



MOLECULAR INTERACTIONS BETWEEN METHANOL – BENZENE AND METHANOL–ACETONE MOLECULES

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ABSTRACT

Densities and viscosities of binary mixtures of methanol with benzene and acetone have been measured at 298.15, 303.15, 308.15 and 313.15 K. Using the experimental data, excess molar volumes V^E and deviations in viscosity ($\Delta\eta$) were calculated. The excess molar volumes and deviations in viscosity are fitted to the Redlich–Kister polynomial equation. V^E and $\Delta\eta$ values have been interpreted in terms of intermolecular interactions.

Key words : Density, Viscosity, Excess molar volume, Deviation in viscosity.

INTRODUCTION

Thermodynamic and transport property studies of binary liquid mixtures containing protic, aprotic and associated liquids have been reported earlier^{1–5}. The calculated excess quantities and other data have been interpreted in terms of difference in size of molecules and strength of the specific and non-specific interactions taking place between the components of the mixtures. In the present study, interactions between benzene, methanol and acetone have been reported. Methanol exists in associated form, whereas benzene and acetone have non-associated structures in liquid state. When associated methanol is mixed with non-associated benzene and acetone, then mixing properties with varying intermolecular interactions may be generated. To investigate this effect, the density (d) and the viscosity (η) of binary mixtures methanol–benzene and methanol–acetone are measured in the present investigation over the entire composition range at 298.15, 303.15, 308.15 and 313.15 K.

EXPERIMENTAL

Methanol (S.D. Fine Chemicals, purity > 99 mol %), benzene (Merck, purity > 99 mol. %) and acetone (Qualigens Fine Chemicals purity > 99.5 mol. %) were used after single distillation. The purity of the liquids after distillation was ascertained by GLC and also by comparing their densities and viscosities with the literature values⁶ at 298.15 K (Table 1). Binary mixtures were prepared by mass in airtight stoppered glass bottles with a precision of 0.01 mg on a Mettler

balance (Switzerland, Model AE-200). Care was taken to avoid evaporation and solvent contamination during mixing. The estimated error in mole fraction was $< 1.0 \times 10^{-4}$. The densities of degassed pure liquids and binary mixtures were measured using the bicapillary pycnometer having a bulb volume of 15 cm^3 and capillary bore with an internal diameter of 1 mm, in a transparent glass walled water bath having a thermal stability of 0.01 K^{7-9} . The pycnometer was calibrated using the conductivity water having a conductivity $< 1.0 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. Density values were reproducible within $5.0 \times 10^{-5} \text{ g cm}^{-3}$.

Table-1 Comparison of experimental densities (d) and viscosities (η) of pure liquids with literature values at 298.15 K.

Liquid	d/g. cm^{-3}		n / m Pa.s	
	Expt.	Lit. ⁶	Expt.	Lit. ⁶
Benzene	0.8739	0.8736	0.6030	0.6028
Methanol	0.7861	0.7864	0.5513	0.5513
Acetone	0.7844	0.7844	0.3030	0.3029

Dynamic viscosities were measured using an Ubbelohde suspended level viscometer^{10,11} calibrated with conductivity water. An electronic digital stopwatch with readability 0.01 s was used for flow time measurement. At least three repetitions of each data point were obtained, which were reproducible to ± 0.05 s and the results were averaged. Since all flow times were > 200 s and the capillary radius (0.5 mm) was far less than its length (50–60 mm), the kinetic energy and the end corrections were negligible. The dynamic viscosity (η) of the liquids was calculated using the relation –

$$\eta/\eta_0 = d \times t/d_0 \times t_0 \quad \dots(1)$$

where d, d_0 , t and t_0 to refer to the density and flow time of the liquid and water, respectively. The values of the dynamic viscosities (η) thus obtained are reproducible to ± 0.001 mPa.s.

RESULTS AND DISCUSSION

Table 2 and 3 summarise the experimental density (d) and viscosity (η) of binary mixtures of methanol with benzene and acetone at 298.15, 303.15, 308.15 and 313.15 K. d has been used to calculate the excess molar volume, V^E with the help of the following equation –

$$V^E(\text{cm}^3 \cdot \text{mol}^{-1}) = \frac{M_1 X_1 + M_2 X_2}{d_{12}} - \frac{M_1 X_1}{d_1} - \frac{M_2 X_2}{d_2} \quad \dots(2)$$

where d_{12} is the density of the mixture and M_1, X_1, d_1 and M_2, X_2, d_2 are molecular weight, mole fraction and density of pure components 1 and 2, respectively. Excess volumes calculated from equation 2 are listed in Tables 2 and 3.

Table 2. Density (d), viscosity (η) excess molar volume (V^E) deviation in viscosity ($\Delta\eta$) for benzene (1) + methanol (2)

T = 298.15 K				
X_1	d (g.cm ⁻³)	η (mPa.s)	V^E (cm ³ mol ⁻¹)	$\Delta\eta$ (mPa.s)
0.0000	0.7864	0.551	0.000	0.0000
0.0422	0.7968	0.557	-0.015	0.0038
0.0904	0.8068	0.564	-0.269	0.0083
0.1474	0.8165	0.569	-0.377	0.0103
0.2149	0.8262	0.574	-0.437	0.0118
0.2893	0.8350	0.577	-0.489	0.0110
0.3836	0.8440	0.58	-0.508	0.0091
0.4897	0.8518	0.583	-0.473	0.0065
0.6103	0.8584	0.587	-0.368	0.0043
0.7878	0.8658	0.593	-0.156	0.0010
1.0000	0.8736	0.603	-0.000	0.0000
T = 303.15 K				
0.0000	0.7698	0.509	0.000	0.0000
0.0422	0.7809	0.516	-0.139	0.0048
0.0904	0.7917	0.522	-0.260	0.0082
0.1474	0.8022	0.527	-0.344	0.0102
0.2149	0.8130	0.532	-0.426	0.0116
0.2893	0.8229	0.535	-0.479	0.0107
0.3836	0.8332	0.539	-0.501	0.0097
0.4897	0.8421	0.542	-0.463	0.0070
0.6103	0.8499	0.545	-0.350	0.0037

Table 2 Continued.....

Table 2. Continued...

X_1	d (g.cm^{-3})	η (mPa.s)	V^E ($\text{cm}^3 \text{mol}^{-1}$)	$\Delta\eta$ (mPa.s)
0.7878	0.8588	0.553	-0.141	0.0022
1.0000	0.8682	0.562	0.000	0.0000
T = 308.15 K				
0.0000	0.7652	0.472	0.000	0.0000
0.0422	0.7761	0.480	-0.124	0.0057
0.0904	0.7867	0.486	-0.249	0.0090
0.1474	0.7973	0.491	-0.366	0.0109
0.2149	0.8080	0.495	-0.417	0.0112
0.2893	0.8179	0.499	-0.473	0.0111
0.3836	0.8281	0.503	-0.497	0.0099
0.4897	0.8370	0.506	-0.451	0.0071
0.6103	0.8484	0.510	-0.344	0.0044
0.7878	0.8536	0.517	-0.134	0.0017
1.0000	0.8630	0.527	0.000	0.0000
T = 313.15 K				
0.0000	0.7607	0.449	0.000	0.0000
0.0422	0.7713	0.457	-0.124	0.0061
0.0904	0.7819	0.462	-0.234	0.0090
0.1474	0.7924	0.466	-0.323	0.0105
0.2149	0.8031	0.469	-0.405	0.0105
0.2893	0.8129	0.472	-0.461	0.0103
0.3836	0.8231	0.475	-0.488	0.0091
0.4897	0.8319	0.477	-0.444	0.0065
0.6103	0.8396	0.480	-0.327	0.0041
0.7878	0.8485	0.486	-0.125	0.0023
1.0000	0.8580	0.493	0.000	0.0000

Table 3. Density (d), viscosity (η), excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), for acetone (1) + methanol (2)

T = 298.15 K				
X_1	d (g.cm ⁻³)	η (mPa.s)	V^E (cm ³ mol ⁻¹)	$\Delta\eta$ (mPa.s)
0.0000	0.7864	0.551	0.000	0.0000
0.0602	0.7879	0.509	-0.096	-0.0271
0.1007	0.7900	0.476	-0.230	-0.0500
0.1790	0.7925	0.445	-0.400	-0.0616
0.2768	0.7949	0.415	-0.589	-0.0674
0.3551	0.7958	0.393	-0.686	-0.0699
0.4531	0.7954	0.369	-0.719	-0.0696
0.5594	0.7939	0.350	-0.677	-0.0623
0.6922	0.7915	0.333	-0.542	-0.0463
0.7889	0.7894	0.324	-0.405	-0.0314
0.8986	0.7869	0.315	-0.213	-0.0131
1.0000	0.7844	0.303	0.000	0.0000
T = 303.15 K				
0.0000	0.7698	0.509	0.000	0.0000
0.0602	0.7729	0.469	-0.120	-0.0271
0.1007	0.7760	0.422	-0.257	-0.0655
0.1913	0.7796	0.415	-0.436	-0.0531
0.2768	0.7830	0.389	-0.617	-0.0608
0.3551	0.7847	0.370	-0.707	-0.0630
0.4531	0.7853	0.348	-0.730	-0.0640
0.5594	0.7849	0.332	-0.679	-0.0573
0.6922	0.7837	0.319	-0.554	-0.0419
0.7889	0.7825	0.311	-0.426	-0.0292
0.8986	0.7808	0.304	-0.230	-0.0127
1.0000	0.7788	0.295	0.000	0.0000

Table 3 Continued,....

Table 3. Continued...

X_1	d ($\text{g}\cdot\text{cm}^{-3}$)	η ($\text{mPa}\cdot\text{s}$)	V^E ($\text{cm}^3\text{ mol}^{-1}$)	$\Delta\eta$ ($\text{mPa}\cdot\text{s}$)
T = 308.15 K				
0.0000	0.7652	0.472	0.000	0.0000
0.0602	0.7684	0.434	-0.132	-0.0266
0.1007	0.7715	0.411	-0.279	-0.0419
0.1913	0.7752	0.385	-0.476	-0.0507
0.2768	0.7782	0.363	-0.639	-0.0564
0.3551	0.7796	0.346	-0.718	-0.0585
0.4531	0.7801	0.327	-0.744	-0.0589
0.5594	0.7796	0.313	-0.693	-0.0527
0.6922	0.7784	0.301	-0.574	-0.0395
0.7889	0.7772	0.295	-0.447	-0.0271
0.8986	0.7753	0.289	-0.248	-0.0123
1.0000	0.7731	0.282	0.000	0.0000
T = 313.15 K				
0.0000	0.7607	0.449	0.000	0.0000
0.0602	0.7639	0.412	-0.142	-0.0267
0.1007	0.7669	0.390	-0.294	-0.0418
0.1913	0.7706	0.368	-0.495	-0.0483
0.2768	0.7734	0.347	-0.660	-0.0547
0.3551	0.7745	0.332	-0.727	-0.0563
0.4531	0.7750	0.315	-0.759	-0.0565
0.5594	0.7743	0.303	-0.704	-0.0503
0.6922	0.7731	0.293	-0.593	-0.0376
0.7889	0.7717	0.287	-0.462	-0.0271
0.8986	0.7698	0.283	-0.265	-0.0123
1.0000	0.7674	0.278	0.000	0.0000

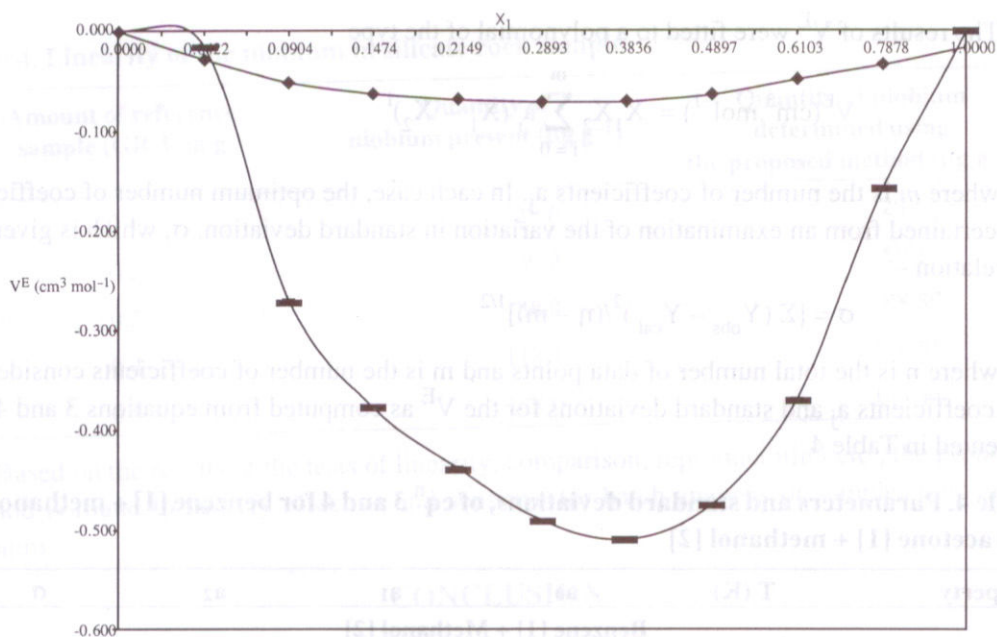


Fig. 1 V^E at 298.15 K for $[X_1][\text{Benzene}] - [1 - X_1][\text{Methanol}]$ ♦ and $[X_1][\text{Acetone}] - [1 - X_1][\text{Methanol}]$ ■

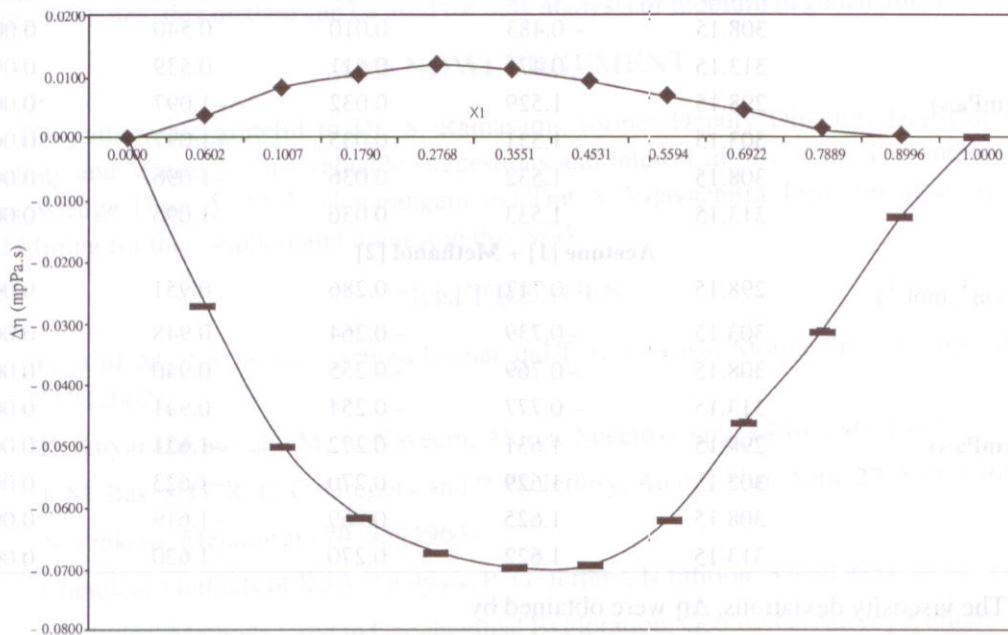


Fig. 2 $\Delta\eta$ at 298.15 k for $[X_1][\text{Benzene}] - [1 - X_1][\text{Methanol}]$ ♦ and $[X_1][\text{Acetone}] - [1 - X_1][\text{Methanol}]$ ■

where η_{12} is the viscosity of the mixtures and η_1, η_2 are the viscosities of pure components 1 and 2, respectively. $\Delta\eta$ values for both mixtures are included in Tables 2 and 3.

The coefficient a_i and standard deviation σ as obtained from equations similar to the equations 3 and 4 are listed in Table 4.

The V^E values are negative for the mixtures of methanol with benzene and acetone. It has been reported that V^E values of binary mixtures result from the chemical, physical and structural characteristics of liquids¹². The physical effects contribute to positive V^E whereas chemical and structural effects contribute to negative V^E . In methanol – benzene mixtures, the negative V^E values are attributed to changes in free volumes in the mixtures due to electron donor – acceptor type of interactions between benzene and methanol molecules leading to H – π bond formation. This is further supported by positive values $\Delta\eta$ in this mixture. The negative V^E and positive $\Delta\eta$ values in acetone – methanol mixtures are attributed to interstitial accommodation of acetone molecules into aggregates of methanol. Fig. 1 and 2 represent dependence of V^E and $\Delta\eta$ with X_1 [benzene or acetone], respectively at 298.15 K. Similar plots are obtained at other temperatures also.

As regards the temperature variation of V^E and $\Delta\eta$, it has been observed that V^E increases and $\Delta\eta$ decreases with increase in temperature suggesting declustering of homo and heteroassociation of molecules.

REFERENCES

1. P. S. Nikam and S. J. Kharat, J. Chem. Eng. Data, **48**, 1291 (2003).
2. P. S. Nikam, Smt. M. C. Jadhav and Mehdi Hasan, J. Mol. Liq., **76** (1998).
3. P. S. Nikam, L. N. Shirsat and Mehdi Hasan, J. Indian Chem. Soc., **77**, 244 (2000).
4. P. S. Nikam, B. S. Jagadale, A. B. Sawant and Mehdi Hasan, J. Chem. Eng. Data., **45**, 214 (2000).
5. P. S. Nikam, T. R. Mahale and Mehdi Hasan, J. Chem. Eng. Data, **41**, 1055 (1996).
6. J. A. Riddick, W. B. Bunger and T. K. Sakano, "Organic Solvents", Wiley, New York, (1986).
7. P. S. Nikam, T. R. Mahale and Mehdi Hasan, J. Chem. Eng. Data, **41**, 1055 (1996).
8. P. S. Nikam, Mehdi Hasan, Neena Nikam and R. R. Ahire, Asian J. Chem., **6**, 789 (1994).
9. P. S. Nikam, and A. B. Sawant, Bull. Chem. Soc. Japan, **71**, 2061 (1998).
10. P. S. Nikam, and A. B. Nikumbh, J. Chem. Eng. Data., **47**, 400 (2002).
11. P. S. Nikam, Neena Nikam, Mehdi Hasan and A. R. Hiray, Asian J. Chem., **7**, 500 (1995).
12. J. Treszczanowicz, O. Kiyohara and G. C. Benson, J. Chem. Thermodyn., **13**, 253 (1981).

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