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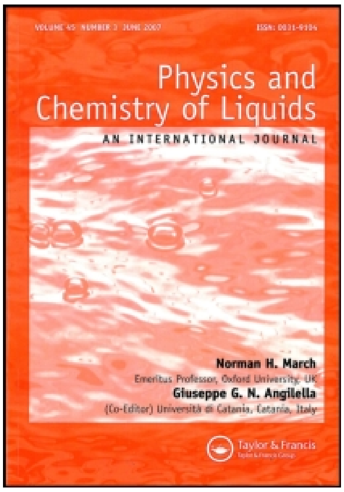

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Dielectric Study of Charge-transfer Complexes in Binary and Ternary Systems at 35°C

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DIELECTRIC STUDY OF CHARGE-TRANSFER COMPLEXES IN BINARY AND TERNARY SYSTEMS AT 35°C

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The measurements of dielectric constant of a number of binary and ternary mixtures of butyl acetate, butyl alcohol, quinoline, pyridine and o-cresol in carbon tetrachloride and benzene have been made at 35°C. Molecular interaction of these aromatic compounds have been studied in terms of variations in parameters; 'dipole moment' (μ), 'interaction dielectric constant' ($\Delta\varepsilon$), 'molecular polarisation' (P) and 'excess polarisation' (P_E). The dipole moment has been calculated using Hysken's method, the interaction dielectric constant utilizing the equation of ideal mole fraction law and excess polarisation using the theory of Erap and Glasstone. The positive values of $\Delta\varepsilon_{12}$ for binary mixtures of quinoline and butyl acetate in carbon tetrachloride and benzene have been attributed to the formation of charge transfer complexes. The negative values of $\Delta\varepsilon_{12}$ and $\Delta\varepsilon_{123}$ with pyridine suggest that charge transfer interaction is weakened by pyridine in its binary and ternary mixtures. The plot between the excess polarisation value and the product of mole fractions yielded a straight line passing through the origin showing the formation of charge transfer complexes.

KEY WORDS: Dipole moment, molecular polarisation.

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INTRODUCTION

The dielectric study has been widely used by many workers$^{1-4}$ to provide important information regarding the interaction between proton donor and proton acceptor molecules in ternary mixtures, having an inert component as a solvent. Misra *et al.*[5] and Jagan Nath *et al.*[6] studied some binary and ternary systems and from the observed positive values of interaction dielectric constants, they suggested the possibility of the formation of charge transfer complexes. With a view to investigate further the dielectric behaviour of the molecular systems, capable of forming charge transfer complexes, the present study in terms of several effective parameters contributing the charge transfer behaviour has been undertaken. In the present paper, the dielectric constant measurements have been made for various binary and ternary solutions consisting of interacting components like butyl acetate, butyl alcohol,

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quinoline, pyridine and o-cresol at 35°C and results have been discussed in terms of $\Delta\varepsilon$, P_E, μ and molecular polarisation.

THEORY

The values of the deviation ($\Delta\varepsilon_{12}$) in the dielectric constants of the various binary mixtures from the ideal mole fraction law, have been calculated using the relation

$$\Delta\varepsilon_{12} = \Delta\varepsilon_{12} - \Sigma x_i \varepsilon_i \tag{1}$$

and

$$\Sigma x_i \varepsilon_i = x_1 \varepsilon_1 + x_2 \varepsilon_2 \tag{2}$$

where ε_1, ε_2 are the dielectric constants of pure components 1 and 2 respectively, x_1 and x_2 refer to the mole fraction of the corresponding components in the binary mixture.

Similarly for ternary systems,

$$\Delta\varepsilon_{123} = \varepsilon_{123} - \Sigma_i x_i \varepsilon_i \tag{3}$$

where $\Sigma x_i \varepsilon_i = x_1 \varepsilon_1 + x_2 \varepsilon_2 + x_3 \varepsilon_3$ and other symbols have their usual meaning.

Further, the molecular polarisation of the binary system has been calculated using the relation.

$$P_{12} = \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \cdot \frac{M_1 x_1 + M_2 x_2}{d_{12}} \tag{4}$$

and the ternary system using;

$$P_{123} = \frac{\varepsilon_{123} - 1}{\varepsilon_{123} + 1} \cdot \frac{M_1 x_1 + M_2 x_2 + M_3 x_3}{d_{123}} \tag{5}$$

where M and x are the molecular weight and mole fraction of a particular component, ε is the dielectric constant and subscripts 12 and 123 refer to the solutions of binary and ternary mixtures respectively.

According to the theory of Erap and Glasstone[7] the total polarisation for binary system is given by:

$$P_T = P_1 x_1 + P_2 x_2 \tag{6}$$

and the excess polarisation by,

$$P_E = P_{12} - P_T \tag{7}$$

Erap and Glasstone model for the polarisation of binary systems has been extended and applied to ternary systems, as the inert solvent is expected to attribute least interference in the presence of both the polar components in the solution. In the case of ternary mixtures under similar conditions, P_T and P_E may be represented as

$$P_T = P_1 x_1 + P_2 x_2 + P_3 x_3 \tag{8}$$

$$P_E = P_{123} - P_T \tag{9}$$

Where all the symbols have their usual meanings.

The dipole moments of solute molecules in inert solvent are calculated using Hysken's[8] method based on the Onsager's theory. The mean square value of the dipole moment can be given as:

$$\mu_{ab}^2 = \frac{9KTV}{4\pi N} \frac{\dfrac{\varepsilon - 1}{\varepsilon} - 3\left\{\dfrac{x_1 V_1}{V}\dfrac{\varepsilon_1 - 1}{2\varepsilon + \varepsilon_1} + \left(1 - \dfrac{x_1 V_1}{V}\right)\left(\dfrac{n_{23}^2 - 1}{n_{23}^2 + 2\varepsilon}\right)\right\}}{x_{23}(2\varepsilon + 1)\left(\dfrac{n_{23}^2 + 2}{n_{23}^2 + 2\varepsilon}\right)^2} \tag{10}$$

Where V and V_1 are the molar volume of the solution and solvent respectively, ε is the dielectric constant of the solution and ε_1 that of the pure solvent and x_1, the mole fraction of the solvent, $x_{23} = 1 - x_1$ and n_{23}, the refractive index of the polar components in the solutions.

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EXPERIMENTAL

The dielectric constant ε of the solution and of the solvent (ε_1) at static frequency (100 kHz) were measured using a Toshniwal RL09 dipole meter and the refractive index using an Abbe's refractometer. The densities of various systems containing varying mole fractions of interacting solutes have been evaluated using a sensitive pyknometer.

The chemicals used were of pure Analar grade and obtained from BDH Ltd., England and High Purity Chemicals Pvt. Ltd., New Delhi (India). The physical parameters of all the chemicals were checked against their literature values. The solvents carbon tetrachloride and benzene were distilled twice before use.

RESULTS

The ε_{12} values, interaction dielectic constant ($\Delta\varepsilon_{12}$), excess polarisation (P_E) and molar polarisation (P_{12}) for binary systems are reported in Table 1. Table 2 contains, ε_{123} values, the interaction dielectric constant ($\Delta\varepsilon_{123}$), P_E, P_{123} and dipole moment 'μ' for ternary systems.

Figure 1 represents plot of P_{12} *vs.* $(\varepsilon_{12} - 1/\varepsilon_{12} + 2)^2$ for butyl acetate + benzene. Figure 2 represents plot of P_E vs. $x_1 x_2$ for butylacetate + carbontetrachloride. Figure 3 represents plot of P_E vs. $x_1 x_2 x_3$ for quinoline + o-cresol + benzene.

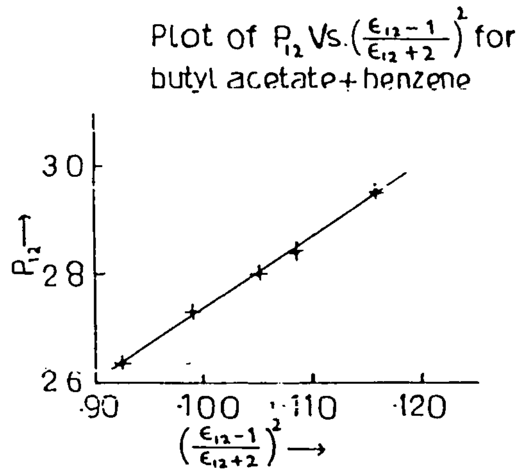

Figure 1 P_{12} vs. $(\varepsilon_{12} - 1/\varepsilon_{12} + 2)^2$ for butyl acetate + benzene.

DISCUSSION

(*1*) *Binary System*

Table 1 shows that the values of $\Delta\varepsilon_{12}$ are positive in the case of various binary mixtures of quinoline and butyl acetate in carbon tetrachloride and benzene respectively. The positive values of $\Delta\varepsilon_{12}$ can be explained due to the increase in the degree of alignment of the molecules of the various components in the binary mixtures, and this can be due to the formation of charge transfer complexes of carbon tetrachloride and benzene respectively with aromatic compounds. Since the plot of P_{12} vs. $(\varepsilon_{12} - 1/\varepsilon_{12} + 2)^2$ for all systems studied here gave a linear behaviour, the possibility was that no chemical interaction was taking place, in the binary systems. This is in agreement with the reported investigation of Srivastava and Talesara.[9]

The negative values of $\Delta\varepsilon_{12}$ for pyridine, o-cresol and butyl alcohol in the inert solvents can be attributed to the decrease in the degree of alignment. As pointed out by Hoover[10], the variation in $\Delta\varepsilon_{12}$ with concentration of the binary system may be explained on the basis of molecular alignment in some preferential direction.

In order to explain the type of interaction, the theory of Erap and Glasstone[7] has been applied. The positive values of excess polarisation (P_E) calculated using Eq. (7) rule out the possibility of dipolar association in these mixtures. The plot of excess polarisation (P_E) vs. product of mole fractions (x_1x_2), yielded a straight line passing through origin, which shows that interaction occuring in these binary systems were also of the charge transfer type of complex formation. These results are consistent with the results of Srivastava and Talesara[9] who studied some binary systems and suggested the formation of charge transfer complexes.

Molecular polarisation in the case of quinoline + benzene varies from 26.01–28.75 and excess polarisation from 1.00–4.99 where as in the case of quinoline + carbon tetrachloride, molecular polarisation and excess polarisation vary from 29.24–35.08 and 2.55–10.92 respectively. The molecular polarisation and excess polarisation for

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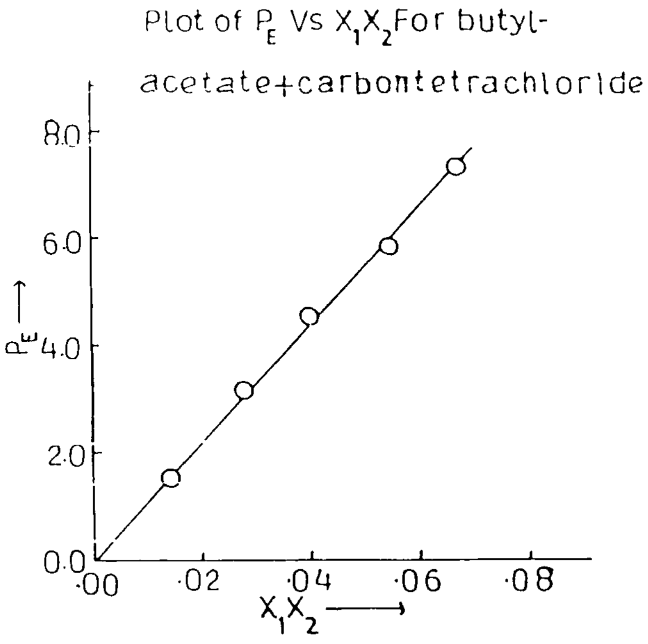

Figure 2 P_E vs. x_1x_2 forbutyl acetate + benzene.

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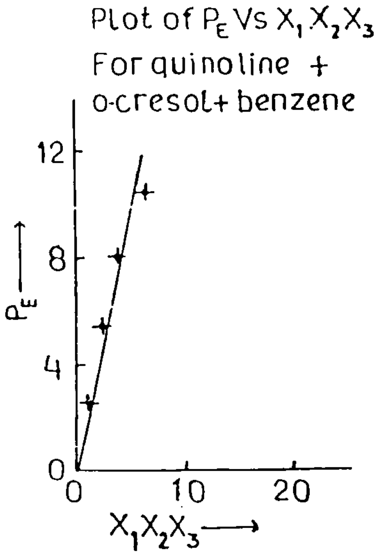

Figure 3 P_E vs. $x_1x_2x_3$ for quinoline + o-cresol + benzene.

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Table 1 Dielectric constant (ε_{12}), interaction dielectric constant ($\Delta\varepsilon_{12}$), molecular polarisation (P_{12}) and excess polarisation (P_E) of binary systems.

Systems	x_1x_2	ε_{12}	$\Delta\varepsilon_{12}$	P_{12}	P_E
Butyl acetate +	0.0073	2.30	0.029	26.12	1.09
Benzene	0.0142	2.337	0.047	26.49	1.81
	0.0207	2.362	0.054	27.10	2.73
	0.0278	2.395	0.066	27.45	3.43
	0.0343	2.453	0.105	28.28	4.52
Butyl acetate +	0.0142	2.258	−0.012	28.10	1.52
Carbon tetrachloride	0.0271	2.337	0.030	29.05	3.15
	0.0391	2.406	0.063	29.81	4.53
	0.0510	2.437	0.058	30.46	5.77
	0.0627	2.516	0.099	31.43	7.31
Butyl alcohol +	0.0114	2.31	−0.025	26.31	1.49
Benzene	0.0217	2.38	−0.034	27.29	2.97
	0.0325	2.437	−0.060	28.06	4.26
	0.0421	2.475	−0.098	28.42	5.05
	0.0515	2.549	−0.101	29.58	6.62
Butyl alcohol +	0.0222	2.30	−0.97	28.24	2.08
Carbon tetrachloride	0.0424	2.39	−0.167	29.75	4.61
	0.0603	2.426	−0.278	30.09	5.76
	0.0777	2.516	−0.339	31.42	7.90
	0.0924	2.560	−0.429	32.05	9.15
Quinoline +	0.0770	2.31	0.006	26.01	1.00
benzene	0.0143	2.405	0.054	27.27	2.59
	0.020	2.465	0.070	27.95	3.57
	0.0254	2.485	0.054	28.12	3.97
	0.0315	2.58	0.107	28.75	4.99
Quinoline +	0.0121	2.31	−0.006	29.24	2.55
Carbon tetrachloride	0.0277	2.416	−0.013	30.71	4.83
	0.0391	2.55	0.036	32.25	6.94
	0.050	2.635	0.036	33.44	8.68
	0.063	2.755	0.054	35.08	10.92
Pyridine +	0.0108	2.354	−0.002	26.87	2.02
Benzene	0.0212	2.416	−0.044	27.41	3.08
	0.0304	2.495	−0.060	28.41	4.53
	0.0395	2.585	−0.066	29.45	6.01
	0.0490	2.675	−0.078	30.51	7.51
Pyridine +	0.0213	2.348	−0.095	28.59	2.40
Carbon tetrachloride	0.0390	2.512	−0.155	30.38	5.12
	0.0561	2.622	−0.191	31.22	6.83
	0.0721	2.776	−0.218	32.53	8.92
	0.0893	2.962	−0.236	33.50	10.71
o-cresol +	0.0083	2.29	−0.066	25.86	0.88
Benzene	0.0146	2.315	−0.125	26.18	1.52
	0.0213	2.355	−0.179	26.63	2.32
	0.0284	2.375	−0.247	27.21	3.21
	0.0356	2.455	−0.266	28.44	4.12

quinoline in carbontetrachloride are higher than in the case of benzene as solvent. In other mixtures also, molecular polarisation and excess polarisation are higher in the solvent carbon tetrachloride in comparison to the solvent benzene.

TERNARY SYSTEMS

The data given in Table 2 shows that the values of $\Delta\varepsilon_{123}$ are positive for the systems, quinoline + butyl acetate + benzene, quinoline + butyl acetate + carbon tetrachloride, quinoline + butyl alcohol + benzene, quinoline + butylalcohol + carbontetrachloride, quinoline + o-cresol + benzene, quinoline + o-cresol + carbon tetrachloride and pyridine + o-cresol + benzene. The positive values of $\Delta\varepsilon_{123}$ can be attributed to the formation of charge transfer complexes since the formation of some new polar species in the solution would increase the dielectric constant of the medium. The values of $\Delta\varepsilon_{123}$ are negative for pyridine + butyl acetate + benzene, pyridine + butyl acetate + carbon tetrachloride, pyridine + butyl alcohol + benzene, pyridine + butyl alcohol + carbon tetrachloride and pyridine + o-cresol + carbon tetrachloride. This shows that in ternary mixtures obtained by the addition of pyridine as the third component to the binary mixtures, pyridine reduces the degree of alignment of the molecules, thus resulting in the weakening of specific interaction between inert solvents and atomatic compounds.

For these systems, in most of the cases, the plot of P_E vs. $x_1x_2x_3$ gives a straight line passing through the origin, thus exhibiting the possibility of charge transfer complex formation. Some ternary systems exhibit a slight bend at the end of straight line on the higher concentration side. This may have been caused from the presence of high polar constituents in these systems.

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Molecular polarisation and excess polarisation for quinoline + butyl acetate + benzene varies from 26.99–31.76 and 2.36–9.41 respectively. But in the solvent carbon tetrachloride with quinoline and butylacetate, molecular polarisation and excess polarisation varies from 29.96–38.68 and 4.22–17.29 respectively. The values of molecular polarisation and excess polarisation in the solvent carbon tetrachloride for all the concentrations are higher than in the solvent benzene. Molecular polarisation and excess polarisation are also higher for all the ternary systems in the solvent carbon tetrachloride than in benzene.

It may be noted here that the process of the complex formation by charge transfer phenomenon between carbon tetrachloride and aromatic molecules may be interpreted on the basis that the aromatic ring acts as π-type electron donor where as carbon tetrachloride molecule acts as type electron acceptor.

The dipole moments calculated using Hysken's method for quinoline + o-cresol + carbon tetrachloride system were found to vary from 3.87D to 5.08D for various concentrations. Similarly for quinoline + o-cresol + benzene μ values were found in the range of 4.09–4.81D. These values are much higher than the dipole moments of the reacting components. The higher values of dipole moment for all these systems are the direct evidence of the presence of complexed species resulting from the interaction between the components forming the charge transfer complexes.

Table 2 Dielectric constant (ε_{123}), interaction dielectric constant ($\Delta\varepsilon_{123}$), molecular polarisation (P_{123}), excess polarisation (P_E) and dipole moment of ternary systems.

Systems	$x_1x_2x_3 \times 10^4$	ε_{123}	$\Delta\varepsilon_{123}$	P_{123}	P_E	μ_{ab}
Quinoline +	0.56	2.37	0.049	26.99	2.36	3.99
Butyl acetate +	1.88	2.455	0.073	28.11	4.09	3.94
Benzene	4.03	2.53	0.086	29.25	5.84	3.97
	6.99	2.635	0.127	30.66	7.85	4.07
	9.93	2.72	0.161	31.76	9.41	4.13
Quinoline +	2.22	2.402	0.029	29.96	4.22	3.83
Butyl acetate +	7.15	2.555	0.063	32.25	7.72	3.96
Carbon tetrachloride	15.13	2.725	0.108	34.83	11.49	4.11
	25.40	2.9	0.165	37.31	15.05	4.19
	36.20	3.01	0.167	38.68	17.29	4.13
Quinoline +	0.73	2.406	0.027	27.60	3.1	4.31
Butyl alcohol +	2.9	2.521	0.011	29.13	5.48	4.11
Benzene	6.0	2.655	0.028	30.96	8.02	4.23
	10.25	2.830	0.081	33.04	10.82	4.37
	15.55	2.962	0.094	33.52	11.96	4.39
Quinoline +	3.26	2.5	−0.006	31.47	6.1	4.20
Butyl alcohol +	11.55	2.777	0.017	35.34	11.6	4.36
Carbon tetrachloride	21.29	2.98	0.020	37.43	14.86	4.29
	33.94	3.237	0.069	40.16	18.67	4.35
	44.76	3.461	0.141	42.17	21.41	4.42
Quinoline +	0.62	2.4	−0.01	27.28	2.69	4.09
o-cresol +	2.16	2.56	0.007	29.49	5.56	4.53
Benzene	4.6	2.702	0.008	31.24	7.95	4.57
	7.19	2.88	0.071	33.34	10.56	4.80
	11.6	3.046	0.079	35.06	12.94	4.81
Quinoline +	2.65	2.5	−0.07	30.86	5.26	3.87
o-cresol +	7.83	2.84	0.023	34.58	10.16	4.44
Carbon tetrachloride	15.28	3.1	0.041	38.79	15.46	4.92
	25.1	3.4	0.093	42.23	19.91	5.08
Pyridine +	0.89	2.375	−0.014	27.26	2.85	3.94
Butyl acetate +	3.07	2.532	+0.029	29.31	5.68	4.17
Benzene	6.35	2.596	−0.016	30.17	7.29	3.96
	10.48	2.718	−0.004	31.72	9.52	4.05
	15.62	2.835	−0.004	33.07	11.54	4.07
Pyridine +	3.28	2.468	−0.023	31.00	5.63	4.03
Butyl acetate +	11.78	2.74	+0.006	34.33	10.65	4.10
Carbon tetrachloride	21.53	2.877	−0.047	36.39	13.84	4.12
	37.78	3.126	−0.055	39.47	18.42	4.11
	53.80	3.286	−0.08	41.15	21.13	4.13
Pyridine +	1.42	2.425	−0.03	27.59	3.89	3.76
Butyl alcohol +	4.95	2.6	−0.038	29.72	6.52	4.00
Benzene	9.73	2.758	−0.04	31.52	9.15	4.03
	16.72	2.933	−0.045	34.49	11.99	4.41
Pyridine +	5.75	2.53	−0.11	31.28	6.47	3.69
Butylalcohol +	17.2	2.785	−0.185	34.34	11.26	3.84
Carbon tetrachloride	40.45	3.27	−0.128	39.45	18.38	4.17
	51.98	3.5	−0.07	41.69	21.35	4.29

(*continued*)

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Table 2 *(continued)*

Systems	$x_1x_2x_3 \times 10^4$	ε_{123}	$\Delta\varepsilon_{123}$	P_{123}	P_E	μ_{ab}
Pyridine +	1.0	2.444	−0.032	28.13	3.76	4.70
o-cresol +	3.27	2.674	0.012	30.91	7.33	4.75
Benzene	6.97	2.87	0.014	33.00	10.22	4.74
	11.65	3.048	0.008	34.87	12.81	4.75
	17.42	3.23	0.005	36.67	15.30	4.76
Pyridine +	3.39	2.521	−0.128	31.39	6.03	4.21
o-cresol +	11.89	2.91	−0.120	36.01	12.30	4.49
Carbon tetrachloride	24.0	3.141	−0.246	38.82	16.52	4.48
	39.2	3.54	−0.195	42.28	21.24	4.63
	51.95	3.742	−0.244	43.75	23.53	4.82

CONCLUSION

It may be concluded that both the binary and ternary systems of the aromatic molecules under investigation exhibited a charge transfer complex formation. It is interesting to note that introduction of pyridine in both binary and ternary systems reduces the preferential alignment of the interacting dipoles, thus weakening the complex formation.

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