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Studies on molar volume, dielectric properties and refractive indices of Cyanex 923 + benzene/xylene at 300 K

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ABSTRACT

The present investigation describes interactions between Cyanex 923 and benzene/xylene at 300 K. The experimental values of molar volume, dielectric constant, refractive index, molar polarisation and molar refraction of pure Cyanex 923, benzene and xylene and their binary mixture over the entire mole fraction range have been determined. The excess parameters, Kirkwood correlation parameter, Gibb's free energy of mixing for these binary mixtures have been evaluated. The excess parameters have been tested using Redlich–Kister equation. The results indicate very weak interactions between Cyanex 923 and benzene/xylene.

1. Introduction

The properties of binary mixtures such as volume, dielectric constant, free energy, refractive index show irregular variation depending upon nature of molecular interactions [1]. In solvent extraction, the detailed studies on interaction between extractant and diluent provide insight to the extraction efficiency of extractant which optimise its use. In order to examine the role of diluent, its interaction with the extractant should be thoroughly studied. Solubility of organic extractants in diluents may be changed by the composition of the diluent. Therefore, a diluent should be free of reactive interaction with extractant in order to maximise the extraction. Nadi has studied effect of various diluents on extraction of Pr (III) and Sm (III) by Cyanex 923 from acidic nitrate medium. He concluded that in benzene the extraction was higher as compared to that in xylene [2]. It has been observed in case of solvent extraction of V (V) from chloride solution using EHEHPA or PC 88A that interaction of diluents having high dielectric constant with organophosphorous extractants is usually stronger as compared to those with low dielectric constant [3]. Panda et al. [4] have investigated the effect of diluents on extraction of Pr (III) using Cyanex 923 as extractant. They observed that in benzene, 4–8% extraction was achieved whereas turbidity appeared in case of xylene. Desirable physico-chemical properties are usually obtained by diluting the extractant with a suitable solvent for better dispersal and rapid phase disengagement [5,6]. Molecular interactions of binary mixtures of polar and non-polar liquids by ultrasonic, dielectric and viscosity studies have been investigated by several researchers [7–10]. The ultrasonic velocities and densities of binary mixtures of Cyanex 272, Cyanex 301 and Cyanex 302 with n-butanol were measured at 303.15 K as reported by Kamila and Dash [9]. The study of dielectric properties of binary mixtures of pure liquids at static and optical frequencies can provide information regarding molecular structure and intermolecular interaction [11]. Dielectric constant is one of the important properties of mixed solvent systems which explain the electrical properties of a system. The dielectric constants and excess values over entire mole fraction range at various temperatures for mixture of acetonitrile with butyl amine/ethyl amine/methyl amine have been reported by Ramana et al. [12].The frequency dependent dielectric behaviour of liquid mixtures provides information on molecular interactions and mechanism of molecular process. Viscosities, densities and excess properties of binary mixture of DEHPA with benzene, toluene and o-xylene have been studied by Swain et al. [13]. Variations in excess properties due to difference in sizes of the components of a mixture have also been investigated [14]. The studies on thermo physical properties such as density, dielectric constant, refractive index are related to molecular interactions present in various liquid mixtures [15]. Literature review shows that so far no reports are there on the molecular interaction studies of binary mixture of Cyanex 923 (trialkyl phosphine oxide) which is a polar compound and solvents such as benzene or xylene. Cyanex 923 is widely used as an effective extractant in the extraction and separation of many metal ions [16–20]. Therefore, the present study has been carried out with Cyanex 923/benzene and xylene in order to have deeper understanding of the intermolecular interactions governed by different types of intermolecular forces such as dispersion force, dipole-dipole interaction and dipole induced dipole forces. The chemical structure of Cyanex 923 is given below in Fig. 1. Despite more electronegativity of oxygen atom, the dipole moment of $R_3P = O$ is directed towards phosphorous, because of $p\pi$-$d\pi$ donation from

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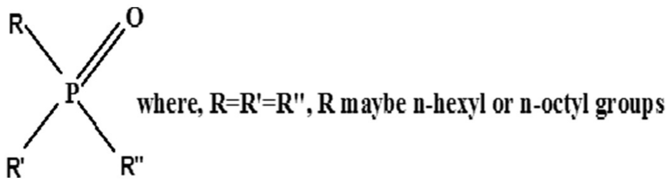

Fig. 1. Chemical structure of Cyanex 923.

oxygen to phosphorous [21]. Cyanex 923 molecules can remain either in "wood-pile" or in "head-tail" structural arrangement.The α- multimers result from head-tail configuration whereas β – multimers are formed due to wood – pile arrangement [22].

In this present investigation, molar volume, dielectric constant, refractive indices, molar polarization, molar refraction of binary mixture of Cyanex 923/benzene and xylene have been determined and corresponding excess parameters have been calculated over entire range of mole fraction in order to get information about the molecular interaction between an extractant which is treated as solute (phosphine oxide) and a diluent taken as solvent (benzene/xylene). The variations in these properties with composition provide information about intermolecular interactions. Redlich-kister polynomial is used to optimise the experimental values of excess parameters for the binary liquid mixtures [23].

2. Materials and methods

Cyanex 923, obtained from Cytec Inc. of Canada was used as received. Benzene and xylene used in the study were of analytical reagent grade. Binary mixture solutions were prepared on the basis of molar concentrations by dissolving required amount of Cyanex 923 in appropriate volume of benzene and xylene. The masses were measured using digital balance. The densities of pure liquids and liquid mixtures were determined using pyknometer. It was calibrated using double distilled water. The dielectric constants were determined by using capacitance measurement method with Dipole meter (Mittal Enterprises, New Delhi). An electronically operated digital constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel at a temperature of 300 K. Refractive indices were measured using Abbe's refractometer (MA-02) having an accuracy of ±0.0001.Calibration of the instruments was done by measuring the refractive indices of double-distilled water and ethanol at a known temperature. Water was circulated into the prism of the refractometer using a circulating pump connected with a constant temperature water bath to maintain the temperature. The sample mixtures were directly injected into the prism assembly of the instrument by means of an airtight hypodermic syringe. FT-IR spectral analysis of Cyanex 923 with benzene/xylene was studied on Perkin-Elmer FT-IR Spectrometer.

3. Theoretical aspects

The molar volume V_{12} of the mixture of Cyanex 923 and the diluents (benzene/xylene) can be defined as follows:

$$V_{12} = (X_1M_1 + X_2M_2)/\rho_{12} \quad (1)$$

Where, X_1, X_2, M_1 and M_2 are the mole fractions and molar masses of diluents and Cyanex 923 respectively: whereas ρ_{12} is the density of the binary mixture in gcm^{-3}. Since the refractive index values are closely related to mean polarizability P and molar refraction R, its measurement gives vital information on the interactions that are only concerned with dispersive forces. Polarizability predicts the interactions between polar and non-polar molecules in terms of dipole moments [24].

The molar refraction R_{12} of the binary mixtures was evaluated using the following equation,

$$R_{12} = \left[\left(n_{D_{12}}^2 - 1\right)/\left(n_{D_{12}}^2 + 2\right)\right][(M_1X_1 + M_2X_2)/\rho_{12}] \quad (2)$$

where $n_{D_{12}}$is the refractive index of the binary mixtures of Cyanex 923 and the diluents (benzene/xylene).

The values of molar polarization P_{12} for the mixtures were evaluated using the following equation:

$$P_{12} = [(\epsilon_{12} - 1)/(\epsilon_{12} + 2)][(M_1X_1 + M_2X_2)/\rho_{12}] \quad (3)$$

Where,ϵ_{12} is the dielectric constant of the binary mixtures.

The information regarding solute-solvent interaction can be obtained from excess properties [25] related to the dielectric constant, density and refractive index in the mixture. The excess properties of the mixture were calculated using the following equation.

$$A^E = A_{12} - (A_1X_1 + A_2X_2) \quad (4)$$

In the present investigation, A^Erepresents the excess parameters (V^E, ϵ^E,Δn_D,P^E,R^E). X_1 and X_2 are the mole fractions of the benzene/xylene and Cyanex 923, respectively in the binary mixtures. A_1 and A_2 are the values of above parameters for diluents and Cyanex 923, respectively. The experimental results of excess parameters have been fitted to a Redlich-Kister polynomial for optimisation of data [26].

$$A^E = X_2(1 - X_2)\left[\alpha_o + \alpha_1(2X_2 - 1) + \alpha_2(2X_2 - 1)^2 + \alpha_3(2X_2 - 1)^3\right] \quad (5)$$

where a_o, a_1, a_2 and a_3 are the adjustable parameters and X_2 is the mole fraction of the solute (Cyanex 923).

The dipole moments of pure liquids are calculated using the following equation [27]:

$$P_M = R_M + (4\pi N\mu^2/9kT) \quad (6)$$

where P_M is the molar polarization, R_M is the molar refraction, N is Avogadro's number, k is Boltzmann constant and T is absolute temperature.

Kirkwood correlation factor, g is a parameter used to obtain information regarding orientation of electric dipoles in polar liquids [28].The value of linear correlation factor g_{12} for the binary mixture is given by Kirkwood-Frohlich equation and expressed as

$$g_{12} = \frac{9kT}{4\pi N{\mu_2}^2X_2}\cdot\frac{(2\epsilon_{12} + \epsilon_{\infty2})^2}{(\epsilon_{\infty2} + 2)^2(2\epsilon_{12} + 1)} \times \left[V_{12}\cdot\frac{(\epsilon_{12} - 1)}{\epsilon_{12}} - \frac{3X_1V_1(\epsilon_{\infty1} - 1)}{(2\epsilon_{12} + \epsilon_{\infty1})} - \frac{3X_2V_2(\epsilon_{\infty2} - 1)}{(2\epsilon_{12} + \epsilon_{\infty2})}\right] \quad (7)$$

where ϵ_{12} is the dielectric constant of the binary mixture: $\epsilon_{\infty2}$, $\epsilon_{\infty1}$ the dielectric constant of the polar solute and non-polar solvent for frequency tends to infinity is taken as the square of the refractive index of the pure solute and non-polar solvent, respectively. V_{12}, V_1, V_2 are the molar volumes of the binary mixture, non-polar solvent and polar solute, respectively and μ_2 is the gas phase dipole moment of the pure solute. For pure liquids the linear correlation factor g is expressed as [29]

$$g_{22} = \frac{9kTM}{4\pi N{\mu_2}^2\rho}\cdot\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} \quad (8)$$

where ϵ is the dielectric constant of pure liquids (polar solute and non-polar solvent), ϵ_∞ is the square of the refractive index of polar and non-polar liquids. The excess free energy of mixing of binary mixture of polar