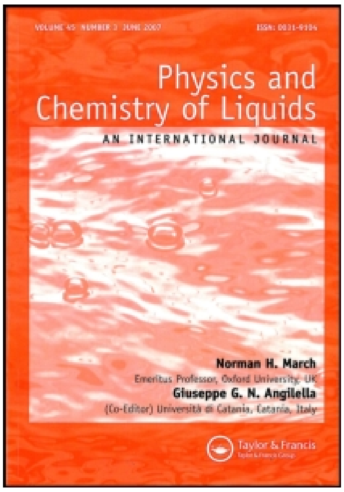


Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Evaluation of excess molar polarization in binary mixtures of Polar-Nonpolar liquids

C. Dwivedy[a]; S. K. Ray[b]
[a] Department of Physics, Government College, Angul, Orissa, India [b] Department of Physics, B.J.B. College, Bhubaneswar, Orissa, India

To cite this Article Dwivedy, C. and Ray, S. K.(2004) 'Evaluation of excess molar polarization in binary mixtures of Polar-Nonpolar liquids', Physics and Chemistry of Liquids, 42: 2, 207 — 213
To link to this Article: DOI: 10.1080/00319100410001679657
URL: http://dx.doi.org/10.1080/00319100410001679657

Physics and Chemistry of Liquids
Vol. 42, No. 2, April 2004, pp. 207–213

EVALUATION OF EXCESS MOLAR POLARIZATION IN BINARY MIXTURES OF POLAR–NONPOLAR LIQUIDS

C. DWIVEDY[a] and S.K. RAY[b,*]

[a]*Department of Physics, Government College, Angul, Orissa, India;*
[b]*Department of Physics, B.J.B. College, Bhubaneswar, Orissa, India*

(Received 2 February 2002)

Excess molar polarization in the binary mixture of polar solutes (acetic acid, *n*-tributyl phosphate) in nonpolar solvents (benzene, tetrachloromethane, *p*-xylene) is evaluated with the help of our proposed equation. The results have been compared with those obtained from a previously proposed equation. It is observed that our proposed equation is more accurate to interpret the liquid structure and molecular association in the binary liquid mixtures.

Keywords: Binary mixtures; Excess molar polarization; Polar solute; Nonpolar solvent

INTRODUCTION

Evaluation and analysis of excess molar polarization [1,2] is useful in the interpretation of molecular association and liquid structure of the liquid mixture. Although the theoretical treatment suggested by Longuet-Higgins [3] is found useful in the interpretation of liquid structure involving weak interactions, it has its own limitation of not being applicable to hydrogen bonded systems, due to the indistinguishability of the long range force from that of the short-range one. In view of this limitation, experimental measurement of excess thermodynamic functions using dielectric properties of liquids is found useful. These excess thermodynamic functions depends on the polarization process in the liquid mixture which arises due to different alignment of molecular dipoles in liquid mixture. Earlier many [4–6] have evaluated the excess molar polarization in the binary mixtures of polar liquids. In this paper we propose an expression for the excess molar polarization of binary mixture of polar and nonpolar liquids to study liquid structure.

---

*Corresponding author.

ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100410001679657

THEORY

Utilizing the concept of structural correlation in the statistical theory of Ramshaw [7] and Wertheim [8], Winkelmann and Quitzsch [9] have developed an expression for the correlation factor for the binary mixture of polar liquids.

For the binary system where one component is nonpolar, the correlation factor for the mixture is given by [10]

$$g_m = \frac{9kT}{4\pi N \mu_{gB} X_B} \frac{(2\epsilon_m + \epsilon_{\infty B})^2}{(\epsilon_{\infty B} + 2)^2 (2\epsilon_m + 1)} \times \left[V \frac{\epsilon_m - 1}{\epsilon_m} - \frac{3X_A V_A (\epsilon_A - 1)}{(2\epsilon_m + \epsilon_A)} - \frac{3X_B V_B (\epsilon_{\infty B} - 1)}{2\epsilon_m + \epsilon_{\infty B}} \right] \tag{1}$$

where A and B represent the nonpolar and polar liquids respectively, X_A and X_B denote the mole fractions of nonpolar liquid respectively, V, V_A, V_B denote the molar volumes of mixture, nonpolar liquid and polar liquid respectively, ε_m, ε_A denote the relative permittivities of mixture and nonpolar liquid respectively, $\epsilon_{\infty B}$ is the square of the refractive index, μ_{gB} is the gas phase dipole moment of polar liquid, k is Boltzmann constant, T is temperature in Kelvin, N is Avogadro's number.

Winkelmann and Quitzsch [11] have developed the expression for polarization in the binary mixture of polar liquids considering the macroscopic reaction field model from Onsager dielectric continuum theory [12] utilizing the concept of correlation factor.

$$P_m = \frac{\epsilon_m}{\epsilon_m + 2} \left\{ \sum_{r=A,B} \frac{3X_r V_r (\epsilon_{\infty r} - 1)}{(2\epsilon_m + \epsilon_{\infty r})} + \sum_{r=A,B} \frac{(\epsilon_{\infty r} + 2)^2 (2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_{\infty r})^2} \frac{X_r \mu_{gr}^2 g_{rr} 4\pi N}{9kT} + \frac{(\epsilon_{\infty A} + 2)(\epsilon_{\infty B} + 2)(2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_{\infty A})(2\epsilon_m + \epsilon_{\infty B})} \frac{4\pi N \mu_{gA} \mu_{gB}}{9kT} (g_{AB} - 1) \right\} \tag{2}$$

where A and B refer to the molecules of variety A and B, g_{rr} represents the correlation factor between the molecules A–A and B–B molecules and g_{AB} represents the mutual correlation factor between molecules A and B.

Swain *et al.* [13] have modified Eq. (2) for the binary mixture of polar and nonpolar liquids assuming the dipole moment of nonpolar liquid in the binary mixture becomes zero and $\epsilon_{\infty A} \approx \epsilon_A$ at high frequency range. Eq. (2) can be expressed as

$$P_{m.\mathrm{I}} = \frac{\epsilon_m}{\epsilon_m + 2} \left\{ 3X_A V_A \frac{(\epsilon_A - 1)}{(2\epsilon_M + \epsilon_A)} + 3X_B V_B \frac{(\epsilon_{\infty B} - 1)}{(2\epsilon_m + \epsilon_{\infty B})} + \frac{(\epsilon_{\infty B} + 2)^2 (2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_{\infty B})^2} \frac{X_B \mu_{gB}^2 g_{BB} 4\pi N}{9kT} \right\} \tag{3}$$

The Eq. (3) represents the polarization due to long range interaction among the similar molecules. The third term in Eq. (3) contains the correlation factor (g_{BB}) of pure polar liquid. But in reality the situation is different. We have observed in Table I, the value of

TABLE I Valuation of ε_m, g_m, $\Delta P_{m.\mathrm{I}}$ and $\Delta P_{m.\mathrm{II}}$ with mole fraction of acetic acid in nonpolar solvents at 303.16 K

Mole fraction of acetic acid X_B	*Relative permittivity of mixture* ϵ_m	*Correlation factor of mixture* g_m	$\Delta P_{m.\mathrm{I}}$ *in* $cm^3\ mol^{-1}$	$\Delta P_{m.\mathrm{II}}$ *in* $cm^3\ mol^{-1}$
(a) Acetic acid + benzene				
0.088	2.298	0.17	1.169	−2.262
0.130	2.332	0.20	1.711	−3.042
0.162	2.382	0.25	2.089	−3.169
0.190	2.410	0.26	2.453	−3.563
0.250	2.505	0.30	3.191	−3.914
0.304	2.762	0.40	3.536	−2.572
0.440	3.110	0.47	4.897	−1.435
0.600	3.603	0.49	6.004	−1.382
0.710	4.050	0.51	6.092	−1.320
(b) Acetic acid + tetrachloromethane				
0.100	2.195	0.01	1.431	−3.769
0.180	2.260	0.10	2.498	−5.605
0.300	2.540	0.33	3.780	−3.994
0.360	2.663	0.36	4.492	−3.954
0.450	2.900	0.40	5.438	−3.620
0.530	3.235	0.46	5.881	−2.055
0.610	3.610	0.51	6.008	−0.464
0.680	4.060	0.56	5.613	−0.296
(c) Acetic acid + *p*-xylene				
0.086	2.450	−0.20	0.592	−5.485
0.106	2.430	−0.29	1.032	−7.245
0.157	2.435	−0.08	1.713	−7.779
0.220	2.539	0.13	2.407	−8.032
0.306	2.597	0.17	3.612	−8.502
0.373	2.832	0.33	4.088	−5.650
0.470	3.277	0.50	4.366	−1.060
(d) TBP + benzene				
0.076	2.873	0.82	3.594	0.632
0.124	3.334	0.93	9.089	1.972
0.180	3.805	0.98	11.047	2.606
0.248	4.385	1.05	11.940	3.457
0.331	5.081	1.13	11.412	4.199
0.435	5.750	1.18	10.551	3.911
0.569	6.436	1.21	8.882	3.624
0.748	7.283	1.28	4.525	3.012
(e) TBP + tetrachloromethane				
0.050	2.815	1.11	3.904	2.335
0.082	3.303	1.16	4.955	4.721
0.133	3.680	1.21	7.552	5.771
0.193	4.138	1.17	9.432	5.899
0.264	4.540	1.12	12.192	5.739
0.349	5.041	1.13	12.420	4.856
0.455	5.732	1.18	11.259	4.824
0.588	6.540	1.24	8.137	4.306
0.763	7.298	1.28	4.488	2.946
(f) TBP + *p*-xylene				
0.060	2.744	1.23	5.005	4.226
0.080	3.000	1.18	5.771	4.320
0.109	3.190	1.12	6.685	3.844
0.150	3.360	1.00	10.434	3.475
0.218	3.750	0.99	13.475	3.506
0.300	4.150	0.97	16.421	2.498
0.450	5.050	1.05	16.899	2.628
0.570	5.680	1.09	15.873	1.678
0.700	6.400	1.15	12.472	0.912

correlation factor of pure polar solute in nonpolar solvent does not remain constant with the change of concentration of the polar solute. This might be due to the short range interaction between polar and induced nonpolar molecules in the binary mixture which in turn affect the nature of molecular orientation of dipoles and induced dipoles. Considering this effect, we have proposed an expression for the molar polarization in the binary mixture of polar and nonpolar liquids by substituting g_m in place of g_{BB}. Hence Eq. (3) can be modified as

$$P_{m.\mathrm{II}} = \frac{\epsilon_m}{\epsilon_m + 2}\left\{3X_A V_A \frac{\epsilon_A - 1}{2\epsilon_M + A} + 3X_B V_B \frac{\epsilon_{\infty B} - 1}{2\epsilon_m + \epsilon_{\infty B}} + \frac{4\pi N \mu_{gB}^2 X_B g_m}{9kT} \frac{(\epsilon_{\infty B} + 2)^2 (2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_{\infty B})^2}\right\} \tag{4}$$

When a binary mixture is formed, the expected properties such as thermodynamic parameters, dielectric properties and refractive index do not vary linearly [14]. So the deviation of these parameters from the linear behaviour termed as excess parameters is considered to be very important to study the nature of cluster formation [15] in the mixture. We intend to evaluate the excess molar polarization using the Eqs. (3) and (4).

$$\Delta P_{mr} = P_{mr} - \sum_{i=A,B} X_i P_i \tag{5}$$

where, $r = \mathrm{I}, \mathrm{II}$ where ΔP_{mr} is excess molar polarization of the mixture, P_i is the molar polarization of components of the mixture.

EXPERIMENTAL

The chemicals used were of analytical grade and of reputed make and redistilled before use. The experimental arrangement used for measurement of relative permittivity, refractive index, density etc. is the same as that used by Ray *et al.* [16] and the reproducibility of the experimental measurements is also same.

RESULTS AND DISCUSSION

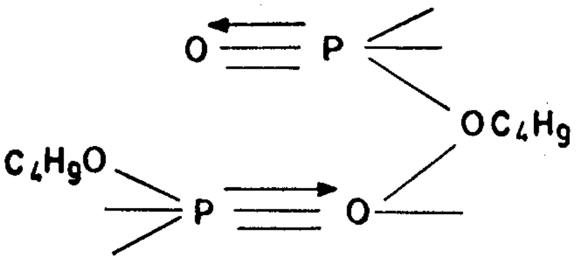
We have evaluated g_m, $\Delta P_{m.\mathrm{I}}\,\mathrm{cm^3\,mol^{-1}}$ and $\Delta P_{m.\mathrm{II}}\,\mathrm{cm^3\,mol^{-1}}$ of binary mixtures of polar solute (acetic acid, tri-butyl-phosphate) in nonpolar solvent (benzene, tetrachloromethane, *p*-xylene) at 303.16 K from the experimental data using the dielectric probe. The results of g_m, $\Delta P_{m.\mathrm{I}}$ and $\Delta P_{m.\mathrm{II}}$ have been presented in Table I.

We have observed in Table I, the correlation factor (g_m) of the binary mixtures increases with the increase of the mole fraction of polar solute in the solution. In case of binary mixtures containing acetic acid, the value of g_m is smaller than the mixture containing TBP. This indicates that the correlation of acetic acid molecules is less than TBP molecules in the solution. This result confirms the experimental results (i.e. the correlation factor of acetic acid is 0.65 and that of TBP is 1.3

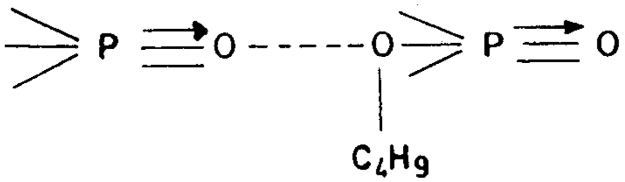
at 303.16 K). Then we have made a comparative study between the excess molar polarization $\Delta P_{m.\mathrm{I}}$ using Eq. (3) and $\Delta P_{m.\mathrm{II}}$ using Eq. (4). We have observed that $\Delta P_{m.\mathrm{I}}$ remains positive in all the mixtures, whereas $\Delta P_{m.\mathrm{II}}$ becomes negative in the binary mixtures of acetic acid in nonpolar solvents and becomes positive in the binary mixtures of TBP in nonpolar solvents. The results obtained from $\Delta P_{m.\mathrm{II}}$ fairly agree with actual dynamic association of the polar molecules in the nonpolar solvents. Acetic acid is a nonassociated liquid as its correlation factor is smaller than unity and TBP is an associated liquid as its correlation factor is greater than unity [17]. Thus acetic acid in the solution favours the formation of β-multimers (antiparallel orientation of the molecular dipoles) and makes the excess molar polarization negative. But TBP due to its associated character favours the formation of α-multimers (parallel alignment of molecular dipoles) and makes the excess molar polarization positive.

We have also observed that $\Delta P_{m.\mathrm{I}}$ increases above the 0.5 mole fraction of polar solute and then decreases. But in case of $\Delta P_{m.\mathrm{II}}$, the magnitude of $\Delta P_{m.\mathrm{II}}$ increases in the lower concentration of polar solute and attains maximas in the region of 0.2–0.35 mole fraction of polar solute in the solution and then decreases with the increase of polar solute in the mixture. While studying the spontaneous polarization in a binary mixture of polar–nonpolar liquids in the dielectric relaxation region, Patapov [18] has found that in a dilute solution the effective dipole moment of the molecules becomes five to six orders greater than the average isotropic dipole moment of the molecules. Thus the maxima or minima of $\Delta P_{m.\mathrm{II}}$ in the lower concentration region of polar solute proves the correctness of our proposed equation for excess molar polarization ($\Delta P_{m.\mathrm{II}}$). We have also observed that the minimas of $\Delta P_{m.\mathrm{II}}$ in the binary mixture of acetic acid in nonpolar solvents are in the order *p*-xylene > tetrachloromethane > benzene. It is due to the fact [19] that $-CH_3$ group of *p*-xylene, being an electron pusher interacts maximum and forms more β-clusters (antiparallel alignment of the molecular dipoles in the mixture). The tetrahedral structure of tetrachloromethane favours formations of β-clusters due to the interaction between polar acetic acid and induced tetrachloromethane molecules. Relatively less interaction in case of benzene with acetic acid is probably due to the presence of aromatic ring in benzene molecule. Thus the minima of excess molar polarization is least in case of binary mixture of acetic acid and benzene. The excess molar polarization depends on the polarization effect due to the interaction between the polar–polar molecules and polar-induced nonpolar molecules. Thus with the increase of concentration polar acetic acid, the interaction between the polar molecules plays the predominant roles and formation of more α-cluster reduces the negative of the $\Delta P_{m.\mathrm{II}}$.

TBP is a mildly associated liquid. In solution TBP can remain in either a wood-pile (Fig. 1(a)) or head–tail (Fig. 1(b)) arrangement [20]. In the lower concentration region of TBP in solution, more TBP molecules in the mixtures favour the formation of a head–tail structure which in turn form more α-clusters. Thus $\Delta P_{m.\mathrm{II}}$ has the maxima in the lower concentration region of TBP in solution. With the increase of mole fraction of TBP in solution wood-pile structure of TBP results in formation β-clusters, thus reducing the magnitude of $\Delta P_{m.\mathrm{II}}$. The maxima of $\Delta P_{m.\mathrm{II}}$ in the binary mixtures of TBP in nonpolar solvents is in the order tetrachloromethane > *p*-xylene > benzene. In case of $\mathrm{TBP} + \mathrm{CCl_4}$, the interaction between oxygen atom of phosphoryl group with chlorine atom of tetrachloromethane due to its high electronegativity favours



(a) Wood - pile arrangement



(b) Head-tail arrangement

FIGURE 1 (a) Wood-pile arrangement. (b) Head–tail arrangement.

the formation of more head–tail arrangement of TBP in solution. In case of *p*-xylene, greater delocalisation found in benzene ring through the hyperconjugative effect of $-CH_3$ group is a possible factor for reinforcing greater angular correlation with TBP molecules, thus forming more α-clusters. But in the case of benzene, the situation is different. When the concentration of TBP is less, the scarce TBP molecules are surrounded by a cage of nonpolar aromatic benzene molecules. The isolated TBP molecules, therefore, fail to establish correlation among themselves of their own. Also the solvent molecules do not help in reinforcing angular correlation. Thus maxima of $\Delta P_{m.\mathrm{II}}$ in case of binary mixture of TBP + benzene is least and TBP + tetrachloromethane is greatest. Thus our proposed equation for excess molar polarization in the binary mixture of polar and nonpolar liquids appears to explain satisfactorily the liquid structures in the solution.

References

[1] M.I. Davis and G. Douheret (1987). *Thermochin Acta*, **116**, 183.
[2] S. Tripathy and B.B. Swain (1991). *Chem. Papers*, **45**, 321.
[3] H.C. Higgins-Longuet (1951). *Proc. Roy. Soc. Ser. A*, **205**, 247.
[4] B.B. Swain (1985). *Acta Chim. Hung.*, **118**, 321.
[5] S. Tripathy, S.K. Dash, K. Garabadu, G.S. Roy and B.B. Swain (1993). *J. Mol. Liq.*, **55**, 137.
[6] S.K. Chakrabarty, J. Rath and S.K. Ray (2000). *J. Ultra Sci.*, **12**, 22.
[7] J.D. Ramshaw (1972). *J. Chem. Phys.*, **57**, 2684.
[8] M.S. Werthein (1973). *Mol. Phys.*, **26**, 1425.
[9] J. Winkelmann and K. Quitzsch (1976). *Z. Phys. Chem. (Leipzig)*, **257**, 678.
[10] S. Ray, B. Mohanty, S.K. Ray and G.S. Roy (1996). *Phys. Chem. Liq.*, **32**, 211.
[11] J. Winkelmann and K. Quitzsch (1976). *Z. Phys. Chem. (Leipzig)*, **257**, 746.

[12] L. Onager (1936). *J. Am. Chem. Soc.*, **58**, 1486.
[13] B.B. Swain and G.S. Roy (1986). *Jpn. J. Appl. Phys.*, **25**, 209.
[14] J.S. Rowlinson (1956). *Liquid and Liquid Mixtures*, 2nd Edn. Butterworth Science Publication, London.
[15] V. Subramanian, B.S. Bellubbi and J. Sobhanadri (1993). *Pramana – J. Phys.*, **41**, 9.
[16] S.K. Ray and G.S. Roy (1996). *Phys. Chem. Liq.*, **31**, 259.
[17] B.B. Swain (1984). *Acta Chim. Hung.*, **117**, 383.
[18] A. Patopov (1993). *Zh. Eksp. Tekh Fiz.*, **103**, 125. Translated by Alferieff, M.E. (1993). *J.E.T.P.*, **76**, 68.
[19] S.K. Ray, S. Tripathy, P.K. Srivastav and G.S. Roy (1993). *Acta Ciencia Indica*, **19**, 3084.
[20] M.A. Aforin, E.V. Kamarov, V.V. Korolev, L.B. Schpunt, V.A. Scheebakov and E.A. Kopylov (1989). *In Proc. Actinides-89. Int. Lint. Taskent.* USSR.