Viscosities, Densities, and Speeds of Sound of Binary Mixtures of *o*-Xylene, *m*-Xylene, *p*-Xylene, and Isopropylbenzene with 4-Methylpentan-2-one at 298.15 K

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The viscosities, densities, and speeds of sound of binary mixtures of 4-methylpentan-2-one with *o*-xylene, *m*-xylene, *p*-xylene, and isopropylbenzene have been determined at 298.15 K over the whole composition range. Excess volume (V^E), excess compressibility (K_s^E), and deviations in viscosity ($\Delta\eta$) were calculated.

Introduction

The studies of liquid mixture behavior of industrially important chemicals have generated considerable interest in recent years. The studies of viscosity, density, and speed of sound are being increasingly used as tools for investigation of the properties of pure components and the nature of intermolecular interactions between the liquid mixture constituents.

As part of the experimental investigation of the excess thermodynamic properties of liquid mixtures, in the present study, measurements of densities, viscosities, and speed of sound of four binary mixtures of 4-methylpentan-2-one with *o*-, *m*-, and *p*-xylene and isopropylbenzene have been made at 298.15 K. This forms a part of a program to study the properties of liquid mixtures with a C_8 or C_9 aromatic hydrocarbon as one of the components, where recently we have reported similar studies with 3-pentanone.[1]

Experimental Section

4-Methylpentan-2-one (Riedel, India), *o*-xylene, *m*-xylene, *p*-xylene (Riedel, Germany), and isopropylbenzene (BDH, Poole England) were purified by standard procedures[2] and stored over molecular sieves. The purity of the samples was checked by comparing measured density and viscosity values with those reported in the literature as shown in Table 1. Densities were measured with an Anton Paar densimeter DMA 60/602 with an uncertainty of $\pm 1.0 \times 10^{-4}$ g·cm^{-3}. The mole fraction of each mixture was obtained to an accuracy of $\pm 1.0 \times 10^{-4}$.

Table 1. Physical Properties of the Pure Components at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s	
component	exp	lit	exp	lit
4-methylpentan-2-one	0.7960	0.7961[2]	0.550	0.542[2]
isopropylbenzene	0.8571	0.85751[2]	0.739	0.739[2]
o-xylene	0.8752	0.87596[2]	0.769	0.760[14]
		0.8744[11]		0.756[2]
		0.87563[13]		0.758[12]
m-xylene	0.8594	0.85990[2]	0.587	0.588[12]
		0.8597[11]		0.581[2]
				0.616[11]
p-xylene	0.8561	0.85669[2]	0.609	0.605[2]
		0.8558[11]		0.614[11]

Table 2. Density, ρ, Viscosity, η, Speed of Sound, u, and Compressibility, k_s, of Binary Systems of *o*-Xylene, *m*-Xylene, *p*-Xylene, and Isopropylbenzene with 4-Methylpentan-2-one at 298.15 K

x_1	ρ/g·cm^{-3}	u/m·s^{-1}	η/mPa·s	10^{12} K_s/Pa^{-1}
o-Xylene (1) + 4-Methylpentan-2-one (2)				
0.0000	0.7960	1215	0.550	850.9
0.0598	0.8013	1214	0.562	846.6
0.1483	0.8089	1220	0.577	830.5
0.2932	0.8207	1237	0.605	796.2
0.4368	0.8322	1263	0.631	753.2
0.5820	0.8434	1294	0.662	708.0
0.7227	0.8545	1318	0.694	673.6
0.8635	0.8651	1336	0.730	647.6
0.9457	0.8712	1345	0.751	634.4
1.0000	0.8752	1349	0.769	627.8
m-Xylene (1) + 4-Methylpentan-2-one (2)				
0.0000	0.7960	1215	0.550	850.9
0.0586	0.8014	1207	0.554	856.4
0.1483	0.8095	1212	0.558	840.8
0.2898	0.8212	1233	0.564	800.9
0.4312	0.8305	1257	0.567	762.0
0.5762	0.8374	1280	0.569	728.8
0.7187	0.8428	1299	0.572	703.1
0.8591	0.8490	1314	0.577	682.1
0.9429	0.8544	1321	0.582	670.7
1.0000	0.8594	1323	0.587	664.8
p-Xylene (1) + 4-Methylpentan-2-one (2)				
0.0000	0.7960	1215	0.550	850.9
0.0590	0.8001	1215	0.553	846.6
0.1454	0.8058	1226	0.556	825.6
0.2887	0.8149	1248	0.562	787.8
0.4325	0.8236	1267	0.567	756.3
0.5735	0.8322	1284	0.572	728.8
0.7166	0.8405	1300	0.579	703.9
0.8587	0.8484	1311	0.591	685.7
0.9419	0.8530	1315	0.600	677.9
1.0000	0.8561	1316	0.609	674.4
Isopropylbenzene (1) + 4-Methylpentan-2-one (2)				
0.0000	0.7960	1215	0.550	850.9
0.0518	0.7994	1227	0.563	830.8
0.1305	0.8046	1231	0.579	820.1
0.2631	0.8134	1234	0.600	807.2
0.4022	0.8226	1246	0.621	782.9
0.5439	0.8315	1262	0.645	755.0
0.6917	0.8403	1282	0.672	724.0
0.8420	0.8487	1309	0.704	687.6
0.9355	0.8537	1325	0.725	667.1
1.0000	0.8571	1338	0.739	651.7

Viscosities were measured by using a modified Ubbelhode viscometer, as described earlier.[3] From the measured values of density, ρ, and efflux time, t, the viscosity, η, was calculated using the relation

$$\eta/\rho = at + b/t \quad (1)$$

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10.1021/je049899g CCC: $27.50
Published on Web 07/07/2004

Table 3. Values of the Coefficients of the Redlich−Kister Eq 8 and Standard Deviations, σ, (Eq 9) at 298.15 K

	A_0	A_1	A_2	A_3	A_4	A_5	σ
			o-Xylene (1) + 4-Methylpentan-2-one (2)				
V^E/cm^3·mol^{-1}	−1.317	0.363	−0.390	-			0.009
$\Delta\eta$/mPa·s	−0.0608	−0.0225	0.0023	−0.0136			0.001
10^{12} k_s^E/Pa^{-1}	−33.692	−192.748	60.486	229.760	1.661	−231.305	0.295
			m-Xylene (1) + 4-Methylpentan-2-one (2)				
V^E/cm^3·mol^{-1}	−3.966	4.713	4.162				0.001
$\Delta\eta$/mPa·s	−0.0006	−0.043	−0.017				0.001
10^{12} k_s^E/Pa^{-1}	−52.401	−97.814	107.813	−11.340	113.080	−179.161	0.191
			p-Xylene (1) + 4-Methylpentan-2-one (2)				
V^E/cm^3·mol^{-1}	−1.177	0.121	−0.255				0.009
$\Delta\eta$/mPa·s	−0.040	−0.043	−0.022				0.001
10^{12} k_s^E/Pa^{-1}	−81.773	−37.189	−34.570	−37.800	163.624	−99.047	0.140
			Isopropylbenzene (1) + 4-Methylpentan-2-one (2)				
V^E/cm^3·mol^{-1}	−0.394	−0.552	0.526				0.001
$\Delta\eta$/mPa·s	−0.031	−0.046	0.053				0.001
10^{12} k_s^E/Pa^{-1}	71.758	5.850	33.709	−100.229	−239.206	332.742	0.241

Table 4. Interaction Parameters for the McAllister Model (Eq 10) for Viscosity at 298.15 K

systems	η_{12}	η_{21}	$\sigma(\eta)$/mPa·s
o-xylene (1) + 4-methylpentan-2-one (2)	0.6781	1.6462	0.237
m-xylene (1) + 4-methylpentan-2-one (2)	0.5575	1.7314	0.199
p-xylene (1) + 4-methylpentan-2-one (2)	0.5617	1.7544	0.207
isopropylbenzene (1) + 4-methylpentan-2-one (2)	0.6561	1.5999	0.183

where *a* and *b* are viscometer constants. The values of these constants were obtained by measuring the flow time with triply distilled water and twice-distilled benzene. The flow measurements were made with an electronic stopwatch with a precision of ±0.01 s. For the purpose of calculation of viscosity, an average of three sets of flow times of each liquid mixture was taken. The uncertainty of the viscosity estimates are found to be within ±0.003 mPa·s.

Speed of sound was determined by using an interferometer (Belen Model UI-751) with an accuracy of ±1.0 m·s^{-1}. All the measurements were made at constant temperature with the help of a circulating-type cryostat (MK70-MLW) where the uncertainty in temperature was ±0.02 K.

Experimental Results and Correlations

The experimental values of viscosity η, density ρ, and speed of sound u are reported in Table 2. The molar volume, V_m, was calculated from

$$V_m = (x_1M_1 + x_2M_2)/\rho_m \quad (2)$$

where x_1 and x_2 are the mole fractions and M_1 and M_2 are molecular weights of components 1 and 2, respectively, and ρ_m is the mixture density. The excess molar volume (V^E) for these binary mixtures was obtained from the following relation

$$V^E = x_1M_1(1/\rho_m - 1/\rho_1) + x_2M_2(1/\rho_m - 1/\rho_2) \quad (3)$$

where ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively.

The values of the speed of sound, u, and mixture density, ρ_m, were used to calculate the isentropic compressibility, K_s by using the relation

$$K_s = u^{-2}\rho_m^{-1} \quad (4)$$

The excess isentropic compressibility, K_s^E was obtained from the relation

$$K_s^E = K_s - K_s^{id} \quad (5)$$

where K_s is the experimental compressibility and K_s^{id} is the isentropic compressibility of an ideal mixture of the components. The values of K_s are reported in Table 2.

K_s^{id} was determined by using the Kiyohara and Benson equation[4]

$$K_s^{id} = \sum \phi_i[k^0_{s,i} + TV_i^0(\alpha_i^0)^2/C^0_{pi}] - T(\sum x_iV_i^0)(\sum \phi_i\alpha_i^0)^2/\sum x_iC^0_{pi} \quad (6)$$

where ϕ_i is the volume fraction of component i in the mixture stated in terms of the unmixed components, T is the temperature, and $k^0_{s,i}$, V_i^0, α_i^0, and C^0_{pi} are the isentropic compressibility, molar volume, coefficient of thermal expansion, and molar heat capacity for the pure component i. The values of α_i^0 were obtained from the density values at two different temperatures. The values of the molar heat capacity were taken from the literature.[2,5,6]

Deviations in viscosity, $\Delta\eta$, were obtained by using the relation

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad (7)$$

where η_m is the viscosity of the mixture and η_1 and η_2 are the viscosities of pure components 1 and 2, respectively.

A Redlich−Kister-type[7] equation was fitted to the excess properties (V^E and K_s^E) and deviations in viscosity ($\Delta\eta$)

$$A = x_1x_2\sum_{j=1}^{n} A_{j-1}(x_1 - x_2)^{(j-1)} \quad (8)$$

where A is the property, A_{j-1} is the polynomial coefficient, and n is the polynomial degree.

The standard deviation in each case is calculated using the relation

$$\sigma(X) = \left[\frac{\sum(X_{expt} - X_{calc})^2}{N - n}\right]^{1/2} \quad (9)$$

where N is the number of data points and n is the number of coefficients. The values of the coefficients of eq 8 as determined by the method of least squares along with the standard deviations for all four systems are reported in Table 3.

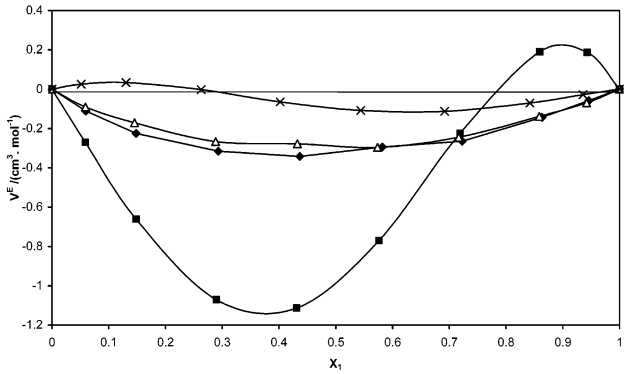

Figure 1. Excess molar volume, V^E (cm^3·mol^{-1}), for the systems of ◆, *o*-xylene; ■, *m*-xylene; △, *p*-xylene; ×, isopropylbenzene with 4-methylpentan-2-one at 298.15 K.

McAllister[8] derived the following equation for the viscosity of a mixture based on Eyring's rate theory[9]

$$\ln \eta_m = x_1^3 \ln \eta_1 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21} + x_2^3 \ln \eta_2 - \ln[x_1 + x_2 M_2/M_1] + 3x_1^2 x_2 \ln[{}^2/_3 + M_2/3M_1] + 3x_1 x_2^2 \ln[{}^1/_3 + 2M_2/3M_1] + x_2^3 \ln[M_2/M_1] \quad (10)$$

where η_{12} and η_{21} are interaction parameters. The constants of eq 10 were determined using the least-squares method and are reported in Table 4 along with standard deviations (σ) for viscosity.

Discussion

The excess molar volume, V^E, for all the four systems is shown in Figure 1. The V^E for all the systems except for [(*m*-xylene) + (4-methylpentan-2-one)] are small, which indicate weak molecular interactions. In the case of the [(*m*-xylene) + (4-methylpentan-2-one)] system, the values are very large and negative up to a *m*-xylene mole fraction of 0.78 and then they becomes positive. The negative excess volume could be attributed to an ordering of molecules in the mixture.

The deviations in viscosity, $\Delta\eta$, for all the four systems are compared in Figure 2. The deviations are negative for systems containing *o*-xylene and *p*-xylene for the entire composition range, whereas for the systems containing *m*-xylene and isopropylbenzene, the deviations are positive initially and then change to negative. The larger negative deviations for systems containing *o*-xylene and *p*-xylene indicate that the dispersion forces are stronger in these systems.[10]

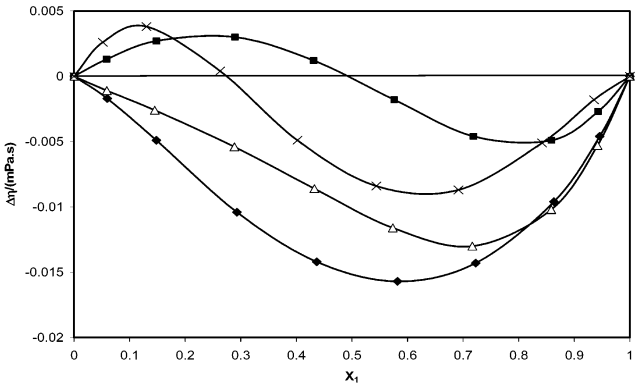

Figure 2. Viscosity deviations, $\Delta\eta$ (mPa·s), for the systems of ◆, *o*-xylene; ■, *m*-xylene; △, *p*-xylene; ×, isopropylbenzene with 4-methylpentan-2-one at 298.15 K.

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Received for review March 11, 2004. Accepted May 27, 2004.

JE049899G