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VOLUMETRIC PROPERTIES OF THE BINARY MIXTURE *n*-HEPTANE+ETHYLBENZENE MIXTURES AT HIGH TEMPERATURES AND HIGH PRESSURES

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New experimental data on the density of three (0.2393, 0.4856 and 0.7390 mole fraction of ethylbenzene) binary *n*-heptane+ethylbenzene mixtures have been measured with a constant-volume piezometer immersed in a precision liquid thermostat. These new experimental data covering a temperature range from 306 to 527 K and a pressure range of 0.1 to 11 MPa. The experimental data reported here have an uncertainty less than 0.06% for the density, 0.05% for the pressure, 15 mK for the temperature, and 0.012% for the concentration. Excess molar volumes were derived using measured values of density for the mixtures and for the pure components calculated with reference equation of state for *n*-heptane (Span and Wagner, 2003) and for the pure ethylbenzene (Frenkel *et al*., 2005). The derived values of excess molar volumes at atmospheric pressure were compared with the values reported by other authors in the literature. The effect of pressure on the excess molar volumes was studied.

Keywords: *density, ethylbenzene, excess molar volume, n-heptane*

Introduction

The volumetric properties of hydrocarbon mixtures are required in many industrial applications such as design calculations in petrochemical industrial equipment. Knowledge of the thermodynamic ($p\rho Tx$) properties of hydrocarbon mixtures is of fundamental importance for the modelling of underground oil flow and in other applications of chemical engineering to develop oil processes, process equipment in the oil and gas industries, oil recovery technology, geology and mineralogy for geothermal processes. All of these processes occur at high temperatures and high pressures. Underground oil comprises the largest reservoirs of hydrocarbon mixtures currently known. Thus, there is great practical interest in the thermodynamic properties of hydrocarbon mixtures at high temperatures and high pressures.

The accurate volumetric properties of hydrocarbon mixtures over a wide range of temperature and pressure are of research interest because of the need for accurate models to predict the density and excess properties to understand and control the processes that involve hydrocarbon mixtures. To test and improve the accuracy of the prediction techniques and to develop effective prediction methods, reliable density data for the mixtures and their pure components are required. The behavior of binary mixture is highly depending on the geometry, relative sizes of components, structure and type of components and the details of the molecular interactions (nature of the molecules, specific interaction). A comprehensive understanding of the nature of intermolecular interactions in binary mixtures is thus only possible from the accurately measurements of thermodynamic properties and treating the derived excess functions.

However, measurements of the density of *n*-heptane+ethylbenzene mixtures have so far been limited to a rather narrow range of temperature. Very few measurements have been made on the densities for this mixture. Previous density measurements by various authors [1–5] for (*n*-heptane+ethylbenzene) mixtures were performed only at atmospheric pressure and temperatures 293, 298, 308 and 313 K only. A survey of the literature reveals the lack of experimental density data for (*n*-heptane+ethylbenzene) mixtures at high temperatures and high pressures. The densities of this mixture have been measured by Díaz *et al.* [1] at temperature of 298.15 K and at atmospheric pressure over the whole composition range. Measurements were performed with an Anton Paar DSA-48 digital densimeter with a precision of ±0.05 kg m^{-3} or 0.006–0.007%. The same technique was used by Qin *et al*. [2] to measure the densities of

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(*n*-heptane+ethylbenzene) mixtures at temperature of 293.15 K and 0.1 MPa. Awwad *et al.* [3] reported densities for (*n*-heptane+ethylbenzene) mixtures at T=298.15 K and 0.1 MPa. They also used the same technique to measure the densities. The estimated precision in the density measurements is better than 0.004 kg m^{-3}. Paul *et al.* [4] used also vibrating U-tube instrument (Paar, DMA 602/60, A) to measure the density of (*n*-heptane+ethylbenzene) mixtures at 298.15 K and 0.1 MPa. Recently Al Gherwi *et al*. [5] reported the densities for (*n*-heptane+ethylbenzene) mixtures over the entire composition range at two temperatures of 308.15 and 313.15 K. They used also an Anton Paar precision densimeter. The authors claimed uncertainty of the density measurements is ±0.0015 kg m^{-3}. Grolier and Faradjzadeh [6] reported excess molar volumes for this mixture at 298.15 K and 0.1 MPa by using the reported density data. The derived values of excess molar volumes were presented analytically as a function of concentration. Cáceres *et al.* [7] reported the excess molar volumes of six binary mixtures of ethylbenzene+*n*-alkanes (C_6, C_8, C_{10}, *n*-dodecane, *n*-tetradecane, *n*-hexadecane). In this study the ethylbenzene+*n*-C_7H_{16} is missing.

Thus, one of the primary objectives of this work was to expand the existing volumetric (pρ*Tx*) properties for this mixture to high temperatures (up to 527 K) and high pressures (up to 11 MPa).

Experimental

The pρ*Tx* relationship of the {(1–*x*) *n*-heptane+ *x* ethylbenzene} mixtures was measured by a constant-volume method. The apparatus, experimental procedure, and the estimation for uncertainty of the measurements were described previously [8–16] was used without modification. The main part of the apparatus consisted of a piezometer, separating the U-shaped capillary tube with mercury, a liquid thermostat, heaters, a temperature regulator, and a 10 Ω platinum resistance thermometer (PRT-10). The internal volume of the piezometer was calibrated by filling it with pure water and then withdrawing the water in small amounts and weighing them. The mass of the water withdrawn $m(H_2O)$ yielded the volume of the piezometer $V_{293}=m(H_2O)/\rho(H_2O)$ from the well established (uncertainty is 0.0001%) density $\rho(H_2O)$=998.207 kg m^{-3} of water at temperature of 293 K and at 0.101325 MPa [17]. The volume of the piezometer at these conditions was V_{293}= (95.545±0.02) cm^3. The piezometer was immersed in a precision liquid thermostat with volume of 0.02 m^3. The temperature inside the thermostat was maintained uniform within 0.02 K with the aid of three guard and regulating heaters. The temperature of the thermostat liquid was measured with PRT-10. The sample temperature was detected with a precision of ±15 mK. The pressure of the mixture was measured with a dead-weight pressure gauge (MP-600) with an uncertainty of 0.015% (maximum uncertainty was 0.05%). The density of the sample at a given temperature T and pressure p is calculated from the simple relation $\rho(T, P)=m/V_{PT}$, where m is the current mass of the sample in the piezometer and $V_{PT}=V_{293}+\Delta V_T+\Delta V_P$ is the temperature- and pressure-dependent volume of the piezometer. The temperature dependence of the piezometer volume at fixed pressure was calculated as $\Delta V_T=V_{293}[1+3\alpha(T-T_0)]$, where V_{293} is the volume of piezometer at the initial reference temperature T_0=293.15 K and $\alpha=1.3\cdot10^{-5}$ K^{-1} is the thermal expansion coefficient of the piezometer material. The pressure dependence of the piezometer volume ΔV_P was calculated from the Love formula [18] for the cylinder and by using the calibration procedure. The uncertainty in piezometer volume V_{PT} at the given temperature and pressure is less than 0.038%. The uncertainty of the mass m of mixture can be estimated to be 0.006%. The experimental uncertainty in the concentration is estimated to be 0.012 %. Based on a detailed analysis of all sources of uncertainties likely to affect the determination of density with the present apparatus, the combined expanded (k=2) uncertainty of measuring the density was 0.06%.

To test the apparatus and procedures, the densities of the pure components *n*-heptane and ethylbenzene were measured at temperatures from 307 to 517 K and from 315 to 470 K, respectively, and at pressures up to 12–14 MPa. The agreement between the reference equation of state (EOS) calculations [19, 20] and the present density results for *n*-heptane and ethylbenzene is within 0.057 and 0.019%, respectively. Majority published density data sets for pure components are good (within 0.01 to 0.06%) agree with the present values. This excellent agreement confirms the reliability and accuracy of the present measurements for (1–*x*) *n*-heptane+ *x* ethylbenzene mixtures and correct operation of the *p*ρ*T* apparatus.

The purities of *n*-heptane and ethylbenzene (Aldrich) were 99.9 and 99.5 mole%, respectively.

Results and discussions

Measurements of the *p*ρ*Tx* properties of the {(1–*x*) *n*-heptane+*x* ethylbenzene}mixtures were performed at three concentrations, *x*=(0.2393, 0.4856, 0.7390 mole fraction of ethylbenzene), for temperatures between 306 and 527 K. The pressure ranged from 0.1 to 11 MPa. The experimental results are presented in Tables 1 and 2. Some selected experimental

Table 1 Experimental densities and excess molar volumes of {(1–*x*)*n*-heptane+*x* ethylbenzene} mixtures at atmospheric pressure

T/K	x=0.2393 mole fraction		x=0.4856 mole fraction		x=0.7390 mole fraction	
	ρ/kg m^{-3}	V_m^E/cm^3 mol^{-1}	ρ/kg m^{-3}	V_m^E/cm^3 mol^{-1}	ρ/kg m^{-3}	V_m^E/cm^3 mol^{-1}
308.15	708.78	0.0536	751.18	0.0657	799.27	0.0314
313.15	704.50	0.0402	746.80	0.0651	794.80	0.0371
318.15	700.12	0.0416	742.35	0.0702	790.34	0.0383
323.15	695.70	0.0470	737.90	0.0714	785.85	0.0411
328.15	691.29	0.0459	733.43	0.0709	781.36	0.0403
333.15	686.78	0.0509	728.95	0.0689	776.92	0.0386
343.15	677.80	0.471	719.85	0.0691	767.74	0.0378
356.15	665.67	0.0403	707.90	0.0630	756.00	–0.0227

results are shown in Figs 1 to 3 as projections in the ρ–x, ρ–T, and ρ–p planes, together with values reported by other researchers [1–6] at atmospheric pressure and various temperatures.

Comparison with literature data

Figures 1 and 2 show the direct comparison the present densities for the {(1–x) *n*-heptane+ x ethylbenzene} mixtures with those reported by various authors [1–6]. As one can see from these figures, generally the agreement between all of the available data sets is good. In order to provide quantitative comparison, we used an analytical interpolation and extrapolation procedures for the present data due to the temperature and concentration differences between the various datasets. All reported data at temperatures from 298.15 to 313.15 K and at 0.1 MPa lies between 0.001 and 0.065%, except two data points at temperatures of 308.15 and 313.15 K and concentration of 0.7390 mole fraction. The agreement between the data of Awwad *et al*. [3] and Díaz *et al*. [1] and the present data is within 0.033 and 0.036%, respectively, while the data by Paul *et al*. [4] deviate from the present results within 0.017%. Excellent agreement within 0.015% was found between the present data and the values reported in [6]. The data by Al Gherwi *et a*l. [5] deviate from the present values

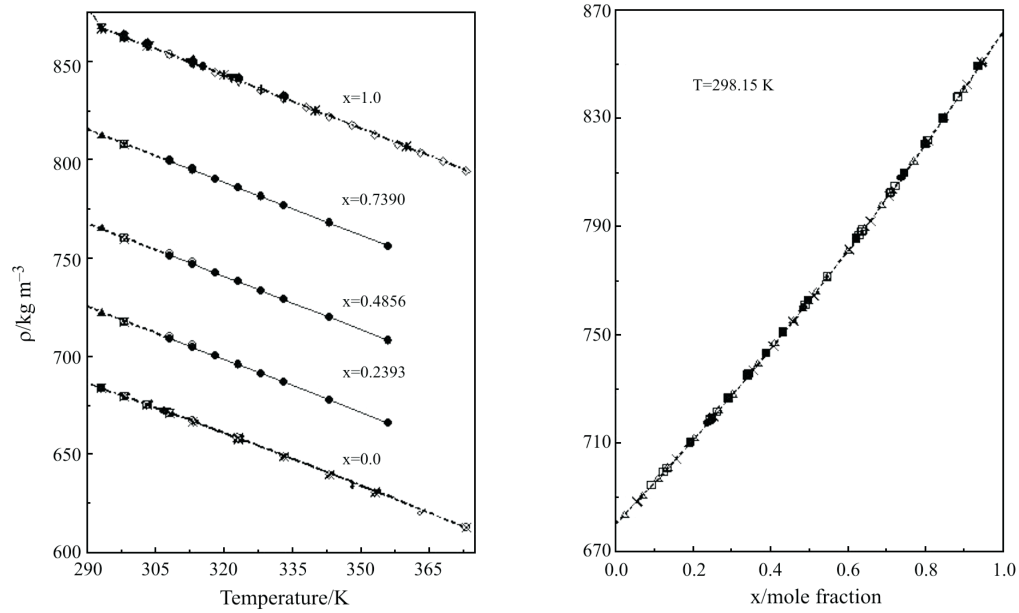

Fig. 1 Measured values of density of *n*-heptane+ethylbenzene mixtures as a function of temperature (left) and concentration (right) at selected isotherm of 298.15 K and various constant concentrations together with the data reported by other authors in the literature. ● – this work; × – [1]; ▲ – [2]; △ – [3]; □ – [6]; ○ – [5]; ▽ – [32]; ■ – [4]; ▼ – [33]; ◇ – [31]; ◆ – [34]; + – [25]; ✠ – [35]; ∗ – [36]; ⊠ – [37]; ⊗ – [26]; ⊠, –[23]; ♂ – [27]; ♀ – [38]; - · - – calculated with EOS for the pure components [19, 20]; – – – – the present data linear extrapolated to low temperatures; ——– linear correlations of the present data

Table 2 Experimental densities of {(1–x) n-heptane+$x$ethylbenzene} mixtures and pure components at high temperatures and high pressures

x=0.2393 mole fraction		x=0.4856 mole fraction		x=0.7390 mole fraction	
p/MPa	ρ/kg m^{-3}	p/MPa	ρ/kg m^{-3}	p/MPa	ρ/kg m^{-3}
T=307.07 K		T=306.26 K		T=317.45 K	
8.414	716.8	9.218	760.5	4.71	795.5
7.257	715.8	7.257	759.1	7.32	797.9
1.961	711.3	3.256	755.6	9.21	799.6
T=387.93 K		T=379.29 K		T=385.65 K	
10.69	655.1	9.179	701.8	4.84	737.0
8.826	652.2	7.355	699.0	7.61	740.9
3.334	643.4	3.334	693.6	9.32	743.3
T=430.21 K		T=438.57 K		T=446.95 K	
10.12	618.1	10.297	651.1	4.53	679.0
8.237	613.9	9.218	649.1	6.87	683.6
4.315	605.1	3.668	636.6	9.64	688.9
T=480.86		T=485.20 K		T=520.69 K	
9.140	566.6	10.375	607.1	5.94	597.4
7.355	560.9	9.218	603.7	9.05	610.8
3.824	545.5	8.237	600.8	–	–
–	–	4.236	589.8	–	–
T=527.11 K		T=527.26 K			
9.963	519.2	10.611	563.0	–	–
7.747	506.5	8.728	554.7	–	–
5.747	491.6	5.217	534.7	–	–

x=0.0 mole fraction		x=1.0 mole fraction	
p/MPa	ρ/kg m^{-3}	p/MPa	ρ/kg m^{-3}
T=306.90 K		T=315.48 K	
0.100	671.91	5.460	851.86
3.750	675.28	9.820	855.47
12.46	648.19	13.76	858.67
T=382.60 K		T=367.82 K	
4.860	612.51	6.790	807.49
11.56	622.90	11.83	812.93
T=462.32 K		T=408.46 K	
5.760	534.83	6.050	769.71
10.46	550.38	14.16	780.79
T=516.55 K		T=469.83 K	
4.410	451.63	7.340	711.51
11.59	499.63	12.49	722.47

within 0.04–0.06% at temperatures of 308.15 and 313.15 K and at concentration below 0.7390 mole fraction, but at high concentrations above 0.7390 mole fraction the deviations are within 0.16 to 0.21%. To compare with the data at 293.15 and 298.15 K the present data were linearly extrapolated to low temperatures. Our extrapolated to 293.15 K values of density are deviate from the values reported by Qin *et al.* [2] within 0.045–0.065%.

Excess molar volumes

Excess molar volumes are related with structural and physical contributions [21–23] and allow a better un-

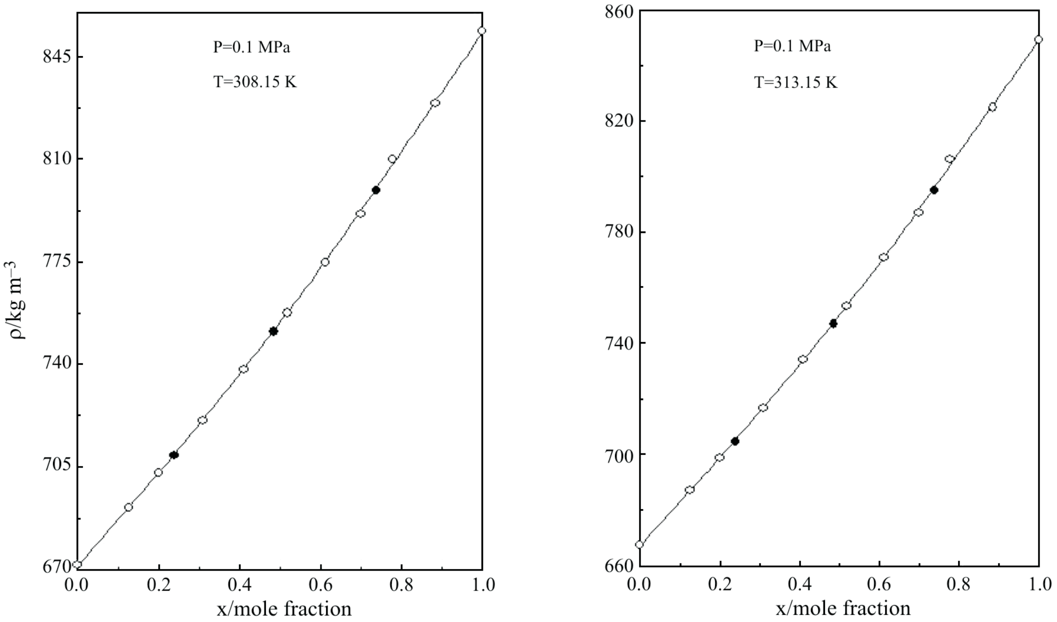

Fig. 2 Measured values of density of *n*-heptane+ethylbenzene mixtures as a function of concentration at two selected isotherms of 308.15 and 313.15 K and at atmospheric pressure together with the data reported by other authors in the literature. ● – this work; ○ – [5]; —— – smoothed curve

derstanding of the phenomena taking place in the liquid mixtures. The excess molar volumes were calculated for the {(1–*x*) *n*-heptane+*x* ethylbenzene} mixtures by using the present molar volume data and pure component values calculated from reference EOS for *n*-heptane [19] and the EOS for ethylbenzene [20] with the following relation

$$V_{\mathrm{m}}^{\mathrm{E}} = V_{\mathrm{m,mix}} - xV_{\mathrm{m,1}} - (1-x)V_{\mathrm{m,2}} \qquad (1)$$

where the *x* is the mole fraction of ethylbenzene. The results are given in Table 1 at atmospheric pressure and in Table 3 at high pressures. The concentration dependences of the derived values of the excess molar volumes at selected temperatures and at atmospheric pressure are demonstrated in Figs 4 to 6 together with published data. The pressure and temperature dependences of the $V_{\mathrm{m}}^{\mathrm{E}}$ at selected concentration and at various temperatures are depicted in Fig. 7. Note

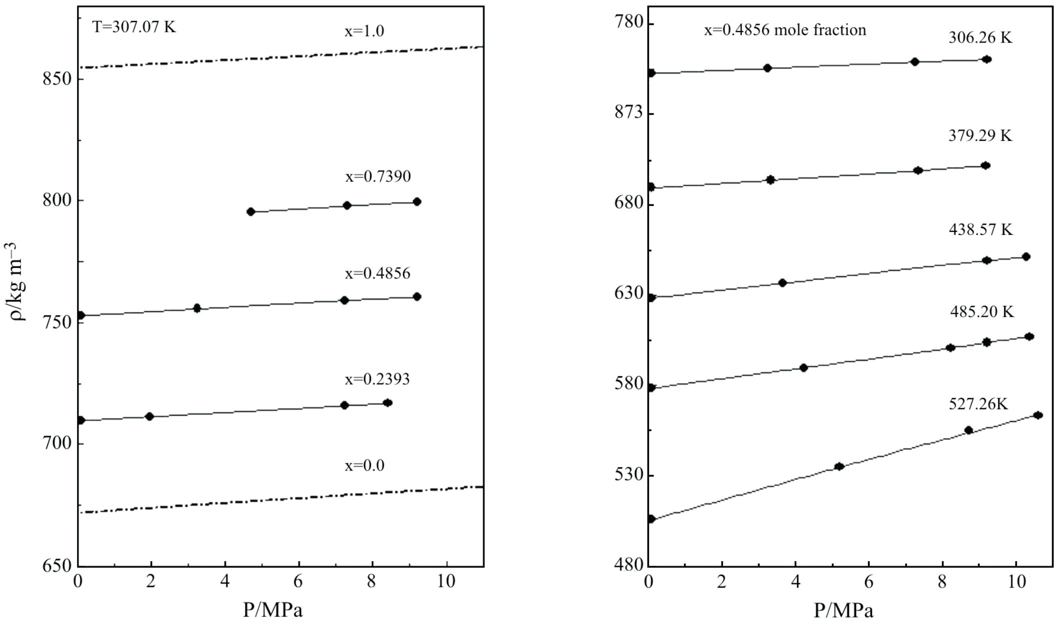

Fig. 3 Measured values of density of *n*-heptane+ethylbenzene mixtures as a function of pressure at various isotherms and at fixed concentration of 0.4856 mole fraction (right) and for various concentrations at fixed temperature of 307.07 K (left), ● – this work; —— – smoothed curve

Table 3 Excess molar volumes of {(1–*x*) *n*-heptane+*x* ethylbenzene} mixtures at high temperatures and high pressures

x=0.2393 mole fraction		x=0.4856 mole fraction		x=0.7390 mole fraction	
p/MPa	V_m^E/cm^3 mol^{-1}	p/MPa	V_m^E/cm^3 mol^{-1}	p/MPa	V_m^E/cm^3 mol^{-1}
T=307.07 K		T=306.26 K		T=317.45 K	
8.414	0.244	9.218	0.195	4.71	–0.190
7.257	0.230	7.257	0.136	7.32	–0.190
1.961	0.109	3.256	0.106	9.21	–0.189
T=387.93 K		T=379.29 K		T=385.65 K	
10.689	–0.361	9.179	–0.388	4.84	–0.247
8.826	–0.357	7.355	–0.349	7.61	–0.244
3.334	–0.487	3.334	–0.508	9.32	–0.244
T=430.21 K		T=438.57 K		T=446.95 K	
10.12	–0.804	10.297	–0.703	4.53	–0.353
8.237	–0.792	9.218	–0.790	6.87	–0.325
4.315	–1.035	3.668	–1.125	9.64	–0.304
T=480.86 K		T=485.20 K		T=520.69 K	
9.140	–1.351	10.375	–1.373	5.94	–0.527
7.355	–1.694	9.218	–1.508	9.05	–0.434
3.824	–2.083	8.237	–1.681	–	–
–	–	4.236	–3.548	–	–
T= 527.11 K		T=527.26 K			
9.963	–2.107	10.611	–2.033		
7.747	–2.638	8.728	–2.639		
5.747	–3.488	5.217	–5.000		

that the values of V_m^E for the {(1–x) n-heptane+ $x$ethylbenzene}mixtures are positive for measured temperatures (up to 356 K) at atmospheric pressure in the whole composition range, except one data point at 356 K and x=0.7390 mole fraction, while at high temperatures (above 306 K) and high pressures (Table 3) the values of V_m^E are negative. The concentration dependence of the excess molar volumes shows a symmetric behavior with x=0.5 mole fraction. The error bar for the present experimental data shown in Fig. 5 for V_m^E at 298.15 K corresponds to the uncertainty of 15%. Therefore, majority available experimental data sets for V_m^E at 298.15 K and 0.1 MPa, except the data from [1, 4], lied within 15%. As one can see from Figs 5 and 6, although the agreement between original densities (see above) reported by various authors and

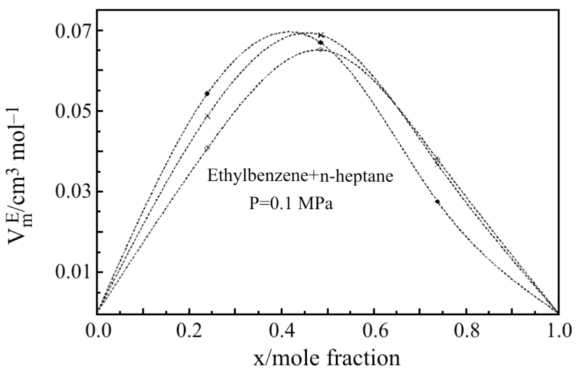

Fig. 4 The derived values of excess molar volume as a function of concentration at three selected temperatures. ○ – 313.15 K; ● – 333.15 K; × – 343.15 K; – – – – smoothed curves

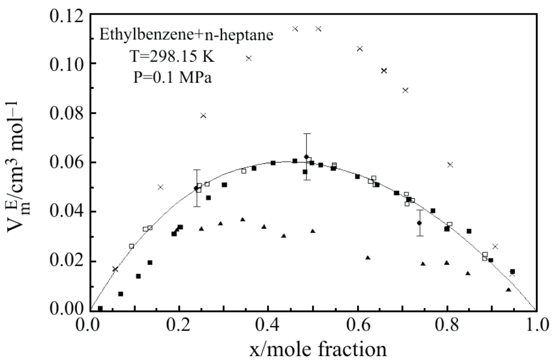

Fig. 5 The derived values of excess molar volume as a function of concentration at temperature of 298.15 K and 0.1 MPa together with the data reported by other authors. ● – this work; ■ – [3]; □ – [6]; × – [1]; ▲ – [4]; —— – calculated with correlation [6]

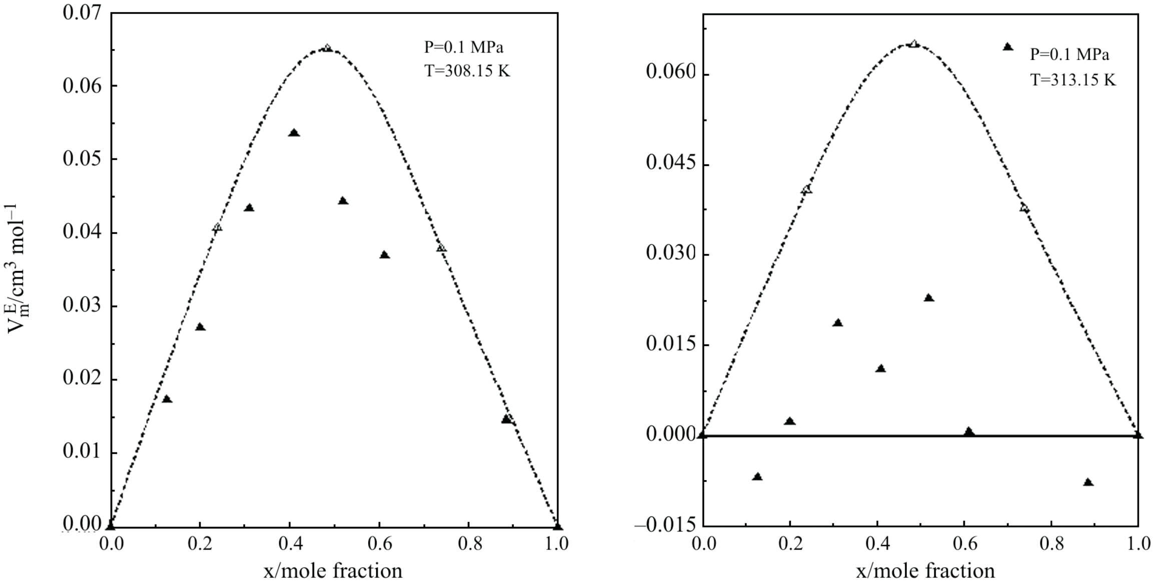

Fig. 6 The derived values of excess molar volume as a function of concentration at two selected temperatures of 308.15 and 313.15 K together with reported data. △ – this work; ▲ – [5]; – – – – – smoothed curves

the present results are good (within 0.001–0.036%), the scattering of the derived values of the excess molar volume by different authors is large (up to 100% and more). As Figs 4 to 6 shows, the difference between mixture molar volumes of mixtures V_m^E and the ideal mixture molar volumes $V_{id}=xV_{m,1}+(1-x)V_{m,2}$ is fairly small (maximum value at temperatures from 298.15 to 313.15 K and 0.1 MPa is about 0.065 cm^3 mol^{-1}), indicating that the mixture exhibits slight deviation from ideality. The maximum relative uncertainty δV_m^E in derived values of V_m^E strongly depends on x, $V_{m,min}$, $V_{m,1}$, $V_{m,2}$ and can be approximately estimated from the following relation

$$\delta V_m^E \cong \delta V_{m,mix} V_{m,mix} / V_{m,mix} - V_{id}) + \delta V_{m1} V_{m1} / (V_{m,mix} - V_{id}) + \delta V_{m2} V_{m2} / (V_{m,mix} - V_{id}) \qquad (2)$$

where $\delta V_{m,mix} \approx 0.06\%$, $\delta V_{m1} \approx 0.2\%$ [19], and $\delta V_{m2} \approx 0.05\%$ [20] are the relative uncertainties in mixture and pure components molar volume determination, respec-

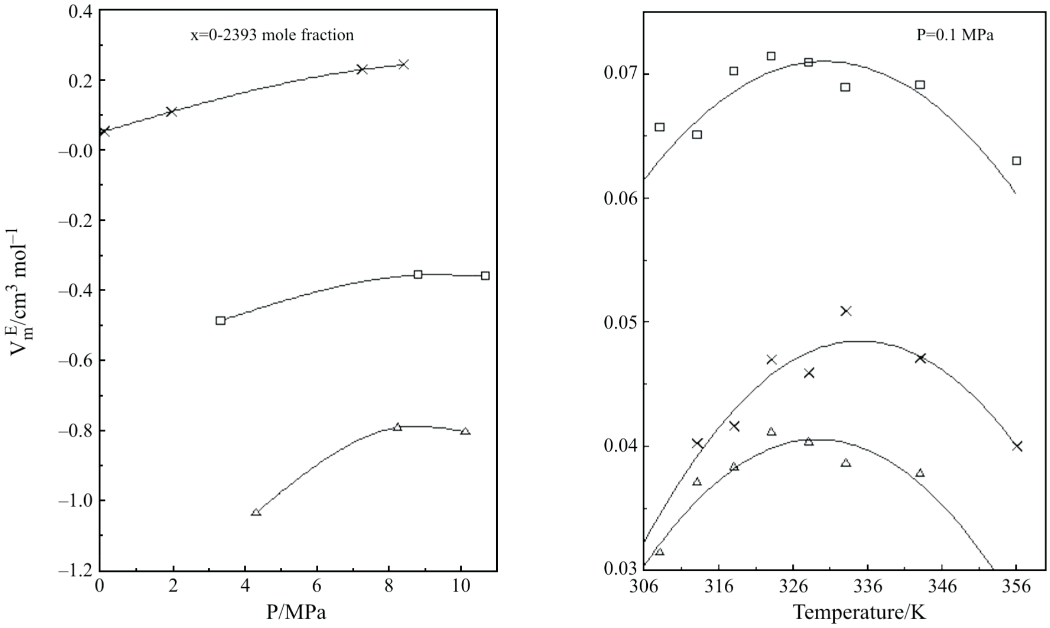

Fig. 7 The derived values of excess molar volumes as a function of pressure (left) and temperature (right). Left – △ – 430.21 K; □ – 387.93 K; × – 307.07 K; Right – △ – 0.7390 mole fraction; □ – 0.4856 mole fraction; × – 0.2393 mole fraction; ——— – smoothed curves

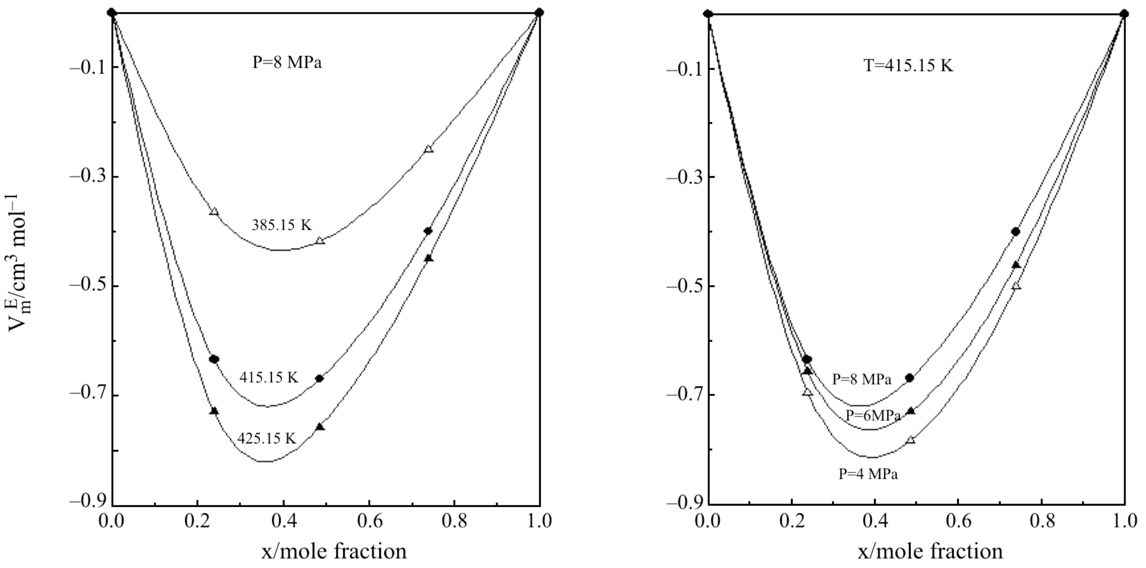

Fig. 8 The derived values of excess molar volume as a function of concentration at high temperatures and high pressures. ——— – smoothed curves

tively. Due to small values of difference ($V_{\rm m,mix}-V_{\rm id}$)), the values of $\delta V_{\rm m}^{\rm E}$ estimated from Eq. (2) is about 100% and more. The present results for excess molar volumes differ from the data reported by Grolier and Faradjzadeh [6] and Awwad *et al*. [3] by 13 and 50–80%, respectively, although the original density data from which $V_{\rm m}^{\rm E}$ were calculated differ by 0.015 and 0.003%. Therefore, these deviations are still acceptable because the uncertainty in the $V_{\rm m}^{\rm E}$ calculation from Eq. (2) is about 113% and more, because the relative uncertainty in $V_{\rm m}^{\rm E}$ is defined as $\delta V_{\rm m}^{\rm E}\cong(V_{\rm m,mix}-V_{\rm id})^{-1}$, where the difference ($V_{\rm m,mix}-V_{\rm id}$) very small and almost zero. This means that the {(1–*x*) *n*-heptane+*x* ethylbenzene}mixture is almost ideal mixture (molecular mass of the pure *n*-heptane and ethylbenzene very close, 100.203 and 106.167 g mol^{-1}, respectively). This is not a surprise because the interac-

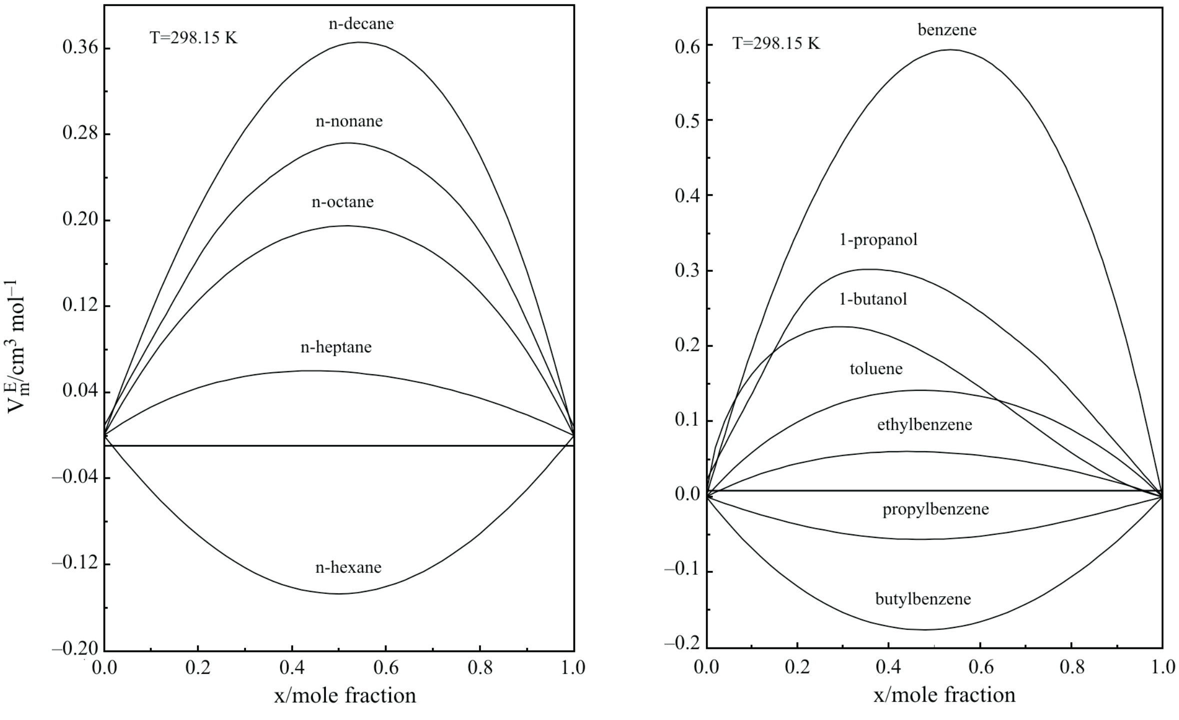

Fig. 9 Excess molar volumes of a series of *n*-heptane and ethylbenzene containing mixtures as a function of composition at a selected temperature 298.15 K and a pressure of 0.1 MPa reported by various authors. Left – ethylbenzene+*n*-alkanes: *n*-decane [7]; *n*-nonane [4]; *n*-octane [7]; *n*-heptane (this work); *n*-hexane [7]; Right – *n*-heptane+another compound: benzene [39]; 1-propanol [40]; 1-butanol [41]; toluene [5]; ethylbenzene; this work – propylbenzene [6]; butylbenzene [6]

tion between the dissimilar molecules of the components *n*-heptane and ethylbenzene is not different much from the interaction between the identical molecules of either *n*-heptane or ethylbenzene.

The ethylbenzene owing to the ethyl group form complexes with *n*-heptane which leads to a volumetric contraction and the values of considerable reduced and at high temperatures and high pressures becomes negative. Therefore, the chemical interactions (non physical nature of the intermolecular interactions) between ethylbenzene and *n*-heptane molecules in this mixture play very important role in determining the volumetric properties (excess molar properties). The addition of ethylbenzene to *n*-heptane may very small result in changes in topology of ethylbenzene or *n*-heptane. As excess molar volume is a packing effect.

As Fig. 7 shows, the excess molar volumes slightly increase when pressure rise. At high *T* and high *p* slightly negative values of excess molar volumes appear (also Fig. 8). As one can see from Fig. 7, the V_m^E increases with temperature, passes through a maximum near 330–336 K, and then decreases at higher temperatures. For the mixtures of ethylbenzene with *n*-alkanes the V_m^E increases as the ratio of the molecular sizes, ethylbenzene-to-*n*-alkane, increases. As well known that V_m^E for mixtures is the result of contributions from the several opposing effects such as chemical, physical, and structural. The structural contributions increases with decreasing length of the *n*-alkane molecule, as can see from Fig. 9.

Cáceres and Núñez [24, 25] studied the effect of the introduction of ethyl and methyl groups in the aromatic ring. They found that methyl groups are decreasing the excess molar volumes. Figure 9 shows the concentration dependence of the excess molar volumes of a series of hydrocarbon mixtures with the same first component (*n*-heptane) and various second component (right) and with the same ethylbenzine and various *n*-alkane (left). This figure demonstrates the effect of the nature of second component on the values and concentration dependence behavior of the excess molar volumes of *n*-heptane+second component (alcohol or hydrocarbon) and ethylbenzene+*n*-alkane. As one can see from Fig. 9 (right), the introduction of ethyl group in the benzene structure is considerable decreasing (from 0.6 to 0.06 cm^3 mol^{-1}, 10 times) the excess molar volumes. Adding the alcohol to *n*-heptene the result in shift of the maximum of V_m^E to low concentration range. The introduction of propyl- and butyl- groups in the benzene structure decreasing the excess molar volumes to negative values at the same thermodynamic (*p*,*T*,*x*) conditions. Figure 9 (left) also shows the concentration dependence of the excess molar volume a series of mixtures ethylbenzene + *n*-alkane with the same first component (ethylbenzene) and various second components (*n*-alkanes from C$_6$ to C$_{10}$). As Fig. 9 (left) shows, among these mixtures ethylbenzene+*n*-heptane shows intermediate values (transition from positive to negative values of V_m^E) of excess molar volumes.

Conclusions

Density for the {(1–*x*) *n*-heptane+*x* ethylbenzene} binary mixtures at *x*=(0.2393, 0.4856, 0.7390 mole fraction of ethylbenzene) have been measured with a constant-volume piezometer. Measurements were made at pressures up to 11 MPa and at temperatures from 306 to 527 K. The measured values of density for pure components are excellent agree (AAD within 0.057% for *n*-heptane and 0.019% for ethylbenzene) with the values calculated with reference EOS for *n*-heptane [19] and ethylbenzene [20]. The present density results for the mixtures are in excellent agreement (within 0.015–0.036%) with the values reported by other author's at atmospheric pressure and at temperatures up to 313.15 K. The excess molar volumes V_m^E were derived using the measured values of density for the mixtures and pure components calculated with reference EOS [19, 20]. The small (within 0.065 cm^3 mol^{-1}) positive deviations of the mixture molar volumes from the ideal mixture values were found at low temperatures (below 343 K) and at atmospheric pressure, while at high temperatures and high pressures the derived values of V_m^E are negative. The discrepancy between various reported values of excess molar volumes for {(1–*x*)*n*-heptane+*x* ethylbenzene} binary mixture is within 100% and more. The introduction of ethyl group in the benzene structure is considerable decreasing (from 0.6 to 0.06 cm^3 mol^{-1}, 10 times) the excess molar volumes of mixture.

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References

1 C. Díaz, B. Orge, G. Marino and J. Tojo, J. Chem. Thermodyn., 33 (2001) 1015.
2 A. Qin, D. E. Hoffman and P. Munk, J. Chem. Eng. Data, 37 (1992) 61.
3 A. M. Awwad, N. K. Al-Nidawy, M. A. Salman and F. A. Hassan, Thermochim. Acta, 114 (1987) 337.

4 H. Paul, J. Krug and H. Knapp, Thermochim. Acta, 108 (1986) 9.

5 W. A. Al Gherwi, A. H. Nhaesi and A. A. Asfour, J. Sol. Chem., 35 (2006) 455.

6 J. P. E. Grolier and A. Faradjzadeh, Int. Data Ser. Selected Data on Mixtures, Ser. A, 8 (1981) 140.

7 M. Cáceres Alonso, J. M. Arsuaga Ferreras and J. Núñez Delgado, Fluid Phase Equilib., 20 (1985) 81.

8 I. M. Abdulagatov and N. D. Azizov, J. Sol. Chem., 32 (2003) 573.

9 I. M. Abdulagatov and N. D. Azizov, Int. J. Thermophys., 24 (2003) 1581.

10 I. M. Abdulagatov and N. D. Azizov, J. Sol. Chem., 33 (2004) 1305.

11 I. M. Abdulagatov and N. D. Azizov, J. Chem. Thermodyn., 36 (2004) 829.

12 I. M. Abdulagatov and N. D. Azizov, Fluid Phase Equlib., 216 (2004) 189.

13 I. M. Abdulagatov and N. D. Azizov, High Temp-High Press., 35/36, (2003/2004) 477.

14 I. M. Abdulagatov and N. D. Azizov, J. Chem. Thermodyn., 36 (2004) 17.

15 I. M. Abdulagatov and N. D. Azizov, Chem. Geology, 230 (2006) 22.

16 I. M. Abdulagatov and N. D. Azizov, J. Chem. Thermodyn., 38 (2006) 1402.

17 W. Wagner and A. Pruß, J. Phys. Chem. Ref. Data, 31 (2002) 387.

18 F. G. Keyes and L. B. Smith, Proc. Amer. Acad. Arts Sci., 68 (1933) 505.

19 R. Span and W. Wagner, Int. J. Thermophys., 24 (2003) 41.

20 M. Frenkel, R. D. Chirico, V. V. Diky, X. Yan, Q. Dong and C. Muzny, J. Chem. Inform. Model., 45 (2005) 816.

21 A. J. Treszczanowicz, O. Kiyohara and G. C. Benson, J. Chem. Thermodyn., 13 (1981) 253.

22 G. Douheret and M. I. Davis, Chem. Soc. Rev., 22 (1993) 43.

23 B. E. de Comindges, M. M. Pineiro, E. Mosteiro, E. M. Ascato, M. M. Mato, T. P. Iglesias and J. L. Legido, J. Therm. Anal. Cal., 70 (2002) 217.

24 M. Cáceres Alonso and J. Núñez Delgado, J. Chem. Thermodyn., 13 (1981) 1133.

25 M. Cáceres Alonso and J. Núñez Delgado, J. Chem. Eng. Data, 27 (1982) 331.

26 I. L. Acevedo, L. Lugo, M. J. P. Comuñas, E. L. Arancibia and J. Fernández, J. Chem. Eng. Data, 48 (2003) 1271.

27 A. K. Doolittle, J. Chem. Eng. Data, 9 (1964) 275.

31 B. M. Westwood and V. N. Kabadi, J. Chem. Thermodyn., 35 (2003) 1965.

32 H. R. Pinnick, Ch. L. Falling, G. C. Allred and W. R. Parrish, J. Chem. Eng. Data, 40 (1995) 950.

33 Y. M. Naziev, A. N. Shahverdiyev and V. H. Hasanov, J. Chem. Thermodyn., 37 (2005) 1268.

34 S. K. Garg, T. S. Banipal and J. C. Ahluwalia, J. Chem. Thermodyn., 25 (1993) 57.

35 S. Malanowski, R. Patz, M. T. Rätzsch and C. Wohlfarth, Fluid Phase Equilib., 3 (1979) 291.

36 D. V. S. Jain, R. Chadha and S. K. Sehgal, Fluid Phase Equilib., 112 (1995) 151.

37 Ch. Yang, W. Yu and P. Ma, J. Chem. Eng. Data, 50 (2005) 1197.

38 G. Chen and H. Knapp, J. Chem. Eng. Data, 40 (1995) 1001.

39 M. Takenaka, R. Tanaka and S. Murakami, J. Chem. Thermodyn., 14 (1982) 399.

40 N. Sastry and M. K. Valand, J. Chem. Eng. Data, 41 (1996) 1421.

41 Ch. Berro and A. Peneloux, J. Chem. Eng. Data, 29 (1984) 206.

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