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Dipolar interaction in binary mixtures of some higher alcohols and polar liquids-mutual correlation factor and excess molar polarization and excess free energy

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Abstract : Dielectric constant of binary mixtures of some long-chain normal aliphatic alcohols namely pentanol, hexanol, heptanol and octanol with aniline and with chlorobenzene has been measured at 303.16 K and 455 kHz. The data are used to calculate g_{ab}, ΔP and ΔG in them using *WQ* equation to study the molecular interaction in them.

Keywords : Dielectric constant, binary mixture, *WQ* equation, mutual correlation factor, excess polarization and free energy

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Winkelmann and Quitzsch [1] developed a relation from statistical-mechanical consideration linking the dielectric constant of binary mixtures with those of pure components. This equation is so comprehensive that the earlier developed relations of Onsagar [2], Kirkwood-Fröhlich [3,4], Hörig and Michel [5] are found to be its special cases. Winkelmann and Quitzsch [6] further extended their dielectric theory to evaluation of excess thermodynamic parameters. Both the equations, are first of its kind as they incorporate molecular interaction according to separation and therefore, contribution due to both long-range and short-range dipolar interaction between the similar as well as dissimilar molecules could be separately evaluated. Besides the Kirkwood-Fröhlich linear correlation factor, they introduced a term

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mutual correlation factor 'g_{ab}' to account for short-range dipolar interaction between molecules of variety *a* and *b*.

Later Davis and Douheret [7] developed a mixture equation purely from empirical considerations and introduced a parameter called excess correlation factor 'Δg' to represent the departure from ideality. The term 'Δg' in effect, is identical to $(g_{ab}-1)$ of the *WQ* equation. Davis and Douheret further extended the dielectric relation to develop relation for thermodynamic excess functions.

Swain [8a,b], Dash and Swain [9] evaluated g_{ab} and Ray and Roy [10a,b] and also Tripathy [11] applied both *WQ* equation and *D.D.* equation for evaluation of g_{ab} and Δg as well as ΔG, the Gibb's excess free energy in number of mixtures. They observed that there is a qualitative agreement but quantitative difference between $(g_{ab}-1)$ and Δg. Identical inference was arrived at for ΔG. Since *WQ* equations recognise the dipolar contribution according to molecular separation while empirical *D.D.* equations express the total contribution, the former have an edge over the *D.D* equations. Furthermore, the fact that the already established equations for pure liquids as well as for binary liquid mixtures are found to be its special cases makes the *WQ* equations more acceptable.

The equations for g_{ab}, ΔP and ΔG based on *WQ* equation and Δg based on *D.D.* equation are taken from the earlier works [7]. The experimental arrangement is also the same as used earlier [8a].

In this study, dielectric constant of binary mixtures of four long chain aliphatic mono-alcohols *i.e.* n-pentanol, n-hexanol, n-heptanol and n-octanol with two polar solvents namely chlorobenzene and aniline has been determined at 303.16 K and 455 kHz. The data are used to calculate mutual correlation factor g_{ab}, excess molar polarization ΔP and Gibb's excess free energy ΔG and excess correlation factor Δg in these mixtures. The relevant data are presented in Table 1(a–d).

The variation of dielectric constant with concentration of alcohols in both sets of mixtures is displayed in Figures 1, 2. The nonlinear characteristic of the curve is an indicator of the mutual interaction between the unlike molecules, which will be better reflected in the other parameters evaluated in this study. Subramanian *et al* [12] and Kolling [13] in their study on excess dielectric constant in binary mixtures of polar liquids reported identical findings.

Winkelmann and Quitzsch [1] postulated the creation of microheterogeneous clusters of unlike molecules due to short-range dipolar interaction in the binary mixtures. Unlike molecules with parallel orientation result in $g_{ab} > 1$ while $g_{ab} < 1$ indicates predominance of antiparallel orientation. In analogy with terms α-multimers and β-multimers characterized by parallel and antiparallel orientation of similar molecules, respectively in a pure hydrogen bonded liquid, the clusters formed in the binary mixtures are named α- and β-clusters [8a] for $g_{ab} > 1$ and $g_{ab} < 1$, respectively.

In all the mixtures investigated here, g_{ab} is less than unity indicating predominance of β-clusters. The extent of departure of g_{ab} from unity, represents the degree of interaction. It is

Table 1. Variation of ε, g_{ab}, Δg, ΔP, ΔG with concentration in different solvents at 303.16 K.

(a) Alcohol-n-pentanol											
Solvent-aniline						Solvent-chlorobenzene					
X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}	X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}
0.114	7.401	0.916	0.873	0.908	-5.156	0.099	6.112	0.913	0.890	1.186	-2.741
0.208	7.899	0.853	0.778	1.502	-1.124	0.209	6.708	0.844	0.800	2.287	3.507
0.302	8.501	0.830	0.732	2.271	1.004	0.299	7.399	0.806	0.746	3.329	14.599
0.399	9.152	0.810	0.694	2.718	11.570	0.421	8.312	0.783	0.709	4.152	34.535
0.510	9.904	0.804	0.677	2.874	26.666	0.495	8.993	0.799	0.720	4.611	40.377
0.609	10.611	0.818	0.698	2.916	32.845	0.596	9.892	0.814	0.735	4.547	50.265
0.719	11.452	0.835	0.727	2.315	44.633	0.689	10.721	0.831	0.759	3.995	57.732
0.804	12.211	0.882	0.800	1.962	34.841	0.800	12.001	0.925	0.870	3.431	29.550
0.898	13.001	0.932	0.883	1.136	23.273	0.902	12.987	0.969	0.930	1.933	15.512
(b) Alcohol-n-hexanol											
0.109	7.202	0.859	0.815	-0.095	-1.896	0.096	5.899	0.845	0.828	-0.345	11.584
0.207	7.399	0.715	0.638	-0.799	15.626	0.199	6.400	0.735	0.696	0.207	16.687
0.301	7.789	0.632	0.528	-0.742	29.178	0.300	7.023	0.670	0.610	1.053	25.293
0.399	8.152	0.538	0.410	-1.124	60.183	0.398	7.679	0.625	0.548	1.615	42.083

Table 1. (*Contd.*)

(b) Alcohol-n-hexanol

Solvent-aniline						Solvent-chlorobenzene					
X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}	X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}
0.502	8.700	0.497	0.354	-1.020	90.266	0.455	8.016	0.593	0.509	1.556	58.374
0.592	9.312	0.496	0.348	-0.805	115.028	0.595	9.204	0.619	0.524	2.158	73.906
0.710	10.298	0.568	0.429	-0.296	126.361	0.694	10.089	0.663	0.571	2.100	77.025
0.811	11.199	0.678	0.564	-0.131	110.457	0.800	11.103	0.738	0.661	1.642	67.759
0.912	12.123	0.775	0.709	-0.345	81.615	0.892	12.029	0.828	0.777	0.940	47.104

(c) Alcohol-n-heptanol

X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}	X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}
0.105	7.008	0.910	0.877	-0.207	19.135	0.053	5.692	0.942	0.931	-0.289	13.218
0.200	7.213	0.851	0.796	-0.171	29.848	0.157	6.025	0.871	0.843	0.119	23.521
0.299	7.498	0.806	0.734	-0.023	38.940	0.358	6.819	0.778	0.732	0.839	48.642
0.405	7.812	0.769	0.689	-0.018	50.496	0.452	7.301	0.765	0.715	1.246	58.534
0.512	8.353	0.777	0.694	0.548	51.437	0.554	7.921	0.777	0.728	1.709	62.624
0.602	8.655	0.760	0.682	0.272	64.278	0.656	8.559	0.797	0.752	1.758	64.493
0.716	9.213	0.780	0.715	0.187	66.992	0.750	9.305	0.858	0.820	1.972	47.554
0.801	9.712	0.821	0.771	0.181	57.696	0.892	10.356	0.939	0.919	1.208	22.580
0.923	10.498	0.906	0.884	0.150	32.203	0.912	10.416	0.929	0.913	0.772	20.139

Table 1. (*Contd.*)

(d) Alcohol-n-octanol

Solvent-aniline						Solvent-chlorobenzene					
X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}	X_2	ε	g_{ab}	$\Delta g+1$	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}
0.110	6.900	0.871	0.821	−0.898	25.538	0.059	5.601	0.898	0.881	−1.263	23.013
0.207	7.005	0.777	0.695	−1.473	39.176	0.115	5.782	0.849	0.820	−1.155	22.844
0.299	7.152	0.704	0.600	−1.917	49.245	0.199	6.008	0.768	0.722	−1.436	29.605
0.401	7.375	0.643	0.526	−2.252	58.829	0.305	6.355	0.699	0.639	−1.416	34.807
0.592	7.902	0.582	0.466	−2.728	79.845	0.413	6.899	0.676	0.606	−0.677	33.861
0.652	8.113	0.583	0.474	−2.766	84.800	0.519	7.403	0.667	0.607	−0.342	40.354
0.715	8.398	0.612	0.514	−2.450	81.962	0.599	7.813	0.677	0.674	−0.147	45.271
0.812	8.803	0.644	0.572	−2.556	84.566	0.689	8.399	0.738	0.742	0.517	37.820
0.905	9.508	0.802	0.759	−1.164	47.493	0.899	9.653	0.889	0.861	0.376	22.366

observed to be concentration dependent. Its value is unity at both ends corresponding to pure liquid while it attains a minimum in the nearly equimolar concentration range. We have also

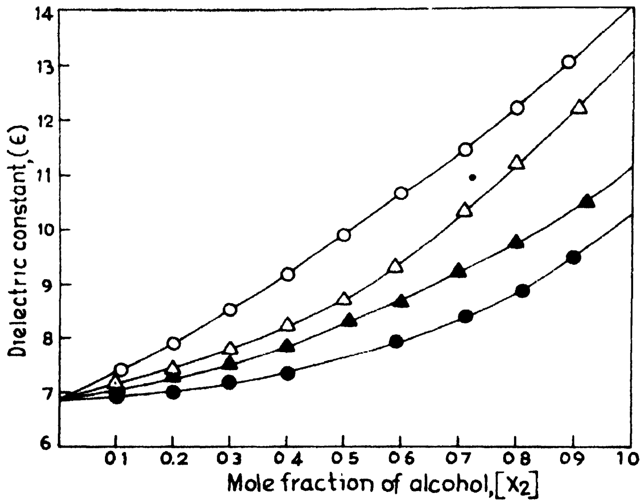

Figure 1. Variation of ε with concentration X_2 of alcohols.
Plots : ⊙ Aniline + Pentanol, △ Aniline + Hexanol,
▲ Aniline + Heptanol, ● Aniline + Octanol.

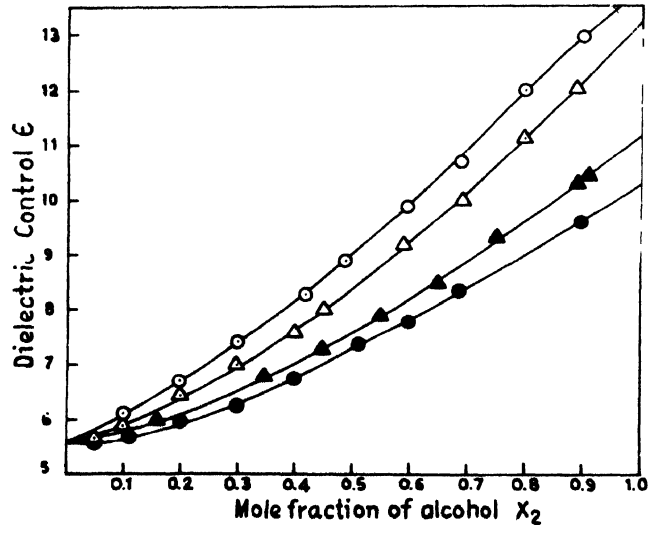

Figure 2. Variation of ε with concentration X_2 of alcohol.
Plots : ⊙ Chlorobenzene + Pentanol, △ Chlorobenzene + Hexanol,
▲ Chlorobenzene + Heptanol, ● Chlorobenzene + Octanol.

included (Δg+1) in the Table 1 with a view to comparing it with the magnitude of g_{ab}. The trends of variation of both (Δg+1) and g_{ab} with concentration of alcohol in the mixtures show qualitative agreement though there is quantitative difference.

The alcohol molecules in the pure state, are arranged in homogeneous clusters of atleast three molecules [14]. There are molecular size holes or voids in such liquid structures [15]. With increase of alcohols concentration more of the chlorobenzene/aniline molecules go to fill the voids in the alcohol structure which attains the saturation limit at nearly equimolar concentration range.

In the alcohol-chlorobenzene mixture, the interaction is expected to be between Cl^{δ^-} of chlorobenzene and H^{δ^+} of alcohol. In the mixture containing aniline, most likely interaction involves N^{δ^-} of aniline and H^{δ^+} of alcohol.

It is observed that in both alcohol-aniline and alcohol-chlorobenzene systems, the departure of $g_{ab(\mathrm{min})}$ from unity is in the order hexanol > octanol > heptanol > pentanol. Excepting pentanol, this is in the same order as the linear correlation factor in the liquids in the pure state *i.e.* hexanol (3.92), octanol (3.08), heptanol (2.43) and pentanol (3.25). The interacting group OH is common to all alcohols investigated here and therefore, the difference in the value of g reflects on the steric hindrance offered by different molecules. Since the other interacting group in the binary mixture remains fixed for a system (Cl or NH), it is logical to expect that the relative orientation of unlike molecules will also be affected by the steric hindrance in alcohols in the same order. As such, the trend of variation of g_{ab} for hexanol, octanol and heptanol fits to the pattern indicating the degree of interaction in that order but pentanol is the exception. Rout and Chakravorty [16] used ultrasonic investigation in binary mixtures of TBP with similar long chain alcohols and reported variation in degree of interaction dependent both on concentration and the chain length of alcohols. Rajendran [17] also determined internal pressure in mixtures of some higher alcohols and reported presence of similar type of interaction.

For the long-chain alcohols, steric hindrance is likely to favour linear linkage between the unlike molecules which results in open chain β-clusters. But with reduced steric hindrance in pentanol some of the molecules may establish strained linkage resulting in formation of α-clusters. Though the β-clusters still predominate, there is gradual conversion of β-clusters to α-clusters. As such, g_{ab} is closer to unity. An identical trend is observed in similar type of mixtures involving lower alcohols [18].

In aniline mixtures, the departure of $g_{ab(\mathrm{min})}$ from unity is more than that in the corresponding chlorobenzene mixture at the same concentration, most probably due to greater activity of NH group than that of the Cl group.

The trend of variation of ΔP mostly shows that in the mixtures with pentanol, it is positive while for octanol and hexanol, it is mostly negative over the entire concentration range in the mixture. For heptanol it is partly positive. Predominance of β-clusters in the mixtures with hexanol and octanol is the probable cause for negative value of ΔP while greater conversion of β to α-multimers is supported by positive ΔP in pentanol mixtures. According to *W.Q.*, the value of g_{aa} and g_{bb} in the mixture equation is the same as that in the pure liquid. It presupposes that the short-range correlation between the like molecules is unaffected. As such, the orienting groups only alter in number and distribution. This assumption is the probable reason for some departures observed.

The trend of variation of ΔG (Table 1) shows that it is positive over the entire concentration range in all mixtures with the exception that it has slight negative value for alcohol deficient region in the mixtures containing pentanol. Formation of β-clusters are expected to cause greater reduction in internal energy. The magnitude of $\Delta G_{\max}$ for hexanol mixtures being highest, corroborates our findings on g_{ab} and ΔP that the extent of formation of β-clusters is maximum in this system. We have not reported ΔG from *D.D.* equation here because ΔG reported on the basis of *WQ* equation reflects on the nature of short-range interaction between unlike molecules which would be used to corroborate our findings on g_{ab} whereas its value from *D.D.* equation includes the contribution due to long-range interactions between like and unlike molecules as well.

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