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Intermolecular interaction in the binary mixtures of ketones with nonpolar molecules

Ranjita Mahapatra [a],*, S.K. Ray [b]

[a] Department of Physics, Institute of Technical Education and Research, Siksha 'O' Anusandhan University, Bhubaneswar, 751 030 Odisha, India
[b] Ravenshaw Junior College, Cuttack, Odisha, India

A B S T R A C T

Excess free energy of mixing and excess molar polarization in the binary mixtures of ketones (acetone, MIBK, DIBK and acetyl acetone) in nonpolar solvents (carbon tetrachloride, Benzene, cyclohexane and n-heptane) is evaluated by Winkelmann–Quitzsch (WQ) and Ray et al. theory by using the experimental findings of relative permittivity and refractive index. The trend of variation of excess free energy of mixing and excess correlation factor depicts a clear picture of molecular association and liquid structure in the binary mixtures. The induction effect is less due to the steric hindrance of isobutyl group of DIBK and the short range interactions between the molecules are least for which WQ and Ray et al. modified equations hold good for the binary mixture of DIBK and nonpolar solvents at the same molar concentration of polar solvents. However, the induction effect is more in acetyl acetone in comparison to acetone and MIBK for which the peak value of $\Delta F_{ab}/\Delta P_{ab}$ lies in the region of 0.2 mol fraction of polar liquids whereas the peak value of $\Delta F_{WQ}/\Delta P_{WQ}$ lies in the equimolar concentration of polar and nonpolar solvents. The observation clearly indicates that the polar-induced nonpolar interaction and induced nonpolar-induced nonpolar interaction in binary liquid mixtures contributes a lot to decrease the excess molar polarization in acetone, MIBK and acetyl acetone.

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1. Introduction

The binary liquid mixtures of polar and nonpolar molecules bear an important ingredient for the separation and extraction of nuclear metals in nuclear industry [1,2] and also act as an absorber to reduce the decanted wastes coming from the industry. Such a chemical technique is known as solvent extraction process. Hence the importance of binary liquid mixtures increases for today's green industry technology [1–3]. It is also necessary to choose suitable liquid mixtures so that 100% purification of metal ingredients can be done. Before approach for the green industry technological application, an analytical treatment is required to evaluate some of the basic parameters like excess correlation factor and excess free energy of mixing which determines the suitability of the solvent extraction process. The evaluation and analysis of excess free energy of mixing is useful in the interpretation of molecular association in the liquid mixtures. Though earlier theoretical treatment suggested by Longuet-Higgins [4] is found useful in the interpretation of liquid structure involving weak interaction, it has its own limitation of not being applicable to hydrogen bonded systems. However a number of theories have been come up with the consideration of long range and short range dipolar interaction in the mixture of polar–polar molecules. Haskell [5] developed an expression for the excess free energy of mixing in the binary mixture of polar–nonpolar liquids

from the experimental value of relative permittivity without considering the short range correlation among the similar and dissimilar molecules. Later Winkelmann–Quitzsch (WQ) [6] extended the dielectric theory and developed the relation for excess free energy of mixing and excess molar polarization taking into account both long range and short range interaction separately between similar molecules as well as dissimilar molecules. Roy, Swain and others [7,8] have studied molecular interaction in the binary mixture of polar–nonpolar liquids using WQ equation. Subsequently Ray et al. [9,10] analyzed the concept of thermodynamic ideality proposed by Davis and Douheret [11] in the binary mixtures of polar liquids and developed the expression for excess free energy of mixing and excess molar polarization for proper study of liquid mixtures [3,12–14]. Many authors [3,14–18] have studied the dielectric properties of binary mixtures of polar liquids and polar nonpolar liquids with the help of Kirkwood correlation factor.

In this paper we have referred to the solvent extraction process which is an important analytical tool used for separation and purification of nuclear metals [19,20]. Various commercial extracting agents namely MIBK (Methyl isobutyl ketone), DIBK (Di isobutyl ketone) and acetyl acetone as a good separator are used in the nuclear energy industry for extraction and purification of metal ions i.e. uranium, thorium, actinide and lanthanide elements [20,21]. The mechanism involved in the solvent extraction process is one of the simple complex formations in which two distinct phases appear – an organic phase which contains the metal ion and aqueous phase which contains the rest of product. But the formation of a third mixed organic – aqueous phase inhibits phase

* Corresponding author. Tel.: +91 9437011558.
E-mail address: ranjitamahapatra@gmail.com (R. Mahapatra).

separation and as such reduces the separation efficiency. However the third phase is eliminated by either addition of a suitable diluent to the extractant or by increasing the temperature of the system [2]. More derivable physico-chemical properties are however obtained by blending the extractant with suitable solvent for greater dispersed and more rapid phase disintegration [22,23]. The dielectric spectroscopy method along with the determination of dielectric permittivity and other physico-chemical studies enable one to assess the 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 non polar solvents which may eventually be correlated with extraction efficiency. When the extractant is blended with diluents the relative permittivity of the organic phase changes [23] and therefore dielectric studies of binary mixtures of acetone, MIBK, DIBK and acetyl acetone with non polar solvents (carbon tetrachloride, benzene, cyclohexane and n-heptane) is undertaken. The excess free energy and excess molar polarization were evaluated using the analytical treatment of Winkelman–Quitzsch and Ray et al. The aspect of the solvent extraction process has been discussed through molecular interaction.

2. Experimental

Keeping in viewpoint of the choice of binary liquid mixtures of polar and nonpolar solvents, different ketones like acetone, MIBK, DIBK and acetyl acetone were considered as polar solvents whereas carbon tetrachloride, benzene, cyclohexane and n-heptane were considered as nonpolar solvents. Spec pure anal grade chemical were used for the mixture. The chemicals were purified and redistilled before taken for the experimental purpose. The purity of the liquids was checked by comparing the experimental data of density, viscosity and velocity of sound at 303 K with those reported in the literature. The accuracy of the measurement of relative permittivity and density were ± 0.003 and ± 0.002 g/cm^3 respectively. Then the mole amount of polar solvent was varied from 0.1 (approximately) to 0.9 (approximately) in the nonpolar solvents. The mixed solutions were stirred for 30 min to have homogeneity in mixture. Then it was placed in a hot bath and the temperature was kept fixed at 30 °C. The dielectric cell was dipped in the liquid to measure the dielectric constant using Dielectric constant instrument supplied by Mittal Enterprises. The cell temperature was controlled with an electronically regulated thermostat arrangement with temperature variation of ± 0.1 °C. The measurement of dielectric constant is carried out at a constant volume of 50 cc for all the mixtures. The general method of determining the dielectric constant of a liquid is defined as the ratio of electric capacitance of a cell when the liquid will be act as a dielectric medium(Cs) to the capacitance of the cell when air forms the dielectric medium (C$_0$) at a given temperature. Here in our experiment, all the measurements were performed at 303 K. The refractive index of the liquids was measured by Pulfrich refractometer. The excess free energy and excess molar polarization of all the mixtures were evaluated using the Winklemann–Quitzsch equation and Ray et al. equation given in theoretical section.

3. Theory

Evaluation of excess free energy of mixing is an important parameter for the determination of liquid structure. The attempt taken by Languet-Higgins [4] found suitable to interpret the liquid structure involving weak interaction. However this theory does not suit to find out the structure for H-bonded system due to the indistinguishability of the long range interaction from short range interaction whereas the presence of H-bonds bring a considerable change in the dielectric properties of liquid mixtures [24]. With the estimation of excess thermodynamic function, Haskell [5] reform the Onsagars equation with the accountability of long range electrostatic dipolar interaction without

considering the short range interaction. This shortfall in the Haskells theory has been extended by Winkelmann and Quitzch to estimate the excess thermodynamic functions of both long range and short range interaction in polar–polar binary liquid mixtures [6]. This theory establishes a relation between dielectric properties and thermodynamic functions. Henceforth, Davis–Douheret expression [11] includes the mutual correlation factor to prove it superiority for the detail study of liquid structure and the molecular associations in the liquid.

$$g = \left[\frac{9KT(2\varepsilon_m + \varepsilon_{\infty b})^2}{4\pi N\mu_b^2 X_b(\varepsilon_{\infty b}+2)^2(2\varepsilon_m+1)} \right] \tag{1}$$

$$\left[\left(\frac{\varepsilon_m - 1}{\varepsilon_m} \right) V_m - \left\{ \frac{3X_a V_a(\varepsilon_{\infty a}-1)}{(2\varepsilon_m + \varepsilon_{\infty a})} \right\} - \left\{ \frac{3X_b V_b(\varepsilon_{\infty b}-1)}{(2\varepsilon_m + \varepsilon_{\infty b})} \right\} \right]$$

The excess free energy of mixing of binary mixture of a polar liquid in a nonpolar solvent as given by Winkelman and Quitzsch is;

$$\Delta F_{WQ} = -\left(\frac{N}{2} \right) \left[X_b \mu_b^2 \left(R_{fb} - R_{fb}^0 \right) \{ X_b(g_b - 1) + 1 \} \right]$$
$$where$$
$$R_{fb} = \left(\frac{8\pi N}{9V_b} \right) \left\{ \frac{(\varepsilon_m - 1)(\varepsilon_{\infty b}+2)}{(2\varepsilon_m + \varepsilon_{\infty b})} \right\} R_{fb}^0 = \left(\frac{8\pi N}{9V_b} \right) \left\{ \frac{(\varepsilon_b - 1)(\varepsilon_{\infty b}+2)}{(2\varepsilon_b + \varepsilon_{\infty b})} \right\} \tag{2}$$

The expression for molar polarization for binary mixture of polar and nonpolar liquids as given by Winkelman and Quitzsch is

$$P_{WQ} = \left\{ \frac{\varepsilon_m}{\varepsilon_m + 2} \right\} \left[\left\{ \frac{3X_a V_a(\varepsilon_{\infty a}-1)}{(2\varepsilon_m + \varepsilon_{\infty a})} \right\} + \left\{ \frac{3X_b V_b(\varepsilon_{\infty b}-1)}{(2\varepsilon_m + \varepsilon_{\infty b})} \right\} \right.$$
$$\left. + \left\{ \frac{(\varepsilon_{\infty b}+2)^2}{(2\varepsilon_m + \varepsilon_{\infty b})^2} \right\} \left\{ \frac{(2\varepsilon_m + 1)4\pi N\mu_{gb}^2 X_b g_b}{9KT} \right\} \right] \tag{3}$$

Where a, b and m represent the non polar liquid, polar liquid and mixture respectively. X_b, X_a denote the mole fraction of polar and non polar liquids respectively. The other parameters are dielectric constant (ϵ), square of refractive index (ϵ_∞), dipole moment (μ), molar volume (V), Boltzmann constant (K), Temperature (T) in Kelvin and Avogadro's number (N).

Both WQ and DD theory could not be able to solve the problems of polar and nonpolar binary liquid mixtures as both the theory established a relation between molecular structure and excess thermodynamic functions in consideration of the long range and short range interaction of polar–polar (similar molecules). However a possibility of an interaction between the dissimilar molecules might be possible. Hence, the consideration of long range and short range electrostatic interaction with the interaction between the dissimilar molecules establishes a new equation and new theory by Swain et al. [7]. This equation reaches at a conclusion that the excess free energy does not depend on only one factor but it depends on dielectric constant, refractive index of polar liquid, dielectric constant of mixture, molar volume of pure polar liquid in the mixture. This equation gives an indication of the existence of induced effect on nonpolar molecules due to polar molecules in the binary mixture. For this reason, Ray et al. considered all type interaction associated in the polar–nonpolar binary liquid mixtures namely; polar–polar molecules; polar-induced nonpolar molecules and induced nonpolar-induced nonpolar molecules [25].

Hence Ray and others [13,26] have substituted excess correlation factor δg in place of g_b used by WQ in Eq. (2).

$$\Delta F_{ab} = -\left(\frac{N}{2} \right) \left[X_b \mu_b^2 \left(R_{fb} - R_{fb}^0 \right) \{ X_b(\delta g - 1) + 1 \} \right] \tag{4}$$

Where $\delta g = g - g_{ideal} = g - (X_a g_a + X_b g_b)$; g_a and g_b represent the correlation factor for pure non polar and polar liquids respectively.

It indicates that the expression for excess free energy of mixing for polar and nonpolar liquid mixture derived by Winkelman and Quitzsch refers to an ideal case which is revealed from the experimental