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Volumetric behaviour of binary liquid systems composed of toluene, isooctane, and methyl tert-butyl ether at temperatures from (298.15 to 328.15) K

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ABSTRACT

The densities and speeds of sound of (toluene + isooctane), (MTBE + toluene), and (MTBE + isooctane) were measured at four temperatures from (298.15 to 328.15) K, and the respective values of excess volumes V_m^E and adiabatic compressibility κ_S were calculated. The V_m^E and κ_S values were fitted to the fourth-order Redlich–Kister equation. The V_m^E values for (MTBE + toluene) are negative and decreasing with increasing temperature. The other systems show positive V_m^E with comparatively small temperature dependence.

1. Introduction

Research activities of our laboratory comprise, among others, the systematic measurement of volumetric properties of different groups of organic compounds. Our present project is devoted to the systematic study of liquid systems modelling liquid engine fuels. After measuring (cyclohexane + alkane) at normal pressure and $T = 298.15$ K [1], (cyclohexane + nonane) at temperatures from (298.15 to 328.15) K and at pressures up to 40 MPa [2], (octane + benzene, or +toluene, or +1,3-xylene, or +1,3,5-trimethylbenzene) at temperatures between (298.15 and 328.15) K [3], and (octane + benzene) at temperatures from (298.15 to 328.15) K and at pressures up to 40 MPa [4], the binary and ternary systems containing methyl tert-butyl ether (MTBE) have been studied with the aim to decide what and how many ternary constants, in addition to the binary constants, are needed to fit the ternary data to Redlich–Kister equation within the error of experimental results. This measurement is also of practical importance with respect to use of MTBE as the liquid fuel antiknock additive.

The thorough literature search showed that there exist some limited binary data for these systems (for their detailed comparison with our results see Section 3). However, to be able to do the test, we needed more accurate and mutually consistent binary (and ternary) results. Not finding such data sets, we decided to measure the title binary systems as the first step.

The densities and excess volumes of the investigated liquids and their mixtures are required, for instance, for relating excess enthalpy and excess Gibbs free energy values. From a practical point of view, the data are useful for the design of mixing, storage, and process equipment. Last but not least, the measured results reflect interactions between the molecules of the mixtures studied and can serve for testing the theories of the liquid state.

2. Experimental

2.1. Materials

The chemicals used in the experiments were the following products from Fluka: MTBE (methyl 1,1-dimethylethyl ether), puriss., g.c. mass fraction purity ⩾0.95, toluene, RdH, for chromatography, g.c. mass fraction purity ⩾0.995, isooctane (2,2,4-trimethylpentane), RdH puriss. p.a., g.c. mass fraction purity ⩾0.995. The substances were used without further purification and dried and stored over 0.4 nm molecular sieves. In order to check the purity of the substances, their density and refractive index values were determined at $T = 298.15$ K and compared with literature data [5,6] with the agreement being, in general, good (table 1). The contents of the substances were also determined by gas chromatography (HP Ser.II. model 5890 chromatograph with capillary column type 1909 1Z–413E and f.i.d., column temperature 413.3 K, helium flow rate $4.2 \cdot 10^{-4}\ \mathrm{cm^3 \cdot s^{-1}}$).

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TABLE 1

Densities (ρ) and refractive index values (n_D) at T = 298.15 K of the pure components, and their comparison with literature; w is the mass fraction purity as determined by g.l.c.

Component	$\rho/(\text{g} \cdot \text{cm}^{-3})$			n_D			w
	Experimental	Literature	Reference	Experimental	Literature	Reference	
Toluene	0.86227	0.8623	[5]	1.4941	1.49414	[5]	0.9995
Isooctane	0.68779	0.68781	[5]	1.38905	1.38898	[5]	0.9996
MTBE	0.73527	0.7353	[6]	1.36648	1.3664	[6]	0.9989

2.2. Apparatus and procedure

The density and the speed of sound of the pure liquids and mixtures were measured at atmospheric pressure with a digital density and sound velocity analyzer Anton Paar DSA-5000 automatically thermostatted at ±0.001 K by built-in solid state thermostat, with an estimated uncertainty of $\pm 5 \cdot 10^{-6}\ \text{g} \cdot \text{cm}^{-3}$ in density and $\pm 0.5\ \text{m} \cdot \text{s}^{-1}$ in sound velocity.

The samples were prepared by weighing (SCALTEC SBC 21 balance with an accuracy of $\pm 1 \cdot 10^{-5}$ g) and then partially degassed at the respective measurement temperature for 3 h by means of an ultrasonic heated bath (Bandelin RK 100H, Berlin, Germany) to prevent the formation of gas bubbles in the densimeter capillary at higher temperatures.

Attention was paid to changes in the composition of the samples during weighing and partial degassing. To diminish this effect, the samples were weighed, degassed, and stored in vessels ("onion cells") designed and recommended by Takenaka *et al.* [7]. Use of this vessels and procedure ensured that the composition calculated from weighed amounts of pure substances corresponded most accurately to the actual composition of the mixture sample without being necessary to take into account the amount of substances in the vapour phase. The vessels are of a special shape, with a negligibly small vapour space left ($<0.25\ \text{cm}^3$ compared to the total cell volume of about $10\ \text{cm}^3$). They are tightly sealed with Teflon stoppers during the operations.

The density of the sample, ρ, was calculated from the measured period of vibration, τ, by using the following relation:

$$\rho = a + b\tau^2. \tag{1}$$

The constants a and b were determined by calibration [8] using double-distilled water and heptane prepared specially for the densimeter calibration. It was doubly distilled in a packed column of 30 theoretical plates. Its density at T = 298.15 K was determined precisely (four repeated runs) in a $25\ \text{cm}^3$ two-arm Sprengel–Ostwald pyknometer with an accuracy of $\pm 1 \cdot 10^{-5}\ \text{g} \cdot \text{cm}^{-3}$. The values of density of water were taken from the tables in the densimeter manual.The V_m^E values were calculated from the mixtures densities, ρ, and the densities, ρ_i, and molar masses, M_i, of pure components i (i = 1,2) by using the relation:

$$V_m^E = \{xM_1 + (1-x)M_2\}/\rho - \{xM_1/\rho 1 + (1-x)M_2/\rho_2\}, \tag{2}$$

where subscript 1 refers to the first component of the binary, 2 to the respective second component, and x stands for the mole fraction of the first component.

The experimental uncertainty in the mole fraction composition is less than $\pm 5 \cdot 10^{-5}$, in density is approximately $\pm 2 \cdot 10^{-5}\ \text{g} \cdot \text{cm}^{-3}$, in sound velocity $\pm 0.5\ \text{m} \cdot \text{s}^{-1}$, and in V_m^E is estimated to be about $\pm 2 \cdot 10^{-3}\ \text{cm}^3 \cdot \text{mol}^{-1}$. However, for both the systems with MTBE at higher and especially the highest temperature, this value might be, due to high volatility of the ether, several times higher.

3. Results and correlation

The results of the measurements of densities and sound velocities of the three binary systems are given in tables 2 to 4 together with the calculated values of V_m^E and adiabatic compressibility κ_S and illustrated in figures 1 to 3 for the temperature dependence of V_m^E and in figures 4 to 6 for the temperature dependence of κ_S. The adiabatic compressibility κ_S was calculated from the relation

$$\kappa_S = 1/(u^2\rho), \tag{3}$$

where u is the measured sound velocity. For fitting the adiabatic compressibility data, the following excess quantity analogue defined by the equation:

$$\kappa_S^E = \kappa_S - x\kappa_{S1} - (1-x)\kappa_{S2} \tag{4}$$

was applied. κ_{S1} and κ_{S2} are compressibility values of pure components.

Both the quantities, V_m^E and κ_S^E denoted generally as Q were fitted to the fourth-order Redlich–Kister type equation:

$$Q = x(1-x)\left[\sum_{n=0}^{2} A_n(1-2x)^n\right], \tag{5}$$

where A_n are disposable parameters which were determined by the weighted gnostic method [9,10]. The number of parameters A_i (3 for V_m^E and 2 for κ_S^E) was predetermined by the statistical F-test. The parameters A_i and standard deviations $\sigma(V_m^E)$ and $\sigma(\kappa_S^E)$ of the fit are summarized in table 5.

Density of pure MTBE at T = 328.15 K is not, due to its high volatility, experimentally accessible with sufficient accuracy and thus had to be determined as another adjustable parameter. For this purpose, equations (1) and (5) can be combined and rewritten as

$$\begin{aligned} &xM_1 + (1-x)M_2/\rho - (1-x)M_2/\rho_2 \\ &\quad = xM_1/\rho_1 + x(1-x)\left[\sum_{n=0}^{2} A_n(1-2x)^n\right]. \end{aligned} \tag{6}$$

The additional adjustable parameter is then $1/\rho_1$ where ρ_1 is the required value of the MTBE density. Both the binary systems containing MTBE were correlated simultaneously in order to determine the common value of ρ_1. Correlation was performed by the linear gnostic regression [9,10] adopting the minimum penalty estimate algorithm suggested by Kovanic [11,12] in order to achieve better stability. The set of linear equations was solved by the singular value decomposition [13]. The method was compared to nonlinear optimization at lower temperatures where the pure component densities are known, and it is therefore possible to verify whether the algorithm leads to reasonable values. It was found that the linear algorithm is faster and more reliable. It is also easier to use because no initial approximation is needed. Since the difference in the density obtained by the linear and nonlinear algorithms is negligible, the use of the linear regression should be preferred.

The comparison of literature data of V_m^E with those of this work is given in figure 7 for (toluene + isooctane), in figure 8 for (MTBE + toluene), and in figure 9 for (MTBE + isooctane). The comparison for single systems appears as follows.

3.1. (Toluene + isooctane)

The V_m^E values for the system are comparatively low (maximum at about $0.1\ \text{cm}^3 \cdot \text{mol}^{-1}$). The literature V_m^E data at T = 298.15 K by