

## APPLICATION OF NON-AQUEOUS SOLVENTS TO BATTERIES PART I. PHYSICO-CHEMICAL PROPERTIES OF PROPIONITRILE/ WATER TWO-PHASE SOLVENT RELEVANT TO ZINC-BROMINE BATTERIES

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### Summary

The properties of bromine/propionitrile solution are investigated with a view to its use as an electrolyte in zinc-bromine batteries which use circulating electrolyte. The solution, which forms a two-phase system with water, has higher conductivity than the oils formed by complexation of bromine with organic salts such as *N,N*-methoxymethyl methylpiperidinium bromide and *N,N*-ethyl methylmorpholinium bromide. The activity of bromine in the aqueous phase of the bromine-propionitrile/water two phase system is very low, thus coulombic efficiencies of greater than 85% are achieved. Zinc-bromine batteries containing this solvent system show good charge/discharge characteristics.

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### Introduction

There has been renewed interest in the zinc-bromine battery in the past few years because of its inherent attractive features which make it a suitable candidate for electric vehicle and utility load-levelling applications. The zinc-bromine battery is based upon the use of abundant and relatively inexpensive reactants, has high energy density, good energy efficiency, and operates at room temperature.

In the past, a number of novel approaches has been tried to overcome the traditional high rate of self-discharge and short cycle life associated with zinc-bromine batteries. Liquid bromine has been complexed with tetramethylammonium perchlorate to form a solid [1] or with other organic salts, such as *N,N*-ethyl methylmorpholinium bromide, to form an oil-like complex [2], both with low water solubility. These techniques decrease bromine ac-

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tivity in the aqueous phase of a complexed-bromine/water two-phase system and, hence, lower the rate of self-discharge. Another approach is to use membranes which are permeable to cations but impermeable to bromine [3]. Water-immiscible, bromine-inert organic solvents such as carbon tetrachloride and dichloromethane, etc., have also been used as electrolyte solvents [4]. However, the high cost of ion-exchange membranes and of bromine-complexing reagents limits their usefulness, while the low conductivities of electrolytes dissolved in carbon tetrachloride or dichloromethane are unacceptable for practical applications.

TABLE 1

Physical properties of propionitrile\*

Density ( $\text{g cm}^{-3}$ ), 25 °C	0.7768
Viscosity (cP.), 30 °C	0.389
Freezing point (°C)	-92.8
Boiling point (°C), 760 mm	97.4
Dielectric constant, 20 °C	27.2
Miscibility with water, 25 °C	10.3% by weight
Specific conductance ( $\Omega^{-1} \text{cm}^{-1}$ ), 25 °C	$8.51 \times 10^{-8}$
Acute toxicity level oral LD <sub>50</sub> (rat)	39 mg/kg**

\*Data from A. Weissberger (ed.), *Organic Solvents — Physical Properties and Methods*, Wiley-Interscience, 3rd Edn., 1970.

\*\*Data from N. Irving Sax (ed.), *Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold Co., London, 5th Edn., 1979.

We have recommended the use of a relatively inexpensive, dipolar aprotic solvent, propionitrile (PN) in zinc-bromine batteries [5]. Table 1 shows the relevant physical properties of PN. The nitrile is moderately toxic, is immiscible with water, inert towards bromine, and a very good solvator of  $\text{Br}_3^-$  ion. More importantly, it forms charge-transfer complexes with bromine [6], resulting in highly conducting solutions. Thus a zinc-bromine battery based on PN/ $\text{H}_2\text{O}$  two-phase solvent should have low rates of self-discharge and a moderate internal resistance-voltaic loss.

In solutions containing bromide ions, bromine exists predominantly as  $\text{Br}_3^-$  which is formed according to equilibrium 1.



Equilibrium 1 is dependent on bromide ion concentration, temperature, and the nature of the solvent. Likewise, zinc halides, which are formed during discharge of a zinc-halogen cell, exist mostly as complex anions of general formula  $\text{ZnX}_3^-$  and  $\text{ZnX}_4^-$ , at high concentrations of the salt and in the presence of other halides [7]. This affects the distribution of bromine between the organic and water phases of the cell during a charge/discharge cycle as the bromine and zinc-halide concentrations alter.

This paper describes the changes in the distribution of bromine between the two phases of  $\text{Br}_2$ , PN/ $\text{H}_2\text{O}$  solvent systems during charge/discharge cycles of zinc–bromine cells. The conductivities of the two phases and the effects of PN and other complexing reagents on the electrochemical behaviour of bromine are also reported. The charge/discharge characteristics of zinc–bromine cells are also discussed.

## Experimental

Aqueous and organic solutions, prepared separately, were thoroughly mixed by agitation and the two phases allowed to separate before analysis.

Simulated-discharge mixtures were prepared by adding known quantities of granulated A.R. zinc to 4M  $\text{Br}_2$ , PN/3M NaCl,  $\text{H}_2\text{O}$  and allowing the mixture to react.

Discharge/charge curves were obtained galvanostatically using a cell containing  $20 \text{ cm}^2$  graphitic carbon electrodes (X8888 Morganite Carbon, Australia Pty. Ltd.), separated by a polypropylene separator (Daramic, 0.010 in., W. R. Grace, Australia Ltd.). A schematic diagram of the cell is shown in Fig. 1. The electrolyte was circulated through the two cell compartments at  $5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$  flow rate. In the fully discharged state the electrolyte consisted of 4M  $\text{ZnBr}_2$ , 3M NaCl in the aqueous part of the cell loop, and the organic part consisted of 2M  $\text{ZnBr}_2$ , 2M  $\text{Br}_2$  dissolved in propionitrile which had been previously saturated with water.

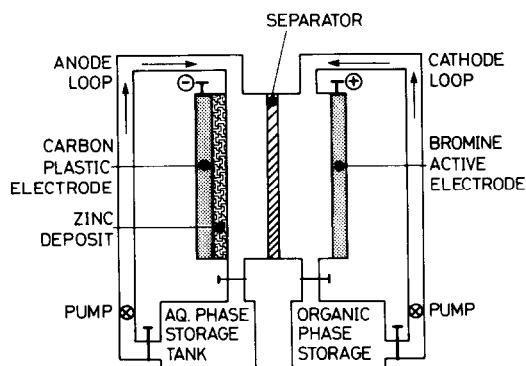


Fig. 1. Schematic diagram of a zinc–bromine cell.

The bromine electrode polarizations (current–potential performance of bromine electrolyte) at various current densities were measured by introducing a platinum pseudo reference electrode which responds to the  $\text{Br}_2/\text{Br}^-$  redox couple near to the graphite electrode in the organic electrolyte side of the cell — shown in Fig. 1. The cell had an appropriate electrolyte circulating at  $5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$  flow rate.

In all experiments, bromine concentrations were determined iodometrically by reacting the sample with excess potassium iodide and titrating against standard thiosulphate solution using starch (Vitex) indicator.

Sodium was analysed by flame photometry (Corning Eel flame photometer) and zinc was determined by atomic absorption spectrometry (Varian Techtron Model 1100 and G.B.S. Scientific Equipment Pty. Ltd. Model SB-900). Conductivities were measured with a Philips PW 9501 conductivity meter.

## Results and discussion

### A. Distribution of bromine between organic/water phases

Bromine has an infinite miscibility with propionitrile and when distributed between propionitrile and water phases, the distribution coefficient,  $K_{Br_2} = ([Br_2]_{org}/[Br_2]_{aq})$ , is  $> 50$  and is independent of the concentration of bromine in the absence of halide salt (Fig. 2). The Figure shows that the presence of NaCl alone does not alter this behaviour to any great extent. However, sodium bromide and zinc bromide exert a very strong influence on bromine distribution. The distribution coefficient of bromine decreases in the presence of sodium bromide and shows an even greater fall in the presence of zinc bromide. This phenomenon is presumably related to the relative changes in the free bromine concentrations of equilibrium (1) and to the ability of zinc bromide to form  $ZnBr_3^-$  and  $ZnBr_4^{2-}$  species which could be solvated

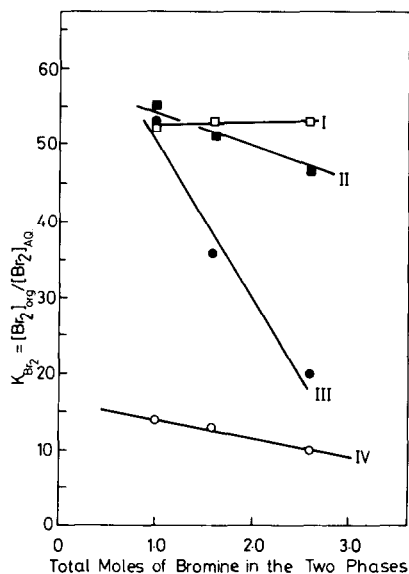


Fig. 2. Distribution of bromine between propionitrile/water phases (25 °C). The  $Br_2$  distributed between equilibrated phases consisting of 1 litre of PN and 1 litre of aqueous solution. The aqueous solution: I, pure water; II, 4M NaCl(aq); III, 4M NaBr(aq); IV, 2M  $ZnBr_2$ (aq).

TABLE 2

Distribution of sodium and zinc ions between PN/H<sub>2</sub>O/Br<sub>2</sub> equilibrated phases\* (25 °C)

Concentration** of bromine (M)	Concentration*** of electrolyte	Sodium		Zinc	
		Fraction in PN phase	Fraction in H <sub>2</sub> O phase	Fraction in PN phase	Fraction in H <sub>2</sub> O phase
1.0	4M NaBr	0.07	0.93	—	—
1.6	4M NaBr	0.12	0.88	—	—
2.6	4M NaBr	0.22	0.78	—	—
1.0	2M ZnBr <sub>2</sub>	—	—	0.32	0.68
1.6	2M ZnBr <sub>2</sub>	—	—	0.34	0.66
2.6	2M ZnBr <sub>2</sub>	—	—	0.36	0.64

\*Equal volumes of PN and H<sub>2</sub>O phases equilibrated.

\*\*Concentration with respect to the PN phase.

\*\*\*Concentration with respect to the aqueous phase.

by the dipolar aprotic nitrile. The distribution of the bromide salts between the nitrile and water phases, as shown in Table 2, is consistent with this hypothesis. Increasing the concentration of sodium chloride in a system where bromine has been distributed between propionitrile and water phases in the presence of zinc bromide, increases the  $K_{Br_2}$  value, as is shown in Fig. 3. This is probably due to the "salting out" of bromine from the aqueous

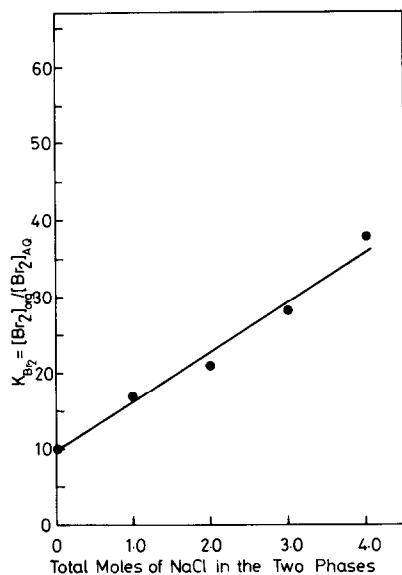


Fig. 3. Distribution of bromine between propionitrile/water phases as a function of NaCl concentration. Sodium chloride added to the equilibrated phases consisting of 1 litre 2.6M Br<sub>2</sub> in PN and 1 litre 2M ZnBr<sub>2</sub> in water.

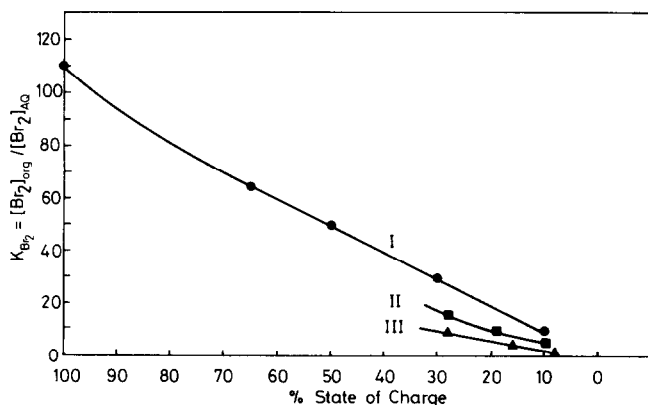


Fig. 4. Distribution of bromine between organic and aqueous phases of a zinc-bromine cell as a function of state of charge. The concentration of bromine in the organic phase at 100% state of charge: I, 4M Br<sub>2</sub> in PN; II, 4M Br<sub>2</sub> complexed with 1.4M *N*-methoxymethyl *N*-methylpiperidinium bromide\*; III, 5M Br<sub>2</sub> complexed with 1.4M *N*-methoxymethyl *N*-methylpiperidinium bromide\*.

\*Data taken from ref. 8.

phase by ionic sodium chloride. The effect of simultaneous changes in the concentrations of zinc bromide and bromine, which would be encountered during the charge/discharge of an actual cell on the distribution of bromine between PN/H<sub>2</sub>O phases, can be seen from Fig. 4. The Figure also compares results from a zinc-bromine cell using *N,N*-methoxymethyl methylpiperidinium bromide (reagent I) as a bromine complexing reagent. It is quite evident from this Figure that PN is more effective in reducing the bromine activity in the aqueous phase than is the complexing reagent I.

The temperature affects the distribution of bromine between PN/H<sub>2</sub>O phases significantly. For example, when equal volumes of 5.4M Br<sub>2</sub> in PN and 3M NaCl in H<sub>2</sub>O are equilibrated at 25 °C, the distribution coefficient of bromine was found to be 37. This dropped to 27 when the temperature was raised to 50 °C. This behaviour is analogous to that observed for the bromine distribution between water and the bromine complex (Br<sub>2</sub> + reagent I) phases [8].

### B. Electrolyte conductivity

The effect of zinc bromide concentration on the conductivity of an aqueous solution can be seen from Fig. 5. The effect of adding sodium chloride to the electrolyte is shown in the same Figure. In the absence of sodium chloride, the conductivity goes through a maximum at approximately 1.5M ZnBr<sub>2</sub>. The initial increase in conductivity is due to an increase in the number of conducting ions, whereas the decrease at higher concentrations of zinc bromide may be attributed to the increase in solution viscosity and to the formation of less mobile zinc-halo complex ions. The addition of sodium chloride leads to increased conductivity relative to zinc bromide alone (Fig. 5). The changes in conductivity of the aqueous and organic phases of an

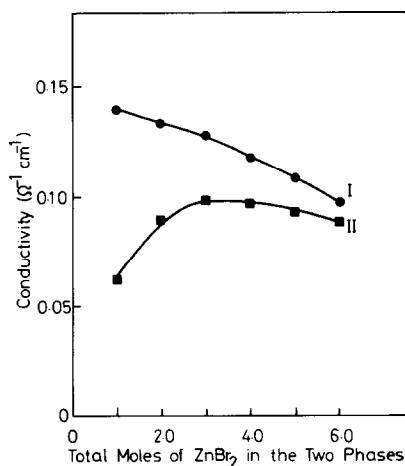


Fig. 5. Conductivity changes of the aqueous phase on addition of  $\text{ZnBr}_2$  to  $\text{PN}/\text{H}_2\text{O}$  (1 litre each) equilibrated two phase system (25 °C). I, solution contains 3M  $\text{NaCl}$  with respect to the aqueous phase; II, solution contains no other electrolyte.

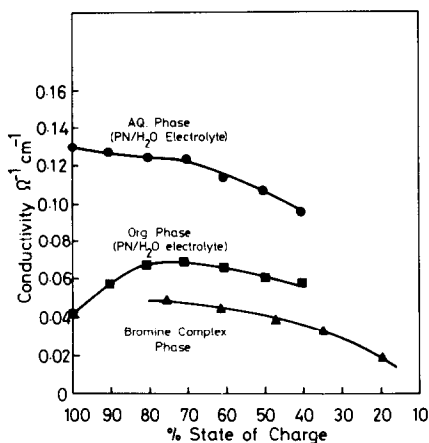


Fig. 6. Conductivities of the organic and aqueous phases as a function of the state of charge of a zinc-bromine cell (25 °C). 100% state of charge electrolyte:  $\text{PN}/\text{H}_2\text{O}$ , 4M  $\text{Br}_2$ ,  $\text{PN}/3\text{M NaCl}$ ,  $\text{H}_2\text{O}$ . Bromine complex phase obtained by electrolysis of an aqueous solution of 1M *N*-ethyl *N*-methylmorpholinium bromide; 3M  $\text{ZnBr}_2$  and 0.2M  $\text{ZnSO}_4$  (data from ref. 8).

actual cell (5M  $\text{Br}_2$ , saturated  $\text{NaBr}$ ,  $\text{PN}/3\text{M NaCl}$ ,  $\text{H}_2\text{O}$ ) undergoing discharge can be seen from Fig. 6. The conductivity of the aqueous phase shows a slight decrease which is due to an increase in the concentration of zinc bromide in the electrolyte during discharge of the cell.

The conductivity of the propionitrile phase goes through a maximum during the discharge cycle. This observation is similar to that observed for the organic phase of a cell using bromine complexed with *N,N*-ethyl methylmorpholinium bromide (complexing reagent II), as is shown in Fig. 6. The conductivity of the propionitrile phase, however, is higher than that of the bromine-complex phase. Solutions of bromine in nitriles are conducting due to the formation of charge transfer complexes [6]. In the presence of bromide ions, the high conductivity of these solutions is related to the "hopping" mechanism hypothesised by Gileadi *et al.* [9]. Additionally, a slight miscibility of  $\text{PN}$  with water further improves the conductivity of  $\text{Br}_2$ ,  $\text{Br}^-$ ,  $\text{PN}$  phases when equilibrated with water. Since the conductivity of the propionitrile phase containing bromine and bromide ions is higher than that of the organic salt-bromine complex, cells using propionitrile-water two phase electrolyte have lower internal resistance, and exhibit smaller voltaic losses than the cells using the bromine complex. For example, data from Fig. 6 show that for a 5 mm thickness of the organic phase between the electrodes of a zinc-bromine cell, the propionitrile phase will contribute  $7.9 \Omega \text{cm}^2$  to the overall specific resistance of the cell, compared with  $12.2 \Omega \text{cm}^2$  for a cell using complexing reagent II under identical conditions. The use of 5 mm

thickness of the electrolyte between the electrodes is for comparison only; in actual cells the electrode spacings of 0.2 - 2 mm will be more appropriate to reduce the ohmic loss to a minimum.

### C. Bromine electrode polarizations on platinum substrate

The current-potential performance of bromine dissolved in propionitrile in the presence of bromide ions and that of bromine complexed with reagent I are compared in Fig. 7. The polarization curves are essentially linear. This

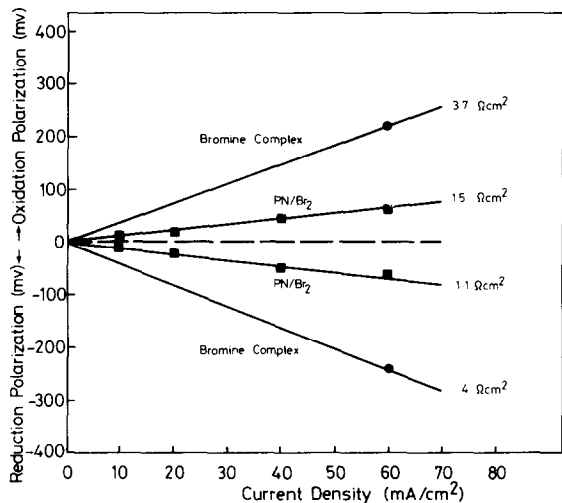


Fig. 7. Current-potential performance of bromine electrolyte. The PN/Br<sub>2</sub> electrolyte from the cell 4M Br<sub>2</sub>, PN/3M NaCl, H<sub>2</sub>O. Data for the bromine complex electrolyte were taken from ref. 8 which was obtained by electrolysing an aqueous solution of 1M *N*-ethyl *N*-methylmorpholinium bromide; 3M ZnBr<sub>2</sub> and 0.2M ZnSO<sub>4</sub>.

linearity is due to ohmic voltage drop between the bromine electrode and the tip of the reference electrode. The slopes of these curves are 1.5 Ω cm<sup>2</sup> and 1.1 Ω cm<sup>2</sup> for the oxidation and reduction of bromine in propionitrile phase, respectively. The corresponding values for the bromine complex as derived from the data in ref. 8 are 3.7 Ω cm<sup>2</sup> and 4 Ω cm<sup>2</sup>. Will *et al.* [10] obtained 0.4 Ω cm<sup>2</sup> for the anodic process and 0.28 Ω cm<sup>2</sup> for the cathodic process of bromine in aqueous solution on a glassy carbon electrode. These results suggest that the activation polarization for the oxidation/reduction of bromine is not affected, to any large extent, by complexation with reagent I, or by the presence of propionitrile. The observed differences in the slopes of the current-voltage curves are essentially due to the differences in the ohmic drops between the bromine electrode and the reference electrode tip in the three electrolytes compared.

### D. Charge/discharge behaviour of zinc-bromine cells

Typical charge/discharge curves for a zinc-bromine cell at 50 mA/cm<sup>2</sup> are shown in Fig. 8. After an initial drop from the open circuit voltage, 1.85



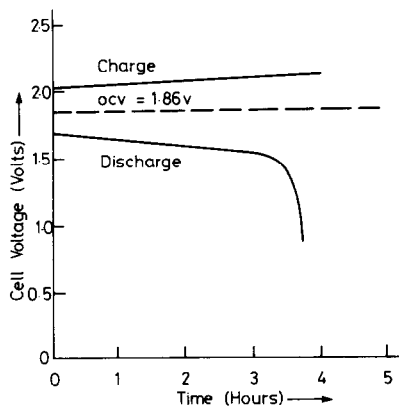


Fig. 8. Galvanostatic charge/discharge curves of a zinc-bromine cell with flowing electrolyte solution. 4 hour charge cycle; 1 A current ( $50 \text{ mA/cm}^2$ ). Electrode separation 4 mm.

V, the discharge voltage decreases gradually until the last stages of discharge, when the potential drops more rapidly due to depletion of zinc from the electrode surface. The charging potential is approximately 2.1 V and remains essentially constant. Taking 1.6 V as the average discharge potential, the voltaic efficiency of the cell is 76%. The coulombic efficiency is found to be *ca.* 85%.

## Conclusion

Propionitrile is an excellent solvent for use in zinc-bromine batteries which use circulating electrolytes. Solutions of bromine in propionitrile show high conductivity and are very effective in decreasing the activity of bromine in the aqueous phase of propionitrile/water electrolytes. As a result of this lowered bromine activity, the self-discharge in zinc-bromine cells is small and the cells show coulombic efficiencies in excess of 85%. The cells using the propionitrile/water system can deliver more power than cells using water-immiscible bromine complexes, under otherwise identical conditions, due to the higher conductivity of the organic phase in the propionitrile-based system. Further improvements in power are possible by circulating an emulsion of the  $\text{Br}_2/\text{PN}/\text{H}_2\text{O}$  phases through the cathode loop of the cell. This is because the emulsion will cause lower ohmic losses than the  $\text{Br}_2/\text{PN}$  electrolyte.

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