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Articles

Density and Viscosity for Mixtures of Propanoic Acid with Aromatic Hydrocarbons at 298.15 K

Mukhtar Singh* and Prakash Chandra Gupta

Department of Chemistry, Agra College, Agra 282002 U.P., India

Ramesh Narain Kesharwani

Department of Chemistry, Ganjdundwara College, Ganjdundwara 207242 U.P., India

The density and viscosity of binary mixtures of propanoic acid + benzene, + toluene, and + *o*-, + *m*-, and + *p*-xylenes have been measured at 298.15 K. Excess volumes have been calculated. The interactions existing between the components have been discussed. The results are used to theoretically justify the validity of the viscosity models.

Introduction

Several workers (*1−4*) have shown the existence of weak specific interactions of electron donor−acceptor type in which the aromatic hydrocarbon behaves as an electron donor. A literature survey reveals that binary systems comprising propanoic acid and aromatic hydrocarbons have not been investigated so far. Hence, the title study has been undertaken in which we report theoretical analysis of the validity of several viscosity models based on density and viscosity data of five binary mixtures at 298.15 K over the entire mole fraction range. Further, an attempt has been made to predict the thermodynamic quantity, viz. the excess molar volume (V^E). The main thrust of these investigations is to correlate the experimental data in terms of the nature of the interacting components of the mixtures and to stress the factors affecting the interactions.

Experimental Section

Propanoic acid, benzene, toluene, and *o*-, *m*-, and *p*-xylenes (all Analar) were purified according to the standard procedures (*5*). Their purities were checked by density determination dilatometrically (*6*) at 298.15 ± 0.1 K, which almost agreed within the accuracy of $\pm 1 \times 10^{-4}$ g·cm^{-3} with the available literature (*7, 8*) values and are given in Table 1. All of the solutions were prepared gravimetrically in stoppered bottles. We charged the heavier components first to minimize the errors in composition due to evaporation during the solution preparation. This led to an accuracy of the order of 3×10^{-4} in the mole fraction. The change of composition due to vaporization during the measurement was minor as confirmed by gas chromatography.

Table 1. Densities (ϱ) and Viscosities (η) for Propanoic Acid + Aromatic Hydrocarbons at 298.15 K

x_1	ϱ/g·cm^{-3}	η/mPa·s	x_1	ϱ/g·cm^{-3}	η/mPa·s
Propanoic Acid (1) + Benzene (2)					
0.0000	0.8794	0.603	0.6403	0.9420	0.723
0.1165	0.8885	0.610	n0.7347	0.9542	0.787
0.2288	0.8975	0.622	0.8260	0.9660	0.863
0.3372	0.9080	0.634	0.9144	0.9778	0.952
0.4417	0.9185	0.647	1.0000	0.9898	1.048
0.5427	0.9303	0.672			
Propanoic Acid (1) + Toluene (2)					
0.0000	0.8623	0.552	0.6817	0.9364	0.772
0.1369	0.8740	0.570	0.7691	0.9498	0.835
0.2630	0.8860	0.595	0.8510	0.9632	0.901
0.3796	0.8980	0.630	0.9278	0.9766	0.974
0.4877	0.9098	0.672	1.0000	0.9898	1.048
0.5881	0.9229	0.720			
Propanoic Acid (1) + *o*-Xylene (2)					
0.0000	0.8744	0.754	0.7087	0.9398	0.854
0.1527	0.8853	0.768	0.7910	0.9519	0.888
0.2885	0.8962	0.781	0.8665	0.9644	0.931
0.4101	0.9070	0.796	0.9359	0.9772	0.986
0.5196	0.9175	0.812	1.0000	0.9898	1.048
0.6187	0.9280	0.829			
Propanoic Acid (1) + *m*-Xylene (2)					
0.0000	0.8597	0.616	0.7122	0.9335	0.742
0.1550	0.8717	0.629	0.7938	0.9467	0.818
0.2920	0.8836	0.643	0.8684	0.9610	0.897
0.4142	0.8956	0.656	0.9369	0.9754	0.973
0.5238	0.9077	0.671	1.0000	0.9898	1.048
0.6227	0.9197	0.698			
Propanoic Acid (1) + *p*-Xylene (2)					
0.0000	0.8558	0.614	0.7132	0.9327	0.809
0.1558	0.8685	0.642	0.7946	0.9467	0.869
0.2930	0.8812	0.671	0.8689	0.9610	0.930
0.4153	0.8940	0.692	0.9372	0.9752	0.984
0.5250	0.9064	0.715	1.0000	0.9898	1.048
0.6237	0.9191	0.745			

Viscosities of the systems were determined with an accuracy of $\pm 3 \times 10^{-3}$ mPa·s using an Ostwald viscometer, which was suspended in a thermostat maintained at 298.15 ± 0.1 K. By comparing the flow time of the pure liquid or the mixture with that of water, the viscosity (η) was calculated from the relation

$$\eta = (t_m/t_w)(\varrho_m/\varrho_w)\eta_w \qquad (1)$$

where η_w is the coefficient of viscosity of water, ϱ_m and ϱ_w are densities, and t_m and t_w are times of flow for the mixture and water, respectively. The values of ϱ_m and ϱ_w were measured dilatometrically. The viscometer was calibrated

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* Author to whom correspondence should be addressed.

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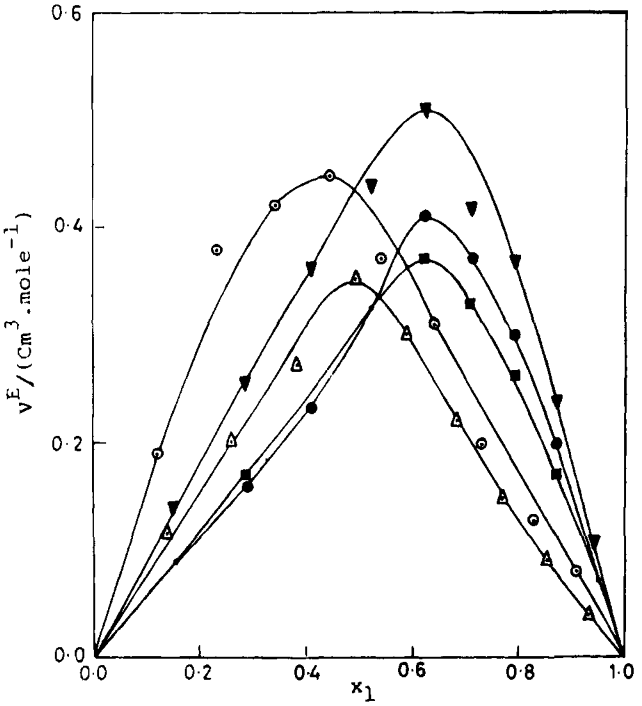

Figure 1. Excess molar volumes, V^E, at 298.15 K of propanoic acid (1) + aromatic hydrocarbon (2): ○, benzene; △, toluene; ●, *o*-xylene; ▼, *m*-xylene; ■, *p*-xylene.

by measuring viscosities of *N*-methylformamide and *N*,*N*-dimethylformamide relative to water at the experimental temperature. The experimental values were in close agreement with the literature (*7*, *8*) values. At least four flow time measurements were made at each mole fraction and a mean deviation from the mean of all measurements not exceeding 0.1 s was taken. The reproducibility was better than ±0.5%.

Results and Discussion

The density and viscosity data as a function of mole fraction (x_1) for propanoic acid (1) + aromatic hydrocarbon (2) mixtures at 298.15 ± 0.1 K are reported in Table 1. The observed excess molar volume of mixing (V^E) values were calculated from these density values. The V^E values were found to be positive for all of the mixtures, indicating the existence of weak interactions (*9*). The plots of V^E vs x_1 (Figure 1) show that maxima occur around the middle of the mole fraction range, confirming the maximum specific interactions at equimolar composition. This interaction strength varies in the order *o*-xylene < *p*-xylene < toluene < benzene ≈ *m*-xylene, which is attributed to a cumulative effect of the two factors (*10*): (i) specific interactions of the electron donor–acceptor type between propanoic acid and aromatic hydrocarbons, where the latter components behave as electron donors; (ii) the disruption in the orientational order of pure components.

The electron donating power of benzene will increase with the introduction of methyl groups in the ring. Consequently, the interactions will also increase and the V^E values for xylene mixtures and toluene mixtures would be less than those of benzene mixtures. Our experimental results support this conjecture. Further, there is steric repulsion between the propanoic acid molecule and the two bulky methyl groups, which hinders their proper orientation. The positions of methyl groups in *m*-xylene are such that steric repulsion is maximum. This is why *m*-xylene shows the weakest interactions with propanoic acid.

The polynomial function of the Redlich–Kister type

$$V^E_{\mathrm{cal/cm^3\,mol^{-1}}} = x_1x_2\left[\sum_{i=0}^{k} A_i(x_1 - x_2)^i\right] \tag{2}$$

was fitted to each set of results by the method of least squares with all points weighed equally. Table 2 gives the values of coefficients A_i and the standard deviations $\sigma(V^E)$ as defined by the equation

$$\sigma(V^E) = [\sum(V^E_{\mathrm{obsd}} - V^E_{\mathrm{cal}})^2/(n - p)]^{0.5} \tag{3}$$

where n is the number of data points and p is the number of coefficients. The standard errors in all of the mixtures were found to be less than 2%.

Tamura and Kurata (*11*) proposed the viscosity model

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1x_2\phi_1\phi_2)^{0.5}T_{12} \tag{4}$$

for the binary mixtures where ϕ_1 and ϕ_2 are the volume fractions and T_{12} is the interaction parameter. The T_{12} values, found to be positive, support the existence of weak interactions. At equimole fraction, T_{12} values and hence the strength of interaction varies in the order *o*-xylene > *p*-xylene > toluene > *m*-xylene > benzene.

The interaction parameter, H_{12}, values were also calculated using the viscosity model

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \tag{5}$$

proposed by Hind et al. (*12*). The H_{12} values are found to be positive and almost resemble the T_{12} values. However, the values of T_{12} seem to provide a better measure. These values support the existence of weak interactions and indicate a similar trend as discussed earlier.

McAllister (*13*), on the basis of the three-body interaction model, proposed the equation

$$\ln \eta = x_1^3 \ln \eta_1 + 3x_1^2x_2 \ln Z_{12} + 3x_1x_2^2 \ln Z_{21} + x_2^3 \ln \eta_2 - \ln(x_1 + x_2M_2/M_1) + 3x_1^2x_2 \ln[(2 + M_2/M_1)/3] + 3x_1x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \tag{6}$$

for the viscosity of binary mixtures where Z_{12} and Z_{21} are the interaction parameters of components 1 and 2, respectively. The values of Z_{12} and Z_{21}, evaluated in the volume fraction range 0.4–0.6 of propanoic acid using the least-squares method, are found to be positive (Table 3), which supports the existence of weak interactions (*9*). The interaction parameter, Z_{12}, values vary in the order *o*-xylene > *p*-xylene > toluene > benzene > *m*-xylene, while those of Z_{21} values are almost the reverse, which also reflects a pattern similar to the models discussed earlier.

Heric and Brewer (*14*) suggested the equation

$$\lambda = x_1\lambda_1 + x_2\lambda_2 + x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2] \tag{7}$$

for the kinematic viscosity ($\lambda = \eta/\varrho$) of binary mixtures, where λ_1 and λ_2 are kinematic viscosities of components 1 and 2, respectively. The values of parameters a, b, and c were evaluated in the volume fraction range 0.4–0.6 of propanoic acid using the least-squares method. The values of parameter a are found to be negative for all of the mixtures as shown in Table 3. Their gradation indicates a pattern similar to that of previous models. However, no regular gradation is shown by parameters b and c. This

Table 2. Coefficient A_i and Standard Deviation $\sigma(V^E)$ for Representation of Excess Functions of Propanoic Acid + Aromatic Hydrocarbons at 298.15 K

aromatic hydrocarbon	A_0	A_1	A_2	$\sigma(V^E)$/cm^3·mol^{-1}
benzene	1.6642	−1.3919	0.2825	0.0080
toluene	1.3895	−0.9640	−0.1071	0.0040
o-xylene	1.2068	2.8674	−3.2383	0.0075
m-xylene	1.7222	1.7557	−1.5786	0.0082
p-xylene	1.2092	2.0876	−2.4625	0.0072

Table 3. Values of McAllister Parameters (Z_{12} and Z_{21}) and Heric and Brewer Parameters (*a*, *b*, *c*) at 298.15 K

system	Z_{12}	Z_{21}	10^2a/ cm^2·s^{-1}	10^2b/ cm^2·s^{-1}	10^2c/ cm^2·s^{-1}
propanoic acid +					
benzene	0.6557	0.5922	−0.6423	−0.3553	0.7686
toluene	0.7264	0.5889	−0.4224	−0.0480	−0.1796
o-xylene	0.7428	0.4401	−0.3069	−0.2927	−0.0979
m-xylene	0.5945	0.6646	−0.6060	−0.5001	0.0594
p-xylene	0.7305	0.5264	−0.3874	−0.9598	1.8735

analysis suggests that the McAllister (*13*) model fits the data better than Heric and Brewer (*14*) model.

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