



Thermodynamic Study on Molecular Interactions in Ternary Liquid Mixture of Morpholine, Cyclohexanone and Isoamyl Alcohol at 308.15 and 318.15 K

A. ROSE VENIS^{1,*} and X. ROSARIO RAJKUMAR²

¹Department of Chemistry, St. Joseph's College (Autonomous), Tiruchirappalli-620 002, India

²Oxford Engineering College, Tiruchirappalli-620 009, India

*Corresponding author: E-mail: rosevenis@gmail.com

(Received: 5 March 2011;

Accepted: 11 November 2011)

AJC-10622

Densities, viscosities and ultrasonic velocities has been measured for the ternary mixture involving morpholine(1) + cyclohexanone(2) + isoamyl alcohol(3) at 308.15 and 318.15 K over the entire range of mole fraction. Thermodynamic parameters like excess volume, adiabatic compressibility, free volume, linear free energy, acoustic impedance, relative association and isentropic compressibility have been calculated. From these values the excess values 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 ternary³⁻⁵, 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 through various thermodynamic parameters. A close study of literature shows that only few work have been done using morpholine⁶⁻⁸, a liquid commonly used in petrochemical industries. In the present study the nature of molecular interaction in the ternary liquid mixture involving morpholine (1), cyclohexanone⁹ (2) and isoamyl alcohol¹⁰ (3) at 308.15 and 318.15 K has been carried out.

EXPERIMENTAL

Morpholine (Merck, Mumbai), cyclohexanone (Merck, Mumbai) and isoamyl alcohol (Qualigens, Mumbai), all AnalaR grades, were dried using suitable drying agents and distilled based on standard methods¹¹. Ternary liquid mixtures of various compositions were prepared by mixing measured amount of pure liquids in air tight stoppered bottles of 50 mL capacity. Densities of pure liquids and liquid mixtures were measured by relative density method using 10 mL relative density bottle with an accuracy of $\pm 0.001 \text{ kg m}^{-3}$. Viscosities of all pure and liquid mixtures were measured using Ostwald viscometer of 10 mL capacity with an accuracy of $\pm 0.001 \text{ cP}$. 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 2 MHz with an accuracy of $\pm 0.02 \%$. All the measurements were made at both 308.15 and 318.15 K with the help of a digital thermostat with a temperature accuracy of $\pm 0.01 \text{ K}$.

RESULTS AND DISCUSSION

The experimental densities (ρ), viscosity (η) and ultrasonic velocity (u) for the pure liquids and ternary system are presented in Tables 1 and 2, 2(308.15 K) and Table-3 3(318.15 K).

TABLE-1
DENSITIES, VISCOSITIES AND ULTRASONIC
VELOCITIES OF PURE LIQUIDS

	Temp. (K)	Density ($10^{-3} \text{ Kg m}^{-3}$)	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
Isoamyl alcohol	308.15	0.7981	3.7191	1220
	318.15	0.7927	2.8387	1180

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

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

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

Acoustic impedance (Z) has been calculated by the relation¹²

$$Z = \rho u \quad (2)$$

Linear free energy has been calculated by Jacobson's relation^{13,14}

$$Lf = \frac{K}{\rho u^{1/2}} \quad (3)$$

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

$$\eta = \left(At - \frac{B}{t} \right) \rho \quad (4)$$

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

Surianarayana¹⁵ proposed a relation to calculate free volume

$$V_f = \left(\frac{M_{\text{eff}} u}{K \eta} \right)^{3/2} \quad (5)$$

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

$$M_{\text{eff}} = x_1 M_1 + x_2 M_2 + x_3 M_3$$

where x_1 , x_2 , x_3 , M_1 , M_2 , M_3 are mole fractions and molar masses of the morpholine, cyclohexanone and isoamyl alcohol, respectively.

Relative association has been calculated using the relation

$$Ra = \left(\frac{\rho}{\rho_1} \right) \left(\frac{u_1}{u} \right)^{1/3} \quad (6)$$

Isothermal compressibility has been calculated using the relation

x_1	x_2	ρ (10^{-3} Kg m ⁻³)	V^E (10^{-3} m ³ mol ⁻¹)	U (ms ⁻¹)	ϕ_1	ϕ_2	ΔK_s (Tpa ⁻¹)
0.0504	0.8513	0.9193	0.0544	1358	0.0424	0.8542	-13.0583
0.0541	0.4477	0.8692	-0.4917	1298	0.0447	0.4410	-28.0999
0.0544	0.2200	0.8370	-0.2581	1258	0.0445	0.2144	-15.7571
0.0507	0.6990	0.9002	-0.1703	1350	0.0423	0.6963	-34.9969
0.0968	0.8518	0.9274	-0.1194	1370	0.0822	0.8632	-12.8266
0.0979	0.0524	0.8219	-0.2535	1244	0.0800	0.0511	-15.7043
0.1466	0.7042	0.9214	-0.5038	1362	0.1249	0.7161	-26.8357
0.1514	0.5472	0.8982	-0.2794	1340	0.1282	0.5528	-33.7627
0.1471	0.2489	0.8570	-0.3534	1292	0.1226	0.2476	-37.0029
0.2007	0.1016	0.8460	-0.3448	1268	0.1681	0.1015	-24.2242
0.2510	0.7000	0.9384	-0.2435	1378	0.2188	0.7278	-16.4455
0.2509	0.5000	0.9113	-0.4430	1356	0.2165	0.5148	-37.7084
0.2523	0.2478	0.8761	-0.4701	1300	0.2151	0.2520	-28.7679
0.3597	0.4916	0.9284	-0.1673	1372	0.3177	0.5181	-27.8210
0.3481	0.3021	0.9023	-0.5795	1344	0.3038	0.3146	-44.6858
0.4971	0.1016	0.9002	-0.4587	1350	0.4438	0.1082	-56.5892
0.5013	0.2482	0.9214	-0.3053	1362	0.4513	0.2666	-36.8585
0.5975	0.0495	0.9113	-0.3856	1356	0.5442	0.0538	-50.3281
0.6492	0.2990	0.9595	-0.2901	1396	0.6063	0.3332	-18.1328
0.7001	0.1493	0.9475	-0.3611	1386	0.6564	0.1670	-30.6532
0.8480	0.1028	0.9696	-0.1001	1400	0.8216	0.1188	-11.7141
Ra	$\Delta \eta$ (cP)	ΔL_f (10^{12} m)	ΔZ (Kg m ⁻² s ⁻¹)	$\Delta \beta_T$ (10^{12} K ⁻¹ Kg ⁻¹ sm ²)	$\Delta \alpha$ (10^6 K ⁻¹ Kg ⁻¹ sm ²)	ΔV_f (10^9 m ³ mol ⁻¹)	
0.6725	0.1605	-0.1565	6.0897	-2.2694	-5.0026	-15.5086	
0.6455	-0.6631	-0.2216	1.8102	-4.4336	-7.1700	2.8877	
0.6281	-0.6260	-0.0724	-7.3275	-2.3473	-1.8252	0.1167	
0.6598	-0.1562	-0.3727	17.1460	-5.4723	-12.6756	-7.5261	
0.6764	0.3566	-0.1675	8.7185	-2.1296	-5.4446	-21.1745	
0.6190	-0.3092	-0.0567	-7.2014	-1.8851	-1.2842	-0.7245	
0.6733	0.3003	-0.3053	15.3078	-4.1289	-9.8457	-20.6652	
0.6600	0.0234	-0.2024	7.6354	-4.9204	-9.7281	-14.1436	
0.6374	-0.2433	-0.2629	-0.1067	-5.1023	-8.1745	-6.6067	
0.6331	-0.0573	-0.0720	-14.1149	-2.7395	-1.2822	-6.2576	
0.6831	0.3818	-0.1858	11.1511	-2.4414	-6.3246	-20.6025	
0.6669	0.1821	-0.3368	12.0024	-5.2643	-11.2949	-16.5510	
0.6503	-0.0136	-0.1228	-11.9817	-3.5243	-3.0658	-10.8493	
0.6768	0.2670	-0.2412	7.1062	-3.6526	-7.7871	-17.0444	
0.6623	0.1817	-0.4302	6.0176	-5.8019	-10.9639	-14.3582	
0.6598	0.1212	-0.4020	4.7930	-6.8187	-12.8018	-9.4113	
0.6733	0.2976	-0.2480	0.0559	-4.3768	-7.6108	-15.2941	
0.6669	0.1332	-0.3181	-1.4714	-5.7227	-9.7252	-8.8039	
0.6954	0.2955	-0.1610	8.0957	-2.2199	-5.3460	-13.5460	
0.6884	0.2261	-0.2181	4.2015	-3.5382	-6.9572	-11.2708	
0.7021	0.2392	-0.0758	0.2464	-1.2398	-2.0706	-9.7053	

TABLE-3
DENSITIES, VISCOSITIES, ULTRASONIC VELOCITIES AND ACOUSTIC PARAMETERS FOR THE TERNARY MIXTURE AT 318.15 K

x_1	x_2	ρ (10^{-3} Kg m $^{-3}$)	V^E (10^{-3} m 3 mol $^{-1}$)	U (ms $^{-1}$)	ϕ_1	ϕ_2	ΔKs (Tpa $^{-1}$)
0.0504	0.8513	0.9144	-0.2580	1342	0.0424	0.8542	-74.9603
0.0541	0.4477	0.8592	-0.0726	1286	0.0447	0.4410	-78.1548
0.0544	0.2200	0.8300	-0.1373	1252	0.0445	0.2144	-68.5599
0.0507	0.6990	0.8913	0.0297	1328	0.0423	0.6963	-84.4658
0.0968	0.8518	0.9195	0.1329	1352	0.0822	0.8632	-70.1305
0.0979	0.0524	0.8150	-0.1121	1234	0.0800	0.0511	-57.7883
0.1466	0.7042	0.9104	-0.1240	1346	0.1249	0.7161	-78.6268
0.1514	0.5472	0.8893	-0.0835	1306	0.1282	0.5528	-64.1526
0.1471	0.2489	0.8511	-0.4252	1280	0.1226	0.2476	-82.6789
0.2007	0.1016	0.8391	-0.2698	1258	0.1681	0.1015	-65.3175
0.2510	0.7000	0.9295	-0.1533	1348	0.2188	0.7278	-54.8651
0.2509	0.5000	0.9030	-0.4020	1340	0.2165	0.5148	-83.1101
0.2523	0.2478	0.8692	-0.4670	1292	0.2151	0.2520	-74.8790
0.3597	0.4916	0.9215	-0.2816	1356	0.3177	0.5181	-70.7137
0.3481	0.3021	0.8943	-0.5135	1336	0.3038	0.3146	-89.1843
0.4971	0.1016	0.8943	-0.6330	1328	0.4438	0.1082	-79.3917
0.5013	0.2482	0.9154	-0.5089	1350	0.4513	0.2666	-72.6655
0.5975	0.0495	0.9034	-0.3693	1340	0.5442	0.0538	-72.6064
0.6492	0.2990	0.9496	-0.1760	1380	0.6063	0.3332	-44.8371
0.7001	0.1493	0.9365	-0.1129	1368	0.6564	0.1670	-48.9109
0.8480	0.1028	0.9597	-0.0254	1380	0.8216	0.1188	-22.2376
Ra	$\Delta\eta$ (cP)	ΔL_r (10^{12} m)	ΔZ (Kg m $^{-2}$ s $^{-1}$)	$\Delta\beta_T$ (10^{12} K $^{-1}$ Kg $^{-1}$ sm 2)	$\Delta\alpha$ (10^6 K $^{-1}$ Kg $^{-1}$ sm 2)	ΔV_f (10^9 m 3 mol $^{-1}$)	
0.8846	0.0937	-0.9360	64.5812	-1.1303	-3.3317	-9.0317	
0.8431	-0.4354	-0.8191	38.4836	-1.1686	-2.7674	7.0632	
0.8217	-0.4959	-0.6766	27.6783	-1.0188	-2.2437	6.2273	
0.8653	-0.1515	-0.9816	57.8257	-1.2622	-3.4056	0.5731	
0.8873	0.2458	-0.8851	60.9989	-1.0322	-3.1330	-16.9826	
0.8107	-0.1516	-0.5155	16.4974	-0.8122	-1.6618	-0.0177	
0.8798	0.1402	-0.9182	58.0156	-1.1415	-3.2258	-13.7772	
0.8681	-0.0191	-0.6512	30.0119	-0.9176	-2.2111	-10.4984	
0.8364	-0.1686	-0.7846	31.9749	-1.1818	-2.6237	-4.1796	
0.8294	-0.0912	-0.5212	11.2675	-0.8709	-1.6623	-4.0106	
0.8979	0.2856	-0.6426	42.7232	-0.7718	-2.2834	-19.7397	
0.8744	0.1931	-0.8763	48.7453	-1.1673	-3.0458	-16.9983	
0.8516	-0.0440	-0.6490	21.6271	-1.0154	-2.1514	-8.1196	
0.8884	0.1943	-0.7501	44.0503	-0.9618	-2.6289	-15.3579	
0.8664	0.0255	-0.8525	40.0057	-1.2057	-2.9136	-9.1726	
0.8682	0.0370	-0.6327	18.7421	-0.9966	-2.1007	-7.5936	
0.8838	0.0899	-0.6579	29.6667	-0.9356	-2.2591	-10.2468	
0.8744	-0.0499	-0.5473	12.0782	-0.8730	-1.7867	-3.7312	
0.9101	0.2127	-0.4692	29.8757	-0.5711	-1.6800	-12.8050	
0.9002	0.1352	-0.4123	15.3878	-0.5846	-1.4025	-9.9366	
0.9198	0.1256	-0.1884	7.7346	-0.2545	-0.6707	-7.8616	

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

T is absolute temperature.

Thermal expansion coefficient has been calculated using the relation

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

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

$$V^E = \left(\frac{(x_1 M_1 + x_2 M_2 + x_3 M_3)}{\rho} \right) - \left(\frac{x_1 M_1}{\rho_1} \right) - \left(\frac{x_2 M_2}{\rho_2} \right) - \left(\frac{x_3 M_3}{\rho_3} \right) \quad (9)$$

ρ_1 , ρ_2 and ρ_3 are densities of morpholine, cyclohexanone and isoamyl alcohol, respectively.

Excess adiabatic compressibility (ΔKs) has been calculated from the relation:

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

Ks_1 , Ks_2 , Ks_3 are adiabatic compressibility values of pure liquids and ϕ_1 , ϕ_2 and ϕ_3 are volume fraction for pure liquids calculated by the relation

$$\phi_1 = \frac{\left(\frac{x_1 M_1}{\rho_1} \right)}{\left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} + \frac{x_3 M_3}{\rho_3} \right)} \quad (11)$$

Excess values of other parameters are calculated using the relation

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

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

All the calculated excess values were fitted to Redlich-Kister¹⁶ type polynomial equation

TABLE-4
ADJUSTABLE PARAMETERS a, b, c AND STANDARD DEVIATION VALUES FOR
THE EXCESS ACOUSTICAL VALUES AT 308.15 K (A) AND 318.15K (B)

Parameters	A (308.15 K)				B (318.15 K)			
	a	b	c	σ	a	b	c	σ
V^E (10^6 m ³ mol ⁻¹)	-11.8305	55.2962	-427.3040	0.0016	-11.8310	55.2979	-427.3590	0.0016
ΔK_s (T Pa ⁻¹)	-12.7094	3488.94	-38858	0.8776	-2933	1286	-50828	3.6251
$\Delta\eta$ (cP)	-1.1795	62.2740	387.0380	0.0042	-1.1790	62.2693	387.0250	0.0042
ΔL_f (m)	-9.5962×10^6	1.0815×10^6	-2.8610×10^8	0.0069	-2.8509×10^7	-3.1957×10^7	-4.9803×10^8	0.0371
Δz (Kg m ⁻² s ⁻¹)	103.1940	3417.76	6674.02	0.1735	1358	6411	20389	2.1083
$\Delta\beta_T$ (K ⁻¹ Kg ⁻¹ sm ²)	-1.6796×10^{-10}	2.7674×10^{-10}	-4.5169×10^{-9}	0.1254	-4.0199×10^{-10}	5.4844×10^{-11}	-6.9250×10^{-9}	0.4845
$\Delta\alpha$ (K ⁻¹ Kg ⁻¹ sm ²)	-0.2969×10^{-3}	-0.2498×10^{-3}	-0.9590×10^{-2}	0.2309	-0.9727×10^{-3}	-0.1447×10^{-2}	-0.0171	0.1282
ΔV_f (m ³ mol ⁻¹)	-4.3724×10^{-7}	-2.3154×10^{-6}	-1.8347×10^{-5}	0.4602	-2.9092×10^{-7}	-2.5327×10^{-6}	-1.9358×10^{-5}	0.2060

$$A^E = x_1 x_2 x_3 [a + b x_1 (x_2 - x_3) + c x_1^2 (x_2 - x_3)^2] \quad (13)$$

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

$$\sigma = \left[\frac{(A_{\text{exp}}^E - A_{\text{cal}}^E)^2}{(n - m)} \right]^{1/2} \quad (14)$$

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-4.

Excess volume values are negative over entire mole fraction values at 308.15 K predicting the presence of strong intermolecular dipolar interaction^{5,17} between the constituent liquids in the mixture. The interactions may be due to strong hydrogen bonding between isoamyl alcohol 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 318.15 K negative value decreases and this 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 values¹⁸. The positive values of excess viscosity indicate that flow of this mixture is difficult as compared with pure liquids⁵. 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 , a, V_f , which are all negative, also predicts the presence of strong interaction between morpholine, cyclohexanone and isoamyl alcohol at all mole fractions¹⁹⁻²². The excess Ra values are positive supporting strong interaction between constituent liquids predominating over hydrogen bonded interaction. At 318.15 K all the excess values of Z, β , a, V_f shows a similar trend, but their corresponding values decreases, predicting a decrease in the nature of interaction at higher temperatures.

Conclusion

From density, viscosity and ultrasonic velocity, related acoustical parameters and their excess values for the ternary liquid mixtures of morpholine, cyclohexanone and isoamyl alcohol for various mole fractions at 308.15 and 318.15 K 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.

REFERENCES

- X.R. Rajkumar, K.V. Raman and S.J. Arulraj, *Proc. Indian Acad. Sci. (Chem. Sci)*, **90**, 417 (1981).
- R.J. Sengwa, V. Khatri and S. Sankhla, *Indian J. Chem.*, **48A**, 512 (2009).
- S. Thirumaran and E. Jayakumar, *Indian J. Pure Appl. Phys.*, **47**, 265 (2009).
- P. Venkatesu, B. Basa Goud and M.V. Prabhakara Rao, *Fluid Phase Equilibria*, **120**, 205 (1996).
- P. Rathore and M. Singh, *Indian J. Chem.*, **45A**, 2650 (2006).
- C. Pettenati, P. Alessi, M. Fermegila and I. Kikic, *Thermochim. Acta*, **162**, 203 (1990).
- V.G. Kozin and A.A. Mukhamadiev, *Russian J. Appl. Chem.*, **75**, 1061 (2002).
- A.M. Awwad, *J. Chem. Eng. Data*, **53**, 307 (2008).
- M. Kalidoss and R. Srinivasamoorthy, *J. Pure Appl. Ultrasonics*, **19**, 9 (1997).
- B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, *Vogel's Text book of Practical Organic Chemistry*, Longman, London, edn. 5, Ch. 2, p. 165.
- M.N. Roy, R.S. Sah and P. Pradhan, *Int. J. Thermophys.*, **31**, 316 (2010).
- P.S. Nikam and M. Hasan, *Indian J. Pure Appl. Phys.*, **24**, 502 (1986).
- B. Jacobson, *Acta Chem. Scand.*, **6**, 485 (1952).
- B. Jacobson, *J. Chem. Phys.*, **20**, 927 (1952).
- C.V. Suryanarayana, *J. Acoust. Soc. India*, **7**, 107 (1976).
- O. Redlich and A.T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
- T.S. Jyostna and Satyanarayana, *Indian J. Chem.*, **44A**, 1365 (2005).
- G.V. Rama Rao, A. Viswanatha Sarma and C. Rambabu, *Indian J. Chem.*, **43A**, 2518 (2004).
- G. Nath, S. Sahu and R. Paikaray, *Indian J. Phys.*, **83**, 429 (2009).
- S. Acharya, B.K. Das and G.C. Mohanty, *Indian J. Phys.*, **83**, 185 (2009).
- G. Subba Rao, T. Ramajappa and E. Kajagopal, *Indian J. Pure Appl. Phys.*, **26**, 717 (1988).
- A. Ali, A.K. Nain, V.K. Sharma and S. Ahmad, *Indian J. Pure Appl. Phys.*, **42**, 666 (2004).