



DENSITIES AND VISCOSITIES OF BINARY MIXTURES OF XYLENES (o-, m-, AND p-) WITH PROPAN-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-, m-, and p-xylenes with propan -1-ol have been measured over the entire range of composition, at 298.15, 303.15, 308.15 and 313.15 K and 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 xylenes + propan -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.

Key words: Xylenes, Propan-1-ol, Viscosity, Density.

INTRODUCTION

Transport and thermodynamic properties of binary liquid mixtures are frequently needed in chemical processes. The physico-chemical properties of these liquid mixtures are interpreted in terms of 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; three-dimensional network of hydrogen bond is believed to be present. Xylenes are non-associated and potential electron donors. Recently, molecular interactions between toluene having $-\text{CH}_3$ as electron donating group, and alkanols have been reported.¹⁻³ There are few reports⁴⁻⁷ on the density measurements of binary mixtures of o-, m-, and p-xylenes with propan -1-ol at 298.15 and 303.15K, but there are no reports on the viscosity measurement of binary mixtures of xylenes with propan-1-ol

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at various temperatures. Therefore in the present investigation, we report density and viscosity studies of binary mixtures of xylenes with propan -1-ol over entire range of composition at 298.15, 303.15, 308.15, and 313.15 K and atmospheric pressure. In the present work, efforts are made to study the effect of additional $-\text{CH}_3$ group (xylenes) and the position of $-\text{CH}_3$ groups of xylenes on molecular interactions between propan -1-ol and o-, m-, and p-xylenes from densities and viscosities studies of their binary mixtures. Since intermolecular interactions are sensitive to temperature variations, density and viscosity studies of binary mixtures of xylenes with propan-1-ol are made at 298.15, 303.15, 308.15, and 313.15 K.

EXPERIMENTAL

o-xylene, m-xylene, p-xylene and propan-1-ol (s.d.fine chemicals, Lancaster, Purity > 99) were purified by standard pocedures⁸. 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 (Table1).

Table 1: Comparison of experimental and literature values of densities and viscosities for pure liquids

Liquid	Temp. (K)	ρ (g.cm ⁻³)		η (mPa.s)	
		Expt.	Lit.	Expt.	Lit.
o-xylene	298.15	0.87596	0.87594 ^a	0.748	0.756 ^a
	303.15	0.87161	0.87174 ^a	0.702	0.709 ^c
	308.15	0.86724	0.86754 ^a	0.660	0.662 ^f
	313.15	0.86275	0.86320 ^b	0.622	0.629 ^d
m-xylene	298.15	0.86050	0.86009 ^a	0.578	0.579 ^f
	303.15	0.85608	0.85581 ^a	0.546	0.546 ^a
	308.15	0.85158	0.85154 ^a	0.515	0.517 ^f
	313.15	0.84707	0.84726 ^a	0.492	0.496 ^a
p-xylene	298.15	0.85674	0.85661 ^a	0.598	0.605 ^a
	303.15	0.85226	0.85225 ^a	0.565	0.566 ^a

Cont...

Liquid	Temp. (K)	ρ (g.cm ⁻³)		η (mPa.s)	
		Expt.	Lit.	Expt.	Lit.
	308.15	0.84773	0.84778 ^c	0.528	0.545 ^c
	313.15	0.84317	0.84352 ^a	0.502	0.514 ^a
Propan-1-ol	298.15	0.80015	0.79997 ^f	1.948	1.943 ^a
	303.15	0.79609	0.79600 ^a	1.737	1.725 ^a
	308.15	0.79187	0.79170 ^a	1.559	1.623 ^a
	313.15	0.78758	0.78785 ^a	1.403	1.428 ^a

^aRef 15. ^bRef 16. ^cRef 17. ^dRef 18. ^eRef 19. ^fRef 20.

The observation of Table 1 reveals that the literature values and our measured values match very well. Binary mixtures were prepared by mass in airtight stoppered glass bottles. The masses were recorded on an Adairdutt balance to an accuracy of $\pm 1 \times 10^{-4}$ g. The more volatile component, (propan-1-ol) was filled directly into the bottle, and closed bottle was weighed. The second component, (xylene) was injected into the bottle through the stopper by means of syringe. This method allowed negligible vapour loss and contamination. The estimated uncertainty in mole fraction was $< 1 \times 10^{-4}$.

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 density¹¹ at 298.15 K. The pycnometer filled with air-bubble-free experimental liquids was kept in a transparent walled water bath (maintained constant to ± 0.01 K) for 10 to 15 min to attain thermal equilibrium. The positions of the liquid levels in the two arms of pycnometer were recorded with the help of a traveling microscope, which could read to 0.01 mm. The estimated uncertainty of density measurements of solvent and binary mixtures was 0.0005 g.cm⁻³. At least three to four measurements were made, which had an average deviation of ± 0.00005 g. cm⁻³.

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 200s and capillary radius (0.5 mm) 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,

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

Where ρ , ρ_w and t , t_w 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.

RESULTS 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 Tables 2, 3 and 4.

Table 2: Density, viscosity, excess molar volumes, deviation in viscosities for propan-1-ol (1) + o-xylene (2)

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
298.15	0.0000	0.87596	0.748	0.000	0.000
	0.0992	0.87024	0.750	0.118	-0.117
	0.2013	0.86450	0.766	0.158	-0.223
	0.2996	0.85889	0.809	0.148	-0.298
	0.3984	0.85293	0.867	0.117	-0.359
	0.5013	0.84632	0.961	0.063	-0.389
	0.5993	0.83948	1.066	0.002	-0.401
	0.6998	0.83171	1.208	-0.059	-0.379
	0.7994	0.82280	1.390	-0.082	-0.317
	0.8991	0.81229	1.627	-0.051	-0.200
	1.0000	0.80015	1.948	0.000	0.000

Cont...

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
303.15	0.0000	.0877161	0.702	0.000	0.000
	0.0992	0.86581	0.706	0.132	-0.099
	0.2013	0.86004	0.715	0.179	-0.195
	0.2996	0.85449	0.747	0.164	-0.266
	0.3984	0.84862	0.798	0.123	-0.316
	0.5013	0.84192	0.876	0.082	-0.345
	0.5993	0.83505	0.965	0.026	-0.357
	0.6998	0.82730	1.099	-0.034	-0.327
	0.7994	0.81852	1.251	-0.068	-0.279
	0.8991	0.80805	1.455	-0.038	-0.178
1.0000	0.79609	1.737	0.000	0.000	
308.15	0.0000	0.86724	0.660	0.000	0.000
	0.0992	0.86136	0.664	0.146	-0.085
	0.2013	0.85559	0.670	0.194	-0.171
	0.2996	0.85005	0.693	0.178	-0.236
	0.3984	0.84410	0.737	0.148	-0.281
	0.5013	0.83745	0.806	0.101	-0.305
	0.5993	0.83058	0.879	0.045	-0.320
	0.6998	0.82283	0.990	-0.014	-0.299
	0.7994	0.81409	1.139	-0.052	-0.240
	0.8991	0.80373	1.314	-0.030	-0.154
1.0000	0.79187	1.559	0.000	0.000	

Cont...

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
313.15	0.0000	0.86275	0.622	0.000	0.000
	0.0992	0.85664	0.618	0.181	-0.081
	0.2013	0.85099	0.626	0.214	-0.153
	0.2996	0.84542	0.647	0.203	-0.209
	0.3984	0.83946	0.683	0.175	-0.251
	0.5013	0.83282	0.741	0.127	-0.272
	0.5993	0.82595	0.807	0.073	-0.283
	0.6998	0.81825	0.908	0.008	-0.260
	0.7994	0.80958	1.021	-0.036	-0.226
	0.8991	0.79932	1.174	-0.022	-0.150
	1.0000	0.78758	1.403	0.000	0.000

Table 3: Density, viscosity, excess molar volumes, deviation in viscosities for propan-1-ol (1) + m-xylene (2)

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
298.15	0.0000	0.86050	0.578	0.000	0.000
	0.0991	0.85574	0.582	0.135	-0.132
	0.1996	0.85123	0.607	0.176	-0.245
	0.2996	0.84679	0.651	0.160	-0.338
	0.4001	0.84198	0.715	0.135	-0.411
	0.4997	0.83688	0.802	0.095	-0.460
	0.5998	0.83125	0.992	0.052	-0.478
	0.7004	0.82497	1.074	0.010	-0.463

Cont...

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
	0.7993	0.81799	1.276	-0.022	-0.397
	0.8990	0.80992	1.554	-0.036	-0.255
	1.0000	0.80015	1.948	0.000	0.000
303.15	0.0000	0.85608	0.546	0.000	0.000
	0.0991	0.85127	0.549	0.146	-0.116
	0.1996	0.84680	0.570	0.185	-0.214
	0.2996	0.84236	0.609	0.172	-0.294
	0.4001	0.83759	0.665	0.146	-0.358
	0.4997	0.83249	0.739	0.109	-0.403
	0.5998	0.82690	0.842	0.064	-0.419
	0.7004	0.82062	0.977	0.025	-0.404
	0.7993	0.81369	1.152	-0.009	-0.346
	0.8990	0.80568	1.396	-0.024	-0.221
	1.000	0.79609	1.737	0.000	0.000
308.15	0.0000	0.85158	0.515	0.000	0.000
	0.0991	0.84672	0.518	0.157	-0.101
	0.1996	0.84227	0.537	0.196	-0.187
	0.2996	0.83784	0.570	0.184	-0.258
	0.4001	0.83309	0.619	0.158	-0.314
	0.4997	0.82800	0.683	0.122	-0.354
	0.5998	0.82240	0.772	0.080	-0.370
	0.7004	0.81614	0.888	0.041	-0.358
	0.7993	0.80925	1.041	0.006	-0.309

Cont...

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
	0.8990	0.80132	1.253	-0.015	-0.201
	1.0000	0.79187	1.559	0.000	0.000
313.15	0.0000	0.84707	0.493	0.000	0.000
	0.0991	0.84211	0.491	0.175	-0.092
	0.1996	0.83771	0.506	0.209	-0.169
	0.2996	0.83329	0.534	0.198	-0.231
	0.4001	0.82854	0.577	0.172	-0.280
	0.4997	0.82347	0.632	0.135	-0.315
	0.5998	0.81786	0.710	0.097	-0.329
	0.7004	0.81162	0.812	0.057	-0.319
	0.7993	0.80477	0.943	0.019	-0.278
	0.8990	0.79693	1.129	-0.008	-0.182
	1.000	0.78758	1.403	0.000	0.000

Table 4: Density, viscosity, excess molar volumes, deviation in viscosities for propan-1-ol (1) + p-xylene (2)

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
298.15	0.0000	0.85674	0.598	0.000	0.000
	0.0989	0.85243	0.601	0.109	-0.131
	0.1994	0.84821	0.627	0.149	-0.240
	0.2994	0.84403	0.667	0.138	-0.335
	0.3991	0.93965	0.728	0.106	-0.409
	0.4995	0.83494	0.811	-0.056	-0.462

Cont...

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
	0.5991	0.82992	0.922	-0.009	-0.485
	0.6994	0.82421	1.072	-0.063	-0.470
	0.7989	0.81765	1.276	-0.093	-0.401
	0.8991	0.80960	1.557	-0.060	-0.254
	1.0000	0.80015	1.948	0.000	0.000
303.15	0.0000	0.85226	0.565	0.000	0.000
	0.0989	0.84782	0.566	0.133	-0.116
	0.1994	0.84367	0.590	0.166	-0.210
	0.2994	0.83951	0.623	0.156	-0.293
	0.3991	0.83513	0.675	0.127	-0.358
	0.4995	0.83045	0.747	0.077	-0.404
	0.5991	0.82541	0.843	0.019	-0.424
	0.6994	0.81975	0.974	-0.039	-0.411
	0.7989	0.81331	1.151	-0.077	-0.351
	0.8991	0.80532	1.401	-0.045	-0.218
	1.0000	0.79609	1.737	0.000	0.000
308.15	0.0000	0.84773	0.528	0.000	0.000
	0.0989	0.84323	0.533	0.145	-0.098
	0.1994	0.83911	0.551	0.178	-0.183
	0.2994	0.83496	0.581	0.169	-0.256
	0.3991	0.83058	0.627	0.142	-0.313
	0.4995	0.82591	0.690	0.094	-0.354
	0.5991	0.82090	0.772	0.033	-0.374

Cont...

Temp. (K)	x_1	$\rho_{\text{mix}} \times 10^{-3}$ (kg. m ⁻³)	η_{mix} (m Pa.s)	$V^E \times 10^6$ (m ³ . mol ⁻¹)	$\Delta\eta$ (m Pa. s)
	0.6994	0.81525	0.887	-0.023	-0.362
	0.7989	0.80884	1.040	-0.061	-0.312
	0.8991	0.80094	1.258	-0.035	-0.197
	1.0000	0.79187	1.559	0.000	0.000
313.15	0.0000	0.84317	0.502	0.000	0.000
	0.0989	0.83858	0.504	0.162	-0.087
	0.1994	0.83450	0.520	0.192	-0.162
	0.2994	0.83037	0.546	0.182	-0.226
	0.3991	0.82602	0.585	0.154	-0.277
	0.4995	0.82135	0.639	0.107	-0.314
	0.5991	0.81632	0.710	0.051	-0.332
	0.6994	0.81080	0.809	-0.004	-0.323
	0.7989	0.80429	0.943	-0.043	-0.279
	0.8991	0.79651	1.155	-0.025	-0.158
	1.0000	0.78758	1.403	0.000	0.000

The density values have been used to calculate excess molar volumes (V^E) using the following equation :

$$V^E / \text{m}^3 \cdot \text{mol}^{-1} = (x_1 M_1 + x_2 M_2) / \rho_{12} - (x_1 M_1 / \rho_1) - (x_2 M_2 / \rho_2) \quad \dots(2)$$

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 as -

$$\Delta\eta / \text{m Pa.s} = \eta_{12} - x_1 \eta_1 - x_2 \eta_2 \quad \dots(3)$$

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–Kister¹³ equation of the type

$$Y = x_1 x_2 \sum_i^n a_i (x_2 - x_1)^i \quad \dots(4)$$

Where Y is either V^E or $\Delta\eta$ and n is the degree of polynomial. Coefficients a_i were obtained by fitting Eq. 3 to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ).

σ was calculated as -

$$\sigma(Y) = \left[\frac{\sum (Y_{\text{expt}} - Y_{\text{calc}})^2}{N - n} \right]^{1/2} \quad \dots(5)$$

where N is the number of data points and n is the number of coefficients. The calculated values of the coefficients (a_i) along with the standard deviations (σ) are given in Table 5.

Table 5: 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
Propan-1-ol + o-xylene :						
298.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.2108	1.2032	0.2120	-	0.0091
	$\Delta\eta/\text{mPa.s}$	-1.5663	0.4310	-0.3066	0.1919	0.0022
303.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.2777	1.2100	0.3370	-	0.0113
	$\Delta\eta/\text{mPa.s}$	-1.3853	0.3292	-0.2348	0.3169	0.0034
308.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.3569	1.2288	0.3959	-	0.0115
	$\Delta\eta/\text{mPa.s}$	-1.2414	0.3151	-0.1349	0.2204	0.0048

Cont...

Temp. (K)	Property	a_0	a_1	a_2	a_3	σ
313.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.4450	1.3336	0.5875	-	0.0184
	$\Delta\eta/\text{mPa.s}$	-1.0855	0.2668	-0.2978	0.3124	0.0037
Propan-1-ol + m-xylene :						
298.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.3729	0.8148	0.2729	0.5803	0.0023
	$\Delta\eta/\text{mPa.s}$	-1.8339	0.7116	-0.4797	0.1939	0.0012
303.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.4180	0.7828	0.3990	0.6300	0.0029
	$\Delta\eta/\text{mPa.s}$	-1.6019	0.6328	-0.4104	0.1230	0.0011
308.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.4686	0.7401	0.4981	0.7144	0.0034
	$\Delta\eta/\text{mPa.s}$	-1.4069	0.5670	-0.4105	0.1740	0.0013
313.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.5221	0.6739	0.6139	0.9436	0.0051
	$\Delta\eta/\text{mPa.s}$	-1.2494	0.4984	-0.4197	0.1732	0.0017
Propan-1-ol + p-xylene :						
298.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.8121	1.2069	0.0970	-	0.0076
	$\Delta\eta/\text{mPa.s}$	-1.8448	-0.7912	-0.4509	0.0761	0.0009
303.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.2588	1.2338	0.2780	--	0.0118
	$\Delta\eta/\text{mPa.s}$	-1.6165	0.7190	-0.3707	-0.0316	0.0018
308.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.3123	1.2337	0.3945	--	0.0135
	$\Delta\eta/\text{mPa.s}$	-1.4181	0.6308	-0.3438	0.0737	0.0010
313.15	$V^E/\text{cm}^3 \text{ mol}^{-1}$	0.3665	1.2481	0.5382	--	0.0152
	$\Delta\eta/\text{mPa.s}$	-1.2756	0.6501	-0.1694	-0.2578	0.0068

The variations of V^E and $\Delta\eta$ with mole fraction of propan-1-ol (x_1) for the three binary systems, (x_1) propan-1-ol + (1- x_1) o-xylene, (x_1) propan-1-ol +(1- x_1) m-xylene, and (x_1)propan-1-ol+(1- x_1)p-xylene at 298.15 K are represented in Figs. 1 and 2. Similar plots were obtained at other temperatures (not shown). V^E values of the propan-1-ol with o-, m-, and p-xylene systems at 298.15⁴⁻⁶ K and 303.15⁷K are also reported in literature. Their values are lower than our values. The V^E curves for binary mixtures of propan-1-ol with o-, m-, and p-xylene are sigmoids. The excess volumes for these mixtures are positive at lower mole fraction and negative at higher mole fraction of propan-1-ol. It is interesting to note that values of V^E for propan-1-ol + m- xylene mixtures are positive over most of the concentration range. They are negative with very low magnitude at $x_1 \approx 0.8$. All the V^E

curves are skewed towards the low mole fraction of alcohol. For propan-1-ol + xylene mixtures, the V^E follows the order

$$m\text{-xylene} > o\text{-xylene} \approx p\text{-xylene}$$

Treszczanowicz¹⁴ observed that V^E may be discussed in terms of several effects, which may be arbitrarily divided into physical, chemical and geometrical contributions. The physical interaction involved mainly dispersion forces giving a positive contribution. The chemical or specific interactions result in a volume contraction and these include charge-transfer type forces, forming or breaking of H-bonds and other complex forming interactions such as donor-acceptor, dipole-dipole, dipole-induced dipole. Structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volume and free volume between the components lead to negative contribution to V^E .

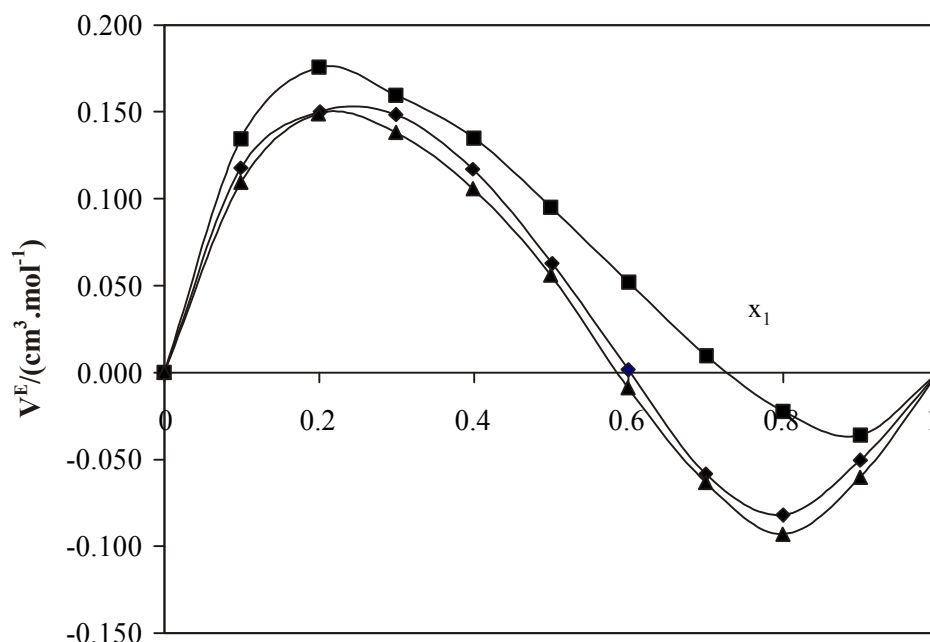


Fig. 1: Excess molar volumes (V^E) at 298.15 K for x_1 propan- 1-ol + (1- x_1) xylenes : o-xylene (\blacklozenge) ; m-xylene (\blacksquare) ; p-xylene (\blacktriangle)

The positive V^E values arise due to breaking of hydrogen bonds in the self associated propan-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 (propan-1-ol) type interactions. The positive V^E values of xylenes + propan -1-ol

may also be explained on the basis of steric hindrance to the molecular interaction by two CH_3 groups, which are attached to the aromatic ring in xylene molecules. The geometrical positions of two CH_3 groups of *m*-xylene are such that they offer maximum steric hindrance yielding maximum positive values of V^E . The negative V^E values of these mixtures may arise due to interstitial accommodation of xylene molecules in the aggregates of propan-1-ol at $x_1 > 0.6$, due to the differences in the free volume and molar volumes of xylenes and propan-1-ol. The molar volumes of *o*-xylene, *m*-xylene, *p*-xylene, and propan-1-ol are 121.20, 123.38, 123.92 and 75.11 cm^3 / mol respectively at 298.15 K. These molar volume values of xylenes and propan-1-ol differ considerably and hence, non-associated xylene molecules are interstitially accommodated into clusters of propan-1-ol, yielding few negative values of V^E . This further implies that complex forming interactions are almost absent in xylenes (*o*-, *m*-, and *p*-) + propan-1-ol systems and therefore observed $\Delta\eta$ values are negative (Fig. 2).

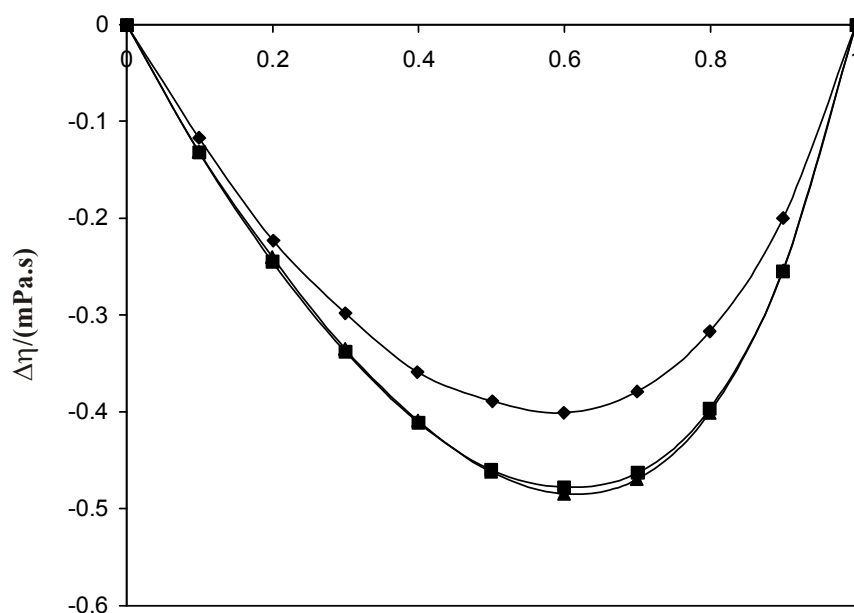


Fig. 2: Deviations in viscosity ($\Delta\eta$) at 298.15 K for x_1 propan-1-ol + $(1-x_1)$ xylenes : *o*-xylene (◆) ; *m*-xylene (■) ; *p*-xylene (▲)

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 propan-1-ol and also to steric hindrance to intermolecular interactions by two

bulky $-\text{CH}_3$ 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 (propan-1-ol.) due to differences in the free and molar volumes between components of binary mixtures.

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