5. Densities and Viscosities of Binary Mixtures of ortho-Xylene with Butan-1-ol and Pentan-1-ol at (298.15, 303.15, 308.15 and 313.15) K

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Abstract

Densities and viscosities for binary mixtures of o-xylene with butan-1-ol and pentan-1-ol have been measured over the entire range of composition, at (298.15,303.15,308.15 and 313.15) K and at atmospheric pressure. From the experimental data, excess molar volumes (V^E) and deviations in viscosities ($\Delta\eta$) have been calculated. The excess molar volumes for o-xylene + butan-1-ol and pentan-1-ol system are sigmoids while deviations in viscosity are negative. The results have been interpreted in terms of molecular interactions. These are further fitted to the Redlich-Kister polynomial equation.

Keyward :- Excess Molar Volumes, O-xylene, Butan-1-ol , Pentan-1-ol.

Introduction

Transport and Thermodynamic properties of binary liquid mixtures are frequently needed in chemical processes. Specific and non–specific interactions taking place between the components of mixtures. Alcohols are strongly self-associated molecules through Hydrogen–bonding and for binary solutions rich in alcohols. Xylenes are non-associated and potential electron donors. Recently molecular interactions between toluene having $-CH_3$ as electron donating group, and alkanols have been reported.[1-3] In the present investigation, we report density and viscosity studies of binary mixtures of o-xylene with butan-1-ol and pentan-1-ol over entire range of composition at (298.15, 303.15, 308.15, and 313.15) K at atmospheric pressure. More work has been reported about excess, transport and thermodynamic properties of binary liquid mixtures.[4-7]

Experimental Section

O-xylene, butan-1-ol and pentan-1-ol (s.d.fine chemicals, Lancaster, Purity>99) were purified by standard procedures[8]. The purity of the solvents, after purification, was ascertained by comparing their densities and viscosities with the corresponding literature values at (298.15,303.15,308.15 and 308.15)K. Binary mixtures were prepared by mass in airtight stoppered glass bottles. The masses were recorded on an Adairdutt balance to an accuracy of + 1 x 10^{-4} g. Densities of pure liquids and their mixtures were determined by using a 15 cm3 bicapillary pycnometer as described earlier.[9,10] The pycnometer was calibrated using conductivity water with 0.99705 g cm^{-3} as its density[11] at 298.15K. The dynamic viscosities were measured using an Ubbelohde suspended level viscometer,[12] calibrated with conductivity water. An electronic digital stop watch with readability of + 0.01 s was used for the flow time measurements. At least three repetitions of each data reproducible to + 0.05 s were obtained, and the results were averaged. Since all flow times were greater than 200 sec and capillary radius (0.5mm) was far less than its length (50 to 60) mm, the kinetic energy and end corrections, respectively , were found to be negligible. The viscosity,(η) of the liquids was calculated by ,

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \quad \ldots\ldots\ldots (1)$$

Where ρ, ρw and t, tw refer to the density and flow time of the experimental liquids and water, respectively. The uncertainties in dynamic viscosities are of the order of + 0.001 m Pa.s.

Result and Discussion

Experimental values of densities (ρ), and viscosities (η) of mixtures at (298.15,303.15, 308.15 and 313.15)K are listed as a function of mole fraction in Table 1. The density values have been used to calculate excess molar volumes (V^E) using the following equation.

$$\mathbf{V^E = (x_1M_1 + x_2 M_2) /\rho_{12} - (x_1M_1/\rho_1) - (x_2M_2/\rho_2)} \quad \ldots\ldots..(2)$$

where ρ_{12} is the density of the mixture and x_1 , M_1, ρ_1, and x_2 , M_2 , ρ_2 are the mole fraction, the molecular weight, and the density of pure components 1 and 2 , respectively.

The viscosity deviations ($\Delta\eta$) were calculated using

$$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad \ldots\ldots(3)$$

Where η_{12} is the viscosity of the mixture and x_1, x_2 and η_1,η_2 are the mole fraction and the viscosity of pure components 1 and 2, respectively.

The excess molar volumes, and deviations in viscosity were fitted to a Redlich– Kister[13] equation of the type

$$_{i}Y = x_1 x_2 \sum_{i}^{a} a_i (x_2 - x_1)^{i} \quad \ldots\ldots(4)$$

Where Y is either V^E or $\Delta\eta$ and n is the degree of polynomial. The calculated values of the coefficients (ai) along with the standard deviations (σ) are given in Table 3.

The variations of V^E and $\Delta\eta$ with mole fraction of o-xylene for the binary systems of o-xylene with butan-1-ol and pentan-1-ol at 298.15K are represented in Figure 1 and 2. Similar plots are obtained at other temperatures. The V^E curves for binary mixtures of o-xylene with butan-1-ol and pentan-1-ol are sigmoids. The excess volumes for these mixtures are negative at lower mole fraction and positive at higher mole fraction of o-xylene.

Treszczanowicz[14] observed that V^E may be discussed in terms of several effects which may be arbitarily divided into physical, chemical and geometrical contributions.

The positive V^E values arise due to breaking of hydrogen-bonds in the self associated butan-1-ol and pentan-1-ol molecules and physical dipole-dipole interaction between alcohol monomers and multimers. Negative V^E values arise from the presence of electron donor (xylene) – acceptor (butan-1-ol and pentan-1-ol) type interactions. The positive V^E values of xylenes + butan-1-ol and pentan-1-ol may also be explained on steric hindrance to the molecular interaction by two $-CH_3$ groups, which are attached to the aromatic ring in xylene molecules. The negative V^E values of these mixtures may arise due to interstitial accommodation of xylene molecules in the aggregates of butan-1-ol and pentan-1-ol due to the differences in the free volume and molar volumes of xylenes and butan-1-ol and pentan-1-ol.The V^E and $\Delta\eta$ increase with increase of temperature suggesting de-clustering of hetero and homo molecular complexes at elevated temperatures.Therefore, it can be concluded that positive V^E values are attributed to dissociation of aggregates of butan-1-ol and pentan-1-ol and also to steric hindrance to intermolecular interactions by two bulky $-CH_3$ groups of xylene molecules. Negative V^E and negative $\Delta\eta$ values may arise due to the structural contribution arising from geometrical fitting (interstitially accommodated) of one component (xylenes) into another (butan-1-ol and pentan-1-ol) due to differences in the free and molar volumes between components of binary mixtures.

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Table 1. Densities (ρ) , Viscosities (η) , Excess Molar Volumes (V^E) , and Deviation in Viscosity (Δη) for the o-xylene (1) + butan-1-ol (2) system.

Temp(K)	X_1	ρ ($g.cm^{-3}$)	η (Poise)	V^E (cm^3mol^{-1})	Δη (cP)
298.15	0.0000	0.80560	0.0259	0.0000	0.000
	0.1002	0.81486	0.0212	-0.0297	-0.282
	0.2004	0.82344	0.0176	-0.0447	-0.462
	0.3012	0.83118	0.0146	-0.0117	-0.572
	0.4017	0.83821	0.0124	0.0515	-0.606
	0.5070	0.84523	0.0106	0.1078	-0.590
	0.6010	0.85126	0.0095	0.1445	-0.529
	0.6921	0.85688	0.0087	0.1726	-0.446
	0.8026	0.86351	0.0080	0.1847	-0.312
	0.9049	0.86974	0.0076	0.1391	-0.167
	1.0000	0.87596	0.0075	0.000	0.000
303.15	0.0000	0.80165	0.0229	0.0000	0.000
	0.1002	0.81080	0.0187	-0.0230	-0.265
	0.2004	0.81930	0.0157	-0.0342	-0.403
	0.3012	0.82685	0.0131	0.0171	-0.500
	0.4017	0.83384	0.0112	0.0812	-0.526
	0.5070	0.84084	0.0097	0.1358	-0.512
	0.6010	0.84687	0.0087	0.1687	-0.460
	0.6921	0.85250	0.0080	0.1914	-0.386
	0.8026	0.85912	0.0074	0.2006	-0.272
	0.9049	0.86531	0.0071	0.1556	-0.146
	1.0000	0.87161	0.0070	0.0000	0.000
308.15	0.0000	0.79760	0.0202	0.0000	0.000
	0.1002	0.80664	0.0166	-0.0151	-0.223
	0.2004	0.81507	0.0140	-0.0224	-0.352
	0.3012	0.82256	0.0118	0.0325	-0.435
	0.4017	0.82952	0.0102	0.0971	-0.456
	0.5070	0.83650	0.0089	0.1508	-0.445
	0.6010	0.84249	0.0081	0.1858	-0.399
	0.6921	0.84810	0.0074	0.2081	-0.335
	0.8026	0.85470	0.0069	0.2163	-0.235
	0.9049	0.86080	0.0066	0.1800	-0.129
	1.0000	0.86724	0.0066	0.0000	0.000
313.15	0.0000	0.79349	0.0180	0.0000	0.000
	0.1002	0.80242	0.0148	-0.0078	-0.196
	0.2004	0.81079	0.0125	-0.0133	-0.307

	0.3012	0.81821	0.0107	0.0457	-0.378
	0.4017	0.82514	0.0093	0.1099	-0.395
	0.5070	0.83208	0.0082	0.1643	-0.385
	0.6010	0.83802	0.0074	0.2020	-0.346
	0.6921	0.84360	0.0069	0.2246	-0.291
	0.8026	0.85015	0.0065	0.2351	-0.205
	0.9049	0.85617	0.0062	0.2055	-0.113
	1.0000	0.86275	0.0062	0.0000	0.000

Table 2. Densities (ρ) , Viscosities (η) , Excess Molar Volumes (V^E) , and Deviation in Viscosity (Δη) for the o-xylene (1) + pentan-1-ol (2) system.

Temp(K)	X_1	ρ ($g.cm^{-3}$)	η (Poise)	V^E (cm^3mol^{-1})	Δη (cP)
298.15	0.0000	0.81128	0.0347	0.0000	0.000
	0.1050	0.81906	0.0276	-0.0398	-0.418
	0.2025	0.82602	0.0225	-0.0622	-0.668
	0.3069	0.83292	0.0180	-0.0341	-0.827
	0.4036	0.83892	0.0150	0.0247	-0.870
	0.5068	0.84525	0.0125	0.0785	-0.839
	0.6035	0.85111	0.0107	0.1197	-0.758
	0.7077	0.85748	0.0094	0.1375	-0.606
	0.8017	0.86319	0.0085	0.1422	-0.441
	0.9051	0.86973	0.0078	0.0929	-0.231
	1.0000	0.87596	0.0075	0.0000	0.000
303.15	0.0000	0.80745	0.0302	0.0000	0.000
	0.1050	0.81508	0.0242	-0.0278	-0.361
	0.2025	0.82197	0.0198	-0.0481	-0.572
	0.3069	0.82877	0.0167	-0.0137	-0.640
	0.4036	0.83474	0.0135	0.0427	-0.740
	0.5068	0.84101	0.0113	0.0980	-0.712
	0.6035	0.84684	0.0098	0.1369	-0.642
	0.7077	0.85315	0.0086	0.1560	-0.516
	0.8017	0.85880	0.0078	0.1626	-0.377
	0.9051	0.86525	0.0072	0.1184	-0.199
	1.0000	0.87161	0.0070	0.0000	0.000
308.15	0.0000	0.80360	0.0265	0.0000	0.000
	0.1050	0.81111	0.0213	-0.0197	-0.313
	0.2025	0.81791	0.0175	-0.0352	-0.493
	0.3069	0.82457	0.0143	0.0111	-0.604
	0.4036	0.83049	0.0121	0.0681	-0.632
	0.5068	0.83673	0.0103	0.1206	-0.608
	0.6035	0.84253	0.0090	0.1573	-0.550
	0.7077	0.84879	0.0079	0.1762	-0.448
	0.8017	0.85437	0.0073	0.1862	-0.325

	0.9051	0.86081	0.0068	0.1359	-0.172
	1.0000	0.86724	0.0066	0.0000	0.000
313.15	0.0000	0.79970	0.0232	0.0000	0.000
	0.1050	0.80710	0.0188	-0.0138	-0.269
	0.2025	0.81380	0.0156	-0.0240	-0.421
	0.3069	0.82036	0.0129	0.0278	-0.515
	0.4036	0.82623	0.0110	0.0843	-0.538
	0.5068	0.83243	0.0094	0.1345	-0.518
	0.6035	0.83817	0.0083	0.1721	-0.470
	0.7077	0.84436	0.0074	0.1927	-0.376
	0.8017	0.84490	0.0068	0.2009	-0.278
	0.9051	0.85624	0.0064	0.1562	-0.148
	1.0000	0.86275	0.0062	0.0000	0.000

Table 3. Coefficients of the Redlich-Kister Equation and Standard Deviation for Excess Molar Volumes and Viscosity Deviations of Mixtures.

Temp (K)	Property	a_0	a_1	a_2	a_3	σ
o-xylene + Butan-1-ol						
298.15	$V^E/cm^3\ mol^{-1}$	0.3629	1.0937	0.3680	0.1910	0.0115
	$\Delta\eta$/mPa.s	-2.3564	0.7975	-0.2648	-0.0913	0.0031
303.15	$V^E/cm^3\ mol^{-1}$	0.4708	1.0244	0.3774	0.4078	0.0135
	$\Delta\eta$/mPa.s	-2.0373	0.6806	-0.3240	0.0208	0.0050
308.15	$V^E/cm^3\ mol^{-1}$	0.5210	0.9759	0.5515	0.6681	0.0167
	$\Delta\eta$/mPa.s	-1.7656	0.6030	-0.3132	0.0093	0.0046
313.15	$V^E/cm^3\ mol^{-1}$	0.5660	0.9577	0.7432	0.8895	0.0194
	$\Delta\eta$/mPa.s	-1.5289	0.5171	-0.3094	-0.0277	0.0045
o-xylene + Pentan-1-ol						
298.15	$V^E/cm^3\ mol^{-1}$	0.2672	0.9949	0.0376	-	0.0089
	$\Delta\eta$/mPa.s	-3.3752	1.1965	-0.3045	-0.1435	0.0041
303.15	$V^E/cm^3\ mol^{-1}$	0.3267	1.0547	0.2477	-	0.0106
	$\Delta\eta$/mPa.s	-2.8084	0.7791	-0.4115	0.3099	0.0222
308.15	$V^E/cm^3\ mol^{-1}$	0.4167	1.1061	0.3352	-	0.0126
	$\Delta\eta$/mPa.s	-2.4490	0.8468	-0.3414	-0.0140	0.0029
313.15	$V^E/cm^3\ mol^{-1}$	0.4710	1.1658	0.4614	-	0.0162
	$\Delta\eta$/mPa.s	-2.0816	0.7413	-0.3224	-0.0440	0.0033