

Dielectric properties of binary mixtures of some amines in nonpolar solvents — linear correlation factor, excess molar polarization, and excess Gibbs energy

S. TRIPATHY and B. B. SWAIN

*Post-graduate Department of Physics, Ravenshaw College,
Cuttack 753003, Orissa, India*

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Relative permittivity of binary mixtures of aniline, pyridine, and dimethylaniline in nonpolar liquids, namely benzene, tetrachloromethane, and *p*-xylene has been measured at $\nu = 455$ kHz for four different temperatures. The Kirkwood—Fröhlich linear correlation factor g , excess molar polarization, excess Gibbs energy of mixing in these mixtures are calculated using the experimentally determined value of relative permittivity on the basis of Winkelmann—Quitze equation.

These parameters are found to be concentration dependent indicating existence of angular correlation between the polar molecules in the nonpolar solvent.

Evaluation of Kirkwood—Fröhlich linear correlation factor [1, 2], excess molar polarization, and excess thermodynamic function from the measured value of relative permittivity in associated systems has been used by many for interpreting liquid structure in such systems.

The linear correlation factor g is a shape dependent correlation factor and is a measure of short-range intermolecular force leading to dipole—dipole interaction. The nature of variation of g with concentration reflects the change in dipolar alignment and hence the nature of multimerization. Though there are many reports in the literature on evaluation of g and excess molar polarization ΔP in binary mixtures of alcohols with nonpolar solvents [3—6], we have come across few such reports for amines [7, 8]. Therefore we have attempted to evaluate these parameters in the binary mixtures of three amines — aniline, pyridine, and dimethylaniline in nonpolar solvents, namely benzene, tetrachloromethane, and *p*-xylene.

Experimental

The chemicals used were of anal. grade and of reputable make, purified and redistilled before use.

The experimental arrangement used for the measurement of relative permittivity, *etc.* is the same as used by one of the authors earlier [5]. The relative permittivity measurements for the 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 with known relative permittivity [9]. The cell temperature was controlled with an electronically regulated thermostatic arrangement with temperature variation of ± 0.1 °C. The refractive indices were measured at the regulated temperature by a Pulfrich refractometer at the sodium D-line. The density measurement was done by a semimicrobalance with a pycnometer of 25 cm³ volume. The reproducibility of relative permittivity measurement at radiofrequency was ± 0.003 and those of refractive index and density measurements were ± 0.00002 and ± 0.00002 g cm⁻³, respectively. For these maximum limits of variation, the value of g , ΔG , and ΔP could be measured accurately up to the second decimal digit.

Calculations

The Kirkwood—Fröhlich relation for linear correlation factor extended to the solutions can be written as

$$g = \frac{9\epsilon_0 k T (2\epsilon_r + \epsilon_x)^2}{N_A \mu^2 x_2 (\epsilon_x + 2) (2\epsilon_r + 1)} \left[V \frac{\epsilon_r - 1}{\epsilon_r} - \frac{3x_1 V_1 (\epsilon_{r,1} - 1)}{(2\epsilon_r + \epsilon_{r,1})} - \frac{3x_2 V_2 (\epsilon_x - 1)}{(2\epsilon_r + \epsilon_x)} \right] \quad (1)$$

where μ is the dipole moment of the solute molecule, V the molar volume of the mixture, V_1 and V_2 are the molar volume of the solvent and the solute, respectively, x_1 and x_2 the mole fractions of the solvent and solute, respectively, ϵ_x is taken as the square of the refractive index of the polar liquid, ϵ_r is the relative permittivity of the mixture, $\epsilon_{r,1}$ the relative permittivity of the nonpolar solvent, ϵ_0 the permittivity of vacuum, k the Boltzmann constant, N_A the Avogadro's constant, and T thermodynamic temperature.

The excess molar polarization of mixing ΔP is calculated taking into account both the long-range and short-range interaction between identical molecules. According to this, the molar polarization of the binary mixtures is given by

$$P_m = \frac{\epsilon_r}{\epsilon_r + 2} \left[\frac{3x_1 V_1 (\epsilon_{r,1} - 1)}{2\epsilon_r + \epsilon_{r,1}} + \frac{3x_2 V_2 (\epsilon_x - 1)}{2\epsilon_r + \epsilon_x} + g \frac{N_A \mu^2 x_2 (\epsilon_x + 2)^2 (2\epsilon_r + 1)}{9\epsilon_0 k T (2\epsilon_r + \epsilon_x)^2} \right] \quad (2)$$

where g is the Kirkwood—Fröhlich linear correlation factor for the solute.

The excess molar polarization is given by

$$\Delta P = P_m - (x_1 P_1 + x_2 P_2) \quad (3)$$

where P_1 and P_2 are molar polarization of the solvent and solute, respectively.

The excess Gibbs energy ΔG of the binary mixture of a polar liquid in a nonpolar solvent is given by the expression [10]

$$\Delta G = -\frac{N_A}{2} [R_{f_2} - R_{f_2}^{\circ}] [x_2 \mu^2 \{x_2 (g' - 1) + 1\}] \quad (4)$$

where

$$R_{f_2}^{\circ} = \frac{2N_A}{9\epsilon_0 V_2} \frac{(\epsilon_{r,2} - 1)(\epsilon_x + 2)}{2\epsilon_{r,2} + \epsilon_x}$$

$$R_{f_2} = \frac{2N_A}{9\epsilon_0 V_2} \frac{(\epsilon_r - 1)(\epsilon_x + 2)}{2\epsilon_r + \epsilon_x}$$

Here, g' and $\epsilon_{r,2}$ are the linear correlation factor and relative permittivity of the pure polar liquid (solute), respectively.

Results and discussion

Relative permittivity of the binary mixtures of aniline, pyridine, and dimethylaniline with three nonpolar solvents, namely benzene, tetrachloromethane, and *p*-xylene was measured at four different temperatures ranging from 304 K to 318 K. The experimental data are used to calculate the value of g , ΔP , and ΔG in these mixtures.

Some of the relevant data are presented in Tables 1—3 and displayed graphically in Figs. 1—6.

The Kirkwood—Fröhlich linear correlation factor g , calculated in pure pyridine and aniline is found to be nearly unity (1) indicating absence of any preferential correlation. However in dimethylaniline, the value of g is less than unity indicating predominance of β -multimers. On dilution, with a nonpolar solvent, the value of g significantly changes, the trend being different in different mixtures. In most of the mixtures, g remains below unity in very dilute solution while in mixtures with aniline it exceeds unity. With increase in concentration, the value of g gradually increases and then falls to a value of g_{\min} beyond which it rises again till it reaches the value in the solute-rich region. This trend at four different temperatures is in conformity with Oster's theoretical curve [11] for associated liquids. It also agrees with the findings of *Sabesan et al.* [12] in carboxylic acids. However, the depth of minima is not as pronounced as in case of alcohols. This is probably due to the fact that amines are mildly associated liquids in these nonpolar solvents.

It is observed that in the low solute concentration region, g_{\max} is highest in the mixtures containing CCl_4 . Furthermore g_{\max} exceeds unity significantly in aniline—tetrachloromethane mixtures. It is probably due to the favourable interaction between lone pair of electrons in the nitrogen atom of aniline or pyridine and positive carbon atom of CCl_4 that helps in establishing angular

Table 1

Variation of g , ΔG , and ΔP with the content of pyridine in different solvents at 35°C ($g' = 1.007$)

Solvent														
Tetrachloromethane					Benzene					<i>p</i> -Xylene				
x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$	x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$	x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$
0.098	2.847	1.04	231.73	5.11	0.096	2.893	0.91	224.62	3.97	0.101	2.820	0.57	242.87	1.07
0.193	3.557	1.02	358.83	8.57	0.197	3.478	0.81	375.08	5.62	0.207	3.283	0.76	420.46	3.42
0.292	4.304	0.98	426.01	10.28	0.293	4.003	0.77	466.31	6.36	0.309	3.800	0.69	530.19	5.10
0.399	5.202	1.03	442.00	12.53	0.400	5.035	0.86	459.74	7.87	0.414	4.560	0.76	558.25	6.71
0.480	5.520	0.94	481.74	10.31	0.488	5.754	0.83	434.78	7.60	0.511	5.416	0.85	529.88	7.49
0.596	6.815	0.91	400.92	8.70	0.589	6.632	0.85	419.81	6.72	0.609	6.221	0.82	493.62	6.76
0.685	7.706	0.92	342.13	7.25	0.719	7.706	0.85	359.27	4.21	0.706	7.197	0.84	420.21	5.39
0.797	8.855	0.92	257.41	4.72	0.788	8.230	0.82	327.84	2.75	0.808	8.202	0.85	338.47	3.66
0.900	10.450	0.97	118.71	2.70	0.900	9.600	0.92	206.12	0.78	0.900	9.800	0.92	185.25	2.19

Table 2

Variation of g , ΔG , and ΔP with the content of aniline in three solvents at 35°C ($g' = 1.03$)

Solvent														
Tetrachloromethane					Benzene					<i>p</i> -Xylene				
x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$	x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$	x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$
0.099	2.599	1.26	87.76	2.52	0.099	2.517	0.67	91.40	0.35	0.106	2.603	0.31	94.06	-1.31
0.197	2.963	1.16	146.53	3.73	0.224	2.817	0.69	179.36	-0.14	0.207	2.809	0.54	166.47	-1.17
0.293	3.162	0.94	198.29	2.58	0.295	2.975	0.68	218.88	-0.75	0.306	3.193	0.78	203.77	0.57
0.393	3.478	0.89	226.85	2.28	0.405	3.400	0.75	243.57	-0.14	0.409	3.560	0.88	226.96	1.40
0.490	3.754	0.88	245.27	1.33	0.451	3.523	0.74	254.91	-0.58	0.499	3.815	0.86	242.61	0.92
0.587	4.109	0.73	244.33	0.73	0.591	3.951	0.72	267.79	-1.69	0.600	4.132	0.89	248.54	0.94
0.761	4.646	0.79	232.54	-1.79	0.691	4.280	0.76	261.45	-2.53	0.698	4.369	0.80	251.34	-1.41
0.877	5.258	0.84	176.27	-2.45	0.761	4.649	0.78	232.10	-2.48	0.797	4.905	0.85	206.25	-0.36
					0.876	5.383	0.84	159.10	-2.49	0.893	5.496	0.90	147.60	-0.33

Table 3

Variation of g , ΔG , and ΔP with the content of dimethylaniline in different solvents at 35°C ($g' = 0.86$)

Solvent														
Tetrachloromethane					Benzene					<i>p</i> -Xylene				
x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$	x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$	x_2	ϵ_r	g	$\frac{\Delta G}{\text{J mol}^{-1}}$	$\frac{\Delta P}{\text{cm}^3 \text{mol}^{-1}}$
0.102	2.329	0.39	58.28	-1.75	0.099	2.450	0.51	52.36	0.61	0.100	2.550	0.14	48.17	-2.58
0.200	2.745	0.78	84.14	1.09	0.199	2.718	0.64	88.71	-0.29	0.200	2.750	0.47	84.62	-2.31
0.299	3.085	0.86	98.08	2.22	0.298	3.065	0.76	98.66	0.89	0.311	2.955	0.55	96.73	-2.18
0.399	3.319	0.82	106.20	1.79	0.398	3.356	0.78	102.65	1.14	0.416	3.200	0.63	122.10	-1.75
0.498	3.601	0.82	101.65	1.85	0.498	3.599	0.78	102.84	0.78	0.513	3.440	0.67	121.74	-1.44
0.582	3.894	0.86	89.92	1.97	0.603	3.823	0.76	97.90	0.07	0.600	3.650	0.70	116.10	-1.42
0.698	4.174	0.84	71.48	1.52	0.696	4.163	0.81	73.72	0.73	0.682	3.954	0.77	94.55	-0.39
0.798	4.466	0.85	43.69	1.26	0.798	4.450	0.83	59.67	0.58	0.768	4.129	0.76	84.85	-1.11
0.898	4.682	0.84	27.62	0.21	0.900	4.750	0.86	23.65	0.44	0.851	4.406	0.79	59.16	-0.83

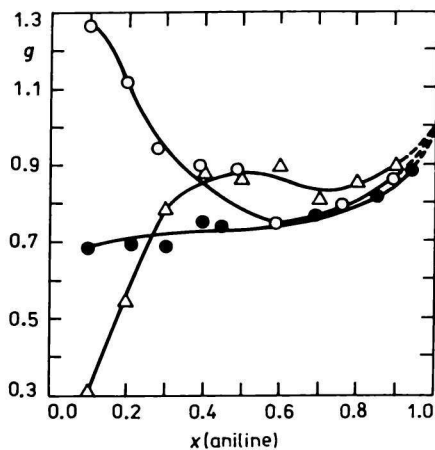


Fig. 1. Variation of g with mole fraction of aniline in three nonpolar solvents: O tetrachloromethane, ● benzene, Δ *p*-xylene.

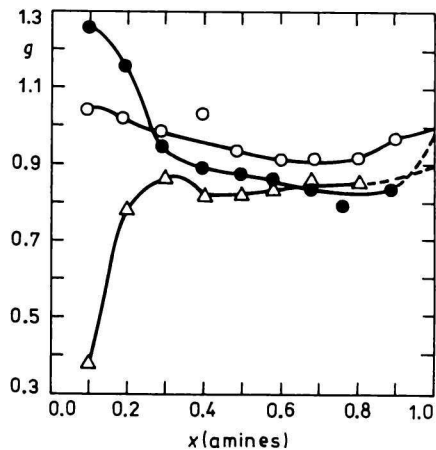


Fig. 2. Variation of g with mole fraction of three amines (O pyridine, ● aniline, Δ dimethylaniline) in tetrachloromethane.

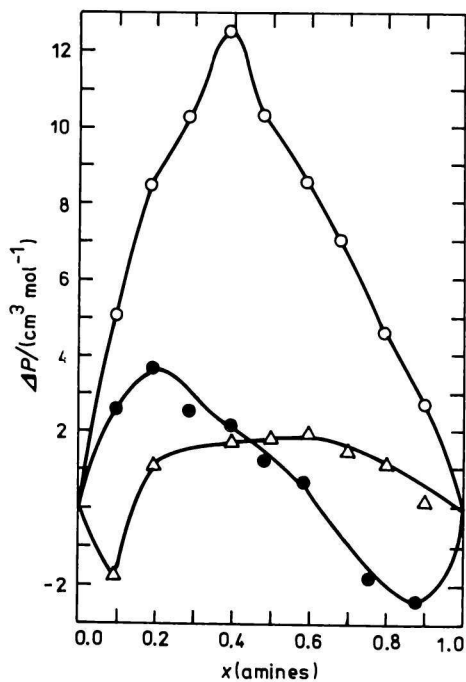


Fig. 3. Variation of ΔP with mole fraction of amines (O pyridine, ● aniline, Δ dimethylaniline) in tetrachloromethane.

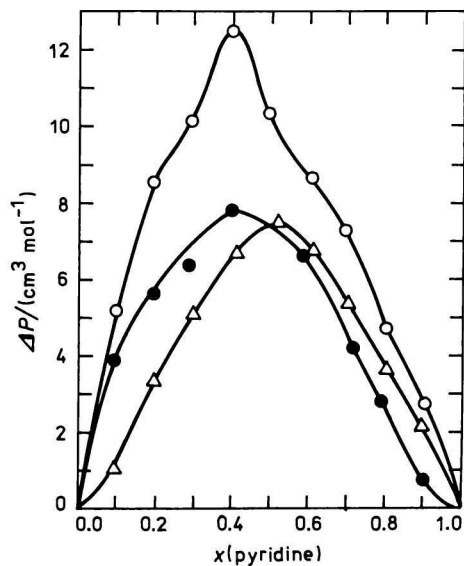


Fig. 4. Variation of ΔP with mole fraction of pyridine in three nonpolar solvents: O tetrachloromethane, ● benzene, Δ *p*-xylene.

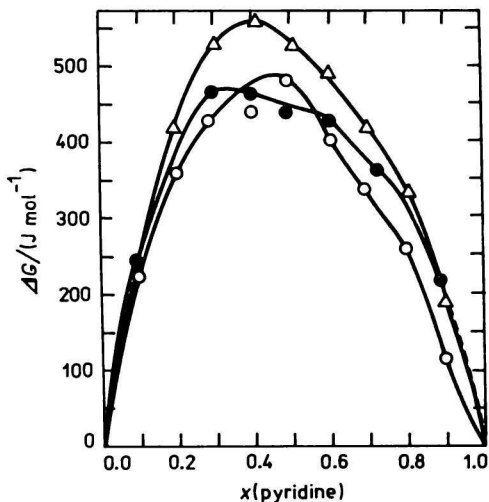


Fig. 5. Variation of ΔG with mole fraction of pyridine in three nonpolar solvents: O tetrachloromethane, ● benzene, Δ *p*-xylene.

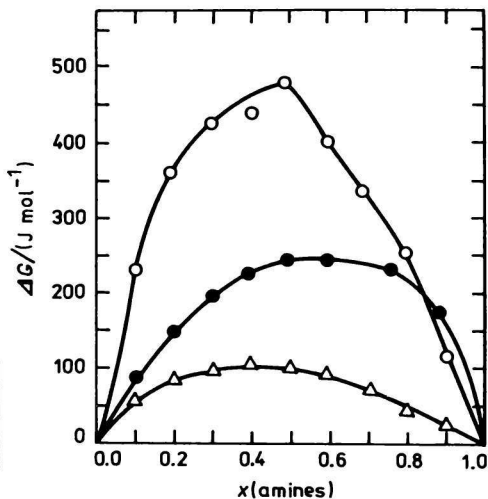


Fig. 6. Variation of ΔG with mole fraction of three amines (O pyridine, ● aniline, Δ dimethylaniline) in tetrachloromethane.

correlation among the solute molecules so that g exceeds unity. The unshared electron pair in the nitrogen atom of dimethylaniline being pushed to C—N bond due to alkyl group leaves a positive charge on nitrogen and causes an electron shift within the ring to put a negative charge on *ortho*- or *para*-carbon atom. As such this interaction is relatively less favoured. The value of g_{\max} in aniline is higher than that of pyridine most probably due to the fact that the nitrogen atom of pyridine is more nucleophilic being an integral part of the ring current.

The variation of excess molar polarization ΔP in the aniline—tetrachloromethane and aniline—benzene mixtures shows a wave-shaped structure. It is positive in the solvent-rich region and negative in the solute-rich region. This is compatible with the fact that α -multimers are predominant in the dilute solutions. Furthermore, ΔP_{\max} is higher in CCl_4 mixture, which agrees with higher magnitude of g_{\max} . However, ΔP in the mixtures of pyridine is positive throughout in all cases. This is probably due to the fact that the g value though less than unity, remains close to unity after the initial increase in the low solute concentration range. Furthermore, ΔP_{\max} is higher in CCl_4 medium as expected. In the mixture of dimethylaniline with tetrachloromethane or benzene ΔP has a low nearly constant positive value after the initial negative value. This agrees with the fact that g in these mixtures attains almost a constant value close to the value beyond the very dilute range. On the other hand, in dimethylaniline—

p-xylene mixture ΔP is negative over the entire concentration range. It may be noted that in these mixtures g is relatively less compared to other mixtures with other solvents.

Excess Gibbs (free) energy is positive in all mixtures probably due to the fact that in all of them there is domination of β -multimers over a greater range and β -multimers are characterized by reduced internal energy making excess energy positive. In the mixtures with CCl_4 as the solvent, the value of ΔG decreases in the order: pyridine, aniline, dimethylaniline. However, for $x_2 > 0.85$, ΔG is found to be higher in aniline mixtures compared to pyridine mixtures. This is compatible with the fact that over a greater range g positive is in aniline mixtures less than in pyridine ones. The lower value of ΔG in the mixtures with dimethylaniline is probably justified by the fact that g is also low in these mixtures. In case of mixtures with benzene and *p*-xylene the same trend is also observed.

The trend of variation at all temperatures of measurement remains nearly identical.

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