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Ultrasonic study of binary mixtures of 1,2-dichlorobenzene with polar diluents at frequency 2MHz and temperature 303.16K vis-a -vis molecular interaction

J. SINGH*, G.C. MOHANTY[1] and S. ACHARYA[2]

*Department of Physics, Synergy Institute of Engg. & Technology,
Dhenkanal-759001, Odisha (INDIA)
[1]Principal, Khallikote Autonomous College, Berhampur -760001, Odisha (INDIA)
[2]Post -Graduate Department of Physics, Ravenshaw University,
Cuttack-753003, Odisha (INDIA)

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Abstract

The Ultrasonic velocities (C) and (ρ) of binary mixture of 1,2-dichlorobenzene with polar diluents have been measured at temperature 303.16 K and frequency of 2MHz.The data of C and ρ have been used to evaluate isentropic compressibility (β) and intermolecular free length (L_f) to study the molecular interaction. The study reveals that interaction is maximum in chloro-benzene 12-dichlorobenzene mixture.

Introduction

Solvent extraction is an important technique used for extraction and purification of actinides and lanthanides in nuclear energy industry[1,2]. The common extractants tri-n-butyl phosphate (TDP), methyl isobutyl ketone (MIBK), ethyl methyl ketone (EMK), di-isobutyl ketone (DIBK) and 1,2-dichloro benzene are used in mixture with polar and nonpolar diluents to give greater dispersal and more rapid phase disengagement[3-5]. How ever 1,2-dichlorobenzene has been employed as both chelating agent and solvent in extraction technology. The liquid-liquid extraction of uranium (VI) with 1,2-dichlorobenzene in different diluents from acidic Ph media has been investigated by various workers.

In recent years, ultrasonic technique has been found to be one of the most powerful techniques for studying the nature of molecular interactions in liquid mixtures. Ultrasonic waves with low amplitude have been used by many workers[6-16] to investigate the structural and physico-chemical behaviour of pure liquid

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*Corresponding Author: Corresponding address
At- Gandhi Mandir Road, (Laxmi Bazar), PO/DIST-Dhenkanal, Pin-759001, Odisha, India.
E-mail: snehaljayashree@gmail.com

and liquid mixtures. It has been reported by many workers[11,13,15] that occurrence of complex formation can be explained successfully by excess parameters such as excess velocity, excess adiabatic compressibility, excess intermolecular free length etc.

The positive values of excess ultrasonic velocity and negative values of excess adiabatic compressibility show strong interaction occurring in liquid mixture showing the possibility of complex formation. This occurs due to the formation of discrete group of molecules arranged in to specific geometric structures which are influenced not only by the shape of molecules but also by the mutual interactions occurring between them. Since the intermolecular interactions under the present investigation are weak type of forces, definite structure of complex could not be predicted[17-19].

Since ultrasonic velocity and related parameters provide better insight into the molecular environment and behaviour in the liquid mixtures, it was considered desirable to study the molecular interaction occurring between the binary mixtures of 1,2-dichlorobenzene with chlorobenzene, bromobenzene and toluene using ultrasonic technique. Ultrasonic velocity, isentropic compressibility, intermolecular free length and their excess value have been calculated for these binary mixtures using ultrasonic data at 2 MHz and temperature303.16K.

Experimental

In the present investigation the chemicals used are of anal R grade purified by standard procedure[20-22] and redistilled before use. Density was determined with a pyknometer of 25cm^3 capacity calibrated at 303.16K. with deionsed doubly distilled water. At a fixed temperature density was determined with an error of one in 104.Ultrasonic velocity was measured by a single crystal variable path interferometer operating at frequency 2MHz. Circulating water from thermostatically regulatory bath around the sample holder with double wall maintains the temperature of the liquid constant with a precision ±0.1 °C.

Theory :

The isentropic compressibility β in the mixture is calculated and from[17],

$$\beta = 1/\rho C^2 \tag{1}$$

Where C is the ultrasonic velocity and ρ is the density of the mixture.

The intermolecular free length L_f in the mixture is given by Jacobson[18].

$$L_f = K \beta^{1/2} \tag{2}$$

Where K is the temperature dependent constant.

The specific acoustic impedance Z in the mixture is given by (19)

$$Z = \rho C \tag{3}$$

The excess isentropic compressibility β^E and excess acoustic impedance Z^E were computed from the expression.

$$\beta^E = (\beta)_{mix} - (X_1\beta_1 + X_2\beta_2) \tag{4}$$

$$Z^E = (Z)_{mix} - (X_1Z_1 + X_2Z_2) \tag{5}$$

Where X indicates mole fraction, the subscripts 1 and 2 referring to the component liquid.

Results and Discussion

The data of C and ρ were used to calculate β, L_f and Z. Excess value of isentropic compressibility β^E and excess intermolecular free-length L_f were computed with accuracy up to third decimal digits. Some of the relevant data are displayed graphically in fig. 1-2.

It is observed that, the values of L_f increases slightly in bromobenzene, while other two liquids show slight decreasing trend. The rate of variation of L_f is rapid in low concentration region of 1,2-dichlorobenzene and is quite significant for 1,2-dichlorobenzene+ bromobenzene mixture. This difference in trend obviously depends on the value of Lf in the components in the pure state and no significance need be attributed to it concerning the nature of interaction.

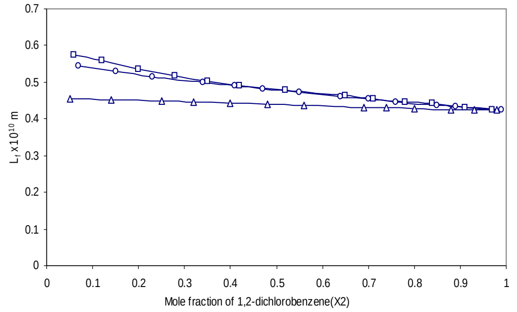

Figure 1.Variation of L_f with mole fraction of 1, 2-dichlorobenzene. (□) 1, 2-dichlorobenzene + chlorobenzene (Δ) 1, 2-dichlorobenzene +bromobenzene, (O) 1, 2-dichlorobenzene + toluene

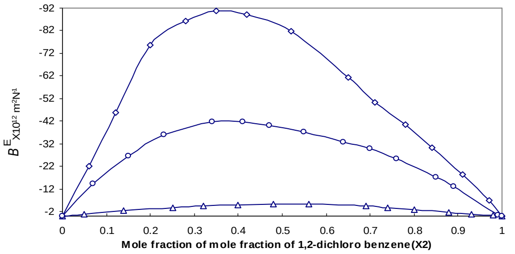

Fig-2:Variation of β^E with mole fraction of 1,2-dichlorobenzene,(□)1,2-dichlorobenzene +chlorobenzene, (Δ) 1,2-dichlorobenzene+bromobenzene,(O)1,2-dichlorobenzene+toluene

According to Subha Rao *et al.*[23] the nature of variation of L_f depends upon the relative size of components. For unequal size it is non linear. Further more, if the molecular size of the diluents is small the deviation is negative, as observed in case of chlorobenzene and toluene. The deviation is positive for bromobenzene where molecular size is relatively larger.

It is observed that the linear correlation factor g for 1,2-dichlorobenzene is 0.926, indicating predominance of β-multimer with antiparallel dipolar orientation. The linear correlation factor g is a shape dependent parameter indicative of short range interaction force leading to dipole -dipole interaction. g is also a useful index to the degree of hindered rotation in a liquid, g > 1 indicates predominance of α-multimers with parallel dipolar orientation, where as g < 1 indicates the predominance of β- multimers with anti-parallel orientation. Furthermore the nature of variation of g with mole fraction of 1, 2-dichlorobenzene reflects upon the dipolar alignment and hence nature of multimerization of solute molecules. Addition of another polar liquid tends to rupture the bond and bi functional groups are free to form intermolecular hydrogen bonding which leads to creation of micro heterogeneous clusters of unlike molecules.

As the trend of variation in L_f, β and Z indicates variation in chlorobenzene is relatively non-linear. In the chlorobenzene deficient region it drops at almost at the same rate as in the other polar media while rate of fall slows down in chlorobenzene rich region and even shows slight decrease in the trend as 1, 2-dichlorobenzene concentration tends to zero. In all

Table 1. Variationof C, ρ, L_f , Z, β with mole fraction X_2 of 1,2-dichlorobenzene in chlorobenzene, bromobenzene and toluene at temperature 303.16K.

X_2	ρ kg m^{-3}	C m s^{-1}	L_f x 10^{-6} m	zx10^{-3} kg m^{-2}s^{-1}	βx10^{12} m ^{2}N^{-1}
			Chlorobenzene		
0.06	1117	1038.18	0.575	1160	829.92
0.12	1129	1065	0.558	1203	780.31
0.2	1145	1104	0.534	1264	716.06
0.28	1161	1132.55	0.517	1315	671.09
0.35	1175	1156	0.504	1359	636.51
0.42	1189	1175.92	0.492	1398	607.92
0.52	1209	1202	0.478	1453	572.25
0.65	1235	1228	0.463	1517	536.8
0.71	1247	1239	0.456	1545	522.26
0.78	1261	1256.65	0.447	1584	502.08
0.84	1273	1271	0.443	1618	486.21
0.91	1287	1288.93	0.432	1658	468.33
0.97	1299	1302.6	0.425	1692	453.68
			Bromobenzene		
0.05	1485	1136.89	0.456	1688	520.82
0.14	1468	1152.68	0.452	1692	512.55
0.25	1447	1172.4	0.448	1697	502.6
0.32	1434	1185.07	0.445	1699	496.48
0.4	1419	1199.5	0.442	1702	489.79
0.48	1403	1214.26	0.439	1704	483.13
0.56	1386	1229	0.436	1706.58	476.78
0.69	1363	1252.08	0.432	1707.71	467.68
0.74	1354	1261.07	0.43	1707.99	464.27
0.8	1343	1271.3	0.428	1707.35	460.71
0.88	1328	1285.49	0.426	1706.87	455.75
0.93	1318	1294.84	0.425	1706.98	452.43
0.98	1308	1304.28	0.424	1707.04	449.14
			Toluene		
0.07	897	1222.8	0.545	1097	745.03
0.15	932	1232.62	0.529	1149	705.66
0.23	967	1242.09	0.515	1202	669.78
0.34	1015	1253	0.5	1272	626.95
0.41	1046	1258	0.491	1316	603.76
0.47	1072	1262	0.483	1353	585.24
0.55	1107	1268	0.473	1404	561.39
0.64	1147	1275.61	0.462	1463	535.64
0.7	1173	1282	0.455	1504	518.49
0.76	1199	1287.32	0.447	1544	502.9
0.85	1239	1295.09	0.438	1605	481.08
0.89	1256	1299	0.434	1632	471.52
0.99	1300	1305.99	0.424	1698	450.78

these three liquids CH_3-, Cl- and Br- are attached to sp^2 hybridized carbon atom of benzene ring. However with the increase of the size of the group or atom attached to the benzene ring, molecular size increases resulting increase of Van der Waals dispersion force which predominates over dipole-dipole interaction in solution. So dispersive force in the solution decreases in the order of B_r - > CH_3 - > Cl -which cause the increase in trend of intermolecular free length. Consequently bromobenzene has the least L_f value as compared to other in pure state.

Due to hyper conjugative effect in the case of toluene, a slight positive charge $\delta+$ develops on the carbon atom of the methyl group. As a result the chlorine atoms of the active 1, 2-dichlorobenzene $Cl^{\delta-}$ interacts with the methyl group of toluene which leads to decrease the value of L_f. On the other hand a slight positive charge $\delta+$ is developed on the chlorine atom of chlorobenzene due to resonance exhibiting decrease of value of L_f in the mixture. Since bromine is less electronegative, double bond character developed between carbon and bromine atom is of less magnitude as compared to that in chlorobenzene (Electro negativity of Br =2.8 and Cl = 3.0) . As a result relatively less positive charge is developed on Br atom of C6H5 -Br causing less interaction between $Br^{\delta+}$ and $Cl^{\delta-}$ of 1, 2-dichlorobenzene leading to slightly increase of L_f. Due to small size of chlorine atom as compared to other two, chlorine atom possesses more mobility and high polarity, as a result molecular interaction is likely to be more affected in case of chlorobenzene resulting greater degree of variation of ultrasonic parameters observed here.

Excess parameters are regarded as more suitable for evaluating the degree of interaction. The result shows that β^E is negative in chlorobenzene, toluene and bromobenzene. The maximum value occurs at around equimolar concentration range. The value of β^E is greater in magnitude in case of chlorobenzene than other two polar liquids. According to Fort and Moore[15] an increasingly negative β^E indicates greater interaction between components. The higher degree of interaction in 1, 2-dichlorobenzene is probably due to the presence of two chlorine groups. The value of Z^E is appreciably positive for chlorobenzene, bromobenzene and negative for toluene. Prakash *et al.*[24] in their study of Z^E reported that more than one type of interaction may be present in any given system. Dispersion force makes a positive contribution to the excess value while dipole-dipole interaction makes negative contribution. The magnitude of Z^E being positive the maximum in chlorobenzene system agrees with the result of β^E.

5. Conclusion

From the experimental findings it appears that the interaction of 1,2-dichlorobenzene in bromobenzene, toluene and chlorobenzene media follows an increasing order. Furthermore, the interaction is relatively stronger in 1,2-dichlorobenzene+chlorobenzene system. This corroborates our findings reported that chlorobenzene is probably a more effective diluent in presence of nuclear extractant 1, 2-dichlorobenzene.

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