

SOME PROPERTIES OF ZINC/BROMINE BATTERY ELECTROLYTES

K. J. CATHRO, K. CEDZYNSKA and D. C. CONSTABLE

CSIRO, Institute of Earth Resources, Division of Mineral Chemistry, P.O. Box 124, Port Melbourne, Victoria 3207 (Australia)

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Summary

The diffusion coefficients for bromine in zinc bromide solutions containing *n*-ethyl *n*-methylnmorpholinium bromide have been determined over a range of temperatures and reagent concentrations relevant to zinc/bromine battery electrolytes. Some data were obtained also for potassium chloride-containing electrolytes. Values for solution resistivity and kinematic viscosity are also reported.

Introduction

One of the serious problems experienced with early zinc/bromine batteries was their high rate of self-discharge. This was due to the solubility of elemental bromine in the zinc bromide electrolyte. This dissolved bromine is transported quite rapidly to the zinc electrode, where it reacts directly with the metal and leads to rapid self-discharge of the battery.

One method of overcoming the above difficulty has been to use an ion-exchange separator between the two electrodes, combined with the use of a circulated electrolyte [1]. The faradaic efficiency of such cells is primarily dependent on the rate of diffusion of bromine in the ion-exchange separator material. A study of bromine diffusion through perfluorinated ion-exchange membranes has been published by Will [2].

However, ion-exchange separators that are resistant to bromine, and that have a sufficiently low rate of bromine (or tribromide ion) transport, are expensive and show a relatively high ohmic resistance. In order to use much less costly porous polyethylene or polypropylene separators, it is necessary to reduce the effective bromine concentration in the positive-side electrolyte from 2 M to about 0.1 M if satisfactory faradaic efficiency is to be obtained. This can be done by adding suitable quaternary ammonium bromides to the electrolyte; these form liquid-phase addition compounds with bromine (termed polybromides [3]) that have a low equilibrium bromine concentration in the aqueous phase. Several zinc/bromine battery systems based on this approach have been described [4 - 6]. An alternative

approach is to use, on the positive side, a conducting organic phase that has a high partition coefficient for bromine against the aqueous phase. Singh *et al.* [7] have described such a system based on the use of propionitrile.

Procedures for calculating the faradaic efficiency of zinc bromide systems using porous separators have been described [8, 9]. These require knowledge of the value of the diffusion coefficient of bromine in the battery electrolyte concerned, but very few such values have been reported.

The present work reports the results obtained for the measurement of bromine diffusion coefficients over a range of solution compositions and temperatures relevant to the operation of a zinc/bromine battery of the polybromide type. In addition, the specific resistances of a number of these solutions have been measured and are reported because of their value in the calculation of the voltaic efficiency of this type of cell.

Experimental

The diffusion coefficient was measured electrochemically using the rotating disc method [10]. The electrolyte was normally a zinc bromide solution of between 1 M and 3 M concentration, containing a quaternary ammonium bromide (hereafter abbreviated to QBr). This QBr was usually *n*-ethyl *n*-methylmorpholinium bromide (EMMB), but some tests were done using *n*-ethyl *n*-methylpyrrolidinium bromide (MEPB). Since the QBr concentration in a battery electrolyte will decrease as the battery is charged (*i.e.*, as the zinc bromide concentration decreases), the range of QBr concentrations studied was varied from zero to 1 M in 3 M ZnBr₂, and from zero to 0.3 M in 1 M ZnBr₂. In addition, some tests were made in the presence of potassium chloride, which is sometimes added to zinc/bromine battery electrolytes in order to improve conductivity. It was necessary to restrict the potassium chloride concentration to 3 M in order to avoid crystallization when working at 0 °C.

As well as the above battery electrolytes, some measurements were made of the diffusion coefficient in 0.1 M KBr and 2.2 M KCl in order to compare the results of our work with values reported previously.

Measurements of electrolyte specific resistance were made on most of the battery electrolytes used for the diffusion coefficient measurements. The detailed procedures used are described as follows.

Reagents

Zinc bromide was prepared by dissolving the stoichiometric weight of reagent grade zinc oxide (analysed for zinc content) in reagent grade hydrobromic acid of known concentration. The resulting solution was evaporated to approximately 8.5 M concentration, and used as a stock solution for the preparation of the battery electrolytes. This stock solution was analysed for both zinc and bromine to ensure the Br:Zn stoichiometry was 2.00 ± 0.01 .

The EMMB was prepared by reaction of bromoethane with n-methylmorpholine in dry acetone. The crude product precipitated slowly, and, after the reaction mixture had stood for about six days, the solvent was decanted and the product purified by recrystallization from anhydrous ethanol, with addition of ethyl acetate to obtain a satisfactory yield. The product analysed contained 37.4% bromide compared with the theoretical value of 38.0%. The MEPB was prepared similarly, but using n-methylpyrrolidine as the starting material. The reaction was much more rapid, and large batches were cooled to prevent thermal runaway. The product analysed contained 40.3% bromide compared with the theoretical 41.2%.

Proton n.m.r. scans were made using the recrystallized material dissolved in dimethyl sulphoxide. The peak patterns obtained were consistent with the structure expected.

Equipment

A Beckman electrode rotator, model 1885, was used. The speed control settings were checked at two values ($\omega = 10$ and 25 Hz) against a stroboscope (calibrated in turn against the a.c. mains frequency), and were found to be within 0.8% of the nominal setting.

The electrode was a platinum disc constructed by fixing a 5.80 mm diameter platinum disc to a 5 mm diameter zirconium rod with silver epoxy cement, and then sheathing the assembly with heat-shrink PVC tubing. Since the shroud-to-disc diameter ratio of 1.1 was below the recommended value [10], the working area of the electrode was determined empirically, as described below. The counter-electrode was a platinum gauze of area 1.5 cm². A platinum wire located close to the edge of the disc served as a reference electrode. Since the diffusion current plateau extends for at least 0.5 V, location of the reference is not critical. Polarization and diffusion current measurements were carried out using a Utah 0152 potentiostat; current and potential readings were taken on digital multimeters of accuracy 0.25% or better.

The cell consisted of a jacketed beaker, with a close-fitting polypropylene lid that carried the counter- and reference electrodes, together with a tube to allow passage of nitrogen either through or over the surface of the solution. Cell temperature was controlled by circulation of 10% aqueous glycerol from an external, temperature-controlled bath.

In addition, it was necessary to know the kinematic viscosity of each solution tested in order to solve the Levich equation for the diffusion coefficient. Viscosities were obtained using a PSL U-tube viscometer, type BS/U size 0, using a calibration factor supplied by the manufacturer. Densities of these same solutions were measured using a specific gravity bottle.

Electrolyte specific resistivities were measured using a General Radio 1650A impedance bridge, operated at 1 kHz, together with a TPS conductivity cell that had a cell constant of approximately 10. The cell constant was checked at each operating temperature using 1 M KCl solution.

Test procedure

The procedure adopted was to pipette 20 ml of electrolyte of the desired composition into the cell, deoxygenate with nitrogen, and then add a known quantity of bromine in the form of a concentrated solution in zinc bromide solution of the same concentration as the test solution. This solution was mixed by bubbling briefly with nitrogen, and the potential was then set to the value at the centre of the diffusion current plateau (approximately -0.6 V to the platinum pseudo-reference). After measuring the diffusion current at a rotation speed of 15 Hz, a 5 ml sample was withdrawn as soon as possible, and its bromine concentration determined iodometrically. The speed was then increased to 25 Hz, and the process repeated. The extent of the diffusion current plateau and the linearity of the current/ $\omega^{1/2}$ relation were confirmed, for each temperature and concentration level examined, by conducting tests prior to the determination of the diffusion coefficient.

Estimation of disc area

The effective area of the disc was estimated by measurement of the limiting current I_L for a material of known diffusion coefficient, the concentration of the material and the rotational speed being known. The species chosen were: (i) 5×10^{-3} M ferrocyanide in 1 M KCl, using the diffusion coefficient data of Hitchman and Albery [11]; (ii) 5×10^{-3} M ferricyanide in 1 M KCl, using the data of Raffel and Van de Graaf [12]; and (iii) 2×10^{-3} M iodine in 0.1 M KI, using the data of Emery and Hintermann [13]. The results obtained are shown in Table 1, and it can be seen that the values for the different species are in good agreement. The average disc area is 0.274×10^{-4} m², the ratio of measured to geometric area being 1.037. The disc area was checked from time to time throughout the test series using the ferricyanide reduction. Six determinations showed a relative standard deviation of 1.1%.

TABLE 1
Area determination of rotating disc

Reaction used	Diffusion coefficient ^a (10^{-9} m ² s ⁻¹)	Kinematic viscosity ^a (10^{-6} m ² s ⁻¹)	Disc area (10^{-4} m ²)
Ferrocyanide oxidation	0.634	0.859	0.275
Ferricyanide reduction	0.762	0.859	0.276
Iodine reduction	1.13	0.874	0.270

^a All measurements at 25 °C.

Results

Plots of $I_L/\omega^{1/2}$ showed excellent linearity and extrapolate to the origin, within experimental error; Fig. 1 shows a typical plot. Again plots of $1/I_L$ against $1/\omega^{1/2}$ give straight lines which, when extrapolated to $1/\omega^{1/2} = 0$, cut the $1/I_L$ axis close to zero. This indicates that the exchange current for this reaction is high, and kinetic effects have a negligibly small effect on the limiting current.

The results obtained for the value of the diffusion coefficient for bromine are given in Table 2 for the ZnBr_2 -EMMB system, and a more restricted set are given for the ZnBr_2 -3 M KCl-EMMB system in Table 3.

Finally, a few values were obtained for the ZnBr_2 -MEPB system, together with the corresponding values for the equivalent EMMB-containing solutions (Table 4). It can be seen that the diffusion coefficients in the MEPB system average about 6% higher than those for the corresponding EMMB systems.

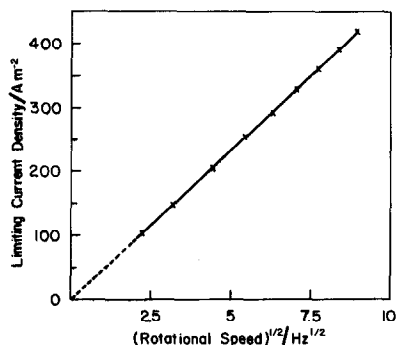


Fig. 1. Plot of current vs. rotational speed for disc. Conditions: 25 °C; 0.016 M bromine; 1 M ZnBr_2 ; -700 mV to Pt wire reference.

TABLE 2

Diffusion coefficients for bromine in the ZnBr_2 -EMMB system

EMMB (M)	Diffusion coefficients for bromine ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)								
	1 M ZnBr_2			2 M ZnBr_2			3 M ZnBr_2		
	0 °C	25 °C	50 °C	0 °C	25 °C	50 °C	0 °C	25 °C	50 °C
0	0.690	1.23	1.96	0.490	1.06	1.57	0.355	0.767	1.15
0.1	0.622	1.16	1.78	0.453	0.973	1.49	0.313	0.670	1.10
0.3	0.501	0.953	1.56	0.357	0.790	1.37	—	—	—
0.5	—	—	—	0.305	0.728	1.16	0.231	0.516	0.891
0.65	—	—	—	0.248	0.587	1.07	—	—	—
0.7	—	—	—	—	—	—	0.185	0.445	0.818
1.0	—	—	—	—	—	—	0.136	0.349	0.650

TABLE 3

Effect of 3 M KCl on bromine diffusion coefficients

Solution composition	Diffusion coefficients for bromine ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)					
	0 °C		25 °C		50 °C	
	0 M KCl	3 M KCl	0 M KCl	3 M KCl	0 M KCl	3 M KCl
1 M ZnBr_2 , 0.3 M EMMB	0.501	0.506	0.953	0.933	1.56	1.47
2 M ZnBr_2 , 0.65 M EMMB	0.248	0.282	0.587	0.588	1.07	0.931
3 M ZnBr_2 , 1 M EMMB	0.136	0.145	0.349	0.330	0.650	0.571

TABLE 4

Diffusion coefficients for MEPB-containing electrolytes

Composition (M)		Diffusion coefficient ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) at 25 °C	
ZnBr_2	QBr	QBr = MEPB	QBr = EMMB
1	0.3	1.00	0.95
2	0.65	0.61	0.59
3	1.0	0.38	0.35

The precision of the results were tested in two ways. Firstly, ten replicate tests were run using 1 M ZnBr_2 and $0.011 \text{ M} \pm 0.0006 \text{ M}$ bromine. The resulting diffusion coefficient of $1.23 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ had a standard deviation of $\pm 0.054 \times 10^{-5}$ or $\pm 4.4\%$. The second approach took advantage of the fact that duplicate estimates were made of the diffusion current for each set of conditions, working at 15 and 25 Hz. The ratio of each of these sets of duplicates was calculated as the ratio (coefficient at 15 Hz)/(coefficient at 25 Hz), and the average ratio and its standard deviation were obtained. The results are shown in Table 5, and it can be seen that the ratio is in fact close to 1.00, while the standard deviation ranges from 0.028 to 0.042, averaging 0.036 over the whole series. A variance ratio test between the results at 0 °C and those at 50 °C is significant ($p = 0.95$), and it is quite possible that measured bromine concentrations were less precise

TABLE 5

Estimate of precision from results of duplicate runs

Temperature (°C)	No. of duplicates	Mean ratio of duplicates	Std. deviation of set
0	16	0.993	0.0283
25	17	0.993	0.0386
50	17	0.993	0.0423

at 50 °C, owing to the much greater volatility of bromine at this temperature.

The nominal bromine concentration was 0.01 M, but in practice this varied from 0.0034 M to 0.020 M, averaging 0.011 M. An attempt was made to assess the effect of variation in bromine concentration on the diffusion coefficient by determining this parameter in 1 M zinc bromide for bromine concentrations from 0.0044 M to 0.022 M. There was no clear variation of the coefficient with concentration, and the average for the ten tests was $1.24 \pm 0.049 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The difference between the standard deviation for these results and that for the tests made under similar conditions, but with constant bromine concentration (described above), was found to be not significant ($p = 0.01$) when analysed using a variance ratio test. The conditions of this work — diffusion in the presence of a high concentration of supporting electrolyte — are quite similar to those applying in polarography, where it has been demonstrated that the diffusion-limited current is strictly proportional to depolarizer concentration over a wide concentration range [14]. This requires constancy of the diffusion coefficient over the same concentration range.

Tables 6 - 8 report measurements of the solution specific resistance for a similar range of reagent concentrations and temperatures as those used for the diffusion current studies. Kinematic viscosity data, useful for calculation of limiting cell currents [15], are given for the ZnBr_2 -EMMB system in Table 9.

Discussion

Comparison with other work

It is of interest to compare the values obtained in the above-described tests with the few that are available from the literature. A value for the diffusion coefficient of bromine in 1 M zinc bromide, obtained from rate-of-

TABLE 6

Electrolyte resistivities for the ZnBr_2 -EMMB system

EMMB (M)	Electrolyte resistivity ($\Omega \text{ cm}$)								
	1 M ZnBr_2			2 M ZnBr_2			3 M ZnBr_2		
	0 °C	25 °C	50 °C	0 °C	25 °C	50 °C	0 °C	25 °C	50 °C
0	15.3	9.3	7.0	14.6	8.7	6.6	17.2	9.9	7.4
0.1	15.6	9.5	7.2	15.2	9.0	7.0	17.4	10.4	7.5
0.3	16.1	9.8	7.5	16.4	9.9	7.4	—	—	—
0.5	—	—	—	17.9	10.9	8.0	22.5	12.7	9.0
0.65	—	—	—	19.0	11.2	8.6	—	—	—
0.7	—	—	—	—	—	—	24.5	14.0	11.4
1.0	—	—	—	—	—	—	30.8	15.9	11.6

TABLE 7

Effect of 3 M KCl electrolyte resistivity

Solution composition	Electrolyte resistivity (Ω cm)					
	1 M ZnBr ₂		2 M ZnBr ₂		3 M ZnBr ₂	
	0 M KCl	3 M KCl	0 M KCl	3 M KCl	0 M KCl	3 M KCl
1 M ZnBr ₂ , 0.3 M EMMB	16.1	6.7	9.8	4.1	7.5	2.9
2 M ZnBr ₂ , 0.65 M EMMB	19.0	8.9	11.2	5.5	8.6	3.9
3 M ZnBr ₂ , 1 M EMMB	30.8	14.7	15.9	8.1	11.6	5.7

TABLE 8

Electrolyte resistivities for MEPB-containing electrolytes

Composition (M)		Electrolyte resistivity (Ω cm); 25 °C	
ZnBr ₂	QBr	QBr = MEPB	QBr = EMMB
1	0.3	11.4	9.8
2	0.65	12.1	11.2
3	1.0	16.5	15.9

TABLE 9

Kinematic viscosity of ZnBr₂-EMMB solutions

EMMB (M)	Kinematic viscosity (10^{-6} m ² s ⁻¹)								
	1 M ZnBr ₂			2 M ZnBr ₂			3 M ZnBr ₂		
	0 °C	25 °C	50 °C	0 °C	25 °C	50 °C	0 °C	25 °C	50 °C
0	2.022	1.040	0.632	2.317	1.165	0.698	2.786	1.371	0.786
0.1	2.071	1.057	0.643	2.429	1.203	0.722	2.866	1.405	0.836
0.3	2.184	1.122	0.663	2.607	1.284	0.759	—	—	—
0.5	—	—	—	2.879	1.378	0.801	3.722	1.665	0.960
0.65	—	—	—	3.059	1.460	0.834	—	—	—
0.7	—	—	—	—	—	—	4.153	1.809	1.048
1.0	—	—	—	—	—	—	4.996	2.175	1.215

dissolution measurements on a zinc hemisphere, is given by Lee and Selman [8]; while Osipov *et al.* [16] have obtained a value for the bromine diffusion coefficient in 0.1 M KBr using a rotating disc, and a set of six replicates were run using this electrolyte to obtain a comparable value. Further, Voloshina *et al.* [17] obtained values in KCl solution using a diffusion cell. Again a set of six replicates were made in 2.2 M KCl to obtain comparable values. Table 10 shows the comparison of the values obtained in this work and those reported. It can be seen that the agreement with the result of Osipov

TABLE 10

Comparison of bromine diffusion coefficients

Ref.	Bromine diffusion coefficient ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) at 25 °C	
	Literature value	This work
16	1.21 ± 0.1	1.23 ± 0.077
8	0.99	1.23 ± 0.054
17	1.44	1.28 ± 0.030

et al., obtained using a rotating disc, is quite good, but the values obtained using non-electrochemical techniques differ from ours by 13% - 24%.

Bellows *et al.* [4] reported a value of $2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the bromine diffusion coefficient in battery electrolyte, but for unstated temperature and electrolyte composition.

Empirical equation for interpolation purposes

Although values of the diffusion coefficient for conditions within the range of variables tested can be obtained from Table 2 by standard interpolation procedures, it is sometimes useful to have an equation for this purpose, particularly when using computer methods to predict cell performance.

Semi-log plots of the diffusion coefficient of bromine in zinc bromide-EMMB solutions against absolute temperature showed that the data approximate to the relation

$$D = K \exp(A/T) \quad (1)$$

where A is a function of the quaternary ammonium bromide concentration Q , and K is a function of both the zinc and quaternary ammonium bromide concentration (Z and Q , respectively), *viz.*,

$$A = -(1958 + 807Q) \quad (2)$$

$$K = K' \exp(1.856Q) \quad (3)$$

$$K' = 10^{-7}(9.56 - 0.79Z - 0.23Z^2) \quad (4)$$

Values of the diffusion coefficient D were calculated for the values of Q , Z and T of Table 2, and these estimated values of D were compared with those measured. The ratio of calculated-to-measured coefficients was 0.998 with a standard deviation of 0.064.

Ionic species

It is unlikely that bromine is present in the uncharged, elemental form; the formation of complex ions, such as tribromide, being most probable at the bromide concentrations used in these tests.

For spherical electroactive species that are larger than the molecules of the solvent, the Stokes-Einstein equation relates particle radius to diffusion coefficient by the relation

$$D = RT/6\pi\eta rN \quad (5)$$

Although the sphericity and size requirements of eqn. (5) are unlikely to be met in the present instance, some comparative values for an ionic radius can be calculated from the experimental values of diffusion coefficient and viscosity. They are shown in Figs. 2(a) - (c) as a function of EMMB concentration and temperature. There is a small increase of ionic radius with increasing EMMB concentration, the trend being less noticeable as the temperature increases.

The changes in ionic radius are consistent with some change in the composition of the diffusing species, but do not seem large enough to suggest that any of the organic compounds is being incorporated in the complex. The observed increase in ionic radius may be due to the increased bromide ion concentration resulting from the addition of the EMMB.

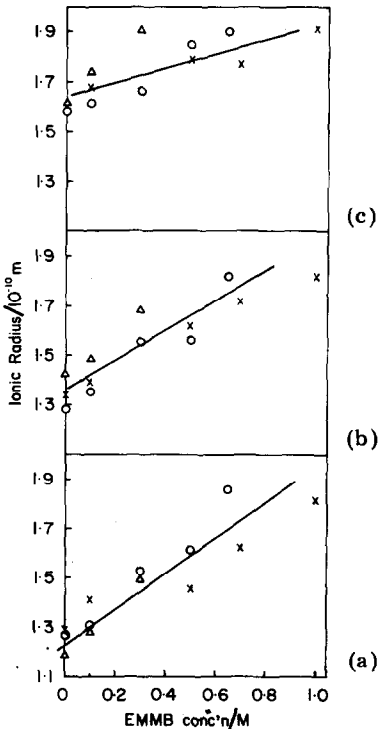


Fig. 2. Effect of EMMB concentration on ionic radius: (a) 0 °C; (b) 25 °C; (c) 50 °C; $ZnBr_2$: Δ , 1 M; \circ , 2 M; \times , 3 M.

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List of symbols

D	Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
I	Current density (A m^{-2})
I_{L}	Limiting current density (A m^{-2})
N	Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$
Q	EMMB concentration
r	Radius of diffusing particles (m)
R	Gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
T	Temperature (K)
Z	Zinc bromide concentration
η	Dynamic viscosity (Pa s)
ω	Rotational speed (Hz)

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