Study of Dielectric behaviour of Binary Liquid by Frequency Domain Technique

***S. M. ANPAT[1], P. W. KHIRADE[2], S. B. SAYYAD[3]**

[1]VP`s Arts, Science & Commerce College Baramati, Maharashtra, India
[2]Department of Physics, Dr. BAMU Aurangabad, (MH), India
[3]Milliya Arts, Science & Management Science College, Beed, Maharashtra, India
***Corresponding Author Email:** sandipanpat2@gmail.com
doi:10.30731/ijcps.7.2.2018.27-35

Abstract

Static dielectric constants and excess properties of sampled binary liquid has been studied at 298k temperature. The frequency domain dielectric sensor technique were used for determination of dielectric constant of binary mixture. The excess dielectric properties such as Kirkwood correlation and Bruggeman factor for binary liquid mixture also determined, which is significant in the study of the intermolecular interaction and hydrogen bonding in the mixture. The binary mixture of Benzene + Ethanol, Benzene + Methanol and Benzene + 1-Propannol has been studied over different concentration. The applicability of the proposed method is verified in experimental studies.

Keywords: Dielectric constant, Excess dielectric constant, Kirkwood correlation factor**,** binary liquid, Bruggeman factor.

Introduction

The study of the dielectric behavior of liquid is very significant in understanding the structure and molecular interactions in the liquid. The dielectric constant specifies the solvent's ability to decrease the field strength of the electric field surrounding the charged particle impressed with it. This decrease is then compared with the field strength of the charged particle in vacuum [1-2]. Macroscopic parameters such as dielectric constant have been extensively used for explanation of solvent effects. The dielectric constant is one of the fundamental properties that must be known to utilize theories of electrolyte solutions [2-3]. The dielectric constant is an important physicochemical parameter, as it is related to many important physical and biological applications [3-4]. The dielectric constant of a solvent is a relative measure of its polarity and its measurements are often used for evaluation of the characteristics of the liquid solutions. In this work, the new technique is used for detection of dielectric constant of binary liquid using a Microcontroller-based sensor system [5-6]. A change in the oscillator frequency of the sensor system resulting from a change in its effective dielectric constant is considered as the index for defining the dielectric constant of the sample liquid. Using this designed sensor system dielectric constant of some binary liquid mixture has been successfully determined over a different concentration.

Experimental Section

Experimental Setup

The experimental setup consists of specially fabricated liquid holder, cell, with Microcontroller-based dielectric constant sensing system. The specially designed dielectric cell, whose capacitance varies with air, reference liquid and the sample liquid, bring into play as a dielectric medium.

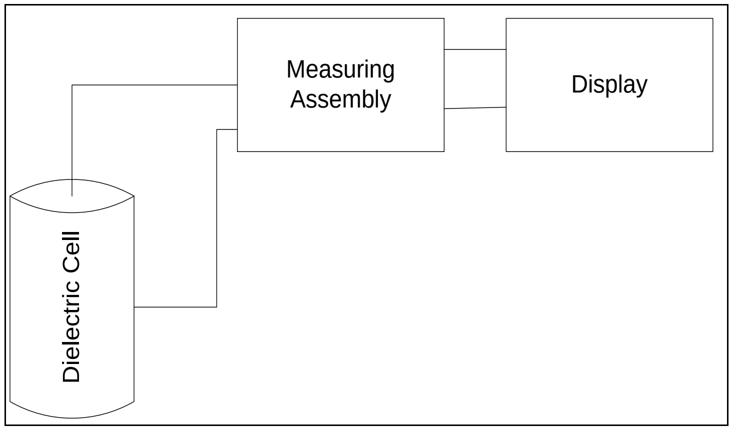

Fig. 1: A simplified block diagram of Microcontroller-based Dielectric Constant Sensing System.

Materials

The spectroscopic grade chemicals with 99.9% purity were used in the present examination. The solutions were prepared by mixing Ethanol, Methanol and 1-Propanol with Benzene at eleven different volume percentage of Benzene as 0 to 100% in steps of 10% at 298 k temperature.

Measurement of dielectric constant

The static dielectric constants of the Benzene-Ethanol, Benzene-Methanol, and Benzene-1-Propanol binary systems were measured using a microcontroller based dielectric spectroscopy liquid sensor [6]. The liquid holder cylindrical cell is used to insert liquid mixture. The capacitance without liquid and with the insertion of a liquid is measured and used further for determination of dielectric constant of binary mixture. The dielectric constant ε is the ratio of the electrical capacitance of a cell when the liquid forms the dielectric medium (C_s) to the capacitance of the cell when air forms the dielectric medium (C_0) at a given temperature.

$$\varepsilon = (C_s) / (C_0) \tag{1}$$

Study of excess permittivity

The information related to interaction of liquid 1 and 2 may be obtained by excess properties like excess permittivity and excess relaxation time in the mixture [4]. In the present study the excess dielectric properties are determined corresponding to static permittivity.

The excess permittivity ε_S^E is defined as

$$\varepsilon_S^E = (\varepsilon_S)_m - [(\varepsilon_S)_1 x_1 + (\varepsilon_S)_2 x_2] \tag{2}$$

Where X is the mole fraction and m, 1, and 2 represent a mixture of liquid 1 and liquid 2. The excess static dielectric constant may provide qualitative information about the formation of structure in the binary liquid mixture as follows:

i) indicates the liquid A and liquid B do not interact and do not change thebehaviordual structural behaviour in the presence of other liquid.
ii) indicates the liquid A and liquid B interact in such a way that the effective dipole moment gets reduced. The liquid A and B may form multimers leading to the less effective dipoles. The negative excess permittivity indicates the formation of multimers in the binary liquid mixtures.
iii) indicates the liquid A and B interact in such a way that the effective dipole moment increases. This may be due to the breaking of the multimers structure in monomer structure in the presence of other molecules.

Study of Kirkwood correlation factor

The Kirkwood correlation factor g [2-4] provides information regarding the orientation of the electric dipoles in polar liquids. For a pure polar liquid, the Kirkwood correlation factor g may be obtained by the expression:

$$g = \frac{\varepsilon_0(\varepsilon_S - \varepsilon_\infty)(2\varepsilon_S + \varepsilon_\infty)9kTM}{\varepsilon_S(\varepsilon_\infty + 2)^2\mu^2 N\rho} \tag{3}$$

Where μ is dipole moment, μ is density at temperature T, M is the molecular weight, k is Boltzmann constant, N is Avogadro's number, (ε_S) is the static dielectric permittivity and ε_0 is free space permittivity**.**
The Kirkwood factor g for mixtures can be expressed by an effective averaged correlation factor g^{eff} such that Kirkwood equation for the mixture can be approximated as

$$g^{eff} = \frac{\varepsilon_0((\varepsilon_S)_m - \varepsilon_{\infty m})(2(\varepsilon_S)_m + \varepsilon_{\infty m})9kT}{N(\varepsilon_S)_m(\varepsilon_{\infty m} + 2)^2\left(\frac{\mu_1^2\rho_1}{M_1}v_1 + \frac{\mu_2^2\rho_2}{M_2}v_2\right)} \tag{4}$$

Where v_1 and v_2 are the volume fractions of liquids 1 and 2, $\varepsilon_{\infty m}$ is high frequency dielectric constant of the liquid mixture. The other way to visualize variation in the Kirkwood correlation factor is to assume that correlation factors for molecules 1 and 2 in mixture contribute to effective g in equal proportion to their values corresponding to pure liquids, i.e., g1 and g2. Under this assumption the Kirkwood equation for the mixture can be approximated as

$$g_f = \frac{\varepsilon_0((\varepsilon_S)_m - \varepsilon_{\infty m})(2(\varepsilon_S)_m + \varepsilon_{\infty m})9kT}{N(\varepsilon_S)_m(\varepsilon_{\infty m} + 2)^2\left(\frac{\mu_1^2\rho_1 g_1}{M_1}v_1 + \frac{\mu_2^2\rho_2 g_2}{M_2}v_2\right)} \tag{5}$$

Where g_f is a fractional change in correlation factor for mixture. The values of g^{eff} in Eq. (5) Will change from g1 to g2 as concentration of varying from 0 to 100%. In Eq. (5), g_f is unity for pure liquids and will remain close to unity if there is no interaction between 1 and 2.

Study of Bruggeman factor

The information related to interaction between two liquid mixtures can be obtained by the Bruggeman factor. The effective volume of the solute gets changed by solute–solvent interactions.

$$f_B = \frac{(\varepsilon_s)_m - (\varepsilon_s)_2}{(\varepsilon_s)_1 - (\varepsilon_s)_2}\left[\frac{(\varepsilon_s)_1}{(\varepsilon_s)_m}\right]^{\frac{1}{3}} = 1 - v_2 \qquad (6)$$

The Bruggeman factor formula state that static permittivity of binary mixture $(\varepsilon_s)_m$, solute $(\varepsilon_s)_1$ and solvent $(\varepsilon_s)_2$ related to volume fraction of solvent (v_2). By observing above equation the linear relationship is expected in Bruggeman factor f_B and v. The deviation from this linear relation indicates molecular interaction in the mixture [2-4].

Results and Discussion

The experimental results of static dielectric constants and the Kirkwood correlation factor of Benzene + Ethanol, Benzene + Methanol and Benzene + 1-Propanol binary solutions are shown in Table 1, 2 and 3 respectively. The variation in static dielectric constant for binary mixtures of Ethanol, Methanol and 1-Propanol with Benzene is shown in figs. 2, 3 and 4 respectively. The dielectric constant of the binary solutions decreases with an increase in the concentration of Benzene. This indicates that the amount of dipoles decreases with increase in mole fraction of Benzene in the mixture. It means that the molecular size of the system decreases with the Benzene concentration.

The experimental excess permittivity for the binary mixture of Benzene - Ethanol, Benzene – Methanol and Benzene – 1-Propanol are presented in figs. 5, 6, and 7 respectively. The observed excess permittivity is found to be negative for all concentrations, indicating that the total number of dipole decreases, which is due to the opposite alignment of the dipoles in the solution. The information related to the molecular interaction in the solution can be obtained by the Bruggeman factor.

The Bruggeman factor plot for binary mixtures of Ethanol, Methanol and 1-Propanol with Benzene are shown in fig. 8, 9, and 10 respectively. It can be observed from these plots that f_B shows a little deviation from the ideal Bruggeman behaviour and this indicates weak intermolecular interaction in the solution.

The value of Kirkwood correlation factor g_f is unity for an ideal mixture and deviation from unity may indicate the interaction between two components of the mixture. The variation of a Kirkwood correlation factor of binary mixture of Benzene with Ethanol is shown in Table 1. It shows the value of geff < 1 suggesting formation of antiparallel arrangement of dipoles and weak dipole-dipole interaction**.** The Table 2 shows the variation of a Kirkwood correlation factor of binary mixture of Benzene with Methanol. It shows that the value of geff > 1 suggesting formation of parallel arrangement of dipoles and weak dipole-dipole interaction. The value of g^{eff} close to unity in the Methanol rich region, indicating weaker intermolecular interaction in the solute solvent, whereas in the Benzene rich region values deviated below unity, indicating antiparallel arrangement of dipoles and weaker intermolecular interaction in that region. The Table 3 shows the variation of a Kirkwood correlation factor of binary mixture of Benzene with 1-Propanol. The value of geff < 1 suggesting formation of antiparallel arrangement of dipoles and weak dipole-dipole interaction.

Table 1: Variation of static dielectric constant and Kirkwood correlation factor of binary mixture of Benzene with Ethanol.

Percentage. Benzene in Ethanol	Static Dielectric Constant 'ε_s'	Kirkwood Correlation Factor g^{eff}
0	23.37	1
10	21.20	0.98
20	19.00	0.96
30	16.60	0.93
40	14.17	0.89
50	11.72	0.85
60	9.38	0.80
70	7.22	0.75
80	5.28	0.71
90	3.58	0.64
100	2.26	1

Table 2: Variation of static dielectric constant and Kirkwood correlation factor of binary mixture of Benzene with Methanol.

Percentage. Benzene in Methanol	Static Dielectric Constant 'ε_s'	Kirkwood Correlation Factor g^{eff}
0	32.79	1
10	31.00	1.02
20	28.89	1.06
30	26.20	1.10
40	23.40	1.14
50	20.30	1.16
60	16.80	1.13
70	12.80	1.02
80	8.20	0.89
90	4.80	0.81
100	2.26	1

Table 3: Variation of static dielectric constant and Kirkwood correlation factor of binary mixture of Benzene with 1-Propanol.

Percentage. Benzene in 1- Propanol	Static Dielectric Constant 'ε_s'	Kirkwood Correlation Factor g^{eff}
0	19.06	1
10	17.29	0.98
20	15.33	0.95
30	13.50	0.93
40	11.50	0.89
50	9.89	0.88
60	8.20	0.87
70	6.60	0.86
80	5.14	0.88
90	3.77	0.99
100	2.26	1

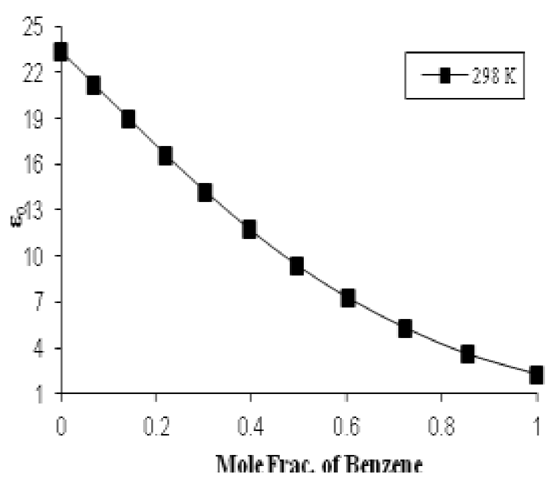

Fig. 2: Variation in static dielectric constant for binary mixture of Ethanol + Benzene at 298 K.

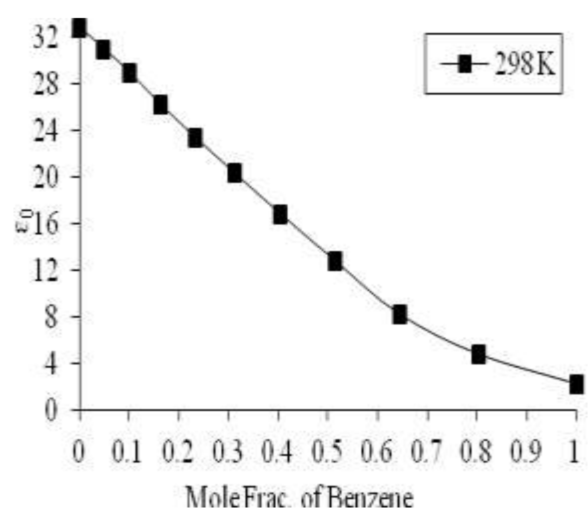

Fig. 3: Variation in static dielectric constant for binary mixture of Methanol + Benzene at 298 K.

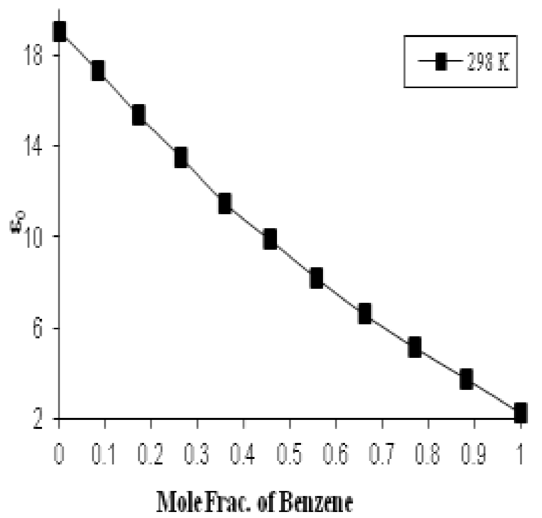

Fig. 4: Variation in static dielectric constant for binary mixture of 1-Propanol + Benzene at 298 K.

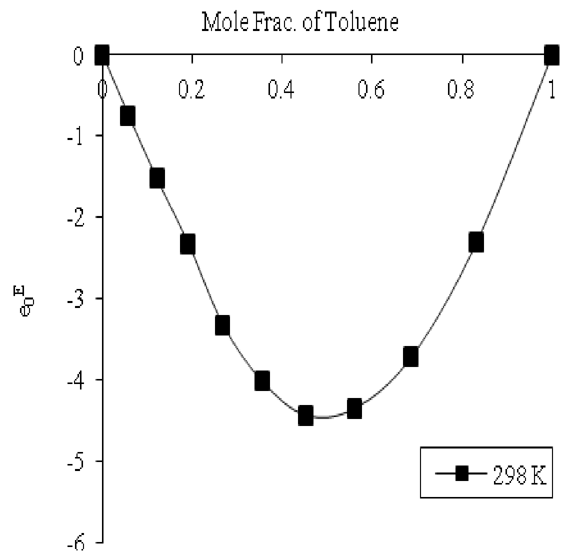

Fig. 5: Variation in excess permittivity ε_0^E for Ethanol +Benzene at 298 K.

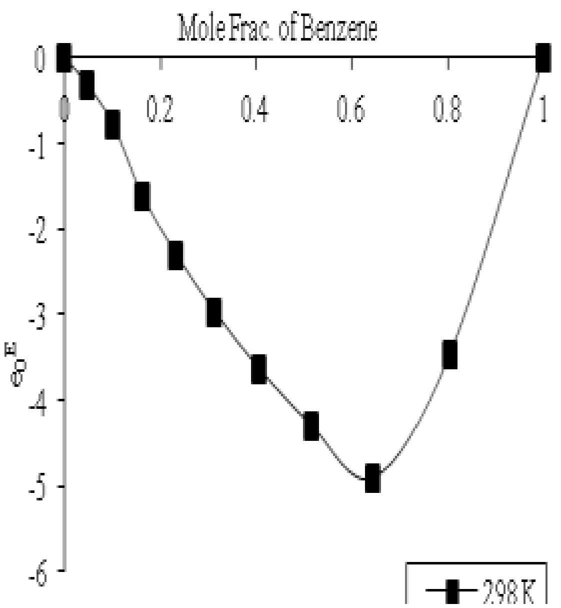

Fig. 6: Variation in excess permittivity ε_0^E for Methanol +Benzene at 298 K.

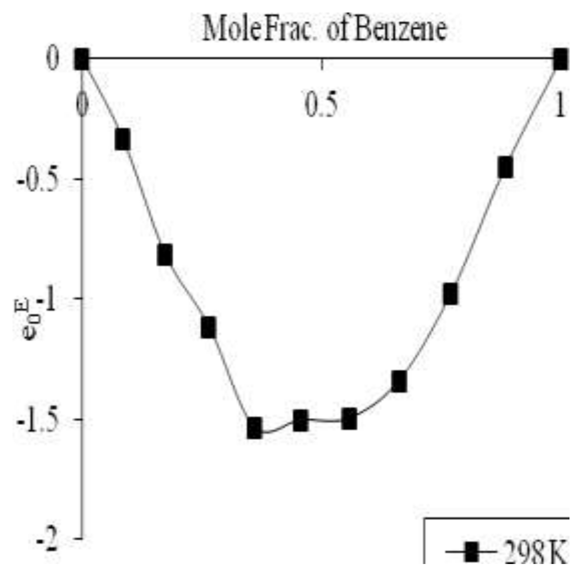

Fig. 7: Variation in excess permittivity ε_0^E for 1-Propanol +Benzene at 298 K.

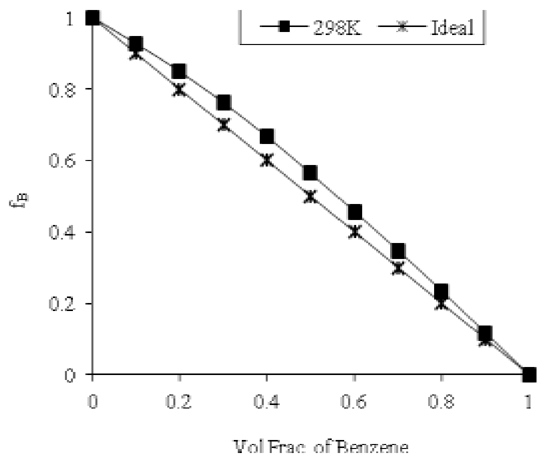

Fig. 8: Bruggeman factor (f_B) plot for binary mixtures of Ethanol + Benzene at 298 K.

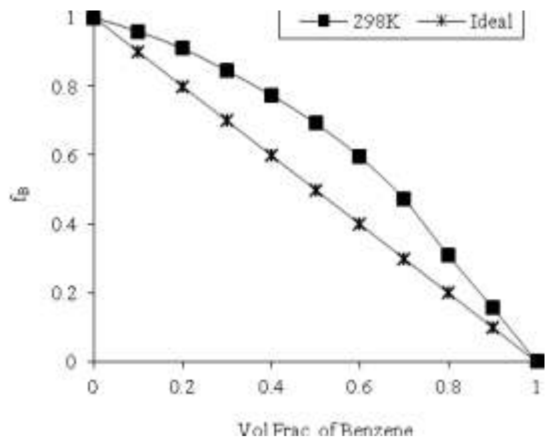

Fig. 9: Bruggeman factor (f_B) plot for binary mixtures of Methanol + Benzene at 298 K.

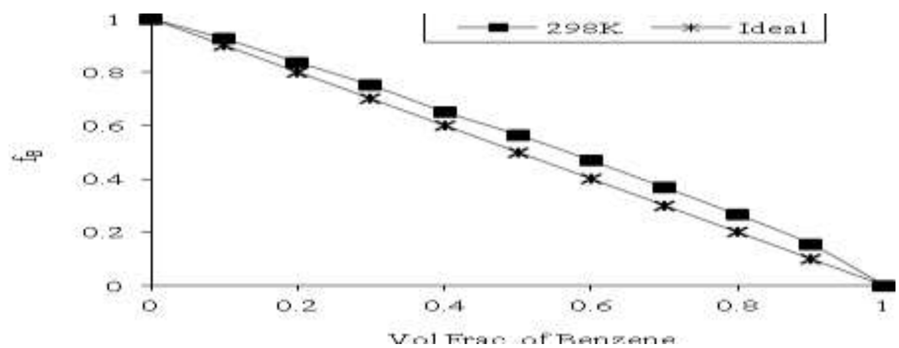

Fig. 10: Bruggeman factor (f_B) plot for binary mixtures of 1-Propanol + Benzene at 298 K.

Conclusions

The static dielectric constant of the binary system decreases with an increase in the percentage of the Benzene increase in the Ethanol, Methanol and 1-Propanol for the studied temperature.

The excess permittivity is negative for the entire mole fraction range of the Benzene- Ethanol, Benzene- Methanol and Benzene-1-Propanol binary systems at the studied temperature indicates the liquid A and liquid B interact in such a way that the effective dipole moment gets reduced.

The Bruggeman factor deviate from ideal behaviour which indicates molecular interactions in the binary solution.

References

[1] S. B. Sayyad, P. B. Undre, P. Yannewar, S. S. Patil, P. W. Khirade and S. C. Mehrotra, "Investigations of intermolecular interactions between 2-metoxyethanol and nitrobenzene through dielectric relaxation study," *Lithuanian J. of Phy*., vol. 51, 2011, pp. 29-37.

[2] R. H. Fattepur, S. B. Sayyad, N. H. Ayachit, P.W. Khirade and S. C. Mehrotra, "Dielectric relaxation study of binary mixtures of 2-methoxyethanol in nitrobenzene and chlorobenzene using time domain reflectometry," IEEE MTT-S International microwave symposium. USA, 2010, pp. 1052-1055.

[3] S. S. Dubal, S. B. Sayyad, S. S. Patil, and P.W. Khirade, "Microwave dielectric characteristics of binary mixture of diethylene glycol monomethyl ether with N, N-dimethylformamide," *Int. Multidisciplinary Reasearch J*., vol. 1, issue 4, 2011, pp. 4-10.

[4] P. W. Khirade, Ajay Chaudhari, J. B. Shinde, S. N. Helambe and S. C. Mehrotra, "Static dielectric constant and relaxation time measurement on binary mixtures of dimethyl sulfoxide with ethanol, 2- ethoxyethanol, and propanol-1-ol at 293, 303, 313, and 323 K.," *J. Chem. Eng*. Vol. 44, 1999, pp. 879-881.

[5] S. M. Anpat and S. B. Sayyad, "Liquid dielectric constant measurement techniques," *International J. of Advanced Research in Basic and Applied Science*s, vol. 1, issue. 1, 2014, pp. 168-171.

[6] Anpat, S. M., Khirade, P. W., and Sayyad, S. B., "Design and development of a dielectric spectroscopy sensor using microcontroller based system," *Bionano Frontier*, vol. 8, issue. 3, 2015, 361-364.