



# The transport properties and the association behavior of some 1:1 and 2:1 electrolytes in some binary alcoholic–aqueous mixtures

Farid I. El-Dossoki <sup>a,\*</sup>, Noraldin E.Y. Abdallah <sup>b</sup>, Saadeldin E.T. Elmasly <sup>b</sup>

<sup>a</sup> Chemistry Department, Faculty of Science, Port-Said University, Port-Said, Egypt

<sup>b</sup> Chemistry Department, Faculty of Arts and Science (Tobruk), Omar Al-Mukhtar University, 919 El-Beida, Libya

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## ABSTRACT

The specific conductance ( $\kappa$ ) of sodium oxalate, ammonium oxalate and ammonium acetate in binary mixtures (methanol–water, ethanol–water and glycerol–water) with the alcohol mass fractions of 10%, 20% and 30% at different temperatures of (293.15, 298.15, 303.15 and 308.15) K was measured experimentally. The conductivity data have been analyzed using the Lee–Wheaton conductivity equation. The molar conductance ( $\Lambda$ ), the limiting molar conductance ( $\Lambda_0$ ), the association constants ( $K_A$ ), the Walden product ( $\Lambda_0\eta_0$ ), the hydrodynamic radii ( $R_H$ ), the activation energy of the transport process ( $E_a$ ) and the standard thermodynamic parameters of association ( $\Delta G^\circ_A$ ,  $\Delta H^\circ_A$  and  $\Delta S^\circ_A$ ) were calculated and discussed. The results show that, the molar conductance and the limiting molar conductance values were decreased as the relative permittivity of the solvent decreased while, the association constant increased. Also the results show that the values of the molar conductance, the limiting molar conductance and the association constant were increased as the temperature increased indicating that the association process is an endothermic one.

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## 1. Introduction

Binary solvent mixtures have been receiving increasing attention in analytical determinations [1]. The transport properties (conductivity, transference number, diffusion coefficient and ionic mobility) in different solvent media give valuable information regarding the behavior of the electrolytes in solutions because the transport properties are mainly related to the effect of collective dynamics (such as ionic atmosphere relaxation) on the single particle properties [2,3]. The concept of ion association is widely used in solution chemistry. A literature survey shows that ion-pair or multiple-ion association phenomena and the nature of the solute–solvent interactions (in aqueous, non aqueous and mixed solutions) have been studied conductometrically [4–10]. In the above references the electrical conductivity has been discussed largely as a function of the dielectric constant and the mathematics of conductance theories has been applied for many electrolytic systems. One of the mathematic of conductance theories is the Lee–Wheaton conductivity equation [11], which is one of the recent conductivity equations based on a more realistic picture or model in which the ions exist in one of three states: as free ions, as solvent-separated ion-pairs and/or as contact ion pairs [12]. Lee–Wheaton conductivity equation has been successfully used

by many researchers for the investigation of many electrolytes in solutions in which ionic association predominates [13–19].

Alcohol–water mixtures at different temperatures exhibit a wide range of dielectric constants, viscosity and a high degree of hydrogen bonding effect, so that the present article aims to study the effect of dielectric constants, viscosity and the hydrogen bonding on the transport properties of sodium oxalate, ammonium oxalate and ammonium acetate in binary mixtures methanol–water (MeOH–H<sub>2</sub>O), ethanol–water (EtOH–H<sub>2</sub>O) and glycerol–water (GlyOH–H<sub>2</sub>O) with the alcohol mass fractions of 10%, 20% and 30% at different temperatures (293.15, 298.15, 303.15 and 308.15) K by applying the Lee–Wheaton conductivity equation.

## 2. Experimental

### 2.1. Materials and solutions

Sodium oxalate (C<sub>2</sub>O<sub>4</sub>Na<sub>2</sub>, 99.5%), ammonium oxalate (C<sub>2</sub>O<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>, 99.7%), ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>, 99.6%), methanol (MeOH, 99%), ethanol (EtOH, 99%) and glycerol (GlyOH, 99%), all were supplied from Riedel–de Haën company (Germany) and used without further purification. Bidistilled water with specific conductivity of 0.06  $\mu\text{S cm}^{-1}$  at 298.15 K was also used for the preparation of the mixed solvents. Binary mixtures methanol–water, ethanol–water and glycerol–water with the alcohol mass fractions of 10%, 20% and 30% were prepared by applying the following equation:

$$\text{Alcohol percentage} = (v_1 d_1) 100 / (v_1 d_1 + v_2 d_2) \quad (1)$$

\* Corresponding author at: Chemistry Department, Faculty of Arts and Science (Tobruk), Omar Al-Mukhtar University, 919 El-Beida, Libya. Tel.: +218 924882037; fax: +218 84637052.

E-mail address: [feldossoki64@yahoo.com](mailto:feldossoki64@yahoo.com) (F.I. El-Dossoki).

where  $d_1$  and  $d_2$  are the density of alcohol and water respectively.  $v_1$  is the volume of alcohol which will be added to the volume  $v_2$  of water to get the mixture of the required percentage. Ten solutions of the salts under investigation with a concentration range of ( $3.98 \times 10^{-4}$ – $3.84 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ), were prepared by take certain volume of the salt standard solution and diluted to the required volume for measurements by the previously prepared mixed solvents.

## 2.2. Conductivity measurement

The conductance measurements of the prepared salt solutions were carried out using Jenway Conductivity Bridge of a cell constant value  $1.15 \text{ cm}^{-1}$  and a deviation of  $\pm 0.1 \mu\text{S} \cdot \text{cm}^{-1}$ . The cell constant was determined with potassium chloride solutions [20]. The Conductivity Bridge was connected to MLW 3230 ultrathermostate to maintain the temperature constant at the desired temperature ( $\pm 0.005 \text{ }^\circ\text{C}$ ).

## 3. Results and discussion

The physical properties, density ( $\rho$ ) [20] viscosity ( $\eta_0$ ) [21] and dielectric constant ( $\epsilon$ ) [22] of (methanol–water, ethanol–water and glycerol–water) with the alcohol mass fractions of 10%, 20% and 30% at temperatures of (293.15, 298.15, 303.15 and 308.15) K were tabulated in Table 1. The unavailable values of the  $\rho$ ,  $\eta_0$  and  $\epsilon$  were evaluated by applying the empirical relations of these properties at the available temperatures taken from the referred references.

The specific conductance ( $\kappa$ ,  $\mu\text{S} \cdot \text{cm}^{-1}$ ) of ten solutions of each salt under investigation with a concentration range of ( $3.98 \times 10^{-4}$ – $3.84 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) in binary mixtures methanol–water, ethanol–water and glycerol–water with the alcohol mass fractions of 10%, 20% and 30% at temperatures of (293.15, 298.15, 303.15 and 308.15) K was measured experimentally. The molar conductance ( $\Lambda$ ) for all studied systems was calculated by applying Eq. (2) and recorded in Tables S2, S3 and S4 (in the Supplemental Materials).

$$\Lambda = 1000 k/c \quad (2)$$

**Table 1**  
The relative permittivity ( $\epsilon$ ), density ( $\rho$ ,  $\text{g} \cdot \text{cm}^{-3}$ ) and viscosity ( $\eta \times 0.1$ ,  $\text{Pa} \cdot \text{s}$ ) at different temperatures in the used solvents.

Solvent	Property	293.15 K	298.15 K	303.15 K	308.15 K
10% methanol–water	$\epsilon$	76.10	74.31	72.33	70.44
	$\rho$	1.0129	1.0110	1.0090	1.0081
	$\eta$	0.7899	0.7459	0.7018	0.6508
20% methanol–water	$\epsilon$	71.60	69.90	68.20	66.10
	$\rho$	0.9913	0.9875	0.9836	0.9848
	$\eta$	0.8159	0.7728	0.7297	0.6708
30% methanol–water	$\epsilon$	67.05	65.40	63.75	61.79
	$\rho$	0.9668	0.9643	0.9600	0.9590
	$\eta$	0.8436	0.7982	0.7528	0.6924
10% glycerol–water	$\epsilon$	77.05	75.60	74.15	72.55
	$\rho$	1.0273	1.0206	1.0139	1.0072
	$\eta$	1.2755	1.1530	1.0305	0.9089
20% glycerol–water	$\epsilon$	74.30	72.70	71.10	69.45
	$\rho$	1.0530	1.0450	1.0370	1.0310
	$\eta$	1.7170	1.5420	1.3670	1.1920
30% glycerol–water	$\epsilon$	71.66	70.00	68.34	66.63
	$\rho$	1.0770	1.0700	1.0630	1.0569
	$\eta$	2.3940	2.1570	1.9200	1.6380
10% ethanol–water	$\epsilon$	74.42	72.80	71.17	69.55
	$\rho$	0.9891	0.9802	0.9713	0.9624
	$\eta$	1.4810	1.3230	1.1650	1.0060
20% ethanol–water	$\epsilon$	68.66	67.12	65.58	63.48
	$d$	0.9695	0.9660	0.9625	0.9611
	$\eta$	2.0225	1.8150	1.6075	1.3321
30% ethanol–water	$\epsilon$	62.50	61.10	59.69	58.02
	$\rho$	0.9592	0.9507	0.9422	0.9447
	$\eta$	2.4800	2.1800	1.8800	1.5800

where  $c$  is the molar concentration,  $\kappa$  is the measured specific conductance of the studied solution from which the specific conductance of the used solvent was subtracted.

### 3.1. Limiting molar conductance

The experimental conductivities were analyzed by means of the Lee–Wheaton [11] conductivity equation. The Lee–Wheaton equation was used in the form suggested by Pethybridge and Taba [23] in Eqs. (3–9):

$$\Lambda_{calc.} = \alpha \Lambda_i \quad (3)$$

$$\Lambda_i = \Lambda^0 [1 + C_1(\beta k) + C_2(\beta k)^2 + C_3(\beta k)^3]^{-s} (k/(1 + kd)) [1 + C_4(\beta k) + C_5(\beta k)^2 + (kd/12)] \quad (4)$$

$$\beta = (z^2 e^2) / (\epsilon_0 \epsilon k_B T) \quad (5)$$

$$k = [(8n N_A e^2 z^2 \alpha c) / (1000 \epsilon_0 \epsilon k_B T)]^{1/2} \quad (6)$$

$$s = (F \xi e z) / (3n \eta^0) \quad (7)$$

$$K_A = (1 - \alpha) / (\alpha^2 f_{\pm}^2 c) \quad (8)$$

$$f_{\pm}^2 = \exp[-(\beta k) / (1 + kd)] \quad (9)$$

where  $C_1$  to  $C_5$  are functions of the product ( $k d$ ) and are given in Ref. [23],  $K_A$  is the thermodynamic ion-pair association constant of the equilibrium;  $M^+ + HA^- = AHM$  in the case of oxalates and of the equilibrium  $M^+ + A^- = AM$  in the case of acetate, where  $M$  is  $\text{Na}^+$  or  $\text{NH}_4^+$ ,  $\alpha$  is the degree of dissociation,  $c$  is the electrolyte concentration,  $f_{\pm}$  is the mean ion activity coefficient of the dissociated species (the activity coefficient for non-conducting species is assumed to be 1),  $e$  the electronic charge,  $z$  the ion charge,  $\epsilon_0$  the permittivity of vacuum,  $\epsilon$  the dielectric constant of the solvent,  $\eta_0$  the viscosity of the solvent,  $F$  the Faraday constant,  $k_B$  the Boltzmann constant,  $N_A$  the Avogadro's number,  $T$  the absolute temperature and the symbol  $\xi$  is equal to  $(1/299.79)$ . The parameter  $d$  represents the center-to-center distance of the formed ion-pairs. Beyond this distance, the ions are considered not to be associated. The computations for calculating the limiting molar conductance ( $\Lambda_0$ ), the association constant ( $K_A$ ), and the distance parameter ( $d$ ) were performed on a computer using the program of successive approximations following the three-parameter optimization as suggested by Pethybridge and Taba [23].

The initial  $\Lambda_0$  values for the procedure were obtained from the Onsager equation [24]. The calculations have been made by finding the values of  $\Lambda_0$ ,  $K_A$ , and  $d$  after obtaining the minimal standard deviation ( $\sigma$ ) between the calculated ( $\Lambda_{calc.}$ ) and the experimental ( $\Lambda_{exp.}$ ) conductivity values for a sequence of  $d$  values. The standard deviation ( $\sigma$ ) is given from the following relation:

$$\sigma = \left[ \sum_{j=1}^n (\Lambda_{j calc.} - \Lambda_{j exp.})^2 / (n-1) \right]^{1/2} \quad (10)$$

The suitable value for the distance parameter  $d$  corresponds to the minimum of the plot  $\sigma$  versus  $d$ . The value of the distance  $d$  which has been selected for the computations was ranging from  $4 \text{ \AA}$  (the sum of the crystallographic radii of the ions) to the maximum value of  $16 \text{ \AA}$ . The derived values of limiting molar conductance ( $\Lambda_0$ ) and distance of closest approach of the ions ( $d$ ) for the studied salts in the used binary mixtures are reported in Table 2 with their standard deviations  $\sigma$ . The calculated and the experimental values of the limiting molar

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