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DENSITIES, EXCESS MOLAR VOLUMES AND VISCOSITIES OF BINARY MIXTURES OF ANILINE WITH METHANOL, ETHANOL, ISOPROPANOL AND BUTANOL AT VARIOUS TEMPERATURES

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ABSTRACT

Experimental values of density and viscosity for the binary mixtures of aniline with methanol, ethanol, isopropanol and butanol at four different temperatures (303.15 – 318.15 K) over the entire mole fraction range of the mixture components at atmospheric pressures have been obtained. From these data, excess molar volume and excess viscosity of the compositions have been calculated. Negative values of excess molar volume and viscosity are exhibited by the systems. The results suggest that various effects such as physical, chemical and geometrical interactions might be developed in the systems.

Key words : Excess molar volume, Geometrical interactions, Viscosity, Density

INTRODUCTION

Thermodynamic properties of various alcohols have been studied in numerous solvents[1–3]. The effect of molecular size, shape and molecular association of alkanol on volumetric, viscometric and acoustic properties of binary liquid mixtures containing alcohols (C_5–C_{10}) have been reported by Nikam *et al.*[4]. Viscosity and density of binary liquid mixtures are extensively used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications, aniline, alkanols and their binary mixtures are generally used as solvents[5]. Considering these significant applications, we are reporting in this communication density and viscosity of these mixtures in the temperature range (303.15–318.15 K) with an interval of 5 K at atmospheric pressure. The objective of this work is to provide an information regarding the types of interaction between aniline and alkanols using derived parameters.

EXPERIMENTAL

Aniline (A.R. grade) was distilled twice and then used. All alkanols were first dried over fused CaO overnight and then distilled twice. The first fraction was discarded. All measurements of density and viscosity were carried out by using single arm pyknometers and SCHOTT GERATE AVS 350 Viscometer equipped with series of Ubbleohde viscometers, respectively. Liquid mixtures of various compositions were prepared by using w/w concept with an accuracy of ± 0.1 mg using Mettler balanace, which can read up to 5th place of decimal. The time given to attain thermal equilibrium for the content of pyknometer and viscometer was 15 min. The efflux time was measured to an accuracy of ± 0.15 till a constant flow time was observed.

RESULTS AND DISCUSSION

The excess molar volume and excess viscosity were calculated from the following relationship :

$$V^E = X_1 M_1 \left[\frac{1}{d} - \frac{1}{d_1}\right] + X_2 M_2 \left[\frac{1}{d} - \frac{1}{d_2}\right] \quad ...(1)$$

where X_1, X_2, M_1, M_2 and d_1, d_2 are the mole fractions, molecular weights and densities of component one and two, respectively. The d is the density of the mixtures.

Excess dynamic viscosity is calculated by using two successive equations. First kinematic viscosity 'ν' is determined by multiplying efflux time with viscometric constant

$$\nu = 0.01 \times t \quad ...(2)$$

Then, η^E excess viscosity is determined by the following equation.

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \quad ...(3)$$

where η, η_1 and η_2 are the viscosity of the mixture, component 1 and component 2, respectively. η, η_1 and η_2 are calculated by multiplying kinematic viscosities with density of mixture, density of component one and component two, respectively. The trend of the data can be easily overlooked from the Tables 1–4.

The graphical presentation of the excess molar volumes is shown in Fig. 1–4. It shows that V^E is negative over the entire range of composition at all measured temperatures. It may be because of physical, chemical and geometrical forces. The chemical or specific interactions result in net decrease in volume, which may be attributed due to charge transfer, dipole–dipole and donor–acceptor types of forces.

Also structural contributions arising from the geometrical fitting of the component into each other, due to differences in the molar volume and free volume between components leads to the negative contribution[6] to V^E. However, with higher alcohols, the latter contribution is

negligible and therefore, association decreases with an increase in the chain length and alcohols[6,7]. Hence, mixtures of aniline with higher alcohols gave larger V^E as compared to lower alcohols (Figures 1 to 4). The higher alcohols possess less proton donating ability than the lower ones (C_1 or C_2) and effects of this kind of hetero–association are smaller in their mixtures and not sufficient to overweigh the positive contribution to V^E. Thus, the specific interaction arising from dipole–dipole interactions follow the order aniline + methanol > + ethanol > + isopropanol > + 1–butanol. The effect of temperature on excess molar volumes does not show any systematic trend. The change of V^E (either positive or negative) depends on X_1.

Table 1. Densities (d), excess molar volumes (V^E) and excess viscositics (η^E) of Aniline + Methanol mixtures at different temperatures

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
	303.15 K		
0.00000	0.782954	0.0000	0.0000
0.01778	0.795425	–0.1631	–0.0178
0.03682	0.807414	–0.3181	–0.0316
0.05724	0.817733	–0.3741	–0.0528
0.07921	0.828825	–0.4520	–0.0733
0.18659	0.874306	–0.7382	–0.1588
0.34043	0.921503	–0.9408	–0.2035
0.57918	0.967793	–0.7848	–0.2452
0.66099	0.979754	–0.6770	–0.2321
0.75590	0.991349	–0.5371	–0.1965
0.86733	1.001946	–0.2811	–0.1496
1.00000	1.01333	0.0000	0.0000
	308.15 K		
0.00000	0.778332	0.0000	0.0000
0.01778	0.790507	–0.1772	–0.0055
0.03682	0.802635	–0.3272	–0.0225
0.05724	0.812964	–0.3799	–0.0386
0.07921	0.823928	–0.4564	–0.0536
0.18659	0.869425	–0.7501	–0.1193
0.34043	0.916952	–0.9539	–0.1574

Contd.,....

Table 1. Continued...

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
0.57918	0.963165	–0.7931	–0.1832
0.66099	0.975364	–0.6871	–0.1719
0.75590	0.986606	–0.5510	–0.1523
0.86733	0.997415	–0.2880	–0.1193
1.00000	1.008900	0.0000	0.0000
	313.15 K		
0.00000	0.773453	0.0000	0.0000
0.01778	0.785853	–0.1872	–0.0098
0.03682	0.798124	–0.3431	–0.0169
0.05724	0.808305	–0.3930	–0.0281
0.07921	0.819524	–0.4780	–0.0405
0.18659	0.864833	–0.7669	–0.0910
0.34043	0.912532	–0.9837	–0.1203
0.57918	0.958857	–0.8080	–0.1498
0.66099	0.970642	–0.6990	–0.1404
0.75590	0.982095	–0.5600	–0.1197
0.86733	0.992912	–0.2910	–0.0944
1.00000	1.004500	–0.0000	0.0000
	318.15 K		
0.00000	0.768310	0.0000	0.0000
0.01778	0.780577	–0.1971	–0.0066
0.03682	0.792996	–0.3552	–0.0102
0.05724	0.803187	–0.4030	–0.0190
0.07921	0.814241	–0.4910	–0.0224
0.18659	0.860111	–0.7935	–0.0721
0.34043	0.907689	–0.9978	–0.0863
0.57918	0.953912	–0.8180	–0.1159
0.66099	0.966172	–0.7073	–0.1040
0.75590	0.977236	–0.5720	–0.0944
0.86733	0.988410	–0.2951	–0.0782
1.00000	1.000062	0.0000	0.0000

Table 2. Densities (d), excess molar volumes (V^E) and excess viscosities (η^E) of Aniline + Ethanol mixtures at different temperatures

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
	303.15 K		
0.00000	0.786012	0.0000	0.0000
0.02538	0.796338	–0.1054	–0.0200
0.05213	0.807258	–0.2398	–0.0592
0.08032	0.818049	–0.3498	–0.0903
0.11010	0.828016	–0.3824	–0.1362
0.24808	0.871088	–0.5830	–0.2672
0.42606	0.916881	–0.6844	–0.3603
0.66438	0.963126	–0.4361	–0.4249
0.73714	0.974767	–0.3045	–0.3745
0.81665	0.987526	–0.2040	–0.3342
0.90387	0.999393	–0.0170	–0.2698
1.00000	1.013330	0.0000	0.0000
	308.15 K		
0.00000	0.781601	0.0000	0.0000
0.02538	0.792636	–0.1350	–0.0303
0.05213	0.803316	–0.2794	–0.0548
0.08032	0.813995	–0.3662	–0.0812
0.11010	0.823993	–0.3990	–0.1114
0.24808	0.866971	–0.5935	–0.2341
0.42606	0.912803	–0.6967	–0.2891
0.66438	0.959184	–0.4612	–0.3322
0.73714	0.970668	–0.3251	–0.3102
0.81665	0.982891	–0.2194	–0.2602
0.90387	0.994946	–0.0453	–0.1827
1.00000	1.00890	0.0000	0.0000

Contd.,...

Table 2. Continued...

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
	313.15 K		
0.00000	0.777141	0.0000	0.0000
0.02538	0.788039	–0.1529	–0.0255
0.05213	0.798865	–0.2845	–0.0432
0.08032	0.809529	–0.3886	–0.0676
0.11010	0.819447	–0.4121	–0.0977
0.24808	0.862405	–0.6072	–0.1976
0.42606	0.908035	–0.7101	–0.2437
0.66438	0.954531	–0.4744	–0.2799
0.73714	0.966130	–0.3371	–0.2585
0.81665	0.978501	–0.2370	–0.2110
0.90387	0.990383	–0.0611	–0.1399
1.00000	1.004500	0.0000	0.0000
	318.15 K		
0.00000	0.772737	0.0000	0.0000
0.02538	0.783686	–0.1790	–0.0210
0.05213	0.794545	–0.2960	–0.0336
0.08032	0.805068	–0.3912	–0.0603
0.11010	0.814965	–0.4215	–0.0809
0.24808	0.857810	–0.6166	–0.1694
0.42606	0.903593	–0.7214	–0.2118
0.66438	0.950197	–0.4916	–0.2379
0.73714	0.961807	–0.3516	–0.2139
0.81665	0.974299	–0.2514	–0.1776
0.90387	0.986004	–0.0740	–0.1218
1.00000	1.000062	0.0000	0.0000

Table 3. Densities (d), excess molar volumes (V^E) and excess viscosities (η^E) of Aniline + Isopropanol mixtures at different temperatures

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
	303.15 K		
0.00000	0.778101	0.0000	0.0000
0.03285	0.788100	–0.0849	–0.0849
0.06690	0.799532	–0.2440	–0.2877
0.10224	0.808994	–0.2170	–0.3520
0.13892	0.820801	–0.4280	–0.4280
0.30080	0.863352	0.5070	–0.5302
0.49186	0.910532	–0.5976	–0.6046
0.72077	0.958986	–0.3051	–0.5250
0.78526	0.972547	–0.2897	–0.4520
0.85311	0.985661	–0.1667	–0.3501
0.92459	0.998831	–0.0480	–0.2480
1.00000	1.013330	0.0000	0.0000
	308.15 K		
0.00000	0.773622	0.0000	0.0000
0.03285	0.784272	–0.1517	–0.1025
0.06690	0.794874	–0.2752	–0.1844
0.10224	0.804162	–0.2458	–0.2619
0.13892	0.816148	–0.4569	–0.3204
0.30080	0.858728	–0.5145	–0.4700
0.49186	0.905903	–0.6019	–0.5341
0.72077	0.954343	–0.3082	–0.4550
0.78526	0.968103	–0.2938	–0.3889
0.85311	0.981024	–0.1748	–0.3024
0.92459	0.994416	–0.0533	–0.1970
1.00000	1.008900	0.0000	0.0000

Contd.,....

Table 3. Continued...

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
	313.15 K		
0.00000	0.768913	0.0000	0.0000
0.03285	0.780233	–0.1890	–0.0856
0.06690	0.790699	–0.3050	–0.1509
0.10224	0.800125	–0.2831	–0.2132
0.13892	0.811908	–0.4802	–0.2631
0.30080	0.185388	–0.5255	–0.3933
0.49186	0.901211	–0.6088	–0.4444
0.72077	0.949879	–0.3126	–0.3828
0.78526	0.963559	–0.2980	–0.3350
0.85311	0.976522	–0.1824	–0.2394
0.92459	0.989974	–0.0612	–0.1628
1.00000	1.004500	0.0000	0.0000
	318.15 K		
0.00000	0.764250	0.0000	0.0000
0.03285	0.775199	–0.2310	–0.0707
0.06690	0.785669	–0.3421	–0.1269
0.10224	0.795069	–0.3071	–0.1700
0.13892	0.773579	–0.4940	–0.2310
0.30080	0.849134	–0.5331	–0.3298
0.49186	0.896606	–0.6134	–0.3726
0.72077	0.945303	–0.3174	–0.3213
0.78526	0.958908	–0.3013	–0.2672
0.85311	0.971951	–0.1911	–0.2194
0.92459	0.985422	–0.0706	–0.1376
1.00000	1.000062	0.0000	0.0000

Table 4. Densities (d), excess molar volumes(V^E) and excess viscosities (η^E) of Aniline + Butanol mixtures at different temperatures

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
	303.15 K		
0.00000	0.803481	0.0000	0.0000
0.04021	0.812719	–0.0741	–0.1075
0.08125	0.823226	–0.2571	–0.2015
0.12316	0.831273	–0.1960	–0.3041
0.16596	0.840405	–0.1870	–0.3769
0.34667	0.878567	–0.2395	–0.6061
0.54419	0.920633	–0.3088	–0.6699
0.760978	0.964388	–0.0808	–0.5831
0.81852	0.976325	–0.1062	–0.4977
0.87750	0.988410	–0.0771	–0.3945
0.93797	1.000607	–0.0030	0.2409
1.00000	1.013330	0.0000	0.0000
	308.15 K		
0.00000	0.799673	0.0000	0.0000
0.04021	0.808683	–0.1310	–0.0925
0.08125	0.818988	–0.2741	–0.1739
0.12316	0.827012	–0.2071	–0.3079
0.16596	0.836042	–0.1957	–0.3235
0.34667	0.874436	–0.2444	–0.5046
0.54419	0.916546	–0.3140	–0.5533
0.760978	0.959693	–0.1017	–0.4798
0.81852	0.971982	–0.1171	–0.3972
0.87750	0.984145	–0.0881	–0.3169
0.93797	0.995995	–0.0210	–0.1980
1.00000	1.008900	0.0000	0.0000
	313.15 K		
0.00000	0.79563	0.0000	0.0000
0.04021	0.804782	–0.1761	–0.0910

Contd.,...

Table 4. Continued...

Mole fraction (X_1)	d (g. cm^{-3})	V^E (cm^3 . mol^{-1})	η^E
0.08125	0.815084	–0.2890	–0.1509
0.12316	0.823338	–0.2261	–0.2194
0.16596	0.832351	–0.2150	–0.2776
0.34667	0.870106	–0.2492	–0.4282
0.54419	0.912181	–0.3233	–0.4700
0.760978	0.955277	–0.1216	–0.3929
0.81852	0.967424	–0.1289	–0.3522
0.87750	0.979797	–0.0940	–0.2684
0.93797	0.991576	–0.0361	–0.1567
1.00000	1.00450	0.0000	0.0000
		318.15 K	
0.00000	0.791505	0.0000	0.0000
0.04021	0.801307	–0.2170	–0.0706
0.08125	0.810849	–0.2990	–0.1335
0.12316	0.818966	–0.2291	–0.1946
0.16596	0.827851	–0.2196	–0.2413
0.34667	0.865705	–0.2540	–0.3737
0.54419	0.907723	–0.3287	–0.4135
0.760978	0.950923	–0.1307	–0.3454
0.81852	0.963077	–0.1406	–0.2951
0.87750	0.975330	–0.1046	–0.2263
0.93797	0.987429	–0.0531	–0.1337
1.00000	1.000062	0.0000	0.0000

This may be attributed to variable degree of depolymerization of aniline and alcohol clusters with varying composition of mixture at different temperatures. In other words, the dipole–dipole interactions arising between aniline and alcohol molecules vary with composition and temperature of the mixture. Such nonsystematic temperature effect on V^E can also be seen in the literature[8,9].

The excess viscosity values for all the systems at four different temperatures over the whole composition range show negative trend, which gives information about the mutual loss of dipolar association and secondly due to strong molecular interactions. Plot of excess viscosity

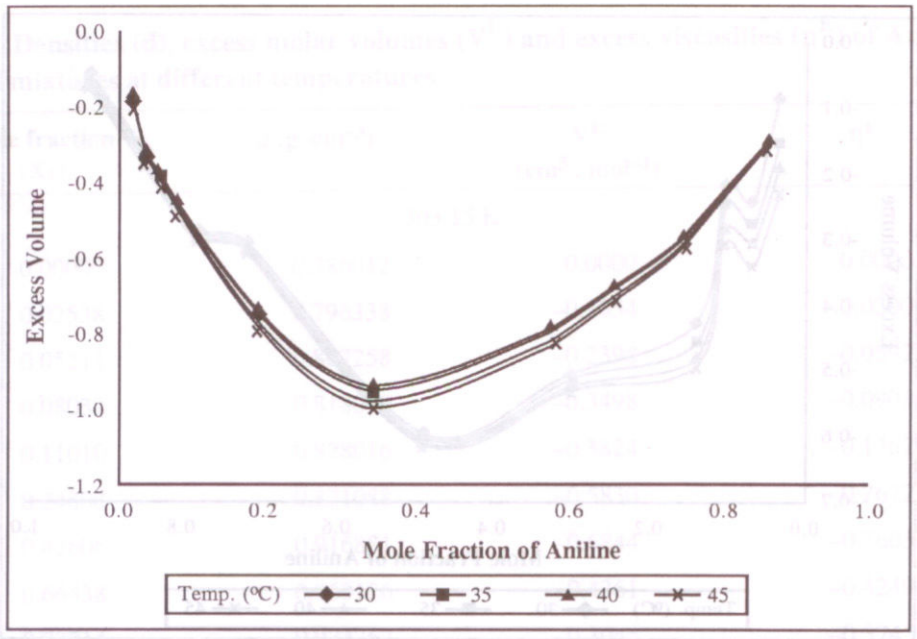


Fig. 1 : Plot of excess volume V/s mole fraction of Aniline in Aniline (1) +methanol (2) at different temperatures

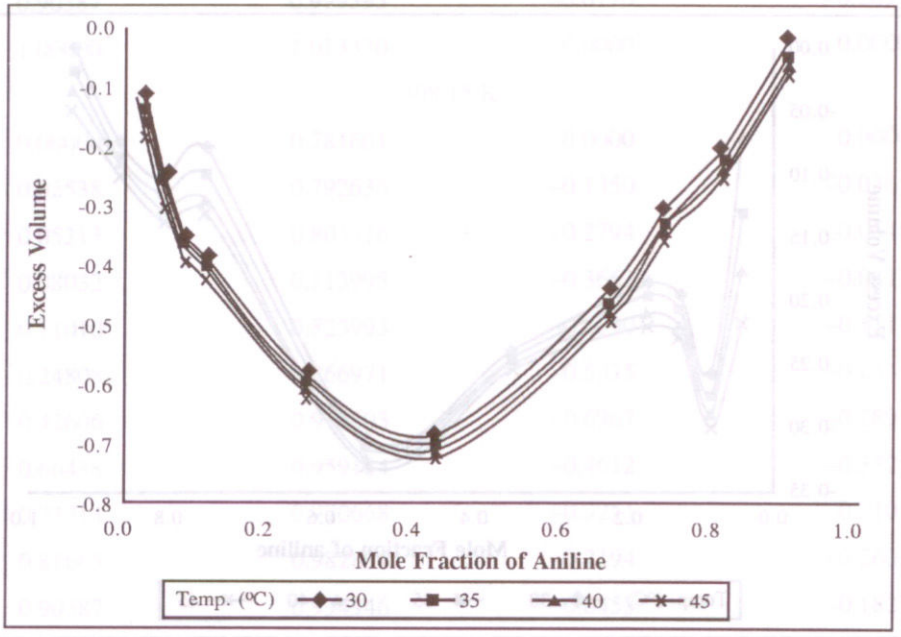


Fig. 2 : Plot of excess volume V/s mole fraction of Aniline in Aniline (1) + ethanol (2) at different temperatures

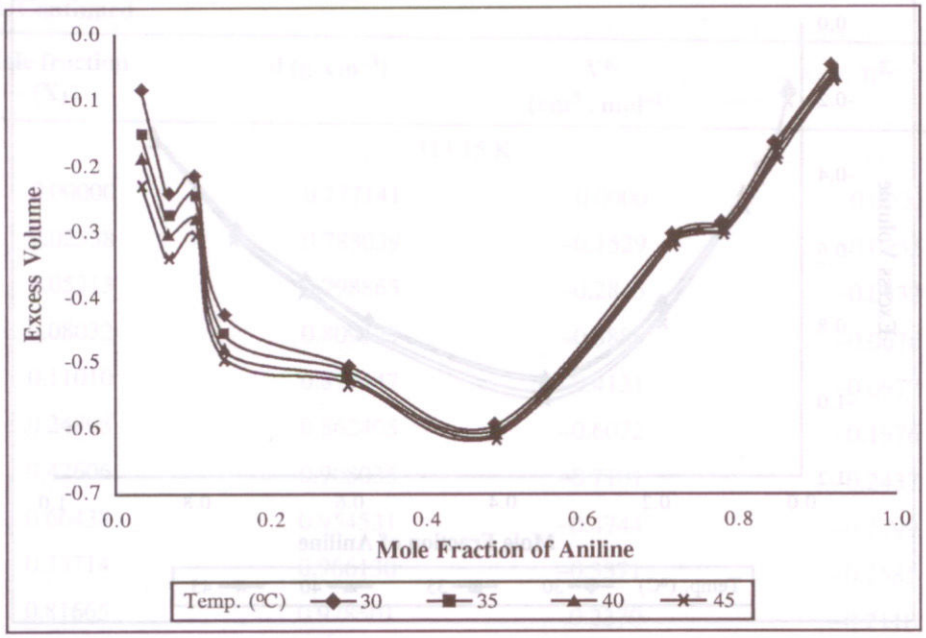


Fig. 3 : Plot of excess volume V/s mole fraction of Aniline in Aniline (1) + isopropanol (2) at different temperatures

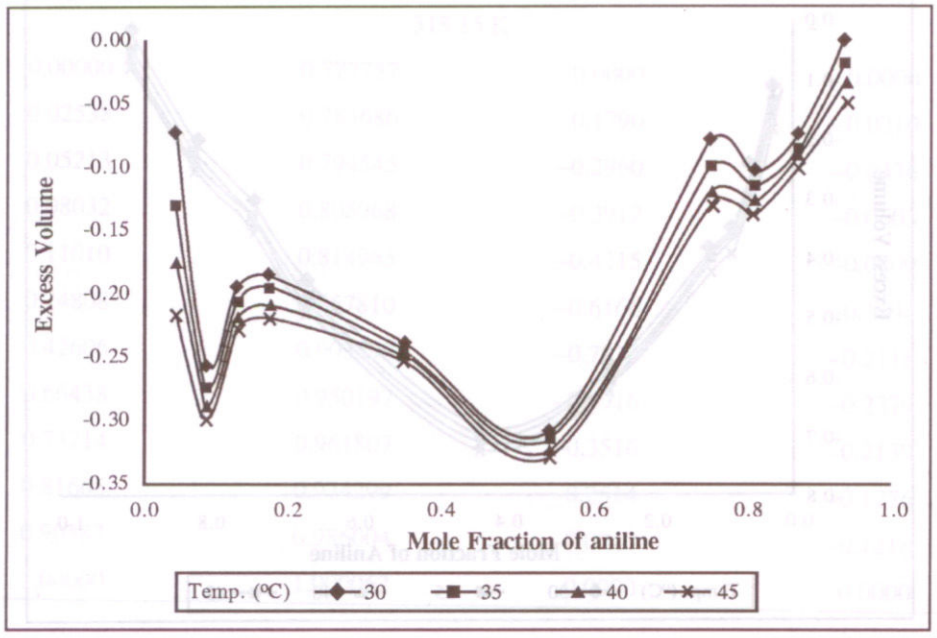


Fig. 4 : Plot of excess volume V/s mole fraction of Aniline in Aniline (1) + butanol (2) at different temperatures

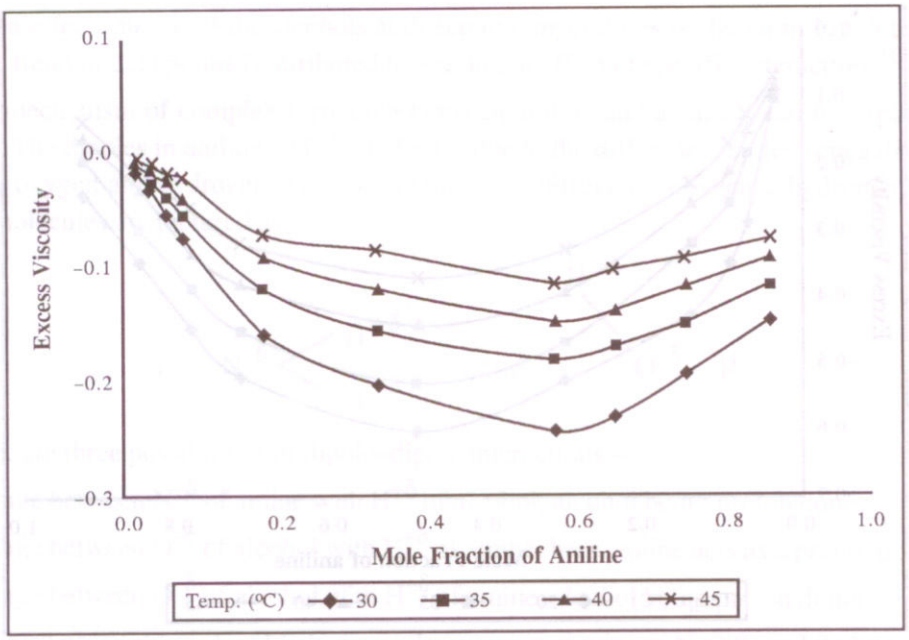


Fig. 5 : Plot of excess viscosity V/s mole fraction of Aniline in Aniline (1) +methanol (2) at different temperatures

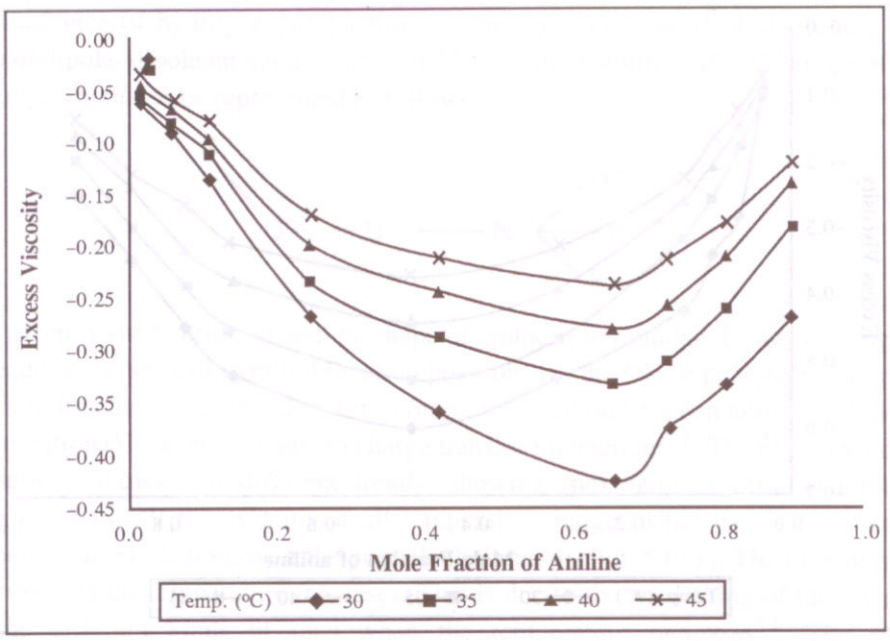


Fig. 6 : Plot of excess viscosity V/s mole fraction of Aniline in Aniline (1) + ethanol (2) at different temperatures

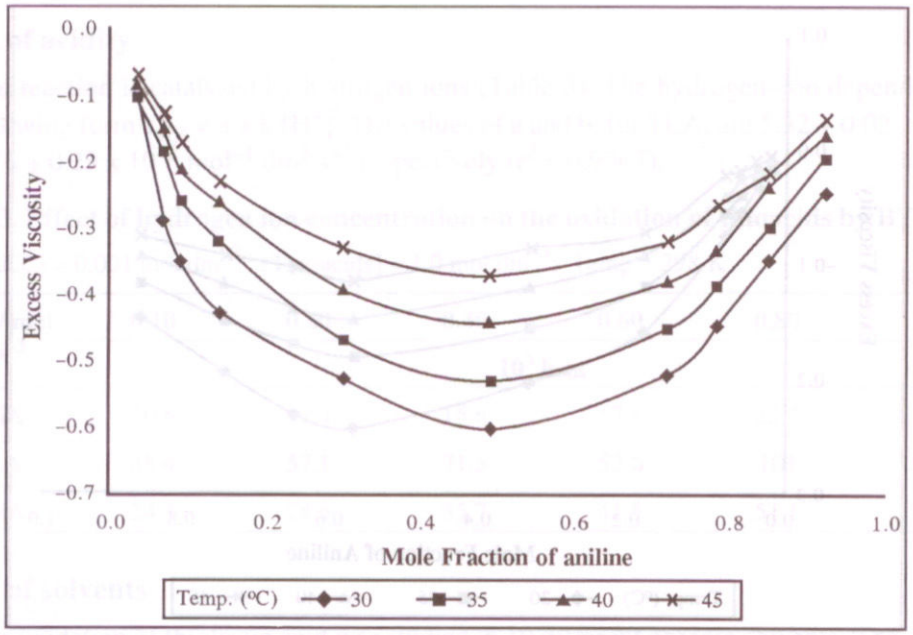


Fig. 7 : Plot of excess viscosity Vs mole fraction of Aniline in Aniline (1) + isopropanol (2) at different temperatures

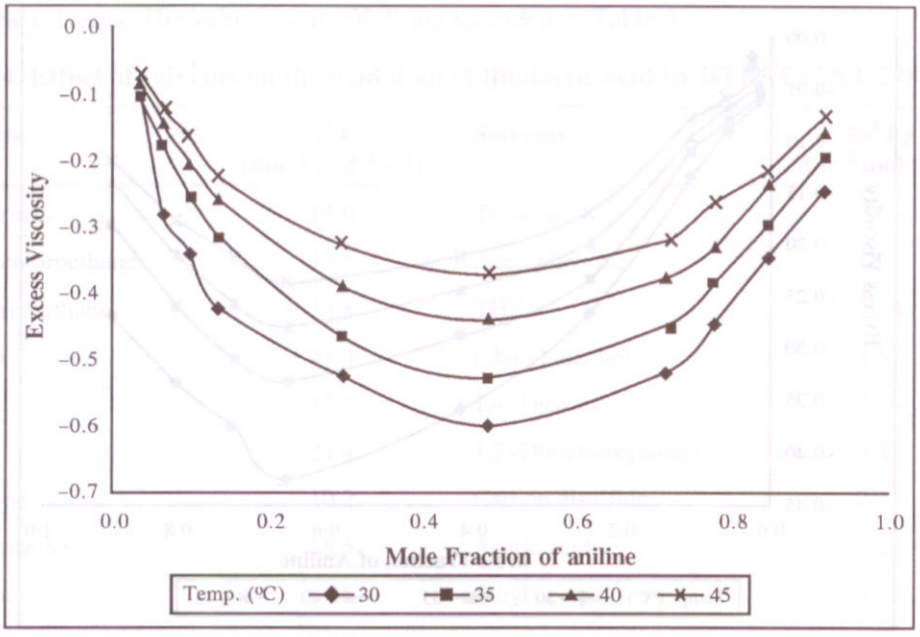
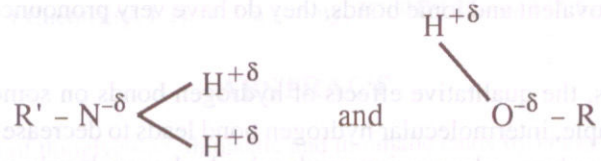


Fig. 8 : Plot of excess viscosity V/s mole fraction of Aniline in Aniline (1) +butanol (2) at different temperatures

versus mole fraction for all the alcohols at different temperatures is shown in Fig. 5 to 8. The observed trend of data points is attributed to a resultant effect of specific interactions[10].

The mechanism of complex formation between aniline and alkanols can be explained as follows : The dipoles in aniline and alcohol arise due to the difference in electronegativities of nitrogen, oxygen and hydrogen. They are in the order nitrogen > oxygen > hydrogen. Hence, dipolar molecules are pictured as



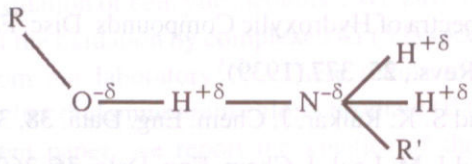
There are three possibilities of dipole–dipole interactions –

i) Linkage between $N^{-\delta}$ of amine with $H^{+\delta}$ of alcohol, alcohol being proton donor.

ii) Linkage between $O^{-\delta}$ of alcohol with $H^{+\delta}$ of amine. here, amine acts as a proton donor and

iii) Linkage between $O^{-\delta}$ of alcohol with $H^{+\delta}$ of amine, alcohol being proton donor.

The third possibility is less likely since electron negativities of N (3.0) and 0 (3.5) are very close. Therefore, the aniline–alcohol complexation takes place due to the first two possibilities. The second possibility of linkage between $O^{-\delta}$ of alcohol and $H^{+\delta}$ of aniline is remote because of steric hindrance of hydrogen groups from aniline to oxygen in alcohol. Hence, the first possibility of dipole–dipole interaction between $N^{-\delta}$ group of aniline with $H^{+\delta}$ group of alcohol is most likely, which can be represented as follows :



The N atom is sp^3 hybridised and the shape of amine is pyramidal. There is enough space on the outside of the apex of pyramid (N atom position) for the OH to penetrate and enter into complexation. It is further assumed that the complex formation between aniline and alcohol is due to polarization effect[1] and not due to charge transfer interactions[11]. The excess volume and excess viscosity shows two different trends, showing maximum at 60% and then give decreasing trend for all the systems at all temperature range, which is clear indication of stronger molecular interactions near the pure alcohol region (Fig. 5 to 8). The maximum in the curve decreases as the temperature increases. This is due to the weakening of the interactions between the different kinds of ions when the temperature increases[12]. The study of intermolecular interactions between aniline and alcohols visualized through hydrogen bonding and also through the several graphs correlating the excess parameters with the mole fraction of

aniline. The plot of excess volume v/s mole fraction (Fig. 1 to 4) have similar pattern for the first two alcohols. Plot of iso–propanol and butanol also show central minimum exhibited by the first two alcohols. In addition to these two minima, two maxima are also seen in these cases.

Such variation in the curves are due to various forces such as electrostatic delocalization, dispersion and repulsion forces also play very important role in changing the thermodynamic properties of the binary liquid–liquid systems. Though hydrogen bonds are relatively weak compared to typical covalent and ionic bonds, they do have very pronounced effects upon these properties[13].

In addition to this, the qualitative effects of hydrogen bonds on some physical properties can be seen. For example, intermolecular hydrogen bond leads to decrease in molar volume and normalized viscosity values, whereas intermolecular hydrogen bonding leads to increase in molar volume and higher viscosity values etc. In many cases, in dilute solution, there is partial hydrogen bonding that is some OH groups are free and some are hydrogen bonded. In such cases, two or more peaks appear[14].

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