Viscosity, Density and Ultrasonic Velocity Studies of Binary Liquid Solutions of Isoamyl Alcohol and Isobutyl Alcohol in Benzyl Amine.

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Abstract:

Viscosity(η),Density(ρ) and Ultrasonic velocities(U) are reported for binary mixtures of of isoamyl alcohol and isobutyl alcohol with benzyl amine over entered range of mole fractions at 298.15 and 308.15 K and atmospheric pressure. The viscosity deviation(Δη) Excess molar volume(V^E) and isentropic compressibility(K_s) have been calculated. The present investigation shows that greater molecular interaction exists in isobutyl alcohol mixtures which may be due to hydrogen bond formation and weak molecular interaction that exists in the isoamyl alcohol mixtures and which may be due to the dominance of dispersion forces and dipolar interaction between the unlike molecules.

Keywords- Viscosity, Density, Ultrasonic velocities, viscosity deviation(Δη) Excess molar volume(V^E) and isentropic compressibility(K_s)

Introduction:

TheViscosity (η), Density (ρ) and Ultrasonic velocities (U)measurements find wide applications in characterizing the physico-chemical behavior of liquid mixtures and in the study of molecular interactions[1-3]. The measurements of Ultrasonic velocity of a liquid and mixtures allows the calculations of compressibility and hence enables to obtain structural information [4], In turn the data of sound velocity can be subjected to scrutiny by applying Jacobins free length and schaaffs collision factor theory. The deviations observed in free length and other parameters have been attributed to dipole-dipole, dipole-induced dipole and other dispersive force interactions[5]. It is well known that aqueous solutions of hydrocarbons, alcohols, amines, ethers are characterized by H-bonding and hydrophobic interactions. The investigations regarding the molecular association in organic binary mixtures having alkanol group as one of the component is of particular interest, since alkanol group is highly polar and can associate with any other group having some degree of polar attractions. benzylamine is aprotic, strongly associated due to highly polar -NH_2 group in the molecule and has large dipole moment [6].

In view of the importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixtures of benzylamine with branched alkanols (C_5 & C_4) at all compositions and four temperatures. In this article only the data of binary mixtures of benzylamine with isoamyl alcohol and isobutyl alcoholrespectively at 298.15 and 308.15 K is reported.

Experimental

All the chemicals used in the present research work are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-Merck, Germany and Sd Fine chemicals, India, which are used as such without further purification. The purities of the above chemicals were checked by density determination at 298.15 and 308.15 K the uncertainty is less than ± $1x10^{-4}$ gcm^{-3}. The binary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density, viscosity and velocity were measured as a function of composition of the binary liquid mixture of benzylamine with isoamyl alcohol and isobutyl alcohol respectively at 298.15 and 308.15 K. The density was determined using a Bi-capillary pyknometer. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.1 mg (Model: Shimadzu AX-200). An Ubbelohde viscometer (20ml) was used for the viscosity measurement and efflux time was determined using a digital clock to within ±0.01s. An ultrasonic interferometer having the frequency of 2 MHz (Mittal Enterprises, New Delhi, Model: F-81) with an overall accuracy of ± 0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with an accuracy of ± 0.01 K.

Theory and Calculations

Excess volumes of the mixtures have been calculated using density and mole fraction data given by equation:

$$V^E = (M_1X_1+M_2X_2)/\rho_{12}-(M_1X_1) /\rho_1 - (M_2X_2) / \rho_2 \quad \text{-- (1)}$$

Viscosity of Binary Mixtures is calculated by:

$$\ln\eta_m=X_1\ln\eta_1+X_2\ln\eta_2 \quad \text{--(2)}$$

The measured viscosities of the mixtures have been used to obtain deviation in Viscosity parameters on the basis of linearity in following way,

Deviation in Viscosity of Binary Mixtures is calculated by :

$$\Delta\eta_m=\eta_{12}-X_1\eta_1-X_2\,\eta_2 \quad \text{--(3)}$$

Deviation in isentropic compressibility have been evaluated by using the equation

$$\Delta k_S=k_S-(\Phi_1\, k_{S1} + \Phi_2\, k_{S2}) \quad \text{--(4)}$$

where k_{S1}, k_{S2} and K_S are isentropic compressibility of liquid mixtures and Φ is volume fraction of pure i^{th} component in the mixture and is defined as

$$\phi = (xi\ Vi) / (\Sigma\ xi\ Vi)$$

where x_1 and V_i are mole fraction and molar volume of ith component in the mixture

The excess properties y^E are fitted by the method of non linear least squares to a Redlich kister type polynomial (5)

$$y^E=X_1X_2\sum Ai(X_1- X_2)^i \quad \text{--(5)}$$

In each case the optimum number of coefficients Ai was determined from an examination of the variation of standard deviation as calculated by :

$$\sigma y^E=[\sum(y^E_{obs} - y^E_{cal}) / (n-m)]^{1/2} \quad --(6)$$

where n represents the number of experimental points and m represents the number of coefficients in fitting the data.

$$Z^E = Z_{mix} - x_1Z_1 - x_2 Z_2 \quad --(7)$$

$$L_f^E=L_{fmix}-x_1L_{f1}-x_2L_{f2} \quad --(8)$$

Various physical and thermo dynamical parameters are calculated from the measured data such as

Adiabatic Compressibility $\beta s=1/(U^2\rho)$ --(9)

Intermolecular freelength $L_f=K\sqrt{\beta}$ -- (10)

where K is a temperature dependent constant.

Free volume $V_f=(M_{ef}U/K\eta)^{3/2}$ --(11)

where M_{ef} is the effective molecular weight (=mM M x, in which m and x are the molecular weight and the mole fraction of the individual constituents respectively). K is a temperature for all liquids.

Available volume $Va=VT(1-U/ U)$ -- (12)

where U is the limiting velocity and is taken as 1600 ms and V is the molar volume at TK.

Excess values of the above parameters can be determined using

$$A^E=A_{exp}-A_{id} \quad --(13)$$

where $A_{id} = \sum$ Ai Xi , Ai is any acoustical parameters and Xi the mole fraction of the liquid component.

In this content, the excess properties like excess volume, excess partial volume, excess free energies and entropies have been found useful in characterizing the molecular interactions. Alcohols are linear H-bonded liquids, have been studied in detail, they show aggregation in non polar solvents like CCl_4[5].In this we thought on the problem that the self association of alcohol molecules can be detected in polar solvents like nitrobenzene. It has been examined by studying the excess volume, excess viscosity and other parameters. The results and other details are given bellow.

Results and Discussion:

In their pure state, the self association of alkanols decreases with increasing chain length, when alkanols are mixed with benzylamne then there is interaction between their individual functional groups (-OH and $-NH_2$). The presence of electron withdrawing group on benzene ring decreases its electron densitie[7] The experimental values of density (ρ) viscosity (η) ultrasonic velocity (U), Excess volume (V^E), viscosity deviations ($\Delta\eta$) and deviation on isentropic compressibility (Δk_S) for the two binary liquid systems at 298.15 and 308.15 K, are given in Tables

1 and 2. The variation of excess parameters with the mole fraction of alkanols (x_2) at 298.15 and 308.15 K are plotted in Fig.1-8.

The curves for V^E, $\Delta\eta$, Δk_S and G^{*E} values are plotted against mole fractions of alkanols, these curves are negative over the most mole fraction of the alkanols at 298.15 and 308.15 K (Fig.1-8). These curves are U-shaped with minima around x_1 = 0.4-0.5 mole fraction of the alkanol. These excess parameters at a particular mole fraction of the alkanols becomes less negative with increase of temperature. The negative values may be attributed to the existence of dispersion and dipolar forces between unlike molecules and related to the difference in size and shape of the molecules[8] The V^E values are less negative at lower temperature as decrease in temperature disturb hereto and homo-association of the molecules which causes decrease in fluidity of the liquid. The V^E values are slight positive at 308.15K for isobutyl alcohol. Values of G^{*E} are more at lower temperature provides additional evidence for the existence of interactions of weak magnitude like dipole-induced dipole type between components of liquid mixtures. The magnitudes of G^{*E} for isoamyl alcohol are slight positive at lower temp. but much negative at higher temp. This trend is exactly reverse in case of isobutyl alcohol. The magnitude of V^E, $\Delta\eta$, Δk_S, and $G^{*E}$the sign and the extent of deviation of these properties from ideality depend on the strength of interaction between unlike molecules. The excess viscosity gives the strength of the molecular interaction between the interacting molecules. For systems where dispersion, induction and dipolar forces which are operated by the values of above excess parameters are found to be negative, the large negative values of excess viscosity for all the systems can be attributed to the presence of the dispersion, induction, and dipolar forces between the components. The magnitude of V^E, $\Delta\eta$ and Δk_S are less at higher temperature provides inverse relation with G^{*E}

V^E values are negative over entire mole fraction of the alkanols The values V^E parameter become more negative with increasing X_1.This is because Δk_S and alkanols are associated[9] The observed V^E may be analyzed in terms of several effects, which may be divided into physical, chemical and geometrical contributions. The physical interactions comprise mainly dispersion forces and non-specific physical interactions giving a negative contribution. The chemical interaction involve the charge transfer complexes, resulting in contraction of volume, geometrical or structural contribution arising from geometrical fitting of one component into other, due to different in molar volume and free volumes between the components increases. In the present investigation the negative deviations of V^E have been attributed to dispersive forces that show weak molecular interaction between the unlike molecules.

Table. 1- Values of density (ρ) viscosity (η) ultrasonic velocity (U), Excess volume (V^E), viscosity deviations and ($\Delta\eta$), deviation on isentropic compressibility (Δk_S) for Binary System of Benzyl amine(1) and Isoamyl alcohol (2) at 298.15 and 303.15 K.

Temp. (K)	x_1	ρ (gm/cm^3)	η10^3 (Nsm^{-2})	U (MS^{-1})	V^E x 10^6(m^3 mole^{-1})	Φ	Δη x 10^3 (Kg m^{-1} s^{-1})	Δk_S x 10^{11}(m^2 N^1)
298.15	0	0.811	4.212065	1232.9	0	0.0000	0	0.00
	0.0842	0.83074	4.10164	1266.4	-0.5939	0.0836	-5.256	-25.49
	0.1716	0.84919	3.815569	1294.4	-0.9194	0.1704	-1.1203	-55.73
	0.2613	0.866038	3.556825	1355.0	-0.9769	0.2597	-27.1234	-64.88
	0.3545	0.88117	3.450918	1363.8	-1.1278	0.3525	-42.5623	-73.90
	0.4518	0.904227	3.28455	1399.2	-1.9682	0.4497	-37.1256	-78.76
	0.5528	0.921459	3.08558	1434.2	-1.2061	0.5507	-34.2156	-75.30
	0.6578	0.938075	2.783418	1461.2	-0.8931	0.6558	-24.1253	-69.60
	0.7673	0.953824	2.57632	1497.4	-0.3968	0.7657	-15.0236	-50.99
	0.8813	0.971072	2.407562	1534.0	-0.0226	0.8804	-8.2365	-25.01
	1	0.992956	2.21512	1560.6	0	1.0000	0	0.00
308.15	0	0.79597	2.637231	1200.4	0	0.0000	0	0.00
	0.0842	0.8224	2.12806	1231.9	0.1122	0.0696	-41.0767	-858.22
	0.1716	0.85227	1.89042	1259.2	0.0286	0.1442	-54.5989	-64.22
	0.2613	0.883196	1.69989	1292.0	0.0436	0.2234	-63.1406	-86.02
	0.3545	0.91565	1.6326	1321.2	0.1546	0.3087	-58.9481	-101.72
	0.4518	0.950118	1.49986	1362.8	0.3401	0.4013	-60.8202	-107.71
	0.5528	0.99158	1.3764	1394.8	0.0948	0.5013	-61.3307	-93.95
	0.6578	1.03375	1.32487	1417.2	0.1259	0.6098	-54.1795	-91.45
	0.7673	1.082137	1.29647	1462.0	0.05512	0.7283	-44.1879	-72.33
	0.8813	1.127457	1.28432	1501.2	0.4009	0.8579	-32.0441	-42.48
	1	1.1881	1.4654	1521.0	0	1.0000	0	0.00

Table. 2- Values of density (ρ) viscosity (η) ultrasonic velocity (U), Excess volume(V^E), viscosity deviations and ($\Delta\eta$), deviation on isentropic compressibility (Δk_S) for Binary System of Benzyl amine(1) and Isobutyl alcohol (2) at 298.15 and 303.15 K

Temp. (K)	x_1	ρ (gm/cm^3)	η10^3 (Nsm^{-2})	U (MS^{-1})	V^E x 10^6(m^3	Φ	Δη x 10^3 (Kg	Δk_S x
298.15k	0	0.805349	4.482728	1183.0	0	0.0000	-0.0001	0
	0.0718	0.82119	3.915317	1224.8	-1.2435	0.0829	-40.5278	-36.36
	0.148	0.856362	3.813343	1265.4	-2.1297	0.1690	-46.2147	-55.12
	0.2291	0.858719	3.427744	1300.1	-3.1241	0.2581	-53.5942	-79.12
	0.316	0.874407	3.215013	1336.9	-4.4231	0.3510	-55.1624	-81.18
	0.4093	0.895254	3.128868	1367.9	-5.124	0.4478	-49.1234	-78.22
	0.5099	0.91086	2.993545	1408.8	-4.2374	0.5491	-44.2563	-74.03
	0.6181	0.942392	2.792046	1446.2	-3.9817	0.6545	-48.2356	-69.89
	0.7351	0.949503	2.653088	1481.7	-2.8673	0.7646	-32.4561	-45.37
	0.8617	0.96527	2.41032	1524.4	-1.8779	0.8794	-22.0147	-24.88
	1	0.992956	2.215198	1560.7	0	1.0000	0.0001	0
308.15k	0	0.7964	3.330054	1154.8	0	0.0000	0	0
	0.0718	0.81187	2.994743	1188.0	-1.0534	0.0827	-12.147	-27.37
	0.148	0.8468	3.09295	1218.7	-2.1048	0.1686	-25.1234	-61.78
	0.2291	0.84915	2.825173	1258.0	-4.4847	0.2576	-34.123	-67.87
	0.316	0.86467	2.81035	1297.9	-4.8536	0.3503	-41.1234	-78.87
	0.4093	0.885377	2.66953	1311.6	-4.1278	0.4471	-55.1203	-69.41
	0.5099	0.9009	2.341685	1360.6	-3.5179	0.5484	-41.7849	-66.06
	0.6181	0.932317	2.271607	1405.3	-2.4518	0.6539	-31.0123	-69.44
	0.7351	0.939832	2.209198	1446.1	-1.3245	0.7641	-15.1203	-48.27
	0.8617	0.9555	1.973911	1478.3	-0.8472	0.8791	-10.2245	-20.29
	1	0.98642	1.874522	1521.0	0	1.0000	0	0

Table. 3- Excess values of free length (L_f^E), Available volume(V_a^E), and Gibb's free energy(G^{*E}) of flow for :

x_1	L_f^E x 10^{10} m		V_a^E x 10^6 m^3mol^{-1}		G^{*E} $Jmol^{-1}$	
	298.15K	308.15K	298.1K	308.15K	298.15K	308.15K
Benzyl amine(1) and Isoamyl alcohol (2)						
0.0000	0	0	0	0	0	0
0.0515	-0.01	-0.02	-0.321	-1.034	-361.4	-428.5
0.1086	-0.022	-0.03	-0.884	-1.354	-734.1	-606.2
0.1727	-0.027	-0.041	-1.237	-1.654	-821.5	-744.5
0.2453	-0.032	-0.045	-1.489	-1.923	-924	-874.1
0.3278	-0.035	-0.047	-1.852	-2.243	-1001.4	-940.2
0.4224	-0.035	-0.046	-2.014	-2.295	-1032.3	-948.3
0.5321	-0.034	-0.044	-1.9	-2.197	-942.3	-865.9
0.6610	-0.026	-0.036	-1.652	-2.015	-823.5	-727.7
0.8143	-0.014	-0.022	-1.098	-1.318	-574	-494.5
1.0000	0	0	0	0	0	0
Benzyl amine(1) and Isobutyl alcohol (2)						
0	0	0	0	0	0	0
0.0627	-0.01	-0.018	-0.401	-0.539	-413.7	-82.8
0.1306	-0.018	-0.027	-0.892	-1.221	-612.3	-261.1
0.2047	-0.024	-0.031	-1.371	-1.633	-782.3	-367
0.2862	-0.029	-0.034	-1.993	-2.334	-893.2	-491.2
0.3755	-0.033	-0.037	-2.128	-2.517	-985.5	-685.3
0.4742	-0.032	-0.035	-2.011	-2.49	-1058.9	-751.9
0.5838	-0.03	-0.031	-1.881	-2.311	-1050.2	-771.2
0.7063	-0.025	-0.024	-1.532	-1.862	-926.6	-744.5
0.8439	-0.016	-0.015	-0.489	-1.107	-606.9	-482.1
1	0	0	0	0	0	0

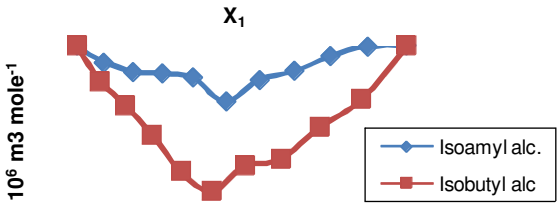

Figure. 1- V^E vs. X_1 for binary systems of benzylamine(1) + alkanols(2) at 298.15 K

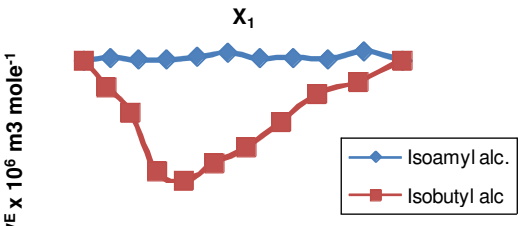

Figure. 2- V^E vs. X_1 for binary systems of benzylamine(1) + alkanols(2) at 308.15 K

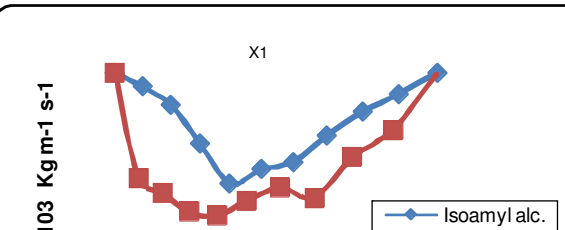

Figure. 3- Δη vs. X1 for binary systems of alkanols (2) + Benzyl amine(1) at 298.15 K

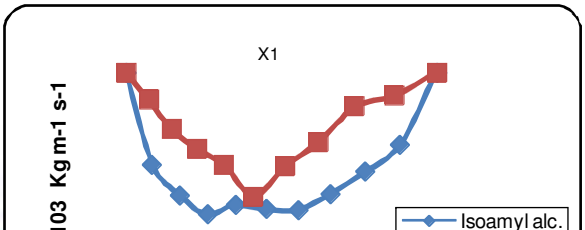

Figure. 4- Δη vs. X1 for binary systems of alkanols (2) + Benzyl amine(1) at 308.15 K

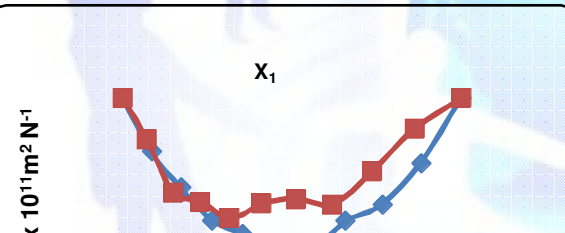

Figure. 5- ΔK_S vs. X_1 for binary systems of benzylamine(1) + alkanols.(2) at 308.15 K

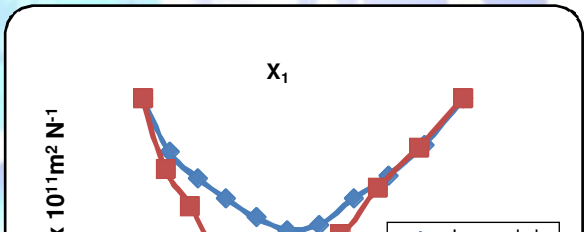

Fig 6. ΔK_S vs. X_1 for binary systems of benzyl amine(1) + alkanols(2) at 298.15 K

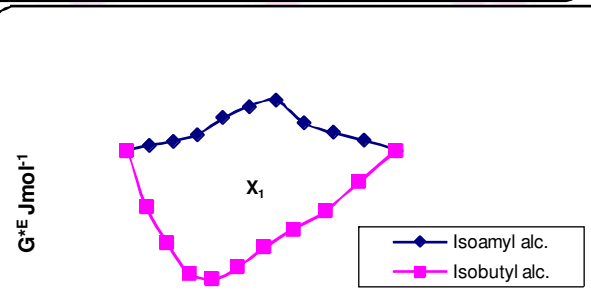

Figure. 7- Excess Gibb's freeenergy vs. X_1 of Benzyl amine(1) + alkanols at 298.15.

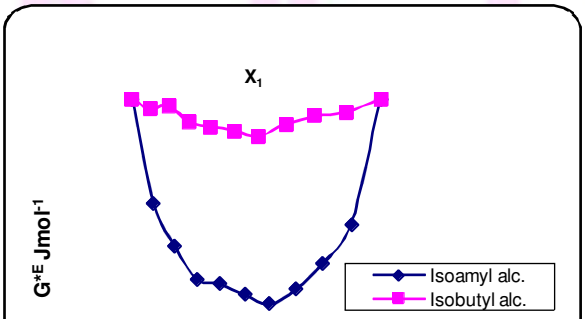

Figure. 8- Excess Gibb's freeenergy vs. X_1 of Benzyl amine(1) + alkanols at 308.15K.

Conclusion:

The experimental data of Ultrasonic velocity (U), density (ρ) and viscosity (η) are reported for binary mixtures of isoamyl alcohol and isobutyl alcoholwith benzylamne over entire range of mole fractions at 298.15 and 308.15 K. Calculated viscosity deviation, excess molar volume and change in isentropic compressibility shows Large negative deviations for both the investigated binary systems. This reveals the existence of molecular interactions in the binary mixtures. The present investigation shows that greater molecular interaction exists in isobutyl alcohol mixtures which may be due to hydrogen bond formation and weak molecular interaction that exists in the isoamyl alcohol mixtures and which may be due to the dominance of dispersion forces and dipolar interaction between the unlike molecules. The interaction tends to be weaker with rise in temperature which may due to weak intermolecular forces and thermal dispersion forces. The existence of molecular interaction in the mixture is in the order: isobutyl alcohol> isoamyl alcohol

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APPENDIX Lists of symbols / abbreviations and units.		
Symbol	Term	Unit
x	Mole fractions.	--
ρ	The Density.	x 10^{-3} kg-m^{-3}
η	The viscosity	mPa s
U	The ultrasonic velocity.	m-s^{-1}
L_f	Intermolecular free length.	x 10^{11}m
Ks	Isentropic compressibility.	x 10^{11}(m^2 N^{-1})
V^E	Excess molar volumes.	x10^6 m^3 $mole^{-1}$
Δη	Deviation in viscosity	mPa s
ΔKs	Deviation in Isentropic compressibility.	x 10^{11}(m^2 N^{-1})
σ	The standard deviation.	--
Φ	Volume fraction.	--
M	Molecular weight.	x 10^{-3} kg
β	The adiabatic compressibility.	x 10^{10} N^{-1} m^2
G^{*E}	Excess Gibbs free energy of flow.	J-mol^{-1}
Z	specific acoustic impedance.	Kg $s^{-1}m^{-3}$
η_m	The viscosity of solution.	mPa s
L_f^E	Excess Intermolecular free length.	x 10^{11}m
V_a^E	Excess available volume.	x10^6 m^3 $mole^{-1}$
Z^E	Excess specific acoustic impedance.	Kg $s^{-1}m^{-3}$