Hindawi Publishing Corporation
Journal of Chemistry
Volume 2013, Article ID 687106, 4 pages
http://dx.doi.org/10.1155/2013/687106

Research Article

Dielectric and Excess Dielectric Constants of Acetonitrile + Butyl Amine, + Ethylamine, and + Methylamine at 303, 313, and 323 K

Ch. V. V. Ramana,[1] A. B. V. Kiran Kumar,[2] M. Ashok Kumar,[3] and M. K. Moodley[1]

[1] *Department of Physics, School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa*
[2] *Department of Chemistry, Kongju National University, 182 Singwandong, Gongju, Chungnam 314-701, Republic of Korea*
[3] *Department of Instrumentation, Sri Krishnadevaraya University, Andhra Pradesh, Anantapur 515055, India*

Correspondence should be addressed to Ch. V. V. Ramana; ramana6@gmail.com

Received 22 June 2012; Revised 12 July 2012; Accepted 12 July 2012

Academic Editor: Pedro M. Mancini

The dielectric constants and excess dielectric constants of the binary systems: acetonitrile + butyl amine, + ethylamine and + methylamine have been studied at 303, 313, and 323 K temperatures and over the complete mole fraction range. The dielectric constants for these mixtures were measured using a microcontroller based system. The results are positive over the entire range of composition. Symmetrical curves were observed for the systems in which the maximum occurs approximately at 0.7-mole fraction of acetonitrile. The results are discussed in terms of intermolecular interactions. The investigation of dielectric constant of mixed solvents bearing amines aims at better comprehension of their biological, chemical, pharmaceutical, technological, and laboratory applications.

1. Introduction

The dielectric constant is an important property of mixed solvents and plays an important role in the characterization of materials electrical properties. When a binary mixture is formed, the expected properties thermodynamic parameters, such as volume, dielectric parameters, and refractive index, do not vary linearly [1]. The concept of an excess thermodynamic property surged in the field of chemical thermodynamics, and therefore physicists and electrical engineers seldom use it. Thus we find of interest to look for the place that the excess dielectric permittivity can occupy in the domain of binary dielectrics. Knowledge of frequency-dependent dielectric properties of binary liquid mixtures is important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical applications. At a fundamental level, the frequency-dependent dielectric behavior of liquid mixtures provides information on molecular interactions and mechanism of molecular process. In pharmaceutical and analytical sciences, the dielectric constant of mixed solvents is required to predict the solubility and chemical stability of the drug [2]. This work is a continuation of our previous studies [3–5] of dielectric and excess dielectric properties of various binary liquid systems, which are of special interest in chemical and electrochemical processes. Acetonitrile is a non-hydrogen-bonded system with large value dipole moment. Its dielectric constant is high (35.09) and allows precise conductometry and potentiometry measurement, yet it is more inert then hydroxylic solvents in that it solvates the majority of the cations and particularly anions much more weakly [6]. Amines have higher boiling points than nonpolar compounds of the same molecular weight but lower boiling points than alcohols. Amines interact more strongly with a component containing electron withdrawing groups than with other molecules. Amines are amongst the most important reagents in organic synthesis and represent an important class of bio-organic solvents. The investigation of dielectric constant of mixed solvents bearing amines aims at better comprehension of their biological, chemical, pharmaceutical, technological, and laboratory applications [7].

The excess dielectric constant ε^E is defined as

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

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 mole fraction represented by mole/L. 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) are explained qualitatively either due to interstitial salvation or due to breaking of aggregates [3–5]. In view of the current interest on dielectric and excess dielectric constant values of the mixed solvents, we report new experimental data for binary systems acetonitrile + butyl amine, + ethylamine, and + methylamine at 303, 313, and 323 K temperatures (keeping the solution in temperature bath at constant temperature and measured the dielectric constant of the solution) over the complete mole fraction range have been carried out. The aim of the study to provides information regarding solute-solvent interaction.

2. Experimental

2.1. Materials. Butyl amine is soluble in all organic solvents. It is used as an ingredient in the manufacture of pesticides (such as thiocarbazides), pharmaceuticals, and emulsifiers. It is also a precursor for the manufacture of N,N′-dibutylthiourea, a rubber vulcanization accelerator, and n-butylbenzene sulfonamide, a plasticizer of nylon. Ethylamine is miscible with virtually all solvents and is considered to be a weak base, as is typical for amines. Ethylamine is widely used in the chemical industry and organic synthesis. Ethylamine is a precursor to many herbicides including atrazine and simazine. Methylamine is the simplest amine. Industrially methylamine is sold in its anhydrous form in pressurized railcars and tank trailers. It has a strong odour similar to fish. Methylamine is used as a building block for the synthesis of many other commercially available compounds. Hundreds of millions of kilograms are produced annually, liquid methylamine can be used as a solvent analogous to liquid ammonia. It shares some of the properties of liquid ammonia, but is better for dissolving organic substances, in the same way that methanol is better than water.

In the present paper analytical-reagent-grade samples were used after necessary purification and distillation mostly as per procedure cited by Weissberger [8]. The chemicals used were acetonitrile, butyl amine, ethylamine, and methylamine. Acetonitrile was purified as described by Putnam et al. [9]. Acetonitrile was purified by treatment with anhydrous potassium carbonate followed by several distillations over phosphorous pentoxide. The acetonitrile so obtained was distilled at atmospheric pressure through a glass helix packed column approximately 90 cm in length. The central cut was redistilled and stored over anhydrous calcium sulphate.

2.2. Measurement. The dielectric constants and excess dielectric constants for the systems acetonitrile + butyl amine, + ethylamine, and + methylamine at 303, 313, and 323 K have been measured using the microcontroller based system [10] for the measurement of dielectric constant. It is based on the principle that the change in frequency of an XR-2206 function generator, when the liquid forms the dielectric medium of the dielectric cell, is measured with a microcontroller. The instrument system covers a wide range of dielectric constants for various liquids at various concentrations and at different temperatures. The system is quite successful in the measurement of dielectric constant in liquids with an accuracy of ±0.2%.

3. Results and Discussion

In recent years there has been considerable advancement in the theoretical and experimental investigation of the dielectric properties of binary liquid mixtures. Liquid mixtures exhibit various phenomena, which cannot be found in pure substances. The most interesting of these are perhaps the new types of phase equilibrium, which arise from the extra degrees of freedom introduced by the possibility of varying the proportions of the components. A limited number of studies have been reported for mixtures.

The dielectric constants of binary liquid mixtures: acetonitrile + butyl amine, + ethylamine and + methylamine are measured at 303, 313, and 323 K and over the complete mole fraction range. The results of measurements for these systems are presented in Tables 1, 2, and 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. Chandrasekhar [11] has reported as that the temperature increases, the dielectric constant decreases. Our results support this viewpoint. In amines lone pair is there, lone pair electrons may interact with carbon in CN group and electron density around nitrogen will decrease. We are expecting interactions between CN and NH_2 groups only not formation of hydrogen bond, because acetonitrile is an aprotic solvent. Based on that dielectric constant will change.

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 excess dielectric constant data provide the following information in relation to the molecular conformation [2–5]:

(i) $\varepsilon^E = 0$ indicates that mixture constituents do not interact and thus have ideal mixing behaviour;

(ii) $\varepsilon^E < 0$ indicates that mixture constituents interact so as to reduce the total number of effective dipoles that contributed to the mixture dielectric polarization;

(iii) $\varepsilon^E > 0$ indicates that the constituents of a mixture interact in such a way that there is an increase in number of effective dipoles contributed in the mixture dielectric polarization;

(iv) the magnitude of ε^E values is the evidence of the strength of unlike molecules H-bond interactions;

Table 1: Dielectric constants for acetonitrile + butyl amine mixture at 303, 313 and, 323 K.

S. No	Concentration (mole fraction)	Dielectric constant at 303 K	Dielectric constant at 313 K	Dielectric constant at 323 K
1	0.0	5.4	5.39	5.29
2	0.1	8.79	8.67	8.54
3	0.2	11.82	11.69	11.57
4	0.3	14.84	14.74	14.62
5	0.4	18.13	18.08	17.85
6	0.5	21.56	21.42	21.26
7	0.6	25.25	25.06	24.75
8	0.7	28.76	28.47	28.26
9	0.8	30.24	30.13	29.87
10	0.9	32.85	32.73	32.61
11	1.0	35.09	34.94	34.79

Table 2: Dielectric constants for acetonitrile + ethylamine mixture at 303, 313 and, 323 K.

S. No	Concentration (mole fraction)	Dielectric constant at 303 K	Dielectric constant at 313 K	Dielectric constant at 323 K
1	0.0	6.30	6.28	6.19
2	0.1	10.06	9.90	9.76
3	0.2	13.08	12.97	12.79
4	0.3	16.17	15.95	15.75
5	0.4	19.53	19.16	18.84
6	0.5	22.75	22.59	22.13
7	0.6	26.19	25.95	25.58
8	0.7	29.54	29.29	28.88
9	0.8	31.35	31.12	30.80
10	0.9	33.62	33.48	33.18
11	1.0	35.09	34.94	34.79

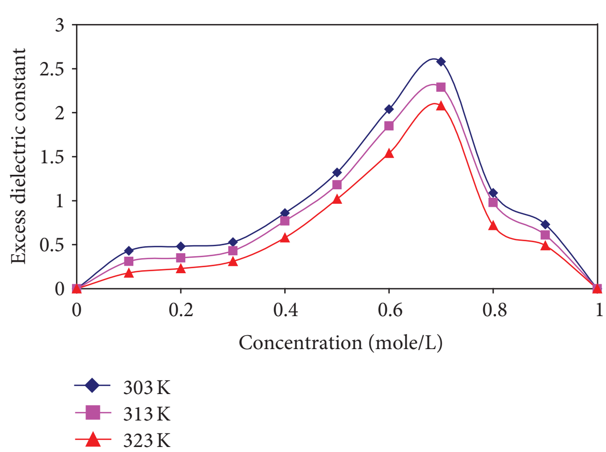

Figure 1: Excess Dielectric constant for acetonitrile + butyl amine mixture versus concentration at 303, 313, and 323 K.

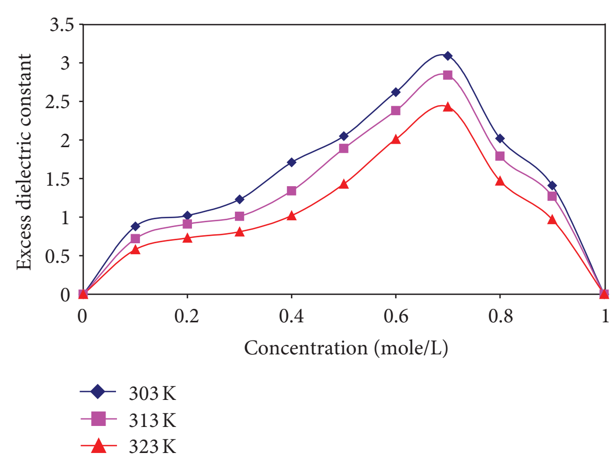

Figure 2: Excess dielectric constant for acetonitrile + ethylamine mixture versus concentration at 303, 313, and 323 K.

that is, higher ε^E values represent the stronger H-bond unlike molecular connectivities between unlike molecules and *vice versa*;

(v) the molar concentration corresponding to pronounced maximum of ε^E values represents the stoichiometric ratio of a stable adduct in the mixture.

The excess dielectric constants for the above binary liquid mixtures were evaluated using (1). The variation of ε^E as a function of concentration is graphically represented in Figures 1, 2, and 3, respectively. Observation of variation of ε^E with acetonitrile in all three binary mixtures indicates that they are positive and less in magnitude. 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. $\varepsilon^E > 0$ indicates that the two solvents interact in such a way that the effective dipole moment increases. There is formation of multimers and

TABLE 3: Dielectric constants for acetonitrile + methylamine mixture at 303, 313 and, 323 K.

S. No	Concentration (mole fraction)	Dielectric constant at 303 K	Dielectric constant at 313 K	Dielectric constant at 323 K
1	0.0	9.40	9.39	9.29
2	0.1	12.95	12.66	12.42
3	0.2	16.00	15.56	15.33
4	0.3	18.92	18.54	18.09
5	0.4	22.03	21.74	21.16
6	0.5	25.11	24.62	24.13
7	0.6	28.12	27.83	26.70
8	0.7	31.27	30.66	30.42
9	0.8	32.73	32.32	31.93
10	0.9	34.41	33.86	33.54
11	1.0	35.09	34.94	34.79

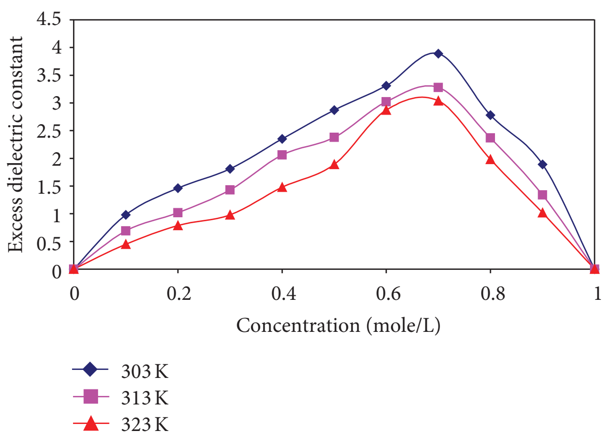

FIGURE 3: Excess dielectric constant for acetonitrile + methyl aminemixture versus concentration at 303, 313, and 323 K.

dimers. A *dimer* is a chemical or biological entity consisting of two structurally similar subunits called monomers, which are joined by bonds, which can be strong or weak. Generally a multimer implies a few monomers attached together. But polymer will be formed with many number of monomers. The excess dielectric constant which varies as a function of concentration and reaches an optimum ration at 0.7 indicates the liquid mixtures in such a way that the total effective dipole moment increases (property of a molecule where the presence of polar bonds generates a centre of positive charge and a centre of negative charge that do not coincide; such molecules have regions that are always positively or negatively charged). There is a tendency of dipole aligned in parallel direction. The nonzero ε^E values over the entire concentration range of these mixtures (Figures 1–3) suggest that electron transport will be made easily from one molecule to other, because electron flow in medium will increase as well as the interactions in between CN and NH_2. We expect that excess dielectric properties depends on electron transport.

4. Conclusion

The positive deviations from ideal behaviour indicate that mixtures can be attributed to an interstitial accommodation of acetonitrile. In view of positive deviation it occurs as a simple "pure dilution" process, as expected for ideal solvents mixtures. The paper presents the precise dielectric constant values of the binary liquid mixtures, which are widely used in biological, chemical, and industrial applications.

References

[1] J. S. Rowlinson, *Liquids and Liquid Mixtures*, Butterworth Science, London, UK, 2nd edition, 1956.

[2] R. J. Sengwa, S. Sankhla, and V. Khatri, "Dielectric constant and molecular association in binary mixtures of N,N-dimethylethanolamine with alcohols and amides," *Fluid Phase Equilibria*, vol. 285, no. 1-2, pp. 50–53, 2009.

[3] Ch. V. V. Ramana and K. Malakondaiah, "Dielectric and excess dielectric constants of binary liquid mixtures: chlorobenzene + nitrobenzene, cyclohexanone + nitrobenzene and benzene + nitrobenzene at 303 K," *Journal of the Indian Chemical Society*, vol. 86, no. 9, pp. 979–981, 2009.

[4] Ch. V. V. Ramana, T. Chandrasekhar, A. B. V. Kiran Kumar, and K. Malakondaiah, "Dielectric and Excess dielectric constants of binary liquid mixtures at 303 K," *Physical Chemistry*, vol. 3, no. 1, 2008.

[5] Ch. V. V. Ramana, G. Ramachandra Reddy, and M. Mohan Reddy, "Dielectric and Excess dielectric constants of acetonitrile + hexane, + heptane and + cyclohexane at 303, 313 and 323 K," *Physical Chemistry*, vol. 4, no. 2, 2009.

[6] F. Franks, *Water: A Comprehensive Treatise*, F. Franks, Ed., vol. 2, Plenum Press, New York, NY, USA, 1976.

[7] R. J. Sengwa, V. Khatri, and S. Sankhla, "Dielectric properties and hydrogen bonding interaction behaviour in binary mixtures of glycerol with amides and amines," *Fluid Phase Equilibria*, vol. 266, no. 1-2, pp. 54–58, 2008.

[8] A. Weissberger, *Technique of Organic Chemistry*, vol. 3, Interscience, New York, NY, USA, 1967.

[9] W. E. Putnam, D. M. Mceachern, and J. E. Kilpatrick, "Entropy and related thermodynamic properties of acetonitrile (Methyl cyanide)," *The Journal of Chemical Physics*, vol. 42, no. 2, pp. 749–755, 1965.

[10] Ch. V. V. Ramana and K. Malakondaiah, "Microcontroller based system for the measurement of dielectric constant in liquids," *Instrumentation Science and Technology*, vol. 35, no. 6, pp. 599–608, 2007.

[11] A. C. H. Chandrasekhar, *[Ph.D. thesis]*, S.V. University, Tirupati, India, 1988.