

Viscometric Properties of Binary Liquid Mixture of Para-xylene with 1-Pentanol at 298.15K Temperature

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Abstract

The densities (ρ) and viscosities (η) of Para-xylene, 1- Pentanol and their binary mixture with the whole composition range have been measured at 298.15 K. From the experimental data the excess molar volume (V^E), deviations in viscosity ($\Delta\eta$), excess Gibbs free energy of activation (ΔG^{*E}), entropies (ΔS^*), and enthalpies (ΔH^*) of activation of viscous flow have been determined. The sign and magnitude of these parameters were found to be sensitive towards interactions prevailing in the studied systems. Moreover, V^E values were theoretically predicted by using Flory's statistical theory. The variations of derived parameters mentioned above with composition offer a convenient method to study the nature and extent of interactions between the component molecules of the liquid mixture not easily obtained by other means.

Key words: Enthalpies, Entropies, Excess molar volume, Interactions, viscosity.

Introduction

Fundamental thermodynamic and thermo physical properties are essential source of information necessary for a better understanding of the non-ideal behavior of complex systems because physical and chemical effects which are caused by molecular interactions, intermolecular forces etc. of unlike molecules¹⁻². Viscometric properties are essential sources of information necessary for a better understanding of the non-ideal behavior of complex system. Excess thermodynamic functions have been used to explain the formation of complexes in liquid mixtures³. The properties of liquid mixtures basically depend on its local structure, expressed in terms of packing density, free volume or radial distribution function. However, this local structure depends on forces between molecules and their forms and volume of molecules. It changes with compositions⁴⁻⁶. Thermodynamic property is one which serves to describe a system. Fundamental variables of thermodynamic properties includes volume, temperature, energy (Enthalpy, Entropy, free energy etc.) and of course, the amount of substance. The nature and type of interactions in binary organic liquid mixtures have been studied in terms of mixing parameters such as excess molar volume⁷⁻⁸. The molecular interactions of binary non-aqueous liquid mixtures using thermodynamic and transport properties⁹⁻¹⁰. Here my study to the binary mixture containing 1-Pentanol and Para-xylene at 298.15K over the whole composition range. The mixture studied are interesting from the experimental as well as from the theoretical point of view because Para-xylene is

mixed with 1- Pentanol. Para-xylene (dimethylbenzene) is a colorless, flammable, liquid hydrocarbon with a characteristic aromatic odor. It is commonly found in products such as varnish, ink, paint thinners, degreasers, and insecticides. Its like benzene and toluene are major components of gasoline and fuel oil. The primary uses of Para-xylene industrially is as solvent and synthetic intermediate. Commercial Para- xylene is often contaminated with other organic compounds such as ethylbenzene, toluene, benzene, trimethylbenzene, phenol, thiophene, and pyridine¹¹. 1-Pentanol is a colourless liquid with a distinctive aroma. 1-Pentanol, also known as 1-pentyl alcohol belongs to the class of organic compounds known as primary alcohols. Thus, 1-pentanol is considered to be a fatty alcohol. 1-Pentanol exists in all eukaryotes, ranging from yeast to plants to humans. 1-Pentanol is one of the promising “next generation” alcohol fuels with high energy density and low hygroscopicity. 1-Pentanol is used as a key starting material in the production of dichloro-acetic acid pentyl ester, 2-methyltetrahydrofuran, dinpenyl ether (DNPE), pentyl butyrate and amyl acetate. As a solvent, it is used for coating CDs and DVDs¹². Whereas 1- Pentanol is polar liquid, strongly self-associated by hydrogen bonding to the extent of polymerization that may differ depending on temperature, chain length, and position of the –OH group. It would be interesting to examine the mixing of Para-xylene with 1-Pentanol and also to observe the effect of the –OH group on the molecular interaction in this binary mixture.

This work reports the experimental densities (ρ) and viscosities (η) of pure Para-xylene, 1- Pentanol and their binary mixture over the entire composition range at 298.15 K. From the above experimental data of ρ , η the excess molar volumes (V^E), deviations in viscosity ($\Delta\eta$), excess Gibbs free energies of activation (ΔG^{*E}), entropies (ΔS^*), and enthalpies (ΔH^*) of activation of viscous flow have been determined. Moreover, V^E values were theoretically evaluated by using Flory’s statistical theory¹³⁻¹⁴. The variations of derived functions, namely, V^E , $\Delta\eta$, ΔG^{*E} , ΔS^* , ΔH^* mixture with composition are discussed in order to gain insight into the type and magnitude of the molecular interactions in binary mixtures of Para-xylene with 1-Pentanol and also the effect of the position of the –OH group on the molecular interactions has been discussed.

Table 1. Comparison of experimental densities ρ and viscosities η of pure components of Para-xylene and 1-Pentanol with literature values at 298.15K¹⁵⁻¹⁷.

S.No.	Component	ρ (kg m ⁻³)		η (m Pas)	
		Expt.	Lit.	Expt.	Lit.
1.	Para-xylene	856.67	856.61	0.6978	0.6975
2.	1-Pentanol	810.82	810.79	3.3691	3.3702

Experimental

Para-xylene 99.7%, 1-Pentanol 99.5% (Sd fine chemicals India) were used as obtained but all the chemicals were stored over 0.4 nm molecular sieves to remove the traces of water, if any, and

degassed just before use. The solutions were prepared by mass using a (Scaletec SAB 200E, India) electronic balance with a precision of 0.1 mg. The densities of pure liquids and their binary mixture were measured using a single-capillary pycnometer as described in the literature⁸⁻¹⁰. The uncertainties in measured density is 0.0001 g cm^{-3} . The viscosities of pure liquids and their binary mixture were measured using Ubbelohde-type suspend level viscometer, calibrated with triple-distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostated water bath (Julabo, Model-MD) having a precision of 0.02 K in order to minimize thermal fluctuations. The uncertainty in viscosity measurement is $\pm 0.003 \text{ mPa} \cdot \text{s}$. A minimum of three readings were taken for each sample and the average values were used in all the calculations. Reliability of the experimental data and the purity of the solvents were ascertained by comparing their densities, and viscosities at different temperatures with the values reported in literature¹⁸⁻²³,

Results and Discussion

The experimental densities (ρ) and viscosities (η) of pure Para-xylene, 1-Pentanol and their binary mixture over the entire composition range, expressed by the mole fraction x_1 of Para-xylene at 298.15 K are presented in Table 2. Thermodynamic excess properties, which are the measure of the deviations from ideal behaviour are found to be influenced by the factors such as: (i) structure of the components i. e., different geometry of the unlike molecules, (ii) reorientation of the component molecules in the mixture, and (iii) intermolecular inter- actions²⁴⁻²⁵. Thus, excess molar volumes (V^E), viscosities ($\Delta\eta$), and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}), were calculated with the help of the following standard relations:

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad (1)$$

Table 2. Values of experimental density ρ and viscosity η of binary liquid mixture of Para-xylene and 1- Pentanol at 298.15K temperature.

x_1	$\rho \text{ (kg} \cdot \text{m}^{-3})$	$\eta \text{ (mPa} \cdot \text{s)}$
0.0000	845.6	6.8752
0.1024	841.5	6.6582
0.2037	838.4	6.4254
0.3036	834.8	6.1425
0.4142	829.6	5.8697
0.5025	824.8	5.5482
0.6087	820.5	5.2547
0.7124	817.4	5.0214
0.8036	814.5	4.8576
0.9004	810.2	4.5243
1.0000	807.5	4.3215

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (2)$$

$$\Delta G^{*E} = R T [\ln(\eta V) - x_1 \ln(\eta_1 V_1) - x_2 \ln(\eta_2 V_2)] \quad (3)$$

where x is the mole fraction. Subscripts 1 and 2 stand for the pure components Para-xylene and 1-Pentanol, respectively, V is the molar volume and can be evaluated by the following reaction

$$V = (x_1 M_1 + x_2 M_2)/\rho \quad (4)$$

where M is the molar mass of the pure components. The values of V^E , $\Delta\eta$ and ΔG^{*E} of the binary mixture were fitted to the Redlich and Kister type equation²⁶:

$$Y^E = x_1 x_2 \sum_i^5 A_i (1 - 2 \cdot x_1)^{i-1} \quad (5)$$

where Y^E stands for V^E , $\Delta\eta$, and ΔG^{*E} . The coefficients A_i of (5), evaluated using least-squares method, and the standard deviations $\sigma(Y^E)$, calculated as

$$\sigma(Y^E) = [\sum \{(Y_{\text{expt}}^E - Y_{\text{cal}}^E)\}^2 / (m - k)]^{1/2} \quad (6)$$

where m is the number of experimental data points and k is the number of A_i coefficients considered, have been listed in Table 3. The variations of V^E , $\Delta\eta$ and ΔG^{*E} with mole fraction x_1 of Para-xylene and 1-Pentanol at 298.15 K.

Table 3. Values of A_i parameters along with standard error, $\sigma(Y^E)$ of binary liquid mixtures at 298.15 K temperature.

Property	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
$V^E \cdot 10^7 \text{ (m}^3 \cdot \text{mol}^{-1})$	13.2154	-1.3254	9.0215	1.6325	8.0214	0.0524
$\Delta\eta \cdot 10^2 \text{ (mPa} \cdot \text{s)}$	-23.2145	-7.0214	-9.2458	-12.2548	20.2145	0.0345
$\Delta G^{*E} \text{ (KJ} \cdot \text{Mol}^{-1})$	-19.0214	2.0214	-7.0214	4.3214	4.0214	0.0201

only, to avoid overcrowding of data points at remaining temperature The observed V^E values exhibit positive deviations over the entire mole fraction range for the binary liquid system. The positive deviations in excess molar volumes can be explained by considering the fact that mixing of Para-xylene with 1-Pentanol leads to (i) the loss of dipolar association between the a molecules which tends to make V^E positive, (ii) dipole-induced- interactions between free Para-xylene and 1-Pentanol molecules (iii) geometrical fitting of smaller molecules of 1-Pentanol molecules into the voids created by the bigger Para-xylene molecules. Thus, the observed positive V^E values suggest that the effect due to (i) dominates over that of (ii) and (iii) effects. Like V^E the behaviour of V^E with x_1 shows positive deviations in the binary system investigated. It should be noted that the extent of positive deviation is more pronounced. This is due to the fact that the excess molar volume is a more powerful parameter in sensing the presence of intermolecular interaction²⁷. The observed positive values of V^E in the mixture over the entire composition range indicate the presence of weak interactions between the component molecules. This is in accordance with the views suggested by Fort and Moore²⁸. The $\Delta\eta$ values are shows entirely negative in the binary system over the complete composition range. Negative deviations in $\Delta\eta$ occur where dispersion and dipole-induced forces are operative in the system²⁹⁻³⁰. The variations of

ΔG^{*E} with mole fraction x_1 of Para-xylene in the binary mixture are presented. The values of ΔG^{*E} , like $\Delta\eta$, are negative in the binary mixture. Similar conclusion the dispersion forces present in the liquid mixtures³¹⁻³². Further, by using the temperature dependence of viscosity data the activation parameters for viscous flow have been investigated. The Eyring viscosity equation³³⁻³⁴ is given as:

$$\eta = \left(\frac{h N}{V}\right)_{\text{exp}} \cdot \left(\frac{\Delta G^*}{RT}\right) \quad (7)$$

where h is Planck's constant, N is Avogadro's number, and ΔG^* is the Gibbs energy of activation of viscous flow. Combining (12) with $\Delta G^* = \Delta H^* - T \Delta S^*$ gives the equation

$$R \ln \left(\frac{\eta V}{h N}\right) = \left(\frac{\Delta H^*}{T}\right) - \Delta S^* \quad (8)$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation of viscous flow respectively. This indicates that ΔH^* values are almost constant in the investigated temperature range, i. e., ΔH^* is independent of temperature. Thus, the values of ΔH^* and ΔS^* were obtained as the slopes and intercepts of the above plots by using a linear regression procedure.

Table 4. Values of enthalpy ΔH^* and entropy ΔS^* of activation of viscous flow of binary liquid mixture at each composition along with the linear correlation factor r

x_1	$\Delta H^* (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S^* (\text{kJ} \cdot \text{mol}^{-1})$	r
0.0000	29.8547	10.0218	0.9985
0.1024	29.5248	10.3458	0.9983
0.2037	29.2548	10.7457	0.9982
0.3036	28.8548	11.1021	0.9980
0.4142	28.6548	11.4187	0.9978
0.5025	28.3254	11.7854	0.9976
0.6087	28.1245	11.9878	0.9976
0.7124	27.8548	12.2145	0.9974
0.8036	27.6254	12.5247	0.9973
0.9004	27.3254	12.8754	0.9972
1.0000	27.1028	13.0012	0.9971

The values of ΔH^* and ΔS^* along with the linear correlation factor r are given in Table 4. A close perusal of Table 4 indicates that in the binary mixture the values of ΔH^* and ΔS^* are positive, show a decrease in ΔH^* and an opposite trend in ΔS^* values with mole fraction x_1 of Para-xylene. It has been suggested earlier³⁵ that the enthalpy of activation of viscous flow may be regarded as a measure of the degree of cooperation between the species taking part in viscous flow. In a highly structured liquid there will be considerable degree of order and hence, for cooperative movement of entities, a large heat of activation is needed for the flow process. Therefore, a perusal of Table 4 indicates that the formation of activated species necessary for viscous flow seems 1- Pentanol rich region owing to the high values of ΔH^* , and become easy as the mole fraction of Para-xylene in the mixture increases. This is supported by the decreasing value of ΔS^* as the amount of Para-xylene in the mixture increases. Furthermore, the extent of interaction between the component

molecules in a mixture is well reflected in the parameters like apparent molar volume, apparent molar compressibility, partial molar volume and partial molar compressibility³⁶⁻³⁸.

This further supports our earlier finding. In the present paper, the excess molar volume V_F^E has also been evaluated by using Flory's statistical theory¹³⁻¹⁴ V_F^E . According to Flory's equation of state¹³⁻¹⁴ V_F^E is given as:

$$V_F^E = [\sum_{i=1}^2 x_i V_i^*] [\tilde{V}^{0\ 7/3} / \{(4/3) - (\tilde{V}^0)^{1/3}\}] \quad (9)$$

The terms and notations used in (9) are the same as given in the literature¹³⁻¹⁴. Flory's statistical theory, though unable to predict excess molar volume quantitatively, seems to be satisfactory in predicting it qualitatively for the present systems studied.

Conclusion

The observed positive V_F^E values, over the entire composition range in the binary systems of Para-xylene and 1-Pentanol at 298.15K temperature indicate that disruption of associated structures of 1-Pentanol by Para-xylene molecules in the mixture dominates over that of the combined effect due to dipole-induced interactions and fitting of smaller molecules of 1-Pentanol into the voids created by bigger Para-xylene molecules. Also, the positive values of V_F^E are more pronounced for the system studied, thereby, suggesting that excess molar volume is a more powerful parameter in sensing the presence of molecular interaction in a mixture. The observed negative values of $\Delta\eta$ and ΔG^{*E} in the binary mixture clearly reinforce the behaviours of V_F^E . In the system have positive ΔH^* and ΔS^* values, show decrease in ΔH^* and reverse trend in ΔS^* values with mole fraction x_1 of Para-xylene. This indicates that the formation of activated species necessary for viscous flow is difficult in 1-Pentanol rich region. The positive values of V_F^E for 1-Pentanol in Para-xylene over the entire composition range in the binary mixture clearly suggest the presence of weak interactions between the component molecules. A comparison between the experimental V_F^E and the theoretically predicted V_F^E , using Flory's statistical theory, suggests that, though, Flory's theory is unable to predict excess molar volume quantitatively is satisfactory in predicting it qualitatively for the systems investigated.

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