

Ionic Equilibria in Aqueous Solutions of Zinc Bromide and the Related Heat Data

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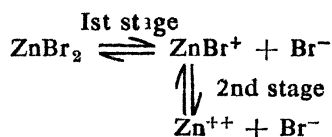
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The dissociation constant of $\text{ZnBr}^+ \rightleftharpoons \text{Zn}^{++} + \text{Br}^-$ has been determined potentiometrically and has been found to be 0.2559, 0.0573, 0.0973 and 0.0339 at 5°, 15°, 25° and 35° respectively. The heat of ionisation ΔH of $\text{ZnBr}^+ = \text{Zn}^{++} + \text{Br}^-$ has been found to be $+1331 \pm 100$ cal/mole.

FERRELL, Ridgion and Riley¹ studied potentiometrically the behaviour of zinc bromide in aqueous solution and suggested the possibility of complex ion formation. Parton and Mitchell² considered zinc bromide to be completely dissociated up to 0.1 M. Egan and Partington³ concluded that zinc bromide behaves as a strong electrolyte up to the concentration range 0.36 molarity. Stokes, Stokes and Robinson's⁴ studies showed that zinc bromide does not dissociate completely even up to 0.1M. Stokes and Stokes⁵ has reported that it is not permissible to regard zinc bromide as fully dissociated even at 0.1M. On account of the different conclusions of the authors, it was decided to study the dissociation of zinc bromide.

Up to 0.1M, it was assumed that the first stage of dissociation of zinc bromide is complete.



Experimental

Anal grade zinc bromide was not available. Hence zinc carbonate was first precipitated by adding hot solution of A.R. sodium carbonate in slight excess to hot zinc chloride (A.R.) solution. The precipitate was washed about 40 times in almost boiling water to remove the chloride completely, though the presence of chloride ion was found to be absent much earlier. Zinc carbonate was dissolved in G.R. hydrobromic acid and a stock solution of zinc bromide in hydrobromic acid was prepared. The zinc and the bromide contents of the solution were respectively estimated gravimetrically by the oxine⁶ and volumetrically by Volhard's⁷ method. Other experimental procedures adopted were similar to those of Sinha and Prasad⁸. The temperature of the thermostat was kept constant within $\pm 0.05^\circ$. Duplicate cells were set up in each case and readings were taken at an interval of one hour after the equilibrium had been established. The readings generally agreed within

0.1mV though in a few cases it went up to 0.15 mV. These mean of four e.m.f values along with the

TABLE 1
Temperature 5°

Mixture of ZnBr_2 & HBr	E in volt	$[\text{Zn}^{++}]$ $\times 10^3$	$[\text{Br}^-]$ $\times 10^3$	$[\text{ZnBr}^+]$ $\times 10^3$	$\mu \times 10^3$
$[\text{ZnBr}_2]_T$ $[\text{HBr}]_T$					
0.008 0.004	0.40060	6.77	18.77	1.23	25.54
0.012 0.006	0.41978	11.23	29.23	0.77	40.46
0.016 0.008	0.43283	14.94	38.94	1.06	53.88
0.020 0.010	0.44283	18.30	48.30	1.70	66.60
0.022 0.011	0.44714	20.04	53.04	1.96	73.08
0.024 0.012	0.45106	21.70	57.70	2.30	79.40
0.026 0.013	0.45467	23.34	62.34	2.66	85.68
0.028 0.014	0.45802	24.98	66.98	3.02	91.96

TABLE 2
Temperature 15°

Mixture of ZnBr_2 & HBr	E in volt	$[\text{Zn}^{++}]$ $\times 10^3$	$[\text{Br}^-]$ $\times 10^3$	$[\text{ZnBr}^+]$ $\times 10^3$	$\mu \times 10^3$
$[\text{ZnBr}_2]_T$ $[\text{HBr}]_T$					
0.008 0.004	0.38891	7.00	19.00	1.00	26.00
0.012 0.006	0.40809	10.68	28.68	1.32	39.36
0.016 0.008	0.42121	13.54	37.54	2.46	51.08
0.020 0.010	0.43162	16.76	46.76	3.24	63.52
0.022 0.011	0.43608	18.37	51.37	3.63	69.74
0.024 0.012	0.44030	20.35	56.35	3.65	76.70
0.026 0.013	0.44404	21.92	60.92	4.08	82.84
0.028 0.014	0.44751	23.49	65.49	4.51	88.98

TABLE 3

Temperature 25°

Mixture of ZnBr ₂ & HBr	E in volt	[Zn ²⁺] × 10 ³	[Br ⁻] × 10 ³	[ZnBr ⁺] × 10 ³	μ × 10 ³
[ZnBr ₂] _T [HBr] _T					
0.012 0.006	0.39734	11.10	29.10	0.90	40.20
0.016 0.008	0.41130	14.84	38.84	1.16	53.68
0.020 0.010	0.42217	18.66	48.66	1.34	67.32
0.022 0.011	0.42677	20.45	53.45	1.55	73.90
0.024 0.012	0.43101	22.32	58.32	1.68	80.64
0.026 0.013	0.43498	24.37	63.37	1.63	87.74
0.028 0.014	0.43861	26.28	68.28	1.72	94.56

TABLE 4

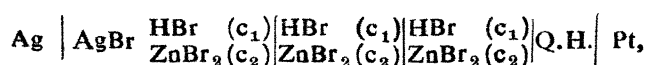
Temperature 35°

Mixture of ZnBr ₂ & HBr	E in volt	[Zn ²⁺] × 10 ³	[Br ⁻] × 10 ³	[ZnBr ⁺] × 10 ³	μ × 10 ³
[ZnBr ₂] _T [HBr] _T					
0.008 0.004	0.36631	6.65	18.65	1.35	25.30
0.012 0.006	0.38650	9.84	27.84	2.16	37.68
0.020 0.010	0.41197	16.29	46.29	3.71	62.58
0.022 0.011	0.41685	18.18	51.18	3.82	69.36
0.024 0.012	0.42122	19.86	55.86	4.14	75.72
0.026 0.013	0.42533	21.78	60.78	4.22	82.56
0.028 0.014	0.42882	22.77	64.77	5.23	87.54
0.030 0.015	0.43260	25.36	70.36	4.64	95.72

concentration of various ions are given in Tables 1 to 4. The symbol []_T represents the stoichiometric concentrations in gm moles/litre. The ionic strength in no case exceeded 0.1.

Discussion

The e.m.f. of the cell,



is given by the equation,

$$E = E^\circ + \frac{2.30259RT}{F} \log [H^+] [Br^-] f_H f_{Br} \quad (1)$$

and the activity coefficient product is given by the expression,

$$-\log f_H f_{Br} = \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} - B\mu \quad (2)$$

where 'A' is the constant of Debye-Hückel equation and B is found from the study of cell reported earlier¹⁰. The values of 'A' and 'B' at various temperatures are given below :

	5°	15°	25°	35°
A	0.4921	0.5002	0.5092	0.5190
B	0.5618	0.5476	0.5274	0.5152

Assuming that the first stage of dissociation, $\text{ZnBr}_2 = \text{Zn}^{2+} + \text{Br}^-$ is complete in very dilute solutions, the only ions present in these solutions can be Zn^{2+} , ZnBr^+ , Br^- and H^+ , and hence the ionic strength of the solution will be given by the equation,

$$\mu = 2[\text{Zn}^{2+}] + \frac{1}{2}[\text{ZnBr}^+] + \frac{1}{2}[\text{H}^+] + \frac{1}{2}[\text{Br}^-] \quad (3)$$

So far $[\text{H}^+]$ is concerned, it is evidently equal to $[\text{HBr}]_T$. For finding the value of other concentration terms, an arbitrary value is given to the ionic strength μ . The corresponding value of $f_H f_{Br^-}$ is calculated from equation (2), there after that of $[\text{Br}^-]$ from equation (1), that of $[\text{ZnBr}^+]$ from the relationship, $[\text{Br}^-] + [\text{ZnBr}^+] = 2[\text{ZnBr}_2]_T + [\text{HBr}]_T$, and that of $[\text{Zn}^{2+}]$ from the relationship, $[\text{ZnBr}_2]_T = [\text{Zn}^{2+}] + [\text{ZnBr}^+]$. With the values of $[\text{H}^+]$, $[\text{Br}^-]$, $[\text{ZnBr}^+]$ and $[\text{Zn}^{2+}]$ thus found, a new value of μ is obtained. This process is repeated till μ becomes constant up to the fifth place of decimal. These final values of $[\text{Zn}^{2+}]$, $[\text{ZnBr}^+]$ and $[\text{Br}^-]$ corresponding to the constant value of μ represent the correct values of concentrations and they are given in the Tables.

The dissociation constant (K_2) of ZnBr^+ is given by,

$$K_2 = \frac{[\text{Zn}^{2+}][\text{Br}^-]}{[\text{ZnBr}^+]} \times \frac{f_{\text{Zn}} f_{\text{Br}}}{f_{\text{ZnBr}}} = K_{A(2)} \frac{f_{\text{Zn}} f_{\text{Br}}}{f_{\text{ZnBr}}}$$

$$\text{Applying the equation, } -\log f_i = \frac{AZ_i^2\sqrt{\mu}}{1+\sqrt{\mu}} - B_i\mu,$$

$$\text{we get, } \log K_{A(2)} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_2 - B\mu \quad (4)$$

The value of $K_{A(2)}$ is next calculated from the values of $[\text{Zn}^{2+}]$, $[\text{Br}^-]$ and $[\text{ZnBr}^+]$ determined, as explained earlier. The left hand side of the equation (4) is plotted against μ and the value of $\log K_2$ is obtained from the intercept of the straight line corresponding to $\mu = 0$.

The values of K and B_1 at various temperatures are given below :

	5°	15°	25°	35°
$K \times 10^3$	25.59	5.73	9.73	3.39
B_1	+1.330	-3.648	-5.916	-5.984

It may be pointed out here that several similar measurements have been made in this laboratory by Prasad and his co-workers. And in no case the value of B has been found to be reversed, which we have found in case of zinc bromide at 5°. This value of B at 5° was checked and was found to be the same. We have not found the reason for this positive value of B at 5°, though such deviations have been found to occur in case of viscosity measurements $\left(\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC \right)$

at lower temperatures in case of some salts. The value of Heat content change ΔH for the reaction $\text{ZnBr}^+ \rightleftharpoons \text{Zn}^{++} + \text{Br}^-$, has been calculated by plotting $\log K$ against $\frac{1}{T}$ and it comes out to be 1331 ± 100 cal/mole. And the values of ΔG° and ΔS° at 25° are respectively -5.482 and 4.486 .

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