

EXCESS VOLUMES IN THE METHANOL-*tert*-AMYL METHYL ETHER SYSTEM AT 298.15 K

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Excess volumes have been measured by means of a vibrating-tube densimeter in the methanol-*tert*-amyl methyl ether system at 298.15 K. The excess volumes are negative over the whole concentration range.

Tert-amyl methyl ether (TAME) is, in addition to methyl *tert*-butyl ether, one of most efficient antiknock additives to gasoline. Continuing the systematic study of systems containing these substances, excess volumes in the methanol-TAME system at 298.15 K have been measured by means of a digital densimeter DMA 60 + 602.

EXPERIMENTAL

Preparation of pure substances. TAME was synthesized and purified as described in our foregoing work¹, where the comparison of its physico-chemical constants with literature data at the temperature of 293.15 K has also been given. At 298.15 K the measured values of its density $\rho^{298.15} = 0.76577 \text{ g cm}^{-3}$ and refractive index $n_D^{298.15} = 1.3858$ (literature values for this temperature were not found).

Purification of methanol has also been given in work¹ along with its criteria of purity. The value of density measured by the densimeter and used through this work is $\rho^{298.15} = 0.78663$.

Procedure. Samples of the methanol and TAME mixtures were prepared by weighing in vessels ("onion cells") designed and recommended by Takenaka and coworkers². Use of vessels of this type ensures that the composition calculated from weighed amounts of components corresponds most accurately to the true composition of the liquid without being necessary to take into account the amount of substances in the vapour phase. The total volume of our vessels amounts to approximately 7 cm^3 . The estimated total error in mole fraction x does not exceed the value $5 \cdot 10^{-4}$ even at the concentration ends.

The density measurements were made with a DMA 60 + 602 vibrating-tube densimeter (A. Paar, Austria). The densimeter measuring cell was tempered with a Heto type CB7 ultra-thermostat maintaining the temperature of vibrating cell with the accuracy of $\pm 0.01 \text{ K}$. The densimeter was tested by measuring the density of five pure substances (water, benzene, cyclohexane, methanol, and TAME) whose density was determined in modified 25 cm^3 two-arm Sprengel-Ostwald pycnometers with the accuracy of $\pm 0.00002 \text{ g cm}^{-3}$. This measurements proved the reproducibility of the density determination with the densimeter to be better than $2 \cdot 10^{-5} \text{ g cm}^{-3}$. Besides, we carried out a check of the entire measuring procedure by deter-

imining the excess volumes of the benzene and cyclohexane mixtures and by comparing the results with the values calculated on using the optimum equation³ for V^E of this test mixture. The found mean deviation in V^E , $\sim 2 \cdot 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$, proved that our apparatus and procedure were reliable. From above mentioned one can deduce that the accuracy of V^E determination is better than $5 \cdot 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$.

RESULTS AND DISCUSSION

Excess volumes V^E at 298.15 K, calculated from the measured density values of samples weighed, are given in Table I. These V^E values were fitted to the equation of the Redlich-Kister type

$$V^E = x_1(1 - x_1) \sum_{i=1}^n A_i(1 - 2x_1)^{i-1}, \quad (I)$$

where x_1 is the mole fraction of methanol and A_i are constants whose values are to be determined from experimental data. Calculations showed that optimum number of constants is $n = 3$.

TABLE I

Experimental excess molar volumes ($\text{cm}^3 \cdot \text{mol}^{-1}$) at 289.15 K and their comparison with calculated values^a in the methanol-TAME system

x_1	V_{exp}^E	V_{calc}^E	$(V_{\text{exp}}^E - V_{\text{calc}}^E) \cdot 10^4$
0.0786	-0.1678	-0.1668	-10
0.1364	-0.2610	-0.2604	-6
0.1866	-0.3254	-0.3244	-10
0.2086	-0.3464	-0.3478	14
0.2527	-0.3881	-0.3873	-8
0.3013	-0.4177	-0.4201	24
0.4342	-0.4615	-0.4611	-4
0.5205	-0.4570	-0.4558	-12
0.6268	-0.4187	-0.4191	4
0.7373	-0.3469	-0.3465	-4
0.8368	-0.2473	-0.2479	6
0.8803	-0.1932	-0.1934	2
0.9202	-0.1366	-0.1365	-1
Deviations:	mean absolute standard		8 12

^a Constants of Eq. (I): $A_1 = -1.836357$, $A_2 = -0.263494$, $A_3 = -0.344726$; mean deviation in $(x_{1,\text{exp}} - x_{1,\text{calc}})$ equals $1.8 \cdot 10^{-6}$, standard deviation $2.6 \cdot 10^{-6}$.

The evaluation of constants A_1 , A_2 , A_3 was carried out by the maximum likelihood method by using the procedures described in work⁴. On using the above-mentioned estimated experimental inaccuracies in composition x and excess molar volume V^E , these values of constants of Eq. (1) were found: $A_1 = -1.836357$, $A_2 = -0.263494$, $A_3 = -0.344726$. The mean and standard deviations of the fit are also given in Table I (the computed values of x_1 are not given because the deviations are here at least an order lower than the number of decimal places of the given experimental values x_1).

The V^E values for the given system are negative over the whole concentration range and, moreover, numerically rather high. Such a shape of V^E can be qualitatively explained on the basis of difference in the size (and shape) of molecules of both components and interactions between them. Mixing the components results in changes of "free volume" and in much close-packed structure in comparison with both pure liquid components.

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