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STUDY OF COMPARATIVE BEHAVIOR OF CERTAIN TYPICAL THERMOACOUSTICAL PARAMETERS OF BINARY MIXTURES OF CYCLOHEXANOL AND CYCLOHEXANE IN METHANOL

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Abstract:
The Literature reveals the extensive use of ultrasonic, thermodynamic and thermoacoustical parameters to characterize physico-chemical behavior of liquid mixtures and study the molecular interactions. In the present investigation an attempt has been made to evaluate and compare thermoacoustical parameters such as volume expansivity[α],Adiabatic compressibility[β_a], Isothermal compressibility[β_T], Molecular weight[M] Specific heat at constant pressure[C_p], Molar Volume[V],Reduced Volume [$\bar{v}$],Characteristic volume[v*], Internal pressure[P_i], Intermolecular energy[Φ], Change in entropy[ΔΦ] etc. of binary liquid mixtures cyclohexanol in methanol and cyclohexanol in cyclohexane for entire range of mole fraction. Experimental and computed results are used to study the type and nature of inter and intra molecular interactions between mixing components. The study of molecular interactions in liquid provides valuable information about internal structure, molecular association etc.

Keywords:- Ultrasonic velocity, Methanol, Cyclohexanol, Cyclohexane, Molecular, Interaction, Molecular association

Introduction

Amongst the four states of matter the solid and the gaseous states have been extensively studied over a long time. It is usually said that the liquid state is intermediate in its properties between a solid and a gas. This statement should not be taken to consider that every property of liquid is intermediate in value between those of the other two states. If numerical values are compared, it is found that in great majority of cases, the values of sufficient representing a property of liquid is quite close either to that of solid or to that of gas.

All theories of liquids developed so far make approximations at some stage of their development. The pair distribution method is best for low density fluids. The solid-like theories of liquid such as the cell, free volumes or partition function methods is best applied for high density fluids i.e. for small cell.

Ultrasonic parameters are being extensively used to study molecular interaction in pure liquids and liquid mixtures[1-2] Early work on non linear behavior of ultrasonic velocity versus concentration curves in different liquid mixtures have been reported by number of workers. [3-8] The empirical relation due to Nomoto [9] and ideal mixing relation [10-11] for ultrasonic velocity have been successively used to investigate the thermodynamic and acoustical behavior of binary liquid mixtures. Interactions in binary liquid mixtures have been studied by Rastogi[12], Jain[13], Hyderkhan[14], Hughes[15], Halzhauer[16], Delmos[17], Sheshadri[18], Naidu19, Tabhane [20-22] and others[23].

Adgaonkar24 studied the hydrogen bonded complex formation in number of binary liquid mixtures.

Experimental Details

The aim of the present study was to attempt to get an insight of the comparison of ultrasonic velocity, density and the thermoacoustical parameters of the binary liquid mixtures namely methanol + cyclohexanol with those of cyclohexane+ cyclohexanol . The experimental data has been generated by measuring u.s. velocity at 2Mhz using interferometer and the density in these pure liquids and their binary liquid mixtures by employing ultrasonic interferometer and hydrostatic plunger method respectively in the temperature range 10- 400c and ultra Thermostat U – 10 min of the samples constant to 0.10c. The accuracy of one part in 104 in the velocity and one part in 104 in the density measurement is achieved. The variation of u and ρ in the mixtures were found to be linear with temperature and hence the method of least square was applied and the values of u and ρ at different temperatures were calculated from the equations 2 and 3 given below. The thermodynamic parameters are calculated for

very small concentration 0.1, 0.2, 0.3..... 1.0 of the two pure liquid components in a given binary liquid mixture of the two components. The result and discussion of the experimental and theoretical investigation on above mentioned systems is presented in comparative manner.

Calculation of Ultrasonic and Thermoacoustical Parameters

1) U.S.Velocity $v = \lambda f$

The values of u and density ρ were used to obtain the

coefficients of following polynomial

2) U S velocity $u = uo + [du/dT] T=0$

3) Density $P = \rho 0 + [d\rho/dT] T=0$

4) Volume expansivity $\alpha = 1/\rho [d\rho/dT]$

5)Adiabatic compressibility $\beta_a = 1/u^2 \rho$

6)Isothermal compressibility $\beta_T = TV\alpha^2/C_p + \beta_a$

7)Molecular weight $M = (1-x) M_1 + xM_2$

8)Specific heat at constant pressure

$C_p = (1-x) C_{p1} + C_{p2}$

9)Molar Volume $V = M/\rho$

10)Reduced Volume $\bar{v} = [(1+4\alpha T)/1 + \alpha T]^{1/3}$

11)Characteristic volume $v^* = v/\bar{v}$

12)Internal pressure $P_i = \rho u^2/(B/A + 1)$

13)Intermolecular energy $\Phi = P_i.v$

14) Change in entropy $\Delta\Phi = \alpha(v- v^*)/B_T$

Table No. 1 : The values of experimentally measured u.s. velocity [Uexpt.] and density [ρ expt], [du/dt] ,[dρ/dt] of systems Methonol + Cyclohexanol and Cyclohaxane+Cyclohexanol at temperature 303.15^{0}K. [u x cm-sec^{-1}, ρ x gm cc^{-1}]

Result and Discussion

A) Methanol + Cyclohexanol :-

It is found that U.S.velocity u, density ρ increase with the increase in mole fraction x. Whereas adiabatic compressibility β_a and isothermal compressibility β_T decrease with the increase in mole fraction x. The characteristic volume v* increases with the increase in mole fraction x.The trend of variation of reduced volume $\bar{v}$ shows overall decrease with the increase in mole fraction x. Variation of internal pressure P_i increases with increase in mole fraction x.

B) Cyclohexane + cyclohexenol :-

The trend of variation of α, β_a, β_T and $\bar{v}$ is opposite to that of velocity u and ρ. The internal pressure P_i rises to highest at 5:5 molar ratio It remains constant for molar ratio 9:1 to 8:2 and also for molar ratio from 2:1 to 1:9. Intermolecular energy Φ of the liquid remains constant from 9:1 to 8:2 molar ratio. It falls at 7:3 and further shows steady rise with the rise in molar concentration of the solute. The characteristic volume **V *** shows a steady rise with increase in mole fraction x.

Table 1

Methonol + Cyclohexanol					**Cyclohaxane+Cyclohexanol**			
Cm	**u**	**du/dt**	**ρ**	**dρ/dt**	**u**	**du/dt**	**ρ**	**dρ/dt**
0	1101.15	-3.018	0.780893	-0.8723	1248.3	-4.68	0.765683	-0.8367
0.1	1169.7	-3.028	0.817368	-0.7653	1251.1	-4.4	0.784603	-0.8959
0.2	1222.83	-3.151	0.848275	-0.757	1263.55	-4.526	0.798808	-0.8557
0.3	1269.88	-3.337	0.868193	-0.6443	1281.85	-4.458	0.81931	-0.8596
0.4	1304.88	-3.153	0.881323	-0.6431	1300.65	-4.198	0.835345	-0.7582
0.5	1347.73	-3.319	0.899548	-0.5861	1230.35	-4.102	0.854888	-0.7565
0.6	1368.27	-3.305	0.891408	-0.6197	1300.65	-4.198	0.835345	-0.7582
0.7	1395.57	-3.413	0.9167	-0.64	1281.85	-4.458	0.81931	-0.7596
0.8	1418.4	-3.508	0.924848	-0.6781	1263.55	-4.526	0.798888	-0.8557
0.9	1433.28	-3.361	0.930468	-0.6333	1251.1	-4.4	0.784603	-0.8959
1	1483.83	-6.459	0.937075	-0.661	1483.83	-6.459	0.937075	-0.661

Table 2 : Some physical parameters (Input data) for pure liquid at 303.15 k.

Liquids	Molecular Weight	Density ρ kg/m^3	U.S. velocity m/s	βε	σ A^0
Methanol	32.04	0.7765	1086.07	28.471	3.832
Cyclohexanol	101.16	0.9338	1451.6	48.68	5.794
Cyclohexane	84.14	0.7615	1225.1	43.08	5.680

Table 3 : some Thermo acoustical parameters SYSTEM A-METHANOL + CYCLOHEXANOL

CM	α	$BaX10^{-11}$	B_TX10^{-11}	M	C_pX10^9	V	v̄	V *	Pi	$ΦX10^{11}$	$ΔΦX10^8$
0.0	0.001117	10.5610	12.432	32.040	0.81574	41.03	1.2711	32.2787	0.8057	1.0987	0.7864
0.1	0.000936	8.9420	10.309	38.952	0.91062	47.655	1.2344	38.6062	0.8749	1.2898	0.8219
0.2	0.000892	7.8837	9.1598	45.864	1.0055	54.067	1.2251	44.1322	0.9638	1.5697	0.9679
0.3	0.000742	7.1426	8.0492	52.776	1.1004	60.788	1.1923	50.9867	0.9636	1.6781	0.9037
0.4	0.000738	6.6638	7.5629	59.688	1.1953	67.725	1.1895	56.9382	1.0190	1.9473	1.041
0.5	0.000652	6.1203	6.8463	66.00	1.2902	74.037	1.1716	63.1952	1.0370	2.0997	1.032
0.6	0.000695	5.9921	6.8497	73.518	1.3851	82.467	1.1816	69.7918	1.0970	2.4942	1.286
0.7	0.000698	5.6011	6.4621	80.424	1.4799	87.732	1.1823	74.2048	1.1720	2.8246	1.461
0.8	0.000733	5.3744	6.3351	87.336	1.5748	94.433	1.1902	79.3389	1.2510	3.2578	1.747
0.9	0.000681	5.2317	6.0691	94.248	1.6697	101.291	1.1783	85.9651	1.2320	3.3851	1.719
1.0	0.000785	4.8469	5.7540	101.160	1.7646	107.953	1.1839	91.1807	1.3500	3.9438	2.056

Table 3 SYSTEM B-CYCLOHEXANE + CYCLOHEXANOL

CM	α′	$B'a X 10^{-11}$	$B'_T X 10^{-11}$	M′	$C'_p x 10^9$	V′	v̄′	V*′	$Pi' X 10^9$	$Φ'X10^{11}$	$ΔΦ'X10^8$
0.0	0.001093	8.3813	10.9490	84.140	1.5229	109.889	1.2663	86.7788	0.9720	3.2683	2.3060
0.1	0.001142	8.1427	10.8900	85.842	1.5471	109.408	1.2760	85.7449	1.0150	3.4185	2.481
0.2	0.001071	7.8410	10.2260	87.544	1.5713	109.593	1.2620	86.8395	1.0290	3.4211	2.384
0.3	0.000927	7.4281	9.1769	89.246	1.5954	108.928	1.2325	88.3820	1.0240	3.2794	2.076
0.4	0.000988	7.0764	8.7267	90.948	1.6196	108.875	1.2284	88.6342	1.0630	3.3745	2.105
0.5	0.000885	6.7099	8.2484	91.650	1.6438	108.377	1.2235	88.5774	1.1060	3.4648	2.154
0.6	0.000908	7.0764	8.7389	94.352	1.6679	112.950	1.2284	91.9516	1.0620	3.4959	2.181
0.7	0.000927	7.4281	9.2028	96.854	1.6921	117.238	1.2325	15.1241	1.0230	3.5196	2.228
0.8	0.0001071	7.8410	1.0279	97.756	1.7163	122.377	1.2620	96.9694	1.0270	3.8004	2.248
0.9	0.001142	8.1427	1.0973	99.458	1.7404	126.762	1.2760	99.3455	1.0120	3.9311	2.853
1.0	0.000705	4.8469	5.7540	101.168	1.7646	107.953	1.1839	91.1807	1.3500	3.9438	2.056

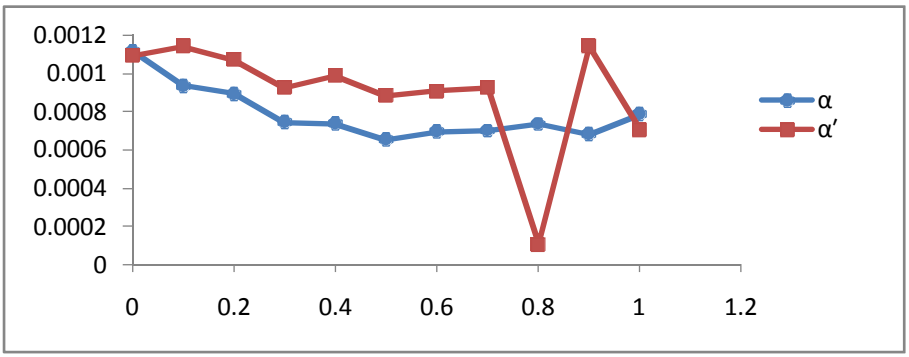

Figure 1: variation of α and α′ in system A and B

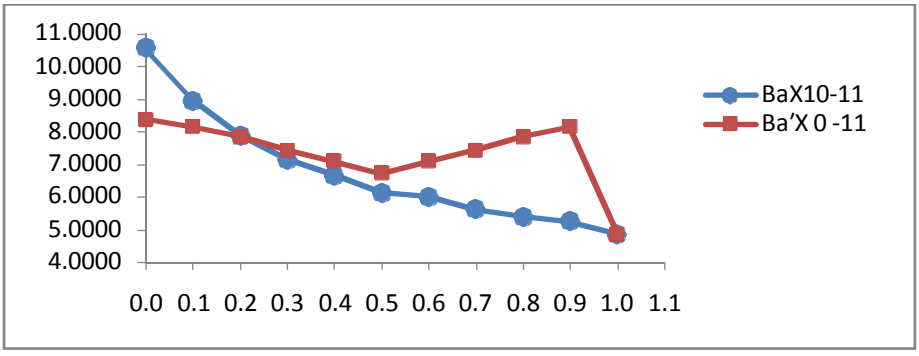

Figure:2 : variation of Ba X 10^{-11} and B′a X 10^{-11} in system A and B .

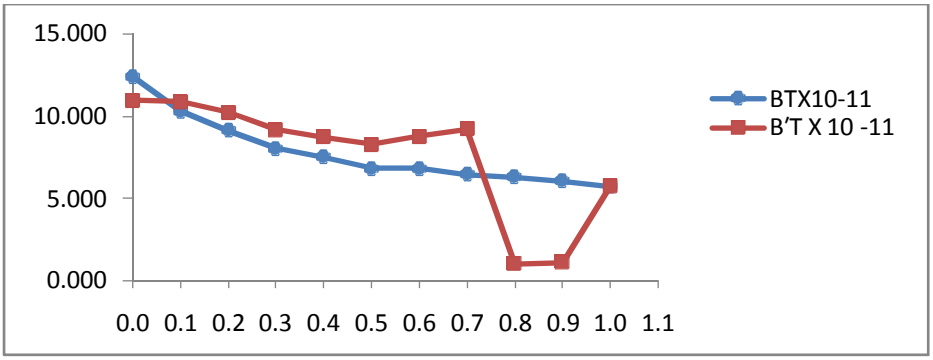

Figure:3 : variation of $BTX10^{-11}$ and $B'_T X 10^{-11}$ in system A and B .

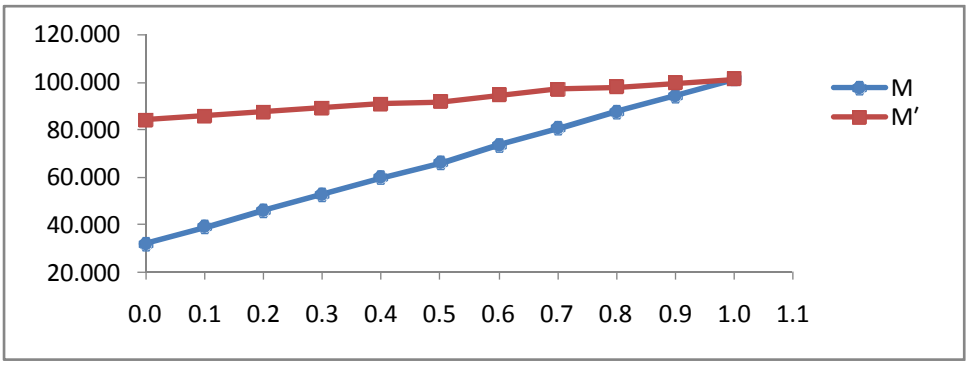

Figure:4 : variation of M and M′ in system A and B .

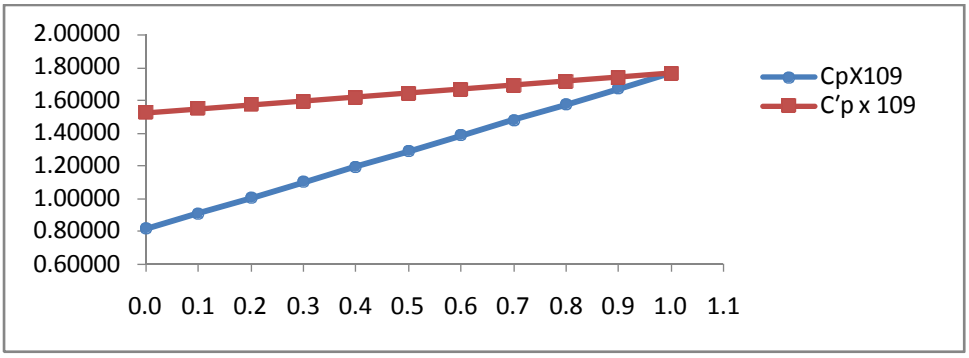

Figure:5 : variation of $CpX10^{9}$ and $C'p \times 10^{9}$ in system A and B .

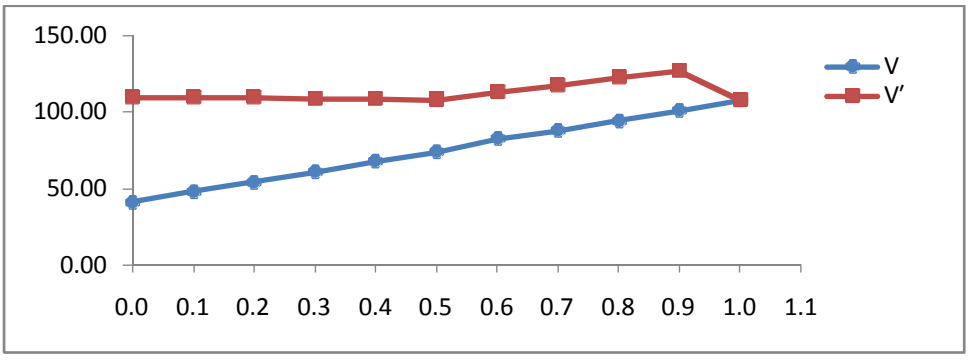

Figure:6 : variation of V and V′ in system A and B .

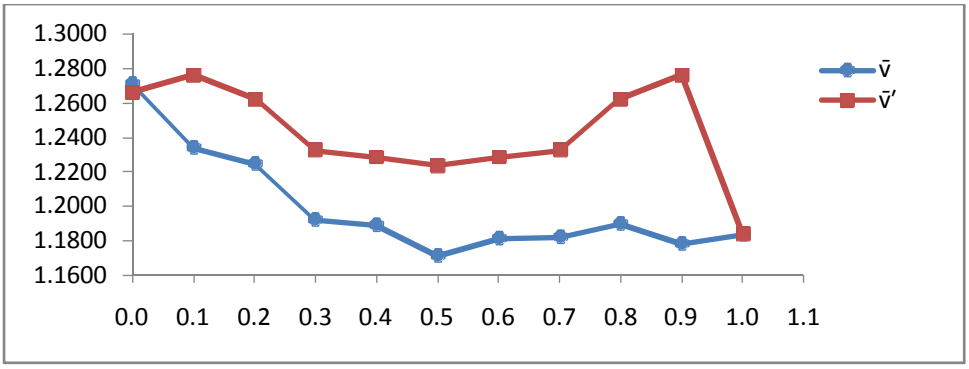

Figure:7 : variation of $\bar{V}$ and $\bar{V}'$ in system A and B .

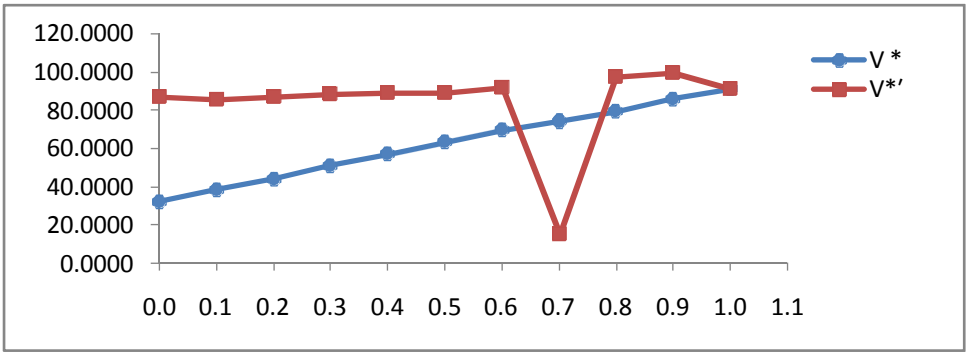

Figure:8 : variation of V * and V *′ in system A and B .

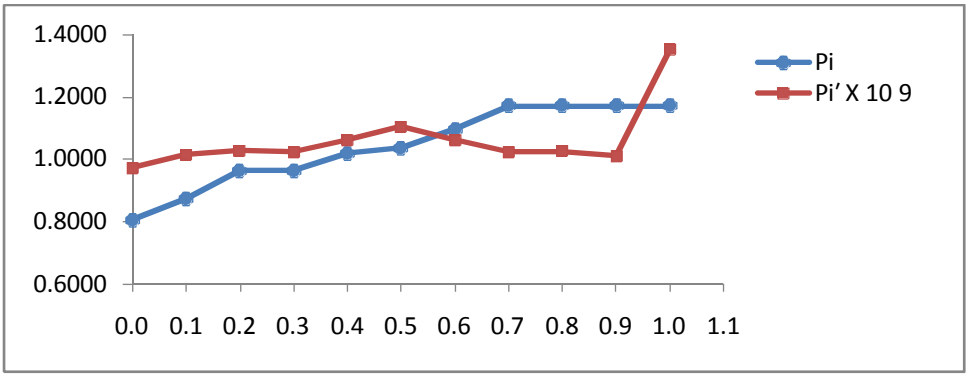

Figure:9 : variation of Pi and Pi′X10^{9} in system A and B .

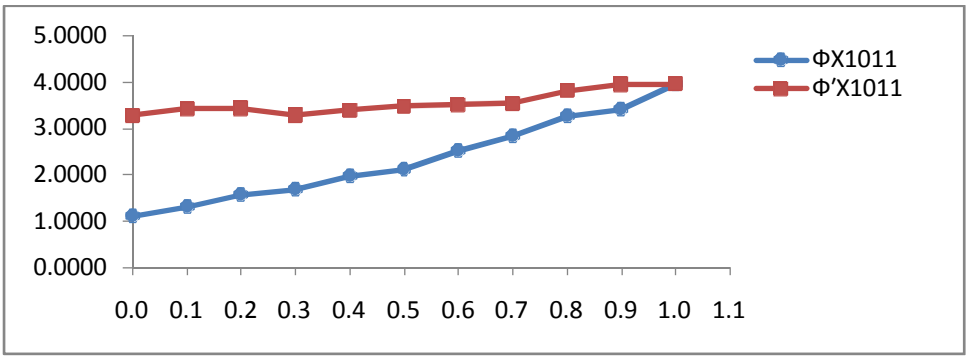

Figure:10 : variation of ΦX10^{11} and Φ′X10^{11} in system A and B .

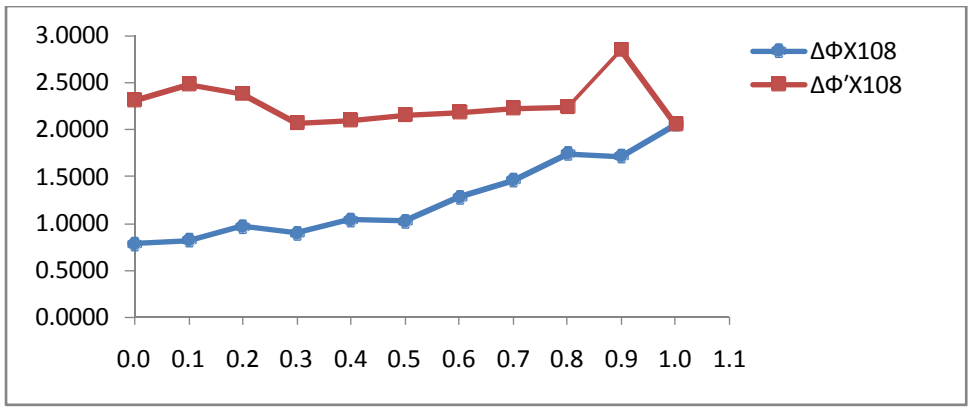

Figure 11 : Variation of $\Delta\Phi X10^8$ and $\Delta\Phi' X10^8$ in system A and B .

Conclusion

In methanol + cyclohexanol an appreciable AB interaction is strong associative nature. The AB interaction of methanol with cyclohexanol results in breaking up the cyclohexanol cluster. The peaking of variation towards the higher concentration of cyclohexanol indicates AB interaction to be stronger than the strength of BB and AA interaction. In cyclohexane + cyclohexanol , cyclohexane is the non associative liquid while cyclohexanaol is the associative liquid due the presence of OH- goup in the later. The associative nature of the liquid may manifest in the form of demarization process due to the possibility of H- bond between H of cyclohexane and OH of cyclohexanol.

References

[1] Murthy N M, Sivkumar, Rajgopal E, & Subrmanium S V Acustica, 48 (1981)341

[2] Reddy R R, Reddy P M, & Murthy N M, Acoustic Leff, 10 (1987) 128

[3] Kannapan A N Rajendra V, Indian J pure & applied Physics, 29(1991) 465

[4] Blokhra R L & Awasthi Aruna, Indian J pure & applied Physics, 30 (1992) 760

[5] Sukla B P, Indian J pure & applied Physics 30 (1992) 754

[6] Vasumathi V & Subranium B & Shobhndri J, J pure & applied Ultrasonics, 15 (1993) 106

[7] Padmashree C & Ravindra Prasad K, Indian J pure & applied Physics 32 (1994) 954

[8] Chauhan S & Syal V K & Chauhan M S, Indian J pure & applied Physics, 33 (1955) 92

[9] Nomoto O J, J of Phys Chem, 13 (1958) 1523

[10] Reddy K G , Subramanium S V & Bhimsenachar J, Trans Far Soc, 68 (1962) 2352

[11] Van Dael W & Vanged E, Proc of the first International conference on colorimetric & T hermodynamics, Warsaw, 955 (1969); Van Dael W Thermodynamic properties and velocity of sound, Chap 5, Butterworth (London) (1975)

[12] Rastogi R P, Jagnnath & Mishra V, J Phys Chem 71 (1967) 1277

[13] Jain D V S, Gupta V K & Lark B S, Indian J Chem, 8 (1970) 815

[14] Hyderkhan V & Subramanium S V, Trans Far Soc, 67 (1971) 815

[15] Hyghes M & Low D R J, Proc Roy Soc (London) 267 A (1962) 384.

[16] Halzauer & Zeigler W T , J Phys Chem, 79 (1975) 590

[17] Delmas G & Turreless, Trans Far Soc , 70 (1974) 572

[18] Sheshadri K , Prabhakar N & Reddy K C , Z Phys Chemie, (Nevie, Folge), 89 (1974) 109

[19] Naidu P R & Krishnan V C , J Phys Soc (Japan) 30 (1965) 1554

[20] Tabhane V A & Patki B A, Nuclear Phys & Solid State Phys Symp. 24C (1981) 131; Acustica, 52(1982) 44; Indian J Pure & Applied Phys, 21 (1983) 155; Nuclear Phys & Solid State Phys symp. 26C (1983) 487; Indian J Pure Applied Phys, 22 (1984) 447; Indian J Pure 7 Applied Phys, 23(19850 58.

[21] Tabhane V A, Acoustic Lett,6(1983)120.

[22] Tabhane V A, Pendse V N & Patki B A, Acustica, 44(1980) 233.

[23] Singh D P & Bhatti S S, Acustica 56(1984) 244.

[24] Adgaonkar C S, Deogaonkar V S & kadu P D, Indian J Pure & Applied Phys, 15 (1977) 98.