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Dielectric and excess dielectric constants of acetonitrile + hexane, + heptane and + cyclohexane AT 303, 313 and 323 K

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ABSTRACT

The dielectric constants and excess dielectric constants of the binary systems: acetonitrile+hexane, +heptane and +cyclohexane have been studied at 303, 313, and 323K temperatures and over the complete mole fraction range. The dielectric constants for these mixtures are measured using a microcontroller based system. The results are negative over entire range of composition. Symmetrical curves are almost observed for all the systems in which the maximum approximately occurs at 0.5mole fraction of acetonitrile. The results are discussed in terms of intermolecular interactions.

KEYWORDS

Dielectric constants;
Excess dielectric constants;
Microcontroller based system.

INTRODUCTION

Dielectric studies have a long and distinguished history. The dielectric data is used to determine the electric dipole moments which reflects the electronic structure of the molecule and helps in understanding the intermolecular interactions. The mixtures containing acetonitrile have been studied rarely. Acetonitrile is a dipolar aprotic solvent and it does not form hydrogen bonds[1], but its large dipole moment may lead to large electrostatic force. The common component acetonitrile, being polar has ability to form complexes. Acetonitrile contains molecules with strong parallel and antiparallel orientation and this strongly ordered structure is stabilized by dipole-dipole interactions[2].

The excess dielectric constant ε^E is defined as

$$\varepsilon^E = \varepsilon_{observed} - \varepsilon_{ideal}$$

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

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 the 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 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[3]. 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.

TABLE 1 : Dielectric constant of acetonitrile + hexane mixture at 303, 313 and 323K

Concentration (mole/l)	Dielectric constant at 303K	Dielectric constant at 313K	Dielectric constant at 323K
0	1.9	1.9	1.9
0.1	2.05	1.92	1.76
0.2	2.86	2.12	2.59
0.3	4.94	4.81	4.51
0.4	7.90	7.13	6.62
0.5	10.84	10.75	10.53
0.6	14.77	14.29	13.37
0.7	19.24	18.82	18.38
0.8	22.71	22.50	22.47
0.9	29.85	29.12	28.86
1.0	35.09	34.94	34.79

TABLE 3 : Dielectric constant of acetonitrile + cyclohexane mixture at 303, 313 and 323K

Concentration (mole/l)	Dielectric constant at 303K	Dielectric constant at 313K	Dielectric constant at 323K
0	2.09	2.29	2.29
0.1	3.68	3.45	3.15
0.2	3.96	3.54	3.24
0.3	5.24	4.92	4.62
0.4	7.98	7.52	7.21
0.5	10.19	9.98	9.62
0.6	14.08	13.89	13.34
0.7	18.00	17.75	17.25
0.8	22.64	22.04	21.85
0.9	28.42	28.01	27.78
1.0	35.09	34.94	34.79

The dielectric constants and excess dielectric constants for the systems: acetonitrile+hexane, +heptane and +cyclohexane at 303, 313 and 323K have been measured using the microcontroller-based system[4] for the measurement of dielectric constant.

EXPERIMENTAL

A microcontroller-based system whose details were published elsewhere[4] is used in the present study for the measurement of dielectric constant in liquids and liquid mixtures. In the present paper acetonitrile was purified as described by Putnam et al.[5] . All the analytical reagent grade samples were used after necessary purification and distillation mostly as per procedure cited by Weissberger[6]. The chemicals used were cyclohexane, heptane and hexane. Refluxing with calcium oxide and distilling from it dried all the chemicals. Comparing measured densities within ±0.002 and ±0.2 with the corresponding literature values[7] checked the purities of the liquids.

TABLE 2 : Dielectric constant of acetonitrile + heptane mixture at 303, 313 and 323K

Concentration (mole/l)	Dielectric constant at 303K	Dielectric constant at 313K	Dielectric constant at 323K
0	1.9	1.9	1.9
0.1	2.15	1.95	1.76
0.2	2.89	2.59	2.39
0.3	5.05	4.76	4.12
0.4	8.09	7.95	7.52
0.5	11.24	10.86	10.16
0.6	14.76	14.46	14.02
0.7	18.89	18.19	17.85
0.8	24.64	24.12	23.75
0.9	29.54	29.01	28.74
1.0	35.09	34.94	34.79

TABLE 4 : Excess dielectric constant of acetonitrile + hexane mixture at 303, 313 and 323K

Concentration (mole/l)	Excess dielectric constant at 303K	Excess dielectric constant at 313K	Excess dielectric constant at 323K
0	0.0	0.0	0.0
0.1	-3.17	-3.30	-3.46
0.2	-5.68	-6.42	-5.95
0.3	-6.92	-7.05	-7.35
0.4	-7.28	-8.05	-8.56
0.5	-7.65	-7.74	-7.96
0.6	-6.04	-7.52	-7.81
0.7	-5.89	-6.31	-6.75
0.8	-5.74	-5.26	-5.98
0.9	-1.92	-2.65	-2.91
1.0	0.0	0.0	0.0

RESULTS AND DISCUSSION

The dielectric constants of binary liquid mixtures: acetonitrile +hexane, +heptane and +cyclohexane are measured at 303, 313 and 323K and over the complete mole fraction range. The results of mea-

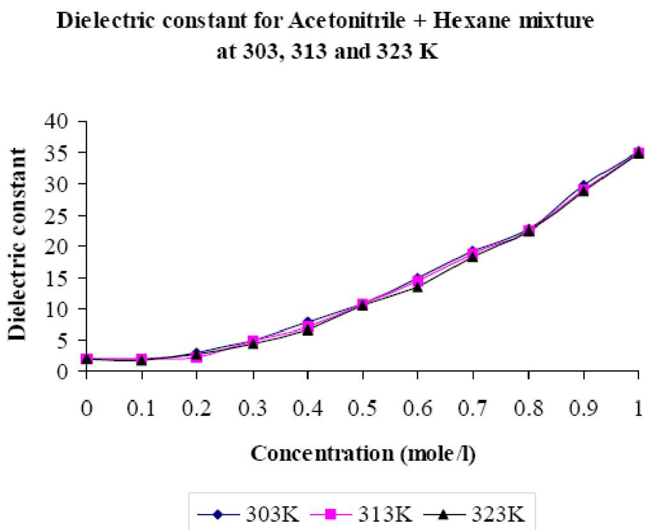

Figure 1 : Dielectric constant for acetonitrile + hexane mixture versus concentration at 303, 313 and 323K

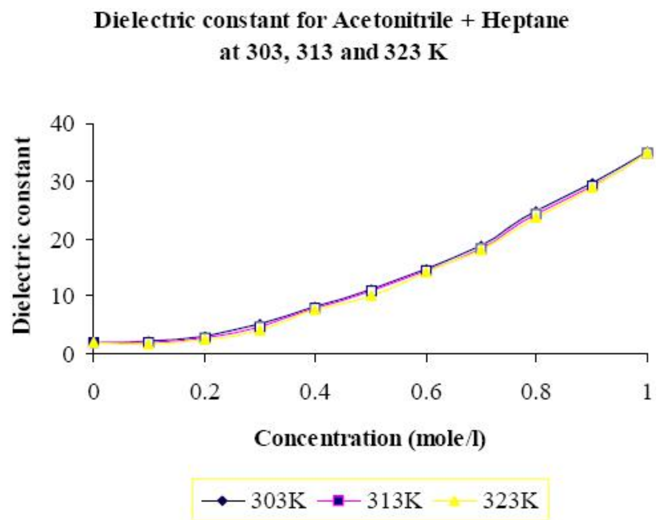

Figure 2 : Dielectric constant for acetonitrile + heptane mixture versus concentration at 303, 313 and 323K

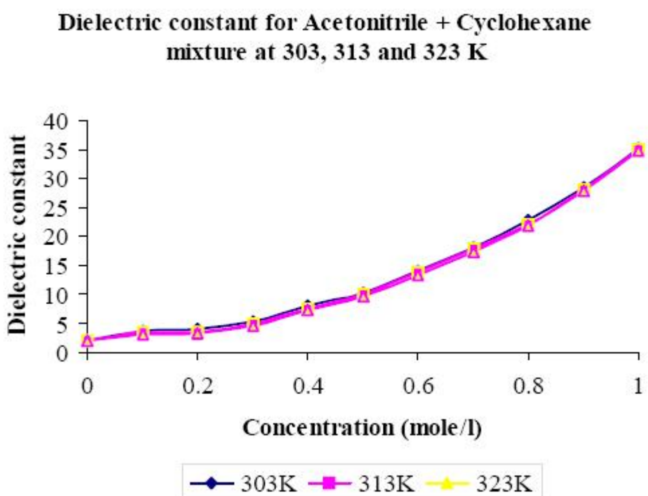

Figure 3 : Dielectric constant for acetonitrile + cyclohexane mixture versus concentration at 303, 313 and 323K

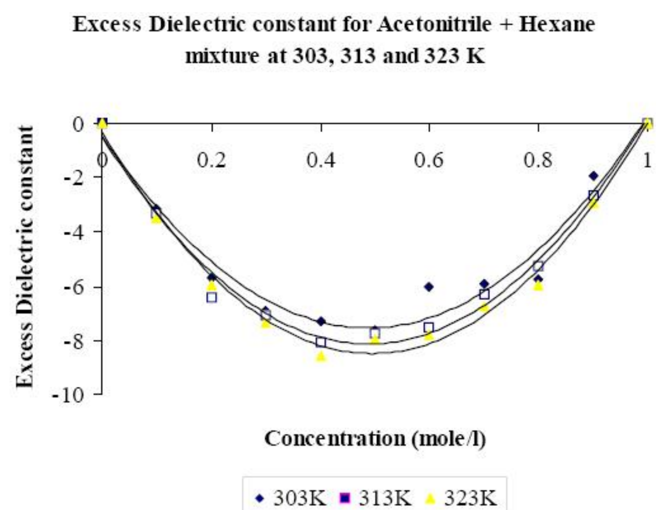

Figure 4 : Excess dielectric constant for acetonitrile + hexane mixture versus concentration at 303, 313 and 323K

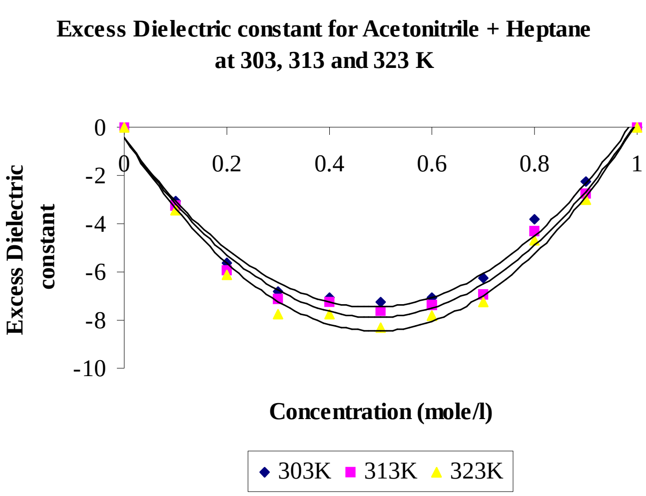

Figure 5 : Excess dielectric constant for acetonitrile + heptane mixture versus concentration at 303, 313 and 323K

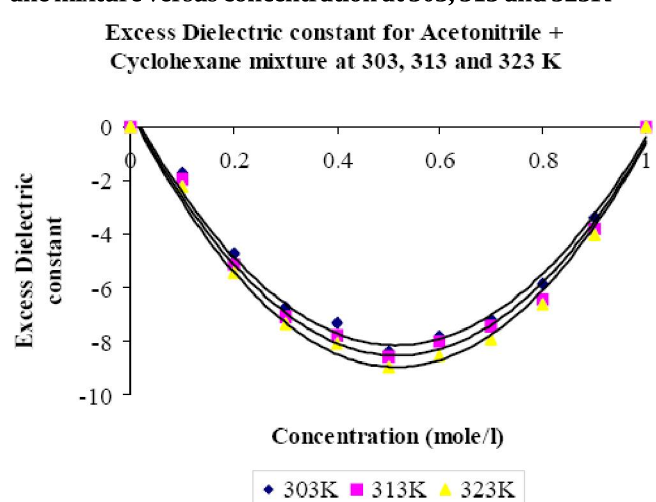

Figure 6 : Excess dielectric constant for acetonitrile + cyclohexane mixture versus concentration at 303, 313 and 323K

TABLE 5: Excess dielectric constant of acetonitrile + heptane mixture at 303, 313 and 323K

Concentration (mole/l)	Excess dielectric constant at 303K	Excess dielectric constant at 313K	Excess dielectric constant at 323K
0	0.0	0.0	0.0
0.1	-3.07	-3.27	-3.46
0.2	-5.65	-5.95	-6.15
0.3	-6.81	-7.10	-7.74
0.4	-7.09	-7.23	-7.76
0.5	-7.25	-7.65	-8.33
0.6	-7.05	-7.35	-7.79
0.7	-6.24	-6.94	-7.28
0.8	-3.81	-4.33	-4.70
0.9	-2.23	-2.76	-3.03
1.0	0.0	0.0	0.0

TABLE 6: Excess dielectric constant of acetonitrile + cyclohexane mixture at 303, 313 and 323K

Concentration (mole/l)	Excess dielectric constant at 303K	Excess dielectric constant at 313K	Excess dielectric constant at 323K
0	0.0	0.0	0.0
0.1	-1.71	-1.94	-2.24
0.2	-4.73	-5.15	-5.45
0.3	-6.75	-7.07	-7.37
0.4	-7.31	-7.77	-8.08
0.5	-8.39	-8.60	-8.96
0.6	-7.81	-8.00	-8.55
0.7	-7.19	-7.44	-7.94
0.8	-5.85	-6.45	-6.44
0.9	-3.37	-3.78	-4.01
1.0	0.0	0.0	0.0

surements for these systems are presented in TABLES 1, 2 & 3 respectively. And also the results are presented graphically as shown in Figures 1, 2 & 3 respectively. 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 TABLES 4, 5 & 6 respectively. The variation of ε^E as a function of concentration is graphically represented in Figures 4, 5 & 6 respectively. Observation of variation of ε^E with acetonitrile 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[8]. The excess dielectric constant varies as a function of concentration and reaches an optimum ratio at X_1=0.5 indicates the extent of intermolecular interactions in binary liquid mixtures.

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