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Measurement and modelling of static dielectric constants of aqueous solutions of methanol, ethanol and acetic acid at $T = 293.15$ K and 91.3 kPa

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ABSTRACT

Static dielectric constants of aqueous solutions of methanol, ethanol and acetic acid at $T = 293.15$ K and 91.3 kPa were measured at weak electromagnetic field ($\ll$0.001 V) and ($\ll$60 Hz). The static dielectric measurements have been achieved by using the new set up presented in the previous work based on a low-pass filter. From the experimental data, excess dielectric constants, ε^E have been calculated and reported. An empirical polynomial equation was used for correlating the data of the dielectric constants for the aqueous solutions. In addition, the measured static dielectric constants data have been calculated on the basis of the empirical modification of the Kirkwood theory for multicomponent systems. According to the average absolute deviations obtained between experimental and calculated data, the calculated dielectric constants of aqueous solutions studied in this work are generally in good agreement with the experimental data.

1. Introduction

The dielectric constant indicates the solvent's ability to reduce the field strength of the electric field surrounding a charged particle immersed in it. This reduction is then compared to the field strength of the charged particle in a vacuum [1]. Macroscopic parameters such as dielectric constant have 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]. The dielectric constant of solvents 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 characteristics of liquid solutions [5]. This property can also be very useful as a support for the efficient design, simulation of separation processes, sample preparation and chromatography techniques in analytical chemistry [6,7]. Additionally, dielectric constants can be used to calculate the ionic activity coefficients of electrolyte solutions at any temperature and composition [8].

It is well known that the thermophysical properties of liquid systems such as dielectric constant are strictly related to the molecular interactions present in different binary liquid mixtures. The variation of this property with composition gives us important data about intermolecular interactions [9]. There is a wide range of possible interactions between the components of a mixture, *e.g.*, hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole-induced dipole interactions [10–12]. As a consequence of these interactions, deviations occur from ideal behaviour of the dielectric constant. These deviations can be defined by excess dielectric constants, ε^E. The dielectric constant decreases as the temperature increases, indicating that the molecular ordering becomes weak at the high-temperature region. Experimental data on excess dielectric constant for a number of binary and ternary liquid mixtures can be found in several articles [13–16]. Dielectric constant data were reported in the literature for electrolyte solutions in both water and other solvents [17–30].

Considering the lack of a theoretical equation for accurate prediction of dielectric constant of solvents and aqueous solutions, search for suitable techniques to provide accurate experimental measurements of the dielectric constants of solvents is still of great interest [31]. In this work, using the set up based on a low-pass filter, the static dielectric constants of the aqueous solutions of methanol, ethanol and acetic acid at $T = (293.15 \pm 0.1)$ K and 91.3 kPa were measured. The static dielectric constant data obtained have been satisfactorily correlated on the basis of the empirical modification of the Kirkwood theory for multicomponent systems. The dependence of the dielectric constant on mole fraction of the aqueous solutions studied is described by an empirical polynomial equation. The coefficients of empirical equation were obtained and are reported in this paper.

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2. Experimental

2.1. Materials

Methanol, ethanol and acetic acid were purchased from Merck Co. Inc., Germany and were used without further purification. The purity of these materials was checked by gas chromatography, and the results confirmed that the mass fraction purity was higher than 0.99%. The densities, refractive indexes and boiling points of the pure components were measured and compared with the literature [32]. The measured physical properties are listed in table 1.

The refractive index was measured using a thermostatically controlled Abbe refractometer (Atago 3T, made in Japan) with an accuracy of ±0.0001n_D. Each measurement was repeated at least three times. The average values were taken for the data reported. The maximum deviations from the average value were less than 0.1%. A 25 cm^3 calibrated glass pycnometer was used for density measurements at $T = 293.15$ K. Each measurement was repeated at least four times. The uncertainty of density measurements was estimated as $\pm 10^{-4}$ g·cm^{-3}. Boiling point measurements were obtained by using a dynamic equilibrium still. The apparatus and procedure were described in the previous work [33]. Each measurement was repeated at least three times. The estimated uncertainty in the boiling point measurements was ±0.05 K. The deionised water was doubly distilled over $KMnO_4$ with conductivity equal to $1.0 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$.

2.2. Measurement of dielectric constants

The dielectric constants were measured using low-pass-filter method which presented in the previous work [1] at weak electromagnetic field (($\ll$0.001 V) and ($\ll$60 Hz)). The experimental data were determined by using a glass cell with a water jacket to maintain a constant temperature at (293.15 ± 0.01) K. The aqueous solutions were made by mass using a Sartorius analytical balance (Model A200S, accurate to 0.0001 g). The estimated uncertainty in the dielectric constant measurements was estimated to be ±0.01. Each measurement was repeated at least three times. The average value was taken as the dielectric constant data measurements. The maximum deviations from the average value were less than 0.1%.

3. Results and discussion

The experimentally measured dielectric constant data of the studied aqueous solutions at $T = 293.15$ K and 91.3 kPa are presented in tables 2–4. According to the data obtained, the dielectric constants values for all the aqueous solutions studied have decreased by increasing of methanol, ethanol and acid acetic concentrations.

TABLE 1
Values of the measured boiling point, density and refractive index of methanol, ethanol and acetic acid.

Component	ρ/(g·cm^{-3})		n_D		T_b/K	
	Exp.	Lit. [32]	Exp.	Lit. [32]	Exp.	Lit. [32]
Water	0.9990	0.9982	1.3342	1.3333	373.10	373.15
Methanol	0.7930	0.7920	1.3280	1.3284	337.85	337.80
Ethanol	0.7900	0.7890	1.3612	1.3614	351.35	351.15
Acetic acid	1.5500	1.5490	1.3720	1.3750	391.10	391.15

The density and refractive index were measured at $T = 293.15$ K. The methanol, ethanol and acetic acid were supplied by Merck, Germany. The verified mass fraction purity was 0.0099.

TABLE 2
Experimental and calculated (empirical equation and Kirkwood model) values of dielectric constant (ε) for {water (1) + methanol (2)} mixture at $T = 293.15$ K and 91.3 kPa (value of the uncertainty = ±0.01).

x_2	ε_{exp}	$\varepsilon_{cal(empirical)}$	$\varepsilon_{cal(Kirkwood)}$
1.00	33.00	33.06	33.00
0.98	33.72	33.64	33.42
0.95	34.65	34.52	34.08
0.90	36.10	36.02	35.22
0.80	39.18	39.15	37.72
0.70	42.54	42.51	40.54
0.60	46.22	46.15	43.77
0.50	50.22	50.16	47.50
0.40	54.70	54.62	51.84
0.30	59.67	59.66	56.97
0.20	65.58	65.43	63.11
0.10	72.27	72.12	70.62
0.05	76.058	75.89	75.03
0.00	79.99	79.99	79.99

TABLE 3
Experimental and calculated (empirical equation and Kirkwood model) values of dielectric constants (ε) for {water (1) + ethanol (2)} mixture at $T = 293.15$ K and 91.3 kPa (value of the uncertainty = ±0.01).

x_2	ε_{exp}	$\varepsilon_{cal(empirical)}$	$\varepsilon_{cal(Kirkwood)}$
1.00	25.02	25.19	25.02
0.98	25.53	25.74	25.36
0.95	26.28	26.59	25.90
0.90	27.55	28.02	26.84
0.80	30.36	31.03	28.95
0.70	33.50	34.29	31.44
0.60	37.01	37.91	34.40
0.50	41.10	42.03	37.98
0.40	46.10	46.84	42.41
0.30	52.20	52.60	48.03
0.20	59.98	59.68	55.40
0.10	69.40	68.58	65.44
0.05	74.70	73.91	71.98
0.00	79.99	79.99	79.99

TABLE 4
Experimental and calculated (empirical equation and Kirkwood model) values of dielectric constants (ε) for {water (1) + acetic acid (2)} mixture at $T = 293.15$ K and 91.3 kPa (value of the uncertainty = ±0.01).

x_2	ε_{exp}	$\varepsilon_{cal(empirical)}$	$\varepsilon_{cal(Kirkwood)}$
1.00	6.15	6.32	6.15
0.98	7.25	7.07	6.84
0.95	8.64	8.30	7.90
0.90	11.11	10.59	9.75
0.80	16.55	15.98	13.80
0.70	22.41	22.12	18.37
0.60	28.50	28.56	23.58
0.50	34.90	35.00	29.54
0.40	41.80	41.38	36.45
0.30	49.40	48.05	44.54
0.20	58.00	55.73	54.14
0.10	67.70	65.67	65.73
0.05	73.50	72.10	72.47
0.00	79.99	79.99	79.99

In this work, the dependence of log ε on mole fraction of the aqueous solutions studied was described by the following empirical equation:

$$\log(\varepsilon/\varepsilon_0) = \sum_{i=1}^{3} a_i x^i \qquad (1)$$

where ε_0 is the dielectric constant of pure water fraction, x is mole fraction of aqueous solutions and a_i are the empirical constants. The results for the aqueous solutions dielectric constants were correlated by the above equation and the values of a_i constants are reported in table 5. The correlated results by equation (1) are presented in tables 2–4. Figure 1 shows the plot of log ($\varepsilon/\varepsilon_0$) versus the aqueous solutions mole fractions. According to this figure,