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Volumes, heat capacities, and compressibilities of the mixtures of acetonitrile and 2-methoxyethanol

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ABSTRACT

Heat capacities and speed of sound of (acetonitrile + 2-methoxyethanol) mixtures at 298.15 K and the densities of the same mixtures at $T = (308.15 \text{ and } 318.15)$ K were determined over the whole composition range. The excess of molar volume and isobaric heat capacity of the mixture, the partial molar volumes and heat capacities of both components of the mixture as well as the adiabatic and isothermal coefficients of compressibility and their excess were calculated from the obtained experimental data. The internal pressure of the examined system was also calculated. The results of investigations were analyzed and discussed. The behavior of the analyzed functions is similar to that observed in the case of the mixtures of acetonitrile with some aprotic solvents examined earlier.

1. Introduction

Systematic studies of thermodynamic properties of electrolyte solutions in binary organic solvents have been carried out in our laboratory for many years. We examined widely the properties of the solutions of electrolytes in the mixtures containing methanol (protic, hydrogen bonded solvent) or N,N-dimethylformamide (aprotic, proton-acceptor, non-hydrogen bonded solvent). As a part of these studies the thermodynamic properties of mixtures used as solvent for electrolytes have been also investigated. Some years ago we have undertaken the examinations of mixtures of several organic solvents with acetonitrile (AN), which due to its polarity is a good solvent for both electrolytes and non-electrolytes. Moreover, acetonitrile molecules, in contrast to the above-mentioned solvents, are not able to form H-bonds in "classical" sense neither as a proton-donor nor as a proton-acceptor. In our previous paper the results of examinations of the mixtures of acetonitrile with N,N-dimethylacetamide (DMA) and propylene carbonate (PC) have been presented [1]. Now we have focused our interest on the mixtures of AN with 2-methoxyethanol (2-ME). The 2-ME belonging to the group of cellosolves has in its molecule both hydroxyl group and ether oxygen, which makes it possible to form intra-molecular hydrogen bond [2]. The physical and chemical properties shown by 2-ME resulting from its associated structure allow one to place it between protic and aprotic solvents. Moreover, following our earlier observations, 2-ME in pure state and in mixtures with water used as a solvent of electrolytes behaves to some extent as an aprotic solvent [3,4]. For that reason it is often defined as a "quasi-aprotic" solvent. Preliminary results of our studies on the volume functions of some electrolyte solutions in (AN + 2-ME) mixtures suggest that also in this system 2-ME shows the features of aprotic solvent [5]. Thus it appeared proper to perform more complex examinations of (AN + 2-ME) mixtures by means of various test methods in order to verify this opinion and assess to what extent the properties of the system under discussion are similar to or differ from those of the mixtures of acetonitrile with typical aprotic solvents such as propylene carbonate and N,N-dimethylacetamide examined by us earlier [1]. Only few results of experiments concerning the system under discussion are available in the literature and they are fragmentary and insufficient for its characteristics [6,7]. For that reason the densities of the mixtures under investigation were measured within the temperature range from (298.15 to 318.15) K and their isobaric heat capacities and speed of sound were measured at a temperature of 298.15 K within the whole composition range. From the measured data the adiabatic and isothermal compressibilities, isobaric thermal expansion, heat capacities at constant volume and internal pressures as well as the appropriate excess functions and partial molar functions were calculated. The obtained results were discussed from the point of view of the effect of mixture composition on the behavior of the system.

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2. Experimental

Acetonitrile (AN), (Sigma–Aldrich, 99.8%, anhydrous) and 2-methoxyethanol (2-ME), (Sigma–Aldrich, 99.9% HPLC grade) were dried and distilled in accordance with the methods described in the literature [8]. The water content in solvents was determined by Carl Fischer's method and was below $1 \cdot 10^{-2}$ wt%. The purity of solvents was verified by NMR spectroscopy. The liquid mixtures were prepared by weight, avoiding contact with air. Each sample was degassed in an ultrasonic cleaner just before experiment.

Densities were measured by means of a vibrating tube densimeter, SODEV Model 03D. The required constant temperature of the measuring cell in the densimeter ($\pm 1 \cdot 10^{-3}$ K) was maintained by means of a thermostat with a closed circulation (SODEV, Model CTL). The density of pure acetonitrile was determined relatively to that of pure propan-2-ol [9]. The densities of the (AN + 2-ME) mixtures were measured in relation to the density of pure acetonitrile. The uncertainty in the density measurements is estimated to be $5 \cdot 10^{-6}$ g · cm^{-3}. Details of the procedure and calibration were reported previously [10–12].

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 with an accuracy of up to 10^{-2} K. The measurements' accuracy in liquids given by the manufacturer is 20 cm · s^{-1} within the (283.15 to 313.15) K temperature range. The speed of sound at the temperature required was determined by linear interpolation of the values of 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 [11–13]. The nitrogen overpressure needed to keep the flow rate at 0.010 cm^3 · s^{-1} never exceeded 0.6.10^{5}Pa. The calorimetric cells were kept at constant temperature to $1 \cdot 10^{-3}$ K.

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

3. Results

3.1. Volumes and thermal expansion coefficients

The densities of binary mixtures, d, at T = (308.15 and 318.15) K are listed in table 1 while those at T = 298.15 K were given in our earlier paper [5].

The densities of pure solvents determined in this work agree well with the corresponding literature data (table 2).

From the densities of (AN + 2-ME) mixtures the excess molar volumes (V^E), partial molar volumes of mixture components (V_i), and the coefficients of thermal expansion (α) were calculated. The molar excess volumes (V^E) of the mixture were calculated according to:

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

where M_i, d_i, and x_i are the molar mass, density, and mole fraction of the component "i", respectively, with i = 1 for AN and i = 2 for 2-ME. The values of V^E for the investigated system are shown in figure 1 as a function of mole fraction of 2-ME 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 is the polynomial coefficient calculated by the least-squares method.

TABLE 1

Experimental densities $d/(\text{g} \cdot \text{cm}^{-3})$ of {acetonitrile (1) + 2-methoxyethanol (2)} mixtures at T = (308.15 and 318.15) K.

x_2	308.15 K	x_2	318.15 K
0.00000	0.765735	0.00000	0.755763
0.00998	0.768618	0.00977	0.758593
0.02137	0.771870	0.02023	0.761593
0.03278	0.775071	0.03040	0.764483
0.04058	0.777238	0.04029	0.767262
0.05050	0.779979	0.04893	0.769671
0.06827	0.784813	0.05932	0.772540
0.07039	0.785413	0.06681	0.774593
0.07541	0.786728	0.07969	0.778086
0.09332	0.791503	0.09100	0.781124
0.10188	0.793744	0.10152	0.783904
0.15115	0.806368	0.15161	0.796793
0.19499	0.817055	0.19502	0.807486
0.24947	0.829827	0.25031	0.820480
0.29811	0.840655	0.30396	0.832469
0.40009	0.861695	0.40125	0.852641
0.50055	0.880458	0.50074	0.871365
0.60170	0.897597	0.60380	0.888921
0.70414	0.913484	0.70311	0.904330
0.80235	0.927171	0.80144	0.918191
0.90660	0.940325	0.90342	0.931153
0.91016	0.940846	0.91327	0.932346
0.92134	0.942098	0.92351	0.933569
0.93158	0.943319	0.93498	0.934916
0.94169	0.944490	0.94341	0.935911
0.95278	0.945766	0.95242	0.936960
0.96324	0.946944	0.96351	0.938217
0.97022	0.947731	0.97234	0.939208
0.98140	0.948974	0.98137	0.940219
0.99313	0.950261	0.99290	0.941484
1.00000	0.951010	1.00000	0.942253

The equation parameters determined by polynomial approximation are given in table 3.

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

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

where $V_{\Phi,i}$ denotes the apparent molar volumes of component i. They were determined from:

$$V_{\Phi,i} = V_i^* + \frac{V^E}{x_i}, \tag{4}$$

where V_i^* is the molar volume of the pure component i.

The partial molar volumes, V_1, of acetonitrile in the mixtures are given in figure 2. The corresponding data that refer to 2-methoxyethanol, V_2, are presented in figure 3. The partial molar volumes of the mixture components at an infinitely diluted solution, equal to their standard values V_i^0, for 2-ME in AN and for AN in 2-ME at temperatures (298.15, 308.15, and 318.15) K and the molar volumes of pure liquids, V_i^*, are listed in table 4.

The mean coefficients of thermal expansion, α, of the (acetonitrile + 2-methoxyethanol) mixtures in the range (298.15 to 318.15) K were calculated from densities at 298.15 K [5], 308.15 K and, 318.15 K

$$\alpha = -d^{-1} (\Delta d / \Delta T) \approx -d^{-1}_{308.15\,\text{K}} ((d_{318.15\,\text{K}} - d_{298.15\,\text{K}})/20). \tag{5}$$

The obtained values are listed in table 5.

The values for pure AN and 2-ME are set up with appropriate literature data in table 2.

3.2. Isobaric heat capacities

The values of molar isobaric heat capacities, C_p, of the examined mixtures at 298.15 K calculated from the heat capacities per unit