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Molecular Interactions in Ternary Liquid Mixture of Morpholine, Cyclohexanone and 1-Hexanol at 308.15K and 318.15K

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ABSTRACT

Densities , viscosities and ultrasonic velocities has been measured for the ternary mixture involving morpholine(1) + cyclohexanone(2) + 1- hexanol(3) at 308.15K and 318.15K over the entire range of mole fraction. Parameters like excess volume, adiabatic compressibility, free volume, linear free energy, acoustic impedance, relative association and isentropic compressibility were calculated. From these values the excess properties are also calculated. The deviations of the liquid mixture from ideality have been explained based on the molecular interaction between unlike molecules.

Key words: Density, Viscosity, Ultrasonic velocity, Adiabatic compressibility, Acoustic impedance.

INTRODUCTION

Knowledge of density, viscosity and ultrasonic velocity of liquids and liquid mixtures, both binary[1-2] and ternary[3-5], is of great importance in predicting the nature of molecular interactions between unlike molecules in industrial process. Various studies have been carried out in the recent past in predicting the nature interactions[6-8] through various thermodynamic parameters. A close study of literature shows that only few work have been done using morpholine[9-11], a liquid commonly used in petrochemical industries. In the present study the nature of molecular interaction in the ternary liquid mixture involving morpholine (1), cyclohexanone[12] (2) and 1-hexanol[13] (3) at 308.15K and 318.15K has been carried out.

MATERIAL AND METHODS

Morpholine (Merck, Mumbai), Cyclohexanone (Merck, Mumbai) and 1- hexanol (Loba Chem, Mumbai), all Analar grades, were dried using suitable drying agents and distilled based on standard methods[14]. Ternary liquid mixtures of various compositions were prepared by mixing measured amount of pure liquids in air tight stoppered bottles of 50ml capacity. Densities of pure liquids and liquid mixtures were measured by relative density method using 10ml relative density bottle with an accuracy of $\pm$ 0.001kgm^{-3}. Viscosities of all pure and liquid mixtures were measured using Ostwald viscometer of 10ml capacity with an accuracy of $\pm$0.001cP. Ultrasonic velocities of pure

and liquid mixtures were measured by a single crystal variable path interferometer (Mittal Enterprises, New Delhi, Model F-80) at a frequency of 2MHz with an accuracy of ±0.02%. All the measurements were made at both 308.15K and 318.15K with the help of a digital thermostat with a

temperature accuracy of ± 0.01K.

RESULTS AND DISCUSSION

The experimental densities (ρ), viscosity (η) and ultrasonic velocity (u) for the pure liquids

Table 1. Densities, viscosities and ultrasonic velocities of pure liquids

	Temperature (K)	Density ($10^3 Kgm^{-3}$)	Viscosity (cP)	Velocity (ms^{-1})
Morpholine	308.15	0.9863	2.0905	1410
	318.15	0.9767	1.7479	1388
Cyclohexanone	308.15	0.9312	1.6562	1358
	318.15	0.9234	1.3809	1275
1- Hexanol	308.15	0.8093	4.4983	1260
	318.15	0.8017	3.3797	1198

Table 2: Densities, viscosities, ultrasonic velocities and acoustic parameters for the ternary mixture at 308.15K

x_1	x_2	ρ ($10^3 Kgm^{-3}$)	V^E ($10^3 m^3 mol^{-1}$)	U (ms^{-1})	ϕ_1	ϕ_2	ΔKs (TPa^{-1})
0.0529	0.8469	0.9224	- 0.3760	1366	0.0438	0.8374	-18.3064
0.0527	0.4509	0.8681	-0.1572	1312	0.0405	0.4138	-15.5830
0.0502	0.2027	0.8390	-0.2130	1288	0.0369	0.1778	-14.4246
0.0489	0.6991	0.8993	-0.1528	1344	0.0393	0.6709	-18.1716
0.0972	0.8534	0.9314	-0.3309	1382	0.0820	0.8585	-22.7027
0.1025	0.0528	0.8299	-0.2618	1278	0.0747	0.0459	-11.3338
0.1477	0.7020	0.9093	-0.3621	1350	0.1231	0.6979	-9.0282
0.1532	0.5465	0.8993	-0.4423	1344	0.1241	0.5282	-23.9157
0.1488	0.2488	0.8591	-0.2622	1306	0.1139	0.2272	-19.9152
0.2001	0.0989	0.8480	-0.1339	1300	0.1516	0.0894	-21.9906
0.2492	0.7023	0.9374	-0.1781	1388	0.2155	0.7246	-22.0392
0.2485	0.5033	0.9133	-0.7744	1360	0.2064	0.4989	-31.3014
0.2492	0.2520	0.8761	-0.3627	1320	0.1973	0.2381	-22.7235
0.3492	0.5009	0.9274	-0.2348	1380	0.3007	0.5147	-28.6194
0.3515	0.2999	0.9003	-0.3981	1364	0.2911	0.2963	-44.0050
0.3967	0.0522	0.8751	-0.4265	1316	0.3182	0.0500	-23.1071
0.4512	0.4997	0.9475	-0.1782	1396	0.4037	0.5335	-21.8699
0.4975	0.3523	0.9344	-0.2253	1382	0.4393	0.3712	-25.9557
0.5010	0.1005	0.9003	-0.4948	1344	0.4208	0.1007	-30.3661
0.5002	0.2499	0.9214	-0.4465	1364	0.4329	0.2580	-27.2771
0.5998	0.0512	0.9093	-0.2295	1368	0.5172	0.0527	-41.3472
0.6483	0.3020	0.9595	-0.3216	1400	0.6005	0.3337	-18.7906
0.7014	0.1490	0.9465	-0.3866	1392	0.6417	0.1626	-28.3892
0.8478	0.1028	0.9686	-0.0757	1404	0.8144	0.1178	-12.5074

Table 2 cont….

Ra	$\Delta\eta$ cP	$\Delta L_f /$ (10^6 m)	$\Delta Z /$ (10^3Kgm^{-2}s^{-1})	$\Delta\beta_T /$ (10^{-12} K^{-1} Kg^{-1}sm^2)	$A\alpha /$ (10^{-6} K^{-1} Kg^{-1}sm^2)	$\Delta V_f /$ (10^{-8} m^{3}mol^{-1})
0.9451	0.2256	-0.2051	13.2912	-2.6767	-7.1120	-1.9510
0.9015	-0.5196	-0.0320	-10.7253	-1.2620	0.0913	-0.7106
0.8767	-0.6477	-0.0404	-7.3413	-1.2400	-0.4225	-2.2529
0.9265	-0.1607	-0.1230	-0.3754	-2.0671	-3.4825	-1.2190
0.9507	-0.3925	-0.2906	22.4625	-3.4380	-10.3820	-2.2562
0.8695	-0.3409	0.0046	-10.0593	-0.6209	1.1652	-0.1609
0.9457	0.1551	-0.0241	-5.3405	-0.8432	-0.1615	-1.8819
0.9265	-0.1085	-0.1360	-1.7024	-2.4595	-3.8836	-1.3727
0.8936	-0.2407	-0.0294	-13.8529	-1.3862	0.4163	-0.9188
0.8834	-0.0564	-0.0295	-15.7648	-1.3759	0.6662	-0.7079
0.9554	0.5070	-0.2521	16.9898	-2.9929	-8.7064	-2.4619
0.9372	0.1951	-0.2229	6.9514	-3.4724	-7.3289	-1.8985
0.9080	0.0545	-0.0188	-17.4134	-1.3995	0.9761	-1.3568
0.9470	0.3512	-0.2288	7.9074	-3.1339	-7.3348	-2.0471
0.9229	0.2744	-0.2963	4.4662	-4.4893	-9.1863	-1.7119
0.9079	0.2144	0.0599	-28.0294	-0.6769	4.2086	-1.0575
0.9638	0.4847	-0.2199	13.2213	-2.6510	-7.4242	-2.1417
0.9538	0.5686	-0.1622	0.8075	-2.4375	-4.7447	-2.2596
0.9275	0.2809	-0.0375	-20.1752	-1.7797	0.5779	-1.3564
0.9445	0.3039	-0.0925	-9.6726	-2.0509	-1.9124	-1.6917
0.9313	0.0981	-0.1751	-10.8357	-3.2107	-4.2168	-0.9666
0.9751	0.4705	-0.1622	9.1419	-2.0659	-5.4015	-1.8437
0.9638	0.4574	-0.1639	1.1340	-2.5149	-4.8901	-1.6825
0.9834	0.3246	-0.0756	0.5239	-1.0692	-2.0038	-1.2203

and ternary system are presented in Table 1, 2(308.15K) and 3(318.15K).

Adiabatic compressibility (Ks) has been calculated from Laplace's equation

$$Ks = 1/\rho u^2 \qquad …(1)$$

in which ρ and u are density and ultrasonic velocity in liquid mixture.

Acoustic impedance (Z) has been calculated by the relation[15]

$$Z= u\rho \qquad …(2)$$

Linear free energy has been calculated by Jacobson's relation[16,17]

$$Lf = K/u\rho^{1/2} \qquad …(3)$$

K is Jacobson's constant which is temperature dependent constant but independent of the nature of the liquid.

Viscosity has been calculated using the relation

$$\eta = (At - B/t)\rho \qquad …(4)$$

A and B are constants characteristic of viscometer calculated using standard liquids water and nitrobenzene, t time of flow.

Surianarayana[18] proposed a relation to calculate free volume

$$V_f = (M_{eff} \, u/K \, \eta)^{3/2} \qquad ...(5)$$

$$\beta_T = 1.71 \times 10^{-3}/(T^{4/9} u^2 \rho^{4/3}) \qquad ...(7)$$

K is a temperature independent constant which is equal to 4.28×10^9 for all liquids; M_{eff} is effective molecular weight of the mixture calculated using the relation

T is absolute temperature

Thermal expansion coefficient has been calculated using the relation

$M_{eff} = x_1 M_1 + x_2 M_2 + x_3 M_3$. Where x_1, x_2, x_3, M_1, M_2, M_3 are mole fractions and molar masses of the pure components 1,2 and 3.

$$\alpha = (0.0191\beta_T)^{1/4} \qquad ...(8)$$

Excess volume (V^E) has been calculated using the relation

Relative association has been calculated using the relation

$$V^E = ((x_1 M_1 + x_2 M_2 + x_3 M_3)/\rho) - (x_1 M_1/\rho_1) - (x_2 M_2/\rho_2) - (x_3 M_3/\rho_3) \qquad ...(9)$$

$$Ra = (\rho/\rho_1)(u_1/u)^{1/3} \qquad ...(6)$$

ρ_1, ρ_2 and ρ_3 are densities of pure components 1,2 and 3.

Isothermal compressibility has been calculated using the relation

Table 3: Densities, viscosities , ultrasonic velocities and acoustic parameters for the ternary mixture at 318.15K

x_1	x_2	ρ $(10^3 Kgm^{-3})$	V^E $(10^3 m^3 mol^{-1})$	U (ms^{-1})	ϕ_1 (TPa^{-1})	ϕ_2	ΔKs
0.0529	0.8469	0.9114	-0.0140	1332	0.0438	0.8374	-62.0006
0.0527	0.4509	0.8602	-0.1452	1292	0.0405	0.4138	-72.6803
0.0502	0.2027	0.8310	-0.1769	1268	0.0369	0.1778	-70.6928
0.0489	0.6991	0.8913	-0.1349	1316	0.0393	0.6709	-68.6069
0.0972	0.8534	0.9235	-0.3408	1350	0.0820	0.8585	-68.2149
0.1025	0.0528	0.8230	-0.3943	1262	0.0747	0.0459	-69.8797
0.1477	0.7020	0.9124	-0.4963	1334	0.1231	0.6979	-64.8808
0.1532	0.5465	0.8903	-0.3234	1312	0.1241	0.5282	-62.9351
0.1488	0.2488	0.8511	-0.2514	1286	0.1139	0.2272	-70.8277
0.2001	0.0989	0.8381	-0.1411	1274	0.1516	0.0894	-61.0710
0.2492	0.7023	0.9285	-0.1003	1358	0.2155	0.7246	-58.0651
0.2485	0.5033	0.9044	-0.6965	1330	0.2064	0.4989	-66.8717
0.2492	0.2520	0.8682	-0.3887	1308	0.1973	0.2381	-75.8492
0.3492	0.5009	0.9195	-0.2842	1344	0.3007	0.5147	-52.7498
0.3515	0.2999	0.8923	-0.4347	1318	0.2911	0.2963	-58.2294
0.3967	0.0522	0.8672	-0.4771	1304	0.3182	0.0500	-66.3588
0.4512	0.4997	0.9396	-0.2450	1364	0.4037	0.5335	-41.9088
0.4975	0.3523	0.9275	-0.4081	1360	0.4393	0.3712	-51.7650
0.5010	0.1005	0.8913	-0.4393	1316	0.4208	0.1007	-49.3565
0.5002	0.2499	0.9114	-0.2873	1332	0.4329	0.2580	-41.9415
0.5998	0.0512	0.9004	-0.2033	1328	0.5172	0.0527	-42.7344
0.6483	0.3020	0.9496	-0.2219	1364	0.6005	0.3337	-18.5187
0.7014	0.1490	0.9365	-0.2805	1362	0.6417	0.1626	-29.4531
0.8478	0.1028	0.9607	-0.2068	1372	0.8144	0.1178	0.6665

Table 3 cont….

Ra	$\Delta\eta$ cP Kg^{-1}sm^2)	ΔL_f/ (10^6 m) Kg^{-1}sm^2)	ΔZ/ (10^{3}Kgm^{-2}s^{-1})	$\Delta\beta_T$/ (10^{-12} K^{-1}	Aα/ (10^{-6} K^{-1}	ΔV_f/ (10^{-8} m^{3}mol^{-1})
0.9460	0.1576	-0.7511	48.9451	-8.9887	-2.6424	-1.6197
0.9020	-0.3583	-0.7077	32.3101	-9.7270	-2.3848	-0.2773
0.8768	-0.3395	-0.6814	29.4623	-9.6712	-2.2812	-0.1512
0.9289	-0.1477	-0.7405	41.5497	-9.4749	-2.5580	-0.5653
0.9543	0.2478	-0.8699	62.7672	-10.1712	-3.1194	-1.8078
0.8698	-0.0631	-0.6496	26.2236	-9.4957	-2.1681	-0.2257
0.9466	0.1333	-0.7339	46.0638	-9.1815	-2.5919	-1.6494
0.9288	-0.1080	-0.6100	28.5501	-8.2788	-2.0768	-0.9461
0.8938	-0.2919	-0.6172	21.3011	-9.0181	-2.0304	-0.3680
0.8830	-0.0181	-0.4633	6.7545	-7.2024	-1.4364	-0.6544
0.9576	0.3694	-0.7322	49.6453	-8.5743	-2.5993	-2.3921
0.9392	0.0990	-0.6674	35.0341	-8.9387	-2.3177	-1.6121
0.9067	0.0618	-0.6498	22.0180	-9.4444	-2.1423	-1.2690
0.9516	0.2204	-0.5551	28.7120	-7.1792	-1.9184	-1.8895
0.9295	0.2196	-0.4651	11.6433	-6.9893	-1.5193	-1.8323
0.9065	0.1891	-0.4503	2.2828	-7.4413	-1.3961	-1.0982
0.9676	0.2985	-0.5349	34.4662	-6.4185	-1.9042	-1.9288
0.9561	0.3479	-0.5459	27.9242	-7.1063	-1.8946	-2.1294
0.9289	0.2026	-0.2832	-7.2929	-5.1959	-0.8303	-1.4163
0.9460	0.1990	-0.3099	1.6524	-4.9241	-0.9781	-1.6792
0.9355	0.0788	-0.2211	-12.8670	-4.3322	-0.5947	-1.0314
0.9779	0.2268	-0.2672	13.0894	-3.4616	-0.9446	-1.5011
0.9649	0.2033	-0.2796	5.5476	-4.1326	-0.9267	-1.4009
0.9874	0.1388	-0.0895	0.2756	-1.4484	-0.3216	-0.9477

Table 4a: Adjustable parameters a, b, c and standard deviation
values for the excess acoustical values at 308.15K

Parameters	a	b	c	σ
V^E (10^3 m^{3}mol^{-1})	-14.6422	9.1755	-208.104	0.0087
ΔKs (T Pa^{-1})	-991.909	1751	-28638	0.6704
$\Delta\eta$ (cP)	1.6980	70.6521	765	0.0030
ΔL_f (m)	-5.1935x10^6	-3.5384x10^7	-1.0368x10^8	0.0039
Δz (10^{3}Kgm^{-2}s^{-1})	-160.58	5849	-7259	0.1568
$\Delta\beta_T$ (K^{-1}Kg^{-1}sm^2)	-8.9291x10^{-11}	-1.9864x10^{-10}	-2.0861x10^{-9}	0.0747
$\Delta\alpha$ (K^{-1}Kg^{-1}sm^2)	-0.1261x10^{-3}	-0.1477x10^{-2}	-0.2743x10^{-2}	0.1528
ΔV_f (m^{3}mol^{-1})	-5.2724x10^{-7}	-2.2476x10^{-6}	-2.1834x10^{-5}	0.0539

Excess adiabatic compressibility (ÄKs) has been calculated from the relation

$$\Delta Ks = Ks - (\phi_1 Ks_1 + \phi_2 Ks_2 + \phi_3 Ks_3) \qquad ...(10)$$

Ks_1, Ks_2, Ks_3 are adiabatic compressibility

**Table 4b: Adjustable parameters a, b, c and standard
deviation values for the excess acoustical values at 318.15K**

Parameters	a	b	c	σ
V^E (10^3 m^3mol^{-1})	-13.0806	-6.4433	-276.993	0.0061
ΔKs (T Pa^{-1})	-2242	2597	`-32277	3.1440
$\Delta \eta$ (cP)	0.5537	38.0996	537	0.0017
ΔL_f (m)	-2.0702×10^7	-3.0841×10^7	-3.8491×10^8	0.0298
Δz ($10^3 Kgm^{-2}s^{-1}$)	811	6709	8106	1.7147
$\Delta \beta_T$ ($K^{-1}Kg^{-1}sm^2$)	-2.9234×10^{-10}	-3.5324×10^{-11}	-5.5615×10^{-9}	0.3826
$\Delta \alpha$ ($K^{-1}Kg^{-1}sm^2$)	-0.6942×10^{-3}	-0.1468×10^{-2}	-0.0126	0.1037
ΔV_f (m^3mol^{-1})	-4.4828×10^{-7}	-1.8033×10^{-6}	-2.2824×10^{-5}	0.0362

values of pure liquids and ϕ_1, ϕ_2 and ϕ_3 are volume fraction for pure liquids calculated by the relation

$$\Phi 1 = (x_1 M_1/\rho_1)/(x_1 M_1/\rho_1 + x_2 M_2/\rho_2 + x_3 M_3/\rho_3)   ...(11)$$

Excess values of other parameters are calculated using the relation

$$A^E = A_{exp} - A_{id}   ...(12)$$

$A_{id} = \Sigma x_i A_i$, x_i and A_i are mole fraction and parameters of the ith component liquid.

All the calculated excess values were fitted to Redlich – Kister[19] type polynomial equation

$$A^E = x_1 x_2 x_3 [a+bx_1(x_2-x_3) + cx_1^2(x_2-x_3)^2]   ...(13)$$

by the method of least squares to derive the adjustable parameters a, b and c. From these a, b and c values theoretical values for all excess parameters were calculated and the standard deviation values were calculated using the relation

$$\sigma = [(A^E_{exp} - A^E_{cal})^2/(n-m)]^{1/2}$$
$$...(14)$$

here n is the number of measurements and m the number of adjustable parameters. The values of a, b, c and σ are given in the table 4a and 4b.

Excess volume values are negative over entire mole fraction values at 308.15K predicting the presence of strong intermolecular dipolar interaction[8,20] between the constituent liquids in the mixture. The interactions may be due to strong hydrogen bonding between 1-hexanol and morpholine, due to electron donor – acceptor complex formation nature of cyclohexanone and geometrical fitting between mixing liquids. Due to this volume contraction takes place. As temperature is raised to 318.15K negative value decreases, except at few mole fractions, that is value become more positive. Since at higher temperatures aggregates of pure liquids open up and move away thus decreasing the excess volume. The above nature of interaction is also predicted by the negative values of adiabatic compressibility and linear free energy values[21]. As the temperature is increased to 318.15K the adiabatic compressibility values becomes more negative. The positive values of excess viscosity at higher mole fraction of morpholine indicate that flow of this mixture is difficult as compared with pure liquids[8]. Few values are negative, at lower concentration of morpholine, indicates the easy flow of the mixture at these compositions.

Close perusal of the excess values of Z, β, α, V_f, which are all negative, also predicts the presence of strong interaction between morpholine, cyclohexanone and isoamyl alcohol at all mole fractions[22-25]. The Ra values are positive supporting strong interaction between constituent liquids predominating over hydrogen bonded interaction. At 318.15K all the excess values of Z, β, α, Vf shows a similar trend, but their corresponding values decreases, predicting a decrease in the nature of interaction at higher temperatures.

CONCLUSIONS

From density, viscosity and ultrasonic velocity, related acoustical parameters and their excess values for the ternary liquid mixtures of morpholine, cyclohexanone and 1- hexanol for various mole fractions at 308.15K and 318.15K has been studied. It is found that there predominates dipole-dipole type of interaction and donor-acceptor type of complex formation in the liquid mixture.

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