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Excess Volumes, Speeds of Sound, Isentropic Compressibilities and Viscosities of Binary Mixtures of *N*-Ethyl Aniline with Some Aromatic Ketones at 303.15 K

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Densities (ρ), Viscosities (η) and ultrasonic speeds (u) of pure acetophenone (AP), propiophenone (PP), *p*-methyl acetophenone (*p*-MeAP), *p*-chloroacetophenone (*p*-ClAP) and those of their binary mixtures with *N*-ethyl aniline (*N*-EA) as a common component, were measured at 303.15 K over the entire composition range. These experimental data were used to calculate the excess volume V^E, deviation in ultrasonic speeds Δu, isentropic compressibility K_s, intermolecular free length L_f, acoustic impedance Z, deviations in isentropic compressibility ΔK_s, deviation in viscosity Δη and excess Gibbs free energy of activation of viscous flow (G^{*E}) at all mole fractions of *N*-ethyl aniline. These parameters, especially excess functions, are found to be quite sensitive towards the intermolecular interactions between component molecules. Theoretical values of viscosity of the binary mixtures were calculated using different empirical relations and theories. The relative merits of these relations and theories were discussed. The experimental results were correlated by using the polynomial proposed by Redlich-Kister equation.

Key Words : Ultrasonic speed, Viscosity, Excess volume, *N*-Ethyl aniline, Ketone

Introduction

Thermodynamic properties derives from the measurement of excess volumes (V^E), Ultrasonic speeds (u) and Viscosities (η) are useful in understanding the nature and type of intermolecular interactions between the component molecules.[1,2] The liquids that were used in the present study are of having many industrial applications. *N*-EA is used as an intermediate to manufacture dyes, agrochemicals and in preparation of some organic compounds. Ketones are used as solvents, polymer precursors and in the preparation of many pharmaceuticals. As far as we are aware that no excess volume, viscosity, ultrasonic speed data is available in the literature for the present systems under consideration. The systems chosen in the present investigation is used to study the effect of position of carbonyl group in a ketone and also their size and shape will give an idea that what type of interactions are occurring between component molecules of ketones when these are mixed with *N*-EA. The densities, viscosities and ultrasonic speeds of pure *N*-EA, AP, PP, *p*-MeAP, *p*-ClAP and those of their binary mixtures with *N*-EA, as common component, were measured at 303.15 K. From these data, various derived parameters such as excess volume V^E, deviations in ultrasonic speed Δu, isentropic compressibility K_s, intermolecular free length L_f, acoustic impedance Z, deviations in isentropic compressibility ΔK_s, deviation in viscosity Δη and excess Gibbs free energy of activation of viscous flow (G^{*E}) were computed. The variations in these parameters with composition of the binary mixtures reveal the qualitative nature and extent of intermolecular interactions between the component molecules. This study will also provide an attest of various interaction parameters. The viscosities were used to test the semi-empirical relations of Grunberg and Nissan[3] Katti and Chaudhri[4] and Hind *et al*..[5] The suitability of these theories and relations for the present liquid mixtures was checked.

Table 1. Physical property of pure compounds at 308.15 K

Component	Densities/gm.cm^{-3}		Viscosities/mpa.s	
	Experimental	Literature	Experimental	Literature
N-ethylaniline	0.95274	0.95260**[a]	1.742	1.741**[a]
acetophenon	1.01937	1.01940**[b]	1.512	1.511**[e]
propiophenone	1.00896	1.0087*[c]	1.469	1.468[d]
p-methylacetophenone	0.99652	0.99630[d]	1.535	1.536[d]
p-chloroacetophenone	1.18125	1.1813[d]	2.292	2.293[d]

*298.15 K. **303.15 k. [a]Reference [6]. [b]Reference [7]. [c]Reference [8]. [d]Reference [9]. [e]Reference [5]

Experimental

Solvents of high purity were used in the present investigation and all the chemicals used were of Analytical reagent grade (S.D. Fine Chemicals Ltd., India). They were further purified by the methods described in the literature.[6] The purities of the samples were checked by comparing the measured densities and viscosities of the compounds with those reported in the literature values are[6-10] shown in Table 1.

Apparatus and Procedure. Binary mixtures were prepared by mass in the air tight stoppered glass bottles. The masses were recorded on a digital electronic balance (Acculab ALC-210.4) to an uncertainty of ± 0.1 mg. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots *via* syringe into stopper bottles. The uncertainty in mole fraction was thus estimated to be less than $\pm 1 \times 10^{-4}$. A set of 13 binary mixtures were prepared for each system and their densities were measured at the respective compositions in the mole fraction scale from 0.1 to 0.9. Densities of the pure liquids and their mixtures were measured by using Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built- in solid-state thermostat and a resident program with accuracy of temperature of 303.15 K ± 0.03 K. Typically, density precisions are $\pm 2 \times 10^{-5}$ gm.cm^{-3}. Proper calibration at each temperature was achieved with doubly distilled, deionized water and with air as standards. Ultrasonic speed of pure liquids and their liquid mixtures were determined by a single-crystal interferometer (Mittal Enterprise, New

Table 2. Experimental values of density, Ultrasonic speed, uand viscosity, η for the binary mixtures at 303.15 K

N-EA (1) + acetophenone (2)				*N*-EA (1) + propiophenone (2)			
303.15 K				303.15 K			
x_1	ρ	u	η	x_1	ρ	u	η
0.0000	1.01937	1465.0	1.512	0.0000	1.00437	1440.0	1.510
0.0651	1.01520	1468.0	1.524	0.0789	1.00105	1445.1	1.524
0.1424	1.01018	1471.8	1.538	0.1541	0.99772	1450.2	1.537
0.2225	1.00493	1475.6	1.554	0.2249	0.99446	1455.0	1.550
0.2977	0.99996	1479.0	1.568	0.3002	0.99089	1460.0	1.565
0.3611	0.99575	1481.7	1.581	0.3862	0.98668	1465.5	1.581
0.4487	0.98991	1484.9	1.599	0.4651	0.98272	1470.3	1.598
0.5162	0.98539	1487.1	1.614	0.5244	0.97967	1473.6	1.612
0.5869	0.98064	1489.0	1.631	0.6049	0.97546	1477.8	1.631
0.6407	0.97703	1490.1	1.644	0.6891	0.97093	1481.8	1.653
0.7083	0.97248	1491.4	1.662	0.7354	0.96838	1483.9	1.666
0.7798	0.96766	1492.5	1.681	0.8005	0.96472	1486.7	1.683
0.8256	0.96457	1493.0	1.694	0.8523	0.96173	1488.8	1.699
0.9025	0.95936	1493.9	1.715	0.9099	0.95831	1491.3	1.716
1.0000	0.95274	1495.2	1.742	1.0000	0.95274	1440.0	1.742

N-EA (1) + *p*-methyl acetophenone (2)				*N*-EA (1) + *p*-chloro acetophenone (2)			
303.15 K				303.15 K			
x_1	ρ	u	η	x_1	ρ	u	η
0.0000	1.00065	1454.0	1.581	0.0000	1.18565	1412.0	2.353
0.0838	0.99752	1458.0	1.587	0.0798	1.16853	1421.5	2.295
0.1427	0.99529	1461.1	1.592	0.1568	1.15173	1429.8	2.242
0.2179	0.99217	1464.9	1.601	0.2321	1.13505	1437.3	2.191
0.2904	0.98904	1468.6	1.608	0.2989	1.12005	1443.6	2.147
0.3608	0.98589	1472.0	1.616	0.3614	1.10586	1449.3	2.106
0.4284	0.98278	1475.2	1.625	0.4467	1.08626	1456.7	2.051
0.4942	0.97969	1478.0	1.635	0.5163	1.07005	1462.6	2.008
0.5577	0.97664	1480.5	1.645	0.5841	1.05411	1468.2	1.967
0.6194	0.97361	1482.8	1.656	0.6601	1.03603	1474.3	1.922
0.6889	0.97012	1485.2	1.670	0.7245	1.02055	1479.1	1.885
0.7467	0.96713	1487.1	1.683	0.7874	1.00530	1483.6	1.850
0.8128	0.96360	1489.1	1.697	0.8487	0.99031	1487.6	1.818
0.9072	0.95831	1492.1	1.718	0.9042	0.97662	1490.8	1.788
1.0000	0.95274	1495.2	1.742	1.0000	0.95274	1495.2	1.742

Delhi, M-82) at a frequency of 3 MHz with an uncertainty of ± 0.2%. The viscosities of pure and liquid mixtures were determined by a suspended Ubbelohole-type viscometer described earlier.[11] The estimated uncertainty in viscosity is ± 0.005 mPa.s. The temperature of the test liquid was maintained to an accuracy of 303.15 ± 0.02 K in an electronically controlled thermostatic water bath.

Results and Discussion

The experimental values of density ρ, viscosity η and ultrasonic u of pure liquids and their mixtures as function of mole fraction x of *N*-EA at 303.15 K are given in Table 2. The derived parameters such as K_s, L_f, and Z were calculated using the following relations

$$K_s = u^{-2}\rho^{-1} \quad (1)$$

$$L_f = K/u\,\rho^{1/2} \quad (2)$$

$$Z = u\,\rho \quad (3)$$

where ρ is the density and u is the ultrasonic speed of solutions. K is a temperature dependent constant.[12] The variations of K_s, L_f, and Z with mole fraction are presented in Table 3. It is obvious from the Table 3 that K_s and L_f increase while Z decreases with increasing mole fraction x of *N*-EA for the two systems (*N*-EA + AP, + *p*-ClAP) under

Table 3. Calculated values of isentropic compressibility, K_s. Deviation in ultrasonic speed Δu, Intermolecular free length, L_f, specific acoustic impedance, Z for the binary mixtures at 303.15 K

N-EA (1) + acetophenone (2)					*N*-EA (1) + propiophenone (2)				
303.15 K					303.15 K				
x_1	Δu	K_s	Z	L_f	x_1	Δu	K_s	Z	L_f
0.0000	0.0000	4.5708	1.4934	1.4324	0.0000	0.0000	4.8015	1.4463	1.5053
0.0651	1.0340	4.5705	1.4903	1.4325	0.0789	0.7447	4.7835	1.4466	1.4996
0.1424	2.4995	4.5699	1.4868	1.4326	0.1541	1.6937	4.7658	1.4469	1.4941
0.2225	3.8805	4.5701	1.4829	1.4327	0.2249	2.5855	4.7499	1.4469	1.4891
0.2977	5.0095	4.5717	1.4789	1.4332	0.3002	3.4290	4.7344	1.4467	1.4842
0.3611	5.7948	4.5743	1.4754	1.4341	0.3862	4.1818	4.7190	1.4460	1.4794
0.4487	6.3493	4.5815	1.4699	1.4363	0.4651	4.6265	4.7071	1.4449	1.4757
0.5162	6.5108	4.5889	1.4654	1.4386	0.5244	4.6531	4.7007	1.4436	1.4737
0.5869	6.2756	4.5994	1.4602	1.4419	0.6049	4.4095	4.6942	1.4415	1.4716
0.6407	5.7509	4.6096	1.4559	1.4451	0.6891	3.7617	4.6906	1.4387	1.4705
0.7083	5.0093	4.6231	1.4504	1.4493	0.7354	3.3059	4.6897	1.4370	1.4702
0.7798	3.9500	4.6393	1.4442	1.4544	0.8005	2.5124	4.6898	1.4342	1.4702
0.8256	3.0669	4.6510	1.4401	1.4581	0.8523	1.7530	4.6911	1.4318	1.4707
0.9025	1.6445	4.6706	1.4332	1.4642	0.9099	1.0735	4.6921	1.4291	1.4710
1.0000	0.0000	4.6949	1.4245	1.4718	1.0000	0.0000	4.6949	1.4245	1.4718

N-EA (1) + *p*-methyl acetophenone (2)					*N*-EA (1) + *p*-chloro acetophenone (2)				
303.15 K					303.15 K				
x_1	Δu	K_s	Z	L_f	x_1	Δu	K_s	Z	L_f
0.0000	0.0000	4.7270	1.4549	1.4819	0.0000	0.0000	4.2303	1.6741	1.3262
0.0838	0.5474	4.7159	1.4544	1.4784	0.0798	2.8606	4.2351	1.6611	1.3277
0.1427	1.2208	4.7064	1.4542	1.4754	0.1568	4.7542	4.2472	1.6467	1.3315
0.2179	1.9225	4.6968	1.4534	1.4724	0.2321	5.9893	4.2647	1.6314	1.3370
0.2904	2.6355	4.6879	1.4525	1.4697	0.2989	6.7315	4.2842	1.6169	1.3431
0.3608	3.1350	4.6812	1.4512	1.4675	0.3614	7.2315	4.3051	1.6027	1.3496
0.4284	3.5499	4.6756	1.4498	1.4658	0.4467	7.5346	4.3384	1.5824	1.3601
0.4942	3.6390	4.6726	1.4480	1.4649	0.5163	7.6438	4.3686	1.5651	1.3696
0.5577	3.5228	4.6714	1.4459	1.4645	0.5841	7.6029	4.4009	1.5476	1.3797
0.6194	3.2807	4.6714	1.4437	1.4645	0.6601	7.3797	4.4407	1.5274	1.3922
0.6889	2.8173	4.6731	1.4408	1.4650	0.7245	6.8216	4.4789	1.5095	1.4041
0.7467	2.3360	4.6756	1.4382	1.4658	0.7874	6.0883	4.5193	1.4915	1.4168
0.8128	1.6126	4.6801	1.4349	1.4672	0.8487	4.9882	4.5631	1.4732	1.4305
0.9072	0.7234	4.6870	1.4299	1.4694	0.9042	3.5706	4.6072	1.4559	1.4443
1.0000	0.0000	4.6949	1.4245	1.4718	1.0000	0.0000	4.6949	1.4245	1.4718

study. The increase in K_s and L_f while opposite trends in Z with x reveal the presence of weak interactions between the component molecules of the mixture.

The deviations in excess functions from ideality provide a relatively better tool to assess the strength of interaction between the component molecules of the binary mixtures. V^E, ΔK_s, $\Delta\eta$ and Δu were calculated from experimental data using the following relevant expressions:

$$V^E = [x_1M_1 + x_2M_2]/\rho_m - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (4)$$

$$\Delta K_s = K_s - [x_1 K_{s1} + x_2 K_{s2}] \quad (5)$$

$$\Delta\eta = \eta - [x_1 \eta_1 + x_2 \eta_2] \quad (6)$$

$$\Delta u = u - [x_1 u_1 + x_2 u_2] \quad (7)$$

where M_1, M_2, Ks_1, Ks_2, η_1, η_2, u_1, u_2, ρ_1, ρ_2, ρ_m, K_s, η, u represent component1, component2 and mixture respectively. The variation of V^E, ΔK_s, $\Delta\eta$ and Δu with x were fitted to the Redlich-Kister equation[13] of the type,

$$Y^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (8)$$

where Y^E is V^E or u^E or K_s^E or $\Delta\eta$. The values of a_0, a_1 and a_2 are the coefficients of the polynomial equation and were obtained by method of least-squares and are given in Table 5 along with standard deviation values σ at 303.15 K.

The excess Gibbs free energy of activation of viscous flow (G^{*E}) is obtained by the equation

$$G^{*E} = RT\,[\ln \eta_m V_m - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (9)$$

where V_m is the molar volume of the mixture, R and T have their usual meanings.

Various equations exist in the literatures were used to estimate the dynamic viscosity η, Gruenberg and Nissan suggested the expression:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2d \quad (10)$$

where d is a parameter proportional to interchange energy, which reflects the non-ideality of the system. This parameter has been considered as valid measure for detecting the presence of interactions between the components. Katti and Chaudhri derived the following equation:

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1x_2W_{vis/RT} \quad (11)$$

where $W_{vis/RT}$ is an interaction term.

Molecular interactions may also be interpreted by the following viscosity model of Hind *et al.*,

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1x_2 H_{12} \quad (12)$$

where H_{12} is Hind interaction parameter.

The excess or deviation values reflect the interactions between the mixing species mainly depend upon the composition, the different molecular size and shape of the components. The important effects, which influence the values of excess thermodynamic function, are divided into physical, chemical and structural contributions.

1. Chemical effect includes charge transfer forces, formation of H-bonds, dipole-dipole interactions and donor-acceptor complex forming interactions making negative contribution towards ΔK_s, V^E and positive contribution towards $\Delta\eta$

2. Physical contributions comprise non-specific physical interactions. *e.g.* dispersion force due to breaking of dipoles or weak dipole-dipole interaction leading to a negative contribution towards $\Delta\eta$ and positive contribution towards ΔK_s, V^E

3. Geometrical fitting of the component molecules into each others structure and due to difference in molar and free volumes.

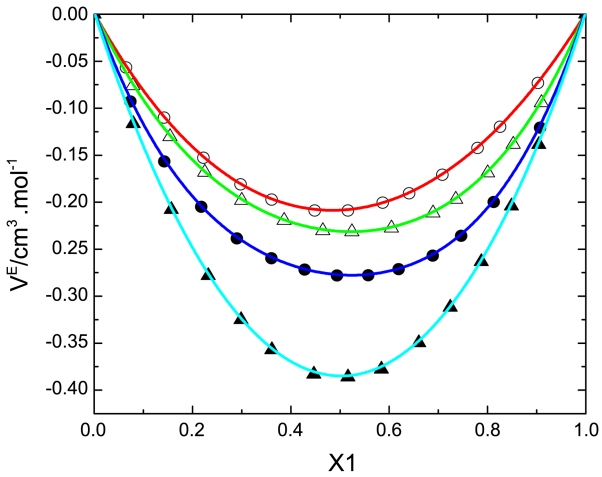

Figure 1. Variation of V^E of the binary liquid mixtures of *N*-EA with acetophenone (○), propiophenone (△), Paramethylacetophenone (●) and parachloroacetophenone (▲) at 303.15 K.

An examination of curves in Figure 1 suggests that the excess volume data for the systems *N*-EA with four ketones are negative over the entire range of mole fraction at 303.15 K.

Ketones AP, PP, *p*-Me-AP, *p*-Cl-AP are strongly dipolar solvents and associated liquids.[14] *N*-ethyl aniline is a basic compound there will be dipole-dipole interactions between component molecules contributing to the reduction in the excess volume. From the above agreement, it is clear that the specific interactions are occurring between the mixtures of aromatic ketones and *N*-ethyl aniline. In addition to strong dipole-dipole interactions, there may be a possibility of charge transfer complex formation between ketones and π-electron cloud of *N*-ethyl aniline. Here the oxygen atom of ketoxy group of aromatic ketones accepts the electrons into its 2P vacant molecular orbital[15] and *N*-ethyl aniline easily donates its mobile π-electrons.

The more negative V^E data for the binary mixture *p*-chloroacetophenone is due to the electron density on the oxygen atom of ketoxy group is highest, because the non-bonded electrons of its chlorine atom when compared to the bonded electrons of *p*-methylacetophenone. A perusal of V^E data for the binary mixtures of *p*-methylacetophenone and propiophenone suggest that the former exhibiting more negative V^E values than the latter. This may be ascribed due to hyper conjugation between hydrogen atom of methyl substituent and π-electrons of phenyl ring. When propiophenone and acetophenone are compared, propiophenone

has an edge over acetophenone due to the large + Inductive effect of its ethyl group compared with methyl group in acetophenone and it was experimental reported in the literature.[16] Hence over all V^E magnitude of aromatic ketones with *N*-EA fall in the following order;

$$p\text{-Cl AP} > p\text{-Me AP} > \text{PP} > \text{AP}$$

Viscosity. A perusal of Table 4 shows that the values of Δη are negative over the entire range of composition in all the binary mixtures of *N*-ethyl aniline with aromatic ketones. The viscosity of a mixture[17,18] depends on the molecular interactions between the components mixture with strong interactions between different molecules show positive viscosity deviations, while for mixtures absence of specific interactions, viscosity deviations are negative. The negative viscosity deviation in the present investigation suggests that without specific interactions between component molecules over the entire composition range in all the binary mixtures.

The algebraic Δη values for the systems containing aromatic ketones fall in the following order

$$p\text{-ClAP} < p\text{-MeAP} < \text{PP} < \text{AP}$$

The observed negative values of Δη in the Table 4 indicate that there are no strong specific interactions present between the mixtures of aromatic ketones and *N*-ethyl aniline which are also reflected from the observed positive value of V^E for system. Thus, the breaking of clusters of ketonic molecules has influencing in the excess molar volume, viscosity,

Table 4. Experimental excess molar volumes (V^E), deviation in viscosities (Δη), excess Gibbs free energy of activation of viscous flow (G^{*E}), Grunberg-Nissan interaction parameters (d), Katti-Chaudhri interaction parameters, ($W_{vis/RT}$) and Hind interaction parameters (H_{12}) at 303.15 K

N-EA (1) + acetophenone (2)							*N*-EA (1) + propiophenone (2)						
303.15K							303.15 K						
x_1	V^E	Δη	G^{*E}	d	$W_{vis/RT}$	H_{12}	x_1	V^E	Δη	G^{*E}	d	$W_{vis/RT}$	H_{12}
0.0000	0.0000	0.0000	0.0000				0.0000	0.0000	0.0000	0.0000			
0.0651	-0.0568	-0.0030	-0.0174	-0.0094	-0.0115	1.6026	0.0789	-0.0762	-0.0043	-0.0274	-0.0122	-0.0151	1.5964
0.1424	-0.1103	-0.0068	-0.0398	-0.0111	-0.0131	1.5994	0.1541	-0.1304	-0.0088	-0.0555	-0.0143	-0.0171	1.5924
0.2225	-0.1529	-0.0092	-0.0527	-0.0103	-0.0122	1.6005	0.2249	-0.1682	-0.0122	-0.0763	-0.0149	-0.0176	1.5911
0.2977	-0.1813	-0.0125	-0.0722	-0.0120	-0.0139	1.5972	0.3002	-0.1982	-0.0146	-0.0906	-0.0147	-0.0173	1.5911
0.3611	-0.1975	-0.0141	-0.0807	-0.0123	-0.0141	1.5965	0.3862	-0.2195	-0.0186	-0.1150	-0.0169	-0.0195	1.5868
0.4487	-0.2091	-0.0162	-0.0928	-0.0133	-0.0151	1.5943	0.4651	-0.2304	-0.0199	-0.1221	-0.0172	-0.0197	1.5860
0.5162	-0.2090	-0.0167	-0.0951	-0.0136	-0.0153	1.5935	0.5244	-0.2315	-0.0197	-0.1196	-0.0167	-0.0193	1.5866
0.5869	-0.2008	-0.0160	-0.0894	-0.0132	-0.0148	1.5940	0.6049	-0.2276	-0.0193	-0.1171	-0.0170	-0.0197	1.5855
0.6407	-0.1907	-0.0154	-0.0854	-0.0133	-0.0149	1.5936	0.6891	-0.2115	-0.0169	-0.1014	-0.0162	-0.0190	1.5866
0.7083	-0.1709	-0.0129	-0.0701	-0.0120	-0.0136	1.5958	0.7354	-0.1969	-0.0146	-0.0874	-0.0152	-0.0180	1.5885
0.7798	-0.1423	-0.0104	-0.0553	-0.0113	-0.0129	1.5969	0.8005	-0.1690	-0.0127	-0.0764	-0.0162	-0.0192	1.5862
0.8256	-0.1200	-0.0079	-0.0410	-0.0098	-0.0114	1.5996	0.8523	-0.1385	-0.0087	-0.0520	-0.0134	-0.0166	1.5913
0.9025	-0.0732	-0.0046	-0.0232	-0.0090	-0.0106	1.6010	0.9099	-0.0941	-0.0051	-0.0302	-0.0114	-0.0148	1.5949
1.0000	0.0000	0.0000	0.0000				1.0000	0.0000	0.0000	0.0000			

N-EA (1) + *p*-chloro acetophenone (2)							*N*-EA (1) + *p*-methyl acetophenone (2)						
303.15 K							303.15 K						
x_1	V^E	Δη	G^{*E}	d	$W_{vis/RT}$	H_{12}	x_1	V^E	Δη	G^{*E}	d	$W_{vis/RT}$	H_{12}
0.0000	0.0000	0	0				0.0000	0.0000	0.0000	0.0000			
0.0798	-0.1165	-0.0092	-0.0199	-0.0057	-0.0109	1.9846	0.0838	-0.0930	-0.0075	-0.0533	-0.0245	-0.0279	1.6127
0.1568	-0.2079	-0.0152	-0.0296	-0.0039	-0.0090	1.9900	0.1427	-0.1569	-0.0120	-0.0856	-0.0245	-0.0281	1.6126
0.2321	-0.2782	-0.0202	-0.0394	-0.0038	-0.0089	1.9909	0.2179	-0.2051	-0.0151	-0.1067	-0.0218	-0.0252	1.6173
0.2989	-0.3250	-0.0234	-0.0454	-0.0036	-0.0087	1.9917	0.2904	-0.2387	-0.0198	-0.1378	-0.0237	-0.0269	1.6136
0.3614	-0.3571	-0.0262	-0.0534	-0.0042	-0.0093	1.9908	0.3608	-0.2598	-0.0231	-0.1594	-0.0247	-0.0278	1.6114
0.4467	-0.3829	-0.0291	-0.0644	-0.0054	-0.0105	1.9887	0.4284	-0.2718	-0.0250	-0.1711	-0.0250	-0.0281	1.6105
0.5163	-0.3860	-0.0295	-0.0675	-0.0058	-0.0109	1.9884	0.4942	-0.2781	-0.0256	-0.1743	-0.0249	-0.0280	1.6104
0.5841	-0.3776	-0.0291	-0.0696	-0.0064	-0.0115	1.9876	0.5577	-0.2778	-0.0258	-0.1750	-0.0254	-0.0285	1.6092
0.6601	-0.3495	-0.0277	-0.0705	-0.0075	-0.0126	1.9858	0.6194	-0.2713	-0.0247	-0.1673	-0.0253	-0.0285	1.6091
0.7245	-0.3117	-0.0253	-0.0682	-0.0086	-0.0137	1.9840	0.6889	-0.2569	-0.0219	-0.1484	-0.0244	-0.0278	1.6104
0.7874	-0.2633	-0.0219	-0.0624	-0.0098	-0.0150	1.9821	0.7467	-0.2359	-0.0182	-0.1238	-0.0227	-0.0263	1.6133
0.8487	-0.2041	-0.0164	-0.0470	-0.0094	-0.0147	1.9835	0.8128	-0.2000	-0.0149	-0.1012	-0.0229	-0.0267	1.6127
0.9042	-0.1386	-0.0125	-0.0411	-0.0137	-0.0191	1.9752	0.9072	-0.1209	-0.0091	-0.0616	-0.0251	-0.0294	1.6077
1.0000	0.0000	0.0000	0.0000				1.0000	0.0000	0.0000	0.0000			

Table 5. Coefficients of Redlich-Kister equation and standard deviation σ value

Binary mixtures	T/K		a_0	a_1	a_2	σ
N-EA + acetophenone	303.15	V^E ($cm^3.mol^{-1}$)	-0.8374	0.0519	-0.0619	0.001
		Δu ($msec^{-1}$)	26.0504	0.2348	-11.3951	0.040
		ΔK_s (TPa^{-1})	-18.3893	0.0668	6.7412	0.025
		Δη (mpa.s)	-0.0653	-0.0018	0.0217	0.001
N-EA + propiophenone	303.15	V^E ($cm^3.mol^{-1}$)	-0.9274	-0.0660	-0.2491	0.001
		Δu ($msec^{-1}$)	18.5789	1.2551	-10.1582	0.029
		ΔK_s (TPa^{-1})	-17.9853	-0.8721	5.5668	0.018
		Δη (mpa.s)	-0.0801	-0.0040	0.0260	0.001
N-EA + *p*-methylacetophenone	303.15	V^E ($cm^3.mol^{-1}$)	-1.1126	-0.0636	-0.4139	0.001
		Δu ($msec^{-1}$)	14.4256	-0.0129	-8.9644	0.034
		ΔK_s (TPa^{-1})	-15.3103	-0.2195	4.0008	0.024
		Δη (mpa.s)	-0.0995	-0.0024	-0.0051	0.001
N-EA + *p*-chloroacetophenone	303.15	V^E ($cm^3.mol^{-1}$)	-1.5466	-0.0105	-0.0681	0.001
		Δu ($msec^{-1}$)	30.6286	1.8786	14.0175	0.024
		ΔK_s (TPa^{-1})	-40.5916	-3.8781	-9.4150	0.015
		Δη (mpa.s)	-0.1160	-0.0124	-0.0217	0.001

ρ = density ($g.cm^{-3}$). u = Ultrasonic speed ($m.s^{-1}$). η = viscosity (mpa.s.). Δu = deviation in Ultrasonic speed ($m.s^{-1}$). K_s = isentropic compressibility (pa^{-1}). L_f = Intermolecular free length (m). Z = acoustic impedance ($kgm^{-2}s^{-1}$). ΔK_s = deviations in isentropic compressibility (TPa^{-1}). V^E = Excess molar volume ($cm^3.mol^{-1}$). Δη = deviation in viscosity (mpa.s). G^{*E} = excess Gibbs free energy of activation of viscous flow ($j.mol^{-1}$). d = Gruenberg-Nissan interaction parameter. $W_{vis}/_{RT}$ = Katti-Chaudhri interaction parameter. H_{12} = Hind interaction parameter. σ = standard deviations

thereby suggesting that dispersive forces are operative in *N*-EA+ aromatic ketones and exhibiting negative values of Δη.[19]

According to Reed and Taylor[20] positive G^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces; similarly, if d values are positive the interactions between in like molecules are strong where weak with negative values. The values of Table 4 incontrovertibly indicate that G^{*E} and d are negative for all the systems over the entire range of mole fraction. Hence, a cerebral conclusion can be made that physical forces are dominating over the chemical forces in all the systems.

Ultrasonic Speed of Sound. All the systems of (*N*-EA + aromatic ketones) show negative deviations in Ks values over the entire range of mole fraction as exhibited by Figure 3.

The value of ΔK_s can be explained in terms of dipole-dipole interactions and charge transfer complex formation between unlike molecules which leads to increase of sound velocity and decrease of isentropic compressibility. As already noted by Benson and Kiyohara[21] that the value and sigh of the deviation in isentropic compressibility, that the resultant of several opposing effects. A strong intermolecular interaction through charge transfer, dipole induced dipole and dipole-dipole interactions, interstitial accommodation and orientation ordering lead to a more compact structure which contributes to negative deviation in isentropic compressibility. The break of solvent structure mainly due to dipole-dipole association and the rupture of the hydrogen-bond liquid structure contribute positive deviation in isentropic compressibility. The more negative ΔK_s values for the system *p*-chloro acetophenone is may be ascribed due to presence of more electronegative chlorine atom.

The negative ΔK_s values decrease fall in the following order:

$$p\text{-Cl-AP} > \text{PP} > \text{AP} > p\text{-Me-AP}$$

The *p*-chloroacetophenone, propiophenone and acetophenone are perfectly in the order of their polarity based on the flexibility of conjugation. The *p*-methyl acetophenone is expected to precede the acetophenone due to its resonance effect. Hence, the above order may be justified.

A careful examination of curves in Figures 1, 2, and 3 that the V^E, ΔK_s values are negative and Δu value is positive, due to dipole-dipole interactions between unlike molecules dominates over the breaking up of the solvent molecules.[22]

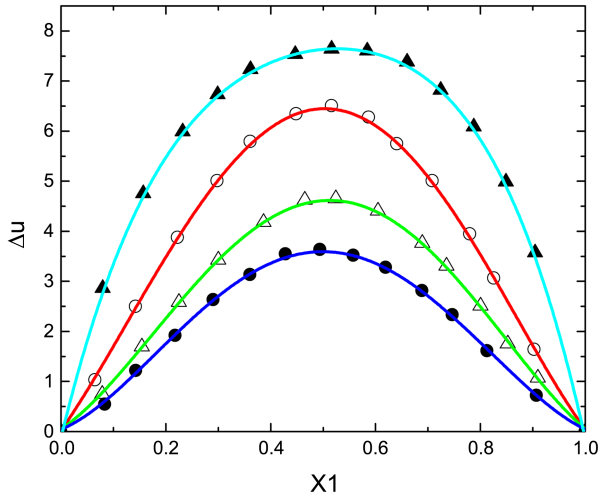

Figure 2. Variation of Δu of the binary liquid mixtures of *N*-EA with acetophenone (○), propiophenone (△) paramethylacetophenone (●) and parachloroacetophenone (▲) at 303.15 K.

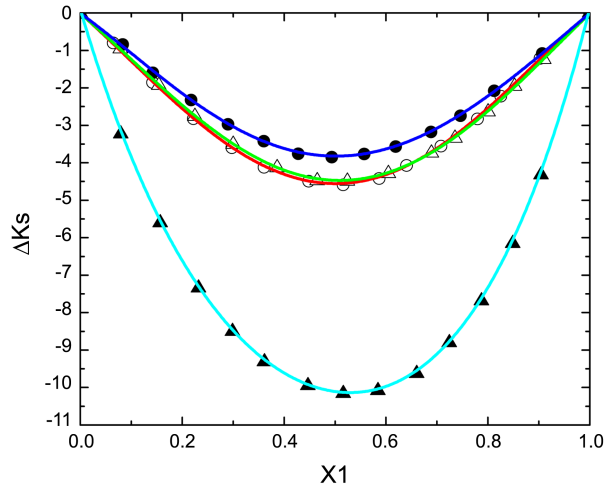

Figure 3. Variation of ΔK_s of the binary liquid mixture of *N*-EA with acetophenone (○), propiophenone (△) paramethylacetophenone (●) and parachloroacetophenone (▲) at 303.15 K.

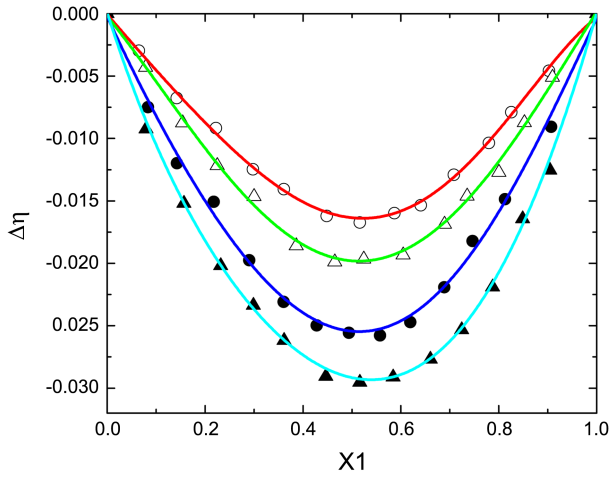

Figure 4. Variation of Δη of the binary liquid mixtures of *N*-EA with acetophenone (○), propiophenone (△), paramethylacetophenone (●) and parachloroacetophenone (▲) at 303.15 K.

Conclusions

Densities of liquid mixtures containing *N*-EA with aromatic ketones have been measured at 303.15 K. The values of the measured densities have been used to compute excess volume (V^E), viscosity, speeds of sound at the same temperature. The experimental data have been analyzed in terms of intermolecular interactions between the component molecules.

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