SELECTION OF QUATERNARY AMMONIUM BROMIDES FOR USE IN ZINC/BROMINE CELLS

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Summary

Various cyclic and aliphatic quaternary ammonium bromides have been tested for use in zinc/bromine battery electrolytes. No single compound can be used over the temperature range 0 - 50 °C due to crystallization of solid materials from either the polybromide or the aqueous phases. Electrolytes containing mixtures of quaternary ammonium bromides can avoid this problem of crystallization, and electrolytes containing 1:1 mixtures of *N*-methyl-*N*-ethylpyrrolidinium bromide with either *N*-methyl-*N*-ethylmorpholinium bromide or dimethylethylpropylammonium bromide have proved acceptable. The performance of a small zinc/bromine cell using electrolytes prepared from various quaternary ammonium bromides is described.

Introduction

Early zinc/bromine cells exhibited rapid self-discharge and poor faradaic efficiency due to the high solubility of bromine in the electrolyte, and its consequent high rate of transport to the zinc deposit. One method of reducing the magnitude of this problem was to incorporate quaternary ammonium salts into the electrolyte. These react with elemental bromine to form an addition compound, which reduces the solubility of bromine in the aqueous phase. Early investigators [1, 2] added tetramethylammonium compounds to the cell electrodes, or, in one case [3], grafted a polymer containing the quaternary ammonium compound onto the positive electrode. While these procedures improved faradaic efficiency, the addition compound was retained within the cell and the self-discharge rate remained high. Clerici *et al.* [2] quote a 50% loss in capacity after about 50 h.

High self-discharge rates can be overcome if circulation of the electrolyte is adopted, and if the quaternary ammonium substrate chosen is such that a liquid bromine addition compound — a polybromide — is formed. This liquid polybromide can then be stored external to the cell, decreasing the

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self-discharge rate substantially when the cell is not in service (*i.e.*, when the electrolyte is not being circulated). During cell operation (electrolyte circulation), access of bromine to the zinc deposit must be restricted by use of a separator. If the bromine concentration in the aqueous phase is sufficiently low (about 0.1 M or lower), a simple, microporous plastic separator is adequate. Several battery systems using this mode of operation have been described [4 - 6].

Eustace [7] studied the formation of liquid-phase polybromides using unsymmetrically substituted cyclic quaternary ammonium bromides (QBr); the polybromide liquid phases formed during battery operation were characterized as "bromine fused salts". Three QBr compounds were studied: *N*-ethyl-*N*-methylmorpholinium bromide (EMMB), *N*-chloromethyl-*N*-methyl-pyrrolidinium bromide (CMPB), and *N*-methoxymethyl-*N*-methylpiperidinium bromide. All these compounds gave liquid polybromide phases which were in equilibrium with an aqueous phase containing 0.03 - 0.3 M bromine. The *N*-methylpiperidinium compound proved unstable, but EMMB has found application in a number of zinc/bromine systems.

The use of unsymmetrical aliphatic QBr compounds was described by Gibbard [8]. A number of such materials were studied, several of which gave liquid-phase polybromides of suitable viscosity and density, in equilibrium with aqueous phase bromine concentrations below 0.1 M. These studies were restricted, however, to the 25 - 60 °C range. It was found that the use of mixtures of QBr compounds may give a liquid polybromide phase, even though the individual constituents give solid or highly viscous polybromides.

Although the above studies contain much useful information, there is little indication of the applicability of the various QBr materials at temperatures below 25 °C, or of the performance of zinc/bromine cells using the different compounds. In the present work, performance tests on zinc/bromine cells using EMMB as the QBr revealed that solid phases could develop when the bromine-to-QBr ratio in the addition compound (QBr_n) was low and the temperature was below 20 °C. This effect was especially marked in the presence of 3 - 4 M potassium chloride, which was added to reduce electrolyte resistance. The formation of these solid phases leads to cessation of electrolyte circulation, with consequent cell failure. As this phenomenon is not referred to in the available literature, a detailed investigation of the zinc bromide/EMMB system has been made. In addition, a number of cyclic and aliphatic QBr materials have been examined using a simple screening test to determine if any are superior to EMMB for zinc/bromine cell use. The more promising of these compounds have been tested in a small cell to assess performance under system operating conditions.

Experimental

Screening tests to assess the suitability of the various QBr compounds, together with more detailed tests to determine bromine distribution in the

cell electrolyte, were conducted by adding known amounts of bromine to zinc bromide/QBr solutions held at a known temperature in stoppered cylinders. The resulting mixtures were shaken to aid equilibration and the phases allowed to separate for inspection and, where appropriate, analysis. Performance tests were carried out using a small polypropylene-bodied cell. Details of the reagents, experimental procedures, and equipment are given in the following sections.

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; this served as a stock solution for the preparation of electrolytes. The stock solution was analysed for both zinc and bromide to ensure the Br:Zn stoichiometry was 2.00 ± 0.01. In some tests, Fluka anhydrous zinc bromide was used, but this did not affect the results obtained. Electrolyte solutions prepared from the stock solution normally had a pH of 3 - 4; when necessary the pH was adjusted to this range by small additions of concentrated hydrobromic acid or sodium hydroxide.

The unsymmetrical cyclic quaternary ammonium bromides were prepared by reacting the desired substrate (*N*-methylmorpholine or *N*-methylpyrrolidine) with the desired adduct (bromoethane or bromochloromethane). Both reagents were dissolved in dry acetone; the adduct: substrate mole ratio was 3:1 for EMMB preparation, and 1:1 for the other QBr compounds. The QBr material was precipitated from the acetone. The reaction varies from quite rapid (bromoethane and *N*-methylpyrrolidine, which is noticeably exothermic) to quite slow (bromochloromethane and *N*-methylmorpholine which requires 10 days to produce a yield of 42%). The crude product was purified by crystallization from either dry ethanol or an ethanol/ethyl acetate mixture. Yields ranged from 40 to 90%, with the highest values being for large batches of EMMB. The compounds prepared are shown in Table 1.

Partial analyses were made on each of the compounds prepared. Elemental microanalysis was carried out by a commercial analytical service, while the ionic bromine was determined volumetrically by the Volhard

TABLE 1

Quaternary ammonium bromides prepared

Adduct	Substrate	
	N-methylmorpholine	N-methylpyrrolidine
Bromoethane	*N*-ethyl-*N*-methylmorpholinium bromide (EMMB)	*N*-ethyl-*N*-methylpyrrolidinium bromide (MEPB)
Bromochloromethane	*N*-chloromethyl-*N*-methylmorpholinium bromide (MCMB)	*N*-chloro-*N*-methylpyrrolidinium bromide (CMPB)

method or gravimetrically by precipitation as the silver halide. The results are shown in Table 2. Purity, based on bromide analysis, was 98 - 99%. In addition to the elemental analyses, a proton NMR scan was made on the supposed EMMB. The shift values obtained were consistent with the EMMB structure.

All the above QBr compounds appeared to be hygroscopic. Thus, the high hydrogen found in CMPB (Table 2) may be due to adsorbed water, even though all materials are vacuum dried at less than 5 kPa for at least 5 h at 70 °C prior to analysis.

The unsymmetrical aliphatic quaternary ammonium bromides were synthesized by reacting an alkyl bromide (bromoethane, bromopropane, or chlorobromomethane) with the appropriate amine (trimethylamine, triethylamine, dimethylethylamine, or methyldiethylamine) in dry acetone. Recovery and purification were as described above for the cyclic compounds. In most cases, the yields were in the 60 - 90% range, averaging 75%. However, triethylpropylammonium bromide (3EP) was difficult to prepare, and the best yield obtained was 22% after 10 days reaction time. The purity of these compounds, as estimated from bromide analysis, ranged from 97.6 to 100.5%, with an average of 99%.

All QBr materials were stored in desiccators using either magnesium perchlorate, or phosphorus pentoxide absorbed on vermiculite, as the drying agent.

Analytical methods

The analytical methods used for determination of bromine and bromide in the different phases were similar to those described by Bellows *et al.* [9]. Dissolved zinc was determined by EDTA titration using xylenol orange indicator, the solution being buffered with ammonium acetate. To avoid attack on the indicator in the presence of free bromine, the latter was reduced with sodium metabisulphite prior to the addition of ammonium acetate.

TABLE 2

Analyses of quaternary ammonium bromides (identified in Table 1)

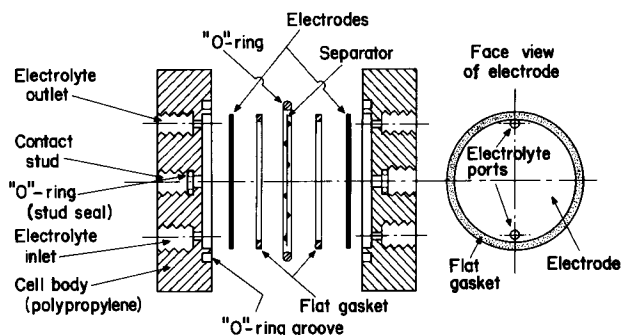| Element	Analyses (wt.%)							
	EMMB		MEPB		MCMB		CMPB	
	Theore-tical	Found	Theore-tical	Found	Theore-tical	Found	Theore-tical	Found
C	40.0	39.6	—	—	—	—	33.6	33.1
H	7.7	7.4	—	—	—	—	6.1	8.2
N	6.7	6.3	—	—	—	—	6.5	6.2
Cl	—	—	—	—	—	—	16.5	14.4
Br	38.0	37.4	41.2	40.3	34.7	34.2	37.3	36.9

Fig. 1. Schematic diagram of experimental Zn/Br$_2$ cell.

Cell test procedures

A schematic of the experimental cell is shown in Fig. 1. The cell body was made from polypropylene, the contact studs from zirconium, and the gaskets (both flat and O-ring) from Viton A (E. I. du Pont de Nemours, Wilmington, DE). The electrodes were 50 mm in diameter and had a working area of approximately 16 cm^2. The positive electrode was a platinum gauze welded to a titanium substrate, while the negative electrode was titanium sheet. Metal electrodes were used, rather than the plastic-bonded-carbon types often used in zinc/bromine cells, to ensure a stable electrode resistance over a series of tests.

The separator material was 0.6 mm thick, flat Daramic (W. R. Grace), a microporous polyethylene. In some cases, this was interleaved between two pieces of Whatman No. 50 filter paper (to give a "sandwich separator") in order to increase the effective thickness. Polyethylene spacer grids, fabricated in these laboratories, were used to support the separator and to provide an electrode-to-separator clearance of approximately 0.7 mm.

The positive- and negative-side electrolytes (35 cm^3 of each) were held in glass reservoirs, and circulated through the appropriate cell compartment by SPM-100, all-PTFE, nutating-disc pumps (Fluocarbon Inc., Anaheim, California), while connecting tubing and fittings were also of PTFE. The cell was cycled by use of a programmable galvanostat constructed in these laboratories. This was controlled, and data recorded, by an AIM-65 microcomputer (Rockwell Corporation, Anaheim, California). The cell was held at 25.0 ± 0.5 °C. The cell resistance was measured continuously during charge and discharge by modulating the current at 1 kHz, and then measuring the amplitude and phase difference of the 1 kHz components of the cell current and voltage.

The test profile used to evaluate the various electrolytes comprised a 2.5 h charge at 25 mA cm^{-2}, followed by a discharge at 25 mA cm^{-2} to a 1.0 V cut-off. The cell was then short-circuited through a 1 Ω resistor with the electrolyte still circulating for 15 min, followed by an open-circuit period, without circulation, of 15 min. Both the zinc- and bromine-side electrolytes

were circulated at approximately 2 cm^3 s^{-1}; the bromine-side electrolyte circulation was arranged so that the positive-side polybromide phase was dispersed throughout the electrolyte.

Results and discussion

Screening tests: cyclic QBr compounds

A qualitative test for the suitability of the four cyclic QBr compounds listed in Table 1 was made by making up a 1 M zinc bromide/1 M QBr solution, and adding 0.2 - 2 cm^3 of bromine to 20 cm^3 of that solution. The samples were equilibrated by shaking, brought to the desired temperature (0, 25, or 50 °C), and re-equilibrated. After standing for about 5 h, the condition of the polybromide and aqueous phases was observed, and the aqueous phase analysed for elemental bromine.

With the two chloro-methyl quaternary ammonium bromides (MCMB, CMPB; Table 1), a copious white precipitate formed when the QBr compound was mixed with the zinc bromide, while a small amount of a similar material separated from MEPB-containing solutions at 0 °C. The composition of these precipitates with respect to zinc and bromide was estimated volumetrically (Table 3). The analyses are consistent with compositions of the general formula ZnBr$_2 \cdot$2QBr. Further investigation showed that these materials were soluble in more concentrated zinc bromide, none precipitating from 3 M zinc bromide solutions.

Because the amount of precipitate formed with CMPB and MCMB was quite large, even at 25 °C, these materials were not tested further. It was later found that addition of bromine re-dissolved the precipitated material, probably due to the formation of a QBr$_n$ addition compound. In a battery system zinc bromide concentrations of about 1 M exist only at full charge, when considerable bromine has been liberated, thus CMPB and MCMB may be worth re-evaluation; especially the former, for which the equilibrium bromine concentration in the aqueous phase is very low.

The compounds EMMB and MEPB (Table 1) were also carried through the screening procedure; the results are given in Table 4, while Table 5 shows the aqueous bromine concentrations for these two compounds at various

TABLE 3

Analysis of precipitates from zinc bromide–QBr solutions

QBr used	Measured			Theoretical for ZnBr$_2 \cdot$2QBr		
	Zn (wt.%)	Br (wt.%)	Br:Zn (mole ratio)	Zn (wt.%)	Br (wt.%)	Br:Zn (mole ratio)
CMPB	10.2	47.7	3.82	10.0	48.9	4.00
MCMB	9.8	46.2	3.90	9.5	46.6	4.00
MEPB	10.6	51.4	3.96	10.7	52.1	4.00

TABLE 4

Polybromide phases from EMMB and MEPB

Temp. (°C)	Quaternary ammonium compound	Bromine added (moles per litre of aqueous phase)									
		0.20		0.49		0.98		1.47		1.96	
		PB*	Aq†	PB	Aq	PB	Aq	PB	Aq	PB	Aq
0	EMMB	solid	clear	solid	clear	solid	clear	oil	clear	oil	clear
	MEPB	semi-solid	white crystals	oil	white crystals	oil	white crystals	oil	white crystals	oil	white crystals
25	EMMB	solid	clear	solid	clear	semi-solid	clear	oil	clear	oil	clear
	MEPB	oil	clear	oil	clear	oil	clear	oil	clear	oil	clear
50	EMMB	oil	clear	oil	clear	oil	clear	oil	clear	oil	clear
	MEPB	oil	clear	oil	clear	oil	clear	oil	clear	oil	clear

*PB = polybromide phase.
†Aq = aqueous phase.

TABLE 5

Aqueous phase bromine concentrations: cyclic QBr compounds

State of charge	QBr used	[Br_2] in aqueous phase (M)		
		0 °C	25 °C	50 °C
Discharged[a]	EMMB	0.095	0.187	0.270
	MEPB	0.043	0.065	0.143
Half charge[b]	EMMB	0.049	0.080	0.136
	MEPB	0.033	0.037	0.066
Full charge[c]	EMMB	0.115	0.141	0.174
	MEPB	0.077	0.054	0.123

[a] Discharged is 0.49 mole Br_2 per litre 3 M $ZnBr_2$/1 M QBr.
[b] Half charge is 1.47 mole Br_2 per litre 2 M $ZnBr_2$/1 M QBr.
[c] Full charge is 2.45 mole Br_2 per litre 1 M $ZnBr_2$/1 M QBr.

states of charge and temperature. It can be seen from Table 4 that both compounds would give unsatisfactory cell operation at 0 °C, due to formation of solid phases. At 25 °C, the polybromide phase formed from EMMB is still solid at low bromine/EMMB ratios, but this phase is liquid throughout with MEPB. At 50 °C, both systems yield a liquid polybromide phase over the whole range of bromine concentrations. The data of Table 5 demonstrate that the equilibrium bromine concentration in the aqueous phase is much lower with MEPB-containing solutions, making them more suitable for use as battery electrolytes.

Screening tests: aliphatic QBr compounds

Although MEPB has satisfactory properties as a QBr for use in zinc/bromine systems, there is a tendency toward the formation of solid phases near 0 °C. It was therefore decided to test a number of unsymmetrical tetra-alkyl ammonium bromides, as suggested by Gibbard [8].

The test procedure used with these compounds differed slightly from that used for the cyclic materials. Again, 20 cm^3 samples of zinc bromide/QBr solution were reacted with bromine to form the polybromide phase. However, 0.5 cm^3 of bromine was used with 3 M zinc bromide/1 M QBr to simulate a discharged electrolyte, 1.5 cm^3 with 2 M zinc bromide/1 M QBr for a half-charge electrolyte, and 2.5 cm^3 was used with 1 M zinc bromide/1 M QBr for a fully-charged electrolyte. The latter would give an n value of 5.8 for the QBr$_n$ addition compound if all the QBr were extracted into the polybromide phase.

The equilibration procedure was similar to that described above. After equilibration at the desired temperature, the sample was allowed to stand to ensure phase separation, and the two phases separated at operating temperature. Each phase was analysed for zinc, bromine and bromide.

The above test procedure was used to screen several unsymmetrical alkyl QBr materials, working first at 25 °C. Any compounds that formed a solid

phase were rejected, as were any that gave high equilibrium bromine concentrations. The remaining compounds were then tested at 0 and 50 °C, and the formation of solid phases or high aqueous bromine concentrations noted.

The results obtained at 25 °C are presented in Table 6. The compounds 3MP, 3MC, 2MEC, and 3EC were eliminated due to solid formation, while 3ME and 2EMC were discarded due to too high an aqueous bromine concentration. Two symmetrical QBr compounds were also tested, namely, tetramethylammonium bromide and tetraethylammonium bromide. As anticipated, both gave solid polybromide phases over the whole composition and temperature range.

Table 7 gives the corresponding results at 0 and 50 °C for the compounds remaining after the elimination of those listed above. Comparing the data of Tables 6 and 7 with those for aqueous bromine concentration in equilibrium with EMMB and MEPB (Table 5), it can be seen that most of the unsymmetrical alkyl compounds are superior to EMMB, and several of them show at least slightly lower aqueous bromine than MEPB, with the 3EP material yielding particularly low values. As is clear from Table 7, however, none of these alkyl QBr compounds can be used over the whole of the temperature range 0 - 50 °C without solid formation.

White crystalline material would sometimes precipitate when unsymmetrical alkyl QBr materials were added to zinc bromide solutions, as was observed for the cyclic compounds. Analyses of the precipitates formed with 2MEP and tetraethylammonium bromide were consistent with the $ZnBr_2 \cdot 2QBr$ composition found previously.

Screening tests: mixed QBr compounds

If the QBr_n addition compounds can be regarded as molten salts [7], it would seem likely that use of mixed QBr materials would give polybromide phases having a lower freezing point. Also, if more than one QBr is used, while a total QBr concentration of 1 M is maintained, the likelihood of exeeding the solubility limit of each $ZnBr_2 \cdot 2QBr$ compound may be less, because of the reduced concentration of each individual QBr. Thus, it seems probable that polybromide phases prepared from mixtures of QBr compounds will show more useful properties than those prepared from single compounds.

Clearly, a very large number of electrolyte compositions based on mixtures of QBr compounds are possible, even if the materials used are restricted to the most promising of those tested. Consequently, tests were confined to 1:1 mole ratio mixtures, the six mixtures being arbitrarily selected from the more promising compounds, as judged from the data in Tables 4 - 7. The test procedure was as described above except that the initial screening was done at 0 °C rather than at 25 °C. The findings are presented in Table 8.

Four QBr mixtures gave satisfactory results at 0 °C in that no solid phase was formed, and three of these were tested further at both 25 and 50 °C. The MEPB/2MEP is clearly the most satisfactory in terms of low aqueous phase bromine concentration, and was selected for cell performance

TABLE 6

Tests on unsymmetrical aliphatic QBr compounds, 25 °C

QBr compound		Discharged			Half charge			Full charge		
Name	Abbreviation	PB[b] state	Aqueous phase		PB state	Aqueous phase		PB state	Aqueous phase	
			State	$[Br_2]$ (M)		State	$[Br_2]$ (M)		State	$[Br_2]$ (M)
Trimethylethyl AB[a]	3ME	oil	clear	0.153	oil	clear	0.080	oil	clear	0.150
Dimethyldiethyl AB	2M2E	oil	clear	0.078	oil	clear	0.094	oil	clear	0.069
Methyltriethyl AB	3EM	oil	clear	0.074	oil	clear	0.035	oil	clear	0.085
Trimethylpropyl AB	3MP	solid	clear	0.046	solid	clear	0.062	semi-solid	clear	0.108
Dimethylethylpropyl AB	2MEP	oil	clear	0.049	oil	clear	0.037	oil	clear	0.110
Methyldiethylpropyl AB	2EMP	oil	clear	0.034	oil	clear	0.026	oil	clear	0.098
Triethylpropyl AB	3EP	oil	clear	0.009	oil	clear	0.019	oil	clear	0.029
Trimethylchloromethyl AB	3MC	solid	clear	0.079	oil	clear	0.15	oil	clear	0.24
Dimethylethylchloromethyl AB	2MEC	semi-solid	clear	0.11	oil	clear	0.064	oil	clear	0.18
Methyldiethylchloromethyl AB	2EMC	oil	clear	0.066	oil	clear	0.058	oil	clear	0.18
Triethylchloromethyl AB	3EC	solid	clear	0.027	solid	clear	0.014	solid	clear	0.16

[a] AB = ammonium bromide.
[b] PB = polybromide phase.

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TABLE 7

Tests on unsymmetrical aliphatic QBr compounds, 0 and 50 °C

QBr Name	Abbreviation	Temp. (°C)	Discharged			Half charge			Full charge		
			PB[b] state	State	$[Br_2]$ (M)	PB state	State	$[Br_2]$ (M)	PB state	State	$[Br_2]$ (M)
				Aqueous phase			Aqueous phase			Aqueous phase	
Dimethyldiethyl AB[a]	2M2E	0	solid	clear	0.048	oil	clear	0.040	semi-solid	clear	0.080
Methyltriethyl AB	3EM	0	oil	clear	0.039	oil	clear	0.023	semi-solid	clear	0.092
Dimethylethylpropyl AB	2MEP	0	solid	clear	0.041	oil	clear	0.024	oil	clear	0.108
Methyldiethylpropyl AB	2EMP	0	semi-solid	clear	0.015	oil	clear	0.017	oil	clear	0.093
Triethylpropyl AB	3EP	0	solid	white crystals	0.006	solid	white crystals	0.008	solid	clear	0.049
Dimethyldiethyl AB	2M2E	50	oil	clear	0.165	oil	clear	0.087	oil	clear	0.141
Methyltriethyl AB	3EM	50	oil	clear	0.121	oil	clear	0.059	oil	clear	0.121
Dimethylethylpropyl AB	2MEP	50	oil	clear	0.104	oil	clear	0.057	oil	clear	0.128
Methyldiethylpropyl AB	2EMP	50	oil	clear	0.082	oil	clear	0.039	oil	clear	0.101
Triethylpropyl AB	3EP	50	oil	clear	0.053	oil	clear	0.028	oil	clear	0.100

[a] AB = ammonium bromide.
[b] PB = polybromide phase.

TABLE 8

Tests on mixtures of QBr compounds

QBr[a] mixture (1:1 mole ratio)	Temp. (°C)	Discharged			Half charge			Full charge		
		PB[b] state	State	[Br$_2$] (M)	PB state	State	[Br$_2$] (M)	PB state	State	[Br$_2$] (M)
			Aqueous phase			Aqueous phase			Aqueous phase	
MEPB/EMMB	0	oil	clear	0.048	oil	clear	0.055	oil	clear	0.116
MEPB/2MEP	0	oil	clear	0.033	oil	clear	0.019	oil	clear	0.073
MEPB/2M2E	0	oil	clear	0.044	oil	clear	0.028	semi-solid	clear	0.066
EMMB/2MEP	0	oil	clear	0.043	oil	clear	0.045	oil	clear	0.099
EMMB/2M2E	0	oil	clear	0.083	oil	clear	0.044	oil	clear	0.104
2M2E/2MEP	0	solid	white crystals	0.034	oil	clear	0.031	oil	clear	0.079
MEPB/EMMB	25	oil	clear	0.118	oil	clear	0.070	oil	clear	0.133
MEPB/2MEP	25	oil	clear	0.069	oil	clear	0.034	oil	clear	0.082
2MEP/EMMB	25	oil	clear	0.100	oil	clear	0.062	oil	clear	0.120
MEPB/EMMB	50	oil	clear	0.166	oil	clear	0.109	oil	clear	0.138
MEPB/2MEP	50	oil	clear	0.118	oil	clear	0.053	oil	clear	0.120
2MEP/EMMB	50	oil	clear	0.153	oil	clear	0.100	oil	clear	0.163

[a]Same notation as in Tables 6 and 7.
[b]PB = polybromide phase.

tests. The MEPB/EMMB mixture, although not outstanding in terms of low aqueous phase bromine, was also used in the cell tests as it appears to have been applied in full-scale battery work [9].

The above results show that the use of mixtures of QBr compounds can be advantageous in obtaining the desired polybromide properties. It is probable that other binary mixtures can be formulated to give liquid phases and yield low aqueous phase bromine concentrations over the desired operating range, even if the choice of materials was restricted to those tested above. Ternary and quaternary mixtures might also be worthy of investigation.

Bromine distribution in zinc bromide/EMMB systems

Prior to the studies on the polybromide-forming reagents reported above, a more detailed study was made of the zinc bromide/EMMB system with, and without, 3 M potassium chloride present. Although EMMB was later found to have some deficiencies as a QBr for use in zinc/bromine cells, the work gave a good indication of the changes in phase composition that can be expected over the operating range, and is therefore worth reporting here.

The experimental method used was similar to that described earlier in that 20 cm^3 volumes of 3, 2, and 1 M solutions of zinc bromide with 1 M EMMB were equilibrated with 0.5, 1, 1.5, 2, and 2.5 cm^3 of bromine. Analyses were made for elemental bromine, bromide, and zinc in the aqueous phase, and for bromine and bromide in the polybromide phase. Tests were made at 0, 25, and 50 °C. The results are presented in Fig. 2(a) - (c) for zinc bromide solutions, and in Fig. 3(a) - (c) for zinc bromide plus potassium chloride. The data are plotted in the form of bromide concentration in the aqueous phase against the number of bromine atoms per EMMB molecule in the polybromide phase, *i.e.*, the value of n in the QBr$_n$ addition compound.

Examination of Fig. 2 reveals that for 3 M zinc bromide, the aqueous bromine concentration is almost independent of the n value in the polybromide phase until this exceeds 6, beyond which there is a rapid increase in the aqueous bromine level. At lower zinc bromide concentrations, the aqueous bromine concentration is reduced for smaller n values, but reaches that found in 3 M zinc bromide solution as n approaches 6. The addition of 3 M potassium chloride (Fig. 3) reduces the bromine concentration slightly but does not change the general character of the curves, except at 0 °C (Fig. 3(a)), at which temperature zinc concentration has little effect on the curve shape. In both the absence and presence of potassium chloride, the effect of elevation in temperature is to increase the aqueous bromine concentration for a given n value. Again, as the temperature decreases, the range of aqueous bromine concentrations for the various zinc bromide levels is reduced.

One set of results was obtained with MEPB as the polybromide-forming reagent using 1 M zinc bromide/1 M MEPB as the electrolyte. The results are plotted in Fig. 4, together with those for an equivalent EMMB solution. It can be seen that the aqueous bromine concentrations are noticeably lower with MEPB, as was shown also in Table 5.
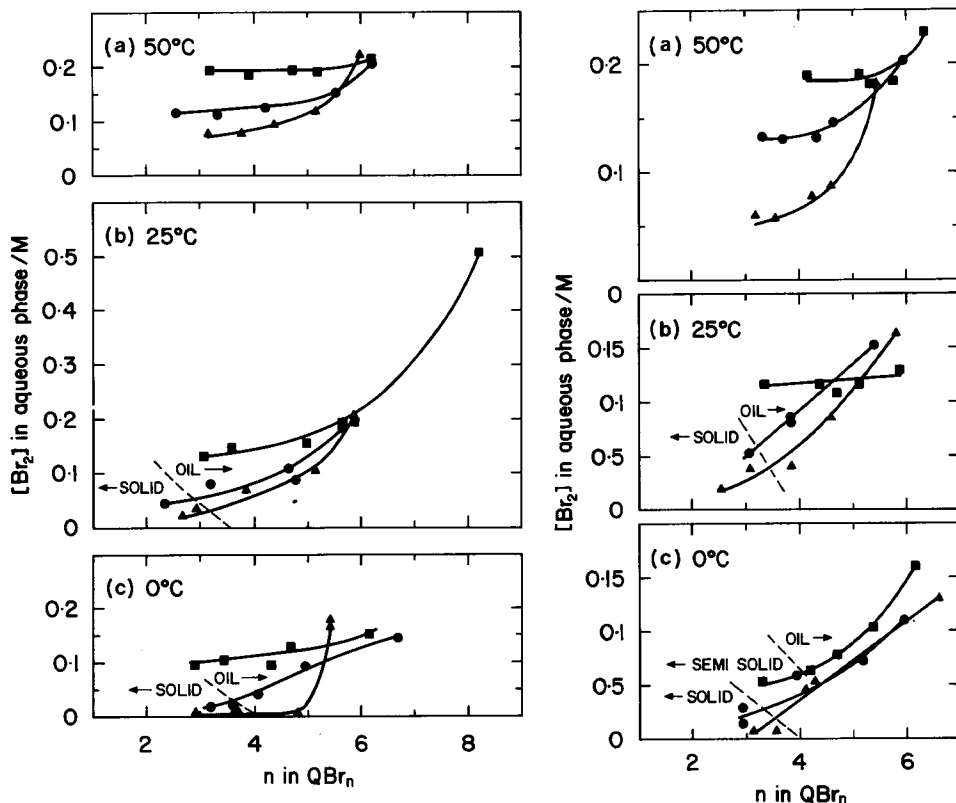
Fig. 2. Bromine distribution in ZnBr₂/EMMB solutions: ■, 3 M ZnBr₂; ●, 2 M ZnBr₂; ▲, 1 M ZnBr₂. (a) 50 °C, (b) 25 °C, (c) 0 °C.

Fig. 3. Bromine distribution in ZnBr₂/3 M KCl/EMMB solutions: ■, 3 M ZnBr₂; ●, 2 M ZnBr₂; ▲, 1 M ZnBr₂. (a) 50 °C, (b) 25 °C, (c) 0 °C.
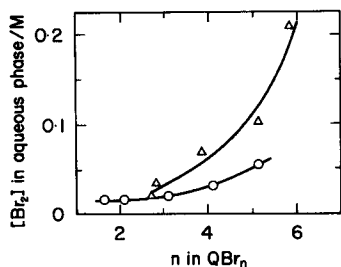
Fig. 4. Bromine distribution in △, 1 M ZnBr₂/1 M EMMB; ○, 1 M ZnBr₂/1 M MEPB.

Composition of solid polybromides

It has been found that solid phases can separate from the polybromide phase, and the data presented in Figs. 2 and 3 show the approximate conditions under which such phases separate. The separation of a solid phase in the polybromide is favoured by lower zinc bromide concentrations, lower

temperatures, and the presence of potassium chloride. Similar solid phases were observed when potassium bromide was substituted for the chloride, showing that a high bromide concentration does not prevent formation of the solid phase.

Analysis of the solid QBr material separating from a 3 M zinc bromide, 4 M potassium chloride, 1 M EMMB electrolyte yielded 38.5% free bromine. The elemental analysis of the remaining 61.5% is shown in Table 9, together with the theoretical values for EMMB. The close correspondence of the composition of the non-bromine fraction to that of EMMB suggests the material is of the form QBr_n with n being 2.65.

The n values for the solid phases formed in the bromine distribution tests were calculated on the assumption that the phases consisted solely of EMMB and bromine. Values of n obtained varied from 2.36 to 3.64, with an average value of 2.95 ± 0.27 for 18 samples. The solid phase thus approximates to the composition QBr_3. With the addition of more bromine, this material liquefies, typically when an n value of 4 is reached. The effect of potassium chloride and bromide can be explained as a "salting-out" effect, but it is not clear why higher zinc bromide concentrations appear to prevent the formation of solid polybromides.

Distribution of EMMB

Several important properties of the electrolyte, such as the diffusion coefficient of bromine and the electrolyte conductance, are a function of the QBr concentration in the aqueous phase [10]. Since much of the QBr is extracted into the polybromide phase, the concentration of that remaining in the aqueous phase is expected to be a function of the amount of elemental bromine present in the system and, hence, of the state-of-charge of the cell.

To test the above hypothesis, the EMMB remaining in the aqueous phase was estimated for the set of tests used to study bromine distribution in the zinc bromide/EMMB system. By assuming that all the bromide in the polybromide phase came from the EMMB present, the EMMB concentration in the aqueous phase could be calculated from the measured volumes of polybromide and aqueous phases, and from the known initial amount of EMMB taken. Curves showing the relation between the EMMB remaining in the

TABLE 9

Analysis of solid polybromide material (elemental analysis excluding "free" bromine)

Element	Found (%)	Theoretical for EMMB (%)
C	40.9	40.0
H	7.8	7.7
N	6.7	6.7
Br	37.9	38.0
O	n.d.	7.6
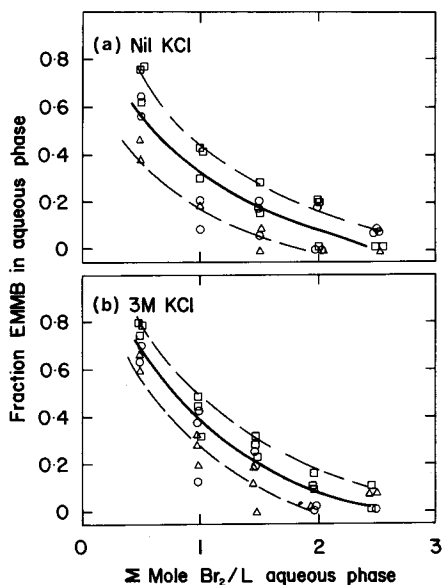
Fig. 5. Distribution of EMMB in ZnBr$_2$/EMMB and ZnBr$_2$/3 M KCl/EMMB solutions: □, 3 M ZnBr$_2$; ○, 2 M ZnBr$_2$; △, 1 M ZnBr$_2$. (a) Nil KCl, (b) 3 M KCl.

aqueous phase and the amount of bromine present are given in Fig. 5. Fitting the data to quadratic equations leads to the following empirical relations:

for the zinc bromide/EMMB system

$$Q = 0.154B^2 - 0.769B + 0.951 \tag{1}$$

while for the zinc bromide/KCl/EMMB system

$$Q = 0.167B^2 - 0.807B + 1.01 \tag{2}$$

where Q is the aqueous phase EMMB concentration (M) and B the number of moles of bromine present (added or generated electrolytically) per litre of aqueous phase. The correlation coefficient for eqn. (1) was 0.952, and the standard deviation of the experimental values from those calculated using eqn. (1) was 0.112 (51 values). The corresponding values for eqn. (2) were 0.976 and 0.083 (53 values).

Closer analysis showed that the zinc bromide concentration had a second-order effect on the equilibrium EMMB concentration, but in view of the poor precision of the results, it was not considered useful to introduce factors into eqns. (1) and (2) to correct for this.

Cell performance with different QBr compounds

Four QBr systems were tested for cell performance, namely, EMMB, MEPB, a 1:1 w/w mixture of MEPB and EMMB, and a 1:1 w/w mixture of MEPB and 2MEP. Each of these systems was tested with 2 M zinc bromide and with 2 M zinc bromide/3 M potassium chloride as the other components of the electrolyte, as well as with each of the separators (flat Daramic and

"sandwich") mentioned above. Bromine equivalent to 1.0 mole per litre of the positive side aqueous phase was added initially to simulate a half-charge electrolyte. The aqueous phase bromine concentration was determined at the end of each run, *i.e.*, when the cell was discharged, and, in a separate series of tests, in the aqueous phase at the end of charge. The bromine concentration shown in Table 10 is the average of these values.

Each electrolyte and separator combination was given four or five charge–discharge cycles. The results of the first of these was discarded, and those of the remaining cycles were averaged to give the data presented in Table 10. The rate of transport of bromine through the separator can be estimated if it is assumed that the faradaic efficiency is determined solely by this rate. and that the cell is zinc-limited and completely discharged each cycle. Under these conditions the rate of bromine transport, expressed as a current density, is given by (charge A h — discharge A h)/(cycle time × area). The values of bromine transport listed in Table 10 were calculated in this way.

A second method of estimating the rate of bromine transport is to substitute a weighed zinc disc for the negative electrode, and operate the cell at open-circuit with the electrolytes being circulated in the normal way. After a suitable time (typically 2 h) the circulation is stopped, the cell drained and disassembled as quickly as possible, and the zinc washed, dried, and weighed. The loss in weight represents any zinc dissolved, whether by reaction with diffused bromine, or by any other mechanism. The values given in Table 11 show the results obtained from these zinc corrosion rate tests, with the corrosion rate expressed as a current density. A blank run was conducted with the separator being replaced by a 1 mm rubber sheet and only the negative-side electrolyte circulated. This gave a corrosion current of 0.03 mA cm^{-2}, which is small by comparison with the rates observed in normal operation. Note that the bromine concentrations during the corrosion tests are lower than for the corresponding cycle test, this is because the cells were not charged prior to the corrosion tests, with the result that the bromine concentration remained near its initial value and did not increase, as normally happens when a cell is charged.

To compare the values of bromine transport estimated independently from the cell performance data and from the zinc corrosion rate tests, some correction must be made for the somewhat different bromine concentrations in the aqueous phase of the positive-side electrolyte. If it is assumed that the electrolyte in each cell-compartment is sufficiently well mixed by the electrolyte circulation for the composition to be taken as uniform, and if it is further assumed that the diffusion calculated through the separator is controlled by the concentration difference between the aqueous phase bromine concentrations, then

$$I_d = [aFD(C_B - C_Z)]/d \tag{3}$$

where I_d is the bromine transport rate expressed as a current, a the number of electrons involved (2 for Br_2), F the Faraday constant, D the diffusion

TABLE 10

Cell performance with various QBr compounds

QBr	Electrolyte composition (M)			Separator	Efficiencies (%)			Aqueous [Br₂] (M)	Bromine transport (mA cm⁻²)	Cell resistance discharge (Ω)
	ZnBr$_2$	KCl	QBr^a		Faradaic	Voltaic	Energy	Aqueous [Br$_2$] (M)	Bromine transport (mA cm^{-2})	Cell resistance discharge (Ω)
EMMB	2	—	0.33	Daramic^b	87.2	84.9	74.0	0.084	1.55	0.29
EMMB	2	3	0.33	Daramic	88.1	90.5	79.7	0.080	1.43	0.16
EMMB	2	—	0.33	Sandwich	93.6	81.1	75.9	0.084	0.75	0.39
EMMB	2	3	0.33	Sandwich	93.9	88.1	82.7	0.080	0.71	0.21
MEPB	2	—	0.15	Daramic	90.6	85.2	77.2	0.041	1.11	0.27
MEPB	2	3	0.15	Daramic	91.0	90.4	82.2	0.036	1.07	0.15
MEPB	2	—	0.15	Sandwich	94.6	81.0	76.6	0.041	0.63	0.38
MEPB	2	3	0.15	Sandwich	95.5	88.4	84.4	0.036	0.53	0.20
MEPB + 2MEP	2	—	0.075/0.10	Daramic	91.7	84.3	77.3	0.037	0.98	0.28
MEPB + 2MEP	2	3	0.075/0.10	Daramic	91.8	88.6	81.3	0.030	0.97	0.18
MEPB + 2MEP	2	—	0.075/0.10	Sandwich	95.3	78.1	74.4	0.037	0.55	0.42
MEPB + 2MEP	2	3	0.075/0.10	Sandwich	96.2	87.4	84.1	0.030	0.43	0.22
MEPB + EMMB	2	—	0.075/0.17	Daramic	87.4	84.2	73.6	0.060	1.53	0.29
MEPB + EMMB	2	3	0.075/0.17	Daramic	87.5	89.2	78.0	0.049	1.51	0.18
MEPB + EMMB	2	—	0.075/0.17	Sandwich	93.4	80.2	74.9	0.060	0.79	0.39
MEPB + EMMB	2	3	0.075/0.17	Sandwich	94.7	87.9	83.3	0.049	0.62	0.22

^{a}QBr concentration is the equilibrium value after bromine addition.
^{b}Daramic separator was acetone extracted and alkaline detergent leached.

TABLE 11

Zinc corrosion rate tests: effect of various QBr compounds

QBr	Electrolyte composition (M)			Separator type	Aqueous $[Br_2]$ (M)	Corrosion rate (mA cm^{-2})
	$ZnBr_2$	KCl	QBr[a]			
EMMB	2	—	0.33	Daramic[b]	0.073	1.22
EMMB	2	3	0.33	Daramic	0.078	1.43
EMMB	2	—	0.33	Sandwich	0.073	0.74
EMMB	2	3	0.33	Sandwich	0.078	0.63
MEPB	2	—	0.15	Daramic	0.033	0.97
MEPB	2	3	0.15	Daramic	0.031	0.90
MEPB	2	—	0.15	Sandwich	0.033	0.45
MEPB	2	3	0.15	Sandwich	0.031	0.40
MEPB + 2MEP	2	—	0.075/0.10	Daramic	0.030	0.73
MEPB + 2MEP	2	3	0.075/0.10	Daramic	0.025	0.72
MEPB + 2MEP	2	—	0.075/0.10	Sandwich	0.030	0.47
MEPB + 2MEP	2	3	0.075/0.10	Sandwich	0.025	0.35
MEPB + EMMB	2	—	0.075/0.17	Daramic	0.050	1.54
MEPB + EMMB	2	3	0.075/0.17	Daramic	0.053	1.43
MEPB + EMMB	2	—	0.075/0.17	Sandwich	0.050	0.58
MEPB + EMMB	2	3	0.075/0.17	Sandwich	0.053	0.57
EMMB	2	—	0.33	Blank test	Nil	0.028

[a]QBr concentration defined as Table 10.
[b]Daramic separator as for Table 10.

coefficient for bromine in the electrolyte used, C_B the positive-side aqueous phase bromine concentration, C_Z the negative-side aqueous phase bromine concentration, and d is the equivalent thickness of the separator, where $d = (T^2/P)L$, with T being the tortuosity factor, P the porosity, and L the physical thickness of the separator [11]. In practice, C_Z is usually negligibly small by comparison with C_B so that

$$I_d/C_B = aFD/d \qquad (4)$$

Since a and F are constants, and d should be a constant for any one separator, the ratio I_d/C_B should vary only as D varies, i.e., this ratio should be constant for a given electrolyte composition.

Since the change in electrolyte composition during the cycle tests used to obtain the data of Table 10 was small, the I_d/C_B values estimated from these tests should be directly comparable with those calculated from the zinc corrosion rate tests. The values of this ratio derived from both the cycle and zinc corrosion rate data are presented in Table 12. It can be seen that there is good agreement between the two procedures.

It is of interest to note that the values of I_d/C_B are much greater for the tests using MEPB-based electrolytes than for EMMB used alone. For both the Daramic and the sandwich separators the ratio of I_d/C_B for MEPB-containing

TABLE 12

Values of I_d/C_B (see eqn. (4))

QBr[a]	Electrolyte composition (M)			Separator type	I_d/C_B	
	$ZnBr_2$	KCl	QBr		Cell	Zn corrosion
EMMB	2	—	0.33	Daramic	18.5	16.7
EMMB	2	3	0.33	Daramic	17.9	18.3
EMMB	2	—	0.33	Sandwich	8.9	10.1
EMMB	2	3	0.33	Sandwich	8.9	8.1
MEPB	2	—	0.15	Daramic	27.0	29.4
MEPB	2	3	0.15	Daramic	29.7	29.0
MEPB	2	—	0.15	Sandwich	15.4	13.6
MEPB	2	3	0.15	Sandwich	14.7	12.9
MEPB + 2MEP	2	—	0.075/0.10	Daramic	26.5	24.3
MEPB + 2MEP	2	3	0.075/0.10	Daramic	32.3	28.8
MEPB + 2MEP	2	—	0.075/0.10	Sandwich	14.9	15.7
MEPB + 2MEP	2	3	0.075/0.10	Sandwich	14.3	14.0
MEPB + EMMB	2	—	0.075/0.17	Daramic	25.5	30.8
MEPB + EMMB	2	3	0.075/0.17	Daramic	30.8	27.0
MEPB + EMMB	2	—	0.075/0.17	Sandwich	13.2	11.6
MEPB + EMMB	2	3	0.075/0.17	Sandwich	12.7	10.8

[a]QBr concentration as in Table 10.

electrolytes to I_d/C_B for electrolytes containing EMMB alone is between 1.5 and 1.6. Part of this difference can be accounted for by the higher diffusion coefficient of bromine in MEPB-based electrolytes, both because it is intrinsically higher in this solution [10], and because the equilibrium QBr concentration is lower in these MEPB-containing systems, again leading to a greater bromine diffusion coefficient. Together, these effects would account for about a ratio of 1.2, at most, in the value of the I_d/C_B between MEPB-containing and EMMB-containing electrolytes. Since this ratio is about 1.55, it seems that the QBr used can affect the value of d, that is, the assumption that only the aqueous phase bromine concentration controls the bromine transport through the separator is, at best, a first-order approximation.

Conclusions

Four cyclic and eleven alkyl quaternary ammonium bromides have been given a screening test in order to evaluate their usefulness in zinc/bromine batteries. No single compound proved entirely acceptable; all produce a solid phase under certain conditions, either by the formation of solid polybromide compounds, or by crystallization from the aqueous phase of compounds having the general formula $ZnBr_2 \cdot 2QBr$. One of the cyclic materials (N-ethyl-N-methylpyrrolidinium bromide), and two of the aliphatics (dimethylethylpro-

pylammonium bromide, diethylmethylpropylammonium bromide) can be used, however, providing the operating temperature is kept above about 10 °C.

The polybromide phases can be regarded as fused salts [7], and it would therefore be expected that polybromides derived from two or more QBr compounds would show a lowering of the freezing point. This has been confirmed; *N*-ethyl-*N*-methylpyrrolidinium bromide/*N*-ethyl-*N*-methylmorpholinium bromide and *N*-ethyl-*N*-methylpyrrolidinium bromide/dimethylethylpropylammonium bromide mixtures have given polybromide phases that remain fluid down to at least 0 °C. It is probable that a number of mixed QBr polybromides would prove satisfactory in terms of reduced freezing points.

Another parameter that requires consideration is the bromine concentration in the aqueous phase. Many of the compounds tested, and all of those listed above, have a sufficiently low equilibrium aqueous phase bromine concentration to be of interest in zinc/bromine cell application. However, when four different QBr materials were incorporated into electrolytes and then tested, the bromine transport rate did not appear to be independent of the QBr used. Proposed models of zinc/bromine cells [9, 12] assume that the bromine transport rate through the separator is proportional to the concentration difference between the aqueous phase bromine in the positive and negative compartments. The results obtained in the cell tests reported here suggest that the presence of the polybromide phase can have an additional effect on this transport rate.

One important aspect of the work which has not been studied is the long-term stability of the compounds tested, especially in the polybromide form. Eustace [7] stated that EMMB-based polybromide is stable for 15 months over the temperature range 0 - 60 °C, but little information is available regarding the other compounds. Further work in this area is desirable.

Acknowledgements

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