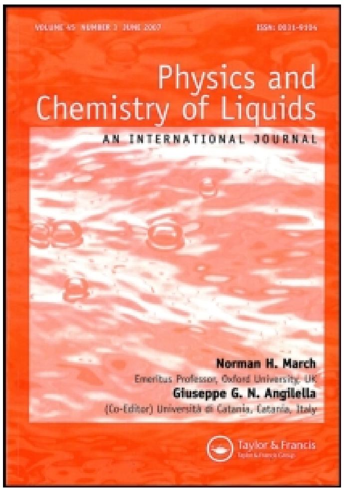

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INFLUENCE OF TEMPERATURE ON MOLECULAR DIPOLE ORIENTATION IN THE BINARY MIXTURE OF POLAR–NONPOLAR LIQUIDS

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The excess correlation factor in the binary mixture of polar liquid (*i.e.*, *i*-butanol and *t*-butanol) in the nonpolar solvent (*i.e.*, benzene, tetrachloromethane, *n*-heptane) has been evaluated at 301°K, 307°K, 313°K and 318°K. An extensive study has been made on the influence of temperature on the orientation of molecular dipoles in the solution with the help of the excess correlation factor.

Keywords: Binary mixture; excess correlation factor; molecular dipoles

INTRODUCTION

One of the important problems in liquid state physics is concerning the structure of multimers in associated liquids in pure state and in different solvents. But the theoretical treatments [1] which are useful in the interpretation of structure and thermodynamic properties in case of weak interactions, give improper results when applied to such hydrogen bonded system [1]. This is due to the fact that the interaction arising out of the short-range forces and long-range forces such as dipole–dipole interaction cannot be readily distinguished in the case of nearest neighbours since the dipole–dipole interaction energy also contributes

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to hydrogen bond energy. However, the experimental method [2] gives useful information regarding such interactions. The I.R. and N.M.R. studies do not give any information concerning the alignment of the neighbouring solute molecules [3], which is essential for the complete knowledge of the configuration of the multimer species. Cole [4] has pointed out that the Kirkood-Fröhlich [5] linear correlation factor 'g' is a measure of short range intermolecular forces that led to dipole – dipole interactions. The factor 'g' cannot be explicitly calculated from statistical-mechanical consideration [5] due to the unknown parameters like mutual correlation factor and number of nearest neighbours. However, experimental determination of linear correlation factor gives quantitative information regarding intermolecular association in polar liquids [6, 7]. But in case of binary mixtures of polar liquids Davis and Douheret [8] have shown that the excess correlation factor has played a vital role in the study of molecular dipole alignment in the solution. Similarly, the excess correlation factor in the binary mixture of polar and nonpolar liquids is considered to be an important parameter [9 – 11] for the study of liquid structure. However much extensive studies have not been made on temperature dependence of excess correlation factor. So we have undertaken this aspect to study the variation of molecular dipole orientation with temperature in the binary mixture of polar and nonpolar liquids with the help of excess correlation factor.

THEORY

Kirkwood-Fröhlich [5] expression for correlation factor for polar and nonpolar liquid mixtures is given by

$$g = \frac{9kT\varepsilon_o}{N\mu_{gB}^2 X_B} \frac{(2\varepsilon_m + \varepsilon_{\infty B})^2}{(\varepsilon_{\infty B} + 2)^2 (2\varepsilon_m + 1)} \left[V\frac{\varepsilon_m - 1}{\varepsilon_m} - \frac{3X_A V_A(\varepsilon_A - 1)}{2\varepsilon_m + \varepsilon_A} - \frac{3X_B V_B(\varepsilon_{\infty B} - 1)}{2\varepsilon_m + \varepsilon_{\infty B}} \right] \tag{1}$$

On the other hand, the expression for excess correlation factor [9 – 13] is given by

$$\delta g = g - (X_A + X_B g_{BB}) \tag{2}$$

where X_A and X_B are the mole fraction of nonpolar and polar liquid respectively, g_{BB} is the correlation factor of polar liquid; N is Avogadro's number; k is Boltzmann constant, ε_o is the vacuum permittivity; μ_{gB} is the gas phase dipole moment; ε_m and ε_A are the dielectric constants of the mixture and nonpolar liquid; V, V_A and V_B are the molar volumes of mixture, nonpolar liquid and polar liquid respectively, $\varepsilon_{\infty B}$ is the square of the high frequency refractive index of polar liquid and T is temperature in kelvin.

EXPERIMENTAL

The experimental devices used for the measurement of dielectric constant, density, refractive index *etc.*, are same as that of Tripathy *et al.* [14].

RESULT AND DISCUSSION

The excess correlation factor is a shape dependent parameter that helps in qualitative interpretation of liquid structure. Since the change of temperature influences the orderliness as well as orientation of molecular dipole moments in the solution, we have evaluated 'δg' in the binary mixtures of *i*-butanol and *t*-butanol in nonpolar solvents (*i.e.*, benzene, tetrachloromethane, *n*-heptane) at 301°K, 307°K, 313°K and 318°K which is presented in Table I.

It is supposed [15] that the dissimilar molecules in the mixture form microheterogeneous clusters that vary in composition over entire concentration range of the mixture. The magnitude of mutual correlation factor reflects the arrangement of the dissimilar molecules in those clusters. When dissimilar molecules align in the same direction they are said to form α-clusters. Alignment of molecular dipoles in opposite direction may be termed as β-clusters.

Swain [16] has found in the binary mixture of polar liquids that mutual correlation factor $g_{AB} > 1$ for all associated + associated liquid mixtures whereas $g_{AB} < 1$ for associated + nonassociated liquid mixtures. Identical results have been obtained by Davis and Douheret [8] basing on the concept of excess correlation factor. Further we have

TABLE I Variation of excess correlation factor with mole fraction of polar liquids at 301°K, 307°K, 313°K, 318°K

		'δg'		
X_B (1)	301°K (2)	307°K (3)	313°K (4)	318°K (5)
		(a) *i*-butanol + benzene:		
0.078	−0.389	−0.333	−0.502	−0.633
0.128	−0.476	−0.496	−0.519	−0.524
0.190	−0.335	−0.369	−0.435	−0.512
0.250	−0.337	−0.387	−0.445	−0.535
0.300	−0.255	−0.341	−0.412	−0.496
0.360	−0.198	−0.249	−0.302	−0.359
0.430	−0.086	−0.162	−0.206	−0.284
0.600	−0.030	−0.072	−0.114	−0.212
		(b) *i*-butanol + tetrachloromethane:		
0.074	−0.639	−0.273	−0.773	−0.794
0.136	−0.807	−0.406	−0.918	−0.942
0.202	−0.635	−0.539	−0.833	−0.918
0.256	−0.640	−0.639	−0.727	−0.926
0.319	−0.603	−0.638	−0.756	−0.858
0.375	−0.556	−0.636	−0.647	−0.832
0.420	−0.431	−0.557	−0.683	−0.922
0.500	−0.395	−0.595	−0.770	−0.900
0.600	−0.070	−0.502	−0.524	−0.802
		(c) *i*-butanol + *n*-heptane:		
0.078	−0.419	−0.401	−0.493	−0.553
0.110	−0.501	−0.417	−0.567	−0.624
0.194	−0.615	−0.470	−0.774	−0.811
0.260	−0.543	−0.585	−0.598	−0.647
0.335	−0.514	−0.648	−0.644	−0.754
0.405	−0.413	−0.534	−0.708	−0.869
0.469	−0.326	−0.522	−0.777	−0.731
0.535	−0.204	−0.418	−0.402	−0.688
0.600	−0.220	−0.326	−0.432	−0.642
		(d) *t*-butanol + benzene:		
0.079	−0.428	−0.467	−0.518	−0.588
0.146	−0.511	−0.432	−0.522	−0.564
0.211	−0.322	−0.459	−0.574	−0.599
0.240	−0.208	−0.323	−0.426	−0.478
0.270	−0.185	−0.289	−0.319	−0.407
0.338	−0.179	−0.279	−0.345	−0.445
0.400	−1.96	−0.252	−0.334	−0.416
0.600	−0.044	−0.210	−0.066	−0.193
		(e) *t*-butanol + tetrachloromethane:		
0.080	−0.189	−0.194	−0.239	−0.279
0.138	−0.451	−0.243	−0.543	−0.537
0.199	−0.487	−0.295	−0.571	−0.577
0.250	−0.360	−0.325	−0.478	−0.457
0.340	−0.372	−0.401	−0.427	−0.436
0.380	−0.281	−0.348	−0.422	−0.466
0.435	−0.269	−0.263	−0.293	−0.381
0.500	−0.110	−0.190	−0.345	−0.375
0.600	−0.104	−0.168	−0.316	−0.364

TABLE I (Continued).

		'δg'		
X_B (1)	301°K (2)	307°K (3)	313°K (4)	318°K (5)
		(f) t-butanol + n-heptane:		
0.080	− 0.489	− 0.504	− 0.579	− 0.609
0.110	− 0.516	− 0.509	− 0.552	− 0.608
0.195	− 0.612	− 0.620	− 0.636	− 0.683
0.268	− 0.682	− 0.693	− 0.707	− 0.745
0.342	− 0.614	− 0.613	− 0.759	− 0.758
0.407	− 0.425	− 0.550	− 0.612	− 0.733
0.480	− 0.415	− 0.536	− 0.603	− 0.685
0.543	− 0.423	− 0.451	− 0.613	− 0.727
0.600	− 0.334	− 0.488	− 0.646	− 0.684

observed that the excess correlation factor 'Δg' proposed by Davis and Douheret is similar to $(g_{AB} - 1)$ of Winkelmann and Quitzsch expression in various types of polar liquids [17]. In view of this, we have defined excess correlation factor 'δg' in binary mixture of polar and nonpolar liquids whose magnitude is taken as the departure from ideality [9–13]. The excess correlation factor is a shape dependent parameter which depends on the orientation of molecular dipoles of polar liquids and induced dipole of nonpolar liquid in the solution.

We have observed in Table I that in the binary mixture of *i*-butanol and *t*-butanol in the nonpolar solvent *i.e.*, benzene, tetrachloromethane and *n*-heptane, the excess correlation factor remains negative and the negativity of excess correlation factor increases with the increase of temperature. Alignment of molecular dipoles in the environment of alcohols (*i.e.*, *i*-butanol, *t*-butanol) in nonpolar solvent is reflected in the value of 'δg'. Therefore, we are of the view that the value of 'δg' at different mole fraction of polar liquid in the binary mixture is an indicator of nature of multimerisation and the type of molecular interaction. Further alcohols being highly associative, molecular interaction takes place between the polar alcohol molecules, polar alcohol and induced nonpolar molecules as well as induced nonpolar molecules. The increase of negativity of 'δg' with the increase in temperature in almost all the mixtures might be due to the fact that with increase in temperature, the randomness of molecular dipoles (polar liquid) and the induced dipoles (nonpolar solvent) increases which reduces the angular correlation among the neighbouring molecules.

Therefore the increase in temperature prevents the formation of α-clusters *i.e.*, parallel orientation of dipoles and induced dipoles and favours the formation of β-clusters [18].

Further it is observed that (δg)-minima in the binary mixture containing *i*-butanol is greater than that of *t*-butanol which is probably due to higher associative character of *i*-butanol in comparison to *t*-butanol.

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