

Ion-solvation studies of chloramine-T species in water, acetonitrile, DMF and their mixture by conductometry

C B Susha & J Ishwara Bhat*

Department of Chemistry, Mangalore University, Mangalagangothri 574 199, India

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Transport property of the species of chloramine-T has been studied in water, acetonitrile, DMF and varying compositions (v/v) of water-acetonitrile, water-DMF mixtures and the data analysed by different conductivity models to identify the involvement of association process in the system. Limiting molar conductance has been found to be maximum in acetonitrile and minimum in DMF indicating the preferential solvation of cation by DMF. Association constant has been identified at all temperatures and compositions. Thermodynamic parameters have been estimated in all the cases. Viscosity of various solvents and solvent mixtures have been determined and used to compute Walden product from which Stoke's molecular radius is estimated. The ion-solvent and solvent-solvent interactions involved in the system have been qualitatively discussed.

Studies on electrolyte conductance of an electrolyte and the effect of ion-solvation on it in aqueous and partially aqueous media have received considerable attention in recent years as they are important both from fundamental and technological points of view¹⁻⁵.

Chloramine-T, CAT, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa}$ is a very stable and inexpensive electrolyte. A detailed examination of this compound as an analytical reagent was reported⁶. Several groups have used CAT as an oxidant in kinetic and mechanistic investigations of several substrates⁷⁻⁹. But very little is known^{10,11} about its conductance behaviour. In continuation with our earlier work¹¹ on ion-solvation of CAT in different solvent and solvent mixtures herein we report its solvation behaviour in water, DMF and acetonitrile in pure and mixed solvent media at 283 to 313 K.

Materials and Methods

Commercially available (E. Merck) chloramine-T after proper purification, triply distilled water and purified solvents (DMF and acetonitrile) were used in the present work. Solution of CAT was prepared in these solvents and their mixtures (v/v), standardized iodometrically and preserved in dark coloured bottle.

Conductance measurements were made with a digital direct reading conductivity meter (Elico, model CM-180) and a calibrated dip type conductivity cell with platinised platinum electrodes (cell constant 0.999 cm^{-1}). All the measurements were made in a thermostat maintained at the desired temp. $\pm 0.01^\circ\text{C}$.

Results and Discussion

The molar conductance (Λ_m) was determined from the solvent corrected¹² specific conductance for chloramine-T in water, DMF, acetonitrile and various compositions (v/v) of water-DMF as well as water-acetonitrile at 283, 293, 303 and 313K. The values were analysed by Debye-Huckel-Onsager and Shedlovsky model of conductivity to evaluate molar conductance at infinite dilution (Λ_m°). Thus obtained values are shown in Table 1.

As expected Λ_m° increased with increase in temperature in all the cases due to increase in thermal energy and mobility of ions. Limiting molar conductance decreased sharply till 80% DMF (slowly till 20-40% CH_3CN) on adding the co-solvent (DMF or CH_3CN) to water. Later it increased sharply till 100% co-solvent.

The observed decrease in limiting conductance clearly indicates the role of the solvation of cation by the non-aqueous solvent (co-solvent). It can be said that cation is more solvated by DMF in comparison with other two solvents. On adding a co-solvent to water, solvent-solvent interaction increases. Due to this conductance decreases. The addition of aprotic and protophilic co-solvent (DMF) to water increases the coordination or three-dimensional structure of water giving a larger solvent molecule (or acts as structure former with water giving $\text{DMF}\cdot 3\text{H}_2\text{O}$). Because of this either the solvation shell increases or captures more number of conducting ions leading to the decrease in conduction. The decrease in conductance may be due to decrease in solubility resulting from the decrease in dielectric constant of the

Table 1—Calculated molar conductance at infinite dilution from different methods for CAT in H₂O-DMF and H₂O-CH₃CN mixtures at different temperatures

T(K)	0		10		20		40		60		80		Cosolvent, %	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
CAT in H ₂ O-DMF mixture														
283	67	66	56	54	47	46	32	31	26	25	24	22	43	45
293	78	79	70	69	59	59	41	42	34	34	31	30	51	52
303	93	96	88	90	69	71	53	55	43	47	40	40	60	62
313	112	118	108	109	86	87	65	68	54	60	50	64	50	69
CAT in H ₂ O-CH ₃ CN mixture														
283	67	66	60	60	57	57	61	62	62	67	80	83	80	80
293	77	79	78	77	73	75	76	79	81	85	96	98	88	88
303	93	96	100	102	96	96	96	100	99	103	113	116	103	104
313	112	118	118	121	114	114	111	116	115	119	130	133	108	117

(1) From D.H.O. model (2) From Shedlovsky eqn.

Table 2—Calculated values of K_a from Shedlovsky plot for CAT in H₂O-DMF and H₂O-CH₃CN mixture at different temperatures

T(K)	In H ₂ O - DMF Mixture (%)							In H ₂ O - CH ₃ CN Mixture (%)						
	0	10	20	40	60	80	100	0	10	20	40	60	80	100
283	5.9	5.2	8.8	5.9	9.4	7.2	6.5	5.9	1.7	2.4	0.8	1.3	17.0	36.1
293	2.9	4.4	6.6	5.6	9.6	9.9	8.2	2.9	2.5	2.0	1.3	2.6	18.4	39.1
303	3.4	5.0	2.4	6.3	12.6	14.1	9.6	3.4	4.5	2.8	1.6	4.8	19.8	49.3
313	4.0	5.4	4.4	6.5	15.7	13.4	11.2	4.0	4.9	4.0	1.9	5.7	20.7	60.2

solvent mixture. If it is so, conductivity should have been the lowest in 100% DMF as its dielectric constant is minimum. But this is not the case, because the effect of molecular size of solvent (DMF) on conductivity cannot be ruled out. The variation in viscosity of the mixture of solvents is also partially responsible for the decrease. As DMF is added to water the system becomes solvent rich (solvent-solvent interaction increases) and conductivity/mobility will vary accordingly. This problem does not arise in the case of 100% DMF. So conductivity marginally increases. But the ion-solvent interaction in this case is more than that in water and almost equal to that in 20% DMF, which is clear from values of Table 1. Hence solvent-solvent and ion-solvent interactions play a definite role in the study of electrical conductivity of chloramine-T in these solvents and solvent mixtures.

In the case of water-acetonitrile mixture the limiting conductance variation trend is slightly different from H₂O-DMF. On adding CH₃CN to H₂O the conductivity decreases till 20-40% of CH₃CN, then increases till 80% and then slightly decreases. This is probably due to the increased three-dimensional structure of water in association with acetonitrile or increased ion-solvent in-

teraction. CAT species is preferentially solvated by acetonitrile in the presence of water. So the molecular size increases and hence conductance decreases. Regular decrease in viscosity with increase in CH₃CN is an indication of higher solvent-solvent interaction and thereby increased ion-solvent interaction. This leads to decrease in conductance. Thereafter system becomes co-solvent rich (middle region), where the solvent-solvent interaction is not predominant and hence the Λ_m° value increases. But Λ_m° is more in water-acetonitrile compared to water-DMF. It may be attributed to the higher dielectric constant, dipole moment and lower molecular size of acetonitrile in comparison with DMF.

Association constant

Association constant, K_a obtained from the slope of Shedlovsky plot is shown in Table 2. It increases with increase in temperature in both the cases of solvents at all compositions indicating endothermic character of the system (Table 2). In the case of water-DMF K_a is maximum at 60% which is in conformity with the observed limiting conductance values, whereas K_a is maximum at 100% in the case of water-acetonitrile system which is slightly going against expected trend. This shows that either the aggregated species is

charged or the solvent molecules have undergone self dissociation in the presence of the electrolyte and became charged leading to higher conductance. In general, it may be stated that the variation in the values of K_a from one composition to another is primarily due to the change in dielectric constant and is also due to the reduction in the thickness of the ionic atmosphere surrounding the ionic species. It may reduce the repulsion between different ionic species by increasing the aggregation number capacity. It may be also due to bulky organic molecules either entering into the solvation shell or coming out of it during the movement of the solvated ion in solution. In general, it can be stated that the ion-solvent and solvent-solvent interactions govern the limiting conductance Λ_m° as well as association constant K_a in different solvents and solvent mixtures. Certain factors related to solvent/solution properties such as dielectric constant, viscosity, chemical effects like short range interaction have been guided by ion-dipole, ion-ion induced dipole, dispersion, hydrophobic-hydrophilic interaction as well as the cavity and related structural effects. Since the data are limited, quantitative analysis of these factors are difficult.

Thermodynamic parameter

The K_a value is used to compute thermodynamic parameters such as change in enthalpy (ΔH_a°), change in entropy (ΔS_a°) and change in free energy (ΔG_a°) of association. Since conductivity increases with increase in temperature it is supposed that this variation has to follow Arrhenius relation, $\Lambda_m^\circ = Ae^{-E_a/RT}$, where E_a is the energy of activation of rate process, R is gas constant and T is the temperature in absolute scale.

From the slope and intercept of the linear plot of $\log \Lambda_m^\circ$ versus $1/T$, E_a and $\log A$ are evaluated ($\log A$ is ~ 2.0). The E_a values (Table 3A) slowly increased upto around 40-60% DMF (20% in acetonitrile) as expected. Slope of $\log K_a$ versus $1/T$ gave ΔH_a° , the heat of association values and are shown in Table 3A. The fact that organic ions, devoid of groups specifically interacting with solvent, exhibit special properties when dissolved in water is well known^{13,14}. The minimum of heat of association appears almost in the intermediate region for H₂O-DMF (water rich region for the acetonitrile). Negative ΔH_a° means that exothermic interaction exists between the ions and becomes very less at 40% for CAT in H₂O-DMF (at 20% in H₂O-CH₃CN). The negative enthalpy of association supports our proposals of association and is supported by the negative free energy change. The minimum of enthalpy of solution may be due to the preferential hydration¹⁵ of ions. The change in standard free energy accompanying the ionization of chloramine-T in pure solvents and their mixtures relative to that of water at 283 to 313K are calculated using the equations¹⁶,

$$\Delta G_t^\circ = RT \ln (wK_s/sK_a)$$

$$\text{and } \Delta G_t^\circ = \Delta G_t^\circ(s) - \Delta G_t^\circ(w)$$

$$= 2.303 RT (pK_s - pK_w)$$

where pK_s and pK_w are the logarithm of the association constant K_a of chloramine-T in solvent mixtures and water respectively. ΔG_t° is the standard free energy of transfer. ΔG_t° was calculated at all temperatures and compositions and is shown in Table 3B. The ΔH_a° is obtained from the slope of the linear plot of $\log K_a$ versus $1/T$. Using these two values, ΔS_t° is also calculated at all temperatures and compositions. All these values are shown in Table 3B. The free energy

Table 3A—Computed values of E_a (kJ mol⁻¹) and ΔH_a° (kJ mol⁻¹) for CAT under varying compositions (v/v) of H₂O-DMF and H₂O-CH₃CN mixtures

		Cosolvent, %						
		0	10	20	40	60	80	100%
E_a	H ₂ O-DMF	13.2	16.3	—	18.3	17.6	17.0	12.0
	H ₂ O-CH ₃ CN	13.2	17.0	17.9	15.5	16.7	11.3	8.6
ΔH_a°	H ₂ O-DMF	-12.7	-8.0	—	-24.8	-16.7	-22.7	-13.8
	H ₂ O-CH ₃ CN	-12.7	-26.8	-26.1	-15.7	-4.2	-4.5	-14.4

Table 3B—Computed change in free energy of transfer (ΔG_t°) and change in entropy of transfer (ΔS_t°) for CAT

		Cosolvent, %					
		10	20	40	60	80	100
ΔG_t°	H ₂ O-DMF	-0.61	—	-1.11	-2.72	-2.55	-2.0
	H ₂ O-CH ₃ CN	0.51	0.88	2.67	0.51	-3.92	-6.09
ΔS_t°	H ₂ O-DMF	-0.02	—	-0.08	-0.05	-0.07	-0.04
	H ₂ O-CH ₃ CN	-0.09	-0.09	-0.06	-0.02	-0.01	-0.03

Table 1—Calculated molar conductance at infinite dilution from different methods for CAT in H₂O-DMF and H₂O-CH₃CN mixtures at different temperatures

T(K)	0		10		20		40		60		80		Cosolvent, %	
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	0	10	20	40	60	80	100	0	10	20	40	60	80	100
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solvent mixture. If it is so, conductivity should have been the lowest in 100% DMF as its dielectric constant is minimum. But this is not the case, because the effect of molecular size of solvent (DMF) on conductivity cannot be ruled out. The variation in viscosity of the mixture of solvents is also partially responsible for the decrease. As DMF is added to water the system becomes solvent rich (solvent-solvent interaction increases) and conductivity/mobility will vary accordingly. This problem does not arise in the case of 100% DMF. So conductivity marginally increases. But the ion-solvent interaction in this case is more than that in water and almost equal to that in 20% DMF, which is clear from values of Table 1. Hence solvent-solvent and ion-solvent interactions play a definite role in the study of electrical conductivity of chloramine-T in these solvents and solvent mixtures.

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Table 4—Calculated Walden product ($\text{ohm}^{-1} \text{cm}^{-1}$ poise) for CAT in H_2O -DMF and H_2O - CH_3CN mixtures at different temperatures

T(K)	Cosolvent, %						
	0	10	20	40	60	80	100
In H_2O -DMF mixture							
283	0.9	0.9	1.0	1.0	1.11	0.8	0.5
293	0.8	0.9	0.9	0.9	1.0	0.7	0.5
303	0.7	0.9	0.8	0.9	0.9	0.7	0.5
313	0.7	0.9	0.8	0.9	1.0	0.8	0.4
In H_2O - CH_3CN mixture							
283	3.3	3.1	2.9	2.2	2.6	3.8	5.6
293	3.6	3.2	2.9	3.01	2.9	3.8	6.1
303	3.6	3.1	3.2	2.9	2.9	3.7	5.9
313	3.6	3.0	3.1	2.9	2.7	3.4	6.9

change of transfer (ΔG_t°) is negative in H_2O - DMF (only at 80 and 100% of CH_3CN in H_2O - CH_3CN mixture) under the studied conditions (Table 3B) indicating the spontaneity of the rate process. These two (exothermic enthalpy and spontaneity) values support the proposed association process. Entropy of transfer process (ΔS_t°) is very small with values slightly negative (Table 3B) indicating the higher electrostriction or slight disorderliness of the process.

The structure making property of acetonitrile with water is evident from the positive solvation and greater slope of the plots of Λ_m° versus T at compositions except at 80% CH_3CN where solvent-solvent interaction is maximum. But in the case of water-DMF the reverse trend is observed.

Walden product

Dependence of conductance on the viscosity of the medium was shown by Walden *et al.* according to whom the product of limiting conductance of an electrolyte and solvent viscosity is inversely proportional to the viscosity of the medium i.e., $\Lambda_m^\circ \eta \propto 1/r$ where r is the effective Stoke's molecular/ionic radius of the species. In H_2O -DMF mixture the Walden product increases slowly and regularly with increase in co-solvent content in water at a given temperature till about 60% DMF and then decreases (Table 4). In the case of water-acetonitrile mixture there is little variation of the product with temperature and with % compo-

sition which proves the fact that the variation in Λ_m° is nullified by the variation in viscosity.

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