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Studies on the effect of dielectric constant on the solvation behaviour of citric acid as a function of temperature

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ABSTRACT

The principle of Electrical conductivity is used in the study of ion-solvation of Citric acid in water, water+CH_3CN *and water+DMSO mixtures (v/v) in the temperature range 283-313K. The conductance data were analyzed by Kraus-Bray and Shedlovsky conductivity models. Limiting molar conductance (*λ_m^0*), dissociation constant (*K_C*) and association constant (*K_a*) were evaluated for all the solvent compositions. The* λ_m^0 *values decreases with the addition of co-solvent* CH_3CN *or DMSO, due to increased solvent-solvent interaction and decrease in dielectric constant. The* λ_m^0 *of water+DMSO mixture is smaller than that in water+*CH_3CN *mixture. The* K_C *values increases with increase in temperature in all the compositions of solvent mixtures. Energy of activation of the rate process and related thermodynamic parameters has been computed. Using viscosity of solvent/solvent mixture, Walden product and corrected Stoke's radius (*r_i*) have also been computed. To identify the formation of ion-pairs and ion-triplets, a plot was drawn on the basis of Fuoss equilibrium equation, the slopes of the plot were found to be around -0.5, indicating the presence of ion-pairs or ion-triplets. These computed values have been used to discuss qualitatively the nature of ion-solvent interaction of Citric acid with water, water+*CH_3CN *and water + DMSO mixture.*

Key words: Electrical conductivity, Ion-solvation, limiting molar conductance, Citric acid.

INTRODUCTION

Studies on electrical conductance of an electrolyte in various aqueous, partial aqueous and non aqueous media have received considerable attention in recent year [1-4]. The effect of ion-solvent interaction on the conductivity of an electrolyte is well known [5-8]. Studies on electrical conductivity of an electrolyte in solution give many important qualitative insights into the properties of electrolyte solution [9-10]. The effect of dielectric constant on the conductance of an electrolyte has formed basis for a number of studies [11-13]. Conductance studies in mixed solvents give information in regard to specific, non specific and preferential solvation effects on ion-association phenomenon. Conductance measurement technique is also a precise information tool for the investigation of ion-pair formation in the system under existing condition. Investigation of solvation process in binary solvent media where one of the solvent being water is an area of study which throws light on ion solvation process [14].

Citric acid [15,16] (2-hydroxy propane-1,2,3-tricarboxylic acid) is a hydroxy tricarboxylic acid which occurs widely in lemon, lime and other citrus fruits. It is a weak organic acid [17]. It is an important intermediate in carbohydrate metabolism [17] (Citric acid cycle or Krebs cycle). It can be used as plasticizers, in the manufacture of soft drinks and candies [15]. It is a white crystalline compound, soluble in water and some non-aqueous solvents [17]. Several groups [18,19,20] have studied solute-solute and solute-solvent interactions of various compounds including citric acid in different solvent media. Seungho Cho et. al [21]., studied the effect of citric acid in the formation of ZnO crystal. The specific interactions of citric acid with anions in acetonitrile have studied at different temperatures [22]. From this laboratory we reported some work on citric acid in water and water+DMF [23]. Literature shows some work on conductivity of citric acid in aqueous solutions at different temperature [24]. Literature reveals the fact that there is little work [25] on the conductometric behaviour of citric acid in aqueous solution. But no report is found in the mixture of solvents (H_2O+non-aqueous) even though several electrolytes have been studied in good number of such solvent mixtures [26]. Solvent mixtures are used in several fields as it gives varied dielectric constant and changed solvent structure. Hence the study of electrolytes in solvent mixtures has much importance. This has made us to take up the work electrical conductivity measurement of citric acid in water, water + CH_3CN and water + DMSO at 283, 293, 303 and 313 K to identify the nature of ion-solvent and solvent-solvent interactions involved in the system.

MATERIALS AND METHODS

Commercially available citric acid (A R grade, Merck make) directly used without further purification[Melting point:152^{0}C(Observed value), 153^{0}C(Literature value)]. Triply distilled water of specific conductivity of the order of ~ 1×10^{-6} S cm^{-1} was used. The solvents acetonitrile and dimethylsulphoxide were purified as reported [27] (specific conductivity of the order of 2.0 - 3.0 $\times10^{-7}$Scm^{-1}). Citric acid solution (0.1M) was prepared in water, water+CH_3CN and water+DMSO mixtures (v/v) as and when required and standardized P^H metrically.

Conductance measurements were made with a digital direct reading conductivity meter (Model CM 180, Elico make) and a calibrated [28] conductivity cell (cell constant 0.975 cm^{-1}). All the measurements were made in a thermostat/cryostat maintained at the desired temperature ± 0.01^{0}C.The instrument was standardized elsewhere [29].

RESULTS AND DISCUSSION

Limiting molar conductance

Solutions of citric acid in water, water+CH_3CN and water+DMSO (in terms of volume ratio) were subjected to conductometric study. The specific conductance (k) of salt solution was directly read from the instrument. To obtain absolute specific conductance of the solution, solvent correction [30] was applied at every case at all temperatures. This corrected k was utilized for determining molar conductance (λ_m) of citric acid for all the cases of solvent mixtures at 283, 293, 303 and 313K using the relation

$$\lambda_m = \frac{1000 \times k}{C} \qquad (1)$$

where C is concentration in molar and k is specific conductance (S cm^{-1}).

As it is known, citric acid is a weak electrolyte, will not follow Onsagers condition. This weak electrolyte is expected to give three protons in the process leading to three ionization values k_1, k_2 and k_3. If it is the case it is possible to get three protons, one could write the following ionization equation.

$$C_6H_8O_7 \rightleftharpoons C_6H_5O^-_7 + 3H^+ \qquad (2)$$

Hence Kraus-Bray equation [31] related to 3:1 electrolyte was used but the plot of ($\lambda_m C$)^3 Vs $1/\lambda_m$ was non-linear (Fig not shown). Then the Kraus-Bray equation related 2:1 electrolyte also tried, but the plot of (λ_m C)^2 Vs $1/\lambda m$ was also non-linear (Fig not shown). This has made us to apply Kraus-Bray equation related to 1:1 electrolyte. According to the equation

$$\frac{1}{\lambda_m} = \frac{1}{\lambda_m{}^0} + \frac{\lambda_m C}{\lambda_m{}^{0\,2} K_c} \qquad (3)$$

where λ_m is the molar conductance, C is the concentration in molar, K_C is the dissociation constant and $\lambda_m{}^0$ is the molar conductance at infinite dilution or limiting molar conductance. A plot of $\lambda_m C$ vs $1/\lambda_m$ was drawn in the cases under study. They are found to be linear. The linearity is an indication of the formation of ion-pair of the electrolyte in equilibrium with ions. The values of $\lambda_m{}^0$ and K_C obtained from the intercept and slope of the above linear plot (Fig.1, as a representative plot) and are presented in the Tables1 and 2 respectively. But, the obtained limiting conductance values are not absolute as they do not account for the effect of ionic mobility and activity co-efficient on conductivity. Therefore, conductance data were further subjected to analysis by Shedlovsky model [32] and which does include corrections for interionic effects on ionic mobilities and for ion activity coefficients. The Shedlovsky equation may be represented as

$$\frac{1}{S\lambda_m} = \frac{1}{\lambda_m{}^0} + \frac{C\lambda_m S f_\pm{}^2 K_a}{\lambda_m{}^{0\,2}} \qquad (4)$$

Where S is Onsagar slope, K_a is the association constant and $f_\pm$ is the mean ionic activity coefficients of the electrolyte. Plot of $1/S\lambda_m$ and $C\lambda m S f_\pm{}^2$ were found to be linear. From the intercept and slope of these plots (Fig.2, as a representative plot), the limiting conductance $\lambda_m{}^0$ and association constant K_a were determined and the values are shown in the Table 1 and 2 respectively.

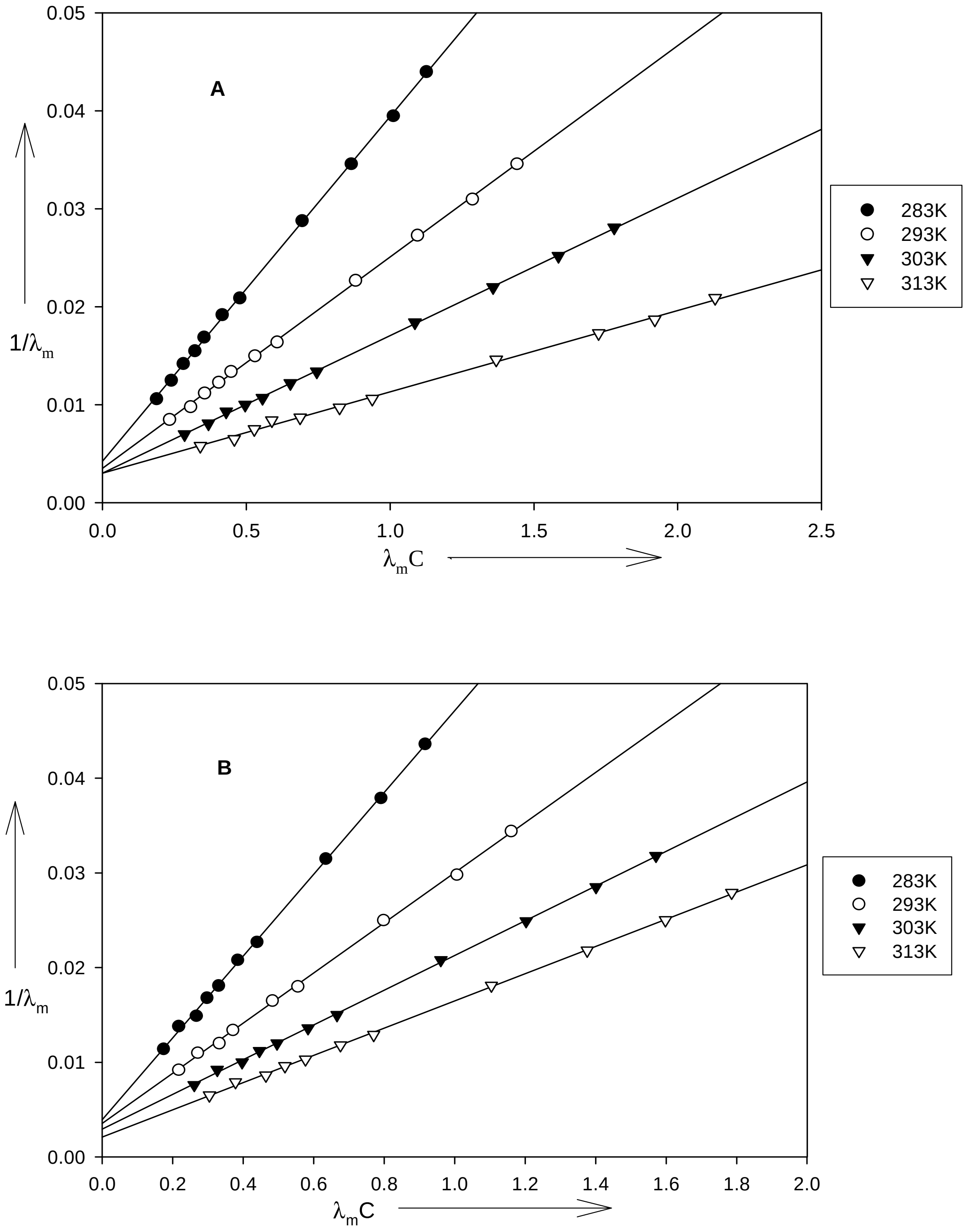


Fig.1. Plot of λ_mC Vs $1/\lambda_m$ for citric acid in A- 10% CH_3CN; B- 10% DMSO

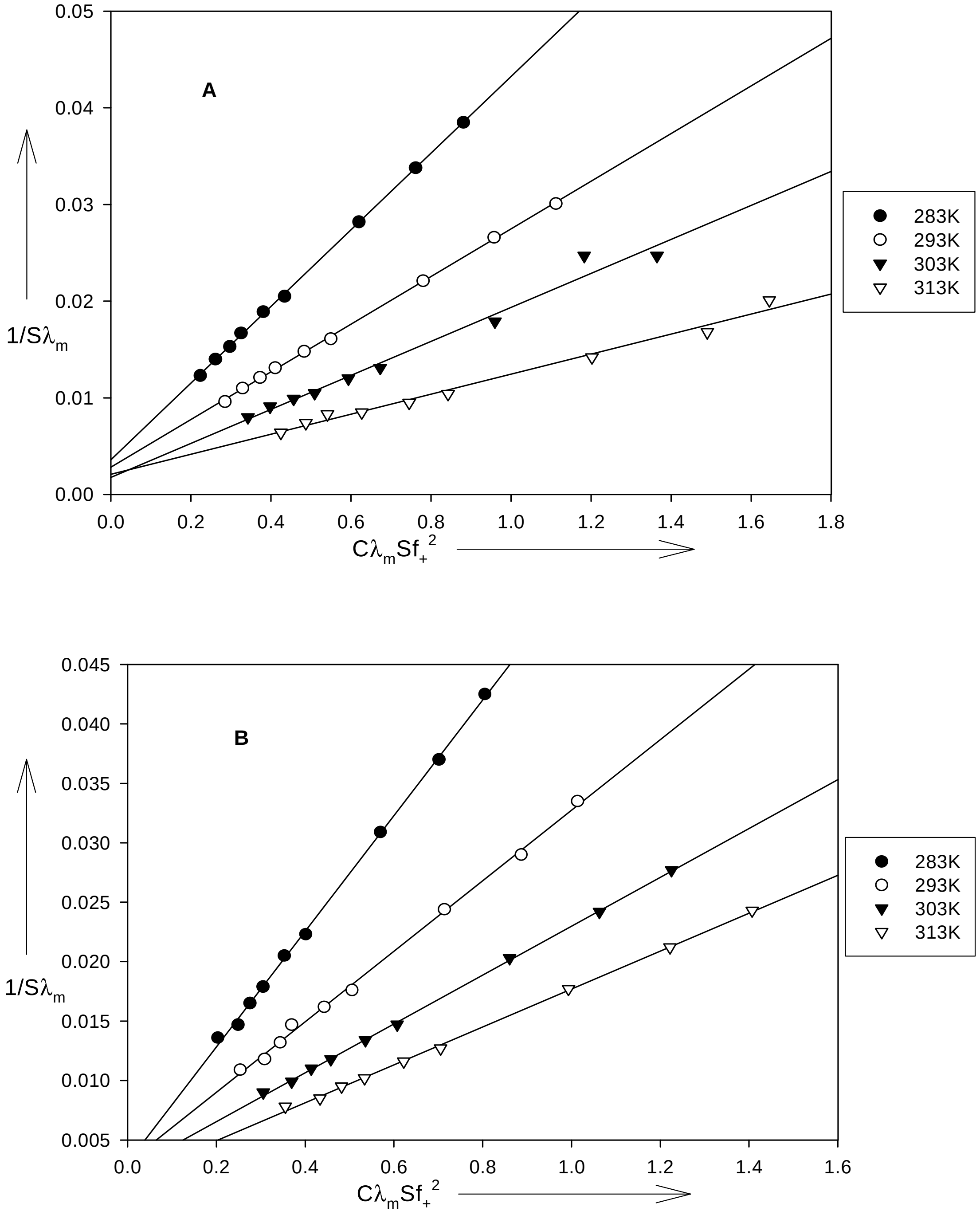


Fig.2. Plot of $1/S\lambda_m$ Vs $C\lambda_m Sf_\pm^2$ for citric acid in A- 10% CH_3CN; B- 10% DMSO

The limiting conductance increased with the increase in temperature due to either increase in the number of conducting ions or due to increased mobility of conducting species or even increase in thermal energy.

The limiting conductance decreased with decrease in dielectric constant obtained by mixing water+CH_3CN/DMSO in required ratio and this decrease continued till the compositions under study.

In case of water+CH_3CN mixture λ_m^0 decreased with increase in CH_3CN content in water probably due to increase in ion-solvent interaction. Acetonitrile being a non-aqueous and aprotic solvent interact with water bringing about solvent-solvent interaction and hence large sized solvent mixture molecule in the system. This in turn solvates the ion and hence the conductivity decreases on adding acetonitrile to water (Table.1). The magnitude of decrease is high in non-aqueous (60-80% CH_3CN) rich region compared to water rich region, indicating higher solvation of the species or increase in ion-ion association.

Table.1: Experimental values of molar conductance at infinite dilution (λ_m^0: mho cm^2 mol^{-1}) for Citric acid from Kraus-Bray (1) and Shedlovsky (2) models in different dielectric constant (ε) or various compositions (v/v) of water + CH_3CN and water + DMSO

λ_m^0 (mho cm^2 mol^{-1})									
T(K)	0%			10%			20%		
	1	2	ε	1	2	ε	1	2	ε
Water + CH_3CN									
283	263	264	84.5	238	240	79.9	208	209	75.4
293	312	313	80.4	277	278	76.0	250	250	71.8
303	385	384	76.7	312	311	72.6	280	279	68.6
313	434	434	73.0	357	358	69.0	317	316	65.3
Water + DMSO									
283	263	264	84.5	217	218	82.9	172	170	81.8
293	312	313	80.4	250	252	79.7	208	208	78.8
303	385	384	76.7	270	271	76.5	225	226	75.2
313	434	434	73.0	295	297	72.98	260	262	72.4

T(K)	40%			60%			80%		
	1	2	ε	1	2	ε	1	2	ε
Water + CH_3CN									
283	125	126	66.0	72	71	56.8	17	19	47.7
293	143	143	63.2	100	99	54.9	22	23	46.3
303	167	168	60.7	125	125	53.0	34	36	44.6
313	200	201	57.7	167	166	50.5	50	52	43.0
Water + DMSO									
283	70	71	81.0	22	23	77.6	-	-	-
293	90	92	77.6	33	35	74.2	-	-	-
303	112	113	74.0	43	44	70.5	-	-	-
313	125	126	70.8	62	64	67.4	-	-	-

Addition of a small amount of DMSO to water or decrease in permittivity rigidifies the three dimensional structure of water and this continues up to till the studied composition. The hydrogen bond between water and DMSO is stronger than in pure water and has been attributed to dipole-dipole interaction [33]. So conductivity decreases. Because of the solvent-solvent interaction might have formed rigid three dimensional structures having some cavity in it. This cavity might trap some of cations leading to lesser number of conducting ions. Conductance of any system is usually reciprocal to viscosity of the solvent/solvent mixture [33].

DMSO is well known to undergo self ionization [34]. DMSO is more protophilic than acetonitrile and forms more close packed structure. Dielectric constant of the solvents varies in the order of water>DMSO>CH_3CN at 30^0C (76.7>44.3>36.7). So one expects maximum conductance in water followed by DMSO and CH_3CN and hence the dielectric constant of mixture of water+DMSO is higher than water+CH_3CN mixture at all temperatures. So $\lambda_m{}^0$ in water+DMSO mixture should be greater than in water+CH_3CN mixture due to higher dielectric constant. But in the present case the result is quit reverse. It says that the dielectric constant of any solvent or solvent mixture is not all sufficient to decide about the solvation/solubility of a solute in a system based on Born model of solvation [35].

The solvation behaviour of the ion by the solvent or solvent mixture molecule, solvent molecular size, solvent-solvent interaction existing in the system. The ionic size of DMSO is greater than CH_3CN molecule. If an isodielectric stage is considered (10% CH_3CN at 283K and 10% DMSO at 293K: ε=79.9 and 79.7 respectively) the $\lambda_m{}^0$ is higher in the case of 10% CH_3CN. Similar such cases can be seen in the present system. All then states that variation of physical properties of the solvent/solvent mixture and the are the deciding factors and take much role in the variation of $\lambda_m{}^0$ with the solvent composition. Such a behaviour was observed in the case of the study of conductivity of CAB in MeOH/ CH_3CN /DMSO/EtOH [12] etc.,

The variation of dielectric constant with temperature for a given composition is smaller compared to the variation of dielectric constant with percentage composition of either CH_3CN or DMSO with water. Hence here onwards variation of dielectric constant with percentage composition only will be considered.

Dissociation and association constants

Dissociation and association constants were obtained respectively from Kraus-Bray and Shedlovsky plots. The values are shown in the Table.2. The K_C value increased with increase in temperature except at 60 and 80% CH_3CN (ε=53.0 and 44.6) where it has found to decrease with temperature. Reverse trend was observed with Ka variation. At high dielectric constant dissociation or forward reaction is favoured and at lower dielectric constant (high % CH_3CN) association or increase the in ion-ion and ion-solvent interaction is favoured at a given temperature. The increase in Ka with the increase in temperature proposes the endothermic character of the system and vice versa. Since the electrolyte under consideration is weak, association process is expected to predominate over dissociation. Increase in Ka with increase in temperature is an indication of ion association.

To identify ion association a plot of log λ_m Vs log C was drawn on the basis of Fuoss equilibrium equation. The plot was linear with a slope around -0.5, indicating the presence of good amount of ion-pairs. To prove this Fuoss-Accascina [36] equation was considered.

$$\lambda_m g(c)\sqrt{C} = \frac{\lambda_m{}^0}{K_p{}^{1/2}} + \frac{\lambda_m{}^{0^T} K_T}{K_p{}^{1/2}}\left[1 - \frac{\lambda_m}{\lambda_m{}^0}\right]C \qquad (5)$$

Table.2: Experimental values of dissociation constant (K_C) and association constant (Ka) for Citric acid in different dielectric constant (ε at 303K) or various compositions (v/v) of water + CH_3CN and water + DMSO

T(K)			$K_C×10^{-4}$						$Ka×10^{3}$			
	0% (76.7)	10% (72.6)	20% (68.6)	40% (60.7)	60% (53.0)	80% (44.6)	0% (76.7)	10% (72.6)	20% (68.6)	40% (60.7)	60% (53.0)	80% (44.6)
Water + CH_3CN												
283	7.71	5.04	3.72	2.46	1.39	1.26	1.317	2.073	2.839	4.186	6.953	7.936
293	7.76	6.20	3.80	3.13	1.19	1.12	1.307	1.700	2.750	3.271	8.246	8.928
303	7.81	7.33	5.31	3.58	1.14	0.86	1.297	1.354	1.946	2.907	8.637	11.697
313	8.28	7.82	6.63	4.54	1.12	0.63	1.230	1.243	1.697	2.300	8.817	15.937
	0% (76.7)	10% (76.5)	20% (75.2)	40% (74.0)	60% (70.5)	- -	0% (76.7)	10% (76.6)	20% (75.2)	40% (74.0)	60% (70.5)	- -
Water + DMSO												
283	7.71	5.54	3.07	2.68	1.54	-	1.317	1.952	3.251	3.920	6.566	-
293	7.76	6.20	3.93	2.88	1.48	-	1.307	1.687	2.568	3.601	6.812	-
303	7.81	7.45	4.93	2.95	1.30	-	1.297	1.392	1.978	3.473	7.680	-
313	8.28	7.92	5.15	3.74	1.13	-	1.230	1.260	1.940	2.752	8.878	-

Table.3: Calculated values of ion pair formation constant (K_P x 10^3) and triple ion formation constant (K_T) for Citric acid in different dielectric constant (ε at 303K) or various compositions (v/v) of water + CH_3CN and water + DMSO at different temperatures

T(K)	0% (76.7)		10% (72.6)		20% (68.6)		40% (60.7)		60% (53.0)		80% (44.6)	
	K_P	K_T	K_P	K_T	K_P	K_T	K_P	K_T	K_P	K_T	K_P	K_T
Water + CH_3CN												
283	2.55	0.15	3.37	0.095	4.50	0.057	5.81	0.053	9.21	0.040	10.24	0.053
293	2.37	0.16	2.73	0.086	3.72	0.047	4.91	0.081	10.20	0.032	10.33	0.071
303	2.31	0.08	2.37	0.082	2.79	0.037	4.32	0.074	10.16	0.026	10.46	0.040
313	2.17	0.07	2.09	0.099	2.24	0.032	3.58	0.058	10.24	0.008	13.20	0.042
	0% (76.7)		10% (76.5)		20% (75.2)		40% (74.0)		60% (70.5)		-	
Water + DMSO												
283	2.55	0.15	3.43	0.128	5.12	0.158	5.41	0.061	9.84	0.091	-	-
293	2.37	0.16	2.83	0.134	4.80	0.151	5.62	0.076	8.87	0.055	-	-
303	2.31	0.08	2.32	0.117	3.16	0.098	5.56	0.109	8.35	0.059	-	-
313	2.17	0.07	2.30	0.110	3.02	0.138	3.90	0.077	8.21	0.040	-	-

Where K_P is the ion-pair formation constant, K_T is triple ion-formation constant, g(c) is a factor which incorporates all inter ionic interaction terms and $\lambda_m^{0\ T}$ is the limiting molar conductance of triple ions. The plot of $\lambda_m g(c)\sqrt{c}$ Vs $\left[1-\frac{\lambda_m}{\lambda_m^0}\right]C$ was found to be linear and the values of K_P and K_T obtained from its slope and intercept and are shown in Table.3. As can be seen from the Table.3, K_T is very small compared to K_P indicating the presence of more ion-pairs than ion triplets hence the conductivity decrease for the increased amount of amount of CH_3CN or DMSO. K_P over weights the K_T leading to the decrease in ions available for conduction and also decreases in total conductance. K_P increased with the increase in percentage composition of either CH_3CN or DMSO with water or with decrease in dielectric constant. Because of this the conductivity decreased with the decrease in dielectric constant (Table.1). K_P decreases with the increase in temperature as required. But the value of K_P relatively smaller in the case of water+DMSO compared to water+CH_3CN. This is going against our proposal of λ_m^0 is greater in water+CH_3CN system.

Walden product

Walden product was obtained by the Stoke – Einstein equation [35] related to diffusion coefficient and the viscosity of the medium. The Nernst-Einstein [35] equation relates the diffusion coefficient to the equivalent/molar conductance. Hence by eliminating diffusion coefficient from these two equations, it is possible to obtain relation between molar conductance and viscosity of the electrolyte solution and hence resulted relation is

$$\lambda_m^0 \eta_0 = \frac{Ze_0F}{6\pi rT} \qquad (6)$$

Where η_0 is the viscosity of the solvent, Z is the charge, e_0 is the electronic charge, r is Stoke's molecular radius and F is Faraday constant. The product of viscosity η_0 of solvent and limiting molar conductance for a particular electrolyte at a given temperature should be a constant. This is called Walden's rule [37]. Since Z, e_0 and F are constants for a given system at a given temperature, the equation (6) takes the form

$$\lambda_m^0 \eta_o \alpha \frac{1}{r} \qquad (7)$$

Where r is the Stoke's radius of the ion. Walden product is calculated at all temperatures and in different dielectric constant or percentage composition of water+CH_3CN and water+DMSO which are shown in Table. 4. Walden product decreased with increase in temperature in both the solvent mixtures except at 60% and 80% CH_3CN (dielectric constant: 53.0 and 44.6 at 303K) where the product increased with increase in temperature for a given composition. The product constantly decreased from water to 80% CH_3CN (dielectric constant: 76.7 to 44.6 at 303K) and 60% DMSO (dielectric constant: 70.5 at 303K). It shows that the effect of variation in limiting conductance is not compensated by the variation in viscosity. From equation.7, it is clear that Walden product is reciprocal to Stoke's molecular radius. But in the present case the corrected Stoke's radius, r_i is calculated and the values are shown in Table.5. The values of corrected Stoke's radius are on expected trend. Walden product and Stoke's radius jointly identifies the solvation behaviour of the ion by the solvent/solvent mixtures. It also gives the solvent-solvent interaction and their role in the mobility of the ionic species.

On addition of non polar solvent to polar solvent, Morinaga et al [38]., observed sharp decrease in the ratio,

$$R_X = \frac{\lambda^0{}_m \eta_0 (solventmixture)}{\lambda^0{}_m \eta_0 (water)} \qquad (8)$$

Table.4: Computed values of Walden product (λ_m^0 η_0: mho cm^2 mol^{-1}Poise) for Citric acid in different dielectric constant (ε at 303K) or various compositions (v/v) of water + CH_3CN and water + DMSO at- λ_m^0 η_0 (mho cm^2 mol^{-1}Poise)

T(K)	0% (76.7)	10% (72.6)	20% (68.6)	40% (60.7)	60% (53.0)	80% (44.6)
Water + CH_3CN						
283	3.44	3.44	2.37	1.58	0.73	0.12
293	3.15	2.96	2.58	1.38	0.79	0.15
303	3.08	2.63	2.41	1.35	0.84	0.18
313	2.85	2.45	2.20	1.26	0.95	0.23
	0% (76.7)	10% (76.5)	20% (75.2)	40% (74.0)	60% (70.5)	--
Water + DMSO						
283	3.44	3.51	3.49	2.37	1.19	-
293	3.15	3.07	3.14	2.27	1.26	-
303	3.08	2.50	2.58	1.98	1.14	-
313	2.85	2.22	2.35	1.71	1.24	-

Table.5: Corrected Stoke's radius (r_i in A^0) of the species of Citric acid in different dielectric constant (ε at 303K) or various compositions (v/v) of water + CH_3CN and water + DMSO

(r_i in A^0)						
T(K)	0% (76.7)	10% (72.6)	20% (68.6)	40% (60.7)	60% (53.0)	80% (44.6)
Water + CH_3CN						
283	2.24	2.19	2.19	2.33	2.84	8.45
293	2.22	2.19	2.19	2.38	2.73	7.07
303	2.19	2.19	2.18	2.36	2.65	6.14
313	2.17	2.18	2.18	2.38	2.51	5.14
	0% (76.7)	10% (76.5)	20% (75.2)	40% (74.0)	60% (70.5)	--
Water + DMSO						
283	2.24	1.94	1.93	2.03	2.34	-
293	2.22	1.94	1.92	2.01	2.27	-
303	2.19	1.97	1.95	2.01	2.29	-
313	2.17	1.97	1.94	2.06	2.21	-

Further they concluded that for a strong indication of selective solvation of the electrolyte or ion by the solvent in the mixture i. e., species of the electrolyte, citrate ion is preferentially solvated by co-solvent and H^+ by water. The preferential solvation of ions depends on the viscosity of the medium and exchange of ions with surrounding solvent molecules. Therefore it can be predicted that the structure of water determines the Walden product in water +cosolvent. Structure of water gets altered either because of solvent-solvent or ion-solvent interaction or both put together. Due to this preferential solvation with the decrease in dielectric constant, ionic size become larger, mobility becomes lower and hence conductivity decreased.

Thermodynamic parameters

The variation of conductance of an ion with temperature can be treated as similar to the variation of the rate constant with temperature which is given by the Arrhenius equation [30] since conductance of an ion is dependent on the rate of movement of ion. Hence

$$\lambda_m^{\ 0} = A.e^{\frac{-Ea}{RT}} \qquad (9)$$

$$\log \lambda_m^{\ 0} = \log A - \frac{Ea}{2.303RT} \qquad (10)$$

Where A is a Arrhenius constant, E_a is the activation energy of the rate process which determines the rate of movement of ions in solution. The slope of the linear plot of log λ_m^0 Vs 1/T (Fig.3) gives the value of E_a (Table.6). E_a slightly decreased with the decrease in dielectric constant in the beginning and increased thereafter in both the cases of solvent mixtures. This initial decrease may be due to the increase in dissociation. This leads to release of ions, which undergo solvation. So even though the E_a is small, λ_m^0 did not increase. Later ions get solvated by the solvent mixture molecule and become bulkier requiring more energy for the transport process. So λ_m^0 decreases. The later increase in E_a is consistent with the decrease in λ_m^0. Thermodynamic parameters of association such as ΔHa, ΔGa and ΔSa were also calculated on the basis of the following equations.

$$\Delta Ha = \frac{RT^2 d \ln Ka}{dT} \qquad (11)$$

$$\Delta Ga = -RT \ln Ka \qquad (12)$$

$$\Delta Sa = \frac{\Delta Ha - \Delta Ga}{T} \qquad (13)$$

The change in enthalpy of the process of association (ΔHa) is calculated from the slope of the plot of log Ka Vs 1/T (Fig not shown). ΔGa was calculated at various temperatures and the average value was considered. ΔSa was obtained from equation.13 at different temperatures and the average value was noted down.

These values with the increase in dielectric constant are shown in Table.6. The heat of association ΔHa was found to be negative till 40% CH_3CN (dielectric constant: 60.7) and 40% DMSO (dielectric constant: 74.0), showing the exothermic behaviour of the system as proposed under dissociation and association constant and then the values become positive indicating the endothermic behaviour of the system. Both the behaviours are feasible, as the ΔGa is found to be negative. ΔSa is very small. The positive values for entropy are an indication of the presence of sterically hindered disordered species in that solvent.

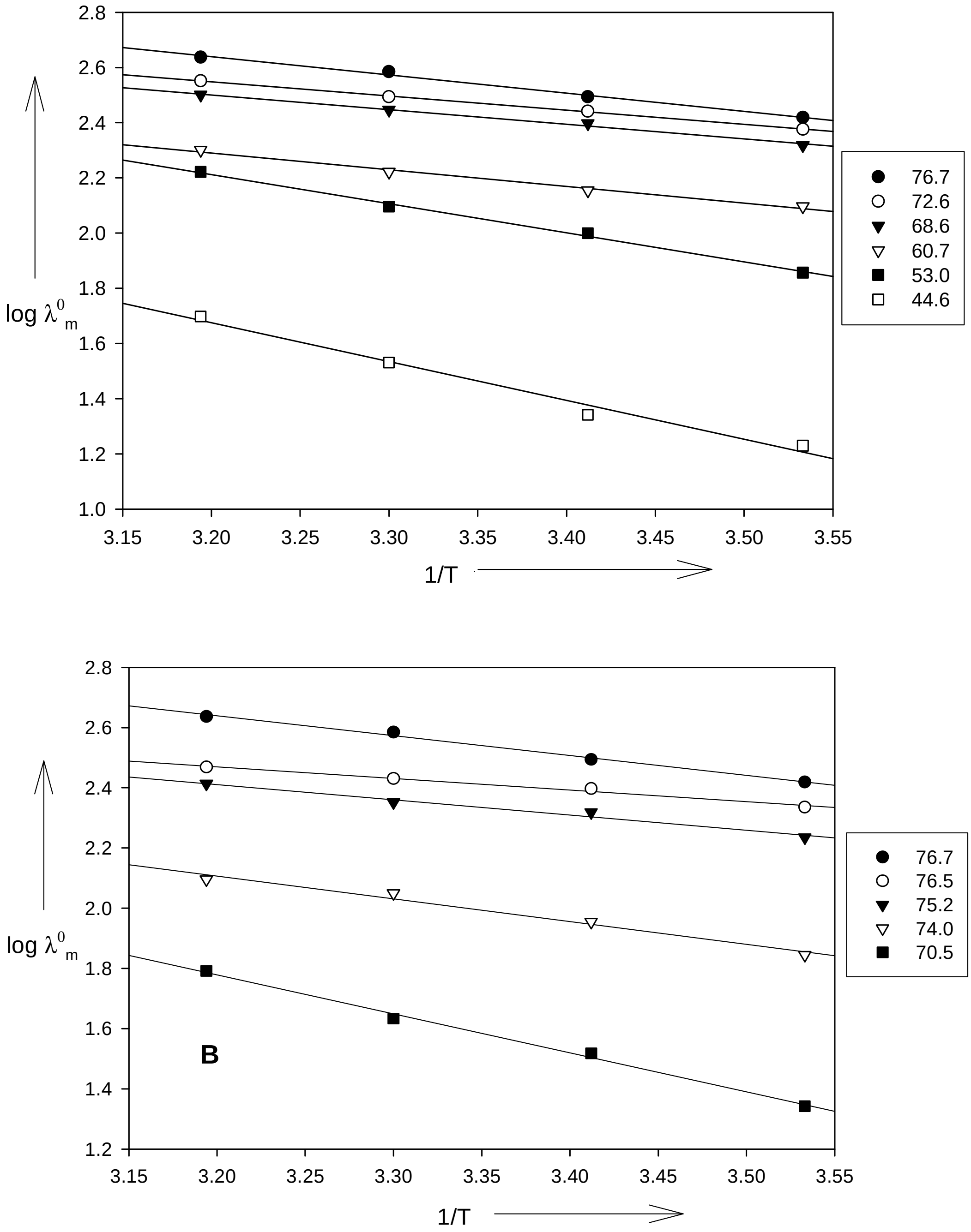


Fig.3. Plot of log λ^0_m Vs 1/T for citric acid in different dielectric constant at 303K, A-water+CH_3CN; B- water+DMSO

Thermodynamics of solvation

Ion-solvent or solute-solvent interaction is the measure of the extent to which the solute dissolves and dissociates an electrolyte in it. The free energy of solvation (ΔGs-s) with a negative value indicates the feasibility of the ion-solvation process and also the capacity to destroy the lattice structure of the crystal. ΔGs-s (s-s stands for solute-solvent interaction) was calculated using the Born relation [35]

Table.6: Computed thermodynamic parameters for Citric acid in different dielectric constant (ε at 303K) or various compositions (v/v) of water + CH_3CN and water + DMSO

Thermo dynamic parameters	Water + CH_3CN					
	0% (76.7)	10% (72.6)	20% (68.6)	40% (60.7)	60% (53.0)	80% (44.6)
Ea ($kJmol^{-1}$)	11.87	10.14	11.10	12.63	20.48	26.04
ΔHa ($kJmol^{-1}$)	-4.46	-16.04	-16.58	-16.88	4.78	24.5
ΔGa ($kJmol^{-1}$)	-17.73	-18.19	-19.10	-19.89	-22.31	-22.70
ΔSa($kJ\ K^{-1}mol^{-1}$)	0.044	0.007	0.008	0.009	0.090	0.157
Water + DMSO						
	0% (76.7)	10% (76.5)	20% (75.2)	40% (74.0)	60% (70.5)	--
Ea ($kJmol^{-1}$)	11.87	8.75	9.57	16.90	25.12	-
ΔHa ($kJmol^{-1}$)	-4.46	-13.97	-20.29	-11.87	8.42	-
ΔGa ($kJmol^{-1}$)	-17.73	-18.15	-19.26	-20.14	-21.95	-
ΔSa($kJ\ K^{-1}mol^{-1}$)	0.044	0.014	-0.005	0.027	0.102	-

$$\Delta G_{s-s} = -\frac{N_A (Z_i e_0)^2}{2r_i}\left(1-\frac{1}{\varepsilon}\right) \qquad (14)$$

Where e_0 is the electronic charge, ε the dielectric constant of the solvent, N_A the Avogadro number and r_i is the corrected Stoke’s radius obtained from the relationship based on Stoke’s law. The corrected Stoke’s radius was calculated using the relation

$$r_i = \frac{0.82Z}{\lambda_m{}^0 \eta_0} + 0.0103\varepsilon + r_y \qquad (15)$$

Where r_y = 0.85A^0 describes dipolar unassociated solvents and r_y = 1.13 applies to protic and associated solvents. The calculated values are shown in Table.5. From the above equation it is clear that change in free energy of the solvation process depends on r_i and dielectric constant of the solvent involved. So larger the dielectric constant and smaller the radius of the ion, larger will be the value of ΔG_{s-s}. in negative direction (Table.7). ΔG_{s-s} increased with the decrease in dielectric constant indicating the decrease in spontaneity of the process. Probably making dissolution/solvation process difficult. This is what experimentally observed in the present case ie., after 80% CH_3CN there was solubility problem and very small value for $\lambda_m{}^0$. Similarly in the case DMSO also.

Negative ΔH_{s-s} values denote the exothermic nature of solvation. High negative value of ΔG_{s-s} denotes the higher stability of the species in solvent water than in solvent mixture.

A plot of -ΔG_{s-s} versus 1/r_i was obtained and found to be linear which indicates that the system is following Born model (Fig. 4).

Table.7. Computed values of thermodynamics of solvation for Citric acid in different dielectric constant (ε at 303K) or various compositions (v/v) of water + CH_3CN and water + DMSO at-

T(K)	0% (76.7)			10% (72.6)			20% (68.6)			40% (60.7)			60% (53.0)			80% (44.6)		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Water + CH_3CN																		
283	318.0	0.018	313.0	324.0	0.020	317.0	325.0	0.021	319.0	303.0	0.020	298.0	249.0	0.015	245.0	83	0.005	82
293	321.0	0.020	315.0	325.0	0.022	318.0	324.0	0.023	318.0	298.0	0.021	292.0	258.0	0.017	253.0	99	0.006	97
303	325.0	0.021	319.0	325.0	0.021	318.0	326.0	0.022	319.0	299.0	0.020	293.0	266.0	0.018	260.0	109	0.009	98
313	326.2	0.023	319.0	326.0	0.025	318.0	326.0	0.025	318.0	296.0	0.027	288.0	279.0	0.028	270.0	133	0.011	99
	0% (76.7)			10% (76.5)			20% (75.2)			40% (74.0)			60% (70.5)			-		
Water + DMSO																		
283	318.0	0.018	313.0	385.5	0.017	360.6	367.3	0.015	363.1	349.2	0.018	344.0	302.7	0.017	297.8	-	-	-
293	321.0	0.020	315.0	365.3	0.018	359.8	369.1	0.016	364.3	352.4	0.020	346.5	311.9	0.019	306.2	-	-	-
303	325.0	0.021	319.0	359.6	0.020	353.5	363.3	0.020	357.1	352.1	0.034	341.6	308.9	0.027	300.8	-	-	-
313	326.2	0.023	319.0	359.3	0.024	351.8	364.8	0.024	357.3	343.5	0.011	340.0	319.9	0.018	314.0	-	-	-

1. –ΔHs-s (kJmol^{-1}) *2. ΔSs-s* (kJK^{-1}mol^{-1}) *3. -ΔGs-s* (kJmol^{-1})

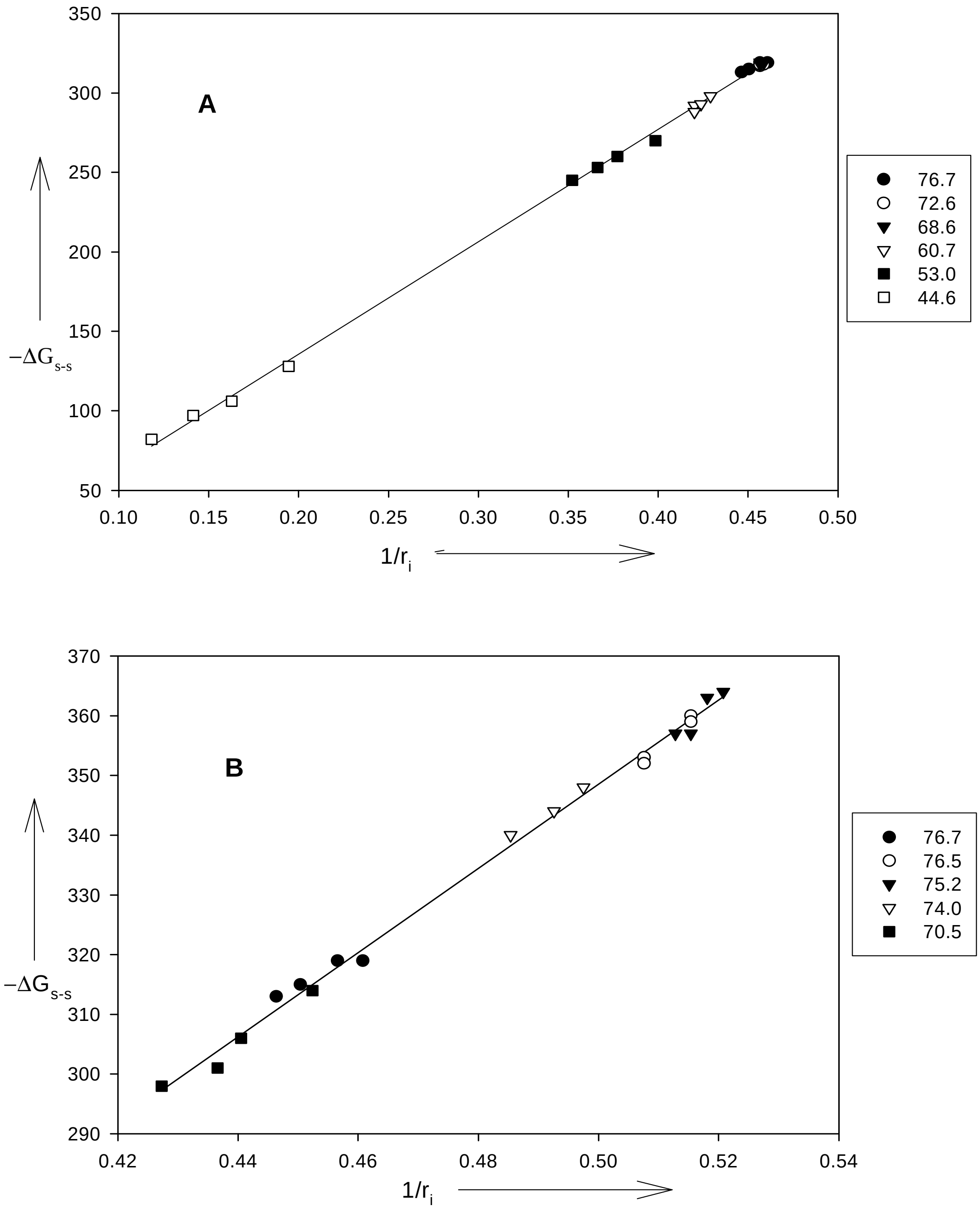


Fig.4. Plot of -$\Delta G_{s\text{-}s}$ Vs $1/r_i$ for citric acid in different dielectric constant at 303K,

***A**-water+CH_3CN; **B**- water+DMSO*

The change in entropy $\Delta S_{s\text{-}s}$ and change in enthalpy $\Delta H_{s\text{-}s}$ of solvation was also calculated using the Born equation and the values are shown in Table.7.

$$\Delta S_{s\text{-}s} = \frac{N_A (Z_i e_0)^2}{2r_i} \frac{1}{\varepsilon^2} \left(\frac{\partial \varepsilon}{\partial T} \right) \qquad (16)$$

$$\Delta H_{s\text{-}s} = \Delta G_{s\text{-}s} + T\, \Delta S_{s\text{-}s} \qquad (17)$$

$\Delta H_{s\text{-}s}$ was also found to be negative indicating the process of solvation to be exothermic in character. Estimated $\Delta S_{s\text{-}s}$ was found positive but small in all the cases indicating the slight disorder ness in the system because of steric hinderence.

Solvation number (S_n)

Solvation number of an ion is the number of solvent molecules that surrenders its translational degree of freedom and get associated to that central ion and always move along with the ion. Solvation number reflects the magnitude of ion-solvent interaction of the system. Solvation number can be calculated by various methods. One of the methods based on the relation [39]

$$S_n = \frac{d_{AB} - r_i}{r_{sol/sol\ mix}} \qquad (18)$$

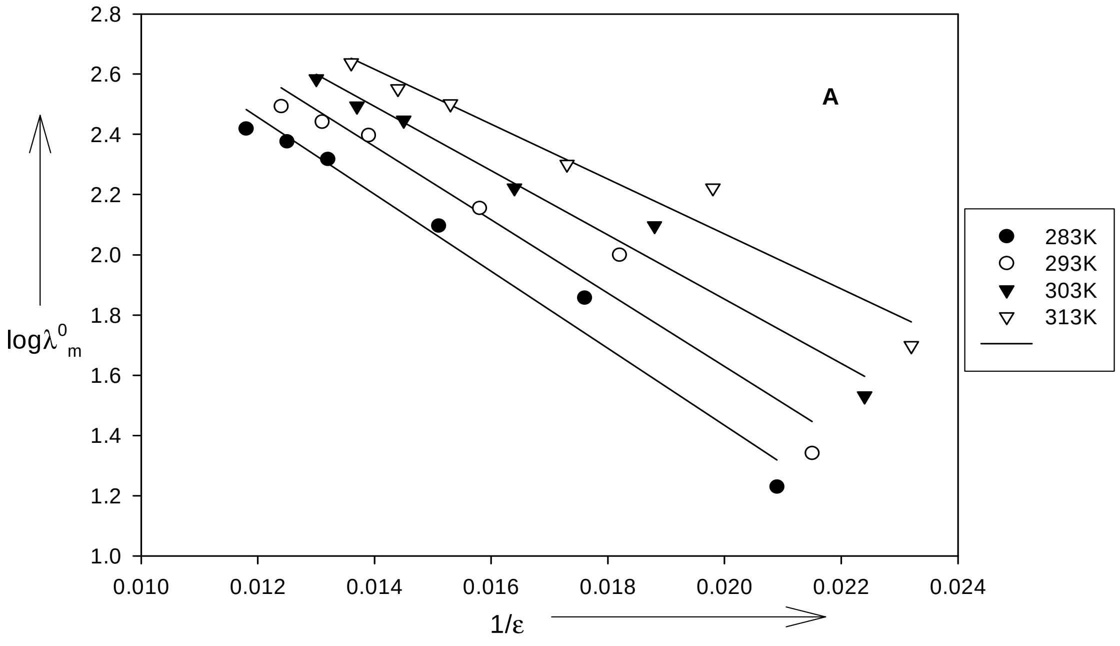
where r_i is the corrected Stoke's radius of an ion. Difference between d_{AB} and r_i gives the surplus number of solvent molecules present around an ion. When it is divided by the radius of solvent/solvent mixture, the resulting value represents the solvation number. The inter nuclear distance or the closest distance of approach was calculated on the basis of the following equation [40].

$$\log \lambda_m^{\ 0} = \log \lambda - \frac{Z_A Z_B e^2}{\varepsilon d_{AB} kT} \qquad (19)$$

Here Z_A, Z_B are the ionic charge on the cation & anion , e is the electronic charge, ε is the dielectric constant, d_{AB} is the inter nuclear distance, k is the Boltzman constant & T is the absolute temperature. The plot of log $\lambda_m^{\ 0}$ versus 1/ε (was obtained by varying % composition of water +CH_3CN & water+DMSO) and found to be linear at all temperatures (Fig.5). It gave a slope of $Z_A Z_B e^2/d_{AB}kT$ from which the value of inter nuclear distance d_{AB} was determined. The value of d_{AB} used in the determination of Solvation number. The calculated values of S_n are presented in the Table.8. The value of S_n is found to be around five (Table.8) indicating the formation of solvent separated ion pair in the system.

Table.8. Computed values of Solvation number of the species of Citric acid in water + CH_3CN and water + DMSO at different temperature

T(K)	Water + CH_3CN	Water + DMSO
283	4.7	3.8
293	5.4	5.4
303	4.2	6.1
313	4.8	7.5



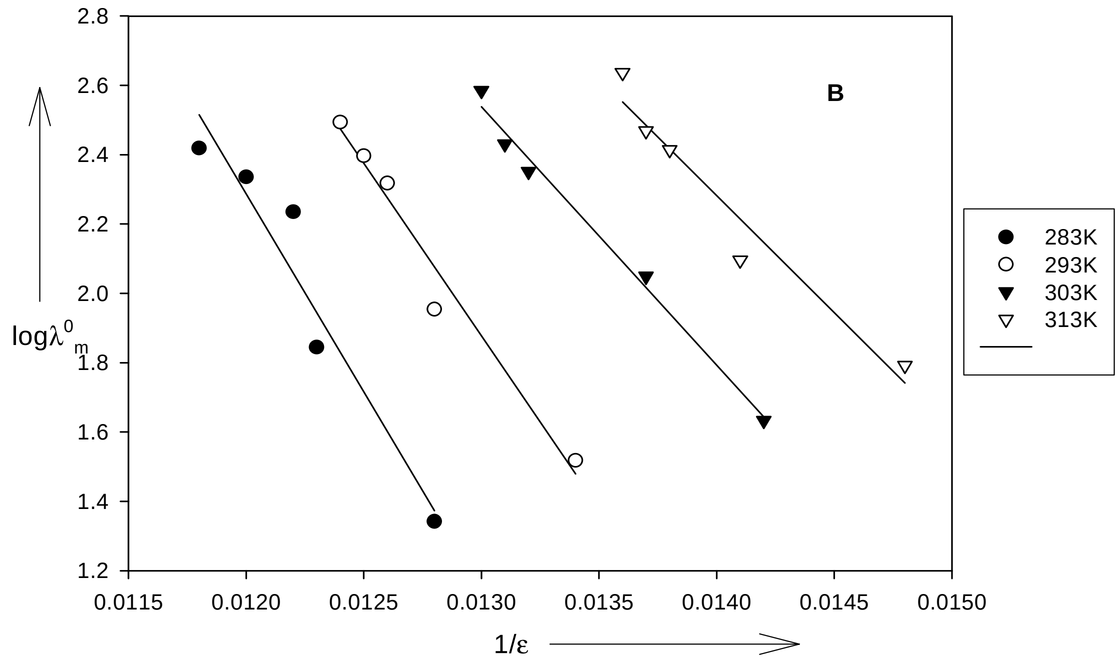


Fig.5. Plot of log λ_m^0 Vs 1/ε for citric acid in A- water+CH_3CN; B- water+DMSO

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