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THE EFFECT OF CATION AND ANION ON THE TRANSPORT PROPERTIES OF SOME 1:1 ELECTROLYTES IN SOME BINARY ALCOHOLIC-AQUEOUS MIXTURES

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ABSTRACT

The specific conductance (κ) of NaCl, KCl, HCOOK and CH₃COOK in binary mixtures (methanol-water, ethanol-water and glycerol-water) with the alcohol mass fractions of 10 %, 20 % and 30 % at different temperatures was measured experimentally. The conductivity data have been analyzed using the Fuoss-Edelson conductivity equation. The molar conductance (Λ), the limiting molar conductance (Λ_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 values of ΔG_A° , ΔH_A° and ΔS_A° were calculated and discussed. The effect of both cation and anion on the association behavior was discussed.

KEYWORDS: Molar conductance; Walden product; Transport Properties.

INTRODUCTION

Binary solvent mixtures have been received 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 of 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 Fuoss-Edelson [11] conductivity equation. Fuoss – Edelson conductivity equation has been successfully used by many researchers for the investigation of many electrolytes in solutions in which ionic association predominates [12-16].

Alcohols-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 chloride, potassium chloride, potassium formate and potassium acetate in binary mixtures methanol-water (MeOH-H₂O), ethanol-water (EtOH-H₂O) and glycerol-water (GlyOH-H₂O) 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 Fuoss-Edelson conductivity equation.

MATERIALS AND METHODS

Materials

Sodium chloride (NaCl, 99.5 %), potassium chloride (KCl, 99.7 %), potassium formate (HCOOK, 99.5 %) and potassium acetate (CH₃COOK, 99.6 %), methanol (MeOH, 99.0 %), ethanol (EtOH, 99.0 %) and glycerol (GlyOH, 99.0 %), 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:

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

where d_1 and d_2 are the density of alcohol and water respectively. v_1 is the volume of alcohol which will 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 $(3.98 \times 10^{-4} - 3.84 \times 10^{-3} \text{ mol.dm}^{-1})$, were prepared by take certain volume of the salt standard solution and dilute to the required volume for measurements by the previously prepared mixed solvents.

Methods

The conductance measurements of the prepared salt solutions were carried out using Jenway Conductivity Bridge of a cell constant value 1.15 cm^{-1} and a deviation of $\pm 0.1 \mu\text{S.cm}^{-1}$. The cell constant was determined with potassium chloride solutions [17]. The Conductivity Bridge was connected to MLW 3230 ultrathermostate to maintain the temperature constant at the desired temperature ($\pm 0.005 \text{ }^\circ\text{C}$).

RESULTS AND DISCUSSION

Molar conductivity and Association constants

The physical properties, density (ρ) [17] viscosity (η_o) [18] and dielectric constant (ϵ) [19] 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 ρ , η_o and ϵ were evaluated by applying the empirical relations of these properties at the available temperatures taken from the referred references.

The specific conductance (κ , $\mu\text{S cm}^{-1}$) of ten solutions of each salt under investigation with a concentration range of $(3.98 \times 10^{-4} - 3.84 \times 10^{-3} \text{ mol.L}^{-1})$ 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 (Λ) for all studied systems was calculated by applying equation (2).

$$\Lambda = 1000 \kappa / c \tag{2}$$

Where c is the molar concentration, κ is the measured specific conductance of the studied solution from which the specific conductance of the used solvent was subtracted. The experimental conductivities were analyzed by means of the Fuoss–Edelson [11] conductivity equation. According to Fuoss–Edelson, the limiting molar conductance (Λ_o) and the association constant (K_A) can be calculated applying the following equations:

$$\Lambda F = \Lambda_o - X K_A / \Lambda_o \tag{3}$$

$$X = C_f \Lambda F (\Lambda F - \Lambda_o / 2) \tag{4}$$

$$F = [(1 - \delta \sqrt{C})^{-1} + (\Lambda_o - \lambda_o^{\circ}) / 2 \Lambda] / [1 + (\Lambda_o - \lambda_o^{\circ}) / 2 \Lambda_o] \tag{5}$$

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

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

Where (A) and (A_0) are the molar and the limiting molar conductances, respectively, λ° is the limiting molar conductance of anion, δ is Onsager's slope, C is the molar concentration and F & X are Fuoss and Edelson functions. The ionic activity coefficient of M^+ , (f_{\pm}), was estimated by the Debye-Huckel second approximation.

$$\log f_{\pm} = -A Z^2 I^{1/2} / (1 + B a I^{1/2}) \quad (6)$$

Where, A , and B are empirical constants. I : ionic strength, a : closest approach distance in \AA (5\AA), Z : valence of cation. Where the constants values of A and B in equation (6) at the various density and dielectric constant are :

$$A = 1.825 \cdot 10^6 \cdot (d)^{1/2} / (DT)^{3/2} \quad (7)$$

$$B = 50.29 \cdot (d)^{1/2} / (DT)^{1/2} \quad (8)$$

Where, d : density of the solvent, D : dielectric constant, T : absolute temperature .

Values of λ° for Cl^- , HCOO^- and CH_3COO^- are 76.35, 54.6, and 40.9 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) [20-22] in water at 25°C . However there are no available data about λ° for methanol- H_2O , ethanol- H_2O , and glycerol- H_2O mixtures, so they were calculated. The value of (A_0) at a given temperature is calculated with an arbitrary estimate of λ° according to Fuoss-Edelson equation which is solved for the two unknown parameters K_A and (A_0) by an iterative procedure. In this way, the (A_0) values have been determined for the different salts at proper temperature. Then, the second estimated of λ° is calculated by multiplying the ratio of the value (A_0) in solvent at 25°C that of water at 25°C by λ° value in water at 25°C [23]. In this way, the λ° values of Na^+ and K^+ in all solvents can be calculated. Also, λ° values at different temperatures were calculated by multiplying the ratio of (A_0) at a given temperatures to that at 25°C by λ° at 25°C . The above procedure is then iterated until λ° attains a constant value. In Fuoss-Edelson program, we plot ΔF against X , which give straight line, its intercept equal (A_0) and the slope equal $-K_A / A_0$, where A_0 and K_A values were evaluated. Then iteration of this processes to fixed the value of limiting (A_0) for all systems under study and the corresponding K_A values can be determined. The A_0 and K_A values for all systems under investigation were represented in Tables 2 and 3 respectively.

Inspection of the results in Table 2, it was noted that the limiting molar conductance of the studied salts in the applied experimental conditions is, in general, in the following order: potassium formate \geq potassium acetate and potassium chloride $>$ sodium chloride. The higher values of potassium chloride than that of sodium chloride can be related to higher ionic mobility of the solvated potassium ion than that of sodium ion. The lower value of the limiting molar conductance of potassium acetate than that of potassium formate in the used alcoholic-aqueous mixtures under study can be related to lower ionic mobility of the acetate ion than that of formate ion.

In comparing the obtained results for the salts under study in alcoholic-aqueous mixtures with that in water solvent [24] at different temperatures, we can observe that the limiting molar conductance of the studied systems in water is higher than that in alcoholic-water mixtures. This may be related to the formation of intermolecular and intramolecular hydrogen bonding with the presence of the alcohol in the solution which reduce the solvation and dissociation of the salts. Also it may be related to a possibility of formation of undissociated molecules and hydrolysis products, which may reduce the conductivity.

The mean values of the ion-pair association constant (K_A) of all systems under study were represented in Table 3. Inspection of the K_A values, it was noted that the association constant for all studied salts in the used solvents, increase as the temperature increase which indicate an endothermic association process. Also this temperature dependence of the association process of ions can be explained on the base of the interplay between dehydration and association of ions where as the temperature increase, the dehydration and/or desolvation process of ions take place, then the ions will has short distance of contact, therefore the association of ions increase.

Table 2. The limiting molar conductance's (Λ_{∞} , ± 0.25 %, $S. mol^{-1}.cm^2$), of sodium and potassium salts in the used solvents at different temperatures

solvent	%	T/K	NaCl	KCl	HCOOK	CH ₃ COOK
MeOH-H ₂ O	10 %	293.15	101.0	113.0	124.4	100.4
		298.15	111.7	124.8	137.6	110.5
		303.15	120.3	131.9	140.5	127.5
		308.15	128.5	138.7	143.3	143.0
	20 %	293.15	79.4	96.3	92.6	86.1
		298.15	86.4	104.9	101.0	95.1
		303.15	96.8	117.3	109.5	108.3
		308.15	106.2	129.7	123.5	123.7
	30 %	293.15	75.1	83.7	86.4	77.6
		298.15	82.8	89.8	93.9	84.8
		303.15	91.1	102.7	105.7	95.2
		308.15	98.9	112.4	117.9	108.3
GlyOH-H ₂ O	10 %	293.15	80.4	113.4	98.2	87.4
		298.15	96.2	118.1	111.1	99.7
		303.15	101.4	123.1	132.7	115.3
		308.15	116.9	128.9	139.1	132.5
	20%	293.15	61.5	82.7	71.4	74.7
		298.15	73.9	97.3	80.2	81.6
		303.15	82.3	107.7	100.2	97.8
		308.15	91.3	117.2	116.3	124.2
	30 %	293.15	52.5	71.3	51.4	70.7
		298.15	61.7	82.8	58.1	78.8
		303.15	67.8	104.3	71.9	90.3
		308.15	74.4	112.7	84.9	102.5

EtOH-H ₂ O	10 %	293.15	76.6	92.5	82.8	76.1
		298.15	92.5	109.1	99.5	81.9
		303.15	101.2	120.0	121.9	94.3
		308.15	112.3	131.6	139.6	116.3
	20%	293.15	61.3	73.6	53.3	67.1
		298.15	71.5	84.4	63.8	74.8
		303.15	81.4	96.4	85.1	82.4
		308.15	90.4	108.0	120.2	91.7
	30 %	293.15	42.4	59.7	52.6	59.1
		298.15	51.6	69.4	58.5	69.4
		303.15	67.1	79.4	78.9	75.9
		308.15	81.4	86.4	117.5	84.9

Table 3: The ion pair association constant (K_A , ± 0.3 %, $\text{dm}^3 \cdot \text{mol}^{-1}$) of sodium and potassium salts in the used solvents at different temperatures

solvent	%	T/K	NaCl	KCl	HCOOK	CH ₃ COOK
MeOH-H ₂ O	10 %	293.15	3.55	3.96	3.27	4.74
		298.15	4.38	4.23	3.35	6.86
		303.15	4.69	4.86	4.52	7.66
		308.15	4.87	6.42	5.35	8.73
	0 %	293.15	3.68	4.17	4.08	4.86
		298.15	5.57	6.89	5.11	7.30
		303.15	10.13	7.04	6.43	7.78
		308.15	10.34	8.33	7.29	8.14
	30 %	293.15	5.92	5.78	4.56	5.95
		298.15	10.59	9.72	5.79	7.52
		303.15	12.62	9.88	8.05	9.05
		308.15	13.31	11.66	12.62	12.36

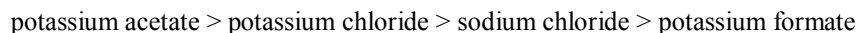
GlyOH-H ₂ O	10 %	293.15	2.41	2.29	4.18	8.25
		298.15	3.02	3.76	4.82	8.73
		303.15	3.12	5.72	5.03	9.46
		308.15	3.66	7.56	6.52	10.33
	20%	293.15	3.34	3.44	4.19	9.53
		298.15	3.39	7.56	5.58	10.05
		303.15	5.59	9.63	5.73	12.02
		308.15	6.85	10.64	7.65	13.09
	30 %	293.15	5.01	5.19	4.65	11.27
		298.15	7.03	10.77	10.59	11.65
		303.15	8.32	10.95	10.93	12.96
		308.15	10.13	12.75	11.73	13.65
EtOH-H ₂ O	10 %	293.15	1.43	2.59	1.76	5.24
		298.15	1.66	4.13	3.09	5.43
		303.15	1.95	4.80	3.22	5.67
		308.15	2.47	6.82	3.59	6.34
	20%	293.15	2.59	6.30	3.5	7.08
		298.15	2.78	7.76	3.64	8.86
		303.15	3.64	8.45	4.08	9.82
		308.15	3.77	9.01	4.55	14.35
	30 %	293.15	3.67	11.87	3.73	7.51
		298.15	3.83	12.56	5.01	9.47
		303.15	5.46	12.92	5.30	13.71
		308.15	5.86	13.16	7.25	19.12

The values of the association constant for all studied systems at the same temperature were found to increase as the proportions of organic solvent increase. This can be explained on the basis of the close relationship between association constant and the strength of the ion solvation in different solvents; that is, the stronger ion is solvated, the weaker the association between cations and anions. This indicate that, as the proportions of organic solvent increase in the mixtures, the mobility's of ions are decreased, giving a chance for ions to associate [25]. This behavior can also relate to the decrease in the dielectric constant of the medium as the proportion of organic solvent increase [26].

Also, it was found that the most predominant order of the association constant values for all studied systems at the same temperature are as the following order with some exceptions:

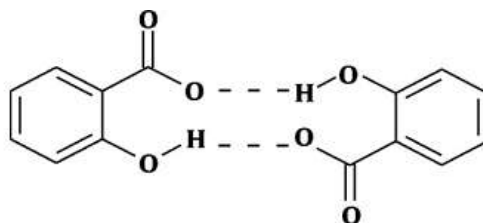
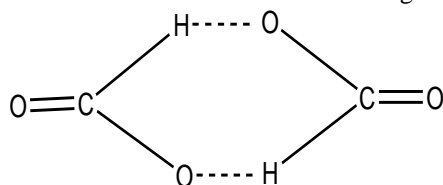


Such order nearly analogous to that observed for the values of (A_1) which interpreted on the basis of the effect of the dielectric constant which play an important role in increasing the association process. The effect of the hydrogen bond on the association process in glycerol (greatest number of -OH groups) is higher than that in ethanol [27-29]. In comparing the association constant values for the studied salts in the same experimental condition, in general, we can note the following order:



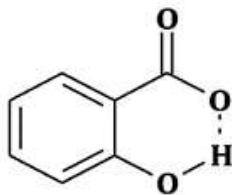
This order is in reverse to that for the limiting molar conductance. The increase of the association constants of the acetate salts than that of formate salt may be related to the higher ability of the formate to form intermolecular hydrogen bonds with the solvent molecules compared to acetate. The formation of intermolecular bonds decreases the association between K^+ and the formate anion. The association constants of ammonium, potassium and sodium salts found in literatures in the same experimental conditions (the same temperature, solvent and anion) [27 and 29] were found to be in the following order: ammonium salts > potassium salts > sodium salts. This may be related to the higher ionic radii and less solvation volume of NH_4^+ than that of K^+ and Na^+ , where it was expected that as the ionic radii increase and the solvation volume decrease, the chance of association increase.

The association constants of sodium chloride (the present study) were compared with other sodium salts (sodium acetate, sodium propionate, sodium formate, sodium benzoate, sodium oxalate, and sodium salicylate) found in literatures in the same experimental conditions (the same temperature and solvent) [27-29]. The association constants of some ammonium salts (ammonium formate, ammonium oxalate, ammonium benzoate, and ammonium acetate) found in literatures in the same experimental conditions (the same temperature and solvent) [27 and 29] were also compared. The comparisons indicate that there are no definite order for formate, oxalate, acetate, propionate, salicylate and benzoate, but it was found that oxalate salts have the highest association constant. This indefinite order of the studied salts may be related to the ability of each system to form intramolecular and intermolecular hydrogen bonds. The formation of intermolecular hydrogen bonds leads to a formation of dimers between each pairs of anions as in the case of formate as in the following scheme;



Intermolecular Hydrogen Bond

where the formic acid or the formate anion has more aldehydic character than acidic one in some of its behaviour. The formation of dimers will decrease the association between cations (Na^+ and NH_4^+) and the formate anions. Also the formation of intermolecular hydrogen bonds between the anions and the solvent molecules is almost likely the reason behind the lower values of association constant as in acetate anion as example, which contains O-H linkage and so cannot undergo intramolecular hydrogen bonding but the possibility of intermolecular hydrogen bonding with the solvent molecules is the highest one compared to other anions. The formation of intramolecular hydrogen bond, as in the following scheme, also leads to lower association process between the cations and anions.



Intermolecular Hydrogen Bond

Plotting of $(\ln K_A)$ versus the reciprocal of the dielectric constant $(1/\epsilon)$ (Figure 1) for all systems under study give a linear relationship. This linearity show that the solvated molecules remain in the ion pairs in those cases where hydrogen bonds form the solvate cluster [25]. Also, this linearity is analogous to that predicted by Fuoss equation [30] over a limited range of composition of the solvent mixtures under study [31]. Fuoss equation can be written in the

following form; $K_A = \frac{4\pi N a^3}{3000} \exp(|Z_+ Z_-| e^2 / a \epsilon K T)$ which composed of two factors, the per-exponential term $K_A = [4 \pi N a^3 / 3000]$, and the exponential term exp (b) with Bjerrum's ratio $B = (|Z_+ Z_-| e^2 / a \epsilon T)$. From this equation, it was noted that K_A depends on the (ϵ) in linear relationship, which achieved in the present study (Figures 1).

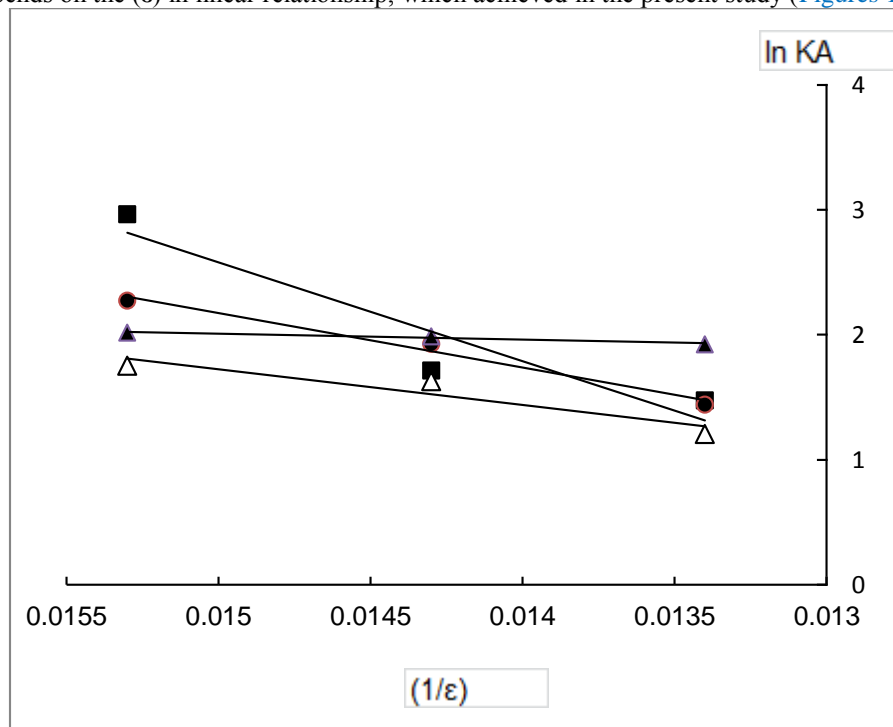
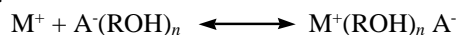


Figure 1. Relation of $\ln K_A$ vs. $(1/\epsilon)$ in 10 %, 20 %, and 30 % (w/w) methanol-water solvent at 298.15 K, (▲) potassium acetate, (△) potassium formate, (●) potassium chloride and (■) sodium chloride.

If the ion-pair is considered as a result of actual contact of two ions i.e. when the sum of their crystallographic radii equal to their separation, another interpretation is that more than one kind of ion-association may be takes place. In this interpretation, the formed ion-pair may initially react to constitute the second type. For the cations Na^+ and K^+ , the ion-pair entity is formed as follow:



In general, we can conclude that, the extent of ion-pairing in salt solutions under study depends upon the nature of the ion-solvent interaction take place in the solution. Moreover it depends on the dielectric constant and the properties of the medium [32, 33], which can be achieved or verified by plotting ($\ln K_A$) values against ($1/\epsilon$) with linearity.

Triple-ions Association Constant

The triple ion association constant (K_3) for the investigated salts, were calculated using Fuoss equation [34]. The small values of K_3 (10^{-4} - 10^{-3}) of the salts, indicate that the triple ion formation can be neglected.

Thermodynamics of Association

The standard free energy of association (ΔG_A°) was calculated for all salts under study using Equation (9) and its values were listed in Table 4.

$$\Delta G_A^\circ = -RT \ln K_A \quad (9)$$

The values of the standard enthalpy (ΔH_A°) and the standard entropy (ΔS_A°) of association process were calculated from the plots of (ΔG_A°) versus the absolute temperature T (Gibbs–Helmholtz relation, $\Delta G_A^\circ = \Delta H_A^\circ - T\Delta S_A^\circ$), where the slope is equal the value of ($-\Delta S_A^\circ$) while the intercept is equal the value of (ΔH_A°). The values of the standard enthalpy (ΔH_A°) and the standard entropy (ΔS_A°) are represented in Table 5. The negative ΔG_A° values indicate that the association processes in all studied systems are spontaneous processes. The positive value of (ΔH_A°), indicate the endothermic nature of the association processes. The positive (ΔH_A°) and (ΔS_A°) values are in a good agreement with several theories in many solvents [35, 36].

Table 4. The free energy of association ($-\Delta G_A^\circ$, kJ/mol) of sodium and potassium salts at different temperature in the used solvents

solvent	%	T/K	NaCl	KCl	HCOOK	CH ₃ COOK
MeOH-H ₂ O	10 %	293.15	3.032	3.296	2.836	3.728
		298.15	3.602	3.572	2.993	4.770
		303.15	3.961	4.047	3.860	5.213
		308.15	4.184	4.914	4.435	5.728
	20 %	293.15	3.116	3.421	3.368	3.788
		298.15	4.254	4.785	4.041	4.926
		303.15	5.506	4.997	4.767	5.253
		308.15	5.616	5.604	5.252	5.544
	30 %	293.15	4.260	4.202	3.633	4.270
		298.15	5.848	5.633	4.350	4.997
		303.15	6.493	5.866	5.339	5.641
		308.15	6.843	6.494	6.702	6.647
GlyOH-H ₂ O	10 %	293.15	2.104	1.993	3.425	5.052
		298.15	2.735	3.279	3.899	5.369
		303.15	2.913	4.467	4.136	5.754

		308.15	3.428	5.347	4.957	6.174
	20%	293.15	2.888	2.955	3.432	5.397
		298.15	3.029	5.013	4.261	5.717
		303.15	4.409	5.800	4.471	6.367
		308.15	5.088	6.252	5.378	6.800
	30 %	293.15	3.859	3.945	3.680	5.799
		298.15	4.833	5.889	5.849	6.083
		303.15	5.424	6.130	6.123	6.560
		308.15	6.123	6.730	6.509	6.911
EtOH-H ₂ O	10 %	293.15	0.857	2.281	1.358	3.966
		298.15	1.253	3.515	2.803	4.192
		303.15	1.711	4.018	2.997	4.446
		308.15	2.391	5.077	3.382	4.882
	20%	293.15	2.280	4.407	3.004	4.686
		298.15	2.540	5.077	3.200	5.405
		303.15	3.309	5.468	3.601	5.851
		308.15	3.509	5.811	4.003	7.034
	30%	293.15	3.114	5.923	3.155	4.826
		298.15	3.325	6.270	3.992	5.569
		303.15	4.346	6.552	3.375	6.705
		308.15	4.675	6.815	5.237	7.801

Table 5: The enthalpy change (ΔH_A , kJ/mol) and the entropy change (ΔS_A , K. kJ/mol) of association for sodium and potassium salts in the used solvents

Solvent % (w/w)		NaCl		KCl		HCOOK		CH ₃ COOK	
		(ΔH_A°)	(ΔS_A°)	(ΔH_A°)	(ΔS_A°)	(ΔH_A°)	(ΔS_A°)	(ΔH_A°)	(ΔS_A°)
MeOH-H ₂ O	10 %	1.383	16.730	1.198	16.962	1.344	16.522	1.599	21.252
	20 %	2.006	21.785	1.582	20.671	1.490	19.235	1.635	21.446
	30 %	2.081	26.127	1.603	23.537	2.557	24.855	1.798	23.645
GlyOH-H ₂ O	10 %	1.330	18.395	2.205	19.595	1.034	16.912	0.571	20.301
	20 %	0.973	18.607	2.337	24.115	1.383	18.981	0.857	22.825
	30 %	1.811	22.735	2.363	26.437	2.121	25.199	0.984	24.147
EtOH-H ₂ O	10 %	0.930	8.135	1.198	13.971	0.660	10.801	0.832	17.157
	20 %	1.053	13.032	1.582	18.991	0.674	13.595	1.673	24.410
	30 %	1.330	17.091	1.603	23.192	1.146	15.980	2.291	28.007

Walden Product and Hydrodynamic Radii

The Walden product ($\Lambda_0 \eta_0$ or $\lambda_0 \eta_0$) which are informative from the point of view of ion-solvent interaction [37, 38], has constant value due to the molar conductance of an ion at infinite dilution depends only upon its speed and hence, the product of ion conductance by the viscosity of the medium should be independent of the solvent nature. Hence, the Walden product ($\Lambda_0 \eta_0$) is expected to be constant for a given electrolyte in a series of solvent mixtures in which the ion-solvent interactions are uniform. Walden has formulated his rule in the form as in equation (10). The values of Walden product were calculated for the salts and ions under study and represented in Table 6.

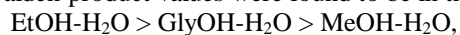
$$\Lambda_0 \eta_0 = 0.82 [1/r_s^+ + 1/r_s^-] \quad (10)$$

The inverse of the factor $[(1/r_s^+) + (1/r_s^-)]$ is a measure of the hydrodynamic radii (R_H) of the ions where r is the radius of a hypothetical sphere that diffuses with the same speed as the particle under examination. In practice, the solute molecules in solution are dynamic and solvated. As such, the radius calculated from the diffusion properties of the particle is indicative of the apparent size of the dynamic hydrated / solvated particle, hence the terminology hydrodynamic radius. This means that the hydrodynamic radius (R_H) includes both solvent (hydro) and Shape (dynamic) effects. The values of the hydrodynamic radii for the salts under study are tabulated in Table 7. We can note that the trend of change in R_H values is completely reversible with that found and discussed for Walden product.

Inspection of the Walden product values, it was noticed that the values of the Walden product decreased with increasing temperature. This negative temperature coefficient of Walden product may be related to the increase in the size of solvated ions in the mixtures as temperature increase as a result of the variation of the proportion of the organic solvent and H₂O molecules in the sheath of solvation with temperature [39].

The two effective factors on the Walden product are the limiting molar conductance and the viscosity, in which the limiting molar conductance is directly proportional with temperature while the viscosity is inversely proportional with temperature. This observation indicates that the contribution of the viscosity value is the most effective factor on the inverse proportional behavior of the Walden product with the temperature. The values of the Walden product were found to decrease as the proportion of methanol solvent increase in the following order: 10% > 20% > 30%, which

may be related to decrease in the limiting molar conductance in the same order. This means that the effect of increase in the limiting molar conductance is higher than the effect of decrease in of the viscosity of the medium. On the other hand the values of Walden product were increase as the proportion of GlyOH and EtOH increase, which may be related to the effect of increase in the viscosity in the same order which is higher than the effect of decrease in limiting molar conductance values. Also the Walden product values were found to be in the following order;



which is due to the decrease in the viscosity in the same order [Table 1](#) which has higher effect than the limiting molar conductance values. The observed trend of change in the values of the Walden product with temperature, solvent composition and nature of electrolyte was also reported by many authors [\[25, 40, and 41\]](#). The relation between the Walden product values and the hydrodynamic radii values is a good inverse linear relationship. This behavior of the hydrodynamic radii was also reported by many authors [\[26, 27\]](#).

Table 6. The Walden products ($\Lambda \cdot \eta$) of sodium and potassium salts at different temperature in the used solvents

solvent	%	T/K	NaCl	KCl	HCOOK	CH ₃ COOK
MeOH-H ₂ O	10 %	293.15	89.79	100.49	110.612	89.13
		298.15	89.14	99.63	109.82	88.23
		303.15	83.27	91.30	97.21	88.22
		308.15	77.61	83.75	86.54	86.37
	20 %	293.15	68.23	82.70	79.51	73.96
		298.15	66.80	81.10	78.06	73.52
		303.15	64.97	78.71	73.47	72.67
		308.15	62.14	75.93	72.25	72.39
	30 %	293.15	62.63	69.81	72.06	64.73
		298.15	61.76	67.02	70.08	63.24
		303.15	59.23	66.76	68.69	61.86
		308.15	55.90	63.54	66.69	61.21
GlyOH-H ₂ O	10 %	293.15	112.43	158.57	137.26	122.20
		298.15	110.91	136.23	128.11	114.93
		303.15	92.44	112.14	120.92	105.06
		308.15	77.20	85.06	91.81	87.45
	20%	293.15	116.45	156.50	135.17	141.25
		298.15	113.96	149.99	123.61	125.75

		303.15	98.11	128.44	119.40	116.62
		308.15	76.67	98.47	97.66	104.35
	30 %	293.15	138.26	187.52	135.16	186.02
		298.15	133.01	178.54	125.26	170.01
		303.15	111.06	170.76	117.67	147.76
EtOH-H ₂ O		308.15	78.17	117.34	89.09	107.61
	10 %	293.15	125.51	151.66	135.66	124.67
		298.15	122.35	144.40	131.65	108.37
		303.15	101.81	120.75	122.60	94.87
		308.15	76.92	90.16	95.61	79.64
	20%	293.15	136.76	164.20	118.74	149.735
		298.15	130.03	153.18	115.77	135.791
		303.15	108.41	128.47	113.41	109.723
		308.15	76.37	91.26	101.58	77.475
	30 %	293.15	117.84	165.94	142.47	164.32
		298.15	112.53	151.34	127.51	151.23
		303.15	105.98	125.43	124.65	119.85
		308.15	78.62	83.35	113.41	81.91

Table 7. The hydrodynamic radii ($R_H \times 10^{-2}$, nm) of sodium and potassium salts at different temperature in the used solvents

solvent	%	T/K	NaCl	KCl	HCOOK	CH ₃ COOK	
MeOH-H ₂ O	10 %	293.15	0.91	0.82	0.74	0.92	
		298.15	0.92	0.82	0.75	0.93	
		303.15	0.98	0.90	0.84	0.93	
		308.15	1.06	0.98	0.95	0.95	
	20 %	293.15	1.20	0.99	1.03	1.11	
		298.15	1.23	1.01	1.05	1.12	
		303.15	1.26	1.04	1.12	1.13	
		308.15	1.32	1.08	1.13	1.13	
	30 %	293.15	1.31	1.17	1.14	1.27	
		298.15	1.33	1.22	1.17	1.30	
		303.15	1.38	1.23	1.19	1.33	
		308.15	1.47	1.29	1.23	1.34	
	GlyOH-H ₂ O	10 %	293.15	0.73	0.52	0.60	0.67
			298.15	0.74	0.60	0.64	0.71
			303.15	0.89	0.73	0.68	0.78
			308.15	1.06	0.96	0.89	0.94
20%		293.15	0.70	0.52	0.61	0.58	
		298.15	0.72	0.55	0.66	0.65	
		303.15	0.84	0.64	0.69	0.70	
		308.15	1.07	0.83	0.84	0.79	
30 %		293.15	0.59	0.44	0.61	0.44	
		298.15	0.62	0.46	0.65	0.48	
		303.15	0.74	0.48	0.70	0.55	
		308.15	1.05	0.70	0.92	0.76	

EtOH-H ₂ O	10 %	293.15	0.65	0.54	0.60	0.66
		298.15	0.67	0.57	0.62	0.76
		303.15	0.81	0.68	0.67	0.86
		308.15	1.07	0.91	0.86	1.03
	20%	293.15	0.60	0.50	0.69	0.55
		298.15	0.63	0.54	0.71	0.60
		303.15	0.76	0.64	0.72	0.75
		308.15	1.07	0.90	0.81	1.06
	30 %	293.15	0.70	0.49	0.58	0.50
		298.15	0.73	0.54	0.64	0.54
		303.15	0.77	0.65	0.66	0.68
		308.15	1.04	0.98	0.72	1.00

Activation Energy of the Transfer Process

Since the conductance of an ion depends on its mobility, it is quite reasonable to treat the rate process taking place with change of temperature on the basis of Equation (11);

$$A_0 = A e^{-Ea/RT} \tag{11}$$

Where A is the frequency factor, R is the gas constant and Ea is the Arrhenius activation energy of the transfer process. From the plot of (ln A₀) vs. (1/T), the Ea values can be evaluated. The values of Arrhenius activation energy of the transfer process of the studied salts in the used solvents are presented in Table 8. The behavior of activation energy change is inverse that of Λ₀. On the other hand there is no definite order of the activation energy of transfer of the studied ammonium and sodium salts, which may be due to the effect of many interfered factors on the association processes and so on the activation energy of transfer. The observed behavior of change in activation energy of transfer was also reported by many authors [27, 42].

Table 8: The activation energy of transfer (Ea, kJ/mol) for sodium and potassium salts in the used solvents

Solvent % (w/w)		NaCl	KCl	HCOOK	CH ₃ COOK
MeOH-H ₂ O	10 %	5.042	6.023	3.356	9.130
	20 %	7.619	7.429	7.143	9.191
	30 %	7.702	7.861	7.959	9.607
GlyOH-H ₂ O	10 %	8.700	9.365	9.229	10.536
	20 %	9.690	9.883	12.728	10.831
	30 %	9.871	17.991	12.992	10.982

EtOH-H ₂ O	10 %	3.213	8.911	13.393	7.505
	20 %	8.684	9.750	18.888	7.778
	30 %	11.670	10.634	19.288	8.888

CONCLUSION

We can conclude that, the extent of ion-pairing in salt solutions under study depends upon the nature of the ion-solvent interaction taking place in the solution. Moreover it depends on the dielectric constant and the properties of the medium. The association increase as the temperature increase and as the proportion of organic solvent increase. Also, it was found that the predominant order of the association constant are in GlyOH-H₂O > in MeOH-H₂O > in EtOH-H₂O and potassium acetate > potassium chloride > potassium formate > sodium chloride. Comparing the association constants of ammonium and sodium salts with other ammonium and sodium salts in literatures we can note that there is no definite order for formate, oxalate, acetate, propionate, salicylate and benzoate, but it was found that oxalate salts have the highest association constant. This indefinite order of the studied salts may be related to the ability of each system to form intramolecular and intermolecular hydrogen bonds.

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