Evaluation of Excess Molar Polarization in Binary Mixtures of Amines in Nonpolar Solvents

C. Dwivedy[a]; S. K. Ray[b]

[a] Department of Physics, Dhenkanal Govt. College, Dhenkanal, Orissa [b] P.G. Department of Physics, Ravenshaw College, Cuttack, Orissa, India

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EVALUATION OF EXCESS MOLAR POLARIZATION IN BINARY MIXTURES OF AMINES IN NONPOLAR SOLVENTS

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

[a]Department of Physics, Dhenkanal Govt. College, Dhenkanal, Orissa;
[b]P.G. Department of Physics, Ravenshaw College, Cuttack-753 003,
Orissa, India

A new expression for the excess molar polarization in binary mixture of polar and nonpolar liquids has been proposed. An experimental assessment of the proposed equation has been made by comparison with an earlier equation in the binary mixtures of amines in nonpolar liquids. The proposed equation for excess molar polarization is found to be more appropriate for detailed study of molecular association in the liquid mixtures.

Keywords: Binary mixtures; Molecular dipoles; Excess molar polarization

INTRODUCTION

Investigation of dielectric properties of the liquid phase over a wide frequency range yield valuable information on the molecular association and molecular interactions among the components of the mixture and the characteristic times of molecular motion [1]. Different equations [2–5] have been proposed to obtain qualitative information on molecular dynamics and molecular association of the liquid mixtures using the dielectric probe. Hörig and Michael [6] have proposed an equation for the relative permittivity for a binary mixtures of polar liquids based on Onsager's equation which takes

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*Corresponding author.

Lagrangian interaction into account but which neglected the short range specific interaction of polar liquids. Kirkwood [7] and Fröhlich [8] theories take into account the short range interaction between similar molecules along with the long range interaction but ignore the short range interaction between dissimilar molecules in the mixture. Winkelmann and Quitzsch [9] have developed an expression for molar polarization considering both short range and long range interaction among the similar and dissimilar molecules in a binary mixture of polar liquids. Later Davis and Douheret [10] have devised an empirical formula for molar polarization of binary mixtures of polar liquids. Chakrabarty *et al.* [11] have made an experimental assessment of the Winkelmann and Quitzsch and the Davis and Douheret expressions for molar polarization and have concluded that the Winkelmann and Quitzsch formula is the more appropriate to study the molecular dynamics in liquid mixtures. Hence we have proposed an expression for the molar polarization in the binary mixture of polar and nonpolar liquids by suitably modifying the Winkelmann and Quitzsch expression and have made an experimental assessment of the proposed equation in the binary mixtures of amines in nonpolar solvents to study the molecular association in the liquid mixtures.

THEORY

Winkelmann and Quitzsch [9] have considered the binary mixture of polar liquids as homogenous medium represented by a uniform relative permittivity ε_m and developed a theory of polarization with the help of the macroscopic reaction field model utilizing the concept of correlation in the statistical theory of Ramshaw [12] and Wertheim [13] mean spherical model.

With this basic concept they have formulated the equation relating to relative permittivity:

$$\frac{\varepsilon_m - 1}{\varepsilon_m} V = \sum_{r=A,B} \frac{3X_r V_r(\varepsilon_{oor} - 1)}{(2\varepsilon_m + \varepsilon_{oor})} + \sum_{r=A,B} \frac{(\varepsilon_{oor} + 2)^2(2\varepsilon_m + 1)}{(2\varepsilon_m + \varepsilon_{oor})^2}$$
$$\frac{4\pi N X_r}{9kT}\mu_{gr}^2 g_{rr} + \frac{(\varepsilon_{ooA} + 2)(\varepsilon_{ooB} + 2)(2\varepsilon_m + 1)}{(2\varepsilon_m + \varepsilon_{ooA})(2\varepsilon_m + \varepsilon_{ooB})}$$
$$\frac{4\pi N}{9kT}\mu_{gA}\mu_{gB}(g_{AB} - 1) \tag{1}$$

where

A and B refer to the molecules of variety A & B,

X_r denotes the respective mole fraction of the component in the mixture,

V_r and V denote the molar volumes of the components and mixtures respectively,

N is Avogadro's number,

k is Boltzmann constant,

T is temperature in Kelvin,

μ_{gr} is the gas phase dipole moment of the component,

ε_m is the relative permittivity of the mixture,

$\varepsilon_{\infty r}$ denotes the square of the refractive index of each component of the mixture,

g_{rr} represents the correlation factor among the identical molecules A–A and B–B,

g_{AB} denotes the mutual correlation factor among different molecules.

Now using the Lorentz–Lorentz expression [14, 15] for molar polarization of binary mixture of polar liquids Eq. (1) can be written as

$$P = \frac{\varepsilon_m}{\varepsilon_m + 2}\left\{ \sum_{r=A,B} \frac{3X_r V_r(\varepsilon_{\infty r} - 1)}{(2\varepsilon_m + \varepsilon_{\infty r})} + \sum_{r=A,B} \frac{(\varepsilon_{\infty r} + 2)^2(2\varepsilon_m + 1)}{(2\varepsilon_m + \varepsilon_{\infty r})^2} \right.$$
$$\frac{4\pi N X_r}{9kT}\mu_{gr}^2 g_{rr} + \frac{(\varepsilon_{\infty A} + 2)(\varepsilon_{\infty B} + 2)(2\varepsilon_m + 1)}{(2\varepsilon_m + \varepsilon_{\infty A})(2\varepsilon_m + \varepsilon_{\infty B})}$$
$$\left. \frac{4\pi N \mu_{gA}\mu_{gB}}{9kT} \times (g_{AB} - 1) \right\} \qquad (2)$$

For binary mixtures of polar and nonpolar liquids Swain and others [16, 17] have assumed that the gas phase dipole moment of nonpolar liquids becomes zero and that the square of the high frequency refractive index is approximately equal to the relative permittivity of nonpolar liquid [18]. Then Eq. (2) for the binary mixture of polar and nonpolar liquid reduces to

$$P_I = \frac{\varepsilon_m}{\varepsilon_m + 2}\left\{ 3X_A V_A \frac{(\varepsilon_A - 1)}{(2\varepsilon_m + \varepsilon_A)} + \frac{3X_B V_B(\varepsilon_{\infty B} - 1)}{(2\varepsilon_m + \varepsilon_{\infty B})} \right.$$
$$\left. + \frac{(\varepsilon_{\infty B} + 2)^2(2\varepsilon_m + 1)}{(2\varepsilon_m + \varepsilon_{\infty B})^2}\frac{X_B\mu_{gB}^2 g_{BB} 4\pi N}{9kT} \right\} \qquad (3)$$

where A and B denote nonpolar and polar molecules in the liquid mixture. Here Eq. (3) takes into the long range interaction as well as the short range interaction between the polar molecules because the third term contains only the correlation factor of pure polar liquids g_{BB}. This indicates that there is no change in g_{BB} with the change of the mole fraction of polar liquid in nonpolar solvent. In reality, when a polar solute is added to nonpolar solvent, there is an induced effect of polar molecules in the mixture and consequently the correlation of polar molecules is affected by the molecular interaction between the polar molecules as well as the polar molecules and induced nonpolar molecules in the mixture. While studying the spontaneous polarization in a binary mixture of polar and nonpolar liquids in the dielectric relaxation region, Patapov [19] has found that in a dilute solution the effective dipole moment of the molecules becomes five to six orders of magnitude greater than the average isotropic dipole moment of the molecules. It is also observed [16] that the correlation factor of the binary mixture of polar and nonpolar liquids changes with the variation of mole fraction of polar solutes in the mixture. In order to obtain an accurate result, we have substituted g_m in place of g_{BB} in Eq. (3). Thus the modified equation becomes

$$P_{II} = \frac{\varepsilon_m}{\varepsilon_m + 2}\left\{ 3X_A V_A \frac{(\varepsilon_A - 1)}{(2\varepsilon_m + \varepsilon_A)} + \frac{3X_B V_B(\varepsilon_{\infty B} - 1)}{(2\varepsilon_m + \varepsilon_{\infty B})} \right.$$
$$\left. + \frac{(\varepsilon_{\infty B} + 2)^2(2\varepsilon_m + 1)}{(2\varepsilon_m + \varepsilon_{\infty B})^2} \frac{X_B \mu_{gB}^2 g_m 4\pi N}{9kT} \right\} \qquad (4)$$

When a binary mixture is formed, the expected properties such as thermodynamic parameters, volume measurements, dielectric parameters and refractive index do not vary linearly [20]. The deviation of these parameters from linear behaviour, termed excess parameters, is considered to be very important and helps to establish the nature of bonding between two liquids [21]. Kolling [22] also, while characterizing the dielectric behaviour of binary mixtures of polar liquid in nonpolar solvent, has considered the excess relative permittivity instead of relative permittivity of the mixture. We have also observed that molar polarizations obtained from Eqs. (3) and (4) do not vary linearly with the mole fraction of solute in mixture. Ray et al. [23], while studying dielectric properties of liquid mixtures, have evaluated

the excess Gibbs energy of mixing. Thus we are interested to evaluate the excess molar polarization to study the molecular association in liquid mixtures from Eqs. (3) and (4) using the formula

$$\Delta P_m = P_m - \sum_{r=A,B} X_r P_r \qquad (5)$$

where m corresponds to I and II in Eqs. (3) and (4), while P_r represents molar polarization of each component of mixture.

EXPERIMENTAL

The experimental device used for measurement of relative permittivity, refractive index *etc.*, was the same as that used by Swain [24]. The reproducibility of the relative permittivity measurements at radio-frequency range was ± 0.003 with wavemeter-oscillator combination. The reproducibility of refractive index and density measurements were ± 0.00002 and $\pm 0.00002 \, gm/cm^3$ respectively.

RESULTS AND DISCUSSION

We have evaluated the excess molar polarization of binary mixtures of amines (aniline, pyridine and dimethyl aniline) and nonpolar liquids (benzene and tetrachloromethane) using relevant experimental data such as relative permittivity, refractive index *etc.*, at 303.16°K which is depicted in Table I and displayed in Figures 1, 2. We have obtained ΔP_I using Eq. (3) and (5) and ΔP_{II} using Eqs. (4) and (5). The excess molar polarization as per Eq. (5) indicates the departure of the molar polarization of binary mixture from its ideal value. One should expect the excess molar polarization should have a low value at low and high mole fraction of the polar solute in nonpolar solvent and have maximum value in between them. But we have observed that magnitude of ΔP_I increases with the increase of mole fraction aniline in tetrachloromethane. In other mixtures also, maxima of ΔP_I falls around 0.7 mole fraction of polar solute. But in case of ΔP_{II}, the maxima peak occurs in almost all mixtures between 0.2 to 0.4 mole fraction of polar solute, which might be a consequence of spontaneous

TABLE I Variation of ε_m, ΔP_I and ΔP_{II} with mole fraction of polar liquids at 303.16°K

Mole fraction of polar liquid X_B	Relative permittivity ε_m	$\Delta P_I \, cm^3 \, mol^{-1}$	$\Delta P_{II} \, cm^3 \, mol^{-1}$
(i) aniline + benzene			
0.099	2.599	1.783	0.149
0.224	2.853	4.290	0.488
0.295	3.095	5.264	1.806
0.405	3.424	6.676	2.555
0.451	3.546	7.245	2.345
0.591	3.996	8.297	1.995
0.691	4.394	8.333	1.192
0.761	4.845	7.254	0.830
(ii) aniline + tetrachloromethane			
0.099	2.607	1.613	4.613
0.197	3.050	2.759	5.671
0.293	3.300	4.260	5.168
0.393	3.500	5.885	3.695
0.490	3.801	6.817	2.850
0.587	4.154	7.263	2.634
0.761	4.955	7.623	1.136
(iii) Pyridine + benzene			
0.096	3.128	4.194	6.838
0.197	3.663	8.753	7.073
0.293	4.184	12.265	7.262
0.400	5.145	13.364	8.895
0.488	5.882	13.799	7.850
0.589	6.767	13.457	7.254
0.719	7.728	13.169	4.407
0.788	8.800	9.873	3.846
(iv) Pyridine + tetrachloromethane			
0.098	2.877	4.970	5.471
0.194	3.689	8.181	9.714
0.292	4.612	9.877	11.456
0.400	5.601	10.759	12.745
0.480	6.001	12.499	10.755
0.596	6.901	12.749	8.873
0.685	7.916	10.825	7.702
0.797	9.156	8.245	5.456
(v) dimethyl aniline + benzene			
0.099	2.500	1.225	0.094
0.199	2.748	2.258	0.121
0.298	3.095	2.661	1.587
0.398	3.402	2.911	1.956
0.498	3.637	3.219	1.489
0.603	3.857	3.447	1.225
0.697	4.216	2.523	1.809
0.798	4.500	1.846	0.750

TABLE I (Continued)

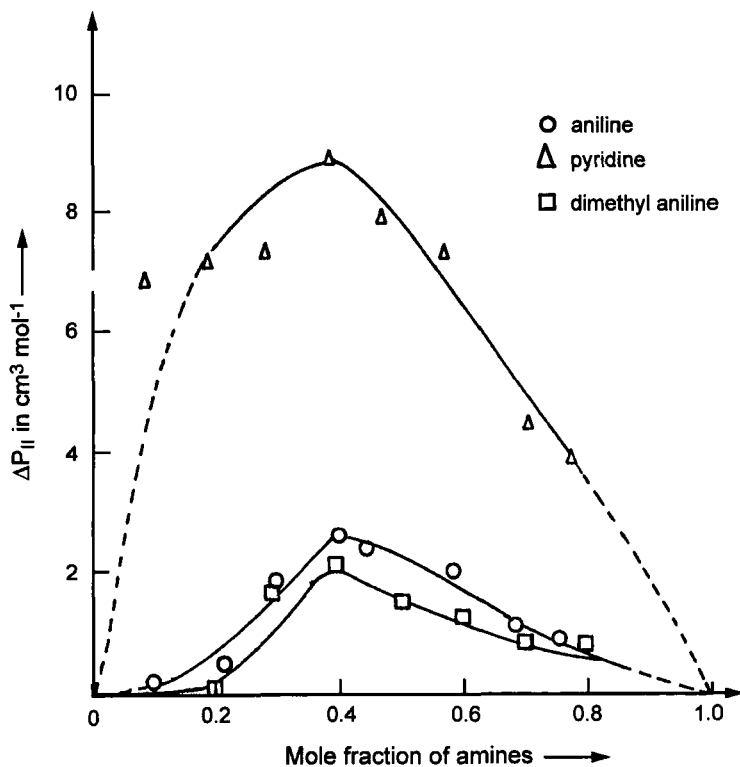| Mole fraction of polar liquid X_B	Relative permittivity ε_m	ΔP_I cm^3 mol^{-1}	ΔP_{II} cm^3 mol^{-1}
(vi) dimethyl aniline + tetrachloromethane			
0.103	2.367	1.550	−1.10
0.200	2.780	2.013	2.633
0.299	3.100	2.482	3.443
0.399	3.364	2.920	2.918
0.498	3.703	2.718	2.431
0.582	3.946	2.549	2.211
0.698	4.286	2.000	1.955
0.798	4.495	1.784	1.689

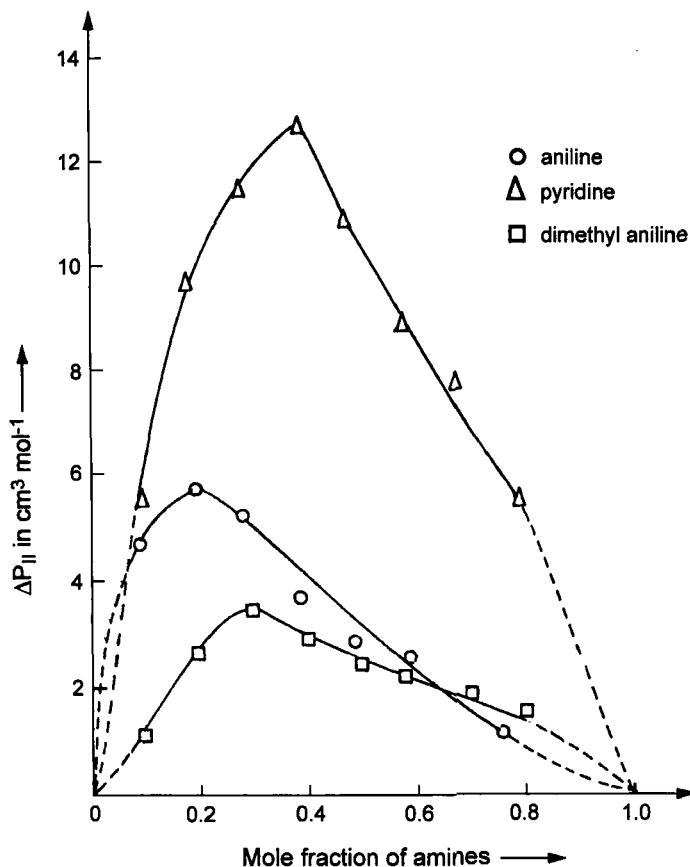FIGURE 1 Variation of ΔP_{II} in cm^3 mol^{-1} with the mole fraction of amines in benzene at 303.16°K.

FIGURE 2 Variation of ΔP_{II} in $cm^3 \ mol^{-1}$ with the mole fraction of amines in tetrachloromethane at 303.16°K.

polarization [19] in dilute solution. After the peak, with the increase of mole fraction of polar solute in the solution, the interaction among polar molecules reduces the molar polarization for which the excess molar polarization (ΔP_{II}) approaches zero as the mole fraction of polar solute tends to one. It is also observed in Figures 1 and 2 that the variation of ΔP_{II} with the mole fraction of solute in all nonpolar solvents (benzene and tetrachloromethane) is in the order pyridine > aniline > dimethyl aniline. It is due to the fact that dimethyl aniline is a nonassociated liquid which favours formation of β-multimers among the similar molecules in solution and thus reduces the magnitude of

excess molar polarization. Aniline and pyridine are associated liquids and thus favours the formation of α-multimers among similar molecules [25]. Again ΔP_{II} in the binary mixture containing pyridine is greater than that of aniline. The presence of delocalised electrons in pyridine helps to have greater polarization in the mixture. But in case of aniline, the nitrogen atom of amino group is out of the ring for which its lone pair does not participate with π-electron within benzene ring and thus reduces the polarization effect of aniline in the mixture [26]. It is also observed in Table I, the maxima of ΔP_{II} in the binary mixture containing amines in tetrachloromethane is more than that of the binary mixture containing benzene. This might be due to the fact that the tetrahedral structure of tetrachloromethane helps to increase polarization effect in the mixture. While studying the variation of the excess Gibbs energy of mixing in binary mixtures of amines in nonpolar solvents Ray *et al.* [25] have obtained the results which tally with our results. But the variation of ΔP_I with mole fraction of polar solute in benzene and tetrachloromethane cannot be satisfactorily explained by the physical and structural property of the liquid. Thus the results based on our proposed equation reflect the actual dynamic characteristic of molecular association and merit consideration.

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