Excess molar volume of the acetonitrile + alcohol systems at 298.15 K. Part I: Density measurements for acetonitrile + methanol, + ethanol systems

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Abstract: The excess molar volume V^E of the binary liquid systems acetonitrile + methanol and acetonitrile + ethanol has been evaluated from density measurements at 298.15 K and at atmospheric pressure over the entire composition range. A vibrating tube densimeter, type Anton Paar DMA 55, was applied for these measurements. The Redlich–Kister equation was used to fit the experimental V^E data.

Keywords: density measurements, excess volume, methanol, ethanol, acetonitrile.

INTRODUCTION

During our thermodynamic studies of non-electrolyte liquid mixtures over a longer period of time, certain efforts have been dedicated to volume changes during mixing.[1–3] As a part of this ongoing work, the non-ideal behavior of two binary mixtures, containing an alcohol and acetonitrile, have been investigated in dependence of the nature of their constituents by determining the excess molar volumes, V^E.

The specific interaction due to hydrogen bond formation between the polar groups of the different compounds is primarily responsible for the non-ideal behavior of binary associated solutions. When an alcohol is mixed with other organic compound which contains a proton acceptor group, such as the nitrogen in the acetonitrile molecule, a part of the alcohol will tend to dissociate and form other kinds of hydrogen bonds within the molecules.

The experimental values of V^E data at 298.15 K and at atmospheric pressure which are calculated from the density measurements of binary liquid mixtures methanol + acetonitrile and ethanol + acetonitrile over the entire composition range are reported in this paper. The measurement technique and the equipment used are briefly described.

In subsequent parts of this study, correlation of V^E these and other higher alcohol systems with acetonitrile will be performed by CEOS and CEOS/G^E thermodynamic models.[4]

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EXPERIMENTAL

Chemicals

The chemicals methanol, ethanol and acetonitrile (all with a purity > 99.8 mass %) were supplied by Merck (methanol) and Riedel-de Haën (ethanol and acetonitrile). The density measurements for the pure components are summarized and compared with the corresponding literature values in Table I. Since the agreement is good, further purification of the employed compounds was not performed.

TABLE I. Densities of the pure compounds at 298.15 K

Compound	Density/g cm^{-3}	
	this work	literature
Methanol	0.78665	078655 – 0.78676[5]
Ethanol	0.78525	0.7852[6] 0.78517[7]
Acetonitrile	0.77669	0.77669[5] 0.77649[8], 0.77673[8]

Apparatus and procedure

All the mixtures were prepared in a septum-capped vial allowing only the needle of a syringe to be introduced. The vapor space in the vessel was limited to a minimum in order to avoid evaporation, which would result in composition errors. The samples were prepared by weight, using a Mettler H20 mass balance with an accuracy $\pm 10^{-4}$ g.

The densities of the methanol + acetonitrile and the ethanol + acetonitrile mixtures, as well as of the corresponding pure compounds, were measured using a vibrating tube densimeter, type Anton Paar DMA 55, with a precision of $\pm 1 \times 10^{-5}$ g cm^{-3}, achieved by determining the period of oscillation of the liquid in a U-tube, thermostated at 298.15$\pm$0.01 K by a constant temperature bath (Lauda E200 T). A pump enabled water from the thermostatic bath to circulate around the brass housing where the U-tube was located. Repetitive measurements of the densities showed that an accuracy better than 3×10^{-5} g cm^{-3} was achieved.

The natural vibration period of the tube, which depends on the density of the liquid, is measured with a high-resolution digital frequency meter. The equation

$$\Delta\rho = \rho - \rho_0 = A(\tau^2 - \tau_0^2) \tag{1}$$

was used to relate the density ρ and the period τ for the investigated liquids to the values ρ_0 and τ_0, corresponding to the reference fluid. The value of the constant A was determined by calibration using fluids of known densities. Air and distilled and deionized water (Millipore quality) were used as the reference fluids to determine the constant of the densimeter. The densimeter was calibrated daily according to the procedure prescribed by the manufacturer.

The density of air was calculated from the equation[9]:

$$\rho_{air}(P, 298.15 \text{ K}) = \frac{P}{101.3} \cdot \rho_{air}(P = 101.3 \text{ kPa}, 298.15 \text{ K}) \tag{2}$$

where P is the absolute pressure and $\rho_{air}(P = 101.3 \text{ kPa}, 298.15 \text{ K}) = 1.185 \times 10^{-3}$ g cm^{-3}. The density of water was taken[9] as $\rho = 0.99707$ g cm^{-3}.

All measurements were made in the "static mode". The U-shaped sample tube was equipped with valves at the entrance and exit. After the sample had been introduced, the valves were closed. The time taken for equilibration was typically between 5 and 7 minutes, after which the period of oscillation was read from the numerical dial. Between two successive measurements, the sample tube was cleaned with acetone and

dried for at least 5 minutes using the built-in air pump. This was the time necessary for the period of the empty sample tube to return to its previous value.

After measuring the densities of the pure fluids and binary liquid mixtures, the excess molar volumes were calculated from the following equation:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{3}$$

where x_1 and x_2 are mole fractions, M_1 and M_2 denote the molecular weights and ρ_1 and ρ_2 stand for the densities of the pure components "1" and "2", respectively. The density of the mixture, ρ was determined from Eq. (1).

RESULTS AND DISCUSSION

The density and excess volume data, evaluated according to Eq. (3), for the binary liquid mixtures methanol(1) + acetonitrile(2) and ethanol(1) + acetonitrile(2) are presented in Table II.

TABLE II. Density and molar excess volume at 298.15 K

x_1	ρ g cm^{-3}	V^E cm^{3}mol^{-1}	x_1	ρ g cm^{-3}	V^E cm^{3}mol^{-1}	x_1	ρ g cm^{-3}	V^E cm^{3}mol^{-1}
			Methanol(1)+acetonitrile(2)					
0.1012	0.77800	− 0.034	0.3869	0.78189	− 0.120	0.6998	0.78583	− 0.155
0.1986	0.77919	− 0.058	0.3995	0.78207	− 0.123	0.7983	0.78675	− 0.140
0.2482	0.77994	− 0.078	0.4990	0.78342	− 0.144	0.8523	0.78709	− 0.122
0.3028	0.78076	− 0.099	0.5871	0.78449	− 0.151	0.9012	0.78731	− 0.101
			Ethanol(1)+acetonitrile(2)					
0.0480	0.77703	0.008	0.4009	0.78044	− 0.007	0.6525	0.78332	− 0.061
0.1474	0.77785	0.015	0.4400	0.78096	− 0.020	0.7842	0.78454	− 0.072
0.2461	0.77882	0.010	0.4878	0.78152	− 0.031	0.8202	0.78479	− 0.069
0.3008	0.77938	0.005	0.5929	0.78259	− 0.044	0.8988	0.78516	− 0.052
0.3523	0.77994	− 0.002	0.6113	0.78287	− 0.053	0.9478	0.78540	− 0.041

The experimental excess volume was fitted to the Redlich-Kister expression (RK)[10]:

$$V^E_{cal} = x_1(1 - x_1) \sum_{i=1}^{k} A_i (2x_1 - 1)^{i-1} \tag{4}$$

where x_1 represents the mole fraction of methanol or ethanol, A_i are fitting parameters obtained by the least square method, k is the degree of the polynomial expansion used. The standard deviation σ of the fit is defined as

$$\sigma = \left[\Sigma (V^E - V^E_{cal})^2 / (N - k) \right]^{1/2} \tag{5}$$

where N represents the number of the experimental data points. The optimized parameters A_i and the standard deviation of the binary V^E data of the investigated mixtures are listed in Table III.

TABLE III. Parameters A_i of Eq. (4) and the standard deviation of the fit σ

System	A_1	A_2	A_3	A_4	A_5	σ
Methanol+acetonitrile	– 0.57521	0.30139	– 0.34919	0.27913	– 0.34176	0.002
Ethanol+acetonitrile	– 0.11803	0.40459	– 0.17328	0.11411	–	0.003

The excess volume for the mixtures investigated in the present work has been reported previously in the literature. The V^E data at 298.15 K for the system methanol + acetonitrile have been measured by several measuring techniques: Nakanishi and Shirai[11] determined V^E by picnometry, while Cibulka *et al.* reported V^E data measured by a digital vibrating-tube densimeter[5] and by a tilting dilution dilatometer.[12] Cibulka *et al.*[12] reported V^E data at 298.15 K for the system ethanol + acetonitrile determined by a tilting dilution dilatometer.

The experimental V^E values at 298.15 K, the fit performed using the RK equation for the investigated binary mixtures, as well as the results of the authors mentioned above are presented in Fig. 1.
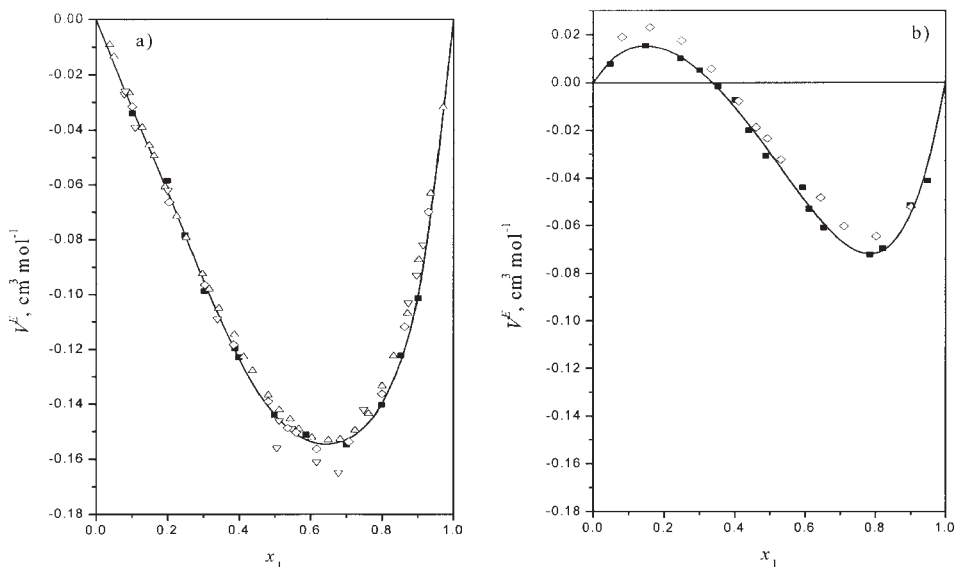

Fig. 1. Excess molar volume of the binary mixtures: a) methanol(1) + acetonitrile(2); b) ethanol(1) + acetonitrile(2) at 298.15 K. Experimental values: ■ – this work; Δ – Cibulka *et al.*[5]; ∇ – Nakanishi and Shirai[11]; ◇ – Cibulka *et al.*[12]; —, calculated by the RK equation with coefficients from Table III.

It can be seen from Fig. 1a that our results for the methanol + acetonitrile system agree very well with those of Cibulka *et al.*[5,12] and satisfactorily with those reported by Nakanishi and Shirai.[11] On the other hand, the results of Cibulka *et al.*[12] for the system ethanol + acetonitrile (Fig. 1b) are slightly higher compared to our results, especially in the regions of the extremes of the $V^E - x_1$ curve.

As can be seen from Fig. 1, the values of V^E for both the investigated systems are very small and close to zero. Also, the excess volume of the alcohol + acetonitrile systems rise with increasing length of the alkyl chain in the alcohol.

The excess volume curve for the system with methanol is negative over the entire composition range and tends to be skewed toward mixtures rich in acetonitrile. This negative effect in V^E is most likely due to the association between the nitrile group and the proton of the methanol hydroxyl group. This effect apparently outweighs the effect due to the dissociation of the alcohol. The excess volume curve for the system with ethanol has an S-shaped form; the values of V^E are slightly positive in the region of low ethanol concentrations and slightly negative for mole fractions of ethanol higher than 0.35.

LIST OF SYMBOLS

A – constant of Eq. (1)
A_i – fitting parameters of Eq. (4)
k – degree of the polynomial expansion
M – molecular weight
N – number of the experimental points
P – absolute pressure
V^E – excess molar volume
x – mole fraction

Greek letters

ρ – density
τ – period of oscillation
σ – standard deviation

Subscripts

0 – reference fluid
1, 2 – compounds
cal – calculated values
i – number of fitting parameters

ИЗВОД

ДОПУНСКА МОЛАРНА ЗАПРЕМИНА СИСТЕМА АЦЕТОНИТРИЛ + АЛКОХОЛ НА 298.15 K. I ДЕО. МЕРЕЊЕ ГУСТИНА СИСТЕМА АЦЕТОНИТРИЛ + МЕТАНОЛ, + ЕТАНОЛ

ИВОНА Р. ГРГУРИЋ, АЛЕКСАНДАР Ж. ТАСИЋ, БОЈАН Д. ЂОРЂЕВИЋ, МИРЈАНА Љ. КИЈЕВЧАНИН и СЛОБОДАН П. ШЕРБАНОВИЋ

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Допунска моларна запремина V^E бинарних течних смеша ацетонитрил + метанол и ацетонитрил + етанол, одређена је мерењем густине на 298.15 K и атмосферском притиску у целом концентрационом опсегу. Мерења су вршена дигиталним густиномером, типа Anton

Paar DMA 55. За корелисање експерименталних података коришћена је Redlich-Kister-ова једначина.

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