

# Study of Dielectric Polarization in Extremely Dilute Solutions of Polar Liquids in Nonpolar Solvents through Evaluation of Excess Correlation Factor and Excess Gibbs Energy of Mixing

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The excess correlation factor  $\delta g$  has been evaluated for a set of binary mixtures of polar liquids (aniline, pyridine, *N,N*-dimethylaniline, methanol, 1-propanol, and 1-butanol) in the nonpolar solvent tetrachloromethane. Also excess Gibbs energy of mixing between induced nonpolar molecules ( $\Delta G_{AA}$ ), between polar molecules ( $\Delta G_{BB}$ ), and between polar-induced nonpolar molecules ( $\Delta G_{AB}$ ) has been evaluated in these binary mixtures.  $\delta g$  changes its sign in case of alcohols, aniline, and pyridine whereas it remains negative in case of *N,N*-dimethylaniline. The results obtained through evaluation of  $\Delta G_{AB}$  have been used to corroborate the findings on  $\delta g$ . The change of the sign of  $\delta g$  is an indicator of the characteristic order—disorder phase transition in extremely dilute polar—nonpolar solutions.

The measurement of molecular characteristics in extremely dilute solutions has given rise to a real possibility of obtaining and interpreting the Debye spectra as a function of temperature. It is an interesting fact that the dipolar molecules acquire a new state [1] in dilute solutions that is qualitatively different from the natural disorder characteristic of the individual liquid. Light scattering experiments confirm that the molecules are in a more ordered state in solution [2], especially in extremely dilute solution than in a pure state. In view of this, we have undertaken this investigation of the dielectric behaviour of extremely dilute binary mixtures of polar—nonpolar liquids. Roy *et al.* [3] while studying the dielectric properties of alcohols and amines in extremely dilute solutions (*i.e.*  $\chi_B \rightarrow 0.1$ ) have shown that the correlation factor  $\delta g$  increases in case of alcohols and decreases in case of amines with a decrease of the mole fraction of the solute in solution. In analogy with the theory proposed by Payne and Theodorou [4], we have proposed a parameter  $\delta g$  [5] called the excess correlation factor – a measure of departure of the correlation factor from its ideal value. Kolling [6] while characterizing the dielectric behaviour of binary solvents containing acetonitrile has considered the excess relative permittivity in lieu of the relative permittivity of the mixture to discuss the nature of the bonding between two liquids. Sobhanadri *et al.* [7] also reported that the excess thermodynamic parameters are more useful than the thermodynamic parameters for a dielectric study of liquid mixtures in the microwave range. It is a matter of interest to note that the excess correla-

tion factor when substituted in the expression for the excess Gibbs energy of mixing proposed by Winkelmann and Quitzsch [8, 9] gives three terms, *i.e.* the excess Gibbs energy of mixing due to interaction between polar and induced nonpolar molecules ( $\Delta G_{AB}$ ), the excess Gibbs energy of mixing due to interaction between induced nonpolar—nonpolar molecules ( $\Delta G_{AA}$ ), and the excess Gibbs energy of mixing due to interaction between polar—polar molecules ( $\Delta G_{BB}$ ). We have made a humble effort to evaluate  $\delta g$ ,  $\Delta G_{total}$ ,  $\Delta G_{AA}$ ,  $\Delta G_{AB}$ , and  $\Delta G_{BB}$  in binary mixtures of alcohols as well as amines in a nonpolar solvent, tetrachloromethane, to throw light on the nature of the molecular association in such mixtures.

## THEORETICAL

Evaluation of the Kirkwood linear correlation factor [10] in dependence on the measured value of the relative permittivity in a binary mixture of polar—nonpolar liquids has been used for interpretation of dynamic characteristics of the molecular association in a liquid mixture. Later Winkelmann and Quitzsch (W. Q.) [8] have developed the expression for the correlation factor using statistical theory which is based on the fact that the polarization of individual molecules in a polar liquid sample is due to a long-range interaction with the bulk of the sample and a short-range interaction with the neighbouring molecules with which it is structurally correlated. W. Q. have developed an expression for the correlation factor  $g$  in a binary mixture of polar—nonpolar liquids

$$g = \frac{9kT\varepsilon_0}{N_A\mu_B^2\chi_B} \frac{(2\varepsilon + \varepsilon_{\infty B})^2}{(\varepsilon_{\infty B} + 2)(2\varepsilon + 1)} \cdot \left[ V \frac{\varepsilon - 1}{\varepsilon} - \frac{3\chi_A V_A(\varepsilon_A - 1)}{(2\varepsilon + \varepsilon_A)} - \frac{3\chi_B V_B(\varepsilon_{\infty B} - 1)}{(2\varepsilon + \varepsilon_{\infty B})} \right] \quad (1)$$

where A and B refer to the nonpolar and polar liquids, respectively,  $\chi$  denotes the mole fraction of a liquid,  $V$  denotes the molar volume of the mixture,  $\varepsilon$ ,  $\varepsilon_A$  are the relative permittivities of the mixture and nonpolar liquid, respectively,  $\mu_B$  is the gas phase dipole moment of the polar liquid,  $\varepsilon_{\infty B}$  is the square of refractive index of the polar liquid,  $N_A$  is Avogadro's constant,  $k$  is the Boltzmann constant,  $\varepsilon_0$  is the vacuum permittivity, and  $T$  is the temperature in K.

Analysis of eqn (1) indicates that  $g$  should increase with  $\chi_B \rightarrow 0$ . In case of amines [11]  $g$  is found to decrease with the decrease in mole fraction of the polar solute. In view of this, we have utilized the concept of *Davis* and *Douheret* [12] to define a new parameter  $\delta g$  known as the excess correlation factor

$$\delta g = g - g_{\text{ideal}} = g - (\chi_A g_A + \chi_B g_B) \quad (2)$$

where  $g_A$  and  $g_B$  represent the correlation factors of pure nonpolar and polar liquids, respectively. In the binary mixture of polar—nonpolar liquids, the nonpolar molecules are slightly polarized so that effective dipole moments of nonpolar molecules are negligibly small. According to *Oster* and *Kirkwood* [13] the correlation factor for the nonpolar liquid in the mixture can be written as

$$g = \lim_{\substack{\mu_{\text{eff}} \rightarrow 0 \\ \mu_g \rightarrow 0}} \frac{\mu_{\text{eff}}^2}{\mu_g^2} = 1 \quad (3)$$

Furthermore, the molecules of a nonpolar liquid and very weak polar liquids [14] lack correlation so that the correlation factor is equal to one. Hence, eqn (2) reduces to

$$\delta g = g - (\chi_A + \chi_B g_B) \quad (4)$$

The excess Gibbs energy of mixing of a binary mixture of a polar liquid in a nonpolar solvent is given [11, 15, 16] by

$$\Delta G_{AB} = -\frac{N_A}{2}(R_{fB} - R_{fB}^0)\{\chi_B\mu_B^2[\chi_B(g_B - 1) + 1]\} \quad (5)$$

where

$$R_{fB}^0 = -\frac{2N_A}{9\varepsilon_0 V_B} \frac{(\varepsilon_B - 1)(\varepsilon_{\infty B} + 2)}{(2\varepsilon_B + \varepsilon_{\infty B})} \quad (6)$$

$$R_{fB} = -\frac{2N_A}{9\varepsilon_0 V_B} \frac{(\varepsilon - 1)(\varepsilon_{\infty B} + 2)}{(2\varepsilon + \varepsilon_{\infty B})}$$

While deriving this expression, W. Q. have assumed that the geometrical arrangement of the identical

molecules will remain unaltered in the mixture, which probably refers to an ideal case. Furthermore, the term in the square bracket in eqn (5) is  $g_{\text{ideal}}$ , which indicates that the expression for the excess Gibbs energy of mixing derived by W. Q. corresponds to the ideal case. On the other hand, by substitution of  $\delta g$  in place of  $g_B$ , we have

$$G_{AB} = -\frac{N_A}{2}(R_{fB} - R_{fB}^0)\{\chi_B\mu_B^2[\chi_B(\delta g - 1) + 1]\} \quad (7)$$

The term in the square bracket on expansion becomes  $\chi_B g + \chi_A^2 - \chi_B^2 g_B$ , which when substituted gives three terms

$$\Delta G_{AB} = \Delta G_{\text{total}} + \Delta G_{AA} - \Delta G_{BB} \quad (8)$$

or

$$\Delta G_{\text{total}} = \Delta G_{AB} - \Delta G_{AA} + \Delta G_{BB}$$

where

$$\Delta G_{\text{total}} = -\frac{N_A}{2}(R_{fB} - R_{fB}^0)(\chi_B\mu_B^2 g)$$

$$\Delta G_{AA} = -\frac{N_A}{2}(R_{fB} - R_{fB}^0)(\chi_A^2\chi_B\mu_B^2) \quad (9)$$

$$\Delta G_{BB} = -\frac{N_A}{2}(R_{fB} - R_{fB}^0)(\chi_B^3 g_B\mu_B^2)$$

The negative sign in  $\Delta G_{AA}$  indicates the excess Gibbs energy of mixing between the nonpolar molecules because of the induction effect. In order to throw light on the molecular association between the hydrogen-bonded liquid molecules, we have used eqn (7) instead of eqn (5) and attempted to corroborate the findings obtained through evaluation of  $\delta g$  and  $\Delta G_{AB}$ .

## EXPERIMENTAL

The chemicals used were of anal. grade and manufactured by Merck. They were redistilled before use. The experimental arrangement used for the measurement of relative permittivity, *etc.* was the same as used by Swain [17]. The relative permittivity measurements for pure substances and mixtures were carried out by a wavemeter—oscillator combination at the frequency 455 kHz. The device was standardized with the help of standard liquids (tetrachloromethane, benzene) with known relative permittivities [18]. The cell temperature was controlled with an electronically regulated thermostatic arrangement at the regulated temperature by a Pulfrich refractometer at the sodium D-line. The density measurements were done by a semimicrobalance with a pycnometer of 25 cm<sup>3</sup> volume. The reproducibility of the relative permittivity measurements at the radio frequency was  $\pm 0.003$  and those of refractive index and density measurements were  $\pm 0.00002$  and  $\pm 0.00002$  g cm<sup>-3</sup>, respectively. The values of  $g$ ,  $\delta g$ ,  $\Delta G_{AB}$ ,  $\Delta G_{BB}$ , and  $\Delta G_{\text{total}}$  could be measured up to the second decimal digit.

**Table 1.** Variation of  $g$ ,  $\delta g$ ,  $\Delta G_{\text{total}}$ ,  $\Delta G_{\text{AA}}$ ,  $\Delta G_{\text{BB}}$ , and  $\Delta G_{\text{AB}}$  with the Mole Fraction of Polar Liquid in Tetrachloromethane at 301 K

$\chi_B$	$g$	$\delta g$	$\frac{\Delta G_{\text{total}}}{\text{J mol}^{-1}}$	$\frac{\Delta G_{\text{AA}}}{\text{J mol}^{-1}}$	$\frac{\Delta G_{\text{BB}}}{\text{J mol}^{-1}}$	$\frac{\Delta G_{\text{AB}}}{\text{J mol}^{-1}}$
Aniline						
0.015	0.86	-0.1399	0.208	15.700	0.003	15.905
0.030	0.86	-0.1397	0.790	29.750	0.020	30.520
0.050	1.02	0.0205	2.590	43.630	0.130	46.090
0.065	1.12	0.1206	4.640	55.780	0.260	60.160
0.080	1.18	0.1807	7.160	64.160	0.480	70.840
0.090	1.25	0.2508	9.310	68.560	0.660	77.210
Pyridine						
0.015	0.88	-0.1198	0.590	43.310	0.010	43.890
0.030	0.88	-0.1197	2.280	81.460	0.070	83.670
0.050	0.89	-0.1095	6.250	126.760	0.340	132.670
0.060	0.87	-0.1294	8.470	143.380	0.670	151.180
0.075	1.11	0.1107	16.270	167.200	1.090	182.380
0.090	1.04	0.0409	21.010	185.860	1.800	205.070
<i>N,N</i> -Dimethylaniline						
0.015	0.17	-0.8276	0.020	9.990	0.002	10.008
0.030	0.24	-0.7552	0.150	19.150	0.020	19.280
0.040	0.26	-0.7336	0.280	24.430	0.040	24.670
0.058	0.29	-0.7008	0.630	33.440	0.100	33.970
0.070	0.36	-0.6289	1.030	39.340	0.070	40.300
0.080	0.39	-0.5973	1.410	43.430	0.090	44.750
0.092	0.43	-0.5554	2.300	47.960	0.410	49.850
Methanol						
0.032	1.83	0.761	4.160	66.550	0.230	70.480
0.059	1.01	-0.117	7.470	110.960	1.390	117.040
0.082	0.76	-0.417	10.190	137.480	3.470	144.500
1-Propanol						
0.021	2.36	1.311	1.170	22.560	0.040	23.690
0.041	1.26	0.163	2.390	42.510	0.270	44.630
0.063	0.83	-0.319	3.610	60.560	0.920	63.250
0.079	0.81	-0.377	5.070	67.190	1.670	70.590
1-Butanol						
0.023	2.142	1.088	1.010	19.520	0.040	20.490
0.039	1.243	0.151	1.710	32.480	0.180	34.010
0.060	0.927	-0.215	3.280	52.120	0.720	54.680
0.077	0.661	-0.521	3.340	55.920	1.310	57.950

## RESULTS AND DISCUSSION

The experimental data of  $g$ ,  $\delta g$ ,  $\Delta G_{\text{AA}}$ ,  $\Delta G_{\text{BB}}$ ,  $\Delta G_{\text{AB}}$ , and  $\Delta G_{\text{total}}$  in the binary mixture of aniline, pyridine, *N,N*-dimethylaniline, methanol, 1-propanol, and 1-butanol in tetrachloromethane are presented in Table 1 and the variation of  $\delta g$  is shown in Fig. 1.

It is seen from Table 1 that the parameters  $g$  and  $\delta g$  exhibit the same type of trend of variation and therefore there is a qualitative agreement between the two terms. The excess correlation factor  $\delta g$  increases in case of alcohols and decreases in case of amines when  $\chi_B \rightarrow 0$ . This variation in the trend is probably due to the difference in the hydrogen bonding capacity of the two groups. A self-association due to the strong

hydrogen bonding is evident in pure alcohols as well as in their solutions. Furthermore, the presence of different, seemingly noninteracting solvents aids to the self-association to a great extent in alcohols. Therefore, even with the dilution to the extent of  $\chi_B \rightarrow 0$ , the hydrogen bonding between the alcohol molecules resulting in a parallel orientation is possible due to a switching mechanism as long as there are at least three molecules in a close vicinity [19–21]. Under such conditions, probably open chain multimers are favoured. With the addition of alcohol molecules, there is a gradual conversion of the parallel orientation of molecular dipoles, *i.e.*  $\alpha$ -multimers, to an antiparallel orientation of molecular dipoles, *i.e.*  $\beta$ -multimers. As a result,  $\delta g$  decreases from positive to negative values. The de-

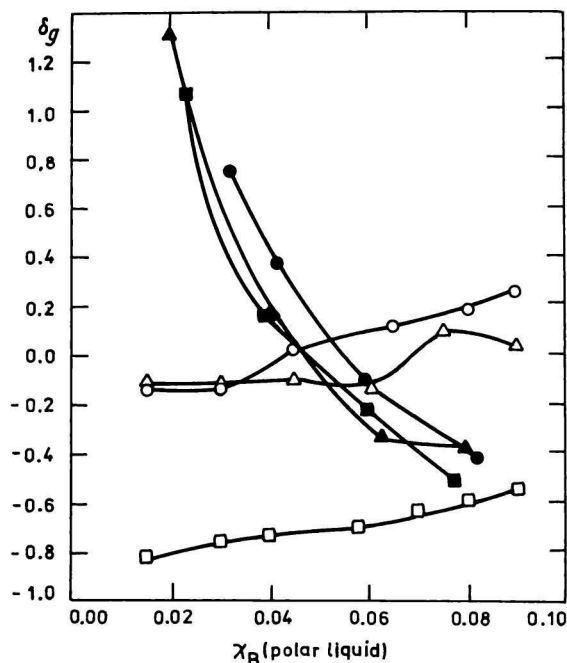


Fig. 1. Variation of  $\delta g$  with the mole fraction of polar liquids in tetrachloromethane at 301 K. ○ Aniline, △ pyridine, □ *N,N*-dimethylaniline, ● methanol, ▲ 1-propanol, ■ 1-butanol.

crease in the value of  $\delta g$  corroborates our findings on the excess Gibbs energy of mixing. The formation of the  $\beta$ -multimers results in the release of internal energy and therefore the excess Gibbs energy of mixing increases with the increase of the concentration of solute. Many authors [15, 16, 22] while studying the dielectric behaviour of alcohols in nonpolar solvent have reported identical results.

On the other hand, amines are very weakly associated liquids and thus the hydrogen bonding becomes nonexistent in very dilute solutions, *i.e.* the measured values of  $\delta g$  probably reflect those for induced nonpolar solvent molecules. The gradual increase of  $\delta g$  with the addition of the polar solute might be probably due to the change of gradual alignment of molecular dipoles [23], which indicates that the induced nonpolar molecules are aligned in a predominant direction leading to the formation of  $\alpha$ -multimers.

The change of the sign of  $\delta g$  can be explained by the theory of Potapov [1]. While studying the spontaneous polarization in a binary mixture of polar—nonpolar liquids in the dielectric relaxation region, Potapov 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. He reported that in dilute solutions most of the molecular dipoles are aligned in a predominant direction and therefore acquire a new state, qualitatively different from the

natural disordered state, characteristic of the individual liquids.

However, the increase of the excess Gibbs energy of mixing with the increase of the concentration of amines is attributed to the reactivity of polar liquid molecules in an environment of nonpolar solvent molecules. In case of pyridine, the presence of delocalized (mobile) electrons causes maximum reactivity which results in the release of the highest excess Gibbs energy. In other two cases, the nitrogen atom of the amino group is out of the ring. As a result, its lone electrons do not participate with the  $\pi$ -electrons within the benzene ring, which makes it less reactive. Consequently, less amount of the Gibbs energy is released. The relatively less excess Gibbs energy in case of *N,N*-dimethylaniline is probably due to steric factors which inhibit the Gibbs energy participation. The lower value of  $\Delta G_{AB}$  in the mixtures with *N,N*-dimethylaniline is probably justified by the fact that  $\delta g$  is also low in these mixtures.

In case of alcohols, a decreasing excess Gibbs energy of mixing is observed in the order  $\Delta G(\text{methanol})$ ,  $\Delta G(\text{1-propanol})$ ,  $\Delta G(\text{1-butanol})$ . It is probably due to the fact that for a hydroxy group containing alcohols, the hydrogen bond formation capacity is enhanced with a lower number of carbon atoms in the chain. The higher is the number of carbon atoms (the length of the alkyl group), due to the hyperconjugation the higher is the electron feeding capability of the carbon atom attached to the OH group. It leads to a higher electron density on the oxygen atom and hence to a less hydrogen-bonding capacity.

In conclusion, our proposition of the term of the excess correlation factor  $\delta g$  as well as its introduction to the expression for the excess Gibbs energy of mixing is significant in the sense that it explains molecular association in a hydrogen-bonded liquid in a more appropriate way than was reflected from the results drawn through the evaluation of the correlation factor  $g$ . Furthermore, the change of the sign of  $\delta g$  is an indicator of the order—disorder phase transition in extremely dilute polar—nonpolar solutions.

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