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Dissociation Constant of Quinic Acid and Association Constants of Some Quinates in Aqueous and in Alcoholic−Aqueous Mixed Solvents

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The dissociation constant of D-(−)-quinic acid {(1*R*,3*R*,4*S*,5*R*)-(−)-1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid} was determined potentiometrically and conductometrically in aqueous, 50 % (v/v) methanol−water, and 50 % (v/v) ethanol−water mixtures at (293.15, 298.15, 303.15, and 308.15) K. In addition, the association constants of lithium, sodium, and potassium salts of quinic acid were determined conductometrically in the same solvents and at the same temperatures. The conductivity data have been analyzed using both the Lee−Wheaton and Shedlovesky conductivity equations. The molar conductance (Λ), limiting molar conductance (Λ_0), limiting ionic molar conductance ($\lambda_{\pm}^{0}$), diffusion coefficients (D_0), ionic mobility ($u_{\pm}$), and transfer numbers of the studied ions ($t_{\pm}$) were calculated and discussed. The association constants (K_A), Walden products ($\Lambda_0\eta_0$ and $\lambda_0\eta_0$), hydrodynamic radii (R_H), fluidity ratio (R), the activation energy of the transport process (E_a), and the standard thermodynamic parameters of association and dissociation ($\Delta G°$, $\Delta H°$, and $\Delta S°$) were also calculated and discussed in terms of solute−solvent interactions. The effect of hydrogen bonds, relative permittivity, and temperature on the transport properties and the dissociation and the association behavior has been studied and discussed. The results show that the dissociation constant, the molar conductance, and the limiting molar conductance decrease as the relative permittivity of the solvent decreased and as the viscosity of the solvent increased. On the other hand, the association constant was found to increase as the relative permittivity of the solvent decreased and as the viscosity of the solvent increased. In addition, the results show that the molar conductance, the limiting molar conductance, and the dissociation and the association constant values increased as the temperature increased, which indicates that the association and the dissociation processes are endothermic. Also, it was found that the predominant order of the association constant values for all studied systems at the same temperature is in the following order with some exceptions: EtOH−H_2O > MeOH−H_2O > H_2O. This order reverses to that observed for Λ_0 values which can interpreted on the basis of the effect of hydrogen bonding and the relative permittivity which plays an important role in changing the association process.

Introduction

Quinic acid is a biogenetic precursor of shikimic acid, which is involved in the biosynthesis of many natural products.[1] It is a white crystalline compound soluble in water, alcohol, and glacial acetic acid but insoluble in ether. The acid is widespread in the plant kingdom, free or as esters,[1] such as in cinchona bark, coffee beans, leaves of tobacco, and carrot. Also, the acid is predominant among the metabolites originating from D-glucose.[2] The acid has five functional groups that can coordinate with metal cations,[3] can yield various kinds of salts, and is an important starting material for the asymmetric multistep synthesis of many natural products and other compounds.[4] Quinic acid is widely used as a chiral building block for the synthesis of pharmaceuticals. An example of an end product is the antiviral drug oseltamivir, a neuraminidase inhibitor used in the treatment and prophylaxis of both influenza A and influenza B. The ion−ion and ion−solvent interactions or the behavior of the electrolytes in solution can be informative depending on the transport properties (conductivity, transference number, diffusion coefficient, and ionic mobility) of these electrolytes in solutions.[5−11]

Because of the importance of quinic acid and in continuation of my previous paper[12] on electrolytic conductance, the present study aims to study the ion−ion and the ion−solvent interactions of quinic acid and some of its salts in different media. The study of the ion−ion and the ion−solvent interactions can be achieved from the determination of the dissociation constant of quinic acid and the association constant of its Li, Na, and K salts in aqueous and in 50 % (v/v) alcoholic−aqueous (mole fraction of alcohol, $x = 0.5$) mixed solvents at different temperatures [(293.15, 298.15, 303.15, and 308.15) K]. In addition, the study aims to estimate and discuss the molar conductance (Λ), limiting molar conductance (Λ_0), limiting ionic molar conductance ($\lambda_{\pm}^{0}$), diffusion coefficients (D_0), ionic mobility ($u_{\pm}$), and transfer numbers of the studied ions ($t_{\pm}$). The association constants (K_a), Walden products ($\Lambda_0\eta_0$ and $\lambda_0\eta_0$), hydrodynamic radii (R_H), fluidity ratio (R), the activation energy of the transport process (E_a), and standard thermodynamic parameters of association and dissociation ($\Delta G°$, $\Delta H°$, and $\Delta S°$) were also calculated and discussed.

In addition, the present article aims to study the effect of relative permittivity, viscosity, temperature, and hydrogen bonding on each of the dissociation and the association phenomena and on the transport properties of some 1:1 electrolytes through re-examination of the mathematics of two

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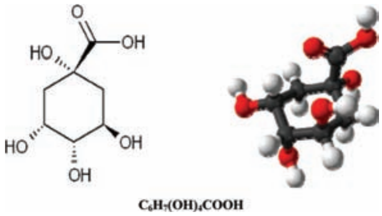
Scheme 1



conductance theories: the Lee−Wheaton and Shedlovesky conductivity equations.

Experimental Section

Materials. D-(−)-Quinic acid {(1*R*,3*R*,4*S*,5*R*)-(−)-1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid}, CAS No. 77-95-2 (Scheme 1) (99.9 %), was supplied by Sigma. Lithium, sodium, and potassium salts of quinic acid were prepared by neutralization of the acid with lithium, sodium, and potassium hydroxides, respectively. The prepared salts were tested using both acid−base titration and elemental analysis. The purity of the prepared monohydrate salts was found to be 99.5 %. Water, with a specific conductance of 0.06 μs·cm^{-1} at 298.15 K, was used as a solvent and for preparation of the mixed solvents. All other chemicals used in this study were either of analytical reagent grade or purified using the recommended methods.[13]

Solutions. Mixed solvents, $x = 0.5$, of methanol−water and ethanol−water were prepared. Many solutions of the quinic acid and its salts under investigation with a concentration range of $(0.2 \cdot 10^{-3}$ to $50.0 \cdot 10^{-3})$ mol·dm^{-3} were prepared in the previously prepared mixed solvents and in pure aqueous media. A solution (0.001 M) of quinic acid, HCl (0.01 M), and KCl (1 M) was prepared in the selected solvents. Carbonate free KOH solution (0.004 M) in the selected solvents was standardized against Analar oxalic acid and used as a titrant.

For the pH measurements, the following mixtures were prepared and titrated potentiometrically two times against standard 0.004 M KOH at (293.15, 298.15, 303.15, and 308.15) K: (i) 1 mL of 0.01 M HCl + 1 mL of 1 M KCl + 5 mL ethanol or methanol, and (ii) 1 mL of 0.01 M HCl + 1 mL of 1 M KCl + 1 mL of 0.001 M quinic acid + 5 mL ethanol or methanol. The pH values were accurate to ± 0.01 pH units.

For each mixture, the volume was made of up to 10 mL of double-distilled water before titration. The same measurements were carried out in aqueous media at the same selected temperatures.

Apparatus. The conductance measurements were carried out for the prepared solutions using a conductivity meter (Jenway 4310). The uncertainty of the conductivity meter is ± 0.1 μS·cm^{-1}. The conductivity bridge was calibrated using a standard solution of KCl to determine the cell constant of the bridge.

The pH measurements were carried out using a pH meter (Mettler Toledo MP 220). The pH was standardized using buffer solutions: pH 7, 4, and 10 containing the same concentration of KCl and wt % methanol. The uncertainty of pH measurements is (± 0.05). Both the pH meter and the conductivity bridge were connected to an Ultrathermostate (type MLW prufgerate-werk) to maintain the proper constant temperature (± 0.05 °C).

Results and Discussion

The physical properties, density (ρ),[14] viscosity (η_0),[15] and relative permittivity (ε)[16,17] of the solvents used at (293.15, 298.15, 303.15, and 308.15) K have been tabulated in Table 1.

Table 1. Relative Permittivity (ε),[16,17] Density (ρ/g·cm^{-3}),[14] and Viscosity (η/cP)[15] of the Used Solvents at Different Temperatures

solvent	property	T/K			
		293.15	298.15	303.15	308.15
water	ε	80.56	78.30	76.21	74.30
	ρ	0.9997	0.9971	0.9942	0.9912
	η	0.8912	0.8903	0.8890	0.8880
50 % (v/v)	ε	58.25	56.30	54.75	52.40
MeOH−H$_2$O	ρ	0.9241	0.9119	0.8990	0.8867
	η	0.7185	0.7174	0.7161	0.7155
50 % (v/v)	ε	53.92	51.90	50.01	48.63
EtOH−H$_2$O	ρ	0.8945	0.8920	0.8900	0.8880
	η	0.9905	0.9895	0.9886	0.9875

1. Potentiometric Studies. Potentiometric (pH) measurements were carried out as explained in the experimental section for quinic acid in aqueous, $x = 0.5$ methanol−water, and $x = 0.5$ ethanol−water mixtures at (293.15, 298.15, 303.15, and 308.15) K. A plot of pH values versus the amount added of KOH solution (mL) is shown in Figure 1.

These curves show that the ionization of quinic acid takes place in the alkaline region starting at pH ∼ 8. The number of protons associated with the quinic acid molecule n_A were determined[18] by applying eq 1:

$$n_A = Y \pm \{(V_1 - V_2)/(V_1 + V°)\}\{(N° + E°)/C°\} \tag{1}$$

where Y is the total number of protons, which are expected to be ionized from the acid, $V°$ is the initial volume of the mixtures, V_1 and V_2 are the volumes of alkali required to reach the same pH in the titration curves of hydrochloric acid and quinic acid, respectively, $C°$ is the total concentration of quinic acid, $N°$ is the normality of potassium hydroxide solution, and $E°$ is the initial concentration of free acid (HCl). The maximum n_A values measured in case of quinic acid in the selected solvents at different temperatures has been found to be ∼ 0.9, revealing that the quinic acid molecule has one dissociable proton (hydrogen ion of the carboxyl group). The values of the ionization constants (pK_d) are obtained from the interpolation at half n_A method[19] where the values of pK_d are the values of pH at n_A equals 0.5 in a plot of pH against n_A. The value of pK_d was also refined with the nonlinear least-squares computer program ESAB2M.[20]

2. Conductometric Studies. 2i. Dissociation Constant of Quinic Acid. The specific conductance of different concentrations of quinic acid with a concentration range of $(0.2 \cdot 10^{-3}$ to $50.0 \cdot 10^{-3})$ mol·dm^{-3}], in aqueous, $x = 0.5$ methanol−water, and $x = 0.5$ ethanol−water mixtures at (293.15, 298.15, 303.15, and 308.15) K were measured experimentally. Using the

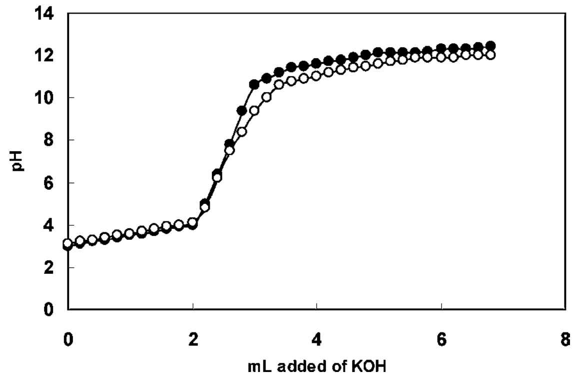


Figure 1. Potentiometric titration curve for quinic acid (○) compared to that of HCl (●) in aqueous solution at 298 K.

Table 2. Molar Conductance (Λ/S·mol^{-1}·cm^2) of Quinic Acid in the Used Solvents at Different Temperatures

$C\cdot10^3$	water				50 % (v/v) MeOH−H$_2$O				50 % (v/v) EtOH−H$_2$O			
mol·dm^{-3}	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.2	210.3	227.7	244.5	262.1	152.3	164.6	177.3	189.9	141.7	153.4	165.1	176.8
0.4	180.1	200.6	220.5	240.1	130.5	144.7	159.2	174.1	121.5	135.1	148.5	162.1
0.6	160.1	180.4	200.1	220.6	117.6	131.2	145.2	159.5	108.1	121.7	135.2	148.8
0.8	152.2	168.9	184.7	200.3	110.2	121.7	133.3	145.1	102.7	113.5	124.1	135.1
1.0	143.1	156.2	167.8	180.5	103.7	112.7	121.7	130.9	96.52	104.8	113.1	121.5
1.5	120.2	130.3	139.5	150.1	87.01	94.25	101.2	108.7	81.01	87.75	94.53	101.3
2.0	109.3	118.6	128.1	136.1	79.03	85.54	92.11	98.61	73.58	79.58	85.51	91.82
3.0	87.14	94.62	101.4	109.2	63.08	68.29	73.58	79.03	58.79	63.72	68.69	73.58
5.0	70.83	76.93	84.61	90.09	51.33	55.75	61.71	65.25	47.81	52.13	56.31	60.75
8.0	56.38	61.43	68.07	73.37	40.61	44.89	49.21	52.93	38.01	41.83	45.63	49.46
12	48.31	52.42	59.34	62.25	34.82	38.19	41.61	45.01	32.63	35.68	38.61	41.85
17	41.01	47.14	50.22	53.53	29.73	32.69	35.71	38.79	27.69	30.51	33.31	36.11
22	36.18	39.36	42.82	46.01	26.11	28.45	30.91	33.35	24.37	26.55	28.75	31.01
26	33.65	38.06	41.02	44.05	24.35	26.83	29.33	31.95	22.65	24.96	27.27	29.71
30	31.63	35.01	38.03	40.76	22.91	25.11	27.31	29.51	21.31	23.35	25.37	27.47
35	31.02	33.91	36.81	38.71	22.51	24.34	26.16	28.06	20.91	22.71	24.41	26.12
40	28.18	30.89	33.73	35.21	20.33	22.09	23.81	25.52	18.91	20.47	21.96	23.64
45	26.53	28.99	31.02	33.11	19.21	20.58	22.21	23.98	17.81	19.29	20.79	22.27
50	25.01	27.55	29.12	30.56	18.13	19.41	20.79	22.17	16.83	18.06	19.58	20.58

measured specific conductance, the molar conductance (Λ) for quinic acid in different solvents and at different temperatures was calculated and is recorded in Table 2.

The change in the molar conductance of the aqueous solution of quinic acid as a function of the molar concentration at different temperatures is shown in Figure 2. Quinic acid is a weak acid dissociate in dilute solution as represented by the following equation:

$$\mathrm{HQ} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{Q^-} \tag{2}$$

The dissociation constant of quinic acid (K_d) can be given by the Shedlovsky[21] equation:

$$\frac{1}{\Lambda\, S(z)} = \frac{1}{\Lambda_0} + \frac{K_a C\Lambda\, S(z)\, \gamma_i^{\,2}}{\Lambda_0^{\,2}} \tag{3}$$

From eq 3, the dissociation constant, K_d, of the acid can be calculated from the reciprocal of the association constant, K_a. Λ_0 is the limiting molar conductance of the acid, which can be calculated from the Kohlorausch law for independent migration of ions at infinite dilution, where the values of $\lambda°_{H^+}$ in aqueous solution are from ref 22 and $\lambda°_{H^+}$ in $x = 0.5$ methanol−water and in $x = 0.5$ ethanol−water mixtures at (293.15, 298.15, 303.15, and 308.15) K were determined from the experimental determination of the limiting molar conductance of HCl and NaCl and by knowing the $\lambda°_{Na^+}$ from ref 12 in the same solvents.

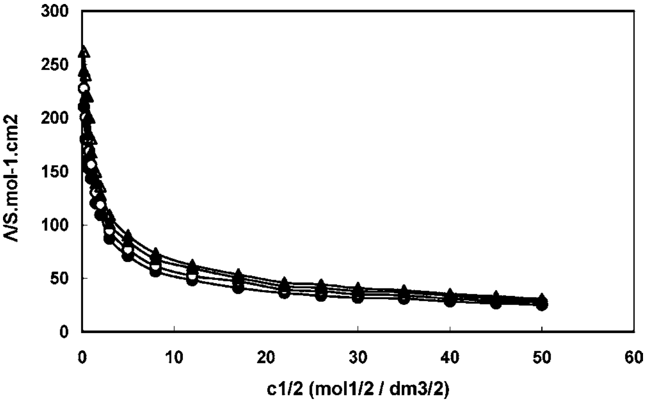


Figure 2. Λ of quinic acid as a function C in aqueous solution at different temperatures (●, for 293 K; ○, for 298 K; ▲, for 303 K; and △, for 308 K).

$S(z)$ is the Shedlovsky function, which can be calculated as follows:

$$S(z) = \left(\frac{Z}{2} + \sqrt{1 + (Z/2)^2}\right)^2 \qquad z = A\frac{\sqrt{C\Lambda}}{\Lambda_0^{\,3/2}} \tag{4}$$

A is the Onsager coefficient and is equal to $(8.2\cdot10^5)\Lambda_0/(\varepsilon T)^{3/2} + (82/\eta_0)(\varepsilon T)^{1/2}$, where ε is the relative permittivity, η_0 is the viscosity of the solvent, and T is the absolute temperature. γ_i is the mean activity coefficient estimated from the Debye−Huckel limiting law as modified by Robinson and Stokes.

The dissociation constant of quinic acid was also determined by applying the Lee−Wheaton[23] conductivity equation in the form of Pethybridge and Taba[24] (from eqs 5 to 11):

$$\Lambda_{\mathrm{calc}} = \alpha\Lambda_i \tag{5}$$

$$\Lambda_i = \Lambda°[1 + C_1(\beta k) + C_2(\beta k)^2 + C_3(\beta k)^3] - [sk/(1 + kd)][1 + C_4(\beta k) + C_5(\beta k)^2 + (kd/12)] \tag{6}$$

$$\beta = (z^2e^2)/(\varepsilon°\varepsilon k_B T) \tag{7}$$

$$k = [(8nN_A e^2 z^2 \alpha c)/(1000\varepsilon°\varepsilon k_B T)]^{1/2} \tag{8}$$

$$s = (F\xi ez)/(3nn°) \tag{9}$$

$$K_a = (1 - \alpha)/(\alpha^2\gamma_\pm^{\,2} c) \tag{10}$$

$$\gamma_\pm^{\,2} = \exp[(-\beta k)/(1 + kd)] \tag{11}$$

where C_1 to C_5 are functions of the product kd and are given in ref 24. K_a is the thermodynamic ion-pair association constant for the equilibrium. α is the degree of dissociation, c the electrolyte concentration, and $\gamma_\pm$ the mean ion activity coefficient of the dissociated species (the activity coefficient for nonconducting species is assumed to be 1). e is the electronic charge, z the ion charge, $\varepsilon°$ the permittivity of a vacuum, ε the relative permittivity of the solvent, $\eta°$ the viscosity of the solvent, F the Faraday constant, k_B the Boltzmann's constant, N_A Avogadro's number, T the absolute temperature, and the symbol ξ equal to (1/299.79). The parameter d represents the center-to-center distance of the formed ion pairs, which is equal to 5 Å where it equals $(1/2)(d_{H^+} + d_{Q^-})$, $d_{Q^-} = 5$ Å,[25] and $d_{H^+} = 5$ Å.[26] Beyond this distance, the ions had been considered not to be associated. The computations for calculating the limiting molar conductance (Λ_0) and the association constant

Table 3. Dissociation Constant Exponent (pK_a ± 0.0030 to 0.0034) and the Standard Thermodynamics of Dissociation (Determined pH Metrically and Conductometrically) for Quinic Acid in the Used Solvents at Different Temperatures

solvent	T / K	pK_d (pot.)	pK_d (cond.)	pK_d (mean)	$+\Delta G°_d$ / $kJ \cdot mol^{-1}$	$+\Delta H°_d$ / $kJ \cdot mol^{-1}$	$-\Delta S°_d$ / $kJ \cdot mol^{-1} \cdot K^{-1}$
water	293.15	3.5720	3.5739	3.5729	20.0240	1.2001	0.0642
	298.15	3.5700	3.5690	3.5695	20.3466		
	303.15	3.5662	3.5645	3.5653	20.6639		
	308.15	3.5618	3.5635	3.5626	20.9890		
50 % (v/v) MeOH−H_2O	293.15	4.9293	4.9320	4.9306	27.6337	5.3424	0.0759
	298.15	4.8905	4.8899	4.8302	27.8747		
	303.15	4.8870	4.8840	4.8855	28.3152		
	308.15	4.8796	4.8809	4.8803	28.7515		
50 % (v/v) EtOH−H_2O	293.15	5.3209	5.3265	5.3237	29.8366	5.4812	0.0829
	298.15	5.2835	5.2820	5.2827	30.1123		
	303.15	5.2779	5.2749	5.2764	30.5808		
	308.15	5.2709	5.2741	5.2725	31.0624		

Table 4. Molar Conductance ($\Lambda/S \cdot mol^{-1} \cdot cm^2$) of the Studied Quinic Acid Salts at Different Temperatures in Aqueous Solution

$C \cdot 10^3$	LiQ				NaQ				KQ			
$mol \cdot dm^{-3}$	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.5	55.51	61.80	66.80	74.80	64.80	73.40	81.20	90.20	91.60	96.40	102.8	109.6
1.0	54.53	61.60	66.60	74.60	64.60	72.80	81.20	90.10	90.50	96.10	102.4	109.4
1.5	54.38	61.40	66.40	74.40	64.40	72.40	80.80	89.80	89.20	95.60	102.2	109.2
2.0	54.00	61.10	66.20	74.20	64.10	72.20	80.60	89.60	88.60	95.40	102.1	109.1
4.0	52.79	59.60	65.80	74.00	63.81	69.40	79.20	88.60	87.50	95.20	101.8	108.6
8.0	50.29	58.32	65.60	73.10	61.35	69.20	77.50	85.50	85.36	93.39	101.5	108.2
12	48.63	56.61	64.59	71.50	59.81	67.75	75.64	83.61	83.84	91.72	99.59	107.7
15	48.17	56.10	63.73	71.20	59.20	67.04	74.81	82.70	83.09	91.10	98.75	106.6
20	47.09	54.78	62.58	69.60	58.21	65.90	73.64	81.36	82.19	89.82	97.59	105.4
25	46.22	53.53	61.25	68.49	57.18	64.63	72.17	79.63	81.21	88.58	96.23	103.5
30	45.11	52.09	59.51	67.19	56.15	63.03	70.63	78.22	80.11	87.10	94.57	102.3
35	44.11	51.15	58.39	65.81	55.09	62.04	69.45	76.78	79.10	86.10	93.39	100.8
40	42.78	49.90	56.81	64.10	53.83	60.85	67.9	75.09	77.75	84.79	91.73	99.19

(K_a) were performed on a computer using the program of successive approximations following the three-parameter optimization as suggested by Pethybridge and Taba.[24]

The initial Λ_0 values for the procedure were obtained from the Onsager equation.[27] The calculations have been made by finding the values of Λ_0 and $K_a = 1/K_d$ after obtaining the minimal standard deviation (σ) between calculated (Λ_{calc}) and experimental (Λ_{exp}) conductivity values. The derived values of the limiting molar conductance (Λ_0) for quinic acid and its ions in the solvents used at different temperatures are reported in Table 6.

The values of the dissociation constant exponent (pK_d) of quinic acid obtained from both the potentiometric and the conductometric measurements are given in Table 3. The values of the dissociation constant of quinic acid ($K_d = 1/K_a$) were found to decrease as the relative permittivity of the solvent decreases and increase as the temperature increases. The values of pK_a are comparable to those obtained potentiometrically in the literature in water at 298.15 K (3.58).[28] The lower values of pK_a for quinic acid were also reported for some other α-hydroxycarboxylic acids such as tartaric acid (3.031) and citric acid (3.154).[29]

The standard free energy ($\Delta G°_d$), the standard enthalpy ($\Delta H°_d$) and the standard entropy ($\Delta S°_d$) of quinic acid dissociation were calculated and reported in Table 3.

The positive $\Delta G°_d$ values indicate that the dissociation processes in all studied systems were nonspontaneous processes. The positive value of $\Delta H°_d$ indicates the endothermic nature of the dissociation processes. The relatively small and negative value of ($\Delta S°_d$) can be explained depending on the solvation effect, where the dissociation process is generally characterized by a decrease in the entropy as a result of the solute−solvent interaction. In such processes, solvation of the free ions due to ion−solvent interactions, together with hydrogen bonding between the solvent molecule and the ions, binds solvent molecules strongly to neighboring ions.

2ii. Association Constant of Quinic Acid Salts. The specific conductance of different concentrations of the lithium, sodium, and potassium salts of quinic acid were measured experimentally in aqueous, $x = 0.5$ methanol−water, and $x = 0.5$ ethanol−water mixtures at (293.15, 298.15, 303.15, and 308.15) K. The molar conductances of the studied salts were calculated from the measured specific conductance and are tabulated in Tables 4 to 6, and some are shown in Figures 3 to 5.

The conductance data were analyzed by applying both the Shedlovesky[21] and the Lee−Wheaton[23] conductivity equation in the form of Pethybridge and Taba[24] equations as discussed in the case of quinic acid. In this case the calculations have been made by finding the values of Λ_0, K_a, and d after obtaining the minimum standard deviation (σ) between the calculated (Λ_{calc}) and the experimental (Λ_{exp}) conductivity values for a sequence of d values. The suitable value for the distance parameter d corresponds to the minimum of a plot σ versus d. The value of the distance d which has been selected for the computations ranged from 3 Å (the sum of the crystallographic radii of the ions) to the maximum value of 20 Å.

The limiting molar conductance (Λ_0) determined and the limiting ionic molar conductance ($\lambda°$) are recorded in Table 7. The limiting molar conductance and the limiting ionic molar conductance are lower in ethanol−H_2O solvent compared to methanol−H_2O and water solvents according to the following order: H_2O > methanol−H_2O > ethanol−H_2O. This may be related to the higher intramolecular hydrogen bonding and higher viscosity of ethanol than that of methanol or water. Also, it can be related to the higher relative permittivity of H_2O and MeOH−H_2O compared to that of EtOH−H_2O.

Table 5. Molar Conductance (Λ/S·mol^{-1}·cm^2) of the Studied Quinic Acid Salts at Different Temperatures in 50 % (v/v) (MeOH−H$_2$O) Solvent

$C \cdot 10^3$	LiQ				NaQ				KQ			
mol·dm^{-3}	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.5	36.25	42.78	49.38	56.21	47.20	53.81	60.43	67.01	71.18	77.73	84.52	91.19
1.0	35.59	42.20	48.65	55.30	46.61	53.16	59.73	66.29	70.59	77.21	83.60	90.31
1.5	35.21	41.79	48.21	54.59	46.39	52.83	59.23	65.61	70.31	76.85	83.20	89.59
2.0	35.01	41.38	47.79	54.41	46.10	52.42	58.81	65.39	70.01	76.51	82.75	89.41
4.0	34.02	40.71	47.31	54.01	45.01	51.61	58.27	65.03	69.03	75.75	82.19	89.11
8.0	31.49	37.91	44.19	50.55	42.54	48.84	55.13	61.51	66.61	72.72	79.19	85.49
12	30.11	36.19	42.41	48.43	41.01	47.17	53.37	59.52	63.52	71.22	77.41	83.51
15	29.39	35.39	41.38	47.51	40.41	46.41	52.41	58.49	64.39	70.39	76.50	82.45
20	28.41	34.31	40.31	46.11	39.38	45.27	51.28	57.08	63.45	69.35	75.33	81.11
25	27.19	32.78	38.40	44.20	38.22	43.85	49.44	55.11	62.31	67.93	73.51	79.20
30	26.21	31.60	37.21	42.59	37.19	42.65	48.16	53.6	61.29	66.59	72.21	77.51
35	25.10	30.51	35.71	41.31	36.09	41.49	46.89	52.29	60.01	65.56	70.91	76.35
40	23.79	29.15	34.39	39.83	34.88	40.15	45.45	50.71	58.61	64.21	69.43	74.92

Table 6. Molar Conductance (Λ/S·mol^{-1}·cm^2) of the Studied Quinic Acid Salts at Different Temperatures in 50 % (v/v) (EtOH−H$_2$O) Solvent

$C \cdot 10^3$	LiQ				NaQ				KQ			
mol·dm^{-3}	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.5	32.78	38.82	44.81	51.15	43.88	49.91	55.92	62.01	67.81	73.82	79.95	86.03
1.0	31.55	37.9	44.00	50.18	42.79	48.93	55.05	61.21	66.79	72.81	79.15	85.25
1.5	31.31	37.45	43.48	49.55	42.55	48.56	54.57	60.61	66.45	72.64	78.45	84.58
2.0	30.75	37.19	43.15	49.32	42.11	48.21	54.19	60.43	66.09	72.19	78.11	84.45
4.0	29.82	35.79	41.71	47.59	40.92	46.81	52.69	58.62	64.83	70.79	76.58	82.59
8.0	27.39	32.81	38.62	44.2	38.41	43.88	49.59	55.15	62.39	67.81	73.51	79.29
12	26.13	31.38	36.75	42.21	37.03	42.41	47.81	53.23	62.01	66.36	71.69	77.31
15	25.36	30.59	35.81	41.09	36.45	41.68	46.91	52.15	60.36	65.51	70.53	76.23
20	24.19	29.48	34.58	39.69	35.39	40.51	45.62	50.73	59.41	64.48	69.65	74.81
25	23.41	28.18	33.11	37.81	34.40	39.23	44.02	48.98	58.38	63.21	68.15	72.89
30	22.42	27.01	31.65	36.48	33.37	38.01	42.71	47.51	57.41	62.01	66.75	71.48
35	21.31	25.79	30.43	35.15	32.34	36.89	41.53	46.12	56.29	60.75	65.62	70.19
40	20.01	24.29	28.85	33.29	30.81	35.33	39.79	44.32	54.81	59.29	63.81	68.39

The limiting molar conductance of the studied salts in the experimental conditions is in the following order: LiQ < NaQ < KQ < HQ and Q$^-$ < Li$^+$< Na$^+$ < K$^+$ < H$^+$, which can be related to higher ionic mobility. The lower value of the limiting ionic molar conductance ($\lambda°$) for Q$^-$ may be related to the intramolecular hydrogen bonding in Q$^-$ and the intermolecular hydrogen bonding with the alcohol and water molecules.

The association constant (K_a) of the studied salts was evaluated using the Shedlovesky method, eq 3, where the following equilibrium was suggested:

$$Q^- + M^+ \rightleftarrows MQ \tag{12}$$

where M$^+$ = Li$^+$, Na$^+$, and K$^+$. The values of K_a for the studied salts in the used solvents at the selected temperatures are listed in Table 8.

During the inspection of the values of K_a, it was noted that the association constant for all studied salts in the used solvents increases as the temperature increases indicating an endothermic association process. Also, it was found that the predominant order of the association constant values for all studied systems at the same temperature are in the following order with some exceptions: EtOH−H$_2$O > MeOH−H$_2$O > H$_2$O. An inverse order was observed for (Λ_0) values which can interpreted on the basis of the effect of hydrogen bond and the relative permittivity which play an important role in changing the association process.[30] In comparing the association constant values for the studied salts in the same experimental conditions, we can note the following order: LiQ > NaQ > KQ. This order may be related to the higher size in the order Li$^+$ < Na$^+$ < K$^+$.

Plotting of ln K_a versus the reciprocal relative permittivity ($1/\varepsilon$) (Figure 6), for all systems, gives a linear relationship. This linearity shows that the solvating molecules remain in the ion pairs in those cases where hydrogen bonds form the solvate cluster.[31] Also, this linearity is analogous to that predicted by the Fuoss equation[32] over a limited range of composition of

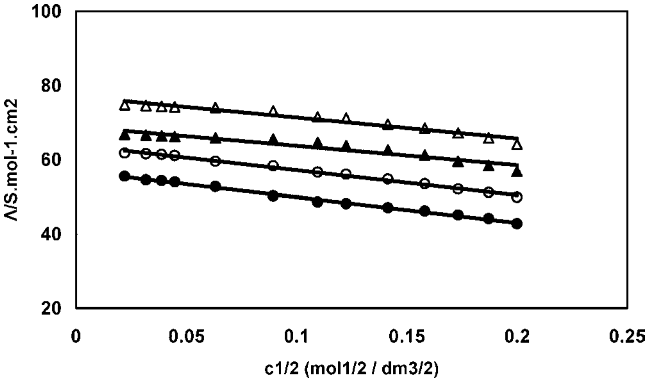


Figure 3. Λ versus $c^{1/2}$ of LiQ in aqueous medium at different temperatures (●, for 293 K; ○, for 298 K; ▲, for 303 K; and △, for 308 K).

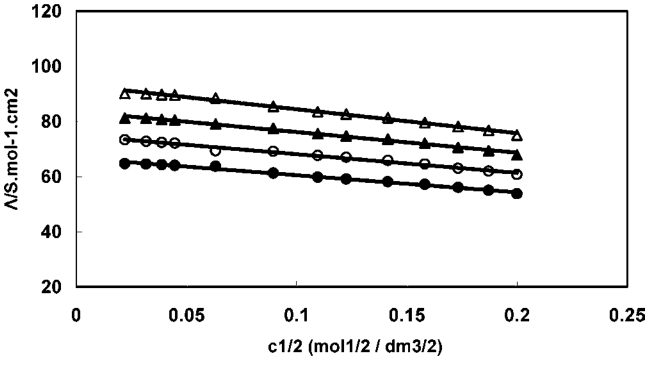


Figure 4. Λ versus $c^{1/2}$ of NaQ in aqueous medium at different temperatures (●, for 293 K; ○, for 298 K; ▲, for 303 K; and △, for 308 K).

Table 7. Limiting Molar Conductances of the Studied Salts (Λ_0/S·mol^{-1}·cm^2) and Ions ($\lambda°$/S·mol^{-1}·cm^2) in the Used Solvents at Different Temperatures

	T	Λ_0, ± 0.25 to 0.52				$\lambda°$				
solvent	K	LiQ	NaQ	KQ	HQ	Q^-	Li^+	Na^+	K^+	H^+
water	293.15	56.91	66.89	92.28	368.3	21.58	35.69	46.59	70.58	346.6
	298.15	63.91	74.95	98.49	374.5	24.63	38.71	50.11	73.52	349.8
	303.15	68.94	83.74	105.1	380.7	27.95	41.71	53.11	76.51	352.8
	308.15	77.03	93.14	111.9	387.5	31.39	45.21	56.22	80.18	356.2
50 % (v/v) MeOH−H_2O	293.15	37.91	48.91	72.84	267.5	15.56	22.35	33.35	57.28	251.9
	298.15	44.79	55.78	79.79	271.9	17.79	27.01	37.99	62.01	254.1
	303.15	52.32	62.64	86.61	275.8	20.22	32.11	42.42	66.39	255.6
	308.15	58.58	69.55	93.58	281.3	22.71	35.87	46.84	70.87	258.6
50 % (v/v) EtOH−H_2O	293.15	33.89	45.15	69.15	249.1	14.49	19.41	30.66	54.66	234.6
	298.15	40.51	51.56	75.52	252.6	16.65	23.95	34.91	58.87	235.9
	303.15	46.89	57.96	81.87	257.2	18.83	28.06	39.13	63.04	238.4
	308.15	53.43	64.43	88.45	261.9	21.25	32.18	43.18	67.21	240.7

Table 8. Association Constant (K_a/dm^3·mol^{-1}) and the Standard Free Energy Change ($\Delta G°_a$/kJ·mol^{-1}) of Association for the Studied Quinic Acid Salts in the Used Solvents at Different Temperatures

	T	K_a, ± 0.41 to 0.49			$-\Delta G°_a$		
solvent	K	LiQ	NaQ	KQ	LiQ	NaQ	KQ
water	293.15	9.89	7.65	5.04	5.578	4.953	3.937
	298.15	9.92	7.62	5.14	5.681	5.091	4.053
	303.15	9.97	7.86	5.19	5.788	5.189	4.145
	308.15	10.0	7.93	5.29	5.891	5.298	4.262
50 % (v/v) MeOH−H_2O	293.15	13.65	10.56	6.95	6.362	5.738	4.719
	298.15	13.70	10.78	7.10	6.480	5.886	4.852
	303.15	13.76	10.85	7.17	6.599	6.001	4.957
	308.15	13.81	10.93	7.31	6.717	6.119	5.089
50 % (v/v) EtOH−H_2O	293.15	14.84	11.48	7.55	6.565	5.940	4.920
	298.15	14.88	11.72	7.71	6.684	6.093	5.055
	303.15	14.96	11.78	7.78	6.809	6.209	5.164
	308.15	14.99	11.90	7.92	6.921	6.336	5.295

the solvent mixtures under study. The Fuoss equation can be written in the following form;

$$K_a = \frac{4\pi Na^3}{3000}\exp(|Z_+Z_-|e^2/a\varepsilon KT) \qquad (13)$$

This equation is composed of two factors, the pre-exponential term $K_a = [4\pi Na^3/3000]$, and the exponential term exp(B) with Bjerrum's ratio $B = (|Z_+Z_-|e^2/a\varepsilon T)$. From this equation, it was noted that ln K_a depends on $1/\varepsilon$ in a linear relationship (Figure 6).

In general, we can conclude that, the extent of ion pairing in the salt solutions under study depends on the nature of the ion−solvent interaction. Moreover, it depends on the relative permittivity and the properties of the medium,[33,34] which can be achieved or verified by a linear plot of ln K_a versus $1/\varepsilon$.

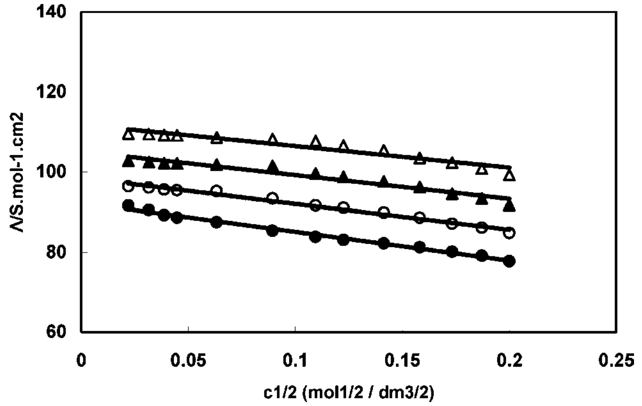


Figure 5. Λ versus $c^{1/2}$ of KQ in aqueous medium at different temperatures (●, for 293 K; ○, for 298 K; ▲, for 303 K; and △, for 308 K).

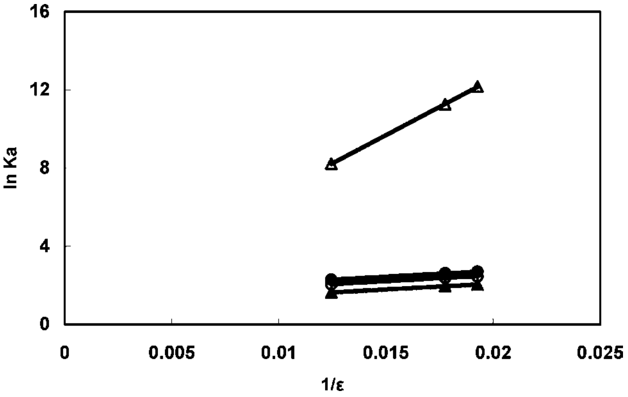


Figure 6. ln K_a versus $1/\varepsilon$ for quinic acid (△) and its salts (●, for LiQ; ○, for NaQ; and ▲, for KQ) at 298 K.

The standard thermodynamics of association ($\Delta G°_a$, $\Delta H°_a$, and $\Delta S°_a$) of quinic acid salts were also calculated and are presented in Tables 8 and 9. The negative $\Delta G°_a$ values indicate that the association processes in all studied systems were spontaneous processes. The positive value of $\Delta H°_a$ indicates the endothermic nature of the association processes. The positive $\Delta H°_a$ and $\Delta S°_a$ values are in a good agreement with several theories in many solvents.[35,36]

2iii. Triple Ion Association Constant. The triple ion association constant (K_3) for the investigated salts was calculated using the Fuoss equation.[37] The small values of K_3 (10^{-4} to 10^{-3}) for the salts indicates that the triple ion formation value can be neglected.

2iv. Walden Product and the Hydrodynamic Radii. The Walden products ($\Lambda_0\eta_0$ and $\lambda_0\eta_0$), which are informative from the point of view of ion−solvent interaction,[38] have a constant value because 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 products ($\Lambda_0\eta_0$ and $\lambda_0\eta_0$) are expected to be constant for a given electrolyte in a series of solvent mixtures in which the ion−solvent interactions are uniform. Walden[39] has formulated the rule (for 1:1 electrolytes) in the form of eq 14. The values of Walden product were calculated for the salts and ions under study and are tabulated in Tables 10 and 11.

$$\Lambda_0\eta_0 = 0.82[(1/r_s^{\,+}) + (1/r_s^{\,-})] \qquad (14)$$

The inverse of the factor $[(1/r_s^{\,+}) + (1/r_s^{\,-})]$ is a measure of the hydrodynamic radii of the ions where the dynamic light scattering (DLS) measured radius is the radius of a hypothetical sphere that diffuses with the same speed as the particle under

Table 9. Enthalpy Change (ΔH°_a/kJ·mol^{-1}) and the Entropy Change (ΔS°_a/kJ·mol^{-1}·K^{-1}) of Association for the Studied Quinic Acid Salts in the Used Solvents

	$+\Delta H^\circ_a$			$+\Delta S^\circ_a$		
solvent	LiQ	NaQ	KQ	LiQ	NaQ	KQ
water	0.5491	1.6873	2.3092	0.0209	0.0227	0.0213
50 % (v/v) MeOH−H_2O	1.3301	1.6405	2.3997	0.0268	0.0252	0.0243
50 % (v/v) EtOH−H_2O	0.5259	1.7003	2.2964	0.0242	0.0261	0.0246

Table 10. Walden Product ($\Lambda_0\eta_0$/S·mol^{-1}·cm^2·cP) and the Hydrodynamic Radii (R_H/Å) of Quinic Acid and the Studied Quinic Acid Salts in the Used Solvents at Different Temperatures

	T	$\Lambda_0\eta_0$				$R_H \cdot 10^2$			
solvent	K	LiQ	NaQ	KQ	HQ	LiQ	NaQ	KQ	HQ
water	293.15	50.71	59.55	82.24	328.22	1.62	1.37	0.99	0.249
	298.15	56.89	66.73	87.69	333.42	1.44	1.23	0.94	0.246
	303.15	61.29	74.44	93.43	338.44	1.34	1.10	0.88	0.242
	309.15	68.40	82.71	99.35	344.10	1.19	0.99	0.83	0.238
50 % (v/v) MeOH−H_2O	293.15	27.24	35.85	52.33	192.19	3.01	2.29	1.57	0.426
	298.15	32.13	40.02	57.24	195.06	2.55	2.05	1.43	0.420
	303.15	37.46	44.86	62.01	197.50	2.19	1.83	1.32	0.415
	309.15	41.91	49.76	66.96	201.27	1.96	1.65	1.22	0.407
50 % (v/v) EtOH−H_2O	293.15	33.56	44.72	68.49	246.63	2.44	1.83	1.19	0.325
	298.15	40.11	51.02	74.72	249.95	2.04	1.61	1.09	0.328
	303.15	46.36	57.29	80.94	254.27	1.77	1.43	1.01	0.322
	309.15	52.76	63.62	87.34	258.63	1.55	1.29	0.94	0.317

examination. In practice, the solute molecules and ions 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 equation for the Walden product can be written in terms of the effective Stokes−Einstein radii, in which the inverse of the factor $[(1/r^+_s) + (1/r^-_s)]$ is a measure of the hydrodynamic radius (R_H) and, in turn, could be used to get information about solute or ion−solvent interactions assuming the applicability of the Walden product. The values of hydrodynamic radii were calculated for the salts and ions under study and are listed in Tables 10 and 11.

It was noticed that the Walden product increased as the temperature increased. This positive temperature coefficient of the Walden product may be related to the increase in the mobility, and so there is an increase in the molar conductance of ions in the solvent as temperature increases. This is because of the variation of the proportion of the organic solvent and H_2O molecules in the sheath of solvation with temperature.[22]

The two effective factors on the Walden product are the limiting molar conductance and viscosity, where the limiting molar conductance is directly proportional, while η_0 is inversely proportional with temperature. This observation indicates that the contribution of the limiting molar conductance is the most effective factor on the behavior of the Walden product with temperature. Also, the Walden product was found to be in the following order: water > EtOH−H_2O > MeOH−H_2O. This may be due to the effect of the viscosity. In addition, the Walden product were found to be in the following order: LiQ < NaQ < KQ < HQ and $Q^- < Li^+ < Na^+ < K^+ < H^+$, which can be related to the change in the limiting molar conductance in the same order. The observed trend in the change of the Walden product with temperature, solvent composition, and nature of electrolyte was also reported by many authors.[40−44]

The relationship between the Walden product values and the hydrodynamic radii values was a good inverse linear relationship. This behavior of the hydrodynamic radii has also been reported by many authors.[16,45]

2v. Transfer Number. The transfer number ($t_\pm$), which is a measure of quantity or fraction of electricity transferred by an ion or a measure of conductance ability of ions, was calculated for all ions under investigation in the experimental conditions using the following equation, and their values are presented in Table 12.

Table 11. Walden Product ($\Lambda_0\eta_0$/S·mol^{-1}·cm^2·cP) and the Hydrodynamic Radii (R_H/Å) of the Studied Ions in the Used Solvents at Different Temperatures

	T	$\lambda_0\eta_0$					$R_H \cdot 10^{2}$				
solvent	K	Q^-	Li^+	Na^+	K^+	H^+	Q^-	Li^+	Na^+	K^+	H^+
water	293.15	19.23	31.81	41.52	62.58	308.15	4.26	2.58	1.97	1.30	0.265
	298.15	21.93	34.46	44.61	65.45	311.43	3.74	2.38	1.84	1.25	0.263
	303.15	24.85	37.08	47.21	68.02	313.64	3.30	2.21	1.74	1.21	0.261
	308.15	27.87	40.15	49.92	71.19	316.31	2.94	2.04	1.64	1.15	0.259
50 % (v/v) MeOH−H_2O	293.15	12.16	17.47	26.06	44.76	196.86	6.43	4.69	3.15	1.83	0.416
	298.15	12.76	19.38	27.25	44.49	182.29	5.66	4.23	3.01	1.84	0.451
	303.15	14.48	22.99	30.38	47.54	183.04	5.65	3.56	2.69	1.72	0.448
	308.15	16.24	25.66	33.51	50.71	185.03	5.05	3.19	2.45	1.62	0.343
50 % (v/v) EtOH−H_2O	293.15	14.35	19.23	30.37	54.14	232.37	5.71	4.26	2.70	1.51	0.353
	298.15	16.47	23.69	34.54	58.25	233.42	4.98	3.46	2.37	1.41	0.351
	303.15	18.61	27.74	38.68	62.32	235.68	4.40	2.96	2.12	1.31	0.348
	308.15	20.98	31.78	42.64	66.37	237.69	3.91	2.58	1.93	1.23	0.345

Table 12. Transfer Number of the Studied Ions in the Used Solvents at Different Temperatures

	T	t_{Q^-}							
solvent	K	LiQ	NaQ	KQ	HQ	Li^+	Na^+	K^+	H^+
water	293.15	0.3793	0.3229	0.2339	0.0586	0.6272	0.6972	0.7648	0.9411
	298.15	0.3854	0.3286	0.2500	0.0658	0.6057	0.6686	0.7465	0.9340
	303.15	0.4054	0.3338	0.2659	0.0734	0.6050	0.6342	0.7279	0.9267
	308.15	0.4075	0.3370	0.2806	0.0809	0.5869	0.6036	0.7167	0.9192
50 % (v/v) MeOH−H_2O	293.15	0.3771	0.3182	0.2136	0.0581	0.5895	0.6820	0.7864	0.9417
	298.15	0.3812	0.3189	0.2229	0.0654	0.6030	0.6811	0.7772	0.9345
	303.15	0.3905	0.3228	0.2335	0.0733	0.6137	0.6772	0.7666	0.9268
	308.15	0.3975	0.3264	0.2426	0.0807	0.6123	0.6735	0.7573	0.9193
50 % (v/v) EtOH−H_2O	293.15	0.3755	0.3169	0.2095	0.0582	0.5727	0.6791	0.7904	0.9420
	298.15	0.3800	0.3179	0.2205	0.0659	0.5914	0.6771	0.7795	0.9338
	303.15	0.3916	0.3219	0.2299	0.0732	0.5984	0.6751	0.7700	0.9269
	308.15	0.3970	0.3248	0.2403	0.0811	0.6023	0.6702	0.7598	0.9190

$$t_{\pm} = \frac{\lambda^0_{\pm}}{\Lambda_0} \tag{15}$$

From inspection of the data in Table 12, we can conclude that the values of transfer number of Q^- are greatly affected by the co-ions in the studied electrolyte and less affected by the temperature and the solvent composition. This can be related to the direct proportionality change in both $\lambda^0_{\pm}$ and Λ_0 by the temperature and the solvent composition, where, as Λ_0 increases with an increase in temperature or with the solvent composition change, $\lambda^0_{\pm}$ will increase directly and vice versa. In each of the two cases, the ratio ($\lambda^0_{\pm}/\Lambda_0$) will remain nearly constant. This behavior was also been reported.[31] On the other hand, Λ_0 of one salt will differ from that of another salt. Therefore, $\lambda^0_{\pm}$ will differ, but the change is not directly proportional to Λ_0 so that the ratio ($\lambda^0_{\pm}/\Lambda_0$) will not be constant and will differ from one ion to another, affected by the co-ion. This can be noted where the values of t are inversely proportional to the values of Λ_0, as in the following order: Q^- in LiQ > NaQ > KQ > HQ. The values of the transfer number of the Q^- anion were found to be less than that of the studied cations which can be related to the interhydrogen bond between the anions and the solvent molecules and so higher molar volumes.

2vi. Ionic Mobility. The ionic mobilities ($u_{\pm}$) of all ions under investigation in the experimental conditions were calculated by applying eq 16:

$$u_{\pm} = \frac{\lambda^0_{\pm}}{Z_{\pm}F} \tag{16}$$

where $\lambda^0_{\pm}$, $Z_{\pm}$, and $u_{\pm}$ are the limiting ionic molar conductance, charges, and ionic mobility of the cations and anions and F is the Faraday constant. The values of u_+ and u_- for all of the studied ions in the used solvents at different temperatures are presented in Table 13. The change in the values of u_+ and u_- are also analogous to that observed for the limiting ionic molar conductance.

2vii. Diffusion Coefficients. Since the determination of diffusion coefficients of electrolytes in dilute aqueous solutions has been made possible by the utilization of electrolytic conductance,[46,47] we aim in the present study to determine the limiting diffusion coefficient, D_0 (diffusion at infinite dilution), of the salts under investigation in applying the following limiting equation originally obtained.[48]

$$D_0 = 17.872 \cdot 10^{-10}\, T\left(\frac{\lambda^0_+\lambda^0_-}{\Lambda_0}\right) \tag{17}$$

The values of D_0 for the studied salts are presented in Table 13. The diffusion coefficient for all studied salts has an analogous trend to that of the limiting molar conductance and the limiting ionic molar conductance.

Table 13. Diffusion Coefficients (D_0/cm$^2\cdot$s^{-1}) of the Studied Salts and the Ionic Mobility ($u_{\pm}$/cm$^2\cdot$s$^{-1}\cdot$V^{-1}) of the Studied Ions in the Used Solvents at Different Temperatures

	T	$(D_0)\cdot 10^6$				$(u_{\pm})\cdot 10^4$				
solvent	K	LiQ	NaQ	KQ	HQ	Q^-	Li^+	Na^+	K^+	H^+
water	293.15	7.09	7.88	8.64	10.6	2.23	3.69	4.84	7.32	35.9
	298.15	7.94	8.77	9.79	12.3	2.55	4.01	5.19	7.62	36.3
	303.15	9.16	9.59	11.0	14.0	2.89	4.32	5.50	7.93	36.6
	308.15	10.1	10.4	12.4	15.9	3.25	4.69	5.83	8.31	36.9
50 % (v/v) MeOH−H_2O	293.15	4.80	5.56	6.41	7.67	1.61	2.32	3.46	5.94	26.1
	298.15	5.71	6.45	7.36	8.85	1.84	2.79	3.94	6.43	26.3
	303.15	6.72	7.42	8.39	10.2	2.09	3.33	4.39	6.88	26.5
	308.15	7.65	8.42	9.46	11.5	2.35	3.72	4.85	7.35	26.8
50 % (v/v) EtOH−H_2O	293.15	4.35	5.15	5.99	7.15	1.50	2.01	3.18	5.66	24.3
	298.15	5.24	6.00	6.91	8.28	1.73	2.48	3.62	6.10	24.5
	303.15	6.10	6.88	7.85	9.45	0.95	2.91	4.06	6.53	24.7
	308.15	7.05	7.84	8.89	10.8	2.20	3.33	4.48	6.97	24.9

Table 14. Activation Energy of Transfer (E_a, kJ$\cdot$mol^{-1}) for Quinic Acid and the Studied Quinic Acid Salts and Ions in the Used Solvents

solvent	LiQ	NaQ	KQ	HQ	Q^-	Li^+	Na^+	K^+	H^+
water	18.907	15.822	9.624	2.488	18.414	11.579	9.331	6.350	1.349
50 % (v/v) MeOH−H_2O	21.914	7.625	2.506	2.441	18.881	23.861	16.968	10.575	1.257
50 % (v/v) EtOH−H_2O	22.702	17.805	12.281	2.546	19.074	25.068	17.104	10.393	1.317

2viii. 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 a change of temperature on the basis of eq 18:

$$\Lambda_0 = A\exp(-E_a/RT) \tag{18}$$

where A is the frequency factor, R is the gas constant, and E_a is the Arrhenius activation energy of the transfer process. From a plot of ln Λ_0 versus $1/T$, the E_a values were evaluated[49] and presented in Table 14. The behavior of the activation energy change is reverse to that of Λ_0. The activation energy of the transfer process for the studied salts is in the order LiQ > NaQ > KQ > HQ. The values of the activation energy of the transfer process for Q^-, Li^+, and Na^+ ions in the used solvents were found to be in the following order: EtOH−H_2O > MeOH−H_2O > water. Also, the values of the activation energy of the transfer process, for quinic acid and the studied salts except LiQ in the used solvents, were found to be in the following order: EtOH−H_2O > water > MeOH−H_2O. The values of the activation energy of the transfer process for K^+ and H^+ ions have different orders. The increase in the relative permittivity, viscosity, and association process of the electrolyte (as a result of the hydrogen bond formation) is always accompanied by an increase in the activation energy of the transfer process. The higher values of the activation energy of the transfer process indicate more energy consumed for the transfer process and vice versa. The observed behavior of change in the activation energy of transfer was also reported by many authors.[16,40,42]

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