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Viscosities and Densities of Binary Mixtures of Toluene with Acetic Acid and Propionic Acid at (293.15, 303.15, 313.15, and 323.15) K

V. K. Rattan,*,† Seema Kapoor,† and K. Tochigi‡

Department of Chemical Engineering & Technology, Panjab University, Chandigarh 160 014, India, and
Department of Materials and Applied Chemistry, Nihon University, Tokyo 101-8308, Japan

Viscosities and densities of binary mixtures of toluene with acetic acid and propionic acid have been measured at (293.15, 303.15, 313.15, and 323.15) K over the complete compositional range. Viscosity deviations are calculated from the experimental data and the results have been fitted to a Redlich−Kister-type equation. The corresponding parameters have been derived. The McAllister equation has also been used to correlate the viscosity data. The results are discussed in terms of molecular interactions.

Introduction

Carboxylic acids are strongly associated liquids showing peculiar mixing properties with various solvents. The temperature dependence of various thermodynamic and transport properties is of considerable importance for understanding the molecular behavior in associated liquid mixtures. Densities and viscosities of toluene with acetic acid and propionic acid were measured at (293.15, 303.15, 313.15, and 323.15) K. In the literature, values for toluene + propionic acid at 308.15 K are reported.[1] Viscosity deviations, $\Delta\eta$, were calculated from the experimental data at different mole fractions. Also, the viscosity data have been fitted to McAllister's[2] model.

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.[3−5]

Experimental Section

Toluene, acetic acid, and propionic acid (BDH, India) were purified by standard procedures[6] and stored over molecular sieves. The purity of the samples was checked by the density and viscosity measurements and the values are compared with literature values as shown in Table 1.

Table 1. Pure Component Properties

component	temp, T (K)	ρ (g cm^{-3}) exptl.	ρ (g cm^{-3}) lit.	μ (mPa s) exptl.	μ (mPa s) lit.
acetic acid	293.15	1.0498	1.04926[6]	1.2150	1.2220[11]
propionic acid	293.15	0.9938	0.99336[10]	1.1026	1.1022[11]
toluene	293.15	0.8670	0.8672[10]	0.5903	0.5876[6]

Densities were measured with an Anton Paar digital densimeter DMA 48, with precision of $\pm 1.0 \times 10^{-4}$ g cm^{-3}.

A calibrated Ubbelohde viscometer was used for viscosity measurements. The reported viscosity is accurate to within ±1%. At each temperature the viscometer was calibrated so as to determine the two constants a and b in the equation

$$\eta/\rho = at - b/t \tag{1}$$

The values of the constants were obtained by measuring the flow time with triply distilled water and twice-distilled benzene and carbon tetrachloride. The flow measurements were made with an electronic stopwatch with a precision of ±0.01 s. An average of three or four sets of flow times for each liquid or liquid mixture was taken for the purpose of calculation of viscosity. The reproducibility of the viscosity estimates was found to be within ±0.003 mPa s.

All measurements were made at a constant temperature with the help of a circulating-type cryostat where the temperature was controlled to ±0.02 K.

The mole fraction of each mixture was obtained to an accuracy of $\pm 1 \times 10^{-4}$.

Experimental Results and Correlation

The experimental data on density and viscosity are recorded in Table 2.

From the experimental data the deviations in viscosity, $\Delta\eta$, were calculated using the relations

$$\Delta\eta = \eta_m - (\eta_1 x_1 + \eta_2 x_2) \tag{2}$$

where η_m, η_1, and η_2 are the viscosities of the mixture and pure components 1 and 2. The values of $\Delta\eta$ were fitted to a Redlich−Kister type of equation[7] using the least-squares method,

$$\Delta\eta = x_1 x_2 \sum_{j=1}^{n} a_{j-1}(2x_1 - 1)^{j-1} \tag{3}$$

where a_{j-1} are constants whose values are listed in Table 3. Figures 1 and 2 show the comparison between the experimental and correlated $\Delta\eta$ for both systems.

McAllister[2] derived the following equation for the viscosity of a mixture based on Eyring's rate theory:[8]

$$\ln \eta_m = x_1^3 \ln \eta_1 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21} + x_2^3 \ln \eta_2 - \ln[x_1 + x_2 M_2/M_1] + 3x_1^2 x_2 \ln[2/3 + M_2/3M_1] + 3x_1 x_2^2 \ln[1/3 + 2M_2/3M_1] + x_2^3 \ln[M_2/M_1] \tag{4}$$

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* To whom correspondence should be addressed. E-mail: vkrattan@pu.ac.in.
† Panjab University.
‡ Nihon University.

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Table 2. Experimental Values of Densities and Viscosities

x_1	ρ / g cm^{-3}	η / mPa s	x_1	ρ / g cm^{-3}	η / mPa s	ρ / g cm^{-3}	η / mPa s	ρ / g cm^{-3}	η / mPa s
Toluene (1) + Propionic Acid (2)									
293.15 K						303.15 K			
0.0000	0.9934	1.1026	0.5550	0.9160	0.6938	0.9820	0.9498	0.9054	0.6095
0.0286	0.9897	1.0604	0.6209	0.9077	0.6768	0.9794	0.9144	0.8970	0.5898
0.0720	0.9824	1.0087	0.6913	0.9003	0.6606	0.9721	0.8713	0.8897	0.5743
0.1175	0.9746	0.9670	0.7372	0.8956	0.6419	0.9641	0.8298	0.8849	0.5603
0.1497	0.9693	0.9304	0.7870	0.8909	0.6276	0.9589	0.7997	0.8805	0.5507
0.2309	0.9572	0.8623	0.8644	0.8835	0.6088	0.9467	0.7424	0.8729	0.5364
0.3182	0.9446	0.8060	0.9714	0.8747	0.5928	0.9342	0.6911	0.8641	0.5259
0.4118	0.9323	0.7554	1.0000	0.8670	0.5903	0.9217	0.6539	0.8580	0.5211
0.5137	0.9199	0.7079				0.9093	0.6205		
313.15 K						323.15 K			
0.0000	0.9710	0.8453	0.5550	0.8947	0.5469	0.9595	0.8102	0.8863	0.4952
0.0286	0.9663	0.8218	0.6209	0.8867	0.5292	0.9586	0.7431	0.8783	0.4824
0.0720	0.9592	0.7818	0.6913	0.8796	0.5131	0.9512	0.6965	0.8711	0.4666
0.1175	0.9515	0.7510	0.7372	0.8750	0.5035	0.9434	0.6720	0.8666	0.4574
0.1497	0.9464	0.7176	0.7870	0.8706	0.4940	0.9383	0.6478	0.8620	0.4506
0.2309	0.9345	0.6663	0.8644	0.8635	0.4799	0.9264	0.5978	0.8549	0.4372
0.3182	0.9224	0.6194	0.9714	0.8551	0.4684	0.9141	0.5682	0.8466	0.4295
0.4118	0.9105	0.5909	1.0000	0.8488	0.4658	0.9021	0.5342	0.8389	0.4285
0.5137	0.8985	0.5536				0.8900	0.5047		
Toluene (1) + Acetic Acid (2)									
293.15 K						303.15 K			
0.0000	1.0493	1.2219	0.5579	0.9189	0.6349	1.0380	1.0394	0.9081	0.5578
0.0220	1.0394	1.1435	0.6302	0.9094	0.6233	1.0293	0.9772	0.8987	0.5464
0.0569	1.0270	1.0599	0.6817	0.9029	0.6144	1.0169	0.9070	0.8921	0.5382
0.1191	1.0080	0.9245	0.7391	0.8967	0.6055	0.9976	0.8216	0.8860	0.5304
0.1879	0.9879	0.8359	0.8610	0.8847	0.5941	0.9774	0.7410	0.8739	0.5201
0.2626	0.9712	0.7694	0.9262	0.8784	0.5880	0.9605	0.6753	0.8678	0.5130
0.3520	0.9526	0.7293	0.9645	0.8747	0.5842	0.9419	0.6216	0.8639	0.5088
0.4459	0.9360	0.6757	1.0000	0.8670	0.5903	0.9251	0.5903	0.8580	0.5211
0.4893	0.9286	0.6542				0.9178	0.5766		
313.15 K						323.15 K			
0.0000	1.0270	0.9003	0.5579	0.8971	0.5022	1.0178	0.7967	0.8885	0.4559
0.0220	1.0145	0.8709	0.6302	0.8881	0.4910	1.0068	0.7709	0.8794	0.4486
0.0569	1.0023	0.8111	0.6817	0.8818	0.4828	0.9945	0.7288	0.8731	0.4384
0.1191	0.9837	0.7310	0.7391	0.8758	0.4757	0.9756	0.6410	0.8672	0.4319
0.1879	0.9640	0.6554	0.8610	0.8644	0.4619	0.9557	0.5900	0.8558	0.4200
0.2626	0.9477	0.6030	0.9262	0.8586	0.4611	0.9393	0.5446	0.8498	0.4194
0.3520	0.9298	0.5610	0.9645	0.8549	0.4574	0.9212	0.5072	0.8464	0.4163
0.4459	0.9135	0.5220	1.0000	0.8488	0.4658	0.9049	0.4740	0.8389	0.4285
0.4893	0.9064	0.5131				0.8978	0.4647		

Table 3. Coefficients of the Redlich−Kister Equation (eq 3) and Standard Deviation (eq 5)

T (K)	a_0	a_1	A_2	a_3	$\sigma(\Delta\eta)$ (mPa s)
Toluene (1) + Propionic Acid (2)					
293.15	−0.0052	−0.0026	−0.0013	−0.0005	0.00003
303.15	−0.0045	0.0025	−0.0014	−0.0006	0.00002
313.15	−0.0039	0.0025	−0.0008	−0.0015	0.00003
323.15	−0.0043	0.0018	−0.0038	0.0044	0.0008
Toluene (1) + Acetic Acid (2)					
293.15	−0.0099	0.0060	−0.0069	0.0051	0.00006
303.15	−0.0082	0.0052	−0.0046	0.0012	0.00006
313.15	−0.0068	0.0046	−0.0026	−0.0015	0.00003
323.15	−0.0052	0.0026	−0.0013	−0.0005	0.00003

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

The standard deviation in each case is calculated using the relation

$$\sigma(X) = \left[\frac{(\sum X_{\text{expt}} - X_{\text{calc}})^2}{N - n}\right]^{1/2} \tag{5}$$

where N is the number of data points and n is the number of coefficients.

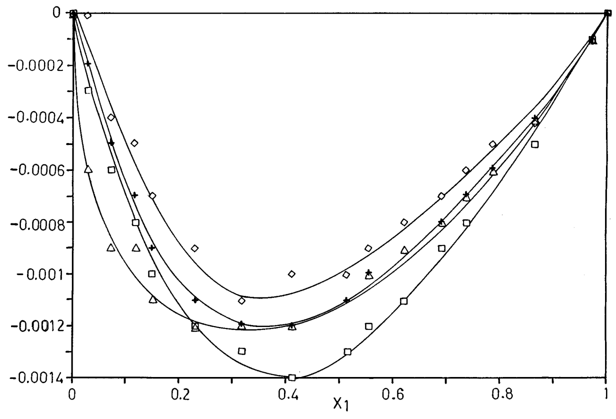

Figure 1. Viscosity deviations, $\Delta\eta$, for the system toluene + propionic acid at □ at 20 °C, + 30 °C ◊ 40 °C and △ 50 °C.

For both systems studied at the four temperatures, it is observed that the density varies almost linearly with increasing temperature. Viscosity changes nonlinearly but without showing any maxima or minima. The type of behavior could be attributed to the presence of secondary forces without any complex formation.

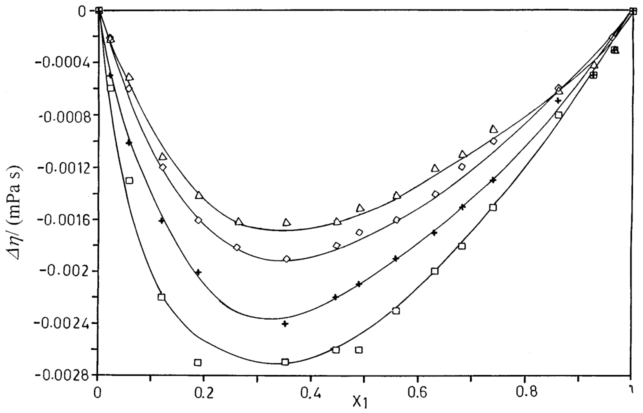

Figure 2. Viscosity deviations, $\Delta\eta$, for the system toluene + acetic acid at □ at 20 °C, + 30 °C ◇ 40 °C and △ 50 °C.

Table 4. Interaction Parameters for McAllister Model (eq 4) for Viscosity

constants	293.15 K	303.15 K	313.15 K	323.15 K
	Toluene (1) + Propionic acid(2)			
η_{12}	0.00650965	0.00572694	0.00501739	0.00484960
η_{21}	0.00729719	0.00624138	0.00574554	0.00467292
$\sigma(\eta)$ (mPa s)	0.00003	0.00003	0.00004	0.00012
	Toluene (1) + Acetic Acid (2)			
η_{12}	0.00641297	0.00543572	0.00471460	0.00429050
η_{21}	0.00554968	0.00507956	0.00474841	0.00432993
$\sigma(\eta)$ (mPa s)	0.00013	0.00008	0.00006	0.00007

The values of viscosity deviations, $\Delta\eta$, are negative over the entire compositional range. The negative values of deviation indicate that only dispersion forces and dipolar forces are operating with the absence of specific interactions.[9]

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