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Temperature dependent excess free energy of mixing and excess molar polarization of the binary mixture of butanols in nonpolar solvents

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ABSTRACT

The excess free energy of mixing and excess molar polarization in the binary mixture of butanols and nonpolar solvents are evaluated at different temperatures starting from 303 K to 318 K. Decreases in correlation factor, excess free energy of mixing and excess molar polarization have been observed with an increase in temperature. However, excess molar polarization does not vary much with respect to temperature at about 0.1 molar concentrations of polar liquids. In some mixtures, at this concentration excess molar polarization increases slightly with an increase in temperature. The excess free energy of mixing and excess molar polarization are higher in the binary mixtures of polar solutes with n-heptane due to the presence of an odd number of carbon atoms. It is important to observe that there is slight variation in excess free energy and excess molar polarization in these polar–nonpolar binary mixtures with respect to temperature. The excess free energy of mixing remains positive at all temperatures for most of the concentrations of polar solvents in polar–nonpolar binary liquid mixtures. This is an advantage to use such polar–nonpolar binary molecules for industrial applications.

1. Introduction

Dielectric investigations of binary mixtures of alcohols with both polar and nonpolar solvents have been studied by many researchers [1–8] due to their various applications in the field of nuclear industry, petrochemical industry, pharmaceutical industry etc. [9–11]. Especially, cyclohexane, t-butanol, n-hexane and their mixtures are used as solvents for biodiesel production [12]. Particularly, the mixture of t-butanol and n-hexane is used as a suitable solvent for biodiesel production due to its ability to eliminate negative effects of excess short chain alcohols on lipases [13]. The binary liquid mixtures of cyclohexane and t-butanol are also used as entertainers in azeotropic distillation process [14]. n-Butanol is the most efficient solvent for the extraction of the lubricating oils [15].

The study and understanding of the various physical and thermodynamical parameters of liquid mixtures become very important to know about the dipolar orientation and molecular association in the liquid mixture. Particularly, the evaluation and analysis of excess parameters like excess correlation factor, excess free energy of mixing and excess molar polarization is very much required as these parameters decide the suitability and the proportion of the solvent in the liquid mixture to industrial use [5]. However, determination of suitable binary liquid mixtures for the industrial use by performing an experiment is not completely possible. Hence, theoretical treatment for the determination of excess thermo-dynamical parameters is adopted to find the suitability of binary liquid mixture for industrial application even if no exact theory has been developed so far due to some limitations.

Though theoretical treatment suggested by Longueet-Higgins [16] is found useful in the interpretation of structures involving weak interaction, but not applicable for those liquids having hydrogen bonds due to the in-distinguishability of the long range force from that of the short range force. Hence, Winkelmann and Quitzsch [17] have developed the dielectric theory in the binary mixtures of polar liquids taking into account both long range and short range interactions. Swain and others [18,19] have studied the molecular interaction in the binary mixture of polar and nonpolar liquids by modifying Winkelmann–Quitzsch equations in which the dipole moment of nonpolar liquid is treated as zero. It has been observed that in several binary mixtures of polar and nonpolar liquids, the value of the correlation factor of pure polar solute in nonpolar solvent does not remain constant with the concentration variation of the polar solute in the mixture [18–24]. This is attributed to the short range interaction between polar and induced nonpolar molecules in the binary mixture [20,21]. Hence, Ray et al. has used the term excess correlation factor in the modified Winkelmann–Quitzsch equations.

Considering the excess correlation factor, we have analyzed the excess parameters of the binary mixtures of butanols with nonpolar solvents (n-hexane, n-heptane and cyclohexane) using Ray et al. equation due to their various applications in the industry and contributions to greenery environment. As, no chemical processes can maintain a constant temperature (a slight variation in the temperature), the excess parameters at various temperatures starting from 303 K to 318 K has

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been evaluated. The temperature range was considered looking into the present maximum environment temperature range in summer to find out the feasibility of the binary liquid mixtures for various industrial applications.

2. Experimental detail

Spec pure anal grade polar liquids (i-butanol, n-butanol and t-butanol) and the non-polar liquids (n-hexane, n-heptane and cyclohexane) were used as binary liquid mixtures. The chemicals were purified and distillated following the experimental procedure reported earlier [25] before preparation of binary liquid mixtures. The density of liquid was measured with the help of a digital balance having an accuracy of 0.001 g and a pycnometer of 25 cm^3 capacity. 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 [26]. The measured instrument was calibrated at every working temperature with air and using liquid with well-known dielectric constant (benzene). The measurement accuracy of relative permittivity and density was ± 0.003 and ± 0.002 g/cm^3 respectively. Then, the mole fractions of i-butanol, n-butanol and t-butanol were varied from 0.1 (approximately) to 0.9 (approximately) in the nonpolar solvents. The mixed solutions were stirred for 30 min to form a homogeneous mixture. Then, it was placed in a hot bath and the temperature was kept varied from 303 K to 318 K. The temperature was considered looking into the present maximum environment temperature range in the summer. The dielectric cell was dipped in the liquid to measure the dielectric constant using a dielectric constant meter associated with LCR meter. 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 cm^3 for all the mixtures. The refractive index of the liquids was measured by Pulfrich refractometer using sodium n-line and the accuracy is 0.00001. The density, refractive index, dielectric constant, and dipole moment of polar liquids are given in Table 1a and the density and refractive index of nonpolar liquids are given in Table 1b.

The values of the dielectric constant and the refractive index found from the experiment has been used to determine the excess correlation factor, excess free energy and excess molar polarization of all the mixtures using the Ray et al. (ab) equations given in Eqs. (1) & (2).

Table 1a
Density, refractive index, dielectric constant, dipole moment of butanols.

Pure polar liquids	Density (g/cm^3)	Refractive index	dielectric constant	Dipole moment
T = 303 K				
n-Butanol	0.802	1.3918	15.828	1.660
i-Butanol	0.801	1.3888	16.768	1.640
t-Butanol	0.778	1.3869	10.900	1.660
T = 308 K				
n-Butanol	0.7996	1.3902	15.052	1.660
i-Butanol	0.7902	1.388	15.959	1.640
t-Butanol	0.774	1.3791	10.598	1.660
T = 313 K				
n-Butanol	0.7946	1.389	14.640	1.660
i-Butanol	0.786	1.3875	15.280	1.640
t-Butanol	0.768	1.3778	9.986	1.660
T = 318 K				
n-Butanol	0.7906	1.3861	14.020	1.660
i-Butanol	0.780	1.387	14.681	1.640
t-Butanol	0.762	1.3761	9.347	1.660

Table 1b
Density, refractive index of non-polar liquids at various temperature.

Pure non-polar liquids	Density (g/cm^3)	Refractive index
T = 303 K		
n-Hexane	0.660	1.375
n-Heptane	0.683	1.3877
Cyclohexane	0.778	1.4265
T = 308 K		
n-Hexane	0.6452	1.3657
n-Heptane	0.672	1.3764
Cyclohexane	0.768	1.4152
T = 313 K		
n-Hexane	0.6409	1.3642
n-Heptane	0.666	1.3738
Cyclohexane	0.76	1.4117
T = 318 K		
n-Hexane	0.6364	1.3614
n-Heptane	0.660	1.3710
Cyclohexane	0.756	1.4085

The excess free energy of mixing of binary mixture of a polar liquid in a nonpolar solvent is given by,

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

where,

$$R_{fb} = \left(\frac{8\pi N}{9V_b}\right)\left\{\frac{(\varepsilon_m-1)(\varepsilon_{\infty b}+2)}{(2\varepsilon_m+\varepsilon_{\infty b})}\right\}, R_{fb}^0 = \left(\frac{8\pi N}{9V_b}\right)\left\{\frac{(\varepsilon_b-1)(\varepsilon_{\infty b}+2)}{(2\varepsilon_b+\varepsilon_{\infty b})}\right\}.$$

The expression for molar polarization for binary mixture of polar and non-polar liquids is given as

$$P_{ab} = \left\{\frac{\varepsilon_m}{\varepsilon_m+2}\right\} \times \left[\left\{\frac{3X_aV_a(\varepsilon_{\infty a}-1)}{(2\varepsilon_m+\varepsilon_{\infty a})}\right\}+\left\{\frac{3X_bV_b(\varepsilon_{\infty b}-1)}{(2\varepsilon_m+\varepsilon_{\infty b})}\right\}+\left\{\frac{(\varepsilon_{\infty b}+2)^2}{(2\varepsilon_m+\varepsilon_{\infty b})^2}\right\}\left\{\frac{(2\varepsilon_m+1)4\pi N\mu^2{}_bX_bg}{9KT}\right\}\right] \quad (2)$$

where a, b and m represent the nonpolar liquid, polar liquid and mixture respectively. X_b and X_a denote the mole fractions of polar and nonpolar liquids respectively. The other parameters are dielectric constant (ϵ), square of refractive index (ϵ_∞), dipole moment of polar liquid (μ_b), molar volume (V), Boltzmann constant (K), Temperature (T) in Kelvin, and Avogadro's number (N) and δg is the excess correlation factor. The evaluation of correlation factor and excess correlation factor is calculated using our earlier report [20,21]. The excess molar polarization in the binary mixture of polar and nonpolar liquids is given by

$$\Delta P = P-\sum_{r=a,b} X_rP_r \quad (3)$$

where P is the molar polarization of the liquid mixture and P_r is the molar polarization of the pure liquid. The detail theory of Ray et al. has been described extensively in our earlier work [20,21].

3. Results and discussion

Tables 2–4 represents the variation of dielectric constant of liquid mixtures with respect to temperature. The dielectric constant increases with the increase in polar solvents but decreases with the increase in temperature. The dielectric constant of mixture is used for the determination of excess free energy of mixing and excess molar polarization for the mixtures.

The correlation factor (g) is a shape dependent parameter that helps in the qualitative interpretation of the liquid structure. Since the change