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Volumes, Heat Capacities, and Compressibilities of the Mixtures of Acetonitrile with *N*,*N*-Dimethylacetamide and Propylene Carbonate[†]

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The densities of the mixtures of acetonitrile and *N*,*N*-dimethylacetamide or propylene carbonate were measured within the whole composition range of the systems at temperatures (308.15 and 318.15) K, while the isobaric heat capacity and speed of sound in these mixtures were measured within the whole composition range at 298.15 K. The results obtained were used to calculate the excess molar volume and isobaric heat capacity and the partial molar volumes and heat capacities of both components of the mixtures as well as the adiabatic (κ_S) and isothermal (κ_T) compressibility and their excess. The internal pressures of the systems were also calculated. The results have been analyzed and discussed.

Introduction

Systematic studies on the solvation of electrolytes in binary solvents have been carried out for many years in our laboratory. At first, we examined widely the electrolyte solutions in numerous water + organic solvent mixtures.[1,2] Then we extended these studies to electrolyte solutions in binary organic solvents containing methanol (protic, hydrogen bonded solvent)[3−7] or *N*,*N*-dimethylformamide (aprotic, proton-acceptor, non-hydrogen bonded solvent).[5−9] As a continuation of these studies, we have undertaken investigations of electrolyte solutions in the mixtures of several organic solvents and acetonitrile, which due to its polarity is a good solvent for both electrolytes and nonelectrolytes. Moreover, acetonitrile molecules, in contrast to the mentioned above solvents, are not able to form H-bonds in the “classical” sense either as a proton-donor or as a proton-acceptor.

To investigate the effect of the properties and structure of binary solvents on the solvation of dissolved electrolytes, at first it is necessary to have wide information about the mixtures used as solvents. The properties of mixtures of acetonitrile with methanol[10,11] as well as with *N*,*N*-dimethylformamide and hexamethylenphosphortriamide have been examined earlier.[12] This work presents our results of the examination of thermodynamic properties of other binaries containing acetonitrile. We measured the densities of mixtures of acetonitrile and *N*,*N*-dimethylacetamide as well as acetonitrile and propylene carbonate within the whole range of the mixture composition at the temperatures (308.15 and 328.15) K. (The measurements at 298.15 K were performed earlier.)[13] Isobaric heat capacities (c_p) and the sound velocities (u) were measured for the same mixtures at 298.15 K. From these data, the molar volumes and molar heat capacities as well as the thermal expansion coefficients (α_T) and adiabatic (κ_S) and isothermal (κ_T) compressibilities were calculated. Then the internal pressure, the excesses of volumes and heat capacities of the mixtures, as well as the partial molar functions of the components of the mixtures examined were determined. We expected that the obtained data would enable us to analyze the effect of the mixture composition and the properties of the mixture components on the observed behavior of the systems from the point of view of molecular interactions.

Experimental Section

Chemicals. Acetonitrile (AN) (Sigma-Aldrich, anhydrous, 99.8 %), propylene carbonate (PC) (Sigma-Aldrich, anhydrous, 99.7 %), and *N*,*N*-dimethylacetamide (DMA) (Lab - Scan, 99.8 % HPLC) were dried and distilled in accordance with the methods described in the literature.[14] The water mass fraction in these reagents determined by Carl Fischer’s method was below $1 \cdot 10^{-4}$. The purity of the liquids examined was verified by NMR spectroscopy. The liquid mixtures were prepared by mass, avoiding contact with air. Each sample was degassed in an ultrasonic cleaner just before experiment.

Measurements. The densities of the AN + DMA and AN + PC mixtures relative to the density of pure acetonitrile were measured with a vibrating tube densimeter (SODEV model 03D). The density of pure acetonitrile was determined relative to that of pure propan-2-ol.[15] The uncertainty of the density measurements was estimated to be $5 \cdot 10^{-6}\ \mathrm{g \cdot cm^{-3}}$. The temperature in the densimeter was held constant to $1 \cdot 10^{-3}$ K.

The measurements of speed of sound were carried out by means of a digital ultrasound wave velocity meter, MPFU from ECOLAB. The temperature was controlled to 10^{-2} K. The uncertainty of measurements in liquids given by the manufacturer is $20\ \mathrm{cm \cdot s^{-1}}$ within the (283.15 to 313.15) K temperature range. The speed of sound at the temperature required was determined by the linear interpolation of the values of the speed at temperatures close to the required one.

Volumetric heat capacity, C_p/V, was measured with a Picker flow microcalorimeter (Setaram Model “chaleur specifique”, Lyon, France) as reported earlier.[16,17] The nitrogen overpressure needed to keep the flow rate at $0.010\ \mathrm{cm^3 \cdot s^{-1}}$ never exceeded 0.6 bar. The calorimetric cells were kept at the temperature constant to $1 \cdot 10^{-3}$ K.

The relative uncertainty of volumetric heat capacity ($\Delta C_p/V$) was 0.3 %.

Results

Volumes and Thermal Expansion Coefficients. The densities of binary mixtures, d, at T = (308.15 and 318.15) K are

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Table 1. Experimental Densities *d* of Acetonitrile (1) + Propylene Carbonate and + *N*,*N*-Dimethylacetamide (2) Mixtures at (308.15 and 318.15) K

d/g·cm^{-3}							
acetonitrile + propylene carbonate				acetonitrile + *N*,*N*-dimethylacetamide			
x_2	308.15 K	x_2	318.15 K	x_2	308.15 K	x_2	318.15 K
0.00000	0.765735	0.00000	0.755763	0.00000	0.765735	0.00000	0.755763
0.00899	0.772153	0.00987	0.762800	0.00994	0.768688	0.01091	0.759018
0.01974	0.779714	0.02015	0.770008	0.02031	0.771713	0.02054	0.761841
0.02827	0.785631	0.04049	0.783973	0.03016	0.774535	0.03090	0.764830
0.03912	0.793054	0.04999	0.790403	0.04069	0.777504	0.04289	0.768228
0.04976	0.800230	0.05968	0.796854	0.05104	0.780389	0.05290	0.771009
0.05955	0.806732	0.06983	0.803478	0.05848	0.782424	0.05906	0.772711
0.06835	0.812468	0.07649	0.807807	0.06932	0.785313	0.06978	0.775606
0.08237	0.821557	0.09048	0.816808	0.08223	0.788745	0.08535	0.779778
0.09065	0.826854	0.10148	0.823802	0.09057	0.790902	0.08742	0.780299
0.09974	0.832541	0.15269	0.855059	0.10089	0.793541	0.10216	0.784094
0.14731	0.861545	0.20113	0.882847	0.14971	0.805533	0.14381	0.794432
0.20176	0.892585	0.25020	0.909428	0.18843	0.814490	0.18341	0.803730
0.25091	0.919090	0.29709	0.933541	0.23703	0.824887	0.23010	0.813975
0.29829	0.943362	0.40373	0.983751	0.30148	0.837769	0.29347	0.826829
0.40083	0.991468	0.50359	1.025462	0.40436	0.856101	0.38700	0.843966
0.49049	1.029073	0.60038	1.061559	0.50855	0.872475	0.50302	0.862530
0.59787	1.069652	0.70161	1.095757	0.62510	0.888440	0.60255	0.876476
0.69017	1.101276	0.79970	1.125730	0.70587	0.898160	0.70466	0.889230
0.79027	1.132312	0.90054	1.153945	0.80344	0.908919	0.80854	0.900680
0.90095	1.163557	0.91132	1.156823	0.90244	0.918675	0.90897	0.910546
0.91207	1.166508	0.93397	1.162752	0.91167	0.919547	0.91440	0.911049
0.92179	1.169024	0.94076	1.164499	0.92160	0.920459	0.92152	0.911696
0.93015	1.171246	0.95195	1.167375	0.93219	0.921402	0.93202	0.912659
0.94112	1.174076	0.96085	1.169623	0.94102	0.922202	0.94143	0.913506
0.95038	1.176447	0.97073	1.172108	0.95154	0.923129	0.95457	0.914681
0.96093	1.179119	0.98154	1.174791	0.96143	0.924000	0.96296	0.915423
0.97151	1.181766	0.99083	1.177075	0.97116	0.924844	0.97164	0.916181
0.98152	1.184241	1.00000	1.179306	0.98112	0.925700	0.98094	0.916988
1.00000	1.188733			0.98934	0.926398	0.99106	0.917856
				1.00000	0.927294	1.00000	0.918616

presented in Table 1. The densities of acetonitrile, propylene carbonate, *N*,*N*-dimethylacetamide, and their mixtures at T = 298.15 K were presented in our earlier paper.[13]

The values for pure solvents are in good agreement with the corresponding literature data: acetonitrile at 308.15 K, d = 0.765735 g·cm^{-3} (0.76576 g·cm^{-3},[18] 0.76575 g·cm^{-3},[19] 0.76564 g·cm^{-3},[11] 0.76586 g·cm^{-3});[20] acetonitrile at 318.15 K, d = 0.755763 g·cm^{-3} (0.75634 g·cm^{-3},[21] 0.75498 g·cm^{-3});[11] propylene carbonate at 308.15 K, d = 1.188733 g·cm^{-3} (1.18864 g·cm^{-3},[22] 1.1887 g·cm^{-3});[23] propylene carbonate at 318.15 K, d = 1.179306 g·cm^{-3} (1.17814 g·cm^{-3},[22] 1.1783 g·cm^{-3},[23] 1.17867 g·cm^{-3});[24] *N*,*N*-dimethylacetamide at 308.15 K, d = 0.927294 g·cm^{-3} (0.9276 g·cm^{-3},[25] 0.9275 g·cm^{-3},[26] 0.9278 g·cm^{-3});[27] *N*,*N*-dimethylacetamide at 318.15 K, d = 0.918616 g·cm^{-3} (0.9186 g·cm^{-3}).[25]

From the densities, the excess molar volumes of the mixtures were calculated according to the equation

$$V^{E} = x_1 M_1\left(\frac{1}{d} - \frac{1}{d_1}\right) + x_2 M_2\left(\frac{1}{d} - \frac{1}{d_2}\right) \tag{1}$$

where M_i, d_i, and x_i are the molar mass, density, and mole fraction of component "i", respectively, with $i = 1$ for AN and $i = 2$ for the other component.

The values of V_m^E for the investigated systems are presented in Figure 1 as a function of the mixture composition and temperature.

The values of excess functions were fitted to the polynomial of Redlich−Kister type

$$Z^{E} = x_1 x_2 \sum_{j=0}^{n} A_j (1 - 2x_1)^j \tag{2}$$

where A_j are the polynomial coefficients calculated by the least-squares method. The A_j coefficients and the mean deviations from the regression lines are given in Table 4.

The partial molar volumes, V_i, of the components were calculated according to

$$V_i = V_{\Phi,i} + x_i(1 - x_i)\left(\frac{\partial V_{\Phi,i}}{\partial x_i}\right)_{x_{j\neq i}} \tag{3}$$

The partial molar volumes of AN, V_1, and the second component in the mixtures, V_2, are included as Supporting Information, Figures S1 and S2.

The mean coefficients of thermal expansion, α, of the AN + PC and AN + DMA mixtures in the range (298.15 to 318.15) K were calculated from the densities at (298.15, 308.15, and 318.15) K

$$\alpha = -\frac{1}{d}\frac{\Delta d}{\Delta T} \approx -\frac{1}{d_{308.15\mathrm{K}}}\frac{(d_{318.15\mathrm{K}} - d_{298.15\mathrm{K}})}{(318.15 - 298.15)} \tag{4}$$

The obtained results are presented in Table 2. Values for pure acetonitrile, $\alpha = 1.355 \cdot 10^{-3}$ K^{-1}; propylene carbonate, $\alpha = 0.845 \cdot 10^{-3}$ K^{-1}; and *N*,*N*-dimethylacetamide, $\alpha = 0.957 \cdot 10^{-3}$ K^{-1}, are in a good agreement with the literature data: acetonitrile, 1.346 K^{-1},[10] 1.368 K^{-1};[14,28] propylene carbonate, 0.84 K^{-1},[14] 0.958 K^{-1};[29] *N*,*N*-dimethylacetamide, 0.918 K^{-1},[29] 0.921 K^{-1}.[30]

Isobaric Heat Capacities. The values of molar isobaric heat capacities, C_p, of the mixtures examined at 298.15 K calculated from the volumetric heat capacities, C_p/V, are presented in Table 3. The molar heat capacities obtained for pure solvents agree reasonably well with the appropriate literature data: acetonitrile C_p = 92.36 J·K^{-1}·mol^{-1} (92.48 J·K^{-1}·mol^{-1},[10] 91.706 J·K^{-1}·mol^{-1},[41] 91.69 J·K^{-1}·mol^{-1});[42] propylene carbonate C_p = 166.98 J·K^{-1}·mol^{-1} (167.6 J·K^{-1}·mol^{-1});[29] and *N*,*N*-dimethylacetamide C_p = 175.49 J·K^{-1}·mol^{-1} (175.15 J·K^{-1}·mol^{-1}).[43]

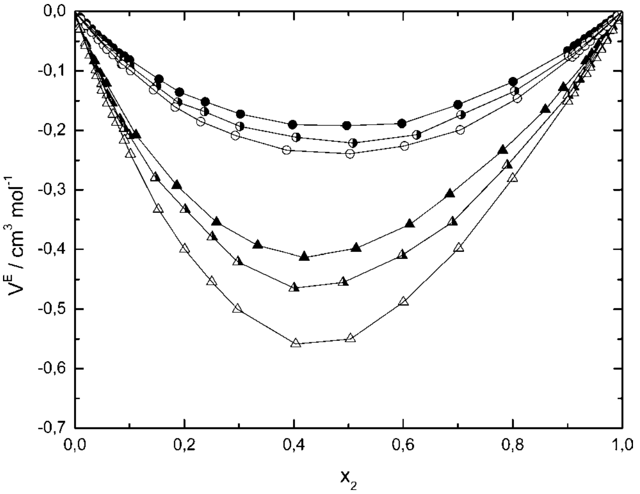

Figure 1. Excess volumes of acetonitrile + propylene carbonate and + *N*,*N*-dimethylacetamide mixtures. ●, PC (298.15 K); ◑, PC (308.15 K); ○, PC (318.15 K); ▲, DMA (298.15 K); ◭, DMA (308.15 K); △, DMA (318.15 K).

Table 2. Thermal Expansion Coefficients of Acetonitrile (1) + Propylene Carbonate and + *N*,*N*-Dimethylacetamide (2) Mixtures

acetonitrile + propylene carbonate				acetonitrile + *N*,*N*-dimethylacetamide			
x_2	$\alpha \cdot 10^3/K^{-1}$	x_2	$\alpha \cdot 10^3/K^{-1}$	x_2	$\alpha \cdot 10^3/K^{-1}$	x_2	$\alpha \cdot 10^3/K^{-1}$
0.00	1.355	0.60	0.912	0.00	1.355	0.60	1.041
0.05	1.298	0.70	0.891	0.05	1.315	0.70	1.013
0.10	1.242	0.80	0.876	0.10	1.277	0.80	0.989
0.15	1.119	0.85	0.869	0.15	1.243	0.85	0.980
0.20	1.114	0.90	0.861	0.20	1.211	0.90	0.972
0.30	1.056	0.95	0.853	0.30	1.157	0.95	0.965
0.40	0.990	1.00	0.845	0.40	1.113	1.00	0.957
0.50	0.943			0.50	1.075		

Table 3. Molar Heat Capacities of Acetonitrile (1) + Propylene Carbonate and + *N*,*N*-Dimethylacetamide (2) Mixtures at 298.15 K

acetonitrile + propylene carbonate		acetonitrile + *N*,*N*-dimethylacetamide	
x_2	$\frac{C_p}{J \cdot K^{-1} \cdot mol^{-1}}$	x_2	$\frac{C_p}{J \cdot K^{-1} \cdot mol^{-1}}$
0.00000	92.36	0.00000	92.36
0.02042	93.86	0.03032	94.92
0.04818	95.91	0.05087	96.66
0.08041	98.29	0.08015	99.14
0.09602	99.45	0.10180	100.97
0.10214	99.90	0.12989	103.36
0.12975	101.95	0.15039	105.10
0.14384	103.00	0.17120	106.87
0.15208	103.61	0.20137	109.43
0.18010	105.69	0.25687	114.15
0.19304	106.65	0.30234	118.01
0.19885	107.08	0.35142	122.17
0.30064	114.62	0.40237	126.48
0.39942	121.92	0.50098	134.78
0.45071	125.72	0.55092	138.97
0.45078	125.72	0.59958	143.03
0.59972	136.77	0.65876	147.96
0.59986	136.78	0.75052	155.56
0.69732	144.05	0.84965	163.68
0.74853	147.88	0.90044	167.77
0.74937	147.94	0.92856	170.00
0.89947	159.26	0.95065	171.73
0.90036	159.33	1.00000	175.49
1.00000	166.98		

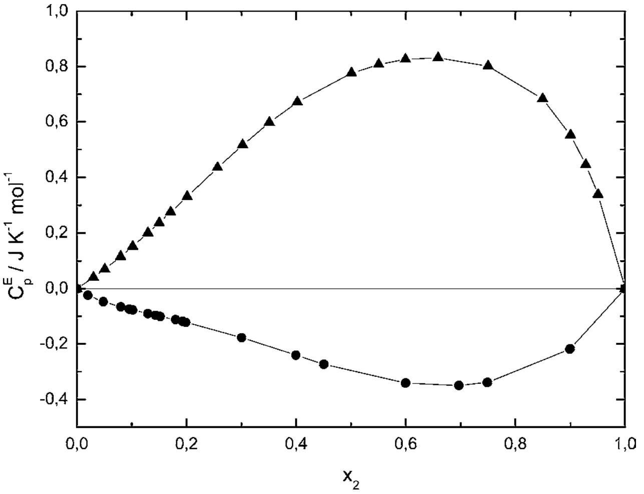

Figure 2. Excess isobaric heat capacities of acetonitrile + propylene carbonate and + *N*,*N*-dimethylacetamide mixtures. ●, PC; ▲, DMA.

The excess molar heat capacities of the mixtures (C_p^E) were calculated according to the formula

$$C_p^{\ E} = C_p - (x_1 C_{p1}* \ + \ x_2 C_{p2}*) \tag{5}$$

where x_i and C_{pi}^* denote the mole fraction and molar heat capacity of the pure components, respectively (1, acetonitrile; 2, the other component). The values of C_p^E of the mixtures are presented in Figure 2 as a function of the mixture composition. The excess functions were then fitted to the polynomial of Redlich−Kister type (eq 2). The coefficients of the polynomial calculated are given in Table 4.

The apparent molar heat capacities and partial molar heat capacities of both components of each mixture were determined in a way similar to that of the volumetric functions. The results are included as Supporting Information, Figures S3 and S4.

Table 6 summarizes the molar and limiting partial molar quantities of the mixture components.

Speed of Sound. The speeds of sound in the mixtures examined within the whole composition range at a temperature of 298.15 K are presented in Table 5. The measured speeds of sound in pure solvents are in good agreement with corresponding literature data: acetonitrile, u = 1279.61 m·s^{-1} (1278.6 m·s^{-1},[31] 1278.7 m·s^{-1},[32] 1280.8 m·s^{-1});[33] propylene carbonate, u = 1442.96 m·s^{-1} (1448.9 m·s^{-1},[34] 1450 m·s^{-1});[35] *N*,*N*-dimethylacetamide, u = 1458.65 m·s^{-1} (1458 m·s^{-1},[27,36] 1462 m·s^{-1},[25] 1468 m·s^{-1}).[26]

From the values of densities, the isobaric heat capacities, and speeds of sound, the adiabatic (κ_S) compressibilities were calculated by the Laplace formula

$$\kappa_S = \frac{1}{du^2} \tag{6}$$

where d is density of mixture and u is speed of sound in the mixture with a given composition.

The values of adiabatic compressibility for pure reagents determined here agree with those given in the literature within the uncertainty limits. For acetonitrile, we have obtained κ_S = 7.865·10^{-10} Pa^{-1}, while the literature reports 7.873·10^{-10} Pa^{-1},[37] 7.876·10^{-10} Pa^{-1},[31] and 7.875·10^{-10} Pa^{-1}.[28,32] Analogously, for propylene carbonate our data are 4.004·10^{-10} Pa^{-1}, and the literature data are 4.020·10^{-10} Pa^{-1},[38] and 4.008·10^{-10} Pa^{-1}.[39] For *N*,*N*-dimethylacetamide, our data are 5.019·10^{-10} Pa^{-1}, and the literature data are 4.996·10^{-10} Pa^{-1},[25] and 4.954·10^{-10} Pa^{-1}.[26]

The isothermal compressibilities (κ_T) for examined mixtures were calculated from the adiabatic one using the well-known relationship

$$\kappa_T = \kappa_S + \left(\frac{\alpha^2 VT}{C_p}\right) \tag{7}$$

The values of isothermal compressibilities of pure solvents agree well with the corresponding literature data: acetonitrile, our data, 10.998·10^{-10} Pa^{-1}; literature data, 10.7·10^{-10} Pa^{-1},[14,29] 11.178·10^{-10} Pa^{-1};[28] propylene carbonate, our data, 5.089·10^{-10} Pa^{-1}; literature data, 5.9·10^{-10} Pa^{-1};[14,29] *N*,*N*-dimethylacetamide, our data, 6.468·10^{-10} Pa^{-1}.

The excess adiabatic and isothermal compressibility coefficients of binary mixtures were then calculated according to the equations given below[40]

$$\kappa_S^{\ E} = \kappa_S - \kappa_S^{id} \tag{8}$$

Table 4. Parameters A_j of Equation 2 and the Standard Deviations for Acetonitrile (1) + Propylene Carbonate and + *N,N*-Dimethylacetamide (2) Mixtures

	T/K	A_0	A_1	A_2	A_3	σ
			x Propylene Carbonate + (1 − x) Acetonitrile			
V^E/cm^3·mol^{-1}	298.15	−1.5936	−0.4643	−0.2108	−0.0301	$1 \cdot 10^{-5}$
	308.15	−1.7882	−0.4595	−0.2581	–	$3 \cdot 10^{-5}$
	318.15	−2.1708	−0.5943	0.0230	–	$2 \cdot 10^{-5}$
C_p^E/J·K^{-1}·mol^{-1}	298.15	−1.175	0.999	−0.636	–	$3 \cdot 10^{-5}$
			x *N,N*-Dimethylacetamide + (1 − x) Acetonitrile			
V^E/cm^3·mol^{-1}	298.15	−0.7755	−0.0640	−0.0784	−0.0784	$1.68 \cdot 10^{-6}$
	308.15	−0.8740	−0.0619	−0.1049	−0.0645	$4.12 \cdot 10^{-6}$
	318.15	−0.9624	−0.0648	−0.0859	−0.0789	$1.28 \cdot 10^{-6}$
C_p^E/J·K^{-1}·mol^{-1}	298.15	3.045	−1.601	1.221	−1.907	$1.1 \cdot 10^{-4}$

Table 5. Experimental Speed of Sound u of Acetonitrile (1) + Propylene Carbonate and + *N,N*-Dimethylacetamide (2) Mixtures at 298.15 K

acetonitrile + propylene carbonate				acetonitrile + *N,N*-dimethylacetamide			
x_2	u/m·s^{-1}	x_2	u/m·s^{-1}	x_2	u/m·s^{-1}	x_2	u/m·s^{-1}
0.00000	1279.61	0.60875	1386.58	0.00000	1279.61	0.80483	1427.46
0.05020	1287.51	0.70348	1399.32	0.04872	1286.50	0.90354	1440.05
0.10219	1296.37	0.70368	1399.42	0.10044	1297.49	1.00000	1458.65
0.15123	1305.13	0.79863	1415.10	0.18975	1315.50		
0.20055	1313.92	0.85596	1422.27	0.29316	1336.44		
0.30313	1331.03	0.90518	1427.84	0.40460	1357.26		
0.30507	1331.64	0.95180	1434.52	0.50298	1375.55		
0.40456	1351.61	0.97655	1438.03	0.60438	1393.68		
0.50666	1369.00	1.00000	1442.96	0.70739	1410.84		

$$\kappa_T{}^E = \kappa_T - \kappa_T^{id} \tag{9}$$

where

$$\kappa_S^{id} = \kappa_T^{id} - \frac{(\alpha^{id})^2 V^{id} T}{C_p^{id}} \tag{10}$$

$$\kappa_T^{id} = \phi_1 \kappa_{T,1}^* + \phi_2 \kappa_{T,2}^* \tag{11}$$

$$\alpha^{id} = \phi_1 \alpha_1^* + \phi_2 \alpha_2^* \tag{12}$$

$$V^{id} = x_1 V_1^* + x_2 V_2^* \tag{13}$$

$$C_p^{id} = x_1 C_{p,1}^* + x_2 C_{p,2}^* \tag{14}$$

and ϕ_i is a volume fraction of component i.

The excess compressibility functions for the AN + DMA and AN + PC mixtures are presented in Figure 3.

Internal Pressure. The internal pressure, p_{int}, defined as

$$p_{int} \equiv \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{15}$$

is a part of the total pressure p of the system illustrating the static pressure due to the intermolecular energy (the other part $T[(dp)/(dT)]_V$ represents the kinetic pressure due to the thermal motion). The internal pressures, p_{int}, of the mixtures under examination were calculated according the formula

$$p_{int} = \frac{T\alpha_p}{\kappa_T} - p \tag{16}$$

The calculated internal pressures as a function of the mixture composition are included as Supporting Information, Figure S5.

Discussion

The molar volumes of the mixtures under investigation exhibit slightly (less than 1 % of the mixture molar volume value) negative deviations from additivity within the whole concentration range for both systems. A similar behavior was observed in the case of acetonitrile mixtures with methanol,[10] *N,N*-dimethylformamide, and hexamethylenphosphortriamide.[12] The volume contraction observed suggests that the interactions between the molecules of the mixture components are somewhat stronger than those between the molecules in pure solvents. Taking into account the properties of the solvents, it can be assumed that in the mixtures under investigation the dipole−dipole interactions are predominant. However, one should bear in mind that the positive charge in the acetonitrile molecule is on the central atom of carbon, while in the *N,N*-dimethylacetamide molecule it is on the nitrogen atom, to which the access is masked by $-CH_3$ groups. This causes interactions between the molecules of both components to be relatively weak and the AN + DMA molecular assembles to be loosely packed despite quite high dipole moments of both solvents (DMA, $\mu = 3.72$;[44] AN, $\mu = 3.44$).[44] A similar situation is in the system of AN + PC. Although the dipole moment of the PC molecule ($\mu = 4.98$)[44] is larger than that of the DMA molecule, the interactions between the molecules of acetonitrile and propylene carbonate

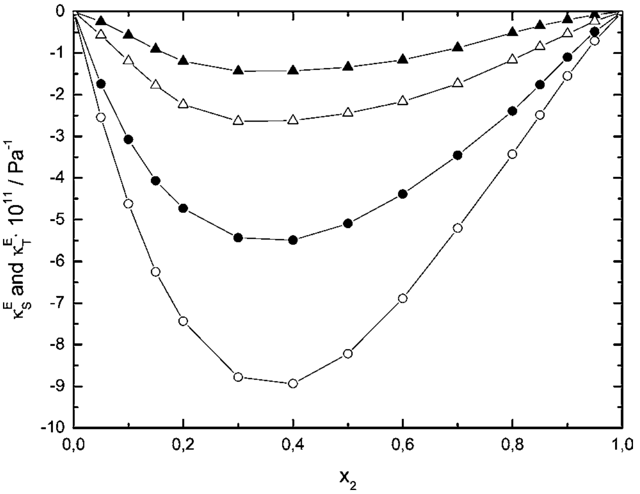

Figure 3. Excess isentropic ($\kappa_S{}^E$) and isothermal ($\kappa_T{}^E$) compressibilities of acetonitrile + propylene carbonate and + *N,N*-dimethylacetamide mixtures. ▲, $\kappa_S{}^E$ (DMA); Δ, $\kappa_T{}^E$ (DMA); ●, $\kappa_S{}^E$ (PC); ○, $\kappa_T{}^E$ (PC).

Table 6. Molar and Limiting Partial Molar Volumes and Heat Capacities in Mixtures of Acetonitrile (1) + Propylene Carbonate (2) and Acetonitrile (1) + *N*,*N*-Dimethylacetamide (2)

system	T K	V_i* $\mathrm{cm^3 \cdot mol^{-1}}$	V_i^0 $\mathrm{cm^3 \cdot mol^{-1}}$	C_{pi}* $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	C_{pi}^0 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
PC in AN	298.15	85.11	82.29	166.98	166.17
	308.15	85.87	83.00	–	–
	318.15	86.56	83.46	–	–
DMA in AN	298.15	93.04	92.06	175.49	176.74
	308.15	93.95	92.76	–	–
	318.15	94.84	93.65	–	–
AN in PC	298.15	52.86	51.45	92.36	89.78
	308.15	53.61	51.96	–	–
	318.15	54.31	52.59	–	–
AN in DMA	298.15	52.86	52.13	92.36	100.61
	308.15	53.61	52.74	–	–
	318.15	54.31	53.42	–	–

are stronger than those between acetonitrile and *N*,*N*-dimethylacetamide, and the minimum in AN + PC mixtures is deeper.

The almost symmetric shape of curves, $V^E = f(x)$, allows us to assume that beyond the areas of solutions diluted in relation to one of the components the molecular units of 1:1 type predominate.

The negative values of V^E increasing with the increase in temperature suggest that higher temperatures break the structure of pure solvents to a larger extent than the structure of their mixtures.

The partial molar volumes of the mixture components (V_1 and V_2) as a function of system concentration (Supporting Information, Figures S1 and S2) exhibit a monotonic trend in all the systems under investigation, which suggests that the structure of these systems changes gradually with the concentration from typical of one pure solvent to typical of the other pure solvent. An increase in temperature results in increased values of V_1 and V_2, but it does not change the shape of the curves.

The standard partial molar volumes of the liquids are slightly smaller than the molar volumes of pure solvents, $V_i^0 < V_i^*$ (Table 6), which indicates that the formation of the mixture is accompanied by a slight volume contraction. One can assume that in consequence of dipole−dipole interactions the solvent molecules around the solute are more closely packed than those in a pure solvent. This conclusion is supported by the fact that the difference $V_1^0 - V_1^*$ is more negative in the case of propylene carbonate solution in acetonitrile (~3 $\mathrm{cm^3}$) than that in *N*,*N*-dimethylacetamide solution in acetonitrile, which is consistent with decreasing dipole moment of the molecules of these solvents. A similar behavior is shown by the standard partial molar volume of acetonitrile in propylene carbonate and *N*,*N*-dimethylacetamide. In this case, the less negative difference, $V_2^0 - V_2^*$, in *N*,*N*-dimethylacetamide may be additionally ascribed to steric hindrances obstructing the close packing of *N*,*N*-dimethylacetamide molecules around acetonitrile.

The negative deviations from additivity in the case of isentropic and isothermal compressibilities of the mixtures under investigation suggest that the interactions between molecules of different components increase the stiffness of the system in comparison with pure solvents (Figure 3). The deviations observed in the case of the AN + PC mixtures are larger than those in the AN + DMA system which indicates that the interactions between the molecules of acetonitrile and *N*,*N*-dimethylacetamide are weaker than those in the AN + PC mixture, and the structure of the former system is quite "loose". The above observations are consistent with the conclusions drawn on the basis of the course of function V^E.

The minima of the excess of both compressibility coefficients fall in the range of mixture composition where one can observe the minima of V^E for the corresponding mixture.

The isobaric heat capacities of the AN + DMA mixtures exhibit positive deviations from additivity (Figure 2). Such a behavior indicates the formation of a different type of unstable, weak associates in the system, as it was suggested earlier. In the AN + PC mixture, one can observe slight (about 0.25 % of C_p value) negative deviations from additivity. This supports the opinion that this mixture has no specified structure despite the relatively strong interactions between the molecules of its components.

The partial molar isobaric heat capacities of mixture components as a function of concentration (Supporting Information, Figures S3 and S4) exhibit monotonic behavior in both systems. The very small changes observed in C_{p1} and C_{p2} functions of the AN + PC system suggest again the absence of any stable structures in this mixture. The partial molar heat capacity of acetonitrile in the mixture under investigation (C_{p1}) within the acetonitrile-rich range (from about (40 to 100) % mol of acetonitrile) is constant within the limits of error and equal to C_{p1}^*. This indicates that in the above given range of mixture compositions the second component of the mixture molecules does not disturb significantly the structure of acetonitrile. The further decrease of acetonitrile content allows the structure typical for the second component of the mixture to start dominating in the mixture which brings about a slight drop of the C_{p1} values in the AN + PC system and an increase in the value of C_{p1} in the AN + DMA system.

The C_{p2} function for propylene carbonate in the mixtures with acetonitrile has a monotonic course within the whole composition range and is almost independent (within the experimental error) of the mixture composition, i.e., $C_{p2} \approx C_{p2}^*$ (Supporting Information, Figure S3). What concerns the AN + DMA mixtures, a slight change in C_{p2} values with the change of the system composition can be observed. Such a monotonic course of the functions is connected with quite a loose structure of the cosolvent of acetonitrile and indicates a lack of significant energetic changes associated with the interactions between the molecules of both solvents.

The values of standard partial molar heat capacities of mixture components, in the AN + PC system (Table 6), are only slightly smaller than the molar heat capacities of pure solvents ($C_{pi}^0 < C_{pi}^*$), which is related to the absence of the structural order in the mixture.

In contrast to that in the AN + DMA system, the values of standard partial molar heat capacities of mixture components are higher than those of pure solvents ($C_{pi}^0 > C_{pi}^*$). The difference $C_{p2}^0 - C_{p2}^*$ for *N*,*N*-dimethylacetamide in acetonitrile is very small (less than 1 %), whereas a considerable difference $C_{p1}^0 - C_{p1}^* > 0$ for acetonitrile in *N*,*N*-dimethylacetamide can be caused by filling up an empty space in the formed *N*,*N*-dimethylacetamide structure by smaller molecules of acetonitrile.

For all the systems under investigation, the internal pressure changes almost linearly along with the increase of the second component of the mixture content (Supporting Information, Figure S5). As the internal pressure can be recognized as a measure of molecular interaction energy, the observed behavior confirms our conclusions about gradual changes of the structure and molecular interactions in the examined systems from those being typical of acetonitrile to typical of the second component of the mixture.

Acknowledgment

The paper is dedicated to the memory of Henry V. Kehiaian.

Supporting Information Available:

The five graphs, from Figure S1 to Figure S5, mentioned in the text, illustrating some of the examined properties of acetonitrile + propylene carbonate and acetonitrile + *N*,*N*-dimethylacetamide mixtures are included. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Piekarski, H. Application of calorimetric methods to investigations of interactions in solutions. *Pure Appl. Chem.* **1999**, *71*, 1275–1283.
(2) Piekarski, H. Calorimetry - An important tool in solution chemistry. *Thermochim. Acta* **2004**, *420* (1−2), 13–18.
(3) Piekarska, A. Ion solvation in methanol-organic cosolvent mixtures. Part 5. Enthalpies of transfer of inorganic ions in mixtures of methanol and propylene carbonate at 298.15 K. *Thermochim. Acta* **1994**, *244*, 61–67.
(4) Taniewska-Osińska, S.; Piekarska, A. Calorimetric investigation of NaI-alcohol interactions in alcohol + alcohol mixtures. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1913–1921.
(5) Taniewska-Osińska, S.; Piekarska, A. Single-ion transfer enthalpies for $Ph_4P^+ = BPh_4^-$, Na^+ and I^- ions in methanol-N, N-dimethylformamide mixtures. *Thermochim. Acta* **1990**, *170*, 189–195.
(6) Piekarska, A.; Piekarski, H.; Taniewska-Osińska, S. Calorimetric studies of NaI solutions in binary organic isodielectric mixtures. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 513–520.
(7) Piekarski, H.; Pietrzak, A. Molecular interactions of alkanediols in methanol and in water: Density and heat capacity measurements. *J. Mol. Liq.* **2005**, *121*, 46–52.
(8) Piekarski, H. Enthalpic pair interaction coefficients of NaI-nonelectrolyte in DMF solution at 25 °C. A comparison of electrolyte-nonelectrolyte interactions in DMF and in aqueous solutions. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 591–599.
(9) Piekarski, H.; Waliszewski, D.; Romanowski, S. Interactions of urea with some non-electrolytes in DMF solution. Calorimetric measurements and quantum-mechanical calculations. *J. Mol. Liq.* **2000**, *88*, 43–54.
(10) Piekarski, H.; Somsen, G. Heat Capacities and Volumes of Metanol + Acetonitrile Mixtures at 5 and 25 °C. *J. Solution Chem.* **1992**, *21*, 557–567.
(11) Saha, N.; Das, B.; Hazra, D. K. Viscosities and Excess Molar Volumes for Acetonitrile + Methanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1264–1266.
(12) Kolker, A. M.; Kulikov, M. V.; Krestov, A. G. Volumes and heat capacities of binary non-aqueous mixtures. Part 2. The systems acetonitrile-N, N-dimethylformamide and acetonitrile-hexamethylphosphoric triamide. *Thermochim. Acta* **1992**, *211*, 73–84.
(13) Piekarski, H.; Piekarska, A.; Kubalczyk, K. Single ionic volumes in acetonitrile-organic cosolvent mixtures at 298.15 K. *Z. Phys. Chem.* **2004**, *218*, 679–698.
(14) Weissberger, A. *Technique of Organic Chemistry, Organic Solvents*; Interscience: New York, 1955; Vol. II.
(15) Hales, J. L.; Ellender, J. H. Liquid densities from 293 to 490 K of nine aliphatic alcohols. *J. Chem. Thermodyn.* **1976**, *8*, 1177–1184.
(16) Picker, P.; Leduc, P.-A.; Philip, P. R.; Desnoyers, J. E. Heat capacity of solution by flow microcalorimetry. *J. Chem. Thermodyn.* **1971**, *3*, 631–642.
(17) Zegers, H. C.; Boegschoten, R.; Mels, W.; Somsen, G. Flow calorimetry of viscous liquids. Volumes and heat capacities of mixtures of N, N-dimethylformamide with N-alkylacetamides. *Can. J. Chem.* **1986**, *64*, 40–45.
(18) Stolypin, V. F. Complexation in the Acetonitrile-15-Crown-5 System at Finite Concentrations. *Russ. J. Phys. Chem.* **1996**, *70*, 1693–1697.
(19) Brown, I.; Smith, F. Volume Changes on Mixing. II. Systems containing Acetone, Acetonitrile and Nitrometane. *Aust. J. Chem.* **1962**, *15*, 9–12.
(20) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry, Vol. II Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.
(21) D'Aprano, A.; Capalbi, A.; Iammarino, M.; Mauro, V.; Princi, A.; Sesta, B. Acetonitrile + nitromethane: An example of ideal solvent mixtures. *J. Solution Chem.* **1995**, *24*, 227–240.
(22) Zhao, Y.; Wang, J.; Xuan, X.; Lu, J. Effect of Temperature on Excess Molar Volumes and Viscosities for Propylene Carbonate + *N*,*N*-Dimethylformamide Mixtures. *J. Chem. Eng. Data* **2000**, *45*, 440–444.
(23) Moumouzias, G.; Panopoulos, D. K.; Ritzoulis, G. Excess properties of the binary liquid system Propylene Carbonate + Acetonitrile. *J. Chem. Eng. Data* **1991**, *36*, 20–23.
(24) Barthel, J.; Utz, M.; Grob, K.; Gores, H. J. Temperature and composition dependence of viscosity I. Propylene carbonate - Dimethoxyethane mixtures and thermodynamics of fluid flow. *J. Solution Chem* **1995**, *24*, 1109–1123.
(25) Ali, A.; Nain, A. K. Ultrasonic study of molecular interactions in N, N-Dimethylacetamide + Ethanol binary mixtures at various temperatures. *Acoust. Lett.* **1996**, *19*, 181–187.
(26) Aminabhari, T. M.; Patil, V. B. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Ethenylbenzene with N,N-Dimethylacetamide, Tetrahydrofuran, N,N-Dimethylformamide, 1,4-Dioxane, Dimethyl Sulfoxide, Chloroform, Bromoform, and 1-Chloronaphthalene in the Temperature Interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 497–503.
(27) Aralaguppi, M. J.; Jadar, C. V.; Aminabhari, T. M.; Ortego, J. D.; Mehrotra, S. C. Density, Refractive Index, and Speed of Sound in Binary Mixtures of 2-Ethoxyethanol with Dimethyl Sulfoxide, N, N-Dimethylformamide, N, N-Dimethylacetamide at Different Temperatures. *J. Chem. Eng. Data* **1997**, *42*, 301–303.
(28) Tamura, K.; Nakamura, M.; Murakami, S. Excess volumes of water + acetonitrile and water + dimethylsulfoxide at 30 °C and the effect of the excess thermal expansivity coefficients on derived thermodynamic properties. *J. Solution Chem.* **1997**, *26*, 1199–1207.
(29) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.
(30) Lagemann, R. T.; McLeroy, E. G.; Milner, O. Ultrasonic Velocity in a Series of Alkyl Acetates. *J. Am. Chem. Soc.* **1951**, *73*, 5891.
(31) Tamura, K.; Murakami, S.; Akagi, Y.; Fukumori, M.; Kawasaki, Y. Thermodynamic properties of binary mixtures: Hexamethylphosphoric triamide + a polar liquid at 25 °C. *J. Solution Chem.* **1994**, *23*, 263–273.
(32) Nakamura, M.; Chubachi, K.; Tamura, K.; Murakami, S. Thermodynamic properties of $[x\{HCON(CH_3)_2$ or $CH_3CN\} + (1\text{-}x)(CH_3)_2SO]$ at the temperature 298.15 K. *J. Chem. Thermodyn.* **1993**, *25*, 1311–1318.
(33) Bakshi, M. S.; Singh, J.; Kaur, H.; Ahmad, S. T.; Kaur, G. Thermodynamic Behavior of Mixtures. 3. Mixtures of Acetonitrile with Dimethylacetamide, Dimethyl Sulfoxide, Nitrobenzene, and Methanol at 25 °C. *J. Chem. Eng. Data* **1996**, *41*, 1459–1461.
(34) Chauhan, S.; Syal, V. K.; Chauhan, M. S. Viscosity and ultrasonic velocity studies of binary mixtures at different temperatures: Part 1 - Acetonitrile - Propylene Carbonate. *Ind. J. Pure Appl. Phys.* **1994**, *32*, 186–188.
(35) Salomon, M.; Plichta, E. Conductivities and ion association of 1:1 electrolytes in mixed aprotic solvents. *Electrochim. Acta* **1983**, *28*, 1681–1686.
(36) Aminabhavi, T. M.; Gopalakrishna, B. Density, Viscosity, Refractive Index, and Speed of Sound in Aqueous Mixtures of N, N-Dimethylformamide, Dimethyl Sulfoxide, N, N-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1,4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856–861.
(37) Miyanaga, S.; Tamura, K.; Murakami, S. Excess molar volumes, isentropic and isothermal compressibilities, and isochoric heat capacities of (acetonitrile + benzene), (benzene + dimethylformamide), and (acetonitrile + dimethylformamide) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1992**, *24*, 1077–1086.
(38) Chauhan, S.; Syal, V. K.; Chauhan, M. S. Ultrasonic studies in binary solvent mixtures at different temperatures: Part II - Acetonitrile + Propylene Carbonate. *Ind. J. Pure Appl. Phys.* **1995**, *33*, 92–94.
(39) Høiland, H. Partial molal volumes of alcohols in propylene carbonate at 25 °C. *J. Solution Chem.* **1976**, *5*, 773–780.
(40) Douheret, G.; Davis, M.; Reis, J. C. R.; Blandamer, M. J. Isentropic compressibilities - Experimental origin and the quest for their rigorous estimation in thermodynamically ideal liquid mixtures. *Chem. Phys. Chem.* **2001**, *2*, 148–161.
(41) deVisser, C.; Somsen, G. Thermochemical behavior of mixtures of N, N-dimethylformamide with dimethylsulfoxide, acetonitrile, and N-methylformamide: Volumes and heat capacities. *J. Solution Chem.* **1979**, *8*, 593–600.
(42) Kolker, A. M.; Kulikov, M. V.; Krestov, A. G. Volumes and heat capacities of binary non-aqueous mixtures. Part 1. The systems acetonitrile-formamide and acetonitrile-N-methylformamide. *Thermochim. Acta* **1992**, *211*, 61–72.
(43) Zegers, H. C.; Somsen, G. Volumes and heat capacities of mixtures of dimethylformamide with several dialkylacetamides. *Fluid Phase Equilib.* **1984**, *18*, 299–311.
(44) Barthel, J. M. G.; Krienke, H.; Kunz, W. *Physical Chemistry of Electrolyte Solutions: Modern Aspects*; Steinkopff: Darmstadt, Springer: New York, 1998.

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