Dielectric and excess dielectric constants of binary liquid mixtures at 303K

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ABSTRACT

The nonideal behaviors of liquid mixtures are characterized by excess thermodynamic properties such as excess volumes, enthalpy of mixing, compressibilities etc. The excess dielectric constant ε^E is also one such parameter that indicates the strength and nature of intermolecular interactions in binary liquid mixtures. The positive deviations from ideal behaviour (ε^E being positive) are qualitatively attributed to a "build in" of components of the mixture in the structure of respective solvent. The negative deviations from ideal behaviour (ε^E being negative) is explained qualitatively either due to interstitial solvation or due to breaking of aggregates. In the present study, the excess dielectric constants for the binary liquid mixtures (1) benzene + nitrobenzene (2) chlorobenzene + nitrobenzene and (3) cyclohexanone + nitrobenzene are measured at 303K and at different concentrations. The dielectric constants for these binary liquid mixtures are measured using a microcontroller based system. The necessary software is developed in C language.
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INTRODUCTION

Dielectric studies have a long and distinguished history, the dielectric data is used to determine the electric dipole moments, which is not only significant as a reflection of electronic structure of the molecule, but is also of prime importance in understanding of molecular interactions and it at least partly controls the transitions between the solid, liquid and gaseous states.

The excess dielectric constant ε^E is defined as

$$\varepsilon^E = \varepsilon_{observed} - \varepsilon_{ideal}$$
$$\varepsilon^E = \varepsilon_{12} - (\varepsilon_1 X_1 + \varepsilon_2 X_2) \qquad (1)$$

Where ε_{12} is dielectric constant of the binary liquid mixture. ε_1 and ε_2 are the dielectric constants of solvent and solute respectively. X_1 and X_2 are mole fractions of solvent and solute respectively. The positive deviations from ideal behaviour (ε^E being positive) are qualitatively attributed to a " build in " of components of the mixture

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TABLE 1 : Dielectric constants of the binary liquid mixtures at 303K

Mole fraction (X_1)	Dielectric constant (ε)		
	benzene + nitrobenzene	chlorobenzene +nitrobenzene	cyclohexanone +nitrobenzene
0.0	34.89	05.96	17.96
0.2	26.13	10.56	21.04
0.4	16.92	15.76	24.08
0.6	12.32	22.18	27.63
0.8	07.26	28.51	31.27
1.0	02.26	34.89	34.89

TABLE 2: Excess dielectric constants of the binary liquid mixtures at 303K

Mole fraction (X_1)	Excess dielectric constant (ε^E)		
	nitrobenzene + chlorobenzene	nitrobenzene + cyclohexanone	benzene + nitrobenzene
0.0	0.000	0.000	0.000
0.2	-1.186	-0.306	-2.236
0.4	-1.772	-0.652	-4.919
0.6	-1.138	-0.488	-2.994
0.8	-0.594	-0.228	-1.524
1.0	0.000	0.000	0.000
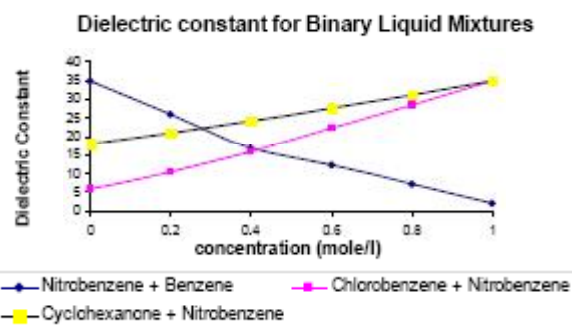
Figure 1: Dielectric constant for three binary liquid mixtures versus concentration at 303K
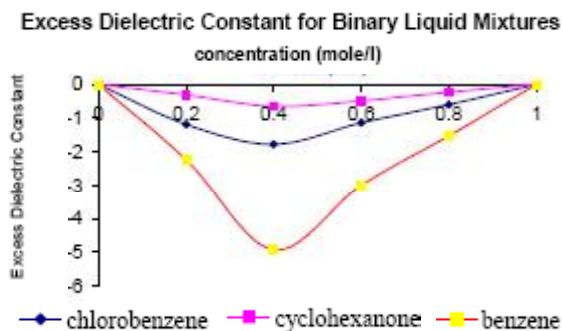
Figure 2: Excess dielectric constant for three binary liquid mixtures versus concentration at 303K

in the structure of respective solvent. The negative deviations from ideal behaviour (ε^E being negative) is explained qualitatively either due to interstitial solvation or due to breaking of aggregates[1]. The excess dielectric

constant ε^E is one of the parameters that indicate the strength and nature of intermolecular interactions in binary liquid mixtures and the nature of solute-solvent interactions.

EXPERIMENTAL

In the present paper analytical reagent grade samples were used after necessary purification and distillation mostly as per procedure cited by Weissberger[2]. The chemicals used were benzene, chlorobenzene, cyclohexanone and nitrobenzene. Benzene was allowed to stand on anhydrous calcium chloride for two days and then filtered. Then the liquid was refluxed with phosphorus pentoxide for six hours and distilled. Spectroscopically pure sodium was drawn in wires in the distillate and redistilled. The liquid was collected at its boiling point 80C. The densities and the dielectric constants of the pure liquids at 303K agreed within ±0.002 and ±0.2 with the corresponding literature values. "A microcontroller based dielectric constant system"[3] (for the measurement of dielectric constant in liquids) is used in the present paper.

RESULTS AND DISCUSSION

The system is used to measure the dielectric constant of binary liquid mixtures (1) benzene+nitrobenzene (2) chlorobenzene+nitrobenzene (3) cyclohexanone + nitrobenzene at 303K and at different concentrations (mole/l). The measurements are made following the procedure mentioned above. The results of measurements for these systems are presented in TABLE 1. And also the results are presented graphically as shown in figure 1. It is observed that at a given temperature the dielectric constant varies as a function of concentration for all the three binary liquid mixtures.

The excess dielectric constants for the above binary liquid mixtures were evaluated using the equation (1). The results of the ε^E measurements are presented in TABLE 2. The variation of ε^E as a function of concentration is graphically represented in figure 2. Observation of variation of ε^E with X_1 in all three binary mixtures indicates that they are negative and large in magnitude. The negative and large values of ε^E may be attributed to the dense solution structure[4]. The excess

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dielectric constant varies as a function of concentration and reaches an optimum ratio in the concentration range $X_1 = 0.3$ to 0.45 indicates the extent of intermolecular interactions in binary liquid mixtures.

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