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Viscosities and Excess Molar Volumes of the Ternary System Toluene (1) + Cyclohexane (2) + Pentane (3) at 298.15 K

H. Iloukhani* and M. Rezaei-Sameti

Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hamadan, Iran

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The viscosity and density of ternary mixtures of toluene (1) + cyclohexane (2) + pentane (3) have been measured at 298.15 K and atmospheric pressure over the entire range of compositions. Excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were obtained from the experimental results for the binary and ternary systems and fitted to Redlich−Kister's and Cibulka's equations in terms of mole fractions. The V_{123}^E data was positive, and inversion of the sign was observed over some concentrations at $x \approx 0.2$ for mixtures at three fixed compositions ($f_m = x_1/x_2$). The $\Delta\eta_{123}$ data were negative values at three fixed compositions. The results obtained for excess molar volume and viscosity of liquid mixtures were used to test the semiempirical relations of Tsao−Smith, Jacob−Fitzner, Kohler, Rastogi et al., Radojkovic et al., Colinet, Toop, and Scatchard et al. The experimental and the constituted ternaries are analyzed to discuss the nature and strength of intermolecular interactions in these mixtures.

Introduction

A knowledge of the densities and viscosities of studied fluids and fluid mixtures is estimated to understand the molecular interactions between the molecules and to develop new theoretical models and also engineering applications of absorption heat pumps and heat transformers.

This paper, as part of a continuing study in our laboratory,[1−4] reports the precise measurement of density and viscosity for the ternary system formed by toluene (1) + cyclohexane (2) + pentane (3). Excess molar volumes and deviation in viscosities were calculated for the studied ternary mixtures, and the excess properties are analyzed because of their importance for inferring which type of interaction predominates in liquid mixtures.

Experimental Section

The substances employed were supplied by Merck. Their mole fraction purities were as follows: toluene (>99 %), cyclohexane (99.5 %), and pentane (>99 %). Toluene and pentane were purified by distillation using a 1 m fractionation column. Cyclohexane was purified by the standard method described by Perrin and Armarego.[5] The purified compounds were stored in brown glass bottles and fractionally distilled immediately before use. The purity of each compound was ascertained by their density and viscosity values, which agreed as shown in Table 1 with the literature values.[6−8]

Table 1. Properties of the Pure Components at 298.15 K

	ρ/kg·m^{-3}		η/mPa·s	
substance	exptl	lit	exptl	lit
toluene	862.19	862.17[a]	0.552	0.550[c]
cyclohexane	773.93	773.89[b]	0.894	0.8921[c]
pentane	621.32	621.36[b]	0.219	0.212[c]

[a] Ref 6. [b] Ref 7. [c] Ref 8.

Apparatus and Procedure. Viscosities at 298.15 K were measured with an Ubbleohde viscometer. The equation for viscosity, according to Poiseuille's law, is

$$\eta = \rho v = \rho(kt - c/t) \tag{1}$$

where k and c are the viscometer constant; t, η, and v are the efflux time, dynamic viscosity, and kinematic viscosity, respectively. The k and c were obtained by measurements on double-distilled water and benzene at 298.15 K. The obtained parameters are $k = 0.010$ m^2·s^{-2} and $c = 1.095$ m^2. The dynamic viscosity was reproducible to within $\pm 2 \times 10^{-3}$ mPa·s. The temperature in the cell was regulated to ± 0.01 K.

The density of the compounds and their binary and ternary mixtures were measured with Anton Paar DMA 4500 oscillating U-tube densitometer. The density measurements accuracy was $\pm 1 \times 10^{-2}$ kg·m^{-3}. The temperature in the cell was regulated to ± 0.01 K with solid-state thermostat. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water. Airtight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle, and the total mass was recorded. Subsequently, the other component was introduced, and the mass of bottle along with the two components was determined. Ternary mixtures were prepared by mixing a measured binary mixture (toluene + cyclohexane at known composition) with pure liquid (pentane as a third component). Each mixture was immediately used after it was well-mixed by shaking. All the weightings were performed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

Results and Discussion

Binary Systems. In Table 2, we show value of densities and dynamic viscosities for binary systems as well as the molar excess volume (V^E) and viscosity deviations ($\Delta\eta$)

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* Corresponding author e-mail: iloukhani@basu.ac.ir.

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computed through the following equations:

$$V^{\mathrm{E}}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = \frac{\sum_{i=1}^{c} x_i M_i}{\rho} - \sum_{i=1}^{c} x_i \frac{M_i}{\rho_i} \qquad (2)$$

$$\Delta\eta/\mathrm{mPa}\cdot\mathrm{s} = \eta - \sum_{i=1}^{c} x_i \eta_i \qquad (3)$$

which are valid for ternary systems as well. In the above equations the presence of the sub index i refers to the property of the pure component, and the quantities without sub index refer to the property of the mixture. M is the molar mass, x is the mole fraction, and c refers to the number of components in the mixture.

Figures 1 and 2 show the variation with composition of V^{E} and $\Delta\eta$ for the systems toluene + cyclohexane, toluene + pentane, and cyclohexane + pentane, respectively. The V^{E} and $\Delta\eta$ values were correlated to composition using the Redlich−Kister equation:

$$Y = x(1-x)\sum_{i=0}^{p} A_i (2x-1)^i \qquad (4)$$

where $Y \equiv V^{\mathrm{E}}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$ or $\Delta\eta/\mathrm{mPa}\cdot\mathrm{s}$, and x is the mole fraction of the first component. The coefficients A_i were calculated by the unweighted least-squares method, and the computed values of standard deviation for each of the properties are shown in Table 3.

Table 2. Densities (ρ), Dynamic Viscosity (η), Viscosity Deviation ($\Delta\eta$), and Excess Molar Volumes (V^{E}) for the Binary Mixtures at 298.15 K

x	ρ / $\mathrm{kg}\cdot\mathrm{m}^{-3}$	η / $\mathrm{mPa}\cdot\mathrm{s}$	$\Delta\eta$ / $\mathrm{mPa}\cdot\mathrm{s}$	V^{E} / $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$
		x Toluene + $(1-x)$ Cyclohexane		
0.0407	776.48	0.8158	−0.0628	0.1380
0.2018	788.44	0.7133	−0.1107	0.4188
0.2798	794.63	0.6687	−0.1287	0.5021
0.3613	801.33	0.6305	−0.1392	0.5573
0.4416	808.17	0.6081	−0.1343	0.5809
0.6003	822.40	0.5660	−0.1224	0.5410
0.6784	829.75	0.5534	−0.1085	0.4809
0.7615	837.82	0.5429	−0.0907	0.3890
0.8396	845.63	0.5395	−0.0676	0.2772
0.9202	853.94	0.5393	−0.0404	0.1368
		x Toluene + $(1-x)$ Pentane		
0.0415	630.69	0.2029	−0.0298	−0.0281
0.2011	668.27	0.2231	−0.0629	−0.2819
0.2799	687.21	0.2386	−0.0736	−0.4039
0.3647	707.61	0.2592	−0.0812	−0.4841
0.4341	724.30	0.2786	−0.0850	−0.5135
0.6011	764.45	0.3367	−0.0824	−0.4636
0.6821	783.95	0.3688	−0.0773	−0.3840
0.7502	800.32	0.3999	−0.0690	−0.2918
0.8213	817.43	0.4371	−0.0554	−0.1725
0.9137	840.19	0.4891	−0.0341	−0.0537
		x Cyclohexane + $(1-x)$ Pentane		
0.0437	627.56	0.2065	−0.0242	−0.0125
0.2145	653.09	0.2555	−0.0936	−0.1342
0.2955	665.44	0.2828	−0.1223	−0.1951
0.3753	677.59	0.3128	−0.1475	−0.2318
0.4595	690.43	0.3503	−0.1683	−0.2467
0.6125	713.75	0.4425	−0.1819	−0.2154
0.7048	727.81	0.5146	−0.1737	−0.1626
0.7791	739.14	0.5847	−0.1550	−0.1029
0.8514	750.15	0.6591	−0.1307	−0.0306
0.9254	761.85	0.7641	−0.0769	−0.0040

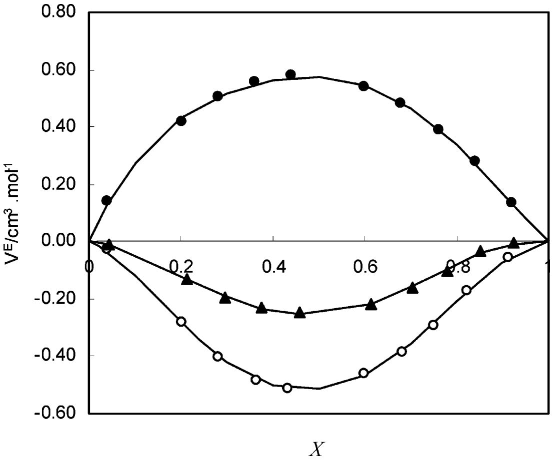

Figure 1. Excess molar volumes of the binary mixtures vs mole fraction x. Experimental results: ●, x toluene + $(1-x)$ cyclohexane; ○, x toluene + $(1-x)$ pentane; ▲, x cyclohexane + $(1-x)$ pentane. Redlich−Kister fit curves (—) at 298.15 K.

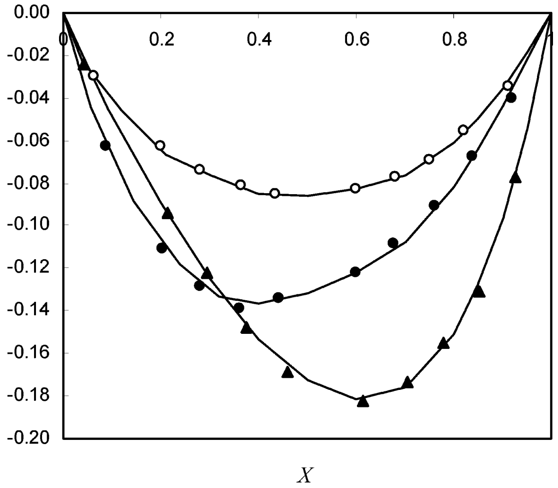

Figure 2. Excess dynamic viscosity of the binary mixtures vs mole fraction x. Experimental results: ●, x toluene + $(1-x)$ cyclohexane; ○, x toluene + $(1-x)$ pentane; ▲, x cyclohexane + $(1-x)$ pentane. Redlich−Kister fit curves (—) at 298.15 K.

In each case, the optimum number of coefficients was ascertained from an examination of the variation of standard deviations (σ) with

$$\sigma = \left[\frac{\sum (Y_{\mathrm{exp}} - Y_{\mathrm{calc}})^2}{(n-p)}\right]^{1/2} \qquad (5)$$

where Y_{exp} and Y_{calc} are the experimental and calculated values of the property Y, respectively, and n and p are the number of experimental points and number of parameters retained in the respective equations. The standard deviations (σ) are also gathered in Table 3.

Table 3. Coefficients A_i of Eq 4 and Standard Deviation (σ) for Binary Mixture at 298.15 K

system	A_0	A_1	A_2	A_3	σ
		x Toluene + $(1-x)$ Cyclohexane			
V^{E}	2.2986	−0.1942	0.2622	−0.8173	0.0067
$\Delta\eta$	−0.5197	0.1509	−0.2929	0.1067	0.0020
		x Toluene + $(1-x)$ Pentane			
V^{E}	−2.1010	0.4110	1.6096	−0.1429	0.0065
$\Delta\eta$	−0.3146	−0.0601	−0.3095	0.2801	0.0054
		x Cyclohexane + $(1-x)$ Pentane			
V^{E}	−1.0154	0.1948	1.1057	0.0173	0.0050
$\Delta\eta$	−1.1015	0.1948	1.1057	0.0173	0.0054

Table 4. Densities (ρ), Dynamic Discosity (η), Viscosity Deviation ($\Delta\eta$), and Excess Molar Volumes (V^E) for the Ternary Mixtures of Toluene (1) + Cyclohexane (2) + Pentane (3) at 298.15 K

		ρ	η	$\Delta\eta_{123}$	V^E_{123}
x_1	x_2	kg·m^{-3}	mPa·s	mPa·s	cm^3·mol^{-1}
		$f_m = x_1/x_2 = 0.3$			
0.2160	0.7067	777.59	0.6670	−0.1011	0.3479
0.1990	0.6509	765.21	0.6164	−0.1084	0.2230
0.1793	0.5866	750.96	0.5421	−0.1327	0.0975
0.1607	0.5257	737.45	0.4834	−0.1441	−0.0025
0.1426	0.4665	724.40	0.4271	−0.1543	−0.0922
0.1053	0.3445	697.27	0.3420	−0.1446	−0.1804
0.0859	0.2812	683.24	0.2965	−0.1410	−0.1965
0.0662	0.2187	669.29	0.2763	−0.1124	−0.1922
0.0397	0.1309	649.71	0.2403	−0.0803	−0.1011
0.0102	0.0318	628.21	0.2068	−0.0371	−0.0142
		$f_m = x_1/x_2 = 1$			
0.4455	0.4768	796.58	0.6006	−0.0886	0.4608
0.4066	0.4352	781.24	0.5527	−0.0955	0.2997
0.3693	0.3952	766.49	0.4912	−0.1175	0.1640
0.3297	0.3528	750.86	0.4351	−0.1318	0.0419
0.2910	0.3114	735.59	0.3906	−0.1355	−0.0546
0.2138	0.2288	705.11	0.3098	−0.1348	−0.1735
0.1759	0.1929	691.04	0.2926	−0.1152	−0.2229
0.1365	0.1497	675.20	0.2663	−0.0992	−0.1966
0.0980	0.1075	659.75	0.2391	−0.0851	−0.1350
0.0197	0.0211	628.78	0.2173	−0.0225	−0.0097
		$f_m = x_1/x_2 = 3$			
0.6943	0.2451	822.54	0.5357	−0.0799	0.2789
0.6683	0.2360	814.98	0.5181	−0.0828	0.2037
0.6154	0.2173	799.55	0.4790	−0.0916	0.0641
0.5442	0.1921	778.77	0.4296	−0.1003	−0.0933
0.4494	0.1587	751.20	0.3624	−0.1134	−0.2524
0.3990	0.1409	736.44	0.3330	−0.1140	−0.2936
0.3284	0.1159	715.85	0.3001	−0.1065	−0.3258
0.2732	0.0965	699.76	0.2746	−0.1005	−0.3180
0.1962	0.0693	677.23	0.2379	−0.0932	−0.2386
0.0301	0.0325	633.20	0.2045	−0.0464	−0.0927

Table 5. Coefficients B_p of Equation 6 and Standard Deviation (σ) for Ternary Mixture of Toluene (1) + Cyclohexane (2) + Pentane (3) at 298.15K

system	B_0	B_1	B_2	σ
		$f_m = 0.3$		
V^E	1.7823	6302.24	−1926.79	0.0060
$\Delta\eta$	−3.0601	−3073.1	949.577	0.0082
		$f_m = 1$		
V^E	2.4513	494.468	−460.86	0.0070
$\Delta\eta$	−2.5775	−351.89	340.43	0.0088
		$f_m = 3$		
V^E	4.4899	1052.36	−3006.3	0.0060
$\Delta\eta$	−1.8796	236.68	−650.673	0.0082

Ternary Systems. In Table 4, we show the densities and dynamic viscosities as well as the computed properties (excess molar volumes (V^E_{123}) and viscosity deviations ($\Delta\eta_{123}$)) for the system toluene (1) + cyclohexane (2) + pentane (3) at 298.15 K. The excess molar volumes, viscosity deviations, and excess Gibbs energy of activation were correlated with ternary composition using the equation proposed by Cibulka:[9]

$$Y_{123} = Y_{bin} + x_1x_2(1 - x_1 - x_2)(B_0 + B_1x_1 + B_2x_2) \quad (6)$$

where $Y \equiv V^E$ or $\Delta\eta$ and $Y_{bin} = Y_{12} + Y_{13} + Y_{23}$ are the so-called "binary contribution".

The coefficients (B_p) and standard deviations (σ) in eq 5 obtained by the least-squares method are shown in Table 5. Figures 3 and 4 show the variation with composition of V^E_{123} and $\Delta\eta_{123}$ for the ternary system toluene (1) + cyclohexane (2) + pentane (3), respectively.

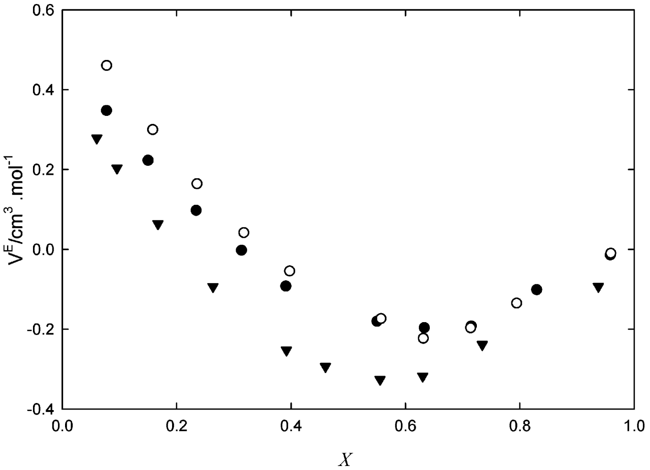

Figure 3. Excess molar volumes of the ternary mixtures formed by addition of pentane (3) to the binary mixtures of toluene (1) + cyclohexane (2) for ●, $f_m = 0.3$; ○, $f_m = 1$; and ▼, $f_m = 3$ at 298.15 K.

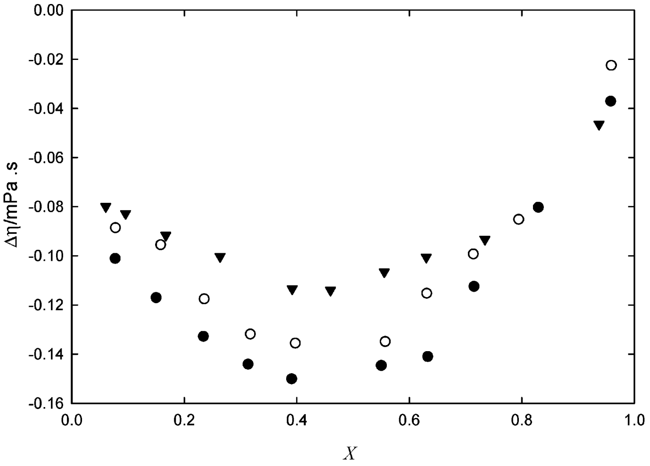

Figure 4. Excess dynamic viscosity of the ternary mixtures formed by addition of pentane (3) to the binary mixtures of toluene (1) + cyclohexane (2) for ●, $f_m = 0.3$; ○, $f_m = 1$; and ▼, $f_m = 3$ at 298.15 K.

Correlating Equations for the Ternary System

Apart from expressing V^E_{123} and $\Delta\eta_{123}$ as a polynomial fit, several semiempirical relations have been proposed to estimate V^E_{123} and $\Delta\eta_{123}$ of liquid mixtures in terms of pure component data. In this work, we applied the models of: Tsao and Smith,[10] Jacob and Fitzner,[11] Kohler,[12] Rastogi et al.,[13] Radojkovic et al.,[14] Colinet,[15] Toop,[16] and Scatchard et al.[17]

Standard deviations (σ) presented in Table 6 were determined for all models as:

$$\sigma = \sqrt{\sum_{i=1}^{n}(Q^E_{exp} - Q^E_{calc})^2/(n - p)} \quad (7)$$

where p is the number of parameters, and n is the number of experimental data.

Conclusions

Comparison of V^E (Figure 1) for different binary systems reveals several interesting features. Excess molar volumes for the binary system formed by toluene with cyclohexane is a positive inversion of the sign that was observed over some concentrations at $x \approx 0.2$ for mixtures at three fixed compositions ($f_m = x_1/x_2$). This model indicates that molecule interactions between different molecules are weaker

Table 6. Standard Deviation (σ) in the Predictions, V^E(cm^3·mol^{-1}), and $\Delta\eta$ (mPa·s) with Different Models for the Ternary Mixture of Toluene (1) + Cyclohexane (2) + Pentane (3) at 298.15 K

	$f_m = 0.3$	$f_m = 1$	$f_m = 3$
	$\sigma\ (V^E_{123})$		
Kohler	0.0320	0.0231	0.0230
Radojkovic et al.	0.0062	0.1040	0.0408
Rastogi et al.	0.1227	0.1311	0.1352
Taso and Smith[a]	0.1590	0.1714	0.0576
Taso and Smith[b]	0.3130	0.1600	0.0651
Taso and Smith[c]	0.1540	0.1461	0.2535
Toop[a]	0.1562	0.1667	0.0435
Toop[b]	0.3143	0.1560	0.0579
Toop[c]	0.0981	0.0826	0.1597
Scatchard et al.[a]	0.1631	0.1838	0.1071
Scatchard et al.[b]	0.3122	0.1673	0.0793
Scatchard et al.[c]	0.1610	0.1592	0.2720
Jacob and Fitzner	0.0770	0.0403	0.0461
Colinet	0.0851	0.1469	0.2204
	$\sigma\ (\Delta\eta_{123})$		
Kohler	0.0280	0.0431	0.0370
Radojkovic et al.	0.0332	0.0406	0.0151
Rastogi et al.	0.0203	0.0091	0.0572
Taso and Smith[a]	0.0222	0.0346	0.4070
Taso and Smith[b]	0.1282	0.0610	0.1082
Taso and Smith[c]	0.2103	0.1472	0.0334
Toop[a]	0.0114	0.0126	0.0410
Toop[b]	0.1108	0.0532	0.0541
Toop[c]	0.1468	0.0896	0.1188
Scatchard et al.[a]	0.0398	0.0721	0.0452
Scatchard et al.[b]	0.1503	0.0780	0.1200
Scatchard et al.[c]	0.2251	0.1660	0.0760
Jacob and Fitzner	0.0463	0.0319	0.0592
Colinet	0.0311	0.0483	0.0371

[a] Toluene is the asymmetric component. [b] Cyclohexane is the asymmetric component. [c] Pentane is the asymmetric component.

than interactions between molecules in the same pure liquid and that repulsive forces dominate the behavior of the solutions. Experimental data for V^E (Figure 3) of the ternary system of toluene (1) + cyclohexane (2) + pentane (3) are positive at three fixed compositions (f_m) over the whole range of composition. As can be seen in Table 6, the standard deviations, $\sigma(V^E)$ represented by various studied models[10–17] for V^E are similar and, although small, are beyond experimental errors. Thus, it is up to the design engineer to consider the advantages of relying on these relations for the description of these properties as continuous models for the whole range of ternary compositions.

The values of $\Delta\eta$ (Figure 2) were negative over the whole composition range for all of the binary systems studied. The sign of $\Delta\eta$ is in agreement with the conclusion by Fort and Moore,[18] who proposed that the negative values of this property are characteristic of systems where dispersion forces predominated.

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