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Determination of Thermodynamic Parameters for Ion Association of N-(2-Fluorophenyl)maleamic acid in Methanol, Ethanol, and Acetone

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Abstract

In this study, As has been determined equivalent conductivity of N-(2-Fluorophenyl)maleamic acid in the solvents (methanol, ethanol, and acetone) that have a different relative permittivity and in concentrations ranging from 1×10^{-5} N to 1×10^{-3} N at 293.15, 303.15, 313.15 and 323.15 K.

Through this study found that equivalent conductivity increases when relative permittivity and temperature increases and equivalent conductivity decreases when the concentration increases. As has been determined Ionization constants and thermodynamic Parameters for organic acid in those polar solvents and temperatures mentioned above.

Keywords

Limiting equivalent conductivity, Ostwald's dilution law, Gibbs free energy, Enthalpy, Entropy.

تقدير القيم الثرموداينميكية للتجمع الايوني لحامض N-(2-فلورو فنيل) الماليميك في الميثانول والإيثانول والأسيتون

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الخلاصة

في هذه الدراسة، تم تقدير المواصلة المكافئة لحامض N-(2-فلورو فنيل) الماليميك في المذيبات (الميثانول والإيثانول والأسيتون) التي لها سماحية نسبية مختلفة وبتراكيز تتراوح من (1×10^{-5} عياري) إلى (1×10^{-3} عياري) عند (293.15، 303.15، 313.15، 323.15 كلفن).

ومن خلال هذه الدراسة وجد أن المواصلة المكافئة تزداد مع زيادة السماحية النسبية، وتقل المواصلة المكافئة مع انخفاض التركيز. كما تم تحديد ثوابت التأين والثوابت الثرموديناميكية للحامض العضوي في المذيبات القطبية ودرجات الحرارة المذكورة آنفا.

Introduction

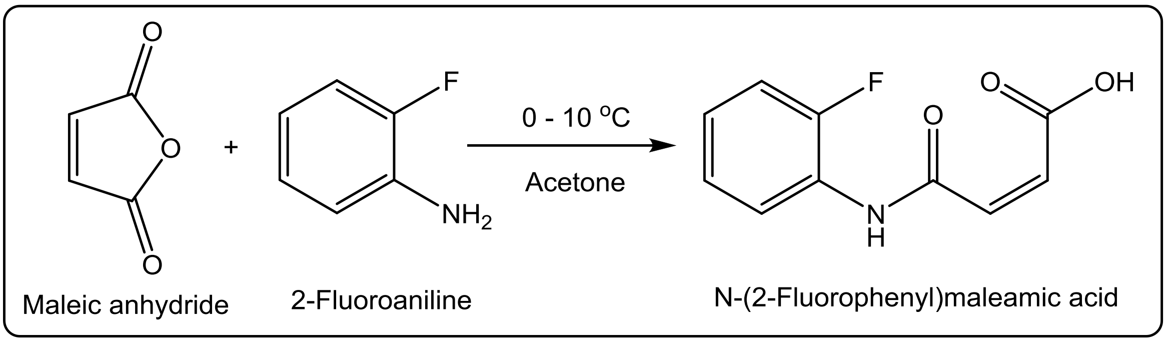
As in other fields of chemistry, some research on compounds has been carried out in nonaqueous media, the use of a nonaqueous solvent may be advantageous [1-7]. Many researchers studied equivalent conductivity [8, 9]. Solvents can be broadly classified into two categories: polar and nonpolar. A special case is a mercury, whose solutions are known as amalgams; also, other metal solutions exist which are liquid at room temperature. Generally, the dielectric constant of the solvent provides a rough measure of a solvent's polarity. The strong polarity of water is indicated by its high dielectric constant of 88 (at 0°C)[10]. Solvents with a dielectric constant of less than 15 are generally considered to be nonpolar. The dielectric constant measures the solvent's tendency to partly cancel the field strength of the electric field of a charged particle immersed in it. This reduction is then compared to the field strength of the charged particle in a vacuum[11]. Heuristically, the dielectric constant of a solvent can be thought of as its ability to reduce the solute's effective internal charge. Generally, the dielectric constant of a solvent is an acceptable predictor of the solvent's ability to dissolve common ionic compounds, such as salts. Donor number and donor-acceptor scale measure polarity in terms of how a solvent interacts with specific substances, like a strong Lewis acid or a strong Lewis base[12]. The electric conductivity is one of the most basic properties in the study of the dynamic processes in electrolyte solutions[13,14]. For a better understanding of the transport mechanism of ions in solutions, conductivity measurements in extreme conditions such as high temperatures and high pressures are of great importance since it can systematically changed the solvent properties in a wide range. In a series of papers [15,16], we have reported electric conductivities of alkali metal and tetra-alkyl ammonium halides in high-temperature liquid methanol along with the liquid-vapor coexistence curve and examined the validity of the Hubbard-Onsager (HO) dielectric friction theory [17,18].

Experiment

Materials and Apparatus: The chemicals used were: Malic Anhydride, 2-Fluoroaniline, Potassium Chloride, Methanol, Ethanol, Acetone, and Water. Moreover, appliance and tools that have been used to track conductivity N-(2-Fluorophenyl)maleamic acid low concentrations and the measurmened from conductivity meter (Wissenschaftlich Technische Werkstatten D 8120 Weilheim), water thermostat, magnetic stirrer, Sartorius 2004 MP6 Electronic Semi-Micro Balance and water distiller were used.

N-(2-Fluorophenyl)maleamic acid was prepared [19] by dissolving 49 g of malic anhydride in 300 ml of acetone. Then the solution is filtered, to get rid of the maleic anhydride non-dissolved if found in the solution. Then for this solution, add 49 g of 2-Fluoroaniline was added drop by drop with continuous stirring using a magnetic stirrer. It was added thru two hours while maintaining the temperature of the solution at less than 10 °C, after the addition process, the stirring process continues for 12 hours at a temperature of 17-20°C. In addition, the precipitation (acetic acid) have been separated that is formed by filtration, then wash several times with chloroform to remove the non-reactive substances that may exist with the acid formed. Moreover, dries under diminished pressure at about

60°C for 24 hours, and was the crystallized acid is reconstituted by using a combination of methanol and chloroform by 1:1, and the color of the formed acid is yellow and its melting point was (135-140°C).



The standard of sodium hydroxide solution is used and titrated it with Sodium hydrogen phthalate solution using phenolphthalein as an indicator, and then it is prepared Sodium salt for organic acid by taking 20 ml of N-(2-Fluorophenyl)maleamic acid whose concentration is 0.001N and add it in equivalent volume of the standardized NaOH solution which leads to its equivalent amount and then the volume is supplemented to 25 ml by the three solvents (methanol, ethanol, and acetone) each separately, from this final solution different solutions of sodium salts were prepared in concentrations range 1×10^{-5} N to 1×10^{-3} N to Measuring the specific conductivity of each solution at 20, 30, 40, and 50°C.

Results and Discussion

After determining, the equivalent conduction values [1-7, 20-22] for each concentration of electrolyte in methanol, ethanol, and acetone at different temperatures Tables (1-3).

Table-1: Equivalent conductivity of each concentration of electrolyte in methanol at different temperatures.

$C_{eq} \times 10^5$	Λ_{eq}			
	293.15 K	**303.15 K**	**313.15 K**	**323.15 K**
8.49	76.3	86.9	97.5	107.9
15.1	62.6	72.3	81.8	91.3
29.7	48.4	56.4	64.5	72.5
44.3	41.2	48.3	55.4	62.5
58.7	36.7	43.1	49.6	56.1
87.2	31.0	36.6	42.2	47.9

Table-2: Equivalent conductivity of each concentration of electrolyte in ethanol at different temperatures.

$C_{eq} \times 10^5$	Λ_{eq}			
	293.15 K	**303.15 K**	**313.15 K**	**323.15 K**
8.58	61.1	70.3	79.3	88.3
15.2	51.3	59.6	67.5	75.5
30.0	40.5	47.4	54.0	60.6
44.8	34.9	41.0	46.8	52.7
59.3	31.3	36.9	42.2	47.4
88.0	26.7	31.6	36.1	40.7

Table-3: Equivalent conductivity of each concentration of electrolyte in acetone at different temperatures.

$C_{eq} \times 10^5$	Λ_{eq}			
	293.15 K	**303.15 K**	**313.15 K**	**323.15 K**
8.41	40.6	49.3	57.8	66.4
14.9	33.5	41.1	48.5	56.0
29.5	26.0	32.2	38.3	44.5
43.9	22.2	27.6	33.0	38.4
58.1	19.8	24.8	29.6	34.5
86.3	16.8	21.1	25.2	29.5

It observed in all experimental tests, that the relationship between $\sqrt{C}$ and Λ_{eq} was not linear، so Electrolyte is weakly dissociation[23,24,25], consequently, one of the theoretical methods should be used to determine the values of some electrolytic conductivity Parameters. In this study, Ostwald's dilution law was used (see Equation 1) to determine the values Λ^{o}_{eq} and K_A by interpreting value and slope value (see Figure 1) [26].

$$\frac{1}{\Lambda_{eq}} = \frac{1}{\Lambda^{o}_{eq}} + \frac{C_{eq} \times \Lambda_{eq} \times K_A}{(\Lambda^{o}_{eq})^2} \qquad \dots (1)$$

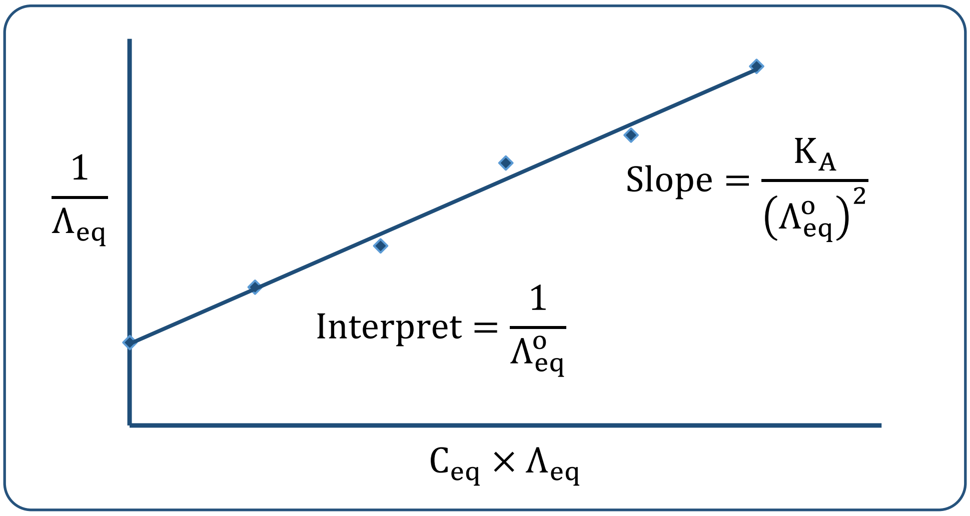


Figure-1: Diagram of Ostwald's dilution law

Table-4: Values Λ_{eq}^{o} of electrolyte in methanol, ethanol, and acetone at different temperatures.

Solvent	Λ_{eq}^{o}			
	293.15 K	**303.15 K**	**313.15 K**	**323.15 K**
Methanol	138.9	147.1	156.3	163.9
Ethanol	95.2	105.3	116.3	126.6
Acetone	70.9	80.0	90.1	101.0

Table-5: Values K_A of electrolyte in methanol, ethanol, and acetone at different temperatures.

Solvent	$K_A \times 10^{-4}$			
	293.15 K	**303.15 K**	**313.15 K**	**323.15 K**
Methanol	1.80	1.40	1.15	0.96
Ethanol	1.05	0.89	0.82	0.75
Acetone	1.58	1.24	1.07	0.97

The Λ_{eq}^{o} values that have been obtained indicate that electrolytic conductivity increases with increasing temperature As a result of increased kinetic energy of electrolyte ions in the solution، as well as that the values of K_A were higher in methanol then in ethanol and in acetone، The reason is that the relative permissibility values are higher in methanol than in ethanol and acetone (least).

The K_A values obtained indicate that the electrolyte ions in the solution tend to the association, therefore, we will focus in this study on the interpretation of the ion association of the thermodynamic by calculating the values of the thermodynamic parameters of the ionic association according to the equations (2-4) [8].

$$K'_A = K_A \times \frac{\rho_o \times 1000}{M_m} \qquad \dots (2)$$

$$\Delta G_A^o = -R_g T \ln K'_A \qquad \dots (3)$$

$$\frac{-\Delta H_A^o}{R_g} = \left(\frac{\partial(\ln K'_A)}{\partial(1/T)}\right)_p \qquad \dots (4)$$

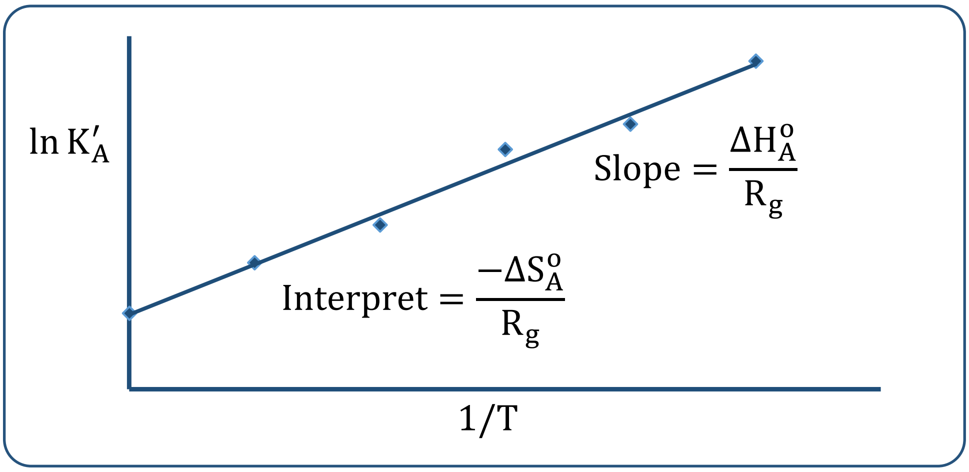


Figure-2: $\ln K'_A$ versus $1/T$ according to van't Hoff equation

Table-6: Values ρ_o of methanol, ethanol, and acetone at different temperatures.

Solvent	ρ_o			
	293.15 K	**303.15 K**	**313.15 K**	**323.15 K**
Methanol	0.7923	0.7831	0.7735	0.7637
Ethanol	0.7889	0.7789	0.7687	0.7583
Acetone	0.7913	0.7802	0.7689	0.7573

Table-7: Values Thermodynamic Parameters of electrolyte in methanol, ethanol, and acetone at different temperatures.

Solvent	ΔG^o_A				ΔH^o_A	ΔS^o_A
	293.15 K	**303.15 K**	**313.15 K**	**323.15 K**		
Methanol	-31700	-32110	-32628	-33151	17434	48.557
Ethanol	-29485	-30050	-30773	-31498	9680.0	67.407
Acetone	-29935	-30301	-30890	-31561	13950	54.265

Through the thermodynamic results obtained for the ionic aggregation of the electrolyte in methanol, ethanol, and acetone, It is obvious that it is an automatic process because of the value of ΔG^o_A is negative It is a heat-absorbent process because of the value of ΔH^o_A is positive and it process leads to a random increase in the system because of the value ΔS^o_A positive, in addition, it is reported that ethanol molecules are more closely associated with their molecules of both acetone and methanol (least) As a result of the nature of the molecules of these compounds from the stereochemistry and molecular interactions.

Nomenclatures

C_{eq}: Equivalent Concentration ($eq.dm^{-3}$)

Λ_{eq}: Experimental Value of Equivalent Conductivity ($S.cm^2.eq^{-1}$)
Λ^o_{eq}: Equivalent Conductivity at Infinite Dilution ($S.cm^2.eq^{-1}$)
K_A: Association Constant ($dm^3.mol^{-1}$)
K'_A: Association Constant (Without Unit)
ρ_o: Density of Solvent ($g.cm^{-3}$)
M_m: Molecular Mass of the Mixture of Solvents ($g.mol^{-1}$)
R_g: Gas Constant ($J.K^{-1}.mol^{-1}$)
T: Thermodynamic Temperature (K)
ΔG^o_A: Standard Value of the Change in Gibbs Free Energy ($J.mol^{-1}$)
ΔH^o_A: Standard Value of the Change in Enthalpy ($J.mol^{-1}$)
ΔS^o_A: Standard Value of Change in Entropy ($J.K^{-1}.mol^{-1}$)

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