Dielectric Investigation of Binary Mixtures Involving a Nuclear Extractant -1, 2- Dichlorobenzene and Nonpolar Solvents

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Abstract- The Relative Permittivity of Binary Mixtures of 1,2-Dichlorobenzene a Nuclear Extractant with Five Nonpolar Solvents is Measured at Frequency 455 Khz and Temperature 303.16K. The Dielectric Constant Data are used to Compute the Linear Correlation Factor and Excess Gibb's Free Energy in the Binary Mixtures. The Molecular Interaction is Found to be Dependent upon Concentration of 1,2-Dichlorobenzene as well as the Nature of the Solvent.

Index Terms- Dielectric constant, binary mixture, Kirkwood Frohlich equation.

I. INTRODUCTION

Solvent extraction is an important experimental tool used for separation and purification of nuclear metals [1].various commercial extracting agents namely , tri-n-butyl phosphate (TBP), methyl Iso-butyl ketone (MIBK), di-(2-ethylhexyl) phosphoric acid (D2EPHA), di-isobutyl ketone (DIBK),ethyl methyl ketone(EMK) and 1,2-dichlorobenzene are used in the nuclear energy industry for extraction and purification of metal ions,viz uranium (VI), thorium (IV), actinide and lanthanide elements [2, 3]. The mechanism involved in the solvent extraction process is one of the simple complex formation in which two distinct Phases appear –an organic phase which contains the metal ion and an aqueous phase which contains the rest of the product. But the formation of a third mixed organo-aqueous phase Inhibits phase separation and as such, reduces extraction efficiency. However, the third phase is eliminated by either addition of a suitable modifier/diluent to the extractant or by increasing the temperature of the system [4]. More desirable physico-chemical properties are ,however, obtained by blending the extractant with a suitable solvent for greater dispersal and more rapid phase disengagement [5,6].the dielectric spectroscopy method along with determination of dielectric permittivity and other physico-chemical studies, enables one to assess dipole moment of the resulting chemical adducts, determine the size of the molecules and complexes etc.

Therefore, it is essential to know the nature of molecular interaction of the extractant with possible polar/nonpolar solvents which may eventually be correlated with extraction efficiency.

Earlier, we have studied [7] the ultrasonic response of binary mixtures of 1,2-dichlorobenzene with several polar liquids. It is indicated that chlorobenzene is probably more effective solvent for used as diluent in solvent extraction process. Many workers [8-13] have also studied molecular interaction of binary mixtures of different solute with polar and non polar liquids by dielectric ultrasonic and viscosity studies.

In the present study therefore we intend to investigate the nature of dipolar interaction of 1,2-dichlorobenzene a nuclear extractant with non polar liquids such as benzene ,CCl4 ,P-xylene, dioxane and n-heptane to assess their suitability as a modifier.

II. THEORY

Considering each kind of multimers as separately entity and assuming that total dipole moment of the cluster of one type has no specific correlation with the other, the value of the linear correlation factor *g* in the binary mixture, is obtained by extending the Kirkwood-Frohlich equation [14, 15] and can be written as

$$g = \frac{9kT}{4\pi N \mu^2 X_2} \frac{(2\varepsilon_m + \varepsilon_\infty)^2}{(\varepsilon_\infty + 2)^2 (2\varepsilon_m + 1)} \left[V\frac{(\varepsilon_m - 1)}{\varepsilon_m} - \frac{3X_1 V_1(\varepsilon_1 - 1)}{(2\varepsilon_\infty + \varepsilon_1)} - \frac{3X_2 V_2(\varepsilon_\infty - 1)}{(2\varepsilon_m + \varepsilon_\infty)} \right]$$

(1)

Where ε_m is the dielectric constant of the mixture : ε_∞ the dielectric constant of the solute for frequency $\to \infty$ is taken as the square of the refractive index of the pure solute; ε_1 is the dielectric constant of the nonpolar liquid ; V,V1,V2 are the molar volumes of the mixture solvent(nonpolar) and solute(polar) respectively; X1,X2 are the mole fraction of nonpolar and polar liquids, respectively and μ is the gas-phase dipole moment of the pure solute. Winkelmann and Quitzsch [16] developed a dielectric model for binary mixtures of the liquids incorporating short-range interaction effects between identical as well as dissimilar molecules which was further extended to link with previously known dipolar theories of the thermodynamics excess functions [17, 18].As such, a comprehensive relation for thermodynamic excess functions of mixing [19] from the measured values of dielectric constant was developed.

The excess Gibb's free energy of mixing ΔG in the binary mixture of an associated liquid and a nonpolar solvent is,

$$\Delta G = \frac{-N}{2} {}_{[}[R_{F2} - R°_{F2}] {}_{[} X_2 \mu^2 \{X_2(g'-1)+\}],$$

(2)

where

$$R°_{F2} = \frac{8\pi N}{9V_2} \frac{(\varepsilon_2 - 1)(\varepsilon_\infty + 2)}{(2\varepsilon_2 + \varepsilon_\infty)}$$

(3)

$$R_{F2} = \frac{8\pi N}{9V_2} \frac{(\varepsilon_m - 1)(\varepsilon_\infty + 2)}{(2\varepsilon_m + \varepsilon_\infty)}$$

(4)

Where R^0_{f2}=Reaction field parameter for the pure liquid

R_{f2}= Reaction field parameter for the binary mixture

ε_2 is the dielectric constant for pure solute (1,2-dichlorobenzene) and the other terms are defined earlier.
g' is the Kirkwood-frohlich linear correlation factor for the polar solute.

III. EXPERIMENTAL

All the chemicals used were of analytical grade (E. Merck, BDH) and were further purified by standard procedures [20].The dielectric constant for the pure liquids as well as for the mixtures was measured by Wave meter-Oscillator combination at frequency 455kHz [21].The device was standardized with liquids of known dielectric constant . The cell temperature was controlled by circulating water maintained at constant temperature by a thermostat with temperature variation of $\pm 0.1^0$C.The refractive indices were measured at the regulated temperature by Pulfrich refractometer at sodium D-line .The reproducibility of dielectric constant measurement is ± 0.003 and refractive index is ± 0.00002. The density measurement was done by a semi-microbalance with a pyknometer of 25 ml capacity placed in a separate thermostatic bath precise up to $\pm 0.01°C$. the pyknometer is calibrated at 303.016 K with deionised double distilled water . The accuracy of measurement of density in this case is $\pm 2 \times 10^{-5}$ g cm^{-3}. In spite of relatively higher isobaric expansivity of benzene i.e.$12.4 \times 10^{-4} K^{-1}$, uncertainties involved in the measurement of density will not be manifested in the computed values of all the parameters to be assessed even for larger variation in the value of density to the extent $\pm 10^{-3}$ g cm^{-3}. For these maximum limits of variation, the evaluation of g, and ΔG could be done precisely up to second decimal digit.

IV. RESULTS AND DISCUSSION

The dielectric constants of 1,2-dichlorobenzene with five nonpolar solvents *viz.* benzene, carbon tetrachloride(CCl$_4$) , p-xylene, n-heptane and dioxane were measured at 303.16 K. The experimental data were used to compute the values of the related parameters listed earlier. Some of the relevant data are displayed graphically in Fig1-2 and presented in table 1.

The result shows that for all five systems studied ΔG is positive over entire range of concentrations of the solute. The trend of variation of g, is how ever different .On the basis of trend of variation of g with mole fraction of 1,2-dichlorobenzene, the non polar liquids can be divided in to three groups . Dioxane falls in the first group, benzene and CCl$_4$ falls in the second group and n-heptane and p-xylene comes in the third group. Also similar type of response is observed in the binary mixtures of Acetyl acetone with above nonpolar liquids [22].

The pure value of g of 1,2-dichlorobenzene is 0.926. This indicates the predominance of β multimers with antiparallel dipolar orientation. The trend of variation of g with changing dilution indicates that its value is dependent upon the concentration of the polar solute as well as the nature of the non polar solvents.

Dioxane exhibits a distinctly different response where the value of g remains greater than unity in low concentration region of solute indicates α-multimers and with increase in concentration of solute its value drops below unity indicates predominance of β-multimers.

The second group benzene and CCl$_4$ value of g is less than unity throughout the whole concentration of solute molecule and steadily attains the value of pure solute with increase in concentration of pure solute. Further solvent in the third group, g is very very less in the low concentration region of the solute. With increase in concentration of solute molecules value of g increases to attain the pure value.

As the trend of variation of g indicates on dilution with solvent like benzene, CCl4, p-xylene, n-heptane demultimerization occurs, but still β-multimers prevail in the mixture. With lowering of 1,2-dichlorobenzene concentration , the scarce of 1,2-dichlorobenzene molecules are surrounded by a cage of isolated nonpolar molecules and there fore fails to establish correlation among themselves on their own and the solvent molecules do not help in reinforcing angular correlation. On the other hand, introduction of dioxane increases angular correlation of solute from β-multimers to α- multimers because of dipole–induced dipole interaction between dioxane and 1,2-dichlorobenzene.

On the other hand benzene molecule has π-electron cloud. The scarce of 1,2-dichlorobenzene solute molecules are completely screened by the abundant of benzene molecules ,as a result demultimerization occurs . So value of g becomes very low at low concentration of the solute molecules.

CCl$_4$ molecules possess spherical structure. At solute deficit region scarce of solute molecules are completely trapped by the rich solvent molecules as a result g value decreases considerably to low value. With increase in solute concentration, large number of solute molecules are surrounded by the smaller CCl$_4$ molecules where many of them are likely to be stacked in wood-pile manner, there fore 'g' increases to attain the value of pure 1,2-dichlorobenzene.

n-heptane molecule is a long chain big molecule having property of steric hindrance .In low concentration region of solute molecules abundant of n-heptane molecules completely hinders the correlation due to above property, which leads to the reduction of value of g to a very low value. With reduction of non-polar molecules, polar molecules could establish correlation among themselves resulting in rapid increase of 'g' value.

Similar type of response has also been observed in TDP+ n-heptane system.

In low concentration region of solute molecules where the isolated 1,2-dichlorobenzene molecules are surrounded by predominantly p-xylene environment , correlation become negligible and the 'g 'value rather reflects that of non-polar solvent. In p-xylene similar type of response has also been observed in MIBK+p-xylene [23].In p-xylene greater delocalization found in the benzene ring through hyper conjugative effect of methyl group, prevents establishment of angular correlation initially where the solvent is in excess .With the increase in the solute molecule, p-xylene environment rapidly changes and correlation among 1,2-dichlorobenzene is referred indicated by ascending value of 'g'

Excess free energy (ΔG) is observed to be positive in all the cases. ΔG (max) decreases in the order n-heptane>p-xylene> CCl_4>benzene> dioxane. The excess of β-multimers are expected to be associated with reduction in internal energy and consequently positive value of ΔG is observed to be maximum in group third liquids. How ever small value of ΔG for dioxane is compatible with trend of variation of 'g', where the value of g is more than 1. There is a considerable conversion of β-multimers to α-multimers in dioxane rich region. The ΔG (max) being highest in n-heptane medium appears to be justified in view of the fact that g value in the mixture is very very less than unity over a large concentration range.

V. ACKNOWLEDGMENTS

VI. CONCLUSION

From the experimental findings it appears that the interaction of 1,2-dichlorobenzene with n-heptane is relatively stronger than other non-polar media. This corroborate our findings reported that n-heptane is probably more effective diluent in presence of the nuclear extractant 1,2-dichlorobenzene.

REFERENCES

[1] G M Ritchey and A W Ashbrook: solvent extraction principle and application to process Metallurgy part וו New York (1979)

[2] P Behera, R Mishra and Vchakravorty: J. Radiational Nucl. Chem. **173** (1993) 161 .

[3] B K Rout and V Chakravortty: Acustica **10,** (1994)203,

[4] P R Vasudev Rao and T G Srinivasan: Proe.lnt.symp.on Radio Chemistry and Radiation Chemistry (BARC.Bombay) (1991)

[5] S K Dash, V Chakravorty and B B Swain: Acta Chim.Hung.**131** (1994)799.

[6] S K Dash and B B swain: Jpn.J.Appl.Phys.**32** (1993)2753 .

[7] J Singh, G C Mohanty and S.Acharya: J. Ultrascientist of Physical Sc **24** (2012)2 .

[8] R. J. Sengwa, Sonu Sankhla and Vinita Khatri: J.Mol. Liquids **151**(2010) 17

[9] T Thenappan and A Prabakar Devaraj : J.Mol. Liquids **123** (2006) 72

[10] (Lovely Sarkar, Mahendra Nath Roy. : Thermochemica Acta; **496** (2009) 124

[11] R.J.Sengwa, Vinita Khatri and Sonu Sankhia: J.Mol. Liquids **144**(2009) 89

[12] T Thenappan and A Prabakar Devaraj: J.Mol. Liquids **126** (2006)38

[13] Susmita Kamila and Jayanta K Dash: J.Mol. Liquids **172** (2012)71-75

[14] J G Kirkwood. : J. Chem.Phys.**7** (1939)911

[15] H Frohlich: Trans. Faraday Soc**. 44**(1949) 238

[16] J Winkelmann, K Quitzsch: Z Phys.Chem (Leipzig) **257** (1976)378

[17] W G Nienhuis,J M Deutch: J. Chem.Phys.**56** (1972)235

[18] J Sutherland G Nienhuis and J M Deutch: Mol. Phys. **26** (1973)999

[19] J Winkelmann and K Quitzsch: Z Phys. Chem. (Leipzig) **257** (1976) 746

[20] J A Riddich and W B Bunger: Organic Solvents (New York: Wiley Interscience) (1970)

[21] S K Dash N D Srichandan. G S Roy.B B Swain and V Chakravorty: Chem.Edun **9**(2) 51(1992)

[22] S Acharya, S K Dash, J N Mohanty and B B Swain J.Mol. Liquids **71** (1997) 73

[23] J K Das S K Dash V Chakravorty and B B Swain: Indian J.Chem.Technol**. 1** (1994)230

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Fig 1 Variation of 'g ' with mole fraction of 1,2-dichlorobenzene
Fig 2. Variation of ΔG with mole fraction of 1,2-dichlorobenzene

Table I. Variation of Єm,g,ΔP,ΔG with the content of 1,2-dichlorobenzene in five nonpolar solvents at 303.16 K

X2	ε_m	g	ΔG(J mol^{-1})
		Benzene	
0.06	2.55	0.58	118.4
0.12	2.89	0.64	216.4
0.2	3.3	0.63	345.15
0.25	3.52	0.61	411.51
0.35	4.08	0.629	501.23
0.46	4.85	0.67	532.34
0.53	5.42	0.71	517.07
0.6	6.03	0.75	479.89
0.67	6.71	0.797	417
0.72	7.14	0.81	375.52
0.85	8.5	0.88	198.87
0.91	8.98	0.89	131.69
0.96	9.37	0.906	71.81
		Carbon tetrachloride	
0.03	2.343	0.48	66.33
0.08	2.55	0.53	169.04
0.16	2.85	0.51	318.72
0.21	3	0.485	409.08
0.28	3.38	0.53	495.53
0.35	3.8	0.57	555.19
0.48	4.69	0.64	596.39
0.57	5.35	0.68	584.14
0.65	6.17	0.74	504.64

0.77	7.15	0.78	410.05
0.87	8.21	0.84	259.13
0.93	8.97	0.88	137.64
0.97	9.46	0.91	57.14
	p-xylene		
0.07	2.658	0.31	140.54
0.12	2.78	0.36	238.52
0.18	2.95	0.4	349.92
0.22	3.09	0.43	416.93
3.43	3.43	0.46	570.76
0.42	3.89	0.51	673.56
0.51	4.51	0.57	688.66
0.56	4.95	0.63	662.41
0.67	5.89	0.71	588.67
0.76	6.87	0.78	460.68
0.83	7.55	0.81	368.98
0.88	8.25	0.85	255.65
0.95	9.14	0.89	110.99

	Dioxane		
0.04	2.615	1.14	79.78
0.095	3.075	1.05	165.25
0.155	3.44	0.91	245.74
0.22	3.92	0.89	306.16
0.28	4.27	0.84	357.42
0.35	4.52	0.76	427.1
0.46	5.16	0.74	474.95
0.53	5.78	0.78	450.11

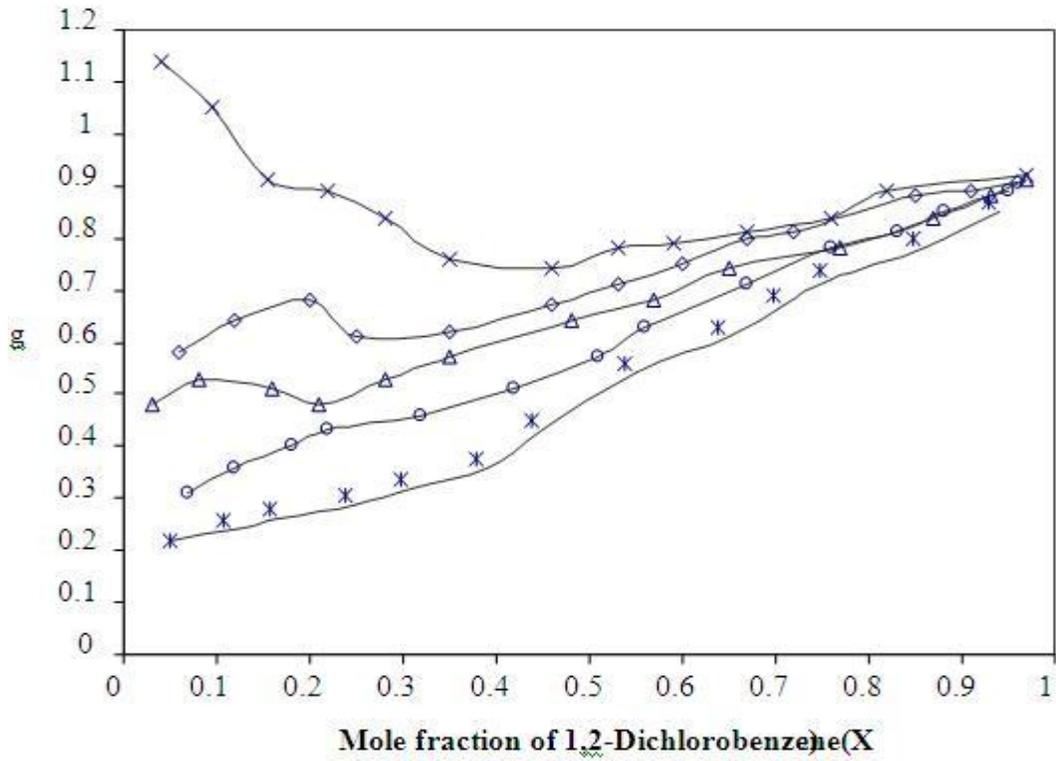|			
0.59	6.21	0.79	436.04
0.67	6.87	0.81	387.57
0.76	7.61	0.84	315.41
0.82	8.4	0.89	205.73
0.97	9.57	0.92	38.25
	n-heptane		
0.05	1.962	0.22	132.29
0.12	2.065	0.24	320.31
0.17	2.155	0.26	452.88
0.25	2.34	0.29	643.27
0.31	2.492	0.32	790.18
0.39	2.77	0.36	936.16
0.45	3.14	0.43	971.24
0.55	3.88	0.54	955.85
0.65	4.72	0.61	879.12
0.71	5.4	0.67	770.13
0.76	6.04	0.72	658.93
0.86	7.06	0.78	500.45
0.94	8.52	0.85	225.54

Fig 1 Variation of 'g ' with mole fraction of 1,2-dichlorobenzene

—◇— Ben —△— Carbon tetrachloride —○— p-xylene —×— Dioxane —∗— n-heptane
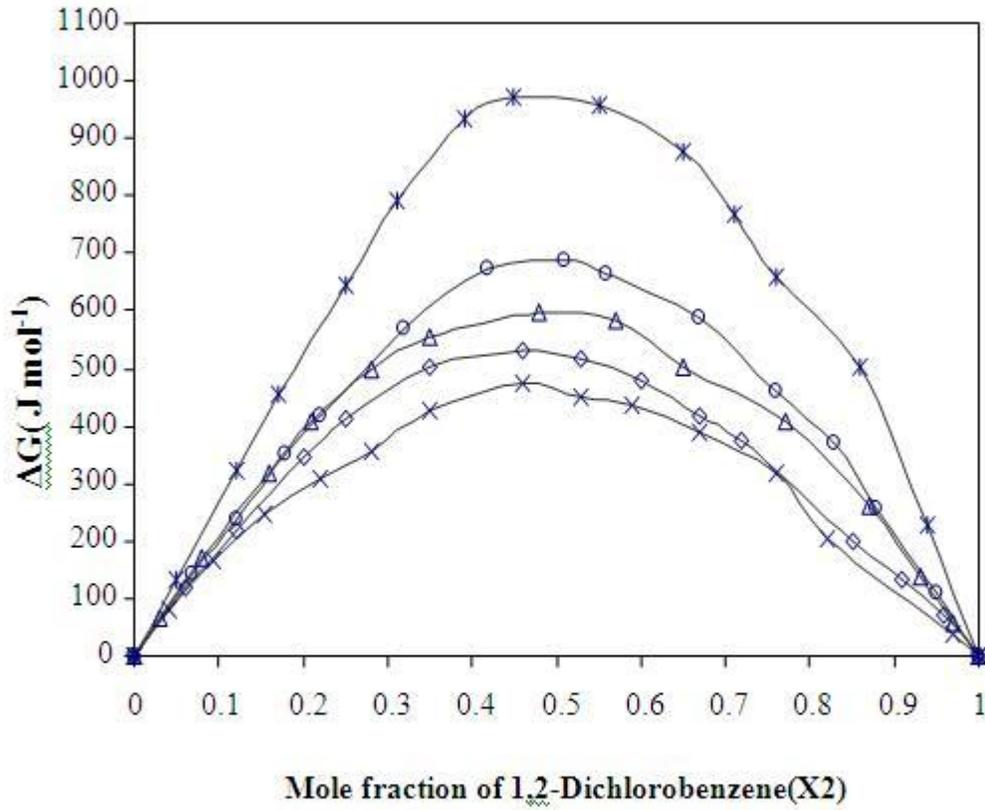
Fig 2. Variation of ΔG with mole fraction of 1,2-dichlorobenzene

—◇— Ben   —△— Carbon tetrachloride —○— P-xylene   —×— Dioxane —⋆— n-heptane