1.746	2.498	3.227
	288.15	0.402	0.973	1.840	2.635	3.402
	298.15	0.337	0.962	1.912	2.828	3.547
	308.15	0.342	1.015	2.023	2.960	3.688
	323.15	0.452	1.151	2.236	3.195	3.897
0.4429	278.15	0.363	0.919	1.785	2.538	3.288
	288.15	0.412	1.002	1.891	2.692	3.466
	298.15	0.346	0.985	1.962	2.906	3.634
	308.15	0.346	1.039	2.081	3.042	3.777
	323.15	0.465	1.185	2.304	3.277	3.982
0.4892	278.15	0.363	0.932	1.815	2.566	3.345
	288.15	0.417	1.016	1.921	2.732	3.511
	298.15	0.351	1.005	1.998	2.959	3.688
	308.15	0.345	1.053	2.121	3.101	3.837
	323.15	0.475	1.210	2.353	3.337	4.041
0.5654	278.15	0.364	0.954	1.864	2.612	3.430
	288.15	0.426	1.042	1.971	2.796	3.600
	298.15	0.376	1.039	2.060	3.054	3.782
	308.15	0.356	1.086	2.188	3.192	3.938
	323.15	0.489	1.253	2.433	3.437	4.142
0.6946	278.15	–	–	–	–	–
	288.15	0.436	1.075	2.048	2.903	3.755
	298.15	0.408	1.104	2.170	3.215	3.958
	308.15	0.409	1.156	2.309	3.358	4.107
	323.15	0.522	1.329	2.574	3.610	4.314
0.8142	278.15	–	–	–	–	–
	288.15	–	–	–	–	–
	298.15	0.447	1.168	2.281	3.373	4.122
	308.15	0.442	1.245	2.430	3.522	4.262
	323.15	0.558	1.404	2.708	3.771	4.471
0.9266	278.15	–	–	–	–	–
	288.15	–	–	–	–	–
	298.15	0.499	1.235	2.376	3.516	4.270
	308.15	0.525	1.335	2.559	3.685	4.410
	323.15	0.589	1.475	2.834	3.921	4.618
0.9836	278.15	–	–	–	–	–
	288.15	–	–	–	–	–
	298.15	0.525	1.264	2.429	–	–
	308.15	0.560	1.374	2.626	3.757	4.484
	323.15	0.609	1.513	2.898	3.998	4.693
1.0000	278.15	–	–	–	–	–
	288.15	–	–	–	–	–
	298.15	0.527	1.275	2.449	–	–
	308.15	0.572	1.389	2.670	3.798	4.522
	323.15	0.615	1.526	2.917	4.021	4.716

studied. The same procedure for data treatment as for κ_T was applied to the α value calculation. The results obtained are presented in the Supporting Information (Table S2).

Thermal pressure coefficients β were calculated by the equation

$$\beta = \left(\frac{dP}{dT}\right)_{V,x} = \left(\frac{\alpha}{\kappa_T}\right)_x \qquad (6)$$

where α and κ_T are the coefficients at the same state parameters.

The maximum uncertainties of κ_T, α, and β coefficients calculated were not in excess of $\pm\, 2 \cdot 10^{-5}$ MPa^{-1}, $\pm\, 3 \cdot 10^{-6}$ K^{-1}, and $\pm\, 0.15$ MPa$\cdot$K^{-1}, accordingly.

Composition dependences of the specific volume of EG−DMSO mixtures at pressures of (0.101 and 100) MPa and at different temperatures are shown in Figure 2. Values of specific volumes were calculated from eq 1. At some state parameters, these dependences have minima, which shift to the lower DMSO concentration with increasing temperature and to the higher DMSO concentrations with rising pressure. At atmospheric pressure, the minima are observed for the concentration dependences at (278.15 and 288.15) K only. With increasing pressure, the minima appear at higher temperatures also. We suppose that it can be connected, on one hand, with different V_m, α, and κ_T values of two structures probably existing in the EG−DMSO mixture (see in Introduction section). On the other hand, possibly in the mixture, the complex with conjectural composition of 1:1 forms, for all that.

As shown in Figure 3, $V_m^E = f(x_2)$ functions are negative over the whole concentration range and have minima at equimolar ratios of the components. Thus, the EG−DMSO mixture formation is accompanied by decreasing volume that is connected with breaking of the structures of initial components and formation of more effective system packing mainly due to H-bond formation between EG and DMSO. With rising pressure and decreasing temperature, V_m^E absolute values decrease like the weakening of EG−DMSO interactions is taking place. Seemingly, it could be connected with the fact that temperature and pressure have a greater influence on association processes in pure components as compared with intermolecular complex formation between EG and DMSO.

As can be seen from Figure 4a, the isothermal compressibility coefficients, κ_T, of EG−DMSO mixtures are steadily increasing

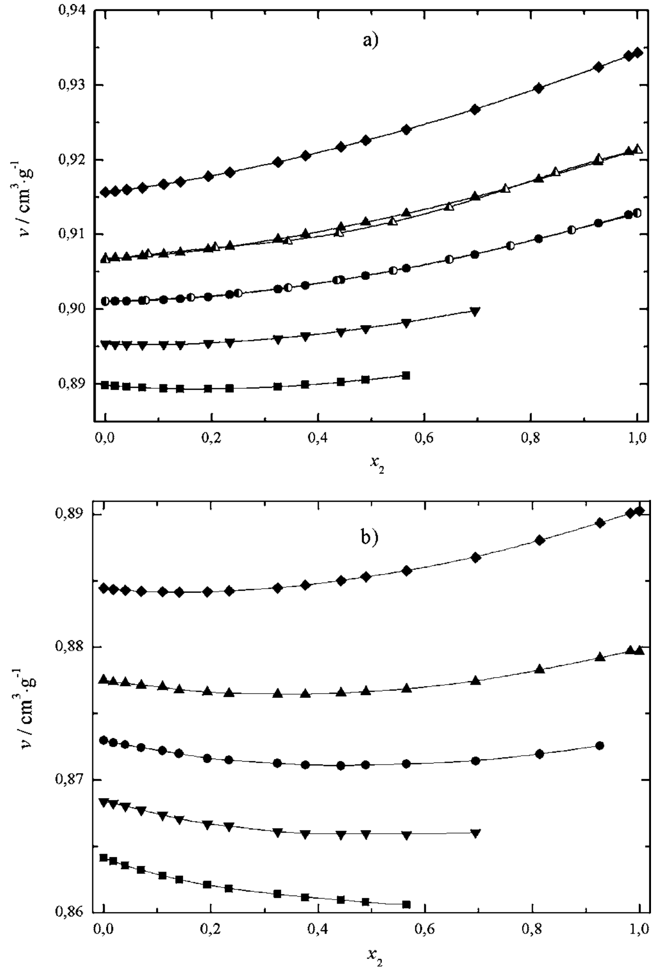

Figure 2. Specific volume v versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at pressures of 0.101 MPa (a) and 100 MPa (b) at different temperatures: ■, 278.15 K; ▼, 288.15 K; ●, 298.15 K; ▲, 308.15 K; ♦, 323.15 K; ◐, ref 22; ◭, ref 23.

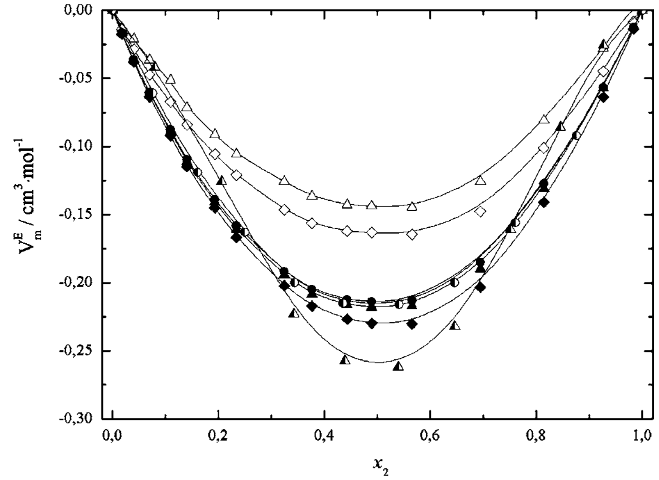

Figure 3. Excess molar volume V_m^E versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at pressures of 0.101 MPa (●, 298.15 K; ▲, 308.15 K; ♦, 323.15 K) and 100 MPa (△, 308.15 K; ◇, 323.15 K) at different temperatures; ◐, ref 22; ◭, ref 23.

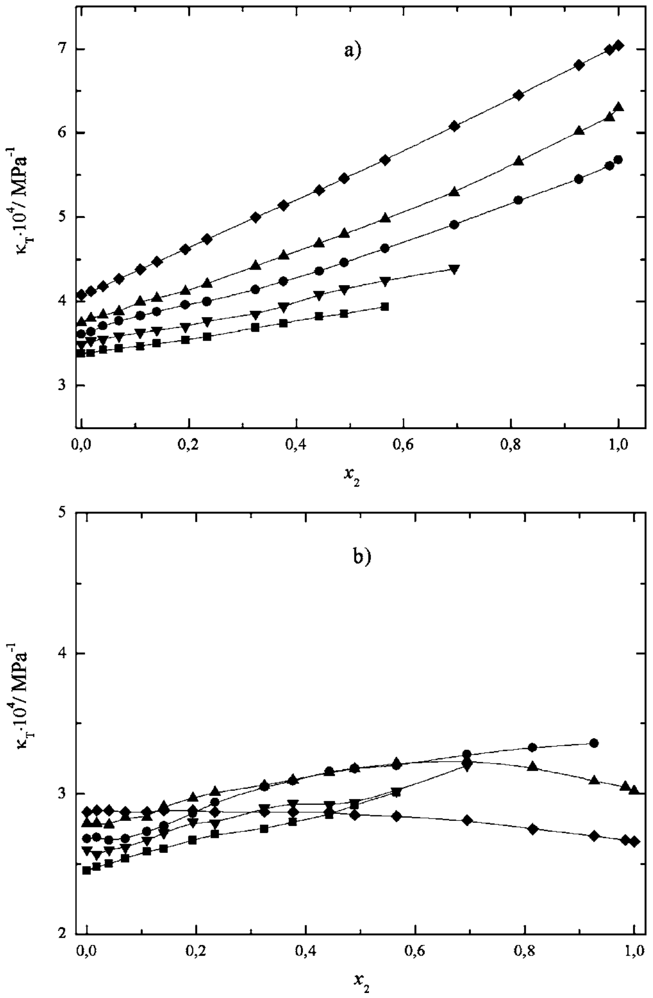

Figure 4. Isothermal compressibility coefficients κ_T versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at pressures of 0.101 MPa (a) and 100 MPa (b) at different temperatures: ■, 278.15 K; ▼, 288.15 K; ●, 298.15 K, ▲; 308.15 K; ♦, 323.15 K.

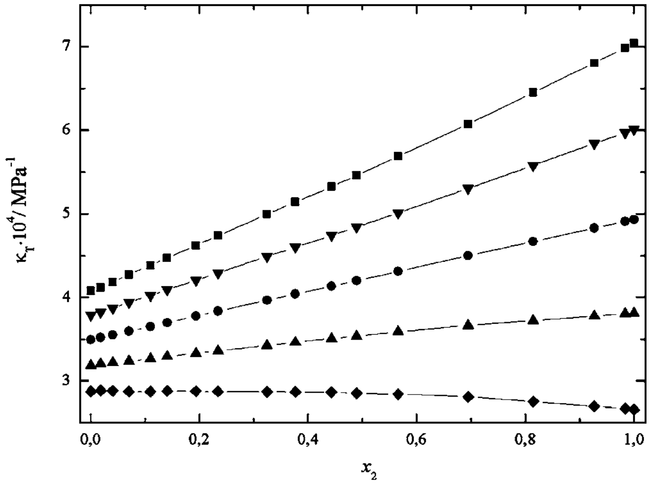

Figure 5. Isothermal compressibility coefficients κ_T versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at 323.15 K and at different pressures: ■, 0.101 MPa; ▼, 25 MPa; ●, 50 MPa; ▲, 75 MPa; ♦, 100 MPa.

with DMSO concentration growth at atmospheric pressure and at all temperatures studied. Pressure build-up from (0.1 to 100) MPa resulted in the changes of character of $\kappa_T = f(x_2)$ dependences at some temperatures (Figures 4b and 5). So at 308.15 K the dependence became extreme, and at 323.15 K κ_T values steadily decreased with rising DMSO concentration. Therefore, the increasing temperature at high pressure made the system less elastic.

The thermal isobaric expansivity coefficients, α, are steadily increasing with DMSO content growth at all temperatures and pressures studied (Figures 6 and 7).

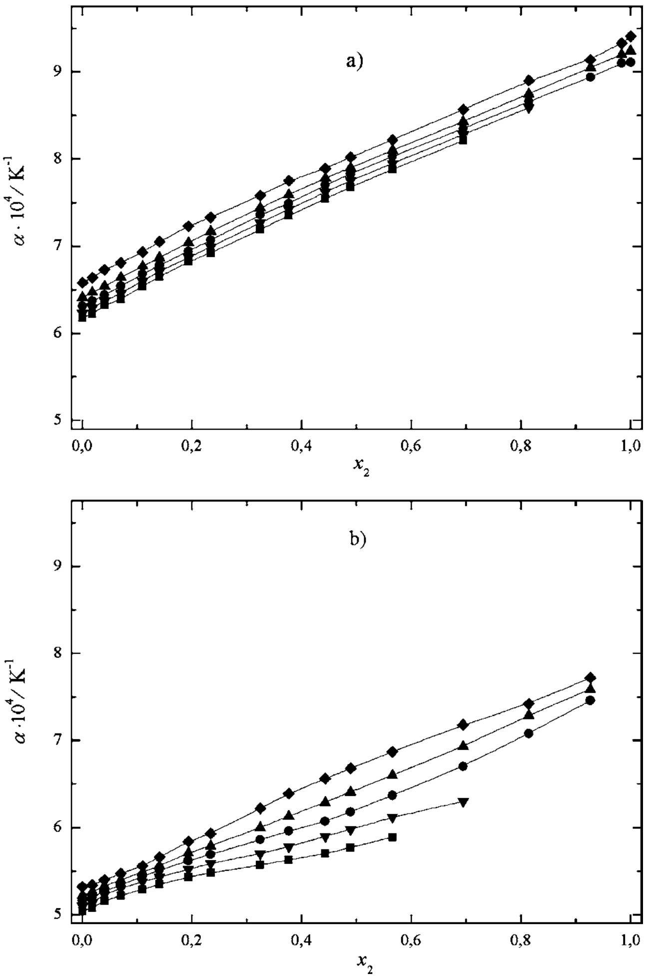

Figure 6. Thermal isobaric expansivity coefficients α versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at pressures of 0.101 MPa (a) and 100 MPa (b) at different temperatures: ■, 278.15 K; ▼, 288.15 K; ●, 298.15 K; ▲, 308.15 K; ♦, 323.15 K.

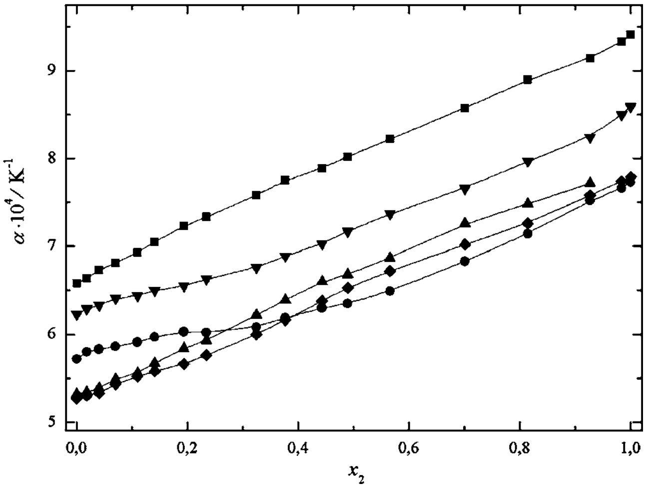

Figure 7. Thermal isobaric expansivity coefficients α versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at 323.15 K and at different pressures: ■, 0.101 MPa; ▼, 25 MPa; ▼, 50 MPa; ▲, 75 MPa; ♦, 100 MPa.

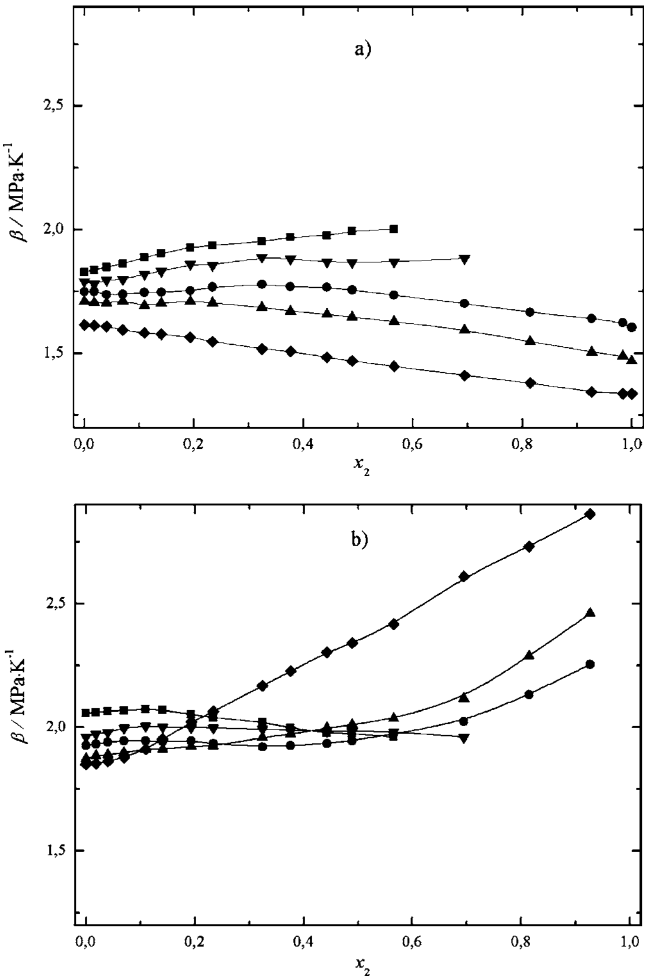

Figure 8. Thermal pressure coefficients β versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at pressures of 0.101 MPa (a) and 100 MPa (b) at different temperatures: ■, 278.15 K; ▼, 288.15 K; ●, 298.15 K; ▲, 308.15 K; ♦, 323.15 K.

The pressure coefficients, $\beta = (\partial p/\partial T)_V$, are sensitive to intermolecular interactions in a liquid, and any displacement of associative equilibria will bring free space changes. At atmospheric pressure, the $(\partial p/\partial T)_V = f(x_2)$ function is positive at 278.15 K, but it becomes negative at 323.15 K (Figure 8a). That means the strengthening of associative interactions or favorable conditions for more packaged system formation arises with increasing temperature. However, at 100 MPa and 323.15 K, β values increase with growth of DMSO concentration (Figure 8b). The same tendency is kept for lower temperatures but in the concentration range enriched with DMSO. It is clear from Figure 9 that at 323.15 K β increasing with DMSO content growth is observed at pressures higher than ~65 MPa. The pressure variation from (0.1 to 100) MPa causes β to increase for pure EG at about 0.2 MPa·K^{-1}, whereas for $x_2 = 0.92$ (the thermal pressure coefficient at 100 MPa is not possible to calculate for higher DMSO concentrations because of the system freezing), $\Delta\beta \approx 0.6$ MPa·K^{-1} at 298.15 K and ≈1.5 MPa·K^{-1} at 323.15 K. Consequently, in the EG−DMSO system at low pressure values, the temperature promotes association processes, and the opposite temperature influence is observed at high pressure.

Conclusions

The volumetric properties indicate that in the associated liquid EG−DMSO mixture the complex changes happen due to either existence of two structures with different dependences of structural properties on pressure and temperature or equimolar complex formation.

The formation of the EG−DMSO mixture is attended by compression. The decrease of the absolute V_m^E values with

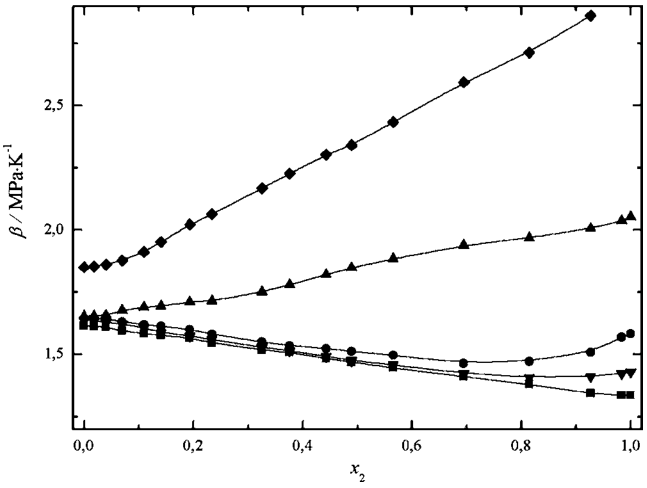

Figure 9. Thermal pressure coefficients β versus composition x_2 for the ethylene glycol (1) + dimethylsulfoxide (2) mixture at 323.15 K and at different pressures: ■, 0.101 MPa; ▲, 25 MPa; ●, 50 MPa; ▲, 75 MPa; ♦, 100 MPa.

decreasing pressure growth and temperature is related with molecule mobility reduction. The temperature and pressure influence on associative equilibria in pure EG and DMSO is probably stronger then on the complex formation between EG and DMSO.

The concentration dependencies of κ_T, α, and β coefficients have monotone character for most state parameters. The association processes in the EG−DMSO mixture strongly depend on temperature and pressure. At low pressures, the increasing temperature contributes to association processes, but at high pressures it does not.

Supporting Information Available:

The calculated coefficients of isothermal compressibility and coefficients of thermal isobaric expansivities of the ethylene glycol (1) + dimethylsulfoxide (2) mixture at temperatures of (278.15 to 323.15) K and pressures of (0.1 to 100) MPa are given Tables S1 and S2, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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