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Molecular Interaction Studies Using Excess Thermodynamic Function in the Binary Mixtures of Cyclohexanol with Bromo, Chloro and Nitro Substituted Benzenes

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The molecular interactions operating in polar liquid mixtures can be studied conveniently by non-spectral methods, namely, excess thermodynamic quantities, as it reflects the solution dynamics and hence helps to understand the type and nature of molecular interactions. Molar excess volume, excess viscosity, Gibbs' free energy change of viscous flow, interaction parameter and interaction energy for the binaries of bromobenzene, chlorobenzene and nitrobenzene with cyclohexanol at selected compositions were determined from the measured values of density and viscosity of pure liquids and their binaries at 303.15 K. FT-IR spectra at chosen composition of titled binaries were recorded with a view to substantiate the conclusion obtained from excess function investigations. Besides, an attempt is made to discern how the substituents present in the solvent molecule affect the solute-solvent interactions by different functional groups of polar aromatic compounds.

INTRODUCTION

The nature of molecular interaction[1,2] in pure liquids and liquid mixtures of non-electrolytes can be understood in terms of excess thermodynamic functions. Attempts were made by several workers[3–6] to evaluate excess thermodynamic quantities to gain more insight into the solution behaviour. The deviation of excess thermodynamic quantities from that expected for ideal behaviour may be directly correlated to the nature of molecular interactions operating in liquid mixtures[7] besides providing a check on different models of solution theory. The possible interactions, most often one encounters in liquid and liquid mixtures, are the familiar charge transfer complexation, loose association and hydrogen bonds arising from dipole-dipole, dispersion and dipole-induced dipole interactions. The present study has been undertaken to understand the type of interactions in the binary mixtures of cyclohexanol (CHL) with bromobenzene (BBE), chlorobenzene (CBE) and nitrobenzene (NBE) besides the effect of functional groups (-Br, -Cl, -NO_2) on the nature of molecular interactions.

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EXPERIMENTAL

The liquids cyclohexanol, bromobenzene, chlorobenzene and nitrobenzene (Qualigens Fine Chemicals, India) are LR grade and they were purified as reported elsewhere[8]. Binary liquid mixtures of cyclohexanol with bromobenzene, chlorobenzene and nitrobenzene were prepared with cyclohexanol concentration (X_2) ranging from 0 to 1 mole fraction. The IR spectrum was recorded for each of the binaries at a concentration of 0.3 molefraction of cyclohexanol using FTIR Spectrometer (Shimadzu, Japan). The densities and viscosities of pure liquids and binary mixtures were determined using volume dilatometer and Ostwald's viscometer respectively. The temperatures of pure liquids and binary mixtures were maintained constant within ±0.1 K using a constant temperature water bath (INSERF, India). The accuracy in the measurement of density and viscosity are ±2 parts in 10^{-5} kg/m^3 and 0.1% respectively.

The excess quantities such as excess volume, excess viscosity, Gibbs' excess energy change for viscous flow, the interaction parameter and interaction energy are evaluated using the following expressions:

$$V^E = V_{obs} - V_{cal} \tag{1}$$

where $V_{obs} = \dfrac{X_1M_1 + X_2M_2}{\rho_{12}}$ and $V_{cal} = \dfrac{X_1M_1}{\rho_1} + \dfrac{X_2M_2}{\rho_2}$

$$\eta^E = \eta_{cal} - \eta_{obs} \tag{2}$$

where $\eta_{cal} = (X_1\eta_1 + X_2\eta_2)$

$$\Delta G^{*E} = \Delta G_{12} - (X_1\Delta G_1 + X_2\Delta G_2) \tag{3}$$

where $\Delta G_{12} = RT\ln\left[\eta_{12}\dfrac{(X_1M_1 + X_2M_2)}{Nh\rho_{12}}\right]$

$$d = \frac{1}{X_1X_2}[\ln\eta_{12} - (X_1\ln\eta_1 + X_2\ln\eta_2)] \tag{4}$$

where $M_1, M_2, X_1, X_2, \rho_1, \rho_2, \rho_{12}, \eta_1, \eta_2, \eta_{12}, \eta_{obs}$ are molecular weight, molefraction, density and viscosity of the components 1 and 2 and their mixtures respectively, d is the interaction parameter and ΔG^* is the Gibbs' free energy change for viscous flow. The interaction parameter was calculated using Grunberg-Nissan equation[9] and ΔG^* by Eyringe equation[10].

RESULTS AND DISCUSSION

The experimental values of excess volume, excess viscosity, excess Gibbs' free energy change for viscous flow and the interaction parameter for all the binaries are given in Table-1. The variation of V^E and η^E with the composition of cyclohexanol in molefraction (X_2) are shown in Figures 1 and 2. The excess volume and the excess viscosity data are fitted to the following polynomial equation by the method of least squares.

$$V^E \text{ or } \eta^E = X_1X_2[A_0 + A_1(2X_2 - 1) + A_2(2X_2 - 1)2 + \ldots + A_n(2X_2 - 1)^n] \tag{5}$$

TABLE-1

EXCESS VOLUME (V^E), EXCESS VISCOSITY (η^E), EXCESS GIBB'S FREE ENERGY CHANGE FOR VISCOUS FLOW (ΔG^{*E}) AND THE INTERACTION PARAMETER (d) FOR ALL THE SYSTEMS STUDIED AT 303.5 K

System	X_2	$V^E \times 10^7$ $m^3\ mol^{-1}$	$\eta^{-E} \times 10^3$ $N\ s\ m^{-2}$	ΔG^{*E} $J\ mol^{-1}$	d
	0.1	2.141	–0.366	–0.718	–3.189
	0.2	2.556	–0.722	–1.236	–3.080
Bromobenzene	0.3	3.297	–1.071	–1.686	–3.201
+	0.5	4.682	–1.724	–2.293	–3.645
Cyclohexanol	0.6	6.819	–1.999	–2.354	–3.918
	0.8	–0.174	–2.242	–1.949	–4.831
	0.9	–0.813	–1.979	–1.476	–6.457
	0.1	0.779	–0.364	–0.569	–2.512
	0.2	1.184	–0.729	–1.233	–3.006
Chlorobenzene	0.3	1.139	–1.084	–1.714	–3.224
+	0.5	1.658	–1.744	–2.259	–3.529
Cyclohexanol	0.6	1.139	–2.026	–2.327	–3.853
	0.8	–0.696	–2.210	–1.709	–4.233
	0.9	–0.879	–1.911	–1.275	–5.614
	0.1	4.144	–0.317	–6.913	–3.093
	0.2	4.683	–0.711	–1.231	–3.081
Nitrobenzene	0.3	5.836	–1.043	–1.631	–3.109
+	0.5	6.545	–1.673	–2.208	–3.521
Cyclohexanol	0.6	4.527	–1.992	–2.258	–3.751
	0.8	1.993	–2.130	–1.863	–6.634
	0.9	–1.879	–1.879	–0.460	–6.273

Here A_n (n = 0–4) are adjustable parameters. In Figures 1 and 2, the experimental points are shown as dark circles while the continuous line drawn by fitting the experimental data to the above polynomial equation. The adjustable parameters estimated for the three binaries studied are given in Table-2. The liquid cyclohexanol, bromobenzene, chlorobenzene and nitrobenzene have high boiling points with appreciable dipole moments. The Trouton's constant for CHL, BBE, CBE and NBE are 25, 21.1, 21.6 and 20.13 kcal mol^{-1} respectively. The high value of Trouton's constant for cyclohexanol indicates that CHL is highly self-associated through hydrogen bonding and its dimerisation energy is expected to be high when compared to other liquids. The dipole-dipole interaction energy is theoretically computed at different bond distances for the binaries using the

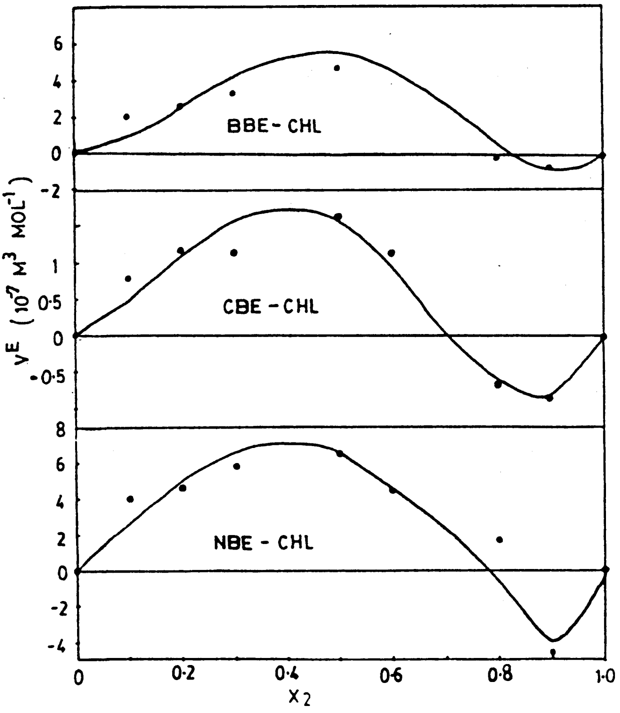

Fig. 1. Excess volume as a function of mole fraction of cyclohexanol

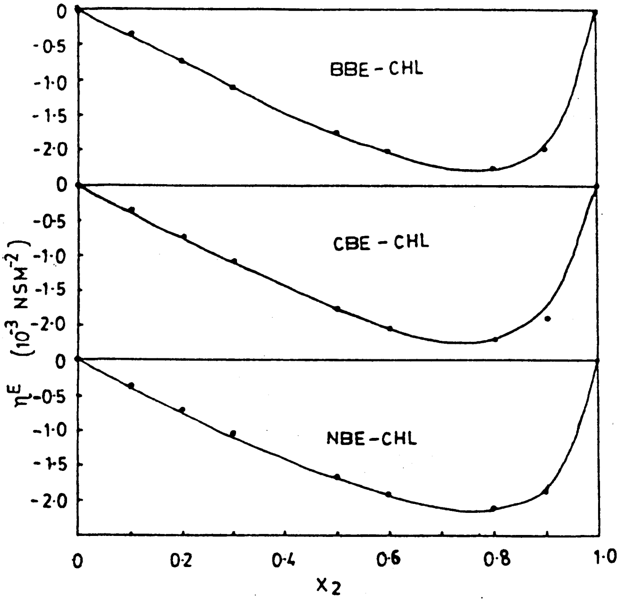

Fig. 2. Excess viscosity as a function of mole fraction of cyclohexanol

equation reported elsewhere[11] and are given in Table-3. The magnitude of the interaction energy is in the order BBE-CHL < CBE-CHL < NBE-CHL indicating significant molecular interaction in NBE-CHL and low for BBE-CHL system compared to other binaries. From Figure 1, it can be seen that the excess volume, V^E, for all the systems studied shows positive deviation at lower composition of CHL and negative deviation at higher composition of CHL. For the NBE-CHL and CBE-CHL systems, the positive deviation of V^E was found to be maximum at $X_2 = 0.4$ molefraction whereas for BBE-CHL system it occurs at $X_2 = 0.5$ molefraction. The maximum negative deviation of V^E for all the binaries occurs at $X_2 = 0.9$ molefraction of CHL. This type of variation of V^E generally indicates the operation of weak interactions between the components of the mixture. The observed positive and negative deviations of V^E for the above binaries may be explained as follows. The dipolar self-association of liquids, *viz.*, BBE, CBE and NBE may be weak compared to CHL due to their low values of dipole moment, dielectric constant and Trouton's constant. But when highly associated CHL molecules enter the solvent the possible effects are self-dissociation of hydrogen bonds in CHL molecules leading to expansion of volume and dipole-dipole, dipole-induced dipole, dispersion interactions, hydrogen bonded interactions and charge transfer complexation between the unlike molecules may also lead to expansion in volume[12] provided such interaction does not lead to compact structure. The actual value of V^E at lower concentrations of CHL may be due to the former effect and the negative deviation of V^E may be due to considerable decrease in the interplay of both effects. Among the three binaries, the maximum negative deviation of V^E is found for NBE-CHL system and is minimum for BBE-CHL system, while CBE-CHL lies in the intermediate range. This is in accordance with the dipole-dipole interaction energy computed for the above binaries. A close examination of the excess volume-composition profiles exhibits a typical sigmoidal behaviour. At low concentration of CHL, V^E is positive and becomes negative at fairly high concentration. The experimental results probably suggest that at lower concentation of CHL loss of dipolar association both for the solvent and the solute molecules occurs resulting in pronounced expansion of volume with simultaneous intermolecular hydrogen bonding[13–16] between unlike molecules. This is obvious as Br-, Cl- and NO_2- groups of benzene form hydrogen bonds with OH- group of cyclohexanol. At fairly appreciable concentration of CHL, V^E decreases and ultimately becomes negative. That is, presumably dipolar interactions may be dominant which entail complexation or loose association resulting in decrease in volume. This can be achieved by hydrogen bonded interactions. Further it also signifies operation of unlike specific interactions between the components. The presence of hydrogen bonding in these binaries has further been confirmed from the IR spectral studies. The stretching frequency of O—H bond ν(OH) is monitored and for CHL it occurs at 3344 cm^{-1} suggesting polymeric hydrogen bonding, while for the binaries BBE-CHL, CBE-CHL and NBE-CHL it is observed at 3376, 3408 and 3392 cm^{-1} respectively thus suggesting intermolecular hydrogen bonds between solvent and solute molecules. This lends additional credence for the excess volume studies.

TABLE-2
THE FITTED PARAMETERS FOR EXCESS VOLUME AND EXCESS VISCOSITY FOR ALL THE THREE SYSTEMS STUDIED AT 303.5 K

Bromobenzene +	$V_0 = 2.406$	$V_1 = 0.426$	$V_2 = -6.667$	$V_3 = -4.043$	$V_4 = 6.298$
Cyclohexanol	$\eta_0 = -7.037$	$\eta_1 = -4.372$	$\eta_2 = -1.955$	$\eta_3 = -10.559$	$\eta_4 = 11.582$
Chlorobenzene +	$V_0 = 6.398$	$V_1 = -5.033$	$V_2 = -1.922$	$V_3 = -1.049$	$V_4 = 1.324$
Cyclohexanol	$\eta_0 = -7.124$	$\eta_1 = -4.502$	$\eta_2 = -1.913$	$\eta_3 = -9.633$	$\eta_4 = 10.743$
Nitrobenzene +	$V_0 = 2.105$	$V_1 = 2.574$	$V_2 = 5.185$	$V_3 = -13.386$	$V_4 = 14.145$
Cyclohexanol	$\eta_0 = -6.830$	$\eta_1 = -4.019$	$\eta_2 = -1.579$	$\eta_3 = -10.075$	$\eta_4 = -11.259$

TABLE-3
CALCULATED VALUES OF INTERACTION ENERGY AT DIFFERENT BOND DISTANCES FOR THE THREE SYSTEMS STUDIED AT 303.5 K

Bond distance R (nm)	Interaction energy (V) kJ mol^{-1}		
	BBE-CHL	CBE-CHL	NBE-CHL
0.150	–666.7	–721.1	–4646.7
0.200	–118.7	–128.3	–827.0
0.250	–31.1	–33.6	–216.8
0.300	–10.4	–11.3	–72.6
0.350	–4.1	–4.5	–28.8

Although several models for the theory of liquids were proposed but the accepted current models[17–22] fairly explain the liquid structure and the processes that occur in them.

The variation of excess viscosity η^E with the concentration of CHL is shown in Figure 2. Examination of the plots reveals that all the systems exhibit negative deviation. This may be explained as follows. In BBE-CHL system, the viscosity becomes increasingly greater with increasing concentration of CHL. This may be due to the possibility that CHL molecule can form clathrate-like structure having large hollow cavities or channels to accommodate BBE molecule in the interstitial space with simultaneous hydrogen bond formation resulting in the lowering of viscosity than the expected theoretical value. As the concentration of CHL increases, the viscosity increases because there is a competitive intermolecular hydrogen bond formation between free CHL and BBE, CBE and NBE molecules. The result of these two opposing processes may lead to net negative excess viscosity[4, 5]. The same explanation also holds good for the other two binaries, namely, CBE-CHL and NBE-CHL.

The Gibbs' free energy change for viscous flow and the interaction parameter are negative for all the systems over the entire concentration range which are indicative of weak hydrogen bond effects. This points out the interplay of hydrogen bonded effects besides appreciable specific and unlike dispersion interaction between the components of the binaries. The trend in the loose hydrogen bonding tendency increases in the order BBE-CHL < CBE-CHL < NBE-CHL. Thus with introduction of systematic increasing polar nature of functional groups in the benzene moiety, the molecular interaction with cyclohexanol is in the same order as one would expect. Thus the present investigations for the titled binaries probably point out that for NBE-CHL system the molecular interaction is quite appreciable while for the other two systems this is of significant interaction and for all the three, hydrogen-bonded effects are the principal contributing factors for molecular interactions. This conclusion is supported by IR evidence. Besides, high values of dielectric constant and dipole moment of components enhance the strength of molecular interactions in binary liquid mixtures.

REFERENCES

1. H. Ratzack and Thomas W.H. Orville, Molecular Interactions, Vols. I, II and III, Wiley-Interscience, New York (1989); B. Pullman, Intermolecular interactions from Diatomics to Biopolymers, Wiley, New York (1978).
2. G. Barone, G. Casstronone, P.D. Vecheri and G.E. Gianathi, *J. Chem. Soc. Faraday Trans. I*, **85,** 207 (1989).
3. K. Govindan and G. Ravichandran, *J. Sol. Chem.*, **25,** 75 (1986).
4. ______, *Indian J. Pure and Appl. Phys.*, **32,** 852 (1994).
5. A.B. Kilkis, S.K. Biswas, M.A. Alamgir and M.A. Seleh, *Indian J. Chem.*, **35A,** 127 (1996).
6. T. Sivaprasad and P. Venkateswaralu, *Acoustic Letters*, **18,** 5 (1994).
7. G. Scatchard and C.L. Raymond, *J. Am. Chem. Soc.*, **60,** 1278 (1938).
8. D.D. Perrin, W.L.E. Armareco and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford (1980).
9. L. Grunberg and A.H. Nissan, *Nature*, **64,** 799 (1949).
10. H. Eyringe and M.H. John, Significant Liquid Structures, Wiley-Interscience, New York (1969).
11. P.S. Sindhu, Electrical and Magnetic Properties of Molecules, Allied Publishers Limited, New Delhi (1989).
12. V.K. Sharma, P.P. Singh, S. Maken and J. Singh, *Indian J. Chem.*, **33A,** 727 (1994).
13. T.M. Aminabhavi, L.S. Manjeswar, S.B. Halligudi and R.H. Balundgi, *Indian J. Chem.*, **27A,** 629 (1988).
14. B. Bhattacharjee and S.N. Bhat, *Proc. Indian Acad. Sci.*, **94,** 461 (1985).
15. K.C. Karra, V.K. Sharma and Katoch Ashma, *Indian J. Chem.*, **35A,** 390 (1996); R. Gopal and S.K. Agarwal, *J. Indian Chem. Soc.*, **60,** 501 (1978).
16. N.V. Sastry and M.M. Raj, *Indian J. Chem.*, **35A,** 49 (1996).
17. J.G. Kirkwood, *J. Chem. Phys.*, **14,** 180 (1946); J.H. Irwing and J.G. Kirkwood, *J. Chem. Phys.*, **18,** 817 (1950).
18. C.N. Andre, *Phil. Mag.*, **17,** 497 (1934).
19. N. Hill, *Proc. Phy. Soc. London*, **678,** 159 (1954).
20. H. Eyringe, The Theory of Rate Processes, McGraw-Hill, New York (1941).
21. R.A. McAllister, *Aich. E.J.*, **6,** 427 (1960).
22. V.A. Bloomfield and R.K. Dewan, *J. Phy. Chem.*, **75,** 3113 (1971).

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