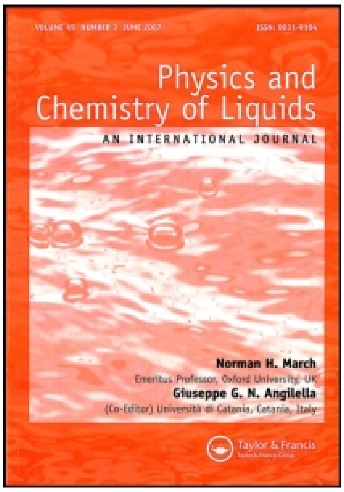

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DIPOLAR INTERACTION IN BINARY POLAR SYSTEMS - A DIELECTRIC STUDY OF ACETYL ACETONE (HAA) AND DI-ISO BUTYL KETONE (DIBK) WITH SOME MONOSUBSTITUTED BENZENES

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Experimentally measured values of dielectric constant (ϵ) at a frequency of 455 kHz and temperature 303.16 K in binary polar mixture of acetyl acetone and of di-iso-butyl ketone in chlorobenzene, bromobenzene and toluene have been used to compute the mutual correlation factor (g_{ab}), the excess molar polarization (ΔP) and the Gibb's free energy of mixing (ΔG_{ab}) using Winkelmann-Quitzsch equations. The results are utilised in interpreting the molecular association and hence the nature of clusters involving unlike molecules.

Keywords: Dielectric constant; mutual correlation factor; excess molar polarization

1. INTRODUCTION

Solvent extraction is an important analytical technique used in the nuclear energy industry for separation and purification of metals (actinides and lanthanides) [1]. There are various extracting agents [2] important ones being tri-n-butyl phosphate (TBP), methyl-iso-butyl ketone (MIBK), acetyl acetone (HAA) and di-iso-butyl ketone (DIBK). In the extraction process, the acidleach solution is put into

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contact with a solvent mixture containing the extractant and another polar liquid (modifier) in a suitable diluent at a definite pH value. As such the separation factor of the organic phase from the aqueous phase seems to be governed by the relative permittivity of the medium [3]. The efficiency of extraction and selectivity depends on the nature of extractant and modifier/diluent used. In order to assess the suitability as a modifier the molecular interaction studies in binary liquid mixtures of TBP, MIBK as one of the components have been carried out in this laboratory using ultrasonic and dielectric techniques [4–6]. In the present study, therefore, we intend to investigate the nature of dipolar interaction in two more extractants, HAA and DIBK with some monosubstituted benzene namely chlorobenzene, bromobenzene and toluene to assess their suitability as modifier.

The Winkelmann-Quitzsch equations [7–8] for binary mixture of polar liquids incorporate both short range dipolar interaction between like and unlike molecules and also long-range electrostatic interaction. These equations are used for evaluation of mutual correlation factor (g_{ab}) between the components a and b in the mixture, the excess molar polarization, ΔP and the excess Gibb's free energy of mixing due to short-range interaction between unlike molecules, ΔG_{ab}.

2. THEORY

The Winkelmann-Quitzsch equation [7] for binary mixture of polar liquids is

$$\begin{aligned}\frac{\epsilon_m - 1}{\epsilon_m} V_m = \sum_{r=a,b} \frac{3\lambda_r V_r(\epsilon_{\infty r} - 1)}{(2\epsilon_m + \epsilon_{\infty r})} + \sum_{r=a,b} \left(\frac{\epsilon_{\infty r} + 2}{2\epsilon_m + \epsilon_{\infty r}}\right)^2 \\ \times (2\epsilon_m + 1)\lambda_r \mu_r^2 g_{rr} \frac{4\pi N}{9kT} \\ + \frac{(\epsilon_{\infty a} + 2)(\epsilon_{\infty b} + 2)(2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_{\infty a})(2\epsilon_m + \epsilon_{\infty b})} \frac{4\pi N}{9KT} \mu_a \mu_b (g_{ab} - 1)\end{aligned} \tag{1}$$

where a and b refer to molecule of variety a and b, ϵ_m is dielectric constant of the mixture, V_r, V_m are molar volume of the component and the mixture, respectively, $\varepsilon_{\infty r}$ is the square of the refractive index of components, respectively, μ_r is the gas-phase dipole moment of the rth component, g_{rr} is linear correlation factor between identical molecules $a-a$ or $b-b$, g_{ab} is mutual correlation factor between the dissimilar molecules $a-b$ and the othe terms convey usual meaning.

The excess molar polarization is given by

$$\Delta P = P_m - \sum \lambda_r P_r \tag{2}$$

where λ_r is the molefraction and P_r is molar polarization of respective components,

$$\begin{aligned} P_m =& \frac{4\pi N\epsilon_m}{\epsilon_m+2}\left[\sum_{r=a,b}\frac{(\epsilon_{\infty r}-1)}{(2\epsilon_m+\epsilon_{\infty r})}\lambda_r\alpha_r + \sum_{r=a,b}\left(\frac{\epsilon_{\infty r}+2}{2\epsilon_m+\epsilon_{\infty r}}\right)^2\right. \\ &\left.\times\,(2\epsilon_m+1)\frac{\lambda_r\mu_r^2 g_{rr}}{9KT} + \frac{(\epsilon_{\infty a}+2)(\epsilon_{\infty b}+2)(2\epsilon_m+1)}{(2\epsilon_m+\epsilon_{\infty a})(2\epsilon_m+\epsilon_{\infty b})}\frac{\mu_a\mu_b}{9kT}(g_{ab}-1)\right] \end{aligned} \tag{3}$$

where α_r is the polarizability of the respective component and all other terms are as defined earlier.

The excess Gibb's free energy of mixing [8] for a condensed phase is given by

$$\begin{aligned} \Delta G =& -\frac{N}{2}\left[\sum_{r=a,b}\lambda_r^2\mu_r^2(R_{fr}-R_{fro})\right. \\ &+\sum_{r=a,b}\lambda_r^2\mu_r^2(g_{rr}-1)(R_{fr}-R_{fro}) \\ &\left.+\,\lambda_a\lambda_b\mu_a\mu_b(g_{ab}-1)(R_{fa}+R_{fb}-R_{fao}-R_{fbo}\right] \\ =&\Delta G_0+\Delta G_{rr}+\Delta G_{ab} \end{aligned} \tag{4}$$

The first term ΔG_0 represents the excess dipolar energy due to long-range electrostatic interaction, the second term ΔG_{rr} gives the excess dipolar energy due to short-range interaction between identical molecules and ΔG_{ab} represents excess dipolar energy due to short-range interaction between dissimilar molecules. The terms R_{fro} and R_{fr} which give the reaction field parameter in the pure liquid and in the mixture are

$$R_{fro} = \frac{8\pi N}{9V_r} \frac{(\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_r + \epsilon_{\infty r})} \tag{5.a}$$

$$R_{fr} = \frac{8\pi N}{9V_r} \frac{(\epsilon_m - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_m + \epsilon_{\infty r})} \tag{5.b}$$

where ϵ_r is the dielectric constant of the pure liquid.

3. EXPERIMENTAL

The dielectric constant measurement for the pure liquids as well as for mixtures were carried out by wavemeter–oscillator combination [9,10] at 455 kHz. The device was standardised with the help of standard liquids of known dielectric constant [11]. The cell temperature was controlled with an electronically regulated thermostatic arrangement with temperature variation of ± 0.1°C. The refractive indices were measured at the regulated temperature by Pulfrich refractometer at sodium D-line. The density of liquids was measured using a pycnometer of 25 mL capacity. The chemicals used were of AR grade, purified by standard procedures [12] and redistilled before use. The reproducibility of dielectric constant measurement was ± 0.003 and those of refractive index and density measurement were of ± 0.00002 and ● 0.00002 g cm^{-3}. For these maximum limit of variation, the value of ΔG_{ab} and ΔP could be measured precisely upto second decimal digit.

4. RESULTS AND DISCUSSION

Relative permittivity (ϵ_m) of binary mixtures of acetyl acetone (HAA) and also of di-iso-butyl ketone (DIBK) with some monosubstituted benzenes namely chlorobenzene, bromobenzene and toluene have been measured at 303.16 K. The experimental data is used to evaluate mutual correlation factor (g_{ab}), excess molar polarization (ΔP) and excess Gibb's free energy of mixing (ΔG_{ab}) in these mixtures. Some of the relevant data are given in Tables I, II and graphically displayed in Figures 1–3.

Mutual association in polar mixtures results in creation of microheterogenous clusters [9,10] of unlike molecules. The mutual correlation factor, g_{ab}, in these mixtures reflects upon the dipolar alignment involved in such clusters and helps in analysis of liquid

TABLE I Variation of ε_m, g_{ab}, ΔP, ΔG_{ab} with the content of acetyl acetone (HAA) in chlorobenzene, bromobenzene and toluene at 303.16 K

λ_2	ε_m	g_{ab}	ΔP ($cm^3 mol^{-1}$)	ΔG_{ab} ($J.mol^{-1}$)
		Chlorobenzene		
0.064	6.39	0.957	4.95	−2.07
0.132	7.28	0.909	4.87	−5.17
0.214	8.50	0.869	4.73	−3.42
0.327	9.90	0.787	8.10	6.54
0.410	11.60	0.795	8.50	20.78
0.500	13.00	0.747	7.41	38.29
0.620	15.00	0.710	6.01	54.08
0.710	16.80	0.710	4.60	55.61
0.850	20.80	0.866	2.46	19.89
0.910	22.40	0.913	2.24	9.40
		Bromobenzene		
0.065	6.03	0.932	1.87	−3.90
0.150	7.40	0.905	6.52	−5.20
0.200	7.84	0.850	6.32	−9.30
0.330	9.96	0.810	8.76	6.50
0.400	11.00	0.785	9.35	17.72
0.520	12.70	0.703	7.49	42.80
0.600	14.30	0.702	6.73	53.60
0.750	17.50	0.733	4.90	50.02
0.820	19.50	0.785	3.25	35.18
0.900	21.80	0.870	2.59	13.76
		Toluene		
0.060	2.55	0.350	−1.71	−18.66
0.150	3.08	0.369	1.33	−60.66
0.207	3.60	−0.726	4.43	−64.64
0.329	5.34	−1.192	11.83	17.60
0.410	6.80	−1.390	14.28	97.49
0.500	8.30	−1.840	11.67	185.40
0.650	11.50	−1.830	11.72	249.00
0.710	13.00	−1.730	10.80	239.70
0.820	16.50	−1.240	8.60	162.80

TABLE II Variation of $\varepsilon_m, g_{ab}, \Delta P, \Delta G_{ab}$ with the content of di-iso-butyl ketone (DIBK) in chlorobenzene bromobenzene and toluene at 303.16 K

λ_2	ε_m	g_{ab}	ΔP $(cm^3 mol^{-1})$	ΔG_{ab} $(J.mol^{-1})$
		Chlorobenzene		
0.060	5.97	0.983	0.39	−0.18
0.120	6.30	0.973	1.01	−0.29
0.192	6.61	0.951	1.25	−0.19
0.350	7.40	0.907	0.69	3.40
0.450	7.80	0.885	1.33	6.50
0.500	8.10	0.882	1.03	8.25
0.700	9.20	0.945	3.10	5.48
0.820	9.80	0.972	2.30	2.20
0.900	10.10	0.977	2.00	1.18
		Bromobenzene		
0.040	5.59	0.978	0.04	−0.24
0.105	5.97	0.958	0.04	−0.70
0.341	7.00	0.868	0.50	2.27
0.420	7.45	0.862	0.60	5.50
0.500	7.83	0.858	1.18	8.63
0.600	8.44	0.886	1.92	9.45
0.800	9.50	0.925	1.72	5.98
0.910	10.00	0.953	−0.97	2.20
		Toluene		
0.050	2.93	0.927	3.39	−0.33
0.150	3.75	0.764	8.37	−0.48
0.230	4.40	0.594	9.83	7.00
0.400	5.70	0.302	10.30	31.80
0.510	6.50	0.165	9.20	51.40
0.650	7.70	0.285	9.30	90.30
0.800	8.75	0.378	3.28	33.10
0.950	10.00	0.736	2.48	4.60

structures. $g_{ab} > 1$, betokens the predominance of parallel orientation leading to α-clusters, whereas $g_{ab} < 1$ indicates predominance of antiparallel orientation leading to β-clusters, and in the ideal case where $g_{ab} = 1$, there is no preferential correlation among the molecules. The terms α-clusters and β-clusters are defined on analogy with the terms α-multimers and β-multimeters formed due to self association in an associating liquid.

When acetyl acetone is blended with either chlorobenzene or bromobenzene, the value of g_{ab} is found to be less than unity throughout and as such β-clusters do predominate. The departure of

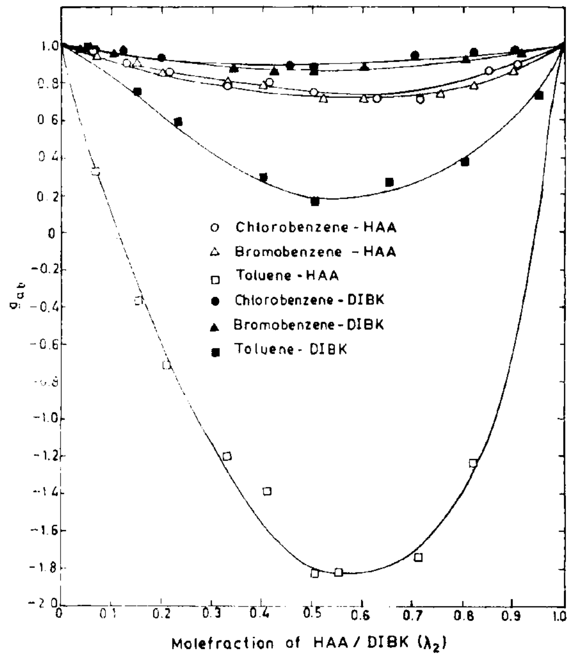

FIGURE 1 Variation of g_{ab} with molefraction of HAA/DIBK.

g_{ab} from unity which can be taken as a measure of degree of interaction is observed to be maximum at around 0.6 molefraction of acetyl acetone. The trend in the mixtures of DIBK with chlorobenzene and bromobenzene are almost identical excepting the fact that the maximum departure from unity is at nearly equimolar concentration range.

The binary mixtures of both acetyl acetone and DIBK with toluene, however, display some significant departure. Though the value of g_{ab} in both cases remain less than unity the departure from unity is remarkably high compared to the earlier cases even to the extent that in the case of acetyl acetone, it is less than zero. The maximum departure, however, occurs at the same concentration in both the cases. This indicates stronger interaction among the unlike molecules. The point of inflexion in the molefraction versus g_{ab} curve is sharp in

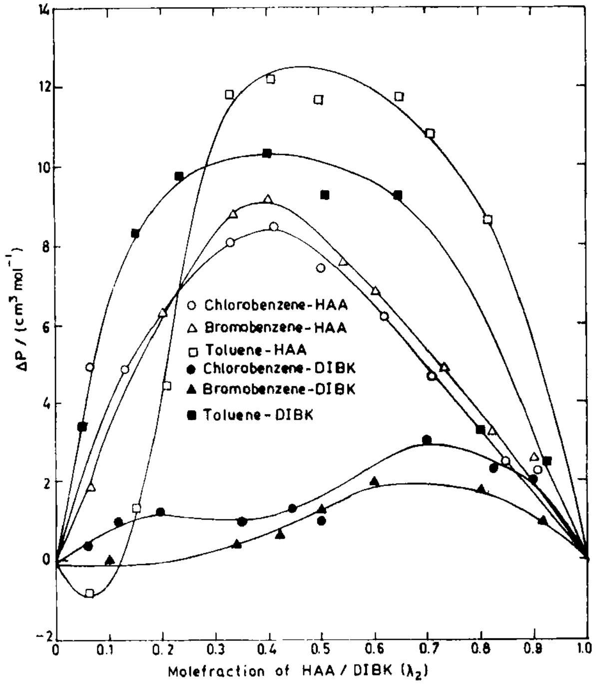

FIGURE 2 Variation of ΔP with molefraction of HAA/DIBK.

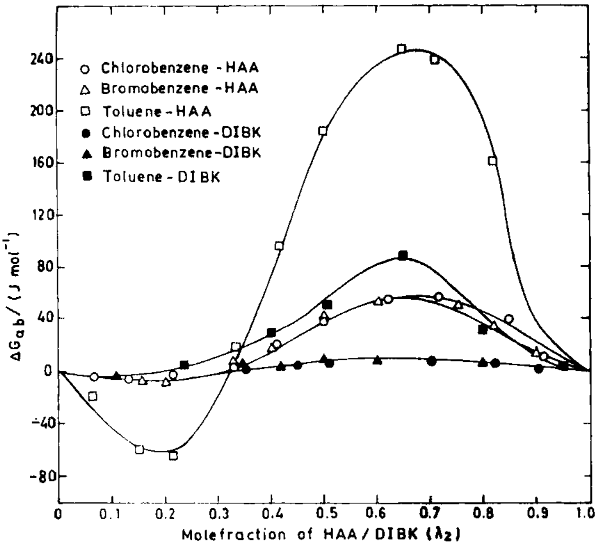

FIGURE 3 Variation of ΔG_{ab} with molefraction of HAA/DIBK.

DIBK + toluene mixture probably due to complex formation. It is worth comparing here the earlier work on mixtures of TBP and of MIBK with chlorobenzene, bromobenzene and toluene. For TBP [13] the value of g_{ab} is observed to be more than unity over the entire compositional range signifying predominance of α-clusters in contrast to predominance of β-clusters in the presently reported case. However, the degree of interaction is observed to be relatively stronger for toluene similar to the one observed by us. In case of MIBK [14] however, the result for toluene is identical to ours with excess of β-clusters whereas for chlorobenzene and bromobenzene the results are identical to those of TBP with excess of α-clusters.

The value of linear correlation factor for pure acetyl acetone and DIBK is 1.56 and 1.64, respectively which betokens the predominance of parallel orientation among the like molecules in both these liquids. But the value of g for chlorobenzene, bromobenzene and toluene, is nearly unity and as such there is no preferential correlation.

The keto-groups in acetyl acetone are symmetrically situated and screened by methyl-group from either end. In pure form acetyl acetone has wood-pile structure due to intramolecular association between $C^{\delta+}$ and $O^{\delta-}$ resulting in α-multimers. On addition of another polar liquid some of the bonds are ruptured and resultant free molecules tend to form cluster with the unlike molecules available in the mixture. The tendency is likely to be maximum when the concentration of both liquids are comparable. It is probable that $C^{\delta+}$ of HAA associates with $Cl^{\delta-}$ or $Br^{\delta-}$ of halogen forming β-clusters. Though toluene is mildly polar yet due to hyperconjugative effect in it methyl group has electron pushing tendency to the benzene ring leaving partially positively charged carbonium ($C^{\delta+}$) ion. As such there is relatively stronger interaction between this $C^{\delta+}$ and $O^{\delta-}$ of the keto-group of HAA because of larger electronegativity difference. Furthermore, the π-electron cloud of the benzene ring also interacts with $C^{\delta+}$ of HAA. In both cases the interaction results in β-clusters. The DIBK molecules can remain in both keto-form and enol-form due to tautomerization [15]. In both forms the molecules are arranged in wood pile structure and results in α-multimers due to intramolecular association. However, the self association in enol-form contributes to higher value of g. The formation of β-cluster as such can be similarly between $C^{\delta+}$ of DIBK and $Cl^{\delta-}$ of the halogen. The intermolecular association between DIBK and toluene is caused in a similar fashion as in case of HAA. However, because of self association in enol form of DIBK the steric factor probably favours complex formation when sufficient number of toluene molecules are trapped in molecular voids. In view of the evidence of stronger interaction in toluene-medium it will be worthwhile attempting the case of toluene as a modifier in an acid leach medium for extraction purpose.

The excess molar polarization ΔP is observed to be positive in both the systems being relatively more when toluene is the second component. The ΔP (max) also occurs when the concentration of both the components in the mixture are comparable. This agrees with findings on 'g_{ab}' in as much as the tendency of clustering is stronger nearly at the same concentration range and large for the same liquid i.e., toluene.

The excess Gibb's free energy (ΔG_{ab}) evaluated here is based on short-range interaction between unlike molecules. It is observed to have a wave-like structure ($\sim$) with a low negative value in acetylacetone/DIBK-deficient region probably due to the fact that the α-multimers present in the pure liquid are gradually converted into β-clusters which necessitates reduction in internal energy and thus ΔG_{ab} becomes positive in HAA and DIBK-rich region. The fact that ΔG_{ab} is more in toluene also corroborates our conclusion from the study of g_{ab} and ΔP that interaction in that system is the strongest.

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