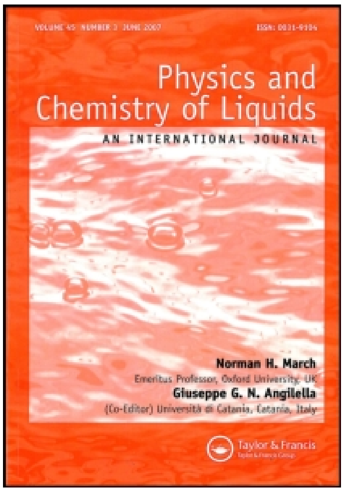

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EXCESS MOLAR POLARIZATION IN BINARY MIXTURES OF POLAR LIQUIDS

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Excess Molar Polarizations ($\Delta P_{\mathrm{W.Q.}}$, $\Delta P_{\mathrm{D.D.}}$) have been evaluated in the binary mixture of associated + associated and associated + nonassociated polar liquids using Winkelmann–Quitzsch and Davis–Douheret equations. It is observed that Winkelmann–Quitzsch equation ($\Delta P_{\mathrm{W.Q.}}$) is the more appropriate one for interpretation of dynamic characteristics of the molecular association in a liquid mixture.

Keywords: Binary mixture; Polar liquid; Excess molar polarization

INTRODUCTION

The study of dielectric properties of binary mixtures of polar liquids over a wide frequency range yields qualitative information on molecular dynamics and molecular interactions in the liquid mixture. Höring and Michael [1] have proposed an equation for a binary mixture of polar liquids based on Onsager's equation which takes Lagragion interaction into account and neglects the short range specific interaction of polar liquids. Theoretical treatments [2] which are useful in the interpretation of structure and thermodynamic properties in case of weak interactions give inaccurate results when applied to such hydrogen bonded systems. This is due to the fact [3]

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that the interaction arising out of the short range forces and long range forces such as dipole–dipole interactions cannot be readily distinguished in case of nearest neighbours since the dipole–diople interaction energy contributes to hydrogen bond energy. Winkelmann–Quitzsch [4] however developed a relation linking the dielectric constant of a binary mixture considering both long range and short range dipolar interaction between similar and dissimilar molecules using the Kirkwood [5] correlation factor of dielectric polarization. Subsequently Davis–Douheret [6] have developed an empirical expression for molar polarization. But the expected properties such as thermodynamic parameters, dielectric parameter *etc.* in a binary mixture do not vary linearly [7]. The deviation of these parameters from the linear behaviour termed as excess parameters is considered to be very important and helps to find the nature of interactions between the two liquids [8]. Again the dynamic molecular aggregation in the binary mixture of polar liquids depends on the polarizability of the polar molecules. So we have evaluated the excess molar polarization using these Winkelmann–Quitzsch (W.Q.) and Davis–Douheret (D.D.) expressions in the associated + associated and associated + nonassociated polar liquid mixtures.

THEORY

Winkelmann–Quitzsch [4] have regarded the binary mixtures of polar liquids as a homogeneous medium represented by a uniform dielectric constant ε_m. They have developed the mixture equation taking into account the reaction field factor on the basis of Onsager's treatment [9] utilizing the concept of statistical theory of Ramshaw [10] and Wertheim [11].

$$\frac{\varepsilon_{m-1}}{\varepsilon_m} V_m = \sum_{r=a,b} \frac{3X_r V_r(\varepsilon_{\infty r}-1)}{(2\varepsilon_m+\varepsilon_{\infty r})} + \sum_{r=a,b} \left(\frac{\varepsilon_{\infty r}+2}{2\varepsilon_m+\varepsilon_{\infty r}}\right)^2 (2\varepsilon_m+1)\frac{4\pi N}{9\mathrm{kT}}$$

$$X_r\,\mu_{gr}\,g_{rr} + \frac{(\varepsilon_{\infty a}+2)(\varepsilon_{\infty b}+2)(2\varepsilon_m+1)}{(2\varepsilon_m+\varepsilon_{\infty a})(2\varepsilon_m+\varepsilon_{\infty b})}\frac{4\pi N}{9\mathrm{kT}}\,\mu_{ga}\,\mu_{gb}\,[g_{ab}-1] \tag{1}$$

where

a, b refer to the molecules of variety of a and b,
X_r denotes the respective mole fraction of the component in the mixture,
V_r and V_m denote the molar volumes of the components and mixture respectively,
N is Avogadro's number,
k is Boltzmann's constant,
T is temperature in kelvin,
μ_{gr} is gas-phase dipolement of the component,
ε_m is the dielectric constant of the mixture,
$\varepsilon_{\infty r}$ is taken as the square of the refractive index of the component,
g_{rr} represents the linear correlation factor between identical molecules $a-a$ and $b-b$,
g_{ab} denotes the mutual correlation factor between the dissimilar molecules.

Winkelmann–Quitzsch [4] have developed the expression for the molar polarization of the binary mixture utilizing the separation of total correlation [12]

$$P_{m\text{.W.Q.}} = \frac{4\pi N\varepsilon_m}{\varepsilon_m+2}\left[\sum_{r=a,b}\frac{(\varepsilon_{\infty r}+2)}{(2\varepsilon_m+\varepsilon_{\infty r})}X_r\alpha_r + \sum_{r=a,b}\left(\frac{\varepsilon_{\infty r}+2}{2\varepsilon_m+\varepsilon_{\infty r}}\right)^2(2\varepsilon_m+1)X_r\,\mu_{gr}^2 g_{rr}/9\text{kT} + \frac{(\varepsilon_{\infty a}+2)(\varepsilon_{\infty b}+2)(2\varepsilon_m+1)}{(2\varepsilon_m+\varepsilon_{\infty a})(2\varepsilon_m+\varepsilon_{\infty b})}\,\frac{\mu_{ga}\mu_{gb}}{9\text{kT}}(g_{ab}-1)\right] \quad (2)$$

where α_r is the polarizability of the respective component in the mixture.

The excess molar polarization is given by

$$\Delta P_{\text{W.Q.}} = P_{m\text{.W.Q.}} - \sum_{r=a,b} X_r P_r \quad (3)$$

Where, P_r is the molar polarization of the component.

Davis–Douheret [13] have defined the excess correlation function 'Δg' as a measure of departure from the ideality.

$$\Delta g = \frac{\mu_{\mathrm{eff}}^2 - \mu_{\mathrm{eff.id}}^2}{\mu_g^2} \tag{4}$$

Where,

$$\mu_{\mathrm{eff}}^2 = \frac{9\mathrm{kT}}{4\pi N} \frac{V_m(\varepsilon_m - \varepsilon_{\infty m})(2\varepsilon_m + \varepsilon_{\infty m})}{\varepsilon_m(\varepsilon_{\infty m} + 2)^2}$$

$$\mu_{\mathrm{eff.id}}^2 = X_a\, g_{aa}\, \mu_{ga}^2 + X_b\, g_{bb}\, \mu_{gb}^2$$

$$\mu_g = X_a \cdot \mu_{ga} + X_b \cdot \mu_{gb}$$

Davis–Douheret have developed an alternative expression [6] for molar polarization from Onsager theory for the binary mixture of polar liquids.

$$P_{m.\mathrm{D.D.}} = \frac{(\varepsilon_m - \varepsilon_{\infty m})(2\varepsilon_m + \varepsilon_{\infty m})}{\varepsilon_m(\varepsilon_{\infty m} + 2)^2} V_m \tag{5}$$

where $\varepsilon_{\infty m}$ is the square of the refractive index of the binary mixture.

The excess molar polarization is given by

$$\Delta P_{\mathrm{D.D.}} = P_{m.\mathrm{D.D.}} - \sum_{r=a,b} X_r P_r \tag{6}$$

EXPERIMENTAL

The experimental methods used for determination of dielectric constant, refractive index, density *etc.*, were same with that of Swain [14]. The experiment was performed at 307°K. The dielectric measurements for liquid mixtures were carried out by a wavemeter–Oscillator combination at 455 kHz. This device was standardised with standard liquids [15] with known dielectric constants (benzene, tetrachloromethane). The cell temperature was controlled with an electronic thermostat arrangement with temperature variation of ± 0.1°C. The refractive indices were measured at the regulated temperature by a Pulfrich refractometer at Sodium D-line. The density measurement was done by semimicrobalance with a py-kno-meter of 25 ml capacity. The chemicals (*n*-proponol, *n*-butanol, *i*-butanol, *t*-butanol, chlorobenzene) used were of reputed make, purified and redistilled before use. The reproducibility of dielectric constant measurement at radio frequency was ± 0.003. The reproducibility of refractive index and density measurements were ± 0.00002 and ± 0.0002 g/cm^3 respectively.

RESULT AND DISCUSSION

We have evaluated $\Delta P_{W.Q.}$ and $\Delta P_{D.D.}$ from data such as dielectric constant, density, refractive index *etc.*, from the experiment at 307°K for the binary mixtures of associated + associated and associated + nonassociated polar liquids. The result of $\Delta P_{W.Q.}$ and $\Delta P_{D.D.}$ at different mole fraction of first component in the mixture are presented in Table I and displayed in Figures 1 and 2.

TABLE I Variation of $\Delta P_{W.Q.}$ and $\Delta P_{D.D.}$ in cm^{3}mol^{-1} in binary mixtures of polar liquids at 307°K

Mole fraction of 1st component	*Dielectric constant (m)*	$(g_{ab}-1)$	'Δg'	$\Delta P_{W.Q.}$ *Cm*^{3} *mol*$^{-1}$	$\Delta P_{D.D.}$ *Cm*^{3} *mol*$^{-1}$
1	2	3	4	5	6
[(A)Associated + Associated]					
		(i) *t*-butanol + *n*-propanol			
.104	18.680	.155	.071	0.70	82.308
.179	18.153	.198	.152	1.13	77.343
.280	17.643	.286	.216	1.68	72.429
.375	16.902	.295	.253	2.02	64.848
.439	16.414	.330	.255	2.18	56.304
.507	15.830	.335	.264	3.32	53.154
.621	14.909	.331	.258	2.40	42.200
.761	13.475	.270	.250	2.30	25.106
		(ii) *t*-butanol + *i*-propanol			
.065	17.000	.068	.061	0.49	2.781
.125	16.706	.080	.099	0.83	4.083
.192	16.291	.162	.122	1.06	4.202
.260	16.000	.168	.125	1.22	5.513
.372	15.196	.181	.161	1.31	3.831
.436	14.805	.190	.184	1.49	3.766
.516	14.337	.154	.149	1.66	3.759
.633	13.410	.132	.127	1.57	0.277
.757	12.532	.075	.072	1.45	– 2.565

TABLE I (Continued)

Mole fraction of 1*st component*	*Dielectric constant* (*m*)	$(g_{ab} - 1)$	'Δg'	$\Delta P_{W.Q.}$ Cm^3 mol^{-1}	$\Delta P_{D.D.}$ Cm^3 mol^{-1}
1	2	3	4	5	6
		(iii) *t*-butanol + *i*-butanol			
.057	16.149	.114	.038	0.28	85.888
.138	15.804	.137	.067	0.53	78.022
.265	15.260	.170	.113	0.92	68.539
.356	14.972	.219	.168	1.31	62.34
.449	14.535	.232	.190	1.49	54.009
.511	4.251	.234	.204	1.53	48.014
.598	13.601	.233	.171	1.49	37.712
.722	12.876	.193	.172	1.41	25.143
[(B)Associated + Non-associated]					
		(iv) *n*-propanol + Chlorobenzene			
0.149	5.519	− 0.063	− 0.144	− 1.69	− 16.982
0.233	5.734	− 0.287	− 0.317	− 1.12	− 22.881
0.319	6.195	− 0.376	− 0.427	− 0.25	− 26.425
0.385	6.915	− 0.425	− 0.463	0.66	− 27.212
0.423	7.649	− 0.430	− 0.519	1.22	− 27.204
0.546	9.988	− 0.358	− 0.482	2.37	− 23.555
0.653	11.902	− 0.275	− 0.409	2.58	− 19.636
0.692	14.416	− 0.151	− 0.292	2.60	− 17.374
0.785	17.053	− 0.036	− 0.147	2.37	− 12.412
		(v) *n*-butanol + Chlorobenzene			
0.11	5.628	− 0.247	− 0.263	− 1.83	− 12.366
0.22	6.020	− 0.366	− 0.386	− 2.26	− 22.47
0.32	6.630	− 0.447	− 0.498	− 1.92	− 27.043
0.43	7.546	− 0.473	− 0.539	− 0.98	− 30.119
0.53	9.048	− 0.369	− 0.449	− 0.90	− 24.906
0.63	10.449	− 0.286	− 0.370	1.71	− 20.591
0.72	11.908	− 0.183	− 0.279	1.96	− 14.818
		(vi) *i*-butanol + Chlorobenzene			
0.102	5.614	− 0.200	− 0.213	− 1.39	− 13.528
0.206	5.866	− 0.384	− 0.413	− 2.72	− 24.416
0.299	6.101	− 0.544	− 0.589	− 3.71	− 33.884
0.397	6.836	− 0.603	− 0.668	− 2.92	− 37.85
0.478	7.498	− 0.640	− 0.712	− 2.36	− 40.463
0.559	8.575	− 0.593	− 0.685	− 1.18	− 38.124
0.658	10.117	− 0.491	− 0.586	− 0.014	− 32.348
0.742	11.575	− 0.384	− 0.469	0.46	− 25.77

For the binary mixtures of associated + associated polar liquids (*i.e.*, *t*-butanol + *n*-Propanol, *t*-butanol + *i*-butanol, *t*-butanol + *i*-propanol), it is observed in Table I and Figure 1, both $\Delta P_{W.Q.}$ and

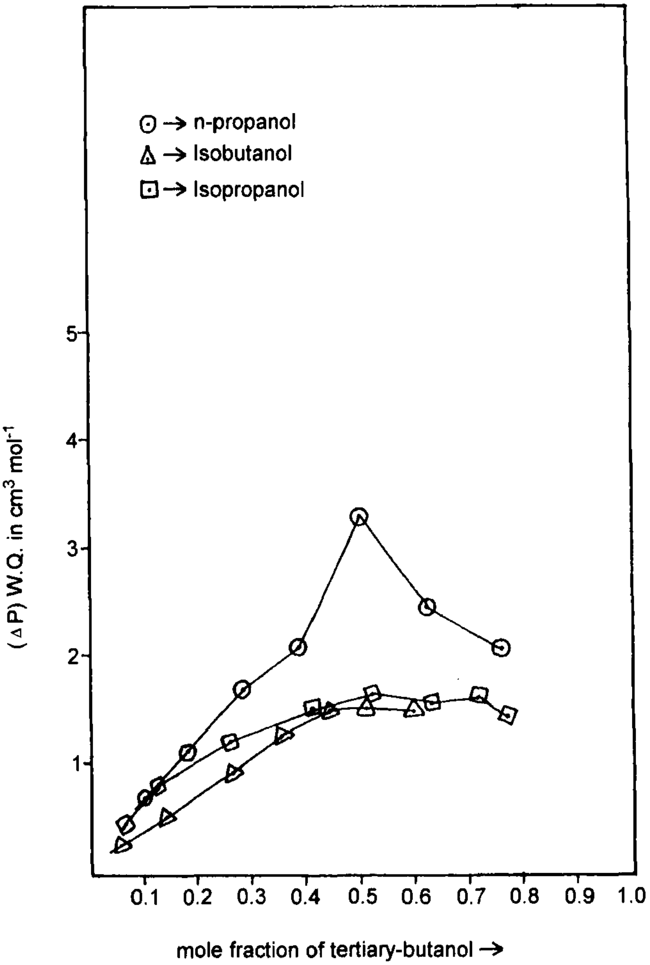

FIGURE 1 Variation of (ΔP)W.Q. with the mole fraction of tertiary butanol in alcohols at 307°K.

$\Delta P_{\mathrm{D.D.}}$ are positive. With increase of concentration of first component in the mixture, the value of excess molar polarization $(\Delta P_{\mathrm{W.Q.}})$ increases and attains a maxima and then decreases. This is probably due to the fact that the associated liquid mixtures favour parallel orientation of molecular dipoles (α-clusters) at lower concentration of one component which becomes maximum at equimole fraction of both components. Thereafter there is a gradual conversion of

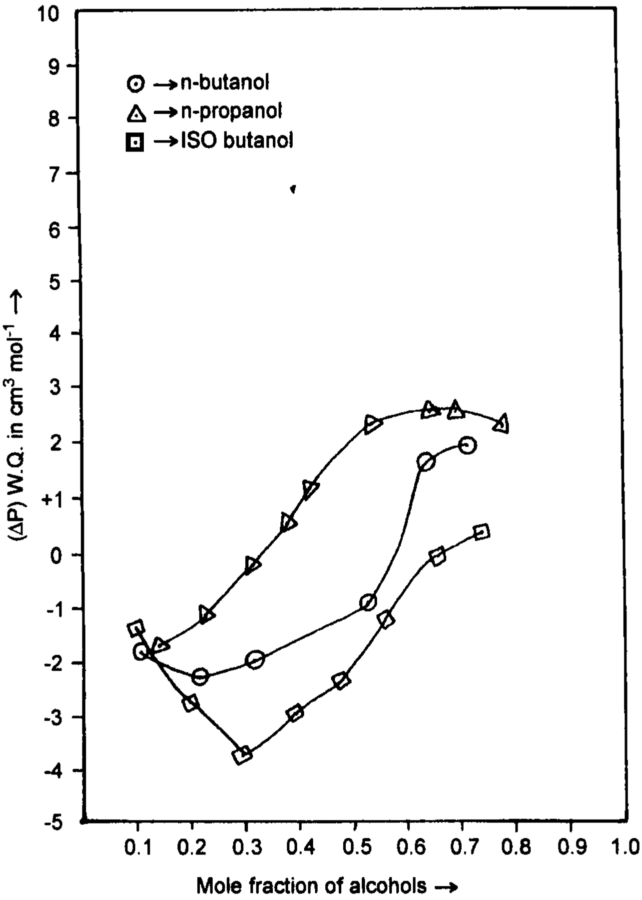

FIGURE 2 Variation of (ΔP)W.Q. with the mole fraction of alcohols in chlorobenzene at 307°K.

molecular dipoles from the parallel orientation (α-cluster) to antiparallel orientation (β-cluster) due to molecular interaction among the similar and dissimilar molecules in the mixture. This corroberates with the finding of Swain [14] and Ray *et al.* [16] that the excess correlation factor $(g_{ab} - 1)$ and Δg are positive for associated + associated polar liquids mixtures. But in case of excess molar polarization $(\Delta P_{\mathrm{D.D.}})$ using Davis–Douheret equation, it has been observed that $(\Delta P_{\mathrm{D.D.}})$ maxima are in lower concentration region of first component in the mixture. Again it is observed in Figure 1 that in the binary mixtures of associated liquids, ($\Delta P_{\mathrm{W.Q.}}$) maxima are in the order, *n*-propanol > *i*-propanol > *i*-butanol which are consistent with the facts that the dipole moment of above polar liquids are in the same order (*i.e.*, μ(*n*-propanol) = 1.68 Debye, μ(*i*-propanol) = 1.66 Debye, μ(*i*-butanol) = 1.64 Debye). On the other hand ($\Delta P_{\mathrm{D.D.}}$) maxima are in order; *i*-butanol > *n*-propanol > *i*-propanol which cannot be explained satisfactorily on the basis of the molecular and physical properties of liquids in the mixtures.

We have observed in the binary mixture of associated liquids (*n*-propanol, *n*-butanol, *i*-butanol) in non-associated liquids (*i.e.*, chlorobenzene), $\Delta P_{\mathrm{D.D.}}$ remains negative throughout all mole fraction of associated liquid in mixture. But it is found in Figure 2 that $P_{\mathrm{W.Q.}}$ remains negative in the associated deficient region and becomes positive in associated rich region. This is presumably due to the fact that the antiparallel alignment of molecular dipole predominate in the region where nonassociated liquid is in excess and parallel alignment of molecular dipoles is the dominant factor in the associated rich region where the long range electrostatic interaction plays a vital role for polarization [17]. It is also observed that the mole fraction of associated liquids in the mixture in which $\Delta P_{\mathrm{W.Q.}}$ remains negative, are in the order, *i*-butanol > *n*-butanol > *n*-propanol. This may be due to the fact that the molecular dipole moments of the above mentioned associated liquids are in the order, μ(*i*-butanol) < (*n*-butanol) < μ(*n*-propanol). As the nonassociated liquids favour antiparallel orientation of molecular dipoles [14], so formation of more β-clusters is feasible in the binary mixture of *i*-butanol + chlorobenzene. As molecular dipole moment of *n*-propanol is larger, $\Delta P_{\mathrm{W.Q.}}$ remains negative in the low concentration region of *n*-propanol and soon with the increase of mole fraction *n*-propanol in the mixture, it favours the formation of α-clusters due to its associated character and hence $\Delta P_{\mathrm{W.Q.}}$ becomes positive. This result tallies with the fact that the magnitude of ($\Delta P_{\mathrm{W.Q.}}$) minima are in the order, *i*-butanol > *n*-butanol > *n*-propanol.

Thus we are led to conclude that though there is a qualitative agreement between both the equations yet quantitative difference makes one superior when compared to the other. The development of W.Q. equation based on the assumptions that the linear correlation factor (g_{aa} or g_{bb}) between similar molecules is the same as that of the pure liquids. With this concept Winkelmann–Quitzsch have developed the expression for the mutual correlation factor (g_{ab}). But Davis–Douheret while attempting to formulate a relation for ideal molar susceptibility of a binary mixture of associated liquids extended the mixture equations of Onsager liquid [9] by incorporating Kirkwood–Fröhlich correlation factor and ignoring the mutual correlation factor g_{ab}. Davis–Douheret have formulated the expression for the excess correlation factor 'Δg' based on the assumption that for a binary mixture of associated liquids to behave ideally, the orientational correlation between the unlike molecules should be a suitably weighted average of the correlation between like pair of components [13]. Thus in the evaluation of Δg, they have not considered the mutual interaction factor between two components of mixtures. Again Davis–Douheret have formulated the expression for molar polarization of pure polar liquids without taking into consideration the molecular properties such as molecular dipole moments of each component and mutual correlation factor of dissimilar molecules in the mixture. But the Winkelmann–Quitzsch expression for excess molar polarization is the only relation that recognises the short range interaction between the dissimilar molecules and similar molecules in the mixtures taking molecular properties of the polar liquids in the mixture into consideration. Hence we are of the view that the Winkelmann–Quitzsch equation for the evaluation of the excess molar polarization is the better choice to analyze the structural and dynamic characteristics of the pattern of molecular association in the binary mixtures of polar liquids.

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