

Conductometric Studies of Sodium Benzoate in Water + 2-Propanol at Different Temperatures

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Summary: Conductance measurements of dilute solutions (1.5×10^{-4} to 4.8×10^{-4} M) sodium benzoate in various binary mixtures of water + 2-propanol were done. The studies were carried out at three different temperatures, i.e. 298.15, 303.15 and 208.15 K. Data was analyzed by using the Fuoss-Kraus equation to obtain the values of the limiting molar conductance, Λ_0 , and the association constant, K_a . It was found that the electrolyte is completely dissociated in pure water and associates with increasing amounts of 2-propanol

Introduction

Conductometric studies on simple (1:1) symmetrical electrolyte in both pure and mixed solvent systems are known [1-6]. The cosolvent can both be organic or aqueous. Various parameters like temperature, pressure and both temperature and pressure are also reported in the literature [6,7]. The present study is an investigation on electrolytic conductance measurements on sodium benzoate in water + 2-propanol mixtures of varying compositions at different temperatures. Analysis of conductance data given in figures (1-3) was done with the help of Fuoss-Kraus equation, which generated the limiting molar conductance (Λ_0), and the association constant

(K_a) for the electrolyte. Normalized Walden Product (NWP) is also reported for the present system. Results are interpreted in terms of solute-solvent interaction.

Results and Discussion

Molar conductance measurements of sodium benzoate in varying compositions of water + 2-propanol mixtures were obtained at three different temperatures. Such values could only be determined for upto 70% 2-propanol due to the solubility limitations of sodium benzoate in the organic

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solvent. The values of molar conductance (Λ_m) obtained were plotted against the concentration of electrolyte to see the general trend. Such plots are given in figures 1-3 at three different temperatures. It is clear from these figures that the Λ_m value

decreases with increasing concentration of the electrolyte in given composition of binary mixture at any fixed temperature. However, the molar conductance value of sodium benzoate is higher at higher temperature in a given composition of water

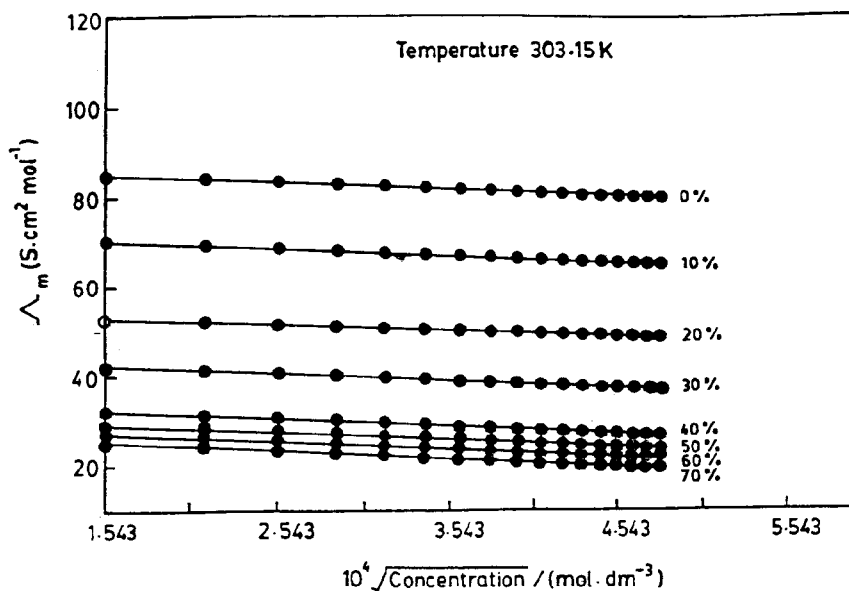


Fig. 1: Dependence of molar conductance of sodium benzoate in various concentrations of water + 2-propanol mixture at 298.15 K.

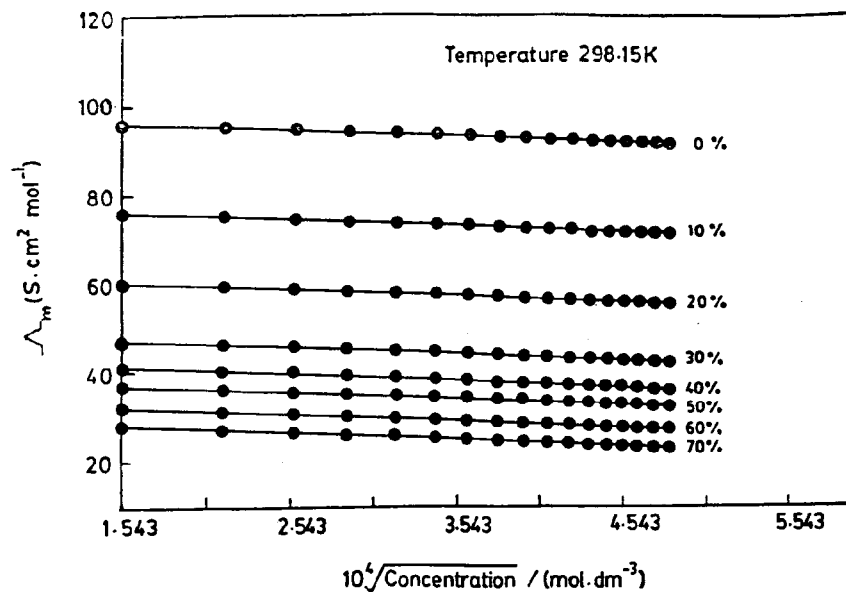


Fig. 2: Dependence of molar conductance of sodium benzoate in various concentrations of water + 2-propanol mixture at 303.15 K.

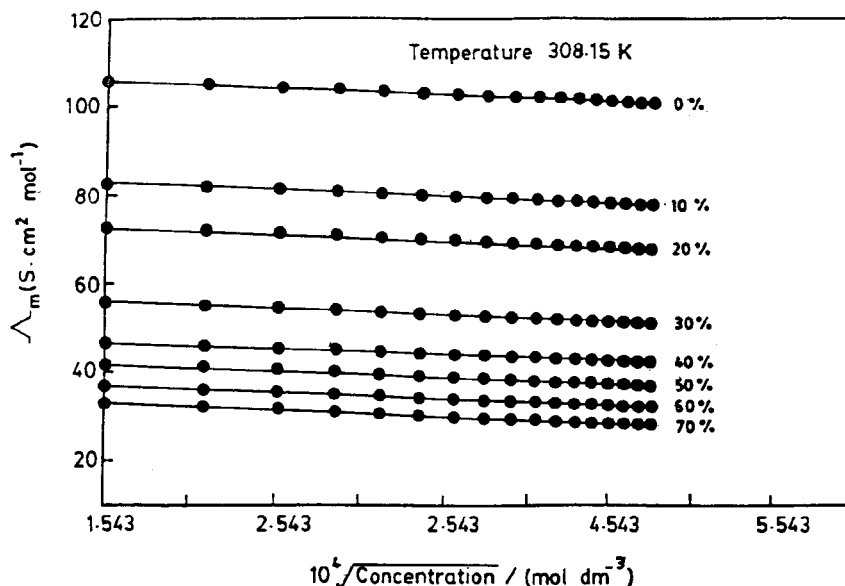


Fig. 3: Dependence of molar conductance of sodium benzoate in various concentrations of water + 2-propanol mixture at 308.15 K.

+ 2-propanol. Concentration values on X-axis ranges from 1.5×10^{-4} to 4.7×10^{-4} M with respect to the analyte which under normal analytical conditions of conductance measurements constitute a very dilute solution. The application of Kohlrausch's law for this concentration range is practically favoured towards a linear plot between $C^{1/2}$ vs Λ_m , which in fact is not an ideal case, however within experimental limits, the observed linearity could be extrapolated to a non linear configuration beyond this concentration range. One also observes that the molar conductance of this electrolyte decreases as the amount of 2-propanol increases. This change might be attributed to the viscosity changes which are greater with increasing amounts of 2-propanol. In other words, the solvent-solvent interaction increases as the amount of 2-propanol increases thereby decreasing the mobility of the ions.

Molar conductance values were fitted to Fuoss-Kraus equation [8] for evaluating the limiting molar conductance (Λ_o) and the association constant (K_a) of the electrolyte.

$$\frac{F(z)}{\Lambda_m} = \frac{1}{\Lambda_o} + \frac{1}{\Lambda_o^2 K} \frac{C^{\pm} \pm \Lambda_m}{F(z)}$$

Where, $F(z) = 4/3 \cos^2 (1/3) \arccos (-3/2.Z.3)^{1/2}$ and the variable Z is given by $Z = S (\Lambda_m C)^{1/2} \Lambda_m^{-3/2} f \pm$ is the ion activity coefficient of the free ions and S is the limiting slope. A plot of $F(z)/\Lambda_m$ versus $C^{\pm} \pm \Lambda_m / F(z)$ gives a straight line with an intercept $1/\Lambda_o$ and a slope of $1/\Lambda_o^2 K_a$.

Values obtained are reported in Table-1. It can be seen from this table that at any given temperature the Λ_o values decrease with increasing amounts of 2-propanol. Also that for any composition of binary mixture, Λ_o increases with increasing temperature. The values for association constant, K_a decrease with increase in temperature

Table-1: Conductance parameters of sodium benzoate in 2-propanol + water at 298.15, 303.15 and 308.15 K.

Weight % of 2-Propanol	298.15 K		303.15 K		308.15 K	
	Λ_o	K_a	Λ_o	K_a	Λ_o	K_a
0	86.290	17.470	97.430	13.010	107.580	9.550
10	71.040	28.620	77.150	23.440	84.290	18.510
20	53.520	35.130	61.040	36.700	74.130	25.360
30	43.010	68.620	48.060	54.680	57.130	39.930
40	33.150	109.130	42.140	69.040	47.730	38.180
50	30.300	132.330	38.280	81.010	43.330	63.110
60	28.490	153.780	33.460	107.550	38.520	76.040
70	26.760	180.890	29.740	135.250	34.730	94.590

Units of Λ_o , S. cm² mol⁻¹
 Units of K_a , dm³ mol

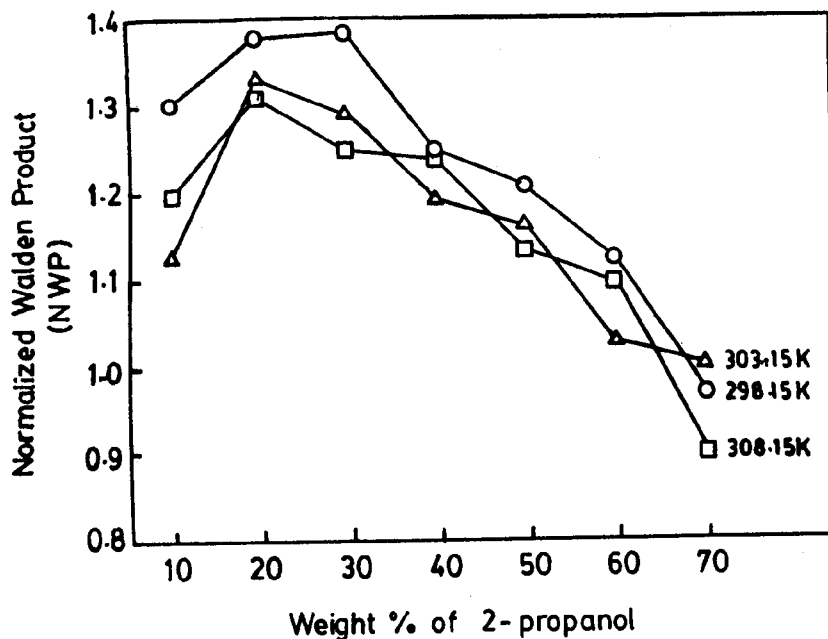


Fig. 4: Normalized Walden Product of sodium benzoate in water + 2-propanol mixture at different temperatures. Δ 298.15 K, O 303.15 K, \square 308.15 K.

and increase with added amounts of 2-propanol. This means that the molecules are more in the associated form in high viscosity mixtures which in term means the formation of more ion pairs. The decrease in K_a value with increasing temperature shows that the heat energy enable the ions to become more mobile and therefore high resistance is offered towards their recombination.

The conductance data was also analyzed in terms of Normalized Walden Product (NWP) which is defined as the ratio of the Walden product of an electrolyte in solvent mixture to that in water [9].

$$NWP = (\wedge_o \eta)^2 / (\wedge_o \eta)^w$$

Where \wedge_o is the molar conductance of an electrolyte at infinite dilution and η is the viscosity of the medium. Such values for sodium benzoate in water + 2-propanol mixture at three different temperatures are plotted in figure 4. The maxima in these curves do not confirm to the maxima in the viscosity composition curve of water + 2-propanol which lies at 70% by weight of 2-propanol [9]. The variation of Walden Products is indicative of relative solvation of ions in this solvent system.

Experimental

Sodium benzoate of 99% purity was obtained from E. Merck and used as such. KCl used for calibration of electrode, was recrystallized from triply distilled water, dried in an oven at 170°C for several days and kept in a desiccator over P_2O_5 for use in determining the cell constant of the conductivity meter. Conductivity grade water was prepared according to the prescribed method [10]. Its specific conductance was found to be $2.5 \times 10^{-7} \text{ S.cm}^{-1}$ at 298.15 K which agreed with the literature value [11]. The purification of 2-propanol was done as suggested in the literature [12]. Its conductance value was found to be $1 \times 10^{-7} \text{ S.cm}^{-1}$ at 298.15 K which was the same as a literature value [13]. The organic cosolvent (2-propanol) was kept over molecular sieves of 4 Å size for further use in the study. Conductance cell was calibrated by usual method [14] and the cell constant was found to be $0.775 \pm 0.001 \text{ cm}^{-1}$. Orion Research conductivity meter (model-101) operating at 1 KHz was employed in this work. The reproducibility of the conductance measurements was better than $\pm 0.01\%$.

Densities of various binary mixtures of water + 2-propanol were determined with a digital

densitometer DMA 48 at all temperatures. Viscosity measurements were done with a Kinematic viscometer. Both density and viscosity values of pure water and 2-propanol those already reported in the literature [4,9,15]. Dielectric constants of cosolvent mixtures were calculated from the empirical relationship $D=ac^{-bt}$ [16], where a and b are empirical constants and T is absolute temperature. The temperature studies were done by varying the temperature of the thermostated oil bath which was heated to a desired value with a temperature control of $\pm 0.01^\circ\text{C}$.

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