Excess Properties of Binary Mixtures of 2-Methoxy-2-methylpropane with *n*-Heptane

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Densities, viscosities, and refractive indexes of the binary system 2-Methoxy-2-methylpropane + n-Heptane have been measured at 293.15, 298.15 and 303.15 K and atmospheric pressure, over the whole composition range. The excess values of molar volume, viscosity, Gibbs free energy of activation of viscous flow, and internal pressure were calculated from experimental measurements. Based on the variation of the excess functions with composition, conclusions about the molecular interactions in these kinds of mixtures were obtained.

Keywords: binary liquid mixtures, excess properties, n-heptane, 2-Methoxy-2-methylpropane

In previous works we studied several binary liquid solutions of C_6-C_8 hydrocarbons with alcohols [1 – 5]. In this contribution we report the following excess properties: molar volumes (V^E), viscosity (η^E), molar free energy of activation of viscous flow (G^{*E}), and internal pressures (P_i^E), for 2-Methoxy-2-methylpropane + *n*-Heptane mixtures, which were calculated from the density, viscosity, and refractive index measured.

Experimental part

The chemicals MTBE (2-Methoxy-2-methylpropane) was obtained from Merck (>99.8 mol %) and *n*-heptane was supplied by Fluka (>99.5 mol %). The chemicals were dried over molecular sieves (Fluka type 4 Å). The purity was checked through chromatographic and refractive index methods. Through weighting, mole fractions were determined. The precision of the mole fraction was ± 0.00005. The densities were determined by hydrostatic weighing method of Kohlrausch. The experimental technique has been previously described [6].

Viscosities of the pure compounds and of the binary mixtures were determined with an Ubbelohde kinematic viscometer [7] that was always kept in a vertical position in a water thermostat. The kinematic viscosity was calculated using the relation:

$$\nu = At - B/t \qquad (1)$$

where t is the flowing time (± 0.1s) of a constant volume liquid through the viscometer capillary; A and B are characteristic constants of the used viscometer, which were determined by taking water and benzene as the calibrating liquids for correction of kinetic energy (Hagen-Poiseuille) deviations. The dynamic viscosity was determined from the equation:

$$\eta = \nu\rho \qquad (2)$$

where ρ is the density of the liquid.

The precision of the densities was ± 0.00005 g/cm^3. The accuracy of the viscosity measurement was estimated to be ± 0.0010 mPa . s. In all determinations, triplicate experiments were performed at each composition and temperature, and the arithmetic mean was taken for the calculations of the viscosity. The flow times were repeatable within 1%. The refractive indices (sodium D line), n_D of pure substances as well as mixtures were measured with an Abbe refractometer. For the density, viscosity and refractive index a thermostatic water bath, whose temperature was controlled to ± 0.05 K was used.

Results and discussion

The measured densities, viscosities and refractive indices of the pure component liquids are listed in table 1 together with published values [8-12]. All measured values show good agreement with data given in the literature. Densities, viscosities and refractive indexes of the binary mixtures of MTBE + *n*-heptane are reported in table 2.

The excess functions of the binary systems can be represented by a Redlich-Kister type equation:

$$X^E = x_i x_j \sum_{k=0}^{3} a_k (2x_i - 1)^k, \qquad (3)$$

where X^E represents any of the following properties: V^E, η^E, G^{*E}, P_i^E; x_i, x_j are the mole fractions of the components i and j, respectively, and a_k denotes the polynomial coefficients.

Component	Purity %mol	Temp. K	Density, kg·m^{-3}		Viscosity mPa·s		n_D^{25}	
			Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
		293.15	739.3		0.3711			
MTBE	>99.8	298.15	735.3	735.7 [8]	0.3560	0.348 [8]	1.3658	1.3660 [9]
		303.15	731.3		0.3359			
		293.15	682.8		0.4255			
n-heptane	>99.5	298.15	679.6	679.4 [12]	0.3965	0.3900 [10]	1.3845	1.3850 [10]
		303.15	676.4	675.1 [11]	0.3785	0.3680 [11]		

Table1
COMPARISON OF EXPERIMENTAL DENSITIES, VISCOSITIES AND REFRACTIVE INDICES n_D^{25} OF PURE LIQUIDS WITH LITERATURE VALUES

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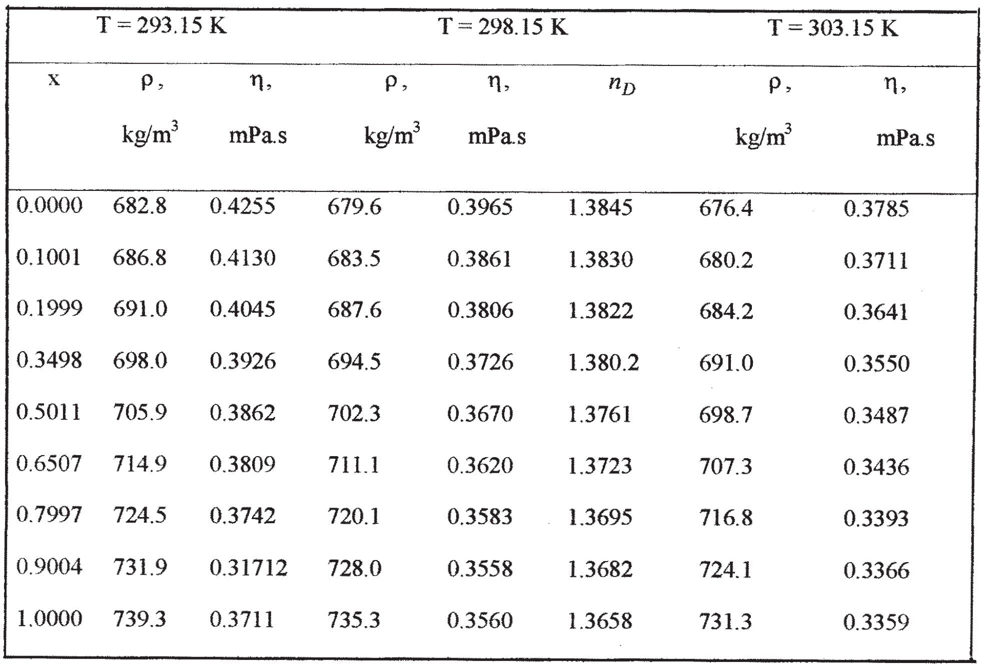
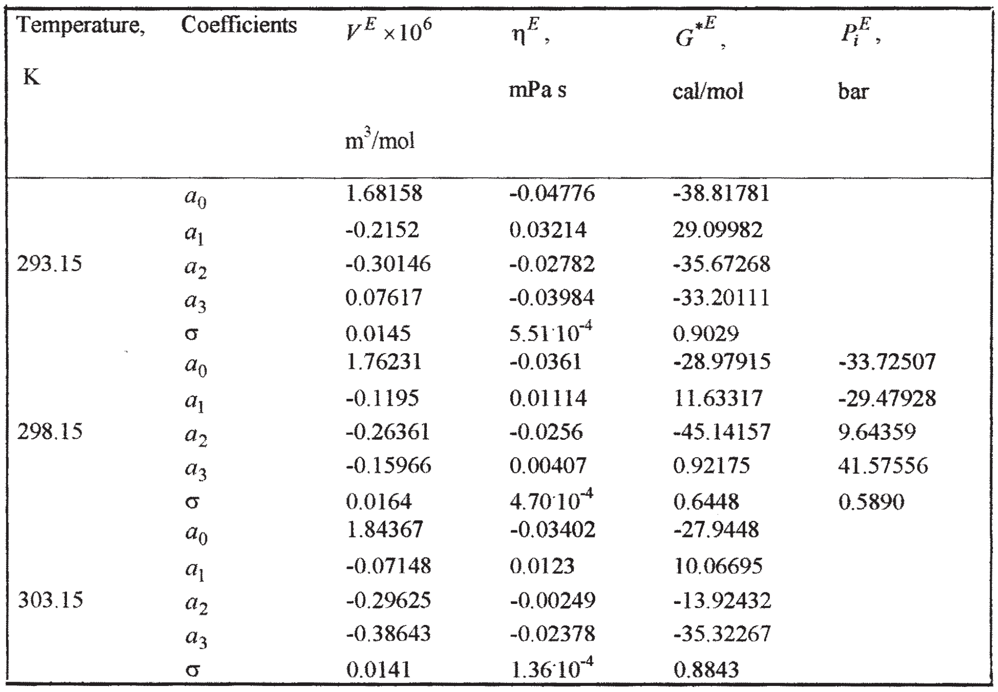
Table 2
EXPERIMENTAL DENSITIES, VISCOSITIES, AND REFRACTIVES OF BINARY MIXTURES OF MTBE (*x*) + *n*-HEPTANE AT DIFFERENT TEMPERATURES



	T = 293.15 K		T = 298.15 K			T = 303.15 K	
x	ρ, kg/m^3	η, mPa.s	ρ, kg/m^3	η, mPa.s	n_D	ρ, kg/m^3	η, mPa.s
0.0000	682.8	0.4255	679.6	0.3965	1.3845	676.4	0.3785
0.1001	686.8	0.4130	683.5	0.3861	1.3830	680.2	0.3711
0.1999	691.0	0.4045	687.6	0.3806	1.3822	684.2	0.3641
0.3498	698.0	0.3926	694.5	0.3726	1.380.2	691.0	0.3550
0.5011	705.9	0.3862	702.3	0.3670	1.3761	698.7	0.3487
0.6507	714.9	0.3809	711.1	0.3620	1.3723	707.3	0.3436
0.7997	724.5	0.3742	720.1	0.3583	1.3695	716.8	0.3393
0.9004	731.9	0.31712	728.0	0.3558	1.3682	724.1	0.3366
1.0000	739.3	0.3711	735.3	0.3560	1.3658	731.3	0.3359

Table 3
COEFFICIENTS a_k FROM EQUATION (3) AND STANDARD DEVIATIONS FOR THE MTBE + *n*-HEPTANE SYSTEM AT DIFFERENT TEMPERATURE



Temperature, K	Coefficients	$V^E \times 10^6$ m^3/mol	η^E, mPa s	G^{*E}, cal/mol	P_i^E, bar
293.15	a_0	1.68158	-0.04776	-38.81781	
	a_1	-0.2152	0.03214	29.09982	
	a_2	-0.30146	-0.02782	-35.67268	
	a_3	0.07617	-0.03984	-33.20111	
	σ	0.0145	$5.51 \cdot 10^{-4}$	0.9029	
298.15	a_0	1.76231	-0.0361	-28.97915	-33.72507
	a_1	-0.1195	0.01114	11.63317	-29.47928
	a_2	-0.26361	-0.0256	-45.14157	9.64359
	a_3	-0.15966	0.00407	0.92175	41.57556
	σ	0.0164	$4.70 \cdot 10^{-4}$	0.6448	0.5890
303.15	a_0	1.84367	-0.03402	-27.9448	
	a_1	-0.07148	0.0123	10.06695	
	a_2	-0.29625	-0.00249	-13.92432	
	a_3	-0.38643	-0.02378	-35.32267	
	σ	0.0141	$1.36 \cdot 10^{-4}$	0.8843	

The values of these coefficients are given in table 3 along with the standard deviation, σ, defined by:

$$\sigma = \left[\frac{\sum (X_{obs.}^E - X_{calc.}^E)^2}{m-n}\right]^{1/2}, \quad (4)$$

where *m* is the number of data points and *n* is the number of estimated parameters.

The excess functions were calculated with the following equations:

$$V^E = V - [x_1V_1 + x_2V_2] \quad (5)$$

$$\eta^E = \eta - [x_1\eta_1 + x_2\eta_2] \quad (6)$$

$$G^{*E} = RT[\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (7)$$

$$P_i^E = P_i - [x_1P_{i1} + x_2P_{i2}] \quad (8)$$

where P_i, P_{i1} and P_{i2} are the internal pressures of the mixtures and the pure components, respectively, which can be obtained from the Buchler-Hirschfelder-Curtis equation of state [13]:

$$P_i = \frac{2^{1/6}RT}{2^{1/6}V - dN^{1/3}V^{2/3}} \qquad (9)$$

where N is Avogadro's number and d the molecular diameter of the mixture or the pure components, calculated by the following relation [14]:

$$d = 2\left[\frac{n_D^2-1}{n_D^2+2}V\frac{3}{4\pi N}\right]^{1/3} \qquad (10)$$

where n_D are the refractive indexes of the mixtures or the pure components.

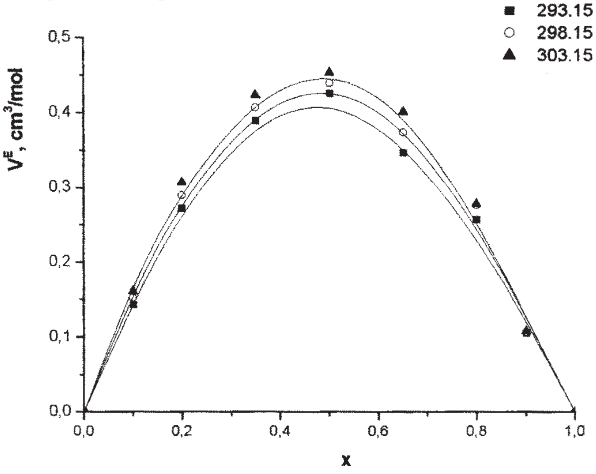


Fig. 1. Molar excess volumes of the MTBE (x) + *n*-heptane system at different temperatures

In figure 1 excess molar volumes are plotted against composition. It can be seen that the isothermal curves at 293.15 K, 298.15 K and 303.15 K are positive for MTBE + *n*-heptane system over the entire range of mole fractions and at all the temperatures. Several effects may contribute to the values of V^E, such as breaking of liquid order on mixing, contribution to the difference in size and shape of the components, difference in free volumes, and dipole-dipole interactions [15].

The positive values of the excess molar volumes indicate that the two former effects are dominant over the latter effects, implying that dispersion forces are dominant in MTBE + *n*-heptane system.

In figure 2, it is observed that excess viscosity for MTBE + *n*-heptane mixture present negative excess values over the entire range of mole fractions and at all the temperatures. The negative deviations occur when dispersion forces are preponderant, which is in complete agreement with the conclusion reached for the V^E behaviour.

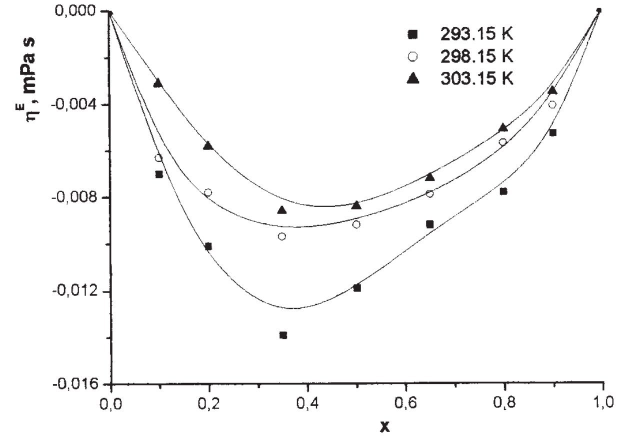


Fig. 2. Excess viscosities of the MTBE (x) + *n*-heptane system at different temperatures

Figure 3 shows the dependence of the calculated G^{*E} values upon composition. The small values of this excess property indicate that in MTBE + *n*-heptane system the molecular interactions are weak.

The values of excess internal pressure calculated at 298.15 K are negative over the entire range of mole fractions. The negative values indicates qualitatively that the repulsion forces are higher than those of attraction in MTBE + *n*-heptane system.

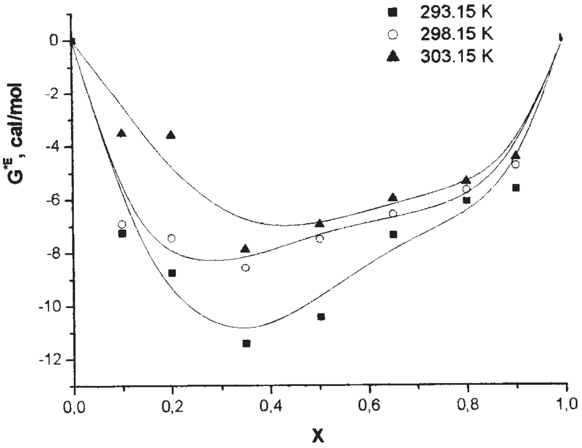


Fig. 3. Molar excess free energies of viscous flow activation of the MTBE (x) + *n*-heptane system at different temperatures

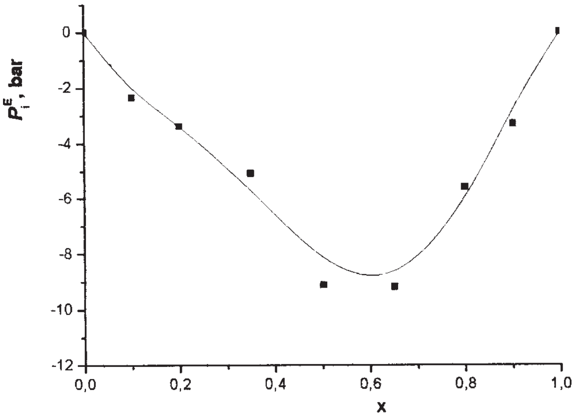


Fig. 4. Excess internal pressures of the MTBE (x) + *n*-heptane system at 298.15 K

Conclusions

The densities and viscosities of binary mixtures of MTBE + *n*-heptane were measured experimentally at 293.15 K, 298.15 and 303.15 K over the entire composition range. From these results, the excess values of molar volume, viscosity, Gibbs free energy of activation of viscous flow, and internal pressure have been computed and fitted to the Redlich-Kister equation. The results show that for the MTBE + *n*-heptane system the dispersion forces are preponderant and also that the repulsion forces have a predominant effect in these mixtures.

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