



## Studies on the Solvation Behaviour of Ammonium Citrate in Aqueous and Partial Aqueous Media

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The paper deals with the study on the solvation behaviour of ammonium citrate in water and various compositions (v/v) of water + acetonitrile and water + dimethyl sulfoxide in the temperature range 283 to 313 K. The electrical conductivity data were analyzed by Kraus-Bray and Shedlovsky models of conductivity. The molar conductance at infinite dilution  $\lambda_m^0$  found to decrease with increase in the amount of co-solvent indicating the increased ion-solvent interaction and solvent-solvent interactions. Association constant  $K_a$  and dissociation constant  $K_c$  have been computed in all the cases. The  $K_a$  value decreased with the increase in temperature indicating exothermic behaviour of the system. Walden product and corrected Stokes radius have been determined in all the cases of solvent mixtures. Thermodynamics of solvation such as  $\Delta G_{s-s}$ ,  $\Delta S_{s-s}$  and  $\Delta H_{s-s}$  have also been evaluated from Born equation. These data were utilized to study the ion-solvent and solvent-solvent interactions.

**Key Words:** Electrical conductivity, Solvation, Ammonium citrate, Acetonitrile, Dimethyl sulfoxide.

### INTRODUCTION

In recent years, the study of conductance behaviour of electrolytes in various non-aqueous media of different dielectric constants has received considerable attention due to its varied applications in several electrochemical investigations<sup>1-4</sup>. Conductivity study is one of the important and the simplest tools to understand the solvation behaviour of the ionic species involved in that electrolyte system under existing conditions<sup>5-7</sup>. The behaviour of electrolytes in solution can be revealed by conductance<sup>1-7</sup> and viscosity investigations<sup>8,9</sup>, which makes one to understand in detail about the nature of ion-ion and ion-solvent interactions operating in the system.

The amount of ammonia in fertilizer can be analyzed in the presence of ammonium citrate<sup>10</sup>. Recently, ammonium citrate used as additive in cyanide free gold plating<sup>11,12</sup>. This paper reports the solvation behaviour of ammonium citrate in aqueous and partial aqueous media.

### EXPERIMENTAL

Ammonium citrate (Loba Chemie, India) was used as received without further purification. Non-aqueous solvents-acetonitrile and dimethyl sulfoxide were purified and triply distilled water (specific conductivity of the order of  $1 \times 10^{-6}$  S cm<sup>-1</sup>) were used in the entire work. The solution of ammonium citrate was prepared (0.01 M) in water and water + acetonitrile/dimethyl sulphoxide in volume ratio.

Conductance measurements were made with a digital direct reading conductivity meter (CM 180, Elico make) and a calibrated dip type conductivity cell with cell constant = 0.975 cm<sup>-1</sup>. All the measurements were made in a thermostat or cryostat maintained at the desired temperature  $\pm 0.01$  °C.

### RESULTS AND DISCUSSION

**Limiting molar conductance:** The solution of ammonium citrate was prepared in water and water + CH<sub>3</sub>CN/ DMSO to get various compositions (v/v) (0, 10, 20, 40 and 60 %) or mole fraction: 0 to 0.368 and 0.272. Specific conductance of the solution was read directly from the instrument and was used after solvent correction<sup>13</sup> for evaluating molar conductance. Then the conductance data were subjected to analysis by Kraus-Bray equation<sup>14</sup>. The chosen electrolyte is of 1:3 type, the Kraus-Bray equation related to that condition was tried but the plot was found non-linear and hence Kraus-Bray equation of 1:2 electrolyte was tried and even that too found non linear. Hence, the Kraus-Bray equation related to 1:1 electrolyte (Eqn.1) was applied.

Kraus-Bray equation may be represented as:

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

where,  $\lambda_m^0$  is the molar conductance at infinite dilution, C is the concentration in molar and  $K_c$  is the dissociation constant. Kraus-Bray plot was drawn for all the cases and found to be

linear. The intercept and slope of the plot gave limiting molar conductance ( $\lambda_m^0$ ) and dissociation constant ( $K_c$ ) respectively and resulted values are shown in Tables 1 and 2. Since Kraus-Bray model is inadequate to explain the effect of ionic mobility or the activity coefficient on conductivity another model which accounts for those effects, namely Shedlovsky model<sup>15</sup>, was used for further analysis of the conductivity data.

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

where,  $K_a$  is the association constant and  $f_{\pm}$  is the mean activity coefficient of the electrolyte,  $C$  is the concentration,  $S$  is the Onsagar slope and  $\lambda_m^0$  is the limiting molar conductance. The plot of  $1/S\lambda_m$  vs.  $C\lambda_m S f_{\pm}^2$  was found to be linear and the intercept and slope of the linear plot gave the limiting molar conductance ( $\lambda_m^0$ ) and association constant ( $K_a$ ). The values are shown respectively in Tables 1 and 2.

T(K)	X = 0.0		X = 0.046		X = 0.096		X = 0.214		X = 0.368	
	1	2	1	2	1	2	1	2	1	2
CH <sub>3</sub> CN										
283	261	263	227	230	208	210	196	196	161	163
293	325	326	292	289	277	281	243	246	196	200
303	398	397	352	357	333	338	294	294	238	243
313	476	476	427	433	408	412	357	357	285	285
DMSO										
	X = 0.0		X = 0.025		X = 0.056		X = 0.139		X = 0.272	
	1	2	1	2	1	2	1	2	1	2
283	261	263	204	210	161	162	87	89	43	43
293	325	326	259	266	205	205	116	116	55	56
303	398	397	322	322	250	252	139	142	69	70
313	476	476	385	390	294	299	166	169	86	87

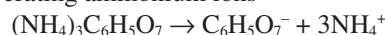
From the Table-1, it is clear that temperature enhanced the conductance values at all mole fractions of CH<sub>3</sub>CN or DMSO in water. This is expected as the increase in temperature increases the thermal energy and mobility of ions, leading to increase in conductivity.

Limiting molar conductance decreased with increase in the amount of co-solvent, CH<sub>3</sub>CN or DMSO due to the increased solvent-solvent interaction and also decreased dielectric constant.

The study was carried out up to  $X = 0.368$  of CH<sub>3</sub>CN or  $X = 0.272$  of DMSO. Beyond that there was solubility problem. But it is certain that decrease in molar conductance with increase in co-solvents is not due to decrease in solubility since citric acid is a weak electrolyte, itself dissociated up to 80 % CH<sub>3</sub>CN ( $X = 0.594$ ) and 60 % DMSO ( $X = 0.272$ ) there is no reason to believe that the relatively strong electrolyte (ammonium citrate) is not dissociated fully above that mole fraction. Therefore, the decrease in limiting molar conductance must be due to the increased solvent-solvent and ion-solvent interactions or the capturing of more number of conducting species by the cavity formed during formation of the solvent-solvent interaction or may be due to the decrease in dielectric constant of the solvent mixture.

In the case of water + acetonitrile mixture the limiting molar conductance decreased with the increase in CH<sub>3</sub>CN which might be due to the increased three dimensional network of water with acetonitrile or increased ion-solvent interaction there by changing the physical properties of the solvent.  $\lambda_m^0$  value appeared to be higher in water + acetonitrile compared to water + DMSO mixture. It may be attributed to the higher dielectric constant, dipole moment, lower molecular size and high viscosity of acetonitrile. Addition of small amount of DMSO to water rigidifies the three dimensional structure of water. The hydrogen bonding between water and DMSO is stronger than that in pure water molecule and has been attributed to dipole-dipole interaction<sup>3</sup>. The size of solvent mixture molecule is larger and hence conductivity is smaller.

**Dissociation and association constants:** Ammonium citrate being a salt of citric acid acts as good electrolyte in solvents, liberating ammonium ions-



The values of dissociation and association constants obtained respectively from the slopes of Kraus-Bray and Shedlovsky plots and are shown in Table-2. There is no notable change either in  $K_c$  or  $K_a$  with the increase in temperature. But  $K_c$  increased in the beginning and then decreased with the increased mole fraction of CH<sub>3</sub>CN in water. But in the case of water + DMSO it increased till 20 % DMSO ( $X = 0.056$ ) and then decreased. Increase in  $K_a$  with the increase in the amount of CH<sub>3</sub>CN or DMSO indicated the possibility of formation of ion aggregation. In general, the variation of these values either with temperature or with the solvent composition is mainly due to the change in dielectric constant and the

T (K)	$K_c$					$K_a$				
	CH <sub>3</sub> CN					DMSO				
	X = 0.0	0.046	0.096	0.214	0.368	X = 0.0	0.025	0.056	0.139	0.272
283	0.020	0.028	0.025	0.014	0.008	47.7	39.1	81.5	82.2	143.4
293	0.024	0.027	0.021	0.015	0.010	42.5	34.2	105.8	67.7	110.8
303	0.021	0.033	0.026	0.019	0.011	40.9	31.8	94.8	52.7	106.8
313	0.020	0.034	0.033	0.021	0.014	49.8	33.9	84.8	39.5	90.1
283	0.020	0.026	0.026	0.020	0.019	47.7	54.6	61.6	56.1	49.7
293	0.024	0.025	0.021	0.021	0.026	42.5	50.6	45.8	52.2	39.2
303	0.021	0.020	0.022	0.028	0.031	40.9	53.9	47.6	40.3	29.8
313	0.020	0.022	0.028	0.029	0.028	49.8	51.7	42.0	33.1	32.8

TABLE-3  
COMPUTED VALUES OF THICKNESS OF IONIC ATMOSPHERE ( $1/k \times 10^{-8}$  cm) FOR AMMONIUM CITRATE IN DIFFERENT MOLE FRACTIONS OF CH<sub>3</sub>CN AND DMSO IN WATER AT DIFFERENT TEMPERATURE

T(K)	CH <sub>3</sub> CN					DMSO			
	X = 0.046	0.096	0.214	0.368	0.025	0.056	0.139	0.272	
283	7.04	6.84	6.40	5.95	7.17	7.12	7.09	6.95	
293	6.98	6.79	6.37	5.94	7.15	7.11	7.06	6.94	
303	6.94	6.75	6.35	5.93	7.13	7.06	7.01	6.84	
313	6.88	6.69	6.29	5.88	7.07	7.05	6.97	6.83	

TABLE-4  
CALCULATED VALUES OF SLOPE OF  $\log \lambda_m$  ( $\text{mho cm}^2 \text{mol}^{-1}$ ) vs.  $\log C$  ( $\text{mol dm}^{-3}$ ) FOR AMMONIUM CITRATE IN DIFFERENT MOLE FRACTIONS OF CH<sub>3</sub>CN AND DMSO IN WATER AT DIFFERENT TEMPERATURE

T(K)	CH <sub>3</sub> CN					DMSO				
	X = 0.0	0.046	0.096	0.214	0.368	0.0	0.025	0.056	0.139	0.272
283	0.072	0.090	0.102	0.133	0.196	0.072	0.091	0.080	0.086	0.090
293	0.078	0.083	0.092	0.132	0.182	0.078	0.091	0.078	0.090	0.080
303	0.077	0.074	0.080	0.113	0.168	0.077	0.073	0.081	0.088	0.068
313	0.064	0.067	0.070	0.092	0.149	0.064	0.073	0.078	0.081	0.061

TABLE-5  
COMPUTED VALUES OF WALDEN PRODUCT ( $\lambda_m^0 \eta_0$ ;  $\text{mho cm}^2 \text{mol}^{-1} \text{poise}$ ) FOR AMMONIUM CITRATE IN DIFFERENT MOLE FRACTIONS OF CH<sub>3</sub>CN AND DMSO IN WATER AT DIFFERENT TEMPERATURE

T(K)	CH <sub>3</sub> CN					DMSO				
	X = 0.0	0.046	0.096	0.214	0.368	0.0	0.025	0.056	0.139	0.272
283	3.41	3.28	2.92	2.47	1.64	3.41	3.30	3.27	2.95	2.33
293	3.28	3.12	2.86	2.35	1.56	3.28	3.18	3.09	2.93	2.10
303	3.19	2.97	2.87	2.37	1.60	3.19	2.99	2.87	2.45	1.82
313	3.12	2.93	2.83	2.24	1.62	3.12	2.89	2.66	2.28	1.72

TABLE-6  
COMPUTED VALUES OF CORRECTED STOKES RADIUS ( $\text{\AA}$ ) FOR AMMONIUM CITRATE IN DIFFERENT MOLE FRACTIONS OF CH<sub>3</sub>CN AND DMSO IN WATER AT DIFFERENT TEMPERATURE

T(K)	CH <sub>3</sub> CN					DMSO				
	X = 0.0	0.046	0.096	0.214	0.368	0.0	0.025	0.056	0.139	0.272
283	2.24	2.20	2.19	2.14	2.22	2.24	1.95	1.94	1.96	2.00
293	2.21	2.18	2.16	2.13	2.22	2.21	1.93	1.93	1.93	2.00
303	2.18	2.15	2.12	2.10	2.19	2.18	1.92	1.92	1.93	2.02
313	2.14	2.12	2.09	2.09	2.16	2.14	1.90	1.90	1.94	2.02

reduction in thickness of ionic atmosphere as shown in Table- 3 surrounding the polar species<sup>13</sup>. Hence, to identify the possible aggregation of ions an attempt has been made by studying to plot  $\log \lambda_m$  vs.  $\log C$  was drawn based on Fuoss equilibrium equation<sup>16</sup> related to the partially dissociated electrolytes. But in the present case, the slope was found to be less than -0.5 as against the expected -0.5 (Table-4) and hence there may not be any notable amount of ion association.

**Walden product** : Walden product<sup>17</sup> depends on limiting conductance of the electrolyte,  $\lambda_m^0$  and the viscosity of the solvent as:

$$\lambda_m^0 \eta_0 = \frac{Z e_0 F}{6 \pi r T} \quad (3)$$

The product was calculated at all temperatures and mole fractions under study and resulted data are shown in Table-5. Walden product slightly decreased with the increase in temperature in both the cases of solvent systems. Walden product decreased for the increased amount of co-solvent in water at all temperatures. From the equation of Walden, it is evident that Walden product is inversely related to the Stokes radius.

In the present case the corrected Stokes radius was calculated (Table-6) instead of Stokes radius for all the cases using the expression as reported<sup>18</sup>. The corrected Stokes radius initially decreased and reaching a minimum at 20 % co-solvent ( $X = 0.096$  or  $0.056$ ) and then increased.

**Thermodynamic parameters**: Since the conductance is believed to be a rate process and hence the Arrhenius equation<sup>13</sup> can be made applicable to this conducting rate process. Accordingly, the energy of activation,  $E_a$  of conducting rate process can be evaluated by:

$$\lambda_m^0 = A e^{\frac{-E_a}{RT}} \quad (4)$$

where, A is the frequency factor, R is the gas constant,  $\lambda_m^0$  is the limiting molar conductance and T is the absolute temperature. The energy of activation was calculated from the slope of the linear plot of  $\log \lambda_m^0$  Vs  $1/T$  (Fig. 1) and the values are shown in Table-7. The energy of activation increased with percentage composition of DMSO ( $X = 0$  to  $0.272$ ) and CH<sub>3</sub>CN ( $X = 0$  to  $0.368$ ).

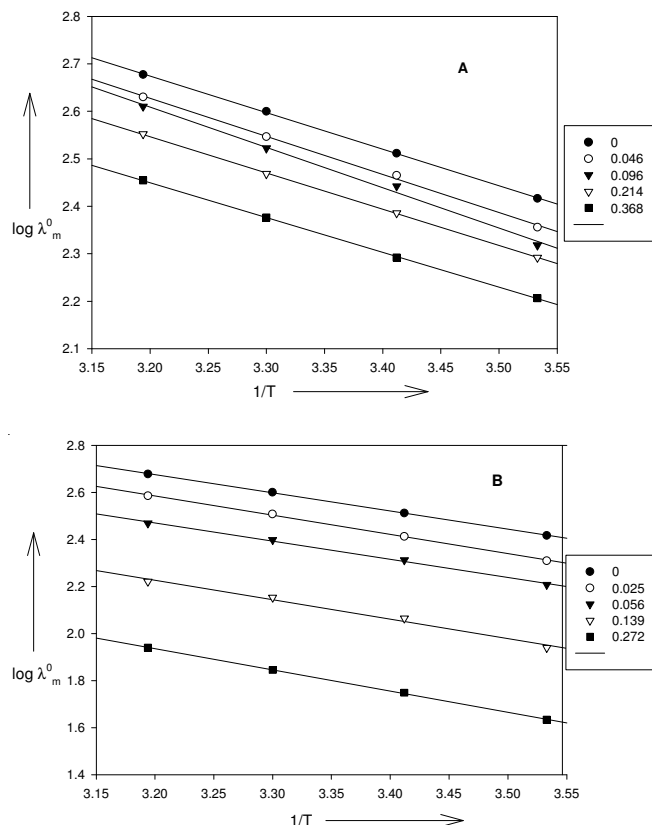


Fig. 1. Plot of  $\log \lambda_m^0$  vs  $1/T$  for ammonium citrate in different mole fractions of  $\text{CH}_3\text{CN}$  (A) and DMSO (B) in water

TABLE-7

COMPUTED VALUES OF ENERGY OF ACTIVATION ( $E_a$ ) FOR AMMONIUM CITRATE IN DIFFERENT MOLE FRACTIONS (X) OF  $\text{CH}_3\text{CN}$  AND DMSO IN WATER

$\text{CH}_3\text{CN}$	X = 0.0	X = 0.046	X = 0.096	X = 0.214	X = 0.368
$E_a$ (kJ mol <sup>-1</sup> )	14.3	15.5	16.75	16.95	17.15
DMSO	X = 0.0	X = 0.025	X = 0.056	X = 0.139	X = 0.272
$E_a$ (kJ mol <sup>-1</sup> )	14.3	14.93	15.5	15.89	17.04

**Thermodynamics of solvation:** Solvation is a process where the ion/solute is covered by solvent molecules and forms an envelope due to ion-dipole interaction. This occurs in the case of all the ions in any solvent but with different magnitude. Certain amount of energy is required for this process which is to be computed in the form of thermodynamics of solvation

such as change in free energy ( $\Delta G_{s-s}$ ), change in enthalpy ( $\Delta H_{s-s}$ ) and change in entropy ( $\Delta S_{s-s}$ ) of solute-solvent interaction. These values can be evaluated using the following Born equations<sup>3</sup>:

$$\Delta G_{s-s} = -\frac{N_A (Z_i e_0)^2}{2r_i} \left(1 - \frac{1}{\epsilon}\right) \quad (5)$$

$$\Delta S_{s-s} = \frac{N_A (Z_i e_0)^2}{2r_i} \frac{1}{\epsilon^2} \frac{\partial \epsilon}{\partial T} \quad (6)$$

$$\Delta H_{s-s} = \Delta G_{s-s} + T \Delta S_{s-s} \quad (7)$$

$\Delta H_{s-s}$  and  $\Delta G_{s-s}$  were found to be negative (Table-8) indicating the feasibility or spontaneity of the exothermic behaviour of the solvation process. The stability of the species in solution depends on the magnitude of free energy change arising from solute-solvent interaction. Larger the  $\Delta G_{s-s}$  higher will be the stability of the species in that solution.  $\Delta G_{s-s}$  decreases with increase in the amount of DMSO in all the cases of solvent mixtures but increased in case of water +  $\text{CH}_3\text{CN}$  till 40% ( $X = 0.214$ ) and later it decreased. Plot of  $-\Delta G_{s-s}$  vs.  $1/r_i$  (Fig. 2) was linear indicating the system to followed Born model<sup>1</sup>.  $\Delta S_{s-s}$  is positive and very small compared either to  $\Delta H_{s-s}$  or  $\Delta G_{s-s}$

**Solvation number ( $S_n$ ):** The solvent molecules which are closely attached to ion surrendering their translation degree of freedom is usually designated by primary solvation layer<sup>1</sup> and beyond this another layer is formed where the molecules are oriented either in the direction of the ion or away from that and which appears before the bulk of the solvents. Number of solvent molecules present in the primary layer is known as solvation number. Solvation number reflects the magnitude of ion-solvent interaction of that ion involved in the system. Solvation number can be calculated using the relation<sup>19</sup>.

$$S_n = \frac{d_{AB} - r_i}{r_{\text{sol}}/r_{\text{solmix}}} \quad (8)$$

where,  $r_i$  is the corrected Stokes radius of an ion,  $d_{AB}$  is the inter nuclear distance and  $r_{\text{sol}}/r_{\text{solmix}}$  is the ratio of radius of solvent and solvent mixture. Difference between  $d_{AB}$  and  $r_i$  gives the number of solvent molecules likely to present around the ion. On dividing this difference by the actual radius of the solvent (water: 1.93 Å) or solvent mixture (water +  $\text{CH}_3\text{CN}$ : 3.0408 Å or water + DMSO: 3.281 Å) and hence resulted

TABLE-8

COMPUTED VALUES OF THERMODYNAMICS OF SOLVATION FOR AMMONIUM CITRATE IN DIFFERENT MOLE FRACTIONS  $\text{CH}_3\text{CN}$  AND DMSO IN WATER AT

T(K)	$\text{CH}_3\text{CN}$ : X = 0.0			X = 0.046			X = 0.096			X = 0.214			X = 0.368		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
283	316.6	0.018	311.4	322.1	0.012	316.5	323.4	0.021	317.5	330.3	0.022	324.2	317.6	0.012	312.2
293	320.7	0.020	314.7	324.9	0.022	318.4	327.4	0.023	320.8	331.6	0.023	324.7	317.4	0.020	311.4
303	324.9	0.021	318.6	329.2	0.021	322.7	333.6	0.023	326.6	336.1	0.023	329.1	321.5	0.022	314.8
313	330.8	0.023	323.5	333.5	0.025	325.6	338.1	0.026	337.4	337.4	0.031	327.7	325.7	0.032	315.5
	DMSO: X = 0.0			X = 0.025			X = 0.056			X = 0.139			X = 0.272		
283	316.6	0.018	311.4	363.6	0.017	358.8	365.4	0.017	360.7	361.6	0.019	356.3	354.2	0.020	345.5
293	320.7	0.020	314.7	367.2	0.019	361.7	367.1	0.018	361.8	367.7	0.021	360.9	354.0	0.022	347.5
303	324.9	0.021	318.6	370.8	0.020	364.6	368.9	0.020	362.7	366.7	0.036	355.8	350.2	0.030	341.0
313	330.8	0.023	323.5	374.5	0.025	366.7	372.5	0.024	364.8	364.7	0.012	361.0	350.0	0.020	343.6

1.  $-\Delta G_{s-s}$  (kJ mol<sup>-1</sup>); 2.  $\Delta S_{s-s}$  (kJ K<sup>-1</sup> mol<sup>-1</sup>) 3.  $-\Delta H_{s-s}$  (kJ mol<sup>-1</sup>)

value represents the solvation number. The inter nuclear distance or the closest distance of approach  $d_{AB}$  was calculated on the basis of the following equation<sup>25</sup> and the plot of  $\log \lambda_m^0$  vs.  $1/\epsilon$ :

$$\log \lambda_m^0 = \log \lambda - \frac{Z_A Z_B e^2}{\epsilon d_{AB} kT} \quad (9)$$

The plot of  $\log \lambda_m^0$  vs.  $1/\epsilon$  was found to be linear (Fig not shown) and slope of it is  $Z_A Z_B e^2 / d_{AB} kT$  where  $Z_A$  and  $Z_B$  are the ionic charges,  $e$  is the electronic charge and  $k$  is the Boltzman constant. From the slope,  $d_{AB}$  was calculated and used for determining the solvation number. The computed values of  $S_n$  are shown in Table-9.  $S_n$  appears to be high indicating the existence of solvent separated ion pair.

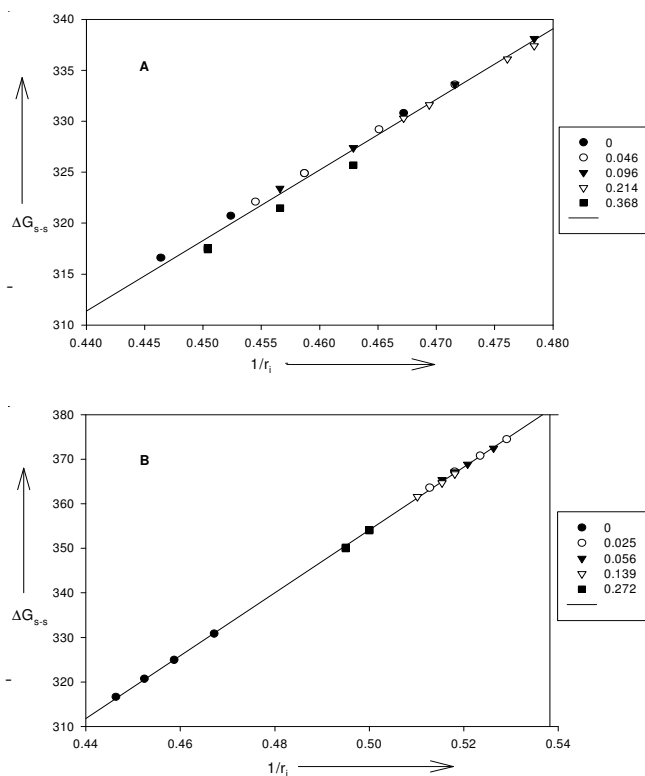


Fig. 2. Plot of  $-\Delta G_{s-s}$  vs.  $1/r_1$  for ammonium citrate in different mole fractions of  $\text{CH}_3\text{CN}$  (A) and DMSO (B) in water

TABLE-9  
COMPUTED VALUES OF SOLVATION NUMBER FOR THE SPECIES OF AMMONIUM CITRATE IN WATER +  $\text{CH}_3\text{CN}$  AND WATER + DMSO AT DIFFERENT TEMPERATURE

T (K)	Water + $\text{CH}_3\text{CN}$	Water + DMSO
283	14.9	6.3
293	13.8	6.1
303	12.8	7.0
313	13.4	7.5

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