

Dielectric studies on binary mixtures of methyl isobutyl ketone (MIBK) in non-polar solvents

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Received 6 December 1993; accepted 14 April 1994

Dielectric constants of binary mixtures of methyl isobutyl ketone (MIBK), an extractant used in nuclear industry, with non-polar solvents, viz., benzene, CCl₄ and *p*-xylene have been measured at 303 K. The results are used to compute linear correlation factor, excess molar polarization and excess free energy of mixing in these mixtures using the Winkelmann-Quitze equation to interpret the liquid structure. The trend of variation of these factors indicates gradual conversion of α -multimers to β -multimers on adding a non-polar diluent to MIBK.

Methyl isobutyl ketone (MIBK) is used for extraction of protactinium-233 from hydrochloric acid solutions containing neutron-irradiated thorium nitrate^{1,2} at a neutron flux of 10^{12} n cm⁻² s⁻¹. The extractant MIBK can be used with water immiscible diluents. Suitable physical properties are obtained by blending the extractant with diluents for greater dispersal and more rapid phase disengagement³. When the extractant is blended with a diluent, the dielectric constant of the organic phase changes and, therefore, we aim to undertake dielectric studies of binary mixtures of MIBK with benzene, carbontetrachloride and *p*-xylene which has practical relevance.

The linear correlation factor (g), mutual correlation factor ($g_{1,2}$), excess molar polarization (ΔP^M) and excess free energy of mixing (ΔG^M) determined from dielectric studies have been used earlier⁴⁻⁷ for interpretation of liquid structure in both polar-polar and polar-nonpolar systems. The linear correlation factor g , is a shape dependent correlation parameter⁸. Its value is an indicator of the nature of short-range intermolecular force leading to dipole-dipole interaction. Furthermore, the variation of g with concentration reflects on the change in dipolar alignment and hence the nature of multimerization. The theoretical curve for g described by Oster⁹ indicates its dependence on concentration of polar liquid in such type of systems and as such its experimental investigation

was undertaken by many resulting in the equations for the dielectric constant of the binary mixture¹⁰⁻²³. However, in view of the versatility of the Winkelmann-Quitze equation^{19,20}, it is used in this investigation for evaluation of g . Winkelmann and Quitze developed a thermodynamical model to consider the short-range specific interaction besides the long-range interaction. Accordingly the excess free energy of mixing ΔG^M in the binary mixture of a polar liquid in a non-polar solvent is given¹⁹ as

$$\Delta G^M = -\frac{N}{2}(R_{12} - R_{12}^0)[X_2 \mu_2^2 \{X_2(g' - 1) + 1\}]$$

where

$$R_{12}^0 = \frac{8\pi N(\epsilon_2 - 1)(\epsilon_\infty + 2)}{9V_2(2\epsilon_2 + \epsilon_\infty)}$$

$$R_{12} = \frac{8\pi N(\epsilon_m - 1)(\epsilon_\infty + 2)}{9V_2(2\epsilon_m + \epsilon_\infty)}$$

Here g' is linear correlation factor for the polar liquid (solute), ϵ_2 is its dielectric constant, ϵ_m is dielectric constant of the mixture, X_2 is mole fraction and V_2 is molar volume of the 2nd component in the mixture, μ_2 is the dipole moment and N is Avogadro's number.

Experimental Procedure

The dielectric constant measurements for the pure liquids as well as for mixtures were carried out by wavenumber-oscillator combination at

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Table 1—Variation of g , ΔP^M and ΔG^M with concentration of MIBK in three different solvents at 303 K

CCl_4					Benzene					<i>p</i> -Xylene				
X_2	ϵ	g	ΔP^M $cm^3 mol^{-1}$	ΔG^M $J mol^{-1}$	X_2	ϵ	g	ΔP^M $cm^3 mol^{-1}$	ΔG^M $J mol^{-1}$	X_2	ϵ	g	ΔP^M $cm^3 mol^{-1}$	ΔG^M $J mol^{-1}$
0.095	2.730	0.635	1.25	208.24	0.041	2.789	1.317	4.12	92.68	0.077	2.583	0.627	1.03	180.08
0.115	3.458	1.197	8.45	208.39	0.087	3.218	1.145	6.13	168.38	0.255	4.437	1.139	13.86	344.34
0.176	4.131	1.197	10.97	260.58	0.170	4.185	1.169	9.84	246.13	0.350	5.600	1.232	15.94	351.77
0.262	5.116	1.211	13.08	295.41	0.250	4.950	1.122	10.67	288.73	0.504	6.720	1.127	12.62	362.53
0.332	5.902	1.218	13.65	303.59	0.357	6.138	1.147	11.41	299.73	0.636	8.580	1.236	11.93	282.24
0.450	7.150	1.216	12.90	294.79	0.597	8.896	1.227	9.53	235.54	0.750	9.850	1.248	8.65	217.97
0.571	8.740	1.282	11.98	242.68	0.740	10.714	1.299	7.30	150.79	0.840	10.830	1.252	5.48	159.96
0.700	9.750	1.238	8.14	208.25	0.850	11.500	1.274	3.87	110.08	—	—	—	—	—
0.850	11.400	1.274	4.32	117.84	—	—	—	—	—	—	—	—	—	—

455 kHz²⁴. The device was standardized with the help of standard liquids with known dielectric constants^{25,26}. The cell temperature was controlled with an electronically regulated thermostatic arrangement, with temperature variation of $\pm 0.1^\circ C$. The refractive indices were measured at the regulated temperature by a Pulfrich-refractometer at sodium D-line. The density was measured using a Pycnometer of 25 mL capacity. The chemicals used were of AR grade purified by standard procedures^{27,28} and redistilled before use. The reproducibility of dielectric constant measurement was ± 0.003 and those of refractive index and density measurements were of ± 0.00002 and $\pm 0.00002 g cm^{-3}$, respectively. For these maximum limits of variation, the values of g , ΔG^M and ΔP^M could be measured precisely upto second decimal place.

Results and Discussion

The dielectric constants of the binary mixtures of MIBK-benzene, MIBK- CCl_4 and MIBK-*p*-xylene, measured at 303 K, were used to calculate the value of g , ΔP^M and ΔG^M in these mixtures. Some of the relevant data are given in Table 1.

The results show that for all the three systems studied g , ΔP^M and ΔG^M are all positive over the entire range of concentration. The trend of variation of g , however, is different. In the mixtures with CCl_4 and *p*-xylene the value of g is less than unity for low MIBK concentration and it increases to near-constant value beyond 0.2 to 0.3 molefraction range. On the otherhand, with benzene as the non-polar component in the mixtures, g decreases from a higher value to attain a minimum at about mole fraction 0.25 of MIBK and, thereafter, steadily increases to attain the value of pure MIBK.

The short-range specific interaction between the polar molecules leads to preferential dipolar

alignment. Reinforcement of angular correlation results in parallel dipolar alignment and such ordering or group of molecules are known as α -multimers. On the otherhand, antiparallel dipolar alignment results in β -multimers. $g > 1$ indicates predominance of α -multimers in the liquid while $g < 1$ shows β -multimers are in excess.

The solute-solvent interaction is the primary factor influencing the change in dipolar alignment in binary mixtures studied. The dipole moment of MIBK (gas phase) is 2.7 D and the value of g in pure liquid is 1.31 which indicates predominance of α -multimers in it. It is likely that MIBK molecules are arranged in wood-pile manner due to $C^{\delta+}$ and $O^{\delta-}$ linkage for intramolecular association in ketones.

The π -electron cloud of the benzene ring can variously interact with $C^{\delta+}$ or $O^{\delta-}$ of the carbonyl group of MIBK. There are also evidences of C-H hydrogen of methyl group entering into such interaction²⁹. At low MIBK concentration in MIBK-benzene mixture, g has a high value which decreases on increase of MIBK concentration. Thereafter, it increases to attain the value of pure MIBK. At extremely low concentration, few MIBK molecules are enclosed by predominantly benzene surrounding where all the three types of interactions of different nature are likely to cancel each others effect. As such, the g value is likely to be close to that of the pure liquid. However, with increasing concentration, the benzene environment around MIBK molecules alters and the interaction of π -electron cloud of the benzene ring with $O^{\delta-}$ becomes predominant leading to gradual conversion of α -multimers to β -multimers with anti-parallel ordering. But the β -multimers, are not likely to be closed-chain ones as the value of g_{min} is still higher than unity. With further increasing of MIBK the solvent effect reduces and g va-

lue approaches to that of pure MIBK. The trends indicated in the mixtures with *p*-xylene and CCl₄ are, however, different. Though *p*-xylene has π -electron similar to benzene, *g* value tends to zero with lowering of MIBK concentration while it increases for benzene. It is most likely due to steric hindrance of isobutyl group of MIBK with the methyl group of *p*-xylene in the lower mole fraction region of MIBK where the isolated MIBK molecules are surrounded by a predominantly *p*-xylene environment. Thus, MIBK molecules fail to establish any correlation among themselves and the *g* value rather reflects that of the non-polar solvent but with increasing MIBK concentration it increases to attain the value of pure MIBK. The trend for CCl₄ mixture, however, is intriguing. The solute-solvent interaction in case of CCl₄ is due to O^{δ-} of MIBK and positive chlorine of CCl₄ and reinforcement of parallel orientation is expected. Probably, for MIBK mole fraction $X_2 \rightarrow 0$, the nearly spherical CCl₄ molecules fill in voids in the MIBK structure, thereby, isolating MIBK molecules. This might be the reason for reduction in *g* value.

The trend of variation of excess molar polarization is nearly identical in all the systems. It is observed that ΔP^M is positive for the whole concentration range and is maximum at about 0.35 mole fraction of MIBK. The low value of ΔP^M in the low concentration range in the MIBK-benzene mixture coincides with lowering in the value of *g* while in the other two systems it coincides with the region where *g* attains the near constant value. Reduction of ΔP^M value for higher concentration of MIBK is probably due to depolymerization of MIBK clusters. The ΔP^M (max) for benzene mixture is minimum most likely due to initial lowering of *g* value from a high value. The excess free energy of mixing ΔG^M in all the systems remain positive over the entire composition range (Fig. 3). It attains a maximum at almost equimolar concentration range for *p*-xylene while the maxima for benzene and CCl₄ systems is at about 0.35 mole fraction of MIBK. The positive value of ΔG^M corroborates our findings in respect of *g* and ΔP^M , since lowering in the value of *g* or *g* value less than unity, both are indicative of creation

of β -multimers which is associated with reduction of internal energy. The ΔG^M (max) is highest in *p*-xylene system where the steric hindrance is maximum to prevent parallel alignment.

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