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CONDUCTIVITIES OF BROMAMINE-T IN WATER AND METHANOL AT VARIOUS TEMPERATURES

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The ionic conductivity of bromamine-T (BAT) in water and methanol as solvent has been studied as a function of temperature. The conductance data have been analysed by the Debye-Huckel, Fuosskraus, Shedlovsky and Fuoss Accascina Equations. The energy of activation of the rate process, thermodynamic parameters, molar conductivity at infinite dilution (λ°_{m}), Walden constant, dissociation and association constants (K's) have been calculated. A comparison of the λ°_{m} and K's values calculated from various equations has been made. An attempt is also made to propose the BAT as a weak electrolyte under the studied experimental conditions.

Key words: Conductivity, Bromamine-T, Temperature.

Introduction

Conductance measurements have been credited as one of the most appreciated techniques to study various types of interactions occuring in solutions. The study of variation of conductance with concentrations and viscosity provides satisfactory informations about the behaviour of solutions.

Bromamine-T (BAT), the sodium salt of *n*-bromo-toluene-*p*-sulphonamide (*p*-$CH_3C_6H_4SO_2NBrNa$),is a stable and inexpensive reagent [1], like chloramine-T, that can be easily prepared, stored and handled. Because of these desirable properties BAT is extensively used as oxidimetric analytical reagent for variety of purposes instead of more expensive iodine solution. A detailed examination of this compound as an analytical reagent was reported by Bishop and Jennings [2]. Several groups [3-6] have studied the kinetic and mechanistic aspects of Bromamine-T reactions. But there are no reports on the transport properties of BAT in the literature. Hence the investigation on the transport properties of BAT in different solvents as a function of temperature is reported here.

Experimental

Bromamine-T (BAT) was obtained [7] by dissolving Dibromamine-T (DBT) in 4 mol dm^{-3} NaOH. Dibromamine-T was prepared [8] by the bromination of chloramine-T (CAT) solution. About 4 cm^3 of liquid bromine was added dropwise to a solution of 20g of CAT in 400 $cm^3$of water with constant stirring of the solution at room temperature. Dibromamine-T separated out was filtered under suction, washed with water until all the bromine absorbed on the compound was completely eliminated, and then dried in a vaccum desiccator for 24 hrs.

About 20 g of dibromamine-Twas dissolved with stirring in 30 $cm^3$of 4 mol dm^{-3}NaOH at room temperature and the resultant aqueous solution was cooled in ice. Pale yellow crystals of BAT were filtered under suction, washed quickly with a minimum quantity of cold water and dried over phosphorus pentoxide.

The purity of the sample was checked by recording its IR spectrum and estimating the amount of active halogen present. Aqueous (~0.01 mol dm^{-3}) and non-aqueous (~0.04 mol dm^{-3}) solution of BAT were standardised by the iodometric [9] method and kept in dark coloured bottles. Doubly distilled water and methanol (purified by refluxing) of conductivity of about 10^{-6} Ω^{-1} cm^{-1} were used for preparing BAT solution.

Conductance measurements were made with a digital direct reading conductivity meter (Model CM-180-Elico Private Limited, Hyderabad). A dip type conductivity cell with plantinised electrodes was calibrated [10] (cell constant = 0.999 cm^{-1}) and used. All the measurements were made in a thermostant maintained at the desired temperature ±0.01°.

Results and Discussion

The specific conductance after correction for solvent conductance at each concentration is used for determining molar conductances λ_m. The molar conductance (λ_m) values of BAT in water and methanol were calculated at three different temperatures and are reported in Tables 1 and 2. Equivalent conductances at infinite dilution (λ°_m) were computed using the following equation.

$$\lambda_m = \lambda^{\circ}_m - [\,A+B\,\lambda^{\circ}_m\,]\,\sqrt{C} \qquad \text{.................................} (1)$$

$$\text{where } A = \frac{82.4}{(DT)^{1/2}\eta} \qquad \text{and} \qquad B = \frac{8.20 \times 10^5}{(DT)^{3/2}}$$

where D is the dielectric constant, η is the viscosity and T is temperature. λ_m values increase with decreasing concentration in both solvent media at all temperatures and a plot of

λ_m vs $\sqrt{C}$ is linear (Figs. 1-2) and the intercept gave molar conductance at infinite dilution (λ^o_m) (Table 3). But in water λ_m increased only down to concentration of about 7.5×10^{-4} mol dm^{-3} and then decreased as shown in Fig.1. This decrease might be due to: (1) the aggregation of ion to form ion pairs or ionic micelli which are uncharged and hence decrease in conductivity, but this is most unlikely since the concentration is so low and; (2) high solvation of solute species due to which their size increases and hence the decrease in conductivity. Slope of the plot λ_m vs $\sqrt{C}$ is calculated and compared with the theoretical slope (Table 4).

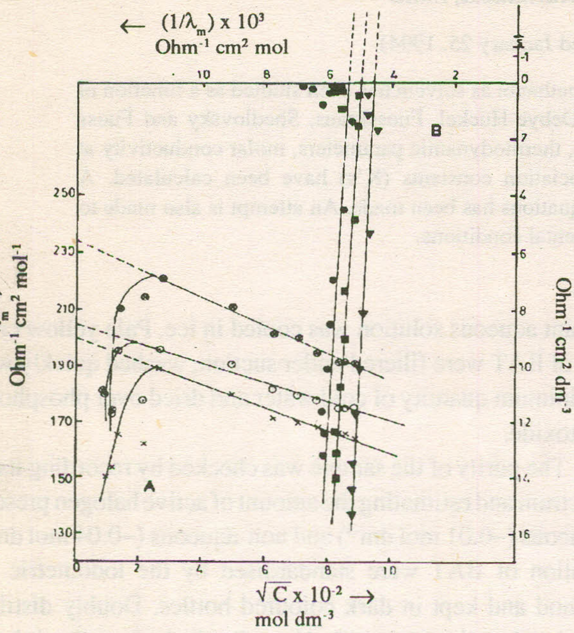

Fig. 1.(A) Plot of λ_m vs $\sqrt{C}$ for BAT in water at X:303K, ʘ308K, ⊗313K. (B) Plot of λ_m C vs $1/\lambda_m$ for BAT in water at ● 303K, ▲301K, ■313K.

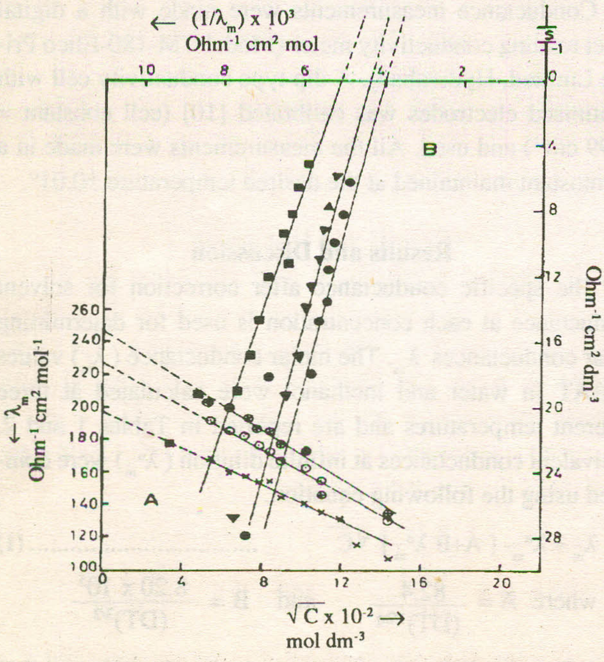

Fig. 2. (A). plot of λ_m vs $\sqrt{C}$ for BAT in methanol at X: 301K, ʘ 308K, ⊗ 313K. (B). Plot of λ_m C Vs $1/\lambda_m$m for BAT in methanol at ■ 301K, ▲ 308K, ● 313K.

As can be seen (Table 4) the agreement is not good between two slope values probably indicating the failure of Debye's limiting law. Therefore Kraus-Bray equation [11] of dilution law is tried as:

$$\frac{1}{\lambda_m} = \frac{1}{\lambda^o_m} + \frac{1}{\lambda^o m^2 K_C} C\lambda_m \quad \text{...} (2)$$

so that a plot of $1/\lambda_m$ against C λ_m should give a straight line for an electrolyte that forms ion-pairs in equilibrium with ions. The plot of $1/\lambda_m$ vs C λ_m were tried (Figs. 1-2) and values of λ^o_m and K_c were calculated and presented in Tables 3 and 5, where K_c is the dissociation constant. Degree of dissociation is calculated by the relationship $\alpha = \lambda_m / \lambda^o_m$ and is given is Tables 1-2.

The values of apparent dissociation constant, K_d of BAT in aqueous and non-aqueous solvents at these temperatures have been calculated using Arrhenius dilution law (where activity coefficient is being considered as equal to unity). The values thus obtained change slightly with the increase in BAT concentration (values are not shown). The average values of K_d are shown in the Table 5. Slight decrease in the value of K_d from water to methanol is primarily due to change in dieletric constant and it also indicates the fact that the electrolyte causes a reduction in the thickness of the ionic atmosphere surrounding the polar species and probably it also reduces repulsion between them with consequent increase in aggregation number and formation of some micelles. The decrease in the hydration/solvation of ions may also be a factor leading to a

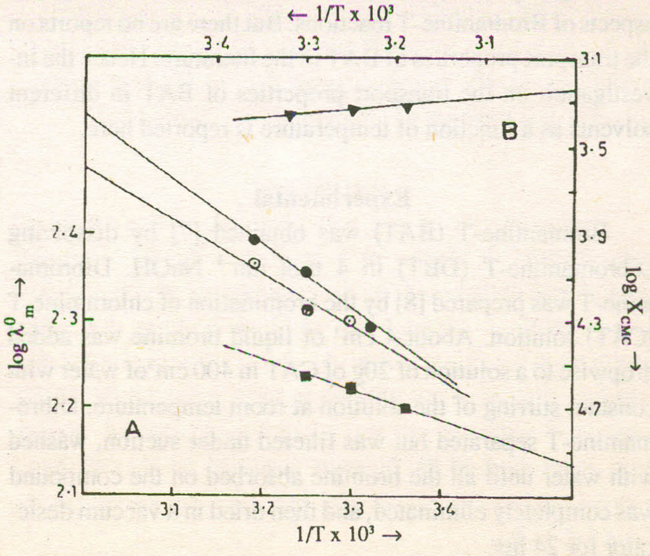

Fig. 3. (A). Plot of log λ^o_m Vs 1/T for BAT in ʘ water, ● methanol. (B). Plot of log x vs 1/T for BAT in ■ water, ▲methanol.

TABLE 1. OBSERVED MOLAR CONDUCTANCE AND CALCULATED DEGREE OF DISSOCIATION OF BROMAMINE-T IN WATER AT THREE TEMPERATURES: (λ_m in ohm^{-1} cm^2 mol^{-1}).

$C\times10^4$	T:303K		308K		313K	
(mol dm^{-3})	λ_m	α	λ_m	α	λ_m	α
80.0	164.3	0.82	175.5	0.85	191.3	0.81
75.0	165.3	0.82	175.0	0.85	191.4	0.81
70.0	165.1	0.82	175.1	0.85	192.2	0.82
60.0	168.6	0.84	178.3	0.86	195.5	0.83
50.0	170.4	0.85	180.2	0.87	200.6	0.85
40.0	171.7	0.85	182.0	0.88	201.7	0.86
25.0	180.4	0.90	191.2	0.93	211.2	0.90
7.5	189.3	0.94	196.0	0.95	221.3	0.94
5.0	162.0	0.81	-	-	214.0	0.91
2.0	165.0	0.82	195.0	0.95	210.0	0.89
1.5	153.3	0.76	173.3	0.84	173.3	0.74
1.0	150.0	0.75	180.0	0.87	180.0	0.76

TABLE 2. OBSERVED MOLAR CONDUCTANCE AND CALCULATED DEGREE OF DISSOCIATION OF BROMAMINE-T IN METHANOL AT THREE TEMPERATURES. (λ_m in ohm^{-1} cm^2 mol^{-1}).

$C\times10^3$	T:301K		308K		313K	
(mol dm^{-3})	λ_m	α	λ_m	α	λ_m	α
20.6	107.9	0.54	130.2	0.57	135.1	0.54
16.5	116.2	0.58	–	–	–	–
14.4	131.7	0.66	–	–	–	–
12.3	136.3	0.68	155.2	0.68	146.0	0.58
10.3	141.5	0.71	163.0	0.71	173.8	0.70
8.2	145.5	0.73	167.6	0.73	177.9	0.71
7.2	155.5	0.78	173.4	0.76	186.5	0.75
6.1	153.9	0.77	176.2	0.77	186.7	0.75
5.1	157.5	0.79	181.2	0.79	193.4	0.77
4.1	160.0	0.80	186.1	0.82	201.2	0.81
3.0	168.9	0.85	191.5	0.84	205.5	0.82

decrease in the value of dissociation constant. The slight drift in the values of K_d may be partly due to the fact that the degree of dissociation is not exactly equal to the conductance ratio, but mainly due to the fact that the assumed activity coefficients of ions are not exactly equal to unity. The deviation from this ideal behaviour may also be due to the failure of simple Debye-Huckel activity equation at the concentration range studied. The true dissociation constant K'_d is obtained from the intercept of the linear plot of $\log K_d$ versus $\sqrt{C\alpha}$ of the following equation.

$$\log K_d = \log K'_d + 2A\ \sqrt{C\alpha} \quad \text{..........................} \quad (3)$$

and the values are given in Table 5. However, the Kraus-Bray equation does not include any correction for interionic effects or for activities of the ions. Hence the data were analysed by Fuoss-Kraus mode [12] and a varient of it developed by Shedlovsky [13] which do include corrections for interionic effects on ionic mobilities and for ion activity coefficients.

K_a and $\lambda^o{}_m$ are calculated from the slope and intercept of the linear plot of the equation of Fuoss-Kraus (F.K) and Shedelovsky (Sh) model and reported in Tables 3 and 5. The molar conductance at infinite dilution $\lambda^o{}_m$ of BAT in water and methanol at various temperatures and K_a obtained in both cases are presented in Tables 3 and 5. The $\lambda^o{}_m$ values obtained by all the four techniques are in good agreement within the experimental error in both solvents at all temperatures $\lambda^o{}_m$ values increase with increase in temperature. K_a value is quite small by both the methods (F.K. and Sh) in the case of water when compared to that in methanol. Therefore, there may not be any notable association. But in methanol the values are very high indicating ion association in the system. K_a values increase with increase in temperature except in the case of water where it varies in zigzag fashion. Variation of $\lambda^o{}_m$ from one solvent to the other is primarily due to viscosity effect, and due to increase in solvation and increased association of salts with decrease in dielectric constant. The values of $\lambda^o{}_m$ increase with increase in temperature indicating increase in ionic mobility (Table 3) or decrease in viscosity. $\lambda^o{}_m$ has been regarded as a

TABLE 3. CALCULATED MOLAR CONDUCTANCE AT INFINITE DILUTE FROM DIFFERENT METHODS FOR BAT IN WATER AND METHANOL AT DIFFERENT TEMPERATURES.

	$\lambda^o{}_m$ Ohm^{-1} cm^2 mol^{-1}							
T (K)	Water				Methanol			
	λ_m vs $\sqrt{C}$	$\lambda_m C$ vs $1/\lambda_m$	F. K.	Sh	λ_m vs $\sqrt{C}$	$\lambda_m C$ vs $1/\lambda_m$	F. K.	Sh
291	–	–	–	–	198.00	197.60	200.00	200.00
303	200.00	194.00	200.00	200.00	–	–	–	–
308	205.00	209.23	204.08	204.08	227.00	229.97	227.27	227.27
313	234.00	228.00	233.00	233.00	248.00	247.11	250.00	250.00

measure of solute-solvent interaction [14], greater the magnitude of λ°_{m}, greater the solute-solvent interaction. The difference in the experimental and calculated K_a ($K_{F.K}$ and K_{Sh}) values and failure to obey Debye-Huckel law leads to the suspicion that ion-ion pair or triple ions may be formed. Based on this, the applicability of the theory of triple ion formation [15] was also tested. To identify the ionic association, a linear plot of log λ_m vs log C was drawn on the basis of Fuoss's [12] equilibrium equation for partially dissociated electrolytes.

From Fuoss equation the plot should be linear with a slope of -0.5. But here was get the slope as -0.024 and -0.143 for water and methanol, respectively. There is no dip in the plot in any one case of the solvent at any temperature. Small slope of the plot predicts the absence of notable association for anions.

Further equations for ion-pair and triple ions given by Fuoss Accascina theory [16] were also tried. The plots for BAT in water and methanol at different temperatures are nonlinear and, therefore, this indicates that there is no triple ion formation in the measured range of concentrations. Hence, the system does not provide any solid evidence for the formation of either an ion-pair or ion triplet except the high values of K_a. But the system obeys log λ_m vs log C plot, indicating the formation of minor amount of ion pairs.

TABLE 4. OBSERVED AND CALCULATED ONSAGER SLOPES FOR BAT IN VARIOUS MEDIA AT DIFFERENT TEMPERATURES.

T(K)	Water		Methanol	
	Experimental	Calculated	Experimental	Calculated
301	–	–	533.33	338.85
303	437.50	106.00	–	–
308	350.00	107.15	642.86	365.62
313	315.79	113.79	714.29	385.00

Above discussions make one to think the formation of micelle or aggregates in the system. Hence, the systems were tested for the formation of micellar aggregation [17] by getting plots of specific conductance (k) versus concentration (C) (plots are not shown). The critical micelle concentration (CMC), which is the point of intersection of two straight lines of k vs C plot, at different temperatures were obtained, and it is expressed in terms of mole fraction (X_{cmc}). X_{cmc} is calculated and found to be $10^5 X_{cmc}$ = 2.65 (303 K), 2.43 (308K), 1.98 (313 K) for water and 42.47 (301 K), 42.82 (308 K), 43.90 (313 K) for methanol solvent. It can be seen that the X_{cmc} slightly decrease with temperature in water medium whereas it increases with temperature in methanol. These values were further used in the evaluation of thermodynamic parameters of ion association.

Walden product. The Walden product of an ion is inversely proportional to the effective radius of the ion in a given solvent [18]. It relates molar conductance at infinite dilution to the viscosity of that solvent as:

$$\lambda^{\circ}_{m}\,\eta_{o} = \text{Constant} / r \quad \text{...} (4)$$

where r is the radius of the ion and η is the viscosity of the solvent in poise.

If the radius of the ion is the same in both solvents the product should be a constant. But here we get a different trend. The values found to be 1.59 ± 0.02 (303 K), 1.50 ± 0.05 (308 K), 1.52 ± 0.04 (313 K) in water medium and 1.04 ± 0.06 (301

TABLE 5. CALCULATED VALUES OF K FROM VARIOUS PROCESSES FOR BAT IN VARIOUS SOLVENTS AT DIFFERENT TEMPERATURES.

T (K)	Water					Methanol				
	K_d	K'_d	K_c	$\leftarrow K_a$ F.K.	$K_a \rightarrow$ Sh	K_d	K'_d	K_C	$\leftarrow K_a$ F.K.	$K_a \rightarrow$ Sh
301	–	–	–	–	–	0.016	0.013	0.019	125.00	87.50
303	0.024	0.039	0.049	46.16	40.00	–	–	–	–	–
308	0.032	0.025	0.044	33.77	25.51	0.016	0.011	0.017	129.13	93.59
313	0.023	0.015	0.040	45.22	42.36	0.014	0.009	0.014	156.25	100.00

K_d = Apparent dissociation constant. K'_d = True dissociation constant. K_c = from $\lambda_m C$ vs $1/\lambda_m$ plot. K_a (F.K. & Sh) = Association constant calculated from Fuoss - Kraus and Shedlovsky Method respectively.

TABLE 6. ENERGY OF ACTIVATION, log A AND THERMODYNAMIC PARAMETERS FOR TRANSPORT PROCESS OF BAT AND ION-ION EQUILIBRIA.

Medium	E_a KJ/mol	log A	ΔH°(kJ/mol)		$\Delta S^{\circ} \times 10^{-1}$ (kJK^{-1} mol^{-1})		ΔG°(kJ/mol)	
			ΔH°_{A}	ΔH°_{D}	ΔS°_{A}	ΔS°_{D}	ΔG°_{A}	ΔG°_{D}
Water	11.60	4.30	31.33	-306.14	2.79	-10.55	-54.60	18.62
Methanol	15.50	4.99	3.83	-264.52	1.41	-8.95	39.61	10.59

K), 1.08 ± 0.02 (308) K), 1.11 ± 0.02 (313 K) in methanol medium. The Walden product varies from water to methanol and hints that ion do not processes the same effective radius in these two solvents; whereas it remains almost a constant from one temperature to another for a given solvent indicating the non-variation of ionic radius under that condition.

It is probable that ions are solvated, that is to say, the ion attaches to itself by physical or chemical forces or both, to a number of molecules of solvent. Since the extent of solvation as well as size of the solvating molecules vary with nature of the solvent, the effective radius will not be constant.

Thermodynamic parameters. Since, the conductance of an ion depends on its rate of movement [15] and also the viscosity and dielectric constant variation of the solvent with temperature, it is quite reasonable to treat conductance similar to the one that employed for the process taking place at a definite rate which increases with temperature, i. e.

$$\lambda^\circ_m = A\, e^{-E_a/RT} \quad \text{.......} \quad (5)$$

or

$$\log \lambda^\circ_m = \log A - \frac{E_a}{2.303\, RT} \quad \text{.......} \quad (6)$$

where A is a constant, E_a is the activation energy of the process which determines the rate of movement of ions.

The slope and intercept of the linear plot of log λ^0_m vs 1/T (Fig.3) gives the values of E_a and log A (Table 6). E_a value is high in the case of methanol, means that the rate of movement of BAT species requires more activation energy in methanol medium than in water medium. The heat of dissociation – the change in enthalpy or heat for the process of dissociation of the species is calculated using the equation.

$$\log \frac{K_{d2}}{K_{d1}} = \frac{\Delta H^\circ_D}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \text{.......} \quad (7)$$

ΔH°_D is calculated for K_d at three different temperatures and the mean value is given in Table 6. The negative values of ΔH°_D indicate that the dissociation process is exothermic in nature. The values of free energy for the dissociation process ΔG°_D has been calculated by the equation:

$$\Delta G^\circ_D = 2.303RT \log K_d \quad \text{.......} \quad (8)$$

Finally ΔS°_D value is also calculated by the relation.

$$\Delta S^\circ_D = \frac{\Delta H^\circ_D - \Delta G^\circ_D}{T} \quad \text{.......} \quad (9)$$

in all cases, the average ΔG°_D and ΔS°_D values are given in Table 6. Since ionic micelles were also thought of once, ΔG°_A and ΔH°_A and ΔS°_A were also calculated. The standard free energy of probable micellisation for the aggregation process [17].

$$G^\circ_A = 2RT \,\text{In}\, X_{cmc} \quad \text{.......} \quad (10)$$

where X_{cmc} is the critical micelle concentration (CMC) expressed in mole fraction and defined as -

$$X_{cmc} = \frac{n_s}{n_s + n_o}\ ; \ \text{indilute solution,}\ X_{cmc} = \frac{n_s}{n_o} \quad \text{.......} \quad (11)$$

The standard enthalpy of micellisation ΔH°_A is given by:

$$\text{In}\, X_{cmc} = -\ (\Delta H^\circ_A / 2RT) + C \quad \text{.......} \quad (12)$$

The values of ΔH°_A have been obtained from the slope of the linear plot of In X_{cmc} vs 1/T (Fig. 3). Even standard entropy of micellisation ΔS°_A can also be calculated by the equation:

$$\Delta S^\circ_A = \frac{\Delta H^\circ_A - \Delta G^\circ_A}{T} \quad \text{.......} \quad (13)$$

All the values are given in Table 6. From a careful examination of thermodynamic parameters (Table 6), it is evident that dissociation is more predominating compared to association process. The change in enthalpy of dissociation and change in entropy of dissociation, both are large negative values, confirm the above statement, and meantime negative value of change in free energy of association supports it.

From the present investigations one may propose that BAT can either be considered as a strong or a weak electrolyte under the present condition but it is better to suggest as a moderate weak electrolyte.

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