

Dielectric investigation in binary mixtures involving a nuclear extractant – di-isobutyl ketone (DIBK) and nonpolar solvents

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Abstract The relative permittivity of di-isobutyl ketone (DIBK), a nuclear extractant with six nonpolar solvents namely benzene, carbon tetrachloride, p-Xylene, n-heptane, cyclohexane and dioxane have been measured at 303.16K and frequency 455 kHz. The data are used to evaluate g , ΔP and ΔG by using Kirkwood-Fröhlich equation. It is observed that in dilute solution, β -multimers with anti-parallel dipolar orientation are predominant for all non-polar liquids except dioxane where α -multimers with parallel orientation are in excess.

Keywords Dielectric constant, binary mixture, Kirkwood Fröhlich equation

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1. Introduction

Solvent extraction is an important analytical 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-ethyl hexyl) phosphoric acid (D2EHPA) and di-isobutyl ketone (DIBK) 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 reported [7] the dielectric response of acetyl acetone (HAA), another nuclear extractant with several nonpolar solvents. The measured values of dielectric permittivity were used to compute linear correlation factor g , excess molar polarization ΔP , and excess free energy of mixing ΔG , in those mixtures. It indicated that *p*-Xylene, cyclohexane and *n*-heptane were probably more effective solvents for use as diluents in the solvent extraction process. The present study, therefore, is designed to measure dielectric permittivity of binary mixtures of DIBK with six nonpolar solvents, and to compute the related parameters and compare their behaviour with those of such mixtures involving HAA. The advantage of using DIBK over HAA is that it can be used in the presence of impurities such as iron, phosphate and rare earths.

2. Theory

Considering each kind of multimers as separate 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 [8,9] and can be written as

$$g = \frac{9kT}{4\pi N\mu^2 X_2} \frac{(\epsilon_m + \epsilon_\infty)^2}{(\epsilon_\infty + 2)^2 (2\epsilon_m + 1)} \left[V \frac{(\epsilon_m - 1)}{\epsilon_m} - \frac{3X_1 V_1 (\epsilon_1 - 1)}{(2\epsilon_\infty + \epsilon_1)} - \frac{3X_2 V_2 (\epsilon_\infty - 1)}{(2\epsilon_m + \epsilon_\infty)} \right] \quad (1)$$

where ϵ_m is the dielectric constant of the mixture ; ϵ_∞ , the dielectric constant of the solute for frequency $\rightarrow \infty$ is taken as the square of the refractive index of pure solute , ϵ_1 is the dielectric constant of the nonpolar liquid ; V , V_1 , V_2 are the molar volumes of the mixture, solvent (nonpolar) and solute (polar) respectively ; X_1 , X_2 are the molefraction of nonpolar and polar liquids, respectively and μ is the gas-phase dipole moment of the pure solute.

The molar polarization of binary mixtures [5] is given by

$$P_m = \frac{\epsilon_m}{(\epsilon_m + 2)} \left[\frac{3X_1 V_1 (\epsilon_1 - 1)}{(2\epsilon_m + \epsilon_1)} + \frac{3X_2 V_2 (\epsilon_\infty - 1)}{(2\epsilon_m + \epsilon_\infty)} + \frac{g' 4\pi N\mu^2 X_2}{9KT} \frac{(\epsilon_\infty + 2)^2 (2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_\infty)^2} \right] \quad (2)$$

where g' is the Kirkwood-Fröhlich linear correlation factor for the polar solute (pure).

The excess molar polarization in the binary mixture is given by

$$\Delta P = P_m - (X_1 P_1 + X_2 P_2), \quad (3)$$

where P_1 and P_2 are the molar polarization of nonpolar and polar liquids, respectively Winkelmann and Quitzsch [10] 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 thermodynamic excess functions [11, 12]. As such, a comprehensive relation for thermodynamic excess functions of mixing [13] 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,

$$\Delta G = \frac{-N}{2} [R_{f_2} - R''_{f_2}] [X_2 \mu^2 \{X_2 (g' - 1) + 1\}], \quad (4)$$

where

$$R''_{f_2} = \frac{8\pi N}{9V_2} \frac{(\epsilon_2 - 1)(\epsilon_\infty + 2)}{(2\epsilon_2 + \epsilon_\infty)} \quad (5.a)$$

and

$$R_{f_1} = \frac{8\pi N}{9V_2} \frac{(\epsilon_m - 1)(\epsilon_\infty + 2)}{(2\epsilon_m + \epsilon_\infty)} \quad (5.b)$$

ϵ_2 is the dielectric constant for pure solute (DIBK) and the other terms are defined earlier.

3. Experimental

All the chemicals used were of analytical grade (E. Merck, BDH) and were further purified by standard procedures [14]. The dielectric constant for the pure liquids as well as for the mixtures was measured by Wavemeter-Oscillator combination at frequency 455kHz [15]. The device was standardised 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 $\pm 0.1^\circ\text{C}$. 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 pycnometer of 25 ml capacity placed in a separate thermostatic bath precise up to $\pm 0.01^\circ\text{C}$. The pycnometer is calibrated at 303.16 K with deionised double distilled water. The accuracy of measurement of density in this case is $\pm 2 \times 10^{-5} \text{ g cm}^{-3}$. In spite of relatively higher isobaric expansivity of benzene *i.e.* $12.4 \times 10^{-4} \text{ K}^{-1}$, 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 $\pm 10^{-3} \text{ g cm}^{-3}$. For these maximum limits of variation, the evaluation of g , ΔP and ΔG could be done precisely up to second decimal digit.

4. Results and discussion

The dielectric constants of DIBK with six nonpolar solvents *viz.* benzene, CCl_4 , *p*-Xylene, cyclohexane 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 trends are displayed graphically in Figures 1-3 and presented in Table 1.

The results show that for all the six systems studied, ΔP and ΔG are positive over the entire range of concentration. The trend of variation of g , however, is different. On the basis of the trend of variation of g with mole fraction of DIBK, the nonpolar liquids can be divided into three groups. Dioxane falls in the first group, benzene and CCl_4 constitute the second while cyclohexane, *n*-heptane and *p*-Xylene comes in the third category. It is worth noting here that these nonpolar solvents exhibited almost identical response in their binary mixtures with HAA.

Dioxane exhibits a distinctly different response where the value of g remains greater than unity throughout. Furthermore, in DIBK-deficient region *i.e.* below 0.2 molefraction of

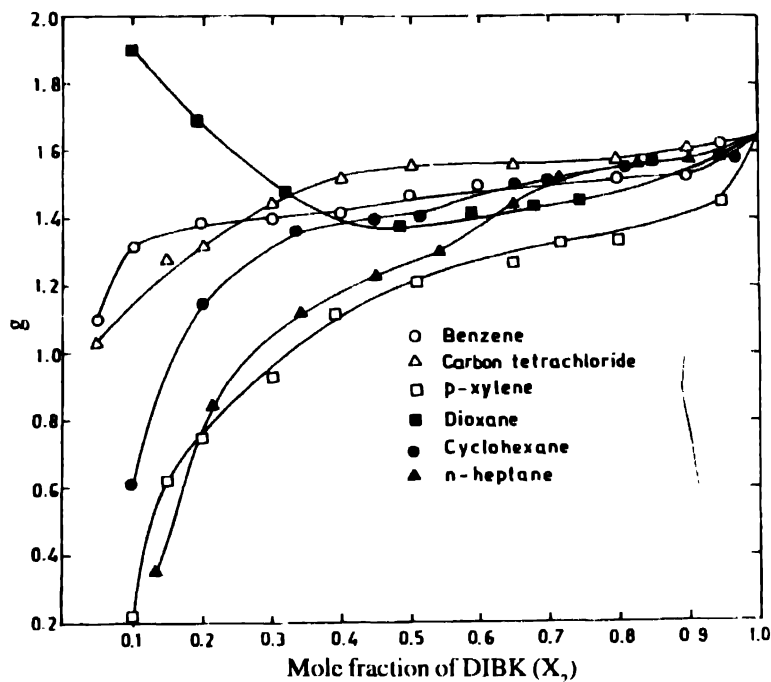


Figure 1. Variation of ' g ' with mole fraction of DIBK

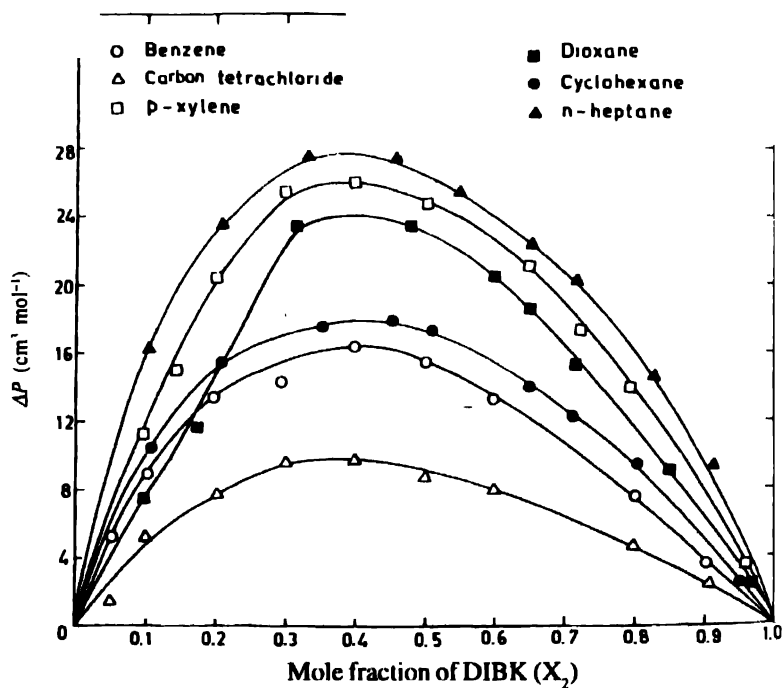


Figure 2. Variation of ΔP with mole fraction of DIBK

DIBK, it even exceeds the value for pure DIBK (1.64). Starting with this higher value, g decreases steadily up to 0.5 mole fraction of DIBK beyond which it increases to attain the value of g for DIBK. For the second group *i.e.* benzene and CCL_4 , the value of g is slightly greater

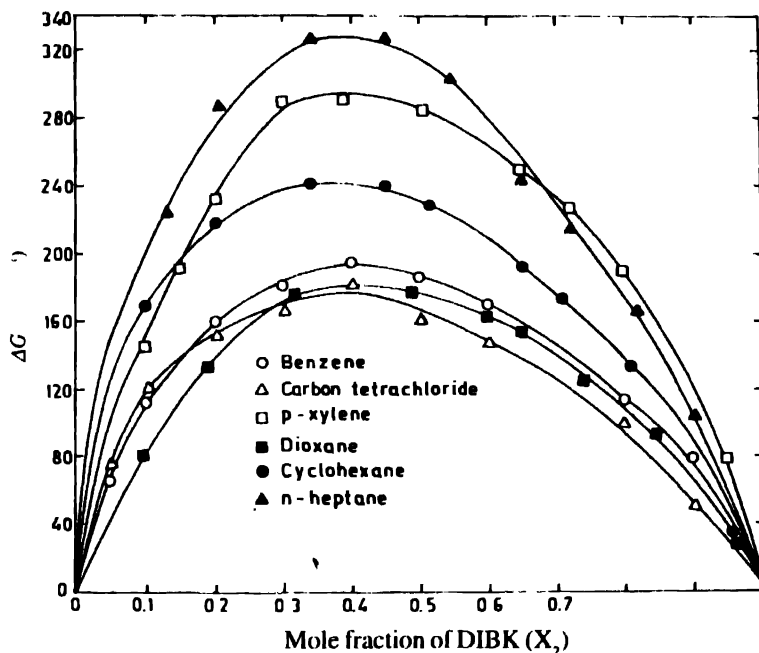


Figure 3. Variation of ' ΔG ' with mole fraction of DIBK

than unity in very low-DIBK concentration region wherefrom it increases steadily to attain the value of pure solute. For the solvents in the third group, g is less than unity in DIBK-deficient region and increases smoothly with increasing concentration of DIBK. Its value goes beyond unity around molefraction 0.35 of DIBK in *n*-heptane and *p*-Xylene while for cyclohexane it exceeds unity for 0.2 mole fraction of DIBK.

Table 1. Variation of ϵ_m , g , ΔP , ΔG with the content of DIBK in six nonpolar solvents at 303.16 K.

X_2	ϵ_m	g	ΔP ($\text{cm}^3 \text{mol}^{-1}$)	ΔG (J mol^{-1})
Benzene				
0.050	2.70	1.10	5.34	67.98
0.100	3.30	1.32	9.02	112.10
0.200	4.40	1.39	13.48	160.00
0.300	6.11	1.40	14.54	181.70
0.400	7.00	1.41	16.87	198.50
0.500	7.80	1.47	15.40	186.30
0.600	9.20	1.58	13.26	171.90
0.800	9.90	1.52	7.62	113.80
0.900	10.00	1.52	3.57	80.09

<i>Table 1 (cont'd)</i>		Carbon tetrachloride		
0.050	2.60	1.03	1.69	70.55
0.100	3.70	1.33	5.51	115.36
0.200	4.10	1.37	7.70	150.00
0.300	5.30	1.44	9.41	164.00
0.400	6.35	1.51	9.75	180.00
0.500	7.34	1.53	8.39	159.48
0.600	8.40	1.65	8.08	148.20
0.800	9.30	1.56	4.40	100.00
0.900	10.10	1.59	2.40	50.00
<i>p</i> -xylene				
0.100	2.60	0.232	11.00	146.19
0.150	3.00	0.629	14.70	192.21
0.200	3.30	0.753	20.47	236.69
0.300	4.00	0.932	25.40	290.57
0.390	4.98	1.120	26.31	290.32
0.510	5.88	1.200	24.46	286.00
0.650	7.15	1.260	20.93	250.20
0.720	7.75	1.320	17.20	228.30
0.800	8.35	1.320	14.53	190.50
0.950	10.00	1.430	3.24	80.00
Dioxane				
0.100	4.30	1.90	6.80	80.00
0.190	4.80	1.69	10.33	132.30
0.325	5.80	1.48	23.76	177.30
0.480	6.97	1.35	23.42	177.10
0.590	7.75	1.43	20.62	168.20
0.650	8.20	1.43	18.80	155.90
0.740	8.85	1.44	15.12	123.10
0.850	9.60	1.57	9.00	98.80
0.960	10.30	1.59	2.80	29.10
Cyclohexane				
0.105	2.42	0.613	10.20	166.00
0.200	3.50	1.150	15.00	220.00
0.340	4.98	1.360	17.40	241.00
0.480	6.00	1.370	18.00	240.00
0.510	6.50	1.360	17.40	229.10
0.650	7.70	1.490	14.00	190.00
0.710	8.20	1.500	12.20	175.00
0.800	8.90	1.540	9.00	136.60
0.950	10.10	1.580	3.00	20.70
<i>n</i> -heptane				
0.130	2.25	0.331	16.20	222.60
0.210	2.95	0.848	23.00	286.90
0.340	4.10	1.120	26.40	327.20
0.450	5.15	1.230	26.40	327.20
0.540	6.00	1.280	25.60	303.80
0.650	7.15	1.440	22.00	242.50
0.720	7.80	1.510	20.00	217.70
0.820	8.75	1.540	15.00	164.70
0.900	9.50	1.570	9.00	106.70

DIBK is a mildly associated polar liquid and the value of linear correlation factor is 1.64 in pure form. It is an equilibrium mixtures of two tautomers [16], the 'keto' and 'enol' forms (Figure 4) and there is a possibility of self association in the pure liquid. Short-range specific interaction between polar molecules leads to preferential dipolar alignment. Reinforcement of

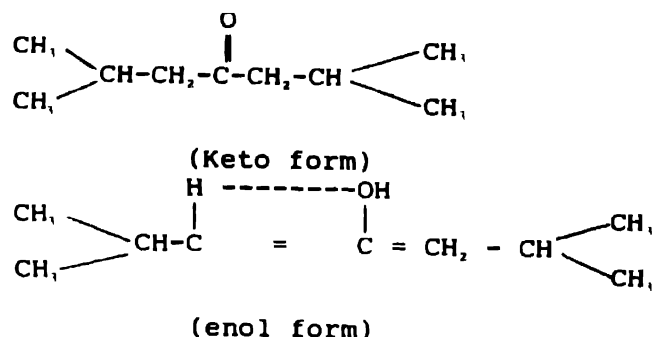


Figure 4. Equilibrium mixtures of two tautomers in DIBK

angular correlation results in parallel dipolar alignment leading to formation of α -multimers where $g > 1$. On the other hand, antiparallel dipolar alignment results in β -multimers where $g < 1$. The value of linear correlation factor ($g' = 1.64$) betokens predominance of α -multimers due to parallel dipolar alignment among the DIBK molecules which is possible due to the wood-pile arrangement (Figure 5) present in both the tautomeric forms.

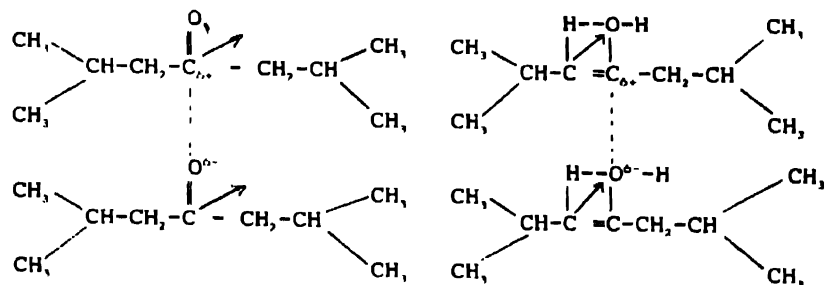


Figure 5. Wood-pile arrangement in two tautomers of DIBK

As the trend of variation of g indicates, on dilution with solvents like benzene, CCl_4 , p -xylene, n -heptane and cyclohexane, α -multimers are gradually converted into β -multimers. With lowering of DIBK concentration, the scarce DIBK molecules are surrounded by a cage of isolated nonpolar molecules and therefore fail to establish any correlation among themselves on their own and the solvent molecules do not help in reinforcing angular correlation. On the other hand, introduction of dioxane has two-fold action. Firstly, the OH hydrogen of DIBK in its enol form probably establishes hydrogen bonding with oxygen of dioxane (ether). This intermolecular interaction reinforces the intramolecular association of DIBK molecules as much as the value of g exceeds the value for pure DIBK in DIBK-deficient region. Secondly, $\text{O}^{\delta-}$ of $\text{C}=\text{O}$ group of DIBK in its keto form, is likely to be influenced by the oxygen of dioxane resulting in breaking of intramolecular bonds in DIBK. The second effect will overtake the first with slight increase in DIBK content as keto form is in excess of enol form [16]. It probably accounts for the subsequent fall in the value of g . With further reduction in availability of

dioxane molecules for higher DIBK concentration, the interaction gradually lapses into that corresponding to pure DIBK. Though the trend of variation of g is similar to that of (HAA + dioxane) system [7], yet the rate of variation of g is more rapid in DIBK (in DIBK-deficient region) and also the lowering in the value of g is more in DIBK which probably indicates that the strength of interaction between DIBK and dioxane is relatively stronger than HAA and dioxane and also the environment undergoes rapid change in it.

The benzene and CCl_4 being relatively smaller molecules, their abundance in DIBK-deficient range effectively screens the scarce neighbouring DIBK molecules, thereby reducing correlation among them. With increase of DIBK concentration, a large number of DIBK molecules are surrounded by these smaller molecules, where many of them are likely to be stacked in woodpile manner and therefore g increases to attain the value of pure DIBK.

In DIBK+cyclohexane system, DIBK molecules are trapped in the cleavage of boat and chair structure of cyclohexane molecules and maintain negligible correlation even when DIBK concentration is low. With further increase in DIBK concentration, more DIBK molecules are available outside the folds of cyclohexane structure reinforcing parallel orientation with consequent steady increase in the value of g .

Furthermore, it is most likely that due to steric hindrance of isobutyl group of DIBK with the methyl group of p -xylene in lower molefraction region of DIBK, where the isolated DIBK molecules are surrounded by a predominantly p -xylene environment, the correlation becomes negligible and the g value rather reflects that of the nonpolar solvent. Though p -xylene has p -electron cloud similar to benzene, g value tends to zero with lowering of DIBK concentration. Similar trends were observed in MIBK + p -xylene and HAA + p -xylene systems studied earlier [17, 7]. But with increasing DIBK concentration, the p -xylene environment rapidly changes and thus correlation among DIBK molecules is reinforced, indicated by the ascending value of g . Normal heptane is relatively bigger molecule and it is likely that in a sea of these molecules, scarce DIBK molecules experience considerable steric hindrance that prevents correlation in DIBK-deficient region. whereas with reduction of nonpolar molecules the polar molecules could establish correlation among themselves resulting in a rapid increase of g value. Similar results were also obtained by Dash *et al.* [5] in TBP+ n -heptane system. In p -xylene, greater delocalisation found in the benzene ring through hyper-conjugative effect of methyl group, prevents establishment of angular correlation initially where the solvent is in excess.

ΔP in all the mixtures is positive. ΔP (max) is in the order n -heptane> $>$ p -xylene $>$ dioxane $>$ cyclohexane $>$ benzene $>$ CCl_4 . It is consistent with the fact that with increasing DIBK concentration in all the six mixtures, the value of g steadily approaches to 1.64, thus increasing polarization.

The excess free energy of mixing ΔG , is also positive in all cases. ΔG (max) decreases in the order n -heptane $>$ p -xylene $>$ cyclohexane $>$ benzene $>$ CCl_4 $>$ dioxane. The excess of β -multimers are expected to be associated with reduction in internal energy and consequently positive value of ΔG is observed in group II and III liquids. However, the small positive value of ΔG for dioxane is compatible with the trend of variation of g where though the value of g is more than one, there is considerable conversion of α -multimers to β -multimers in the 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 this mixture is less than unity over a large concentration range.

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