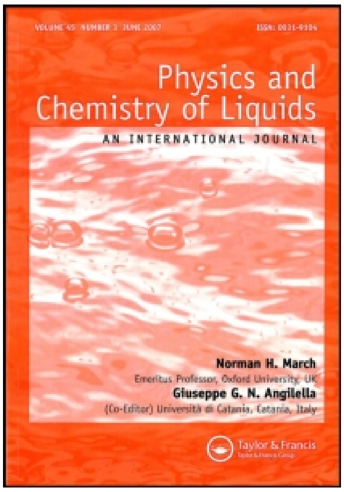

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Susama Tripathy[a]; Bipin Behari Swain[a]
[a] P. G. Department of Physics, Ravenshaw College, Cuttack, Orissa, India

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DIELECTRIC STUDIES OF BINARY MIXTURES OF SOME AMINES—ANILINE AND PYRIDINE—IN NONPOLAR SOLVENTS—SOLUTE-SOLVENT INTERACTIONS

SUSAMA TRIPATHY and BIPIN BEHARI SWAIN

P. G. Department of Physics, Ravenshaw College, Cuttack 753003, Orissa, India.

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Dielectric constant of binary mixtures of aniline and also pyridine in nonpolar liquids namely benzene, carbon tetrachloride, *p*-xylene and *n*-heptane have been measured at 455 kHz for four different temperatures. Eyring's interaction parameter G^* based on the significant structure model is calculated in the mixtures using the experimentally determined value of dielectric constant.

The nature of the solvent is found to influence this parameter G^* reflecting the non-specific solute-solvent interaction. The calculated value of G^* is used for interpreting dipole interaction of solute molecules in the solvent environment.

KEY WORDS: Dielectric constant, binary mixture, significant structure theory, solute-solvent interaction.

1 INTRODUCTION

Investigations in the realm of liquid state have been attempted through variety of experimental methods. Evaluation and interpretation of dielectric properties in hydrogen bonded systems is used by many for such studies. The Kirkwood-Fröhlich[1,2] linear correlation factor g, evaluated from dielectric studies is used for deciding the nature of interaction leading to multimerization in such systems. Oster's theoretical curve[3] describing the concentration dependence of g of a polar liquid in its binary mixture with a nonpolar solvent has been experimentally corroborated by many authors in case of alcohols[4,5,6]. 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 about evaluation of g, Excess Molar Polarization, ΔP and Excess Free Energy of Mixing, ΔF, in binary mixtures of alcohols with nonpolar solvents, we have come across few such reports for amines[7,8]. Therefore, we investigated these aspects in two amines-aniline and pyridine in a number of nonpolar solvents. It is observed that though the trend of variation of g, ΔP and ΔF are identical in seemingly non-interacting nonpolar mediums, yet there is appreciable difference in the value of g and ΔP at the same concentration of the polar liquid for different nonpolar solvents. This obviously points to the presence of nonspecific interaction between solvent and solute molecules specially when the solvent is in excess in addition to the usual dipolar interaction. As such, Mecke-Kempter[9] type of concentration independent equilibrium cannot be assumed for different solvents and as such calculation of g and hence study of dipolar interaction at low concentration is masked by the solvent effect.

On the other hand, the model proposed by Eyring[10] is used in assessing solute-solute interaction in an environment of solute (polar liquid) molecules as well as the solute-solvent contact interaction in the binary mixture. Investigation on dispersion in optical regin and X-ray studies have shown that a liquid has elements of crystalline structure. Eyring and his co-workers using the lattice picture postulated the presence of vacant lattice sites (holes) in the liquid. With this hole concept, they concluded that a liquid possesses dual characteristic of gas and solid, and voids present experiencing gas like freedom and the remaining part of the liquid exhibiting solid like rigidity. Making an Einstein Oscillator approximation for this solid-like portion of the liquid, thermodynamic, transport and dielectric properties of a number of binary mixtures have been explained. Moreover, with addition of nonpolar solvent in an associated liquid, fluidised vacancies can be increased to a large extent and as such short-range correlation of dipoles is significantly altered. Thus this model reveals a significant fact that the solvent effect is directly related to the liquid structure of associated species. Eyring's model is free from certain assumptions used in Kirkwood's model. Singh and Sinha[13] have also shown that the Eyring's relation for binary mixtures give better agreement between theoretical and experimental values of dielectric constant than those obtained from Kirkwood-Fröhlich equations.

This model incorporates two structural parameters G and G^* for the liquids—G reflecting interaction between solute-solute molecules in the pure state of the solute while G^* represents the interaction between solute-solvent molecules. The G^* value changes significantly with various multimer species of the solute in the solution. Here we have evaluated G^* in binary mixtures of two weakly associated systems, aniline and pyridine in four nonpolar solvents namely, Benzene, *p*-Xylene, Carbon tetrachloride and n-heptane. Comparing G^* with the value of G, the liquid structure involving alteration in the process of multimerization could be interpreted.

2 THEORY

According to Significant Structure Theory[10] (S.S.T) there are vacant lattice sites (holes) present in a liquid. These disordered holes of liquid are assumed to be fluidised vacancies, which are supposed to possess gaslike freedom. In one mole of liquid, there will be $V - V_s/V$ moles of such vacancies where V and V_s are the molar volumes of liquid and solid phase, respectively. Thus each of the fluidised vacancies confers gaslike properties on $V - V_s/V$ moles.

Thus the partition function for a mole of liquid is separated into solid like and gaslike degrees of freedom and the mean value of a property χ is given by,

$$\chi = \chi_s\left(\frac{V_s}{V}\right) + \chi_g\left(\frac{V - V_s}{V}\right) \tag{1}$$

where χ_s and χ_g are the values of this property in solid and gaseous states, respectively.

Furthermore, S.S.T[10] envisages associated liquids to be consisting of domains of various sizes containing dipoles in groups. These dipoles have average dipole moment $\mu \cos\theta$ with respect to direction of maximum polarization for the domain. With application of an electric field, direction of maximum polarization will tend to orient in the field resulting in either parallel or antiparallel alignment of the dipoles. This gives rise to the growth of favourably oriented molecules in the domain. The resulting mean dipole moment of solid like structure is given by Eyring to be equal to $\mu^2 GF/kT$ where $G = \cos^2\theta$ and F is the local field. The dielectric polarization P_s is given by $\mu^2 G/kT$. For consideration of fluidised holes, the Kirkwood's factor $\mu^2/3kT$ is still retained since free orientation of the molecules in the local field is also possible for gaseous part.

Basing on the above assumptions coupled with the concept of S.S.T., the following equations for the dielectric constant of a polar liquid is derived.

$$\frac{(\varepsilon_2 - \varepsilon_\infty)(2\varepsilon_2 + \varepsilon_\infty)}{3\varepsilon_2(\varepsilon_\infty + 2)^2} = \frac{4\pi N}{3kT}\frac{\mu^2}{3V_2}\left[\frac{V_s}{V_2}G + \frac{1}{3}\left(1 - \frac{V_s}{V_2}\right)\right] \tag{2}$$

where ε_2 is the dielectric constant of the polar liquid,

ε_∞ is the square of the refractive index of the polar liquid,

V_2 is the molar volume of the polar liquid,

V_s is the molar volume of the polar liquid in solid phase,

μ is the gasphase dipole moment of the polar liquid,

T is the temperature Kelvin,

k is the Bottzmann constant and

G is defined earlier.

When a nonpolar solvent is added, it is expected to alter the liquid structure and hence its dielectric behaviour. The number of domain of the solute species increases as the solvent concentration increases. Then one has to consider the dielectric polarization P_s^* of the domains of the solute species in the solvent environment. P_s^* is now expressed as $\mu^2 G^*/kT$ where G^* replaces G to account for the solute–solvent contact interactions, the occurrence of which is proportional to $X_1 X_2$. Hence Eq. (2) could be modified to take into account the interaction in the altered environment and is given by,

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon(\varepsilon_\infty + 2)^2} = \left(\frac{4\pi N}{3kT}\right)\frac{\mu^2}{3V} X_2\left[\frac{V_s}{V}(X_2 G + X_1 G^*) + \frac{1}{3}\left(1 - \frac{V_s}{V}\right)\right] \tag{3}$$

where X_1 and X_2 are the mole fraction of the solvent and solute respectively,

ε is the dielectric constant of the mixture;

V is the molar volume of the mixture, and other symbols are as defined earlier.

The data for G in pure liquids and G^* for varying composition of amines in nonpolar solvents have been calculated using Eq. (2) and Eq. (3) respectively.

Table 1 Variation of G^* with concentration of aniline in different solvent at 35°C [$G = 0.36$].

Solvent-Benzene			*Solvent-carbon tetrachloride*			*Solvent-p-xylene*		
X_2	ε	G^*	X_2	ε	G^*	X_2	ε	G^*
0.099	2.517	0.05	0.099	2.509	0.03	0.106	2.603	0.02
0.224	2.817	0.05	0.197	2.963	0.20	0.207	2.809	0.07
0.295	2.975	0.04	0.293	3.162	0.15	0.306	3.193	0.21
0.405	3.400	0.08	0.393	3.478	0.13	0.409	3.560	0.22
0.451	3.523	0.05	0.490	3.754	0.13	0.499	3.815	0.19
0.591	3.951	0.00	0.587	4.109	0.07	0.600	4.132	0.20
0.691	4.280	−0.12	0.761	4.646	−0.13	0.698	4.369	−0.00
0.761	4.649	−0.02	0.877	5.258	−0.41	0.797	4.905	−0.07
0.876	5.383	−0.32	—	—	—	0.893	5.496	−0.26

3 EXPERIMENTAL

The experimental arrangement used for the measurement of dielectric constant etc. are the same as used by one of the authors[5] earlier. The accuracy of measurement is also the same.

4 RESULTS AND DISCUSSION

Dielectric constant of the binary mixtures of aniline and pyridine with four nonpolar solvents namely benzene, carbon tetrachloride, *p*-xylene and *n*-heptane was measured at four temperatures between 304 K and 318 K. The experimental data is used to calculate the value of G^* in these mixtures.

Some of the relevant data is presented in Tables 1-2 and graphically displayed in Figures 1-3.

Table 2 Variation of G^* with concentration of pyridine in different solvents at 35°C [$G = 0.33$].

Solvent-Benzene			*Solvent-carbon tetrachloride*			*Solvent-p-xylene*			*Solvent-n-heptane*		
X_2	ε	G^*	X_2	ε	G^*	X_2	ε	G^*	X_2	ε	G^*
0.096	2.893	0.29	0.098	2.847	0.27	0.101	2.820	0.36	0.100	2.501	−0.10
0.197	3.478	0.24	0.193	3.557	0.31	0.207	3.283	0.28	0.198	2.592	−0.13
0.293	4.003	0.22	0.292	4.304	0.30	0.400	3.800	0.19	0.290	3.200	−0.03
0.400	5.035	0.20	0.399	5.202	0.29	0.414	4.560	0.19	0.397	3.711	−0.07
0.488	5.754	0.20	0.480	5.520	0.27	0.511	5.416	0.18	0.497	4.190	−0.07
0.589	6.632	0.18	0.596	6.815	0.23	0.609	6.221	0.14	0.602	4.725	−0.13
0.719	7.706	0.03	0.685	7.706	0.21	0.706	7.197	0.10	0.714	5.234	−0.35
0.788	8.230	0.02	0.797	8.855	0.16	0.808	8.202	−0.03	0.805	6.281	−0.50
0.900	9.600	−0.21	0.900	10.450	0.19	0.900	9.80	0.00	0.900	7.406	−1.06

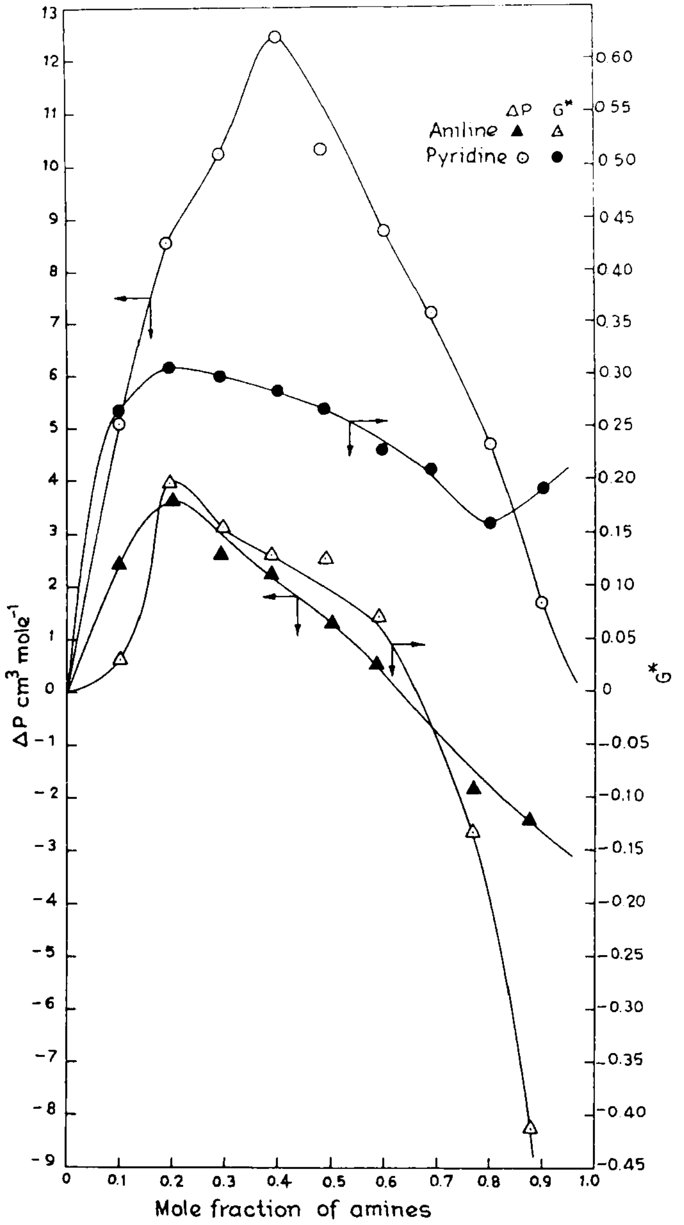

Figure 1 Variation of ΔP and G^* with mole fraction of two amines in carbontetrachloride.

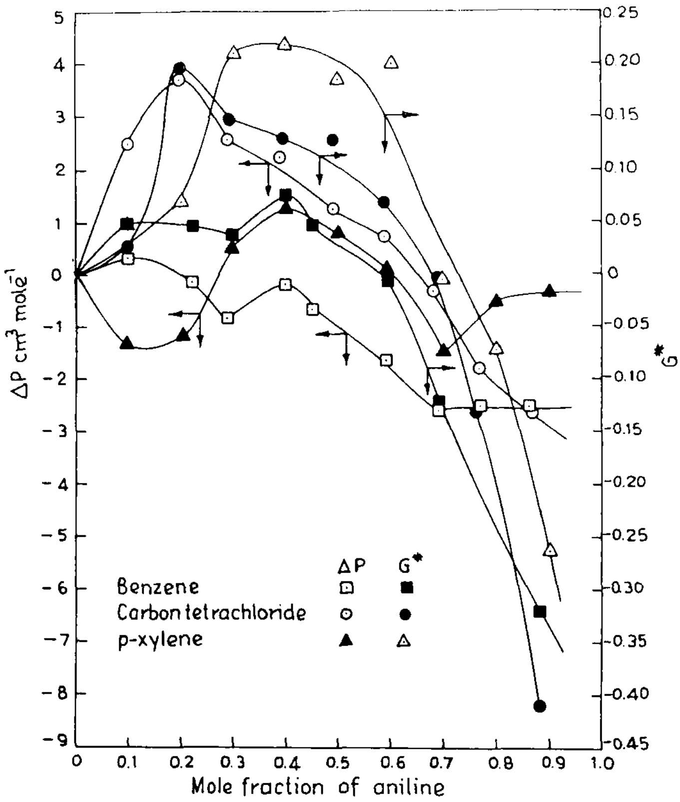

Figure 2 Variation of ΔP and G^* with mole fraction of aniline in three non-polar solvents.

Evaluation of V_s: We have used the relevant data from the international critical tables[11] to extrapolate the density of the polar liquid at its melting point by employing the density temperature relation.

$$dt = d_s + 10^{-3}\alpha(t - t_s) + 10^{-6}\beta(t - t_s)^2 + 10^{-9}\gamma(t - t_s)^3 + \cdots$$

Since β and γ are negligibly small, they are omitted for final calculation and only the term containing α is taken into account. The extrapolated value of density is used to calculate the molar volume at the melting point. Finally this calculated value of V_s is corrected taking into account the fractional volume change on freezing, i.e. $V_{s(\text{corrected})} = V_{s(\text{calculated})}$ − correction factor.

It is observed that the value of g in both the polar liquids, aniline and pyridine is equal to unity at 308 K indicating absence of any preferential correlation between the molecules in the pure state. However, evaluation of G at that temperature shows that its value in aniline is 0.36 while in pyridine, it is 0.33. The slightly higher degree of interaction observed in aniline is probably due to a weak hydrogen bonding between

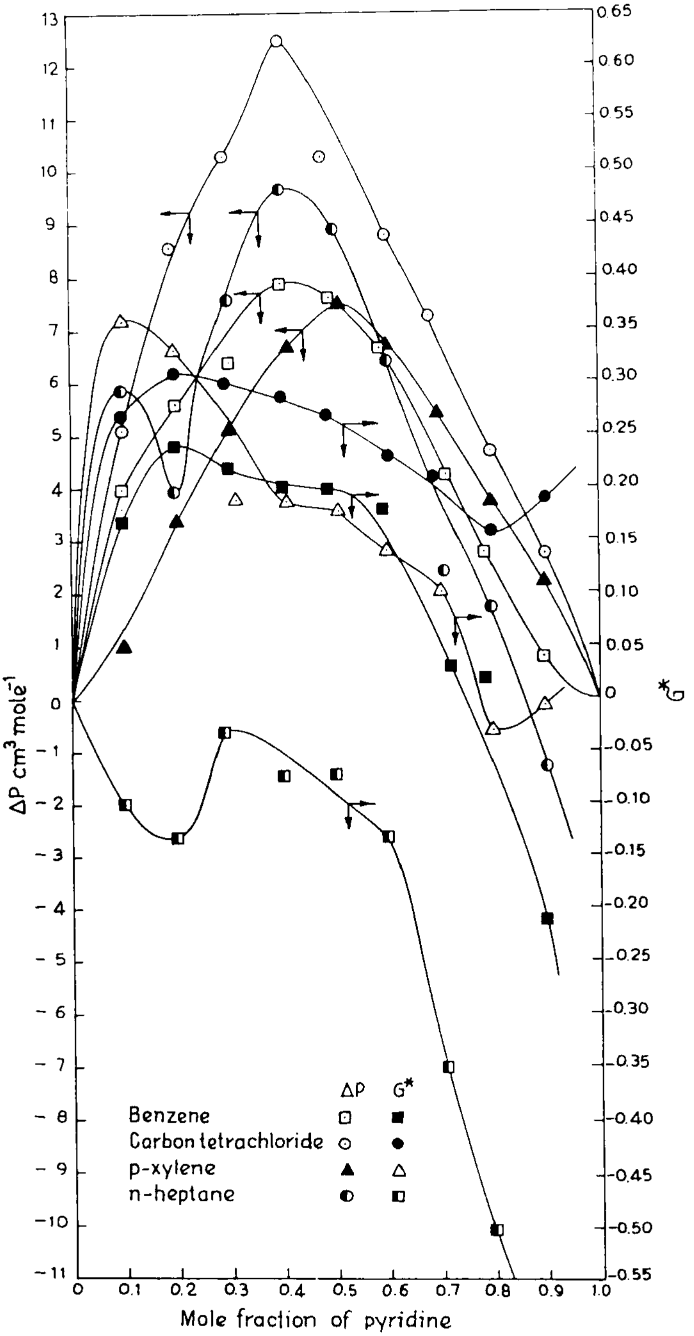

Figure 3 Variation of ΔP and G^* with mole fraction of pyridine in four non-polar solvents.

$N^{\delta -}$ and $H^{\delta +}$ of the aniline molecules. This confirms the view of Eyring *et al.*[10] that evaluation of G and G^* could be used as a better indicator for interaction in a liquid.

On dilution with a nonpolar solvent, G^* significantly changes. The change in the value of G^* reflects the nature of alteration in the process of multimerization of polar solute molecules due to solute-solvent interaction. It is observed that in the systems studies by us G^* is concentration dependent, changing from positive to negative with increase in concentration of the polar solute in four of these systems. Our findings agree in this respect with the observations of Sabesan *et al* . [4], Dwivedi *et al.*[12] and those of Swain and Roy[14] for a number of monoalcohols and carboxylic acids.

Analysing the individual trend it is observed that in the mixtures with CCl_4 the value of G^* increases from a low positive value and reach a maximum value in the solute concentration range of about 0.4 beyond which it decreases. At high solute concentration it attains a negative value in the aniline mixtures while it remains low positive in pyridine mixtures. In aniline-xylene mixture the trend is identical to that of aniline-CCl_4 mixture, but in pyridine-xylene mixture, G^* decreases regularly from positive to negative. In the mixtures containing benzene G^* changes steadily from positive to negative while in *n*-heptane mixture, it is always negative. However at a low temperature, the value of G^* is positive at low concentration even in mixtures containing *n*-heptane.

The change in the nature of environment and hence interaction is reflected in the variation in the value of G^*. At low solute concentration, the solute molecules are confined into a cage limited by the solvent molecules, while at high concentration, the solvent molecules are enclosed within a cloud of solute molecules. Also, the number and size of the domains alter. This probably is the reason for change in the sign of G^* from positive to negative with change in concentration.

For a given solute at a particular concentration higher value of G^* implies better reinforcement of angular correlation. It is observed that G^* decreases in the order:

$$CCl_4 \geq p\text{-xylene} \geq \text{benzene} \geq n\text{-heptane (Pyridine only)}$$

for both the solutes. It indicates CCl_4 and *p*-xylene helps in establishing better angular correlation between the solute molecules in comparison to benzene and *n*-heptane. It is probably due to favourable interaction between lone pair of electrons in the nitrogen atom of amine and positive carbon of CCl_4 that helps in establishing angular correlation between the solute molecules. In case of *p*-xylene, greater delocalization of the electron cloud found in the benzene ring through hyperconjugative effect of the CH_3 group might probably be the reason for better angular correlation between the solute molecules. In case of benzene and *n*-heptane, neither of these factors are present. Moreover, the π-electron in the benzene ring might be the cause of rather unfavourable interaction with the lone electron pair of nitrogen.

The negative value of G^* even at low concentration may probably be attributed to the fact that of all the solvent molecules used in this investigation, *n*-heptane is a straight chain one. As such the cage of solvent molecules around the solute molecules is likely to have a larger domain containing relatively more number of solute molecules. Hence, the liquid environment even at low concentration is akin to that in the high concentration range in other mixtures so that G^* being negative is rather appropriate.

It is further observed that rate of change of G^* with molar concentration is relatively more in aniline systems compared to that of pyridine systems. This goes to show that that change in dipolar alignment responds more quickly to change in environment in aniline because of the difference in dipolar character as reflected in the dipolar moment values of aniline (1.48) and pyridine (2.19).

The Kirkwood-Fröhlich linear correlation factor g and excess molar polarization in these systems have also been evaluated by us (not included in this report). In most of the mixtures, the trend of variation is similar to Oster's theoretical curve[3], i.e., it attains a minimum value at certain concentration. Comparing the trend of variation of g and G^*, it is observed that the change in the sign of G^* from positive to negative occurs in most of the cases at a mole fraction corresponding to $g_{\min}$. Comparison of ΔP and G^* shows that there is certain amount of correlation between them in all the mixtures except pyridine + n-heptane mixtures. It is observed that G^* changes from positive to negative when ΔP tends to become negative. However, the occurrence of zero value of G^* and ΔP do not exactly coincide in some of the mixtures probably due to delayed response to dipolar alignment in them. The trend of variation of G^* at other temperatures remain identical to a large extent in all the systems studied.

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