

Interaction studies in binary liquid mixtures of methyl formate with o-, m- and p-xylenes using viscosity data at 303.15K

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*Densities, viscosities, refractive indices of binary liquid mixtures composed of methyl formate and o-, m- and p-xylenes were determined at 303.15K and atmospheric pressure for the whole range of composition. From the experimental results the deviation in viscosity ($\Delta\eta$), excess Gibbs free energy of activation of flow (DG^*E), and the deviation in molar refraction (ΔR) were deduced. The deviation in viscosities were correlated with Redlich-Kister polynomial equation. The $\Delta\eta$ values are negative while the values of DG^*E are positive and the ΔR values are both positive and negative over the entire range of composition for all the studied systems. The ability of different one parameter and two parameter empirical models to predict mixing viscosities was also studied.*

Keywords : Methyl formate, Viscosity, Molar refraction, Xylenes, Binary mixture.

The interaction of transport properties of dense fluids on a molecular basis is proving extremely difficult due to the problem of accounting many body interactions. For this reason the computer simulation technique of molecular dynamics is becoming more widely used¹⁻⁵, for calculating transport properties of dense fluids. It is, therefore, essential to have accurate transport coefficient data over a wide range of temperature and pressure for liquids and liquid mixtures in order to develop methods of correlation and prediction and theories of transport properties. There are few published thermodynamic and transport studies on binary systems that contain methyl formate⁶⁻¹¹. The formates are the least toxic of the simple esters. The methyl and ethyl esters are quite irritating to the eyes and respiratory track, probably because they hydrolyze readily in contact with water to formic acid. While the aromatic hydrocarbons viz. xylenes were frequently used as octane enhancers in vehicles. In view of their significances it is thought worth while to study the binary mixtures of methyl formate plus o-, m- and p-xylenes in order to understand the interactions between the components. In this work densities, viscosities and refractive indices for the binary mixtures at 303.15K are reported. The experimental viscosities have been fitted to some of the empirical equations.

Experimental Procedure

Methyl formate (Fluka. AG) with a purity of >99.5% on mole basis was used without further purification. o-, m- and p-xylene all (BDH, AR) were purified as per the standard procedure¹². All the chemicals were distilled twice before use. The purities of these chemicals have been verified by measuring their densities, viscosities and refractive indices. Good agreement between the measured and literature values^{12,13} is seen (Table 1). Densities were measured with a pycnometer which is calibrated at 303.15K with doubly distilled water. Viscosities of pure liquids and of mixtures were determined by using an Ubbelohde viscometer. The method and calibration has already been reported¹⁴. Refractive indices for the sodium D line were determined with a Abbe's research refractometer with an estimated accuracy of 0.0002. The temperature of the water thermostat was controlled at 0.01K with a digital thermometer.

Results and Discussion

The densities of pure components and their mixtures were used to determine the dynamic viscosities. The viscosity deviations ($\Delta\eta$) were obtained from the relation.

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad \dots(1)$$

Table 1 - Physical properties of pure liquids at 303.15 K

Liquid	Density, ρ / g.cm ⁻³		Viscosity, η / mPa.s		Refractive index, n_D	
	Expt	Lit ^{12,13}	Exp	Lit ^{12,13}	Expt	Lit ^{12,13}
Methyl formate	0.9681	0.9686	0.323	—	1.3390	1.3393
o-xylene	0.8710	0.8716	0.695	0.693	1.5001	1.5000
m-xylene	0.8553	0.8558	0.557	0.558	1.4920	1.4919
p-xylene	0.8529	0.8523	0.566	0.566	1.4911	1.4905

Where η , η_1 and η_2 are the dynamic viscosities of the mixture and pure components respectively. The viscosity deviations were correlated by three parameter Redlich - Kister¹⁵ equation,

$$\Delta\eta = x_1x_2 [A_1 + A_2(x_1 - x_2) + A_3(x_1 - x_2)^2] \dots(2)$$

Where A_1 , A_2 and A_3 are the fitting coefficients evaluated by method of least squares. Table 2 presents the values thus obtained along with the standard deviation. The Gibbs free energy of activation of viscous flow (DG^{*E}) represents an interesting mixing property because it involves density and viscosity data and is obtained by using the following relation .

$$DG^{*E} = RT [\ln(\eta V) - X_1 \ln(\eta_1 V_1) - X_2 \ln(\eta_2 V_2)] \dots(3)$$

Where $v = (x_1M_1 + x_2M_2)/\rho$ is the molar volume of the mixture and v_1, v_2 are of pure components respectively. The deviations in molar refraction (ΔR) were calculated as a function of volume fraction F_i using the relation,

$$\Delta R = R_M - \sum_i \Phi_i R_i \dots(4)$$

Where R_M is the molar refraction of the mixture obtained by the Lorentz-Lorentz¹⁶ equation, R_i is the molar refraction for component i and Φ_i is the volume fraction of the component given as

$$\Phi_i = \frac{X_i V_i}{\sum_i X_i V_i} \dots(5)$$

Table 3 shows the values of densities (ρ), viscosity (η), Gibbs free energy of activation for viscous flow (DG^{*E}), refractive indices (n_D), molar refraction (R_M) and the deviation in molar refraction (ΔR). The predictive ability of some of the selected viscosity models such as one parameter model by Frenkel¹⁷ and Hind¹⁸ and two parameter model by McAllister¹⁹ (involving three-body interaction) was tested. The equations of these models applied to the studied binary mixtures are as follows.

Table 2 - Parameters of Least Square analysis and standard deviations of binary systems

System	A_1	A_2	A_3	$\sigma(\Delta\eta)$
Methyl formate + o-xylene	-0.0561	-0.0197	-0.0238	0.001
Methyl formate + m-xylene	-0.0281	-0.0136	-0.0028	0.001
Methyl formate + p-xylene	-0.0474	-0.0022	-0.0060	0.001

Frenkel model :

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1x_2 \ln \eta_{12} \dots(6)$$

Hind model :

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1x_2 \eta_{12} \dots(7)$$

where η_{12} is a constant. Its value is obtained from the relation.

$$\eta_{12} = 0.5 \eta_1 + 0.5 \eta_2 \dots(8)$$

McAllister (three-body interaction) model :

$$\ln(\eta) = x_1^3(v_1) + x_2^3 \ln(v_2) + 3x_1^2 x_2 \ln(v_1^2) + 3x_2^2 x_1 \ln(v_2) - \ln [x_1 + x_2 M_2 / M_1] + 3x_1^2 x_2 \ln [2/3 + M_2/3 M_1] + 3x_2^2 x_1 \ln [1/3 + 2M_2 / 3M_1] + x_2 \ln [M_2/M_1] \dots(9)$$

- where v, v_1 and v_2 are the dynamic viscosities of mixture, and their pure components respectively and v_{12} and v_{21} are the other fitting parameters. Table 4 lists these parameters alongwith their average absolute deviation (AAD) for the binary Fig. 1 - Deviations in viscosity as mole fraction of methyl formate + o-xylene (o), +m-xylene (m) and +p-xylene(D) at 303.15K

mixtures studied. The average absolute deviations between the calculated (η_{cal}) and the experimental (η_{expt}) values have been estimated by using the relation.

$$AAD = \dots(10)$$

Figure 1 displays the variation of $\Delta\eta$ with mole fraction. The deviation in viscosities were negative, while the values of DG^*E were positive across the entire composition range for all the systems. The values of DR were found to be both negative and positive for methyl formate + o-xylene and methyl formate + o-xylene and methyl formate + p-xylene systems, while for the system methyl formate + m-xylene they are positive over the entire range of composition. The negative values of Dh suggest the intermolecular interactions become weakend upon mixing, indicating the formation of a complex of low stability in which one component is associated. The negative values may also be due to size differences of molecules of components in mixtures. The large positive values of DG^*E were attributed to the fact that the physical forces rather than the chemical forces are dominant between the dissimilar molecules. Moreover, it was observed that almost all the systems show nearly symmetric values of DG^*E , which may due to the fact that as the composition of xylenes is increased there will be disruption in the ester group, which further confirms the ability of an aromatic xylene as an order destroyer. It is interesting to observe that all of the selected correlative models are capable of representing with higher or lesser degree of accuracy in the viscometric behaviour of the studied mixtures. However, the McAllister equation with two adjustable interaction parameters yields better results. The overall average absolute deviation in all cases was lower than 0.5%.

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