

Dielectric Polarizations of Mixtures of Chlorobenzene with Cyclohexane, *o*-Xylene, *m*-Xylene, and *p*-Xylene

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DIELECTRIC polarizations of chlorobenzene with cyclohexane, *o*-xylene, *m*-xylene, and *p*-xylene have been measured at 303.15 K as a function of composition. Dielectric polarization results show that charge transfer type complexes are formed in these mixtures except in the mixture of chlorobenzene+cyclohexane.

Excess volume V^E of the above mentioned mixtures were reported earlier^{1,2}. In this paper, we report dielectric polarizations of the same mixtures at 303.15 K. Dielectric polarizations may provide information about complex formation in solution. The nature of the complex and stability constant of the complex in solution phase can also be ascertained from dielectric polarizations.

Experimental

Cyclohexane, *o*-, *m*-, and *p*-xylenes (all B. D. H. grade) and chlorobenzene (Reidel) were purified as described earlier^{3,4}. The purities of the samples were checked by measuring their densities; the results agreed to within 0.00002 g cm⁻³ with those in literature^{5,6}.

Dielectric constants of the pure components and their mixtures were determined from capacity measurements using Universal Impedance bridge (type 01-02a, Toshniwal make) at 303.15 K as a function of composition. The samples were placed in a cell containing a coaxial brass cylinder. The mouth of the cell can be closed with a glass stopper to eliminate errors due to evaporation. The cell was immersed in a water-filled thermostat controlled to within 0.01 K with the help of toluene regulator and an electronic relay. The measured dielectric constants were correct to within 0.001.

Results and Discussion

The dielectric constants of the pure components and mixtures are recorded in Table 1 at 303.15 K.

The molar polarizations of the mixtures were calculated using the relation⁷

$$P_{1,2} = (\epsilon_{\text{mix}} - 1)/(\epsilon_{\text{mix}} + 2) \cdot \frac{xM_1 + (1-x)M_2}{d} \quad \dots (1)$$

where $P_{1,2}$ is the molar polarization of the mixture, ϵ_{mix} is the dielectric constant of the mixture, d the density of the mixture, x and $(1-x)$ are the mole fractions of the components 1 and 2 with molecular weights M_1 and M_2 .

The molar polarization of the mixture $P_{1,2}$, calculated from equation (1) were used in calculating the apparent polarization (P_1 or P_2) of the component from the equation

$$P_{1,2} = xP_1 + (1-x)P_2 \quad \dots \quad (2)$$

by assuming the molar polarization of the other component equal to the value for the pure liquid. The values of apparent polarizations so determined are recorded in Table 1.

TABLE—1 DIELECTRIC CONSTANTS AND MOLAR POLARIZATIONS OF MIXTURES CONTAINING CHLOROBENZENE AT 303.15 K

x	ϵ	P_{12}/cc	P_1/cc	P_2/cc	$\left(\frac{\epsilon-1}{\epsilon+2}\right)^2$
Chlorobenzene + (1-x) <i>o</i> -xylene					
1	5.560	68.638	—	—	—
0.9063	5.386	67.866	70.427	1.621	0.3626
0.8118	5.182	65.855	71.124	2.818	0.3391
0.7125	4.802	64.508	73.136	3.604	0.3124
0.6209	4.505	63.203	75.461	4.236	0.2903
0.5184	4.276	60.926	77.461	4.574	0.2725
0.4177	3.912	58.368	79.614	4.585	0.2477
0.3144	3.684	54.983	80.840	3.835	0.2230
0.2165	3.400	51.489	81.751	2.839	0.1976
0.0968	2.906	47.298	86.221	1.702	0.1509
0	2.540	43.127	—	—	—
x chlorobenzene + (1-x) <i>m</i> -xylene					
1	5.560	68.638	—	—	—
0.9077	5.379	67.892	70.884	2.038	0.3522
0.8137	5.106	66.483	72.859	3.438	0.3328
0.7199	4.823	64.854	74.604	4.666	0.3139
0.6306	4.587	63.425	78.043	5.931	0.2965
0.5305	4.272	60.607	80.198	6.133	0.2721
0.4233	3.902	57.408	83.209	6.168	0.2418
0.3212	3.555	53.226	84.410	5.066	0.2155
0.2154	3.200	49.049	87.583	4.081	0.1790
0.1132	2.836	44.527	91.977	2.642	0.1447
0	2.355	38.470	—	—	—
x chlorobenzene + (1-x) <i>p</i> -xylene					
1	5.560	68.638	—	—	—
0.9076	5.400	68.337	71.233	2.354	0.3535
0.8105	5.183	67.065	74.176	3.488	0.3391
0.7152	4.802	64.608	75.740	5.079	0.3124
0.6167	4.398	61.850	77.507	5.469	0.2921
0.5198	4.000	58.841	79.339	5.562	0.2500
0.4934	3.889	57.856	79.626	5.422	0.2406
0.4228	3.586	54.940	79.905	4.764	0.2143
0.2942	3.186	50.503	83.729	4.440	0.1777
0.1875	2.804	45.503	86.853	2.853	0.1410
0.1036	2.412	42.483	92.927	2.516	0.1024
0	2.254	36.653	—	—	—
x chlorobenzene + (1-x) cyclohexane					
1	5.560	68.638	—	—	—
0.8966	5.106	65.605	70.003	—	—
0.7936	4.716	62.686	71.850	—	—
0.6898	4.235	58.368	72.624	—	—
0.6551	4.142	57.686	73.485	—	—
0.4951	3.603	51.897	76.827	—	—
0.3991	3.326	47.724	78.248	—	—
0.2937	3.000	42.669	79.264	—	—
0.1933	2.681	37.915	81.585	—	—
0.0924	2.402	32.770	83.409	—	—
0	2.007	27.451	—	—	—

Molar polarizations of chlorobenzene in *o*-xylene, *m*-xylene, and *p*-xylene increases at infinite dilutions, indicating the complexing nature of chlorobenzene

in these mixtures. Molar polarization of chlorobenzene in cyclohexane is linear even at great dilutions indicating the absence of complex formation between chlorobenzene and cyclohexane.

The complexes in mixtures, of chlorobenzene + *o*-, +*m*-, and +*p*-xylenes, may not be formed due to dipole association because excess polarizations, P^E , are positive in these mixtures.

P_{12} is a linear function of $(\epsilon - 1)^2/(\epsilon + 2)^2$ which shows that no chemical interaction occurs between the components of the solution. It is expected that only contact-pairs are present.

P^E is again a linear function of $x(1-x)$ for chlorobenzene + *o*-, +*m*-, and +*p*-xylenes which indicate the presence of contact-pairs⁹ in these mixtures. It is expected that contact-pairs may be formed between the vacant 3d orbitals of chloro group in chlorobenzene and π -electron cloud of benzene ring in xylenes.

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References

1. R. K. Nigam and P. P. Singh, *Trans. Faraday Soc.*, 1969, **65**, 950.
2. R. K. Nigam, N. N. Maini and M. S. Dhillon, *Indian J. Chem.*, 1973, **11**, 1233.
3. M. S. Dhillon, *J. Chem. Thermodynamics*, 1974, **6**, 1107.
4. M. S. Dhillon, *J. Chem. Thermodynamics*, 1974, **6**, 915.
5. J. Timmermans, "Physico-Chemical Constants of Pure Organic Liquids", Elsevier Pub. Co., New York, 1950.
6. R. C. Weast, "Handbook of Chemistry and Physics", The Chemical Rubber Pub. Co., Ohio, 1972.
7. S. Glasstone, "Textbook of Physical Chemistry", Macmillan and Co. Ltd., London, 1956.
8. D. P. Erap and S. Glasstone, *J. Chem. Soc.*, 1935, **1709**, 1720.
9. I. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839.

Temperature Dependent Paper Chromatography of Co(II), Ni(II), Fe(III), Zn(II) and Mn(II)

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TEMPERATURE dependent paper chromatographic separation has been carried out by many workers¹⁻⁶. The results indicate that the speed of resolution is improved by increasing temperature.

The purpose of this communication is to employ the known solvent systems viz, (i) acetone : HCl : water (87 : 8 : 5)⁷, (ii) acetone : HCl (97 : 3)⁸ and (iii) acetone : HCl : IBMK (85 : 5 : 10)⁹ to study the separation of different cations (a) Co(II), Ni(II) and Fe(III), (b) Co(II), Ni(II) and Zn(II) and (c) Co(II), Ni(II) and Mn(II) at different temperature.

Experimental

All the chemicals used were of AnalaR quality. The usual spraying reagents¹⁰ were used to locate the cations. The solvent mixtures used were (i) acetone : HCl : Water (87 : 8 : 5), (ii) acetone : HCl (97 : 3) and (iii) acetone : HCl : IBMK (85 : 5 : 10). Thermostatic bath with an automatic temperature control was employed to attain a desired temperature. Whatman No. 1 paper was used in glass jar for running the chromatogram.

5.0 μ l of the mixture of the cations viz., (a) Co(II), Ni(II) and Fe(III), (b) Co(II), Ni(II) and Zn(II), and (c) Co(II), Ni(II) and Mn(II) was enacted in the chromatographic separation.

Results and Discussion

The R_f dependence of various cations on temperature in solvent mixture acetone : HCl : water (87 : 8 : 5) resulted the Table-1, the perusal of which shows that in all cases R_f of Ni(II) remains almost constant from 0° to 35° and increases slightly from 35° to 40°. R_f of Fe(III), Zn(II) and Mn(II) show same

TABLE-1 TEMPERATURE DEPENDENCE OF R_f OF CATIONS, FOR SOLVENT MIXTURE ACETONE: HCl : WATER (87:8:5), TIME = 90 MIN.

System	Ions	R_f value at different temperatures(°C)						
		0	10	15	20	30	35	40
1	Ni(II)	0.08	0.08	0.08	0.08	0.08	0.08	0.15
	Co(II)	0.26	0.35	0.40	0.45	0.46	0.69	0.77
	Fe(III)	0.89	0.95	0.95	0.95	0.95	0.95	0.96
2	Ni(II)	0.09	0.09	0.09	0.09	0.09	0.09	0.19
	Co(II)	0.27	0.38	0.41	0.50	0.52	0.70	0.87
	Zn(II)	0.89	0.94	0.94	0.94	0.94	0.94	0.95
3	Ni(II)	0.08	0.08	0.08	0.08	0.08	0.15	0.21
	Co(II)	0.35	0.37	0.46	0.58	0.61	0.83	0.87
	Mn(II)	0.82	0.95	0.95	0.95	0.95	0.95	0.25

behaviour with slight increase in R_f from 0° to 10° and running with solvent front above 10°. This tendency of these three ions to move along with the solvent front depends upon the quality of paper, the nature of the solvent and the temperature at which the experiment is conducted. R_f of Co(II) increases from 0.2 at 0° to about 0.8 at 40° which means that Co(II) has a tendency to reach solvent front as the temperature rises. Thus, separation in all the three cases is improved by increase in temperature. However, after 35°, Co(II) reaches Fe(III), or Zn(II) or Mn(II) as the case may be, thereby after 40° the separation of these ions may become impossible as suggested by earlier workers^{1,11}.

A change in temperature influences the rate of movement of the mobile phase as investigated by Muller and Clogg¹². The rate of movement of given cation and hence its R_f value depends upon its