

“Transport and Thermodynamics Properties of Binary Mixtures of m-Xylene with Propan-1-ol, Butan-1-ol and Pentan-1-ol at Different Temperatures”

¹Tulshidas S. Savale, ²Janardhan M. Shewale.

Post Graduate Department of Physical Chemistry,

M.S.G. Arts, Science and Commerce College, Malegaon Camp - 423105, Dist. Nashik (M.S.)

Email - ¹anilsavale23@gmail.com, ²janshewa@gmail.com

Abstract : The knowledge of thermodynamic mixing properties for binary mixtures of m-xylene with propan-1-ol, 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 m-xylene + propan-1-ol, 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.

Key Words: Density, Viscosity, m-Xylene, Propan-1-ol, Butan-1-ol and Pentan-1-ol.

1. 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. Molecular interactions between toluene, xylenes having $-\text{CH}_3$ as electron donating group, and alkanols have been reported.¹⁻⁵ Measured densities and viscosities of xylene (o-, m- and p-), normal and branched alkanols ($\text{C}_1\text{-C}_{10}$) and their binary mixtures with xylene in the liquid state were reported⁶⁻¹¹ over the whole range of composition at different temperatures and atmospheric pressure. In the present investigation, we report density and viscosity studies of binary mixtures of m-xylene with propan-1-ol, 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.¹²⁻¹⁷

1.1 Experimental Section :

M-Xylene, propan-1-ol, butan-1-ol and pentan-1-ol (s. d. fine chemicals, Lancaster, Purity > 99) were purified by standard procedures¹⁸. 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. 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 $+ 1 \times 10^{-4}$ g. Densities of pure liquids and their mixtures were determined by using a 15 cm³ bicapillary pycnometer as described earlier.¹⁹⁻²⁰ The pycnometer was calibrated using conductivity water with 0.99705 g cm⁻³ as its density²¹ at 298.15K. The dynamic viscosities were measured using an Ubbelohde suspended level viscometer,²² 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,

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

Where, ρ_w and 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.

2. 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 2,3 and 4. The density values have been used to calculate excess molar volumes (V^E) using the following equation.

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

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

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

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–Kister²³ equation of the type

$$Y = X_1X_2 \sum_i^n a_i(X_2 - X_1)^i \quad \text{--- (4)}$$

Where Y is either V^E or $\Delta\eta$ and n is the degree of polynomial. The calculated values of the coefficients (a_i) along with the standard deviations (σ) are given in Table 5.

The variations of V^E and $\Delta\eta$ with mole fraction of m-xylene for the binary systems of m-xylene with propan-1-ol, 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 m-xylene with propan-1-ol, 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 m-xylene.

Treszczanowicz²⁴ observed that V^E may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical and geometrical contributions.

The positive V^E values arise due to breaking of hydrogen-bonds in the self associated propan-1-ol, 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 (propan-1-ol, butan-1-ol and pentan-1-ol) type interactions. The positive V^E values of xylenes + propan-1-ol, butan-1-ol and pentan-1-ol may also be explained on steric hindrance to the molecular interaction by two $-\text{CH}_3$ 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 propan-1-ol, butan-1-ol and pentan-1-ol due to the differences in the free volume and molar volumes of xylenes and propan-1-ol, 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 propan-1-ol, butan-1-ol and pentan-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, butan-1-ol and pentan-1-ol) due to differences in the free and molar volumes between components of binary mixtures.

3. CONCLUSION:

In the present investigation the excess molar volume (V^E) and deviations in viscosities ($\Delta\eta$) of binary mixtures of m-xylene with 1-alkanols ($\text{C}_3\text{-C}_5$) were measured at different temperatures. The excess molar volumes for m-xylene + propan-1-ol, butan-1-ol and pentan-1-ol system are sigmoids while deviations in viscosity are negative. The V^E values for binary mixtures of m-xylene with propan-1-ol, butan-1-ol and pentan-1-ol are negative at lower mole fractions of xylene molecules and positive at higher mole fractions of xylene. The negative V^E values may arise due to π -HO donor-acceptor complex formation between xylene and alkanol molecules. Positive V^E are obtained as a result of dissociation of aggregates of alkanol in presence of xylene molecules. As expected V^E increases with increasing of temperature due to rupture of homo and hetero complexes. The $\Delta\eta$ values for all binary mixtures are negative at all temperatures. These negative $\Delta\eta$ values are attributed to difference in molar volumes and free volumes of propan-1-ol and xylene molecules.

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

Liquid	Temp(K)	ρ (g.cm ³)		η (mPa.s)	
		Expt.	Lit.	Expt.	Lit.
m-Xylene	298.15	0.86050	0.86006 ^a	0.578	0.579 ^c
	303.15	0.85608	0.85581 ^b	0.546	0.546 ^b
	308.15	0.85158	0.85124 ^a	0.515	0.517 ^c
	313.15	0.84707	---	0.492	---
Propan-1-ol	298.15	0.80015	0.79997 ^c	1.948	1.943 ^b
	303.15	0.79609	0.79600 ^b	1.737	1.725 ^b
	308.15	0.79187	0.79158 ^d	1.559	1.537 ^f
	313.15	0.78758	0.78869 ^b	1.403	1.405 ^f
Butan-1-ol	298.15	0.80560	0.80590 ^b	2.586	2.571 ^b
	303.15	0.80165	0.80180 ^e	2.286	2.285 ^e
	308.15	0.79760	0.79815 ^b	2.024	2.000 ^f
	313.15	0.79349	0.79405 ^f	1.797	1.782 ^f
Pentan-1-ol	298.15	0.81128	0.81120 ^g	3.465	3.421 ^d
	303.15	0.80745	0.80740 ^e	3.021	3.054 ^f
	308.15	0.80360	0.8039 ^g	2.648	2.607 ^d
	313.15	0.79970	0.79987 ^e	2.324	2.344 ^e

^aRef 25, ^bRef 26, ^cRef 27, ^dRef 28, ^eRef 29, ^fRef 30, ^gRef 31.

Table 2. Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E), and Deviation in Viscosity ($\Delta\eta$) for the m-xylene (1) + propan-1-ol (2) system.

Temp(K)	X ₁	ρ (g.cm ⁻³)	η (Poise)	V ^E (cm ³ .mol ⁻¹)	$\Delta\eta$ (cP)
298.15	0.0000	0.80015	0.0195	0.0000	0.000
	0.1010	0.80992	0.0155	-0.0361	-0.255
	0.2007	0.81799	0.0128	-0.0224	-0.397
	0.2996	0.82497	0.0107	0.0095	-0.463
	0.4002	0.83125	0.0092	0.0520	-0.478
	0.5003	0.83688	0.0080	0.0950	-0.460
	0.5999	0.84198	0.0072	0.1350	-0.411
	0.7004	0.84679	0.0065	0.1595	-0.338
	0.8004	0.85123	0.0061	0.1756	-0.245
	0.9009	0.85574	0.0058	0.1345	-0.132
303.15	0.0000	0.86050	0.0058	0.0000	0.000
	0.1010	0.80992	0.0174	0.0000	0.000
	0.2007	0.80568	0.0140	-0.0241	-0.221
	0.2996	0.81369	0.0115	-0.0085	-0.346
	0.2996	0.82062	0.0098	0.0252	-0.404
	0.4002	0.82690	0.0084	0.0643	-0.419
	0.5003	0.83249	0.0074	0.1088	-0.403
	0.5999	0.83759	0.0067	0.1458	-0.358
	0.7004	0.84236	0.0061	0.1722	-0.294
	0.8004	0.84680	0.0057	0.1852	-0.214
308.15	0.9009	0.85127	0.0055	0.1461	-0.116
	1.0000	0.85608	0.0055	0.0000	0.000
	0.0000	0.79187	0.0156	0.0000	0.000
	0.1010	0.80132	0.0125	-0.0147	-0.201
	0.2007	0.80925	0.0104	0.0060	-0.309
	0.2996	0.81614	0.0089	0.0414	-0.358

	0.4002	0.82240	0.0077	0.0804	-0.370
	0.5003	0.82800	0.0068	0.1215	-0.354
	0.5999	0.83309	0.0062	0.1575	-0.314
	0.7004	0.83784	0.0057	0.1843	-0.258
	0.8004	0.84227	0.0054	0.1963	-0.187
	0.9009	0.84672	0.0052	0.1572	-0.101
	1.0000	0.85158	0.0052	0.0000	0.000
313.15	0.0000	0.78758	0.0140	0.0000	0.000
	0.1010	0.79693	0.0113	-0.0082	-0.182
	0.2007	0.80477	0.0094	0.0194	-0.278
	0.2996	0.81162	0.0081	0.0573	-0.319
	0.4002	0.81786	0.0071	0.0969	-0.329
	0.5003	0.82347	0.0063	0.1353	-0.315
	0.5999	0.82854	0.0058	0.1722	-0.280
	0.7004	0.83329	0.0053	0.1975	-0.231
	0.8004	0.83771	0.0051	0.2092	-0.169
	0.9009	0.84211	0.0049	0.1752	-0.092
	1.0000	0.84707	0.0049	0.0000	0.000

Table 3. Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E), and Deviation in Viscosity ($\Delta\eta$) for the m-xylene (1) + butan-1-ol (2) system.

Temp(K)	X_1	ρ ($\text{g}\cdot\text{cm}^{-3}$)	η (Poise)	V^E ($\text{cm}^3\text{mol}^{-1}$)	$\Delta\eta$ (cP)
298.15	0.0000	0.80560	0.0259	0.0000	0.000
	0.1006	0.81297	0.0203	-0.0243	-0.355
	0.2012	0.81951	0.0161	-0.0062	-0.568
	0.3014	0.82541	0.0131	0.0385	-0.675
	0.4017	0.83093	0.0107	0.0857	-0.705
	0.5072	0.83639	0.0090	0.1351	-0.664
	0.6010	0.84104	0.0079	0.1686	-0.590
	0.7013	0.84588	0.0070	0.1868	-0.478
	0.8032	0.85063	0.0064	0.1916	-0.337
	0.9021	0.85533	0.0060	0.1491	-0.178
	1.0000	0.86050	0.0058	0.0000	0.000
303.15	0.0000	0.80165	0.0229	0.0000	0.000
	0.1006	0.80883	0.0180	-0.0091	-0.309
	0.2012	0.81527	0.0144	0.0148	-0.494
	0.3014	0.82113	0.0118	0.0589	-0.583
	0.4017	0.82652	0.0098	0.1172	-0.609
	0.5072	0.83205	0.0083	0.1522	-0.571
	0.6010	0.83668	0.0073	0.1835	-0.512
	0.7013	0.84148	0.0065	0.2017	-0.414
	0.8032	0.84618	0.0060	0.2081	-0.292
	0.9021	0.85079	0.0056	0.1729	-0.153
	1.0000	0.85608	0.0055	0.0000	0.000
308.15	0.0000	0.79760	0.0202	0.0000	0.000
	0.1006	0.80455	0.0162	0.0114	-0.249
	0.2012	0.81089	0.0129	0.0417	-0.428
	0.3014	0.81671	0.0107	0.0856	-0.504
	0.4017	0.82217	0.0089	0.1299	-0.526
	0.5072	0.82761	0.0076	0.1712	-0.494
	0.6010	0.83219	0.0068	0.2045	-0.439
	0.7013	0.83697	0.0061	0.2205	-0.355

	0.8032	0.84164	0.0056	0.2259	-0.251
	0.9021	0.84621	0.0053	0.1912	-0.132
	1.0000	0.86724	0.0052	0.0000	0.000
313.15	0.0000	0.79349	0.0180	0.0000	0.000
	0.1006	0.80026	0.0145	0.0270	-0.216
	0.2012	0.80652	0.0116	0.0620	-0.372
	0.3014	0.81229	0.0097	0.1074	-0.438
	0.4017	0.81779	0.0083	0.1420	-0.447
	0.5072	0.82314	0.0071	0.1903	-0.429
	0.6010	0.82773	0.0063	0.2181	-0.383
	0.7013	0.83248	0.0057	0.2336	-0.309
	0.8032	0.83708	0.0053	0.2444	-0.221
	0.9021	0.84158	0.0050	0.2151	-0.118
	1.0000	0.84707	0.0049	0.0000	0.000

Table 4. Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E), and Deviation in Viscosity ($\Delta\eta$) for the m-xylene (1) + pentan-1-ol (2) system.

Temp(K)	X_1	ρ ($\text{g}\cdot\text{cm}^{-3}$)	η (Poise)	V^E ($\text{cm}^3\text{mol}^{-1}$)	$\Delta\eta$ (cP)
298.15	0.0000	0.81128	0.0347	0.0000	0.000
	0.1051	0.81730	0.0266	-0.0306	-0.500
	0.2026	0.82243	0.0209	-0.0173	-0.795
	0.3072	0.82766	0.0161	0.0140	-0.964
	0.4035	0.83226	0.0130	0.0554	-1.000
	0.5070	0.83709	0.0106	0.0977	-0.940
	0.6035	0.84152	0.0089	0.1312	-0.834
	0.7078	0.84628	0.0076	0.1543	-0.662
	0.8019	0.85057	0.0068	0.1605	-0.473
	0.9051	0.85558	0.0061	0.1081	-0.244
	1.0000	0.86050	0.0058	0.0000	0.000
303.15	0.0000	0.80745	0.0302	0.0000	0.000
	0.1051	0.81331	0.0234	-0.0183	-0.426
	0.2026	0.81833	0.0184	0.0019	-0.676
	0.3072	0.82349	0.0144	0.0344	-0.817
	0.4035	0.82806	0.0118	0.0725	-0.848
	0.5070	0.83283	0.0097	0.1152	-0.800
	0.6035	0.83723	0.0082	0.1454	-0.707
	0.7078	0.84196	0.0071	0.1646	-0.563
	0.8019	0.84620	0.0063	0.1705	-0.403
	0.9051	0.85107	0.0057	0.1296	-0.209
	1.0000	0.85608	0.0055	0.0000	0.000
308.15	0.0000	0.80360	0.0265	0.0000	0.000
	0.1051	0.80932	0.0206	-0.0094	-0.367
	0.2026	0.81425	0.0164	0.0142	-0.579
	0.3072	0.81931	0.0130	0.0512	-0.697
	0.4035	0.82382	0.0106	0.0892	-0.723
	0.5070	0.82856	0.0089	0.1270	-0.680
	0.6035	0.83287	0.0076	0.1617	-0.602
	0.7078	0.83756	0.0066	0.1775	-0.480
	0.8019	0.84174	0.0060	0.1838	-0.340
	0.9051	0.84648	0.0054	0.1524	-0.179
	1.0000	0.85158	0.0052	0.0000	0.000

313.15	0.0000	0.79970	0.0232	0.0000	0.000
	0.1051	0.80524	0.0182	0.0058	-0.314
	0.2026	0.81009	0.0146	0.0321	-0.493
	0.3072	0.81508	0.0117	0.0700	-0.592
	0.4035	0.81953	0.0097	0.1085	-0.615
	0.5070	0.82424	0.0082	0.1422	-0.581
	0.6035	0.82852	0.0070	0.1732	-0.515
	0.7078	0.83313	0.0062	0.1919	-0.413
	0.8019	0.83726	0.0056	0.1977	-0.297
	0.9051	0.84193	0.0051	0.1677	-0.158
	1.0000	0.84707	0.0049	0.0000	0.000

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
m-xylene + propan-1-ol						
298.15	V ^E /cm ³ mol ⁻¹	0.3729	1.8148	0.2729	0.5803	0.0023
	Δη/mPa.s	-1.8339	0.7116	-0.4797	0.1936	0.0012
303.15	V ^E /cm ³ mol ⁻¹	0.4180	0.7828	0.3990	0.6300	0.0029
	Δη/mPa.s	-1.6019	0.6328	-0.4104	0.1230	0.0011
308.15	V ^E /cm ³ mol ⁻¹	0.4686	0.7401	0.4981	0.7144	0.0034
	Δη/mPa.s	-1.4069	0.5670	-0.4105	0.1740	0.0013
313.15	V ^E /cm ³ mol ⁻¹	0.5221	0.6739	0.6139	0.9436	0.0051
	Δη/mPa.s	-1.2494	0.4984	-0.4197	0.1732	0.0017
m-xylene + butan-1-ol						
298.15	V ^E /cm ³ mol ⁻¹	0.5038	0.7942	0.2892	0.6642	0.0052
	Δη/mPa.s	-2.6756	1.1506	-0.4606	0.0551	0.0016
303.15	V ^E /cm ³ mol ⁻¹	0.5709	0.6876	0.4894	0.9189	0.0092
	Δη/mPa.s	-2.3118	0.9801	-0.4172	0.1148	0.0022
308.15	V ^E /cm ³ mol ⁻¹	0.6356	0.6477	0.7205	0.9443	0.0100
	Δη/mPa.s	-2.0117	0.9468	-0.2129	-0.2381	0.0058
313.15	V ^E /cm ³ mol ⁻¹	0.6838	0.5686	0.9722	1.1720	0.0138
	Δη/mPa.s	-1.7392	0.8021	-0.2249	-0.2153	0.0069
m-xylene + pentan-1-ol						
298.15	V ^E /cm ³ mol ⁻¹	0.3813	0.8106	0.1226	0.2805	0.0027
	Δη/mPa.s	-3.8080	1.7068	-0.4373	-0.2289	0.0032
303.15	V ^E /cm ³ mol ⁻¹	0.4298	0.6934	0.3167	0.5630	0.0039
	Δη/mPa.s	-3.2288	1.4423	-0.4077	-0.1935	0.0017
308.15	V ^E /cm ³ mol ⁻¹	0.4779	0.6206	0.4847	0.8228	0.0071
	Δη/mPa.s	-2.7458	1.2497	-0.3904	-0.1635	0.0031
313.15	V ^E /cm ³ mol ⁻¹	0.5286	0.5636	0.6597	0.9339	0.0087
	Δη/mPa.s	-2.3389	1.0197	-0.3912	-0.1045	0.0018

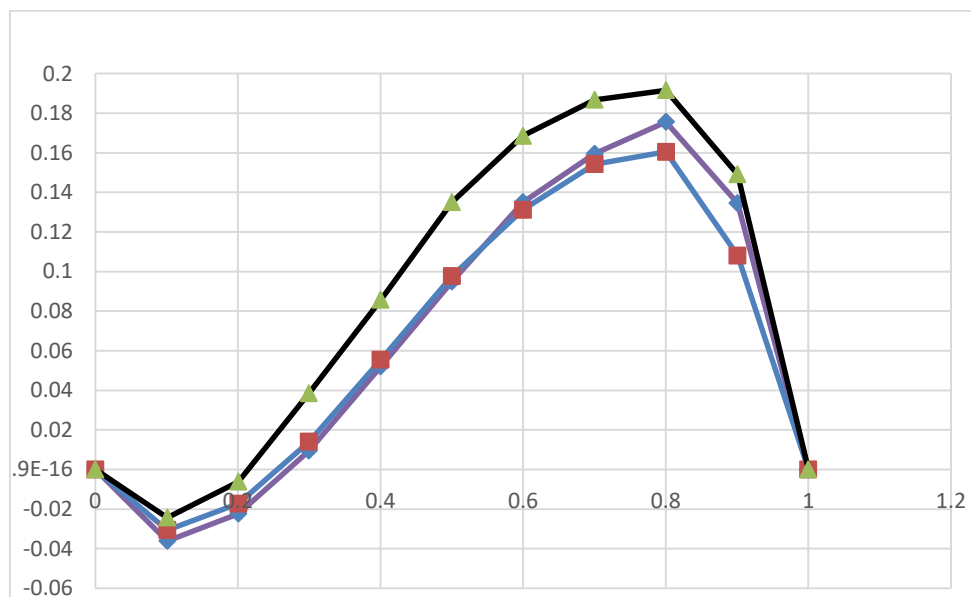


Fig.1. Excess Molar Volume V^E at 298.15K for X_1 m-xylene + $(1- X_1)$ Propan- 1-ol(◆), Butan-1-ol(▲), Pentan-1-ol(■).

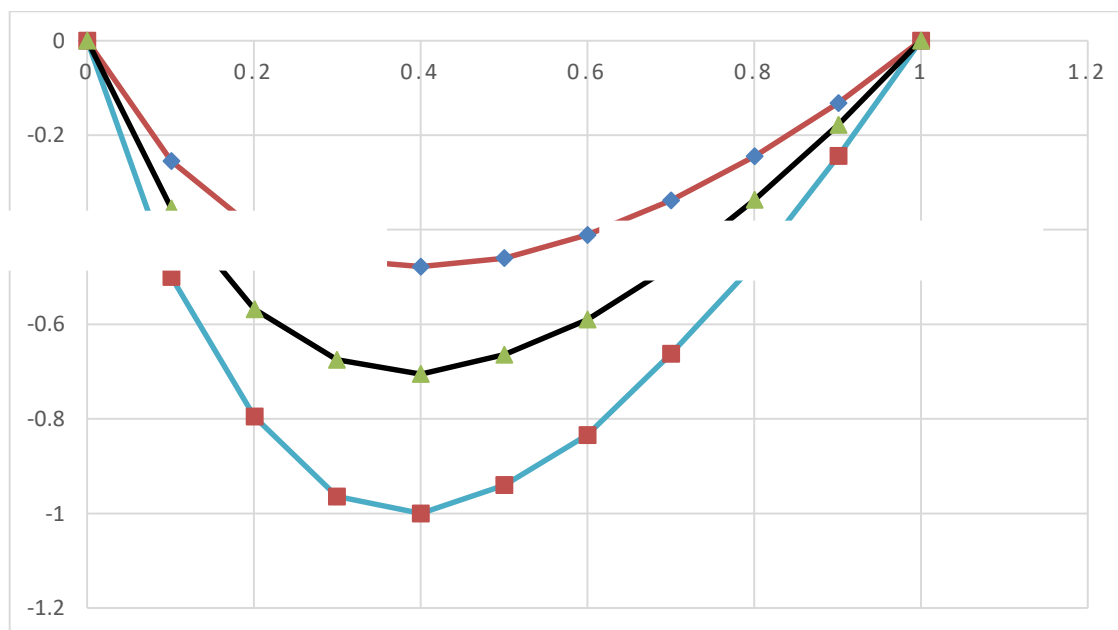


Fig.2. Deviation in viscosity $\Delta\eta$ at 298.15K for X_1 m-xylene + $(1- X_1)$ Propan-1-ol (◆), Butan-1-ol (▲), Pentan-1-ol(■).