Kinetic and Thermodynamic Parameters from the Conductance of Aqueous Solutions of Chloramine-T at Different Temparatures

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The limiting molar condutances of chloramine-T in aqueous solutions in the concentration range 0.005 M to 0.100 M and temparature range 298 to 323K have been determined using Onsager plots. With these values the energy of activation for conductance and Arrhenius parameter have been evaluated. The dissociation constants (K_J) and Thermodynamic parameters are calculated. The temparature coefficient of conductance and the limiting mobilities and transport numbers are also reported.

Chloramine-T (CAT for short) is a versatile analytical reagent [1]. Though elaborate literature is available on the kinetics of oxidation of various substrates [2 - 5] , no work of depth is found on conductance behaviour of CAT in aqueous solutions except the titrimetric work [6] and conductance study by Ishwara Bhat [7]. The latter work is more concerned with nonaqueous media and do not cover wide termperature range. Hence the present investigation on conductance is carried out to evaluate transport, kinetic and thermodynamic properties.

EXPERIMENTAL

All the chemicals used were of AR quality or Merck grade. The aqueous solutions of chloramine-T were prepared in conductivity water and kept in pyrex glass containers. The Elico conductivity bridge, the conductivity cell (cell constant 0.9800) and a thermostat (regulated with a contact thermometer of accuracy ± 0.01°C) were used. The instrument was standardised with standard potassium chloride solution. Aqueous solutions of CAT (of concentrations 0.0050, 0.0100, 0.0250, 0.0400, 0.0500 and 0.1000 M) were prepared. The thermostat was set at different temperatures (298, 303, 308, 313 or 323°K) and conductance of each of the solutions was measured at each of these temperatures after equilibrating for 35-40 minutes. The specific conductance of conductivity water at each of the experimental temperatutres were determined and solvent corrections were made. Each measurement was repeated (after an interval of one week) 4 times to check the reproducibility of results.

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RESULTS AND DISCUSSION

Solvent corrections are made to the measured conductance. Molar conductance (Λ_M) was calculated for each concentration of CAT, at each temperature and a plot of Λ_M *vs* $C^{1/2}$ (Onsager Plot) was found to be linear at all temperatures. The limiting molar conductance (Λ^o_M) are obtained from Onsager plots. These are used to get the values at 1° intervals by interpolation and these values are given in Table 1.

Table 1

Limiting Molar Conductance (Λ^o_M in mho.cm^2.mol^{-1}) of CAT at Different Temperatures

T°K	Λ^o_M	T°K	Λ^o_M	T°K	Λ^o_M
298	104	308	121	316	138
301	108	309	122	317	148
302	110	310	124	318	150
303	114	311	127	319	154
304	115	312	129	320	157
305	116	313	131	321	158.5
306	117	314	132	322	160
307	119	315	135	323	162

log A =2.278, A= 169 & Ea =1.1877 KJ

It is found that around 304 to 309°K, the increase in Λ^o with temperature is comparatively smaller. This is reflected in the low temperature coefficient (a) at this temperature range. Temperature coefficient is calculated using the expression:

$$\Lambda^o_t = \Lambda^o_{25} [1 + a(t - 25)] \quad \ldots (1)$$

The a value is 0.011 at 0.05 M in the range 304 - 309°K. At all other temperatures, this coefficient is 0.02 as expected for a uni-univalent strong electrolyte.

Conductance may be considered as a rate process [7] as it depends on the rate of movement of ions. Hence Arrhenius equation of the type $\Lambda^o_M = A \exp(-Ea/RT)$ is applicable (A is the Arrhenius factor, Ea is the energy of activation and R is the gas constant). From the intercepts and slopes of the linear plots of log Λ^o_M *vs* 1/T over 298 to 323°K, the log A and Ea have been determined and included in the Table 1. The value of "A" is useful to compare conductances in solvents and solvent mixtures of low dielectric constant and higher viscosities. The energy of activation is very low.

Ionic Dissociation

The degree of dissociation is calculated by conductance ratio (Λ_M/Λ^o_M) and presented in Table 2.

Table 2

The degree of dissociation (α) = conductance ratio (Λ_M/Λ^o_M)
At Different Temperatures & Concentrations

T°K	α at 0.1 M	α at 0.05 M	α at 0.04 M
298	0.7820	0.8600	0.8800
302	0.7895	0.8643	0.8834
306	0.7950	0.8683	0.8881
310	0.8085	0.8756	0.8979
314	0.8876	0.8980	0.9158
318	0.8896	0.8990	0.9168
322	0.8400	0.9000	0.9195

At reasonable concentrations (0.04M, 0.05M & 0.10M), α is less than unity. The increase in α with temperature is cosiderably low around 306K showing the probability of conglomeration as suggeseted by Rao *et.al.* [8].

Dissociation Constant

For the dissociation of CAT, the dissociation constant K_d may be given in terms of α as

$$K_d = \alpha^2 C / (1 - \alpha) \quad \ldots (2)$$

The α values in Table 2 are in the higher range of concentrations of CAT. At such concentrations the activity coefficient is much less than unity and can not be ignored. In such cases, K_d may be calculated using

$$K_d = \frac{\alpha^2 C f_\pm}{1 - \alpha} \quad \ldots (3)$$

The mean ionic activity coefficients ($f_\pm$) can be evaluated using the Debye Huckel limiting law

$$- \log f_\pm = \frac{N^2 E^3}{2.303 R^{3/2}} \left(\frac{2\pi}{1000}\right)^{1/3} \frac{Z_i^2}{D^{3/2} T^{3/2}} \mu^{1/2} \quad \ldots (4)$$

This value is computed at each temperature and used in the calculation of K_d. The dissociation contant values (Table 3) increase with increase in dilution and increase in temperature.

$$\Delta G^\circ = -2.303 \, RT \log K_d \quad \ldots (5)$$

Using this relationship ΔG° values are calculated and included in Table 3. The negative values of ΔG° show that dissociation is a spontaneous process. The very small decrease in ΔG° with increase in temperature

Table 3

Dissociation Constant & Thermodynamic Parameters ΔG° in J.mol^{-1}

T°K	Dissociation Const.			-St. Free Energy			St.Entropy		
	0.1 M	0.05 M	0.04 M	0.1 M	0.05 M	0.04 M	0.1 M	0.05 M	0.04M
298	0.1936	0.2032	0.2042	4068.84	3949.02	3936.47	53.8115	53.4096	53.3673
302	0.2045	0.2131	0.2125	3985.83	3882.33	3889.27	52.8239	52.4812	52.5042
306	0.2149	0.2218	0.2244	3912.66	3831.80	3802.51	51.8943	51.6301	51.5343
310	0.2390	0.2395	0.2509	3689.58	3684.24	3564.34	50.5051	50.4979	50.1011
314	0.3040	0.3082	0.3193	3108.91	3074.64	2980.85	48.0124	47.9670	47.6047
318	0.3105	0.3129	0.3248	3092.50	3072.40	2973.77	47.3569	47.2937	46.9836
322	0.3129	0.3175	0.3405	3110.00	3072.21	2884.78	46.8230	46.7056	46.1235

may be attributed to increased thermal motion and chaos at higher temperatures. The values are nearly the same with decreasing concentrations of chloramine-T.

The standard enthalpy of dissociation of CAT on aqueous solutions is obtained from the linear plot of log K_d vs $1/T$. The slope gives $\Delta H°/2.3030$. The value of $\Delta H°$ thus obtained over the experimental temperature range is -11.9679 kJ.mol^{-1}. The negative value indicates that dissociation of CAT is exothermic in aqueous medium.

$$\Delta G° = \Delta H° - T\,\Delta S° \quad \ldots (6)$$

Using this relation, the values of $\Delta S°$ evaluated are included in the Table 3.

The trend in $\Delta S°$ with concentration and temperature is the same as that of $\Delta G°$.

Table 4

Transport Numbers & Mobilities of the Ions

Transport Number of Anions of CAT was
0.4152 at 0.1 M; 0.4400 at 0.05 M;
0.4688 at 0.04 M & 0.4710 at 0.025 M

T°K	t°$_+$	Mobility x 10^{-4} $Cm^2.s^{-1}.V^{-1}$
298	0.5181	5.584
302	0.5080	5.687
306	0.5074	6.204
310	0.4989	6.410
314	0.4989	6.824
318	0.5236	8.275
322	0.5365	8.895

These are positive showing that during dissociation there is increase in entropy. The values decrease with increase in temperature as dissociation is an exothermic process.

The data in Table 4 clearly show that the transport numbers of the anion from CAT increase with increase in dilution and increase in temperature. The slow increase in mobility around 310 to 314°K and the constancy of transport numbers around this range of temperature confirm the probability of conglomeration of chloramine - T.

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REFERENCES

1. E.Bishop and V.J.Jennings, *Talanta*. **1** (1958) 197.
2. B.T.Gowda and B.S.Sherigara, *Microchem. J.*, **34** (1986) 103; *Oxidn. Commun.*, **9** (1986) 103; *Int. J.Chem.Kint.*, **(1986)** 21.
3. K.S. Rangappa, M.P. Raghavendra, D.S. Mahadevappa, *J.Carbohydr. Chem.*, **16(3)** (1997) 359-371.
4. M.P. Raghavendra, D.S. Mahadevappa, K.N.L. Rai, K.S. Rangappa, *J. Carbohydr. Chem.*, **16(3)** (1997) 343-5\358.
5. K.S. Rangappa, Ramachandra, D.S. Mahadevappa, *J. Phys. Org. Chem.*, **10(3)** (1997) 159-166.
6. S.S. Narayana and V.R.S. Rao, *Radio Chem. Radioanal. Lett.*, **49** (1981) 193.
7. J.Ishwara Bhat and P. Bindu, *J. Electrochem. Soc. India*, **42-2** (1993) 103-110.
8. V.R.S. Rao and G. Aravamudan, *Talanta*, **20** (1973) 65.