

SHORT COMMUNICATION

Stability of zinc/bromine battery electrolytes

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1. Introduction

Several zinc–bromine battery systems which utilize an electrolyte containing a quaternary ammonium bromide (QBr) have been described [1–3], the presence of the QBr resulting in the formation of a bromine-rich polybromide phase and an aqueous phase having a low bromine concentration. This low aqueous bromine level results in a high faradaic efficiency being achieved with an inexpensive microporous separator, while the formation of polybromide is a convenient means of storing the bromine generated during charging as a high density phase having a low bromine vapour pressure (4).

There have, however, been few studies as to the long-term stability of such electrolytes. Eustace [5] examined a small range of QBr compounds and reported the polybromide phase for most of these to be stable for 15 months at 60°C, but this study appears to have been made on the polybromide phase alone, not with the polybromide dispersed throughout the aqueous phase as is the case in battery systems. Bellows *et al.* [6] showed the mixture of QBr compounds in a zinc–bromine battery electrolyte to be stable over some 1200 charge/discharge cycles, but gave few details. Therefore, it was considered useful to assess the stability of a range of QBr compounds in a simulated zinc–bromine battery electrolyte, over an extended period.

2. Experimental

The basic procedure was to agitate solutions containing zinc bromide, the QBr under test, and bromine, at 50°C over a six month period. Each phase of the test solution was then examined by ¹⁴N NMR to search for any quaternary ammonium breakdown products of the original QBr, and to establish QBr concentrations in each phase.

In more detail, eight 20 cm³ aliquots of a 2 M zinc bromide/1 M QBr solution, together with 1.2 cm³ (0.023 mole) of bromine (corresponding to the half-charged condition) were placed in extended-neck 100 cm³ Erlenmeyer flasks, a small PTFE-coated stirrer-bar introduced, and the flask sealed. An additional two samples were also carried through this procedure, one having a solution composition 1 M

Table 1. Quaternary ammonium bromides examined

Name	Abbreviation
<i>Cyclic substrates:</i>	
<i>N</i> -ethyl <i>N</i> -methylmorpholinium bromide	EMMB
<i>N</i> -ethyl <i>N</i> -methylpyrrolidinium bromide	MEPB
<i>N</i> -chloromethyl <i>N</i> -methylpyrrolidinium bromide	CMPB
<i>Unsymmetrical aliphatic substrates:</i>	
Dimethyldiethyl ammonium bromide	2M2E
Dimethylethylpropyl ammonium bromide	2MEP
Methyldiethylpropyl ammonium bromide	2EMP
Methyltriethyl ammonium bromide	3EM
Methyldiethylchloromethyl ammonium bromide	2EMC

zinc bromide/1 M 2M2E with 0.042 mole of bromine (corresponding to the fully charged condition), while the other was 3 M zinc bromide/1 M 2M2E with 0.005 mole of bromine (discharged condition). See Table 1 for a list of the QBr compounds tested together with the corresponding abbreviations used in this paper.

The flasks were placed on a multiple-head magnetic stirrer (Variomag® HP 15P) in a controlled-temperature cabinet held at 50°C, and the samples agitated at sufficient intensity to ensure mixing of the aqueous and polybromide phases. These conditions were maintained for 4580 h, after which all samples were removed from the cabinet, the phases re-equilibrated at 25°C, the flasks opened, and the phases separated and stored. The ¹⁴N NMR spectrum of each of these samples was run using a Bruker AM300 NMR spectrometer. The aqueous layer was analysed volumetrically to establish the bromine concentration. A second set of freshly prepared samples, as nearly identical as possible in composition with those taken for the stability test, was taken through the same set of analytical procedures.

The NMR spectra were obtained by introducing the sample to be examined into a 10 mm NMR tube, the reference of nitromethane in dimethylsulphoxide being contained within a concentric capillary. A spectral width of 500 ppm was used to ensure that any signals arising from nitrogen-containing decomposition products would be detected. The acquisition parameters used in these experiments result in a ± 0.2 ppm inherent uncertainty in peak position for constant-temperature operation: moreover, since tem-

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Table 2. ^{14}N NMR peak position

QBr	Peak-position to nitromethane reference/ppm			
	Polybromide phase		Aqueous phase	
	Fresh solution	50° C, 4580 h	Fresh solution	50° C, 4580 h
EMMB	-329.7	-329.5	-330.1	-329.9
MEPB	-308.0	-307.9	-308.5	-308.5
CMPB	-302.0	-301.9	-302.4	-302.4
2MEP	-326.4	-326.6	-327.3	-327.1
2EMP	-321.6	-321.9	-322.3	-322.0
3EM	-322.2	-322.5	-322.7	-322.7
2EMC	-315.5	-316.0	-316.0	-316.1
2M2E, chg	-327.0	-327.0	-327.6	-327.7
2M2E, 1/2 chg	-327.6	-327.9	-326.9	-326.6
2M2E, disch	*	*	-327.2	-327.4

* Insufficient sample volume for analysis.

peratures during acquisition may have varied slightly ($\pm 1^\circ\text{C}$) from sample to sample, larger variations in peak position are possible. For quantitative determination, integrated peak areas were compared to a calibration curve prepared from NMR spectra of a range of solutions of known QBr concentration. Precision of the quantitative QBr determination was estimated from agreement between duplicates during calibration [7], and was approximately $\pm 4.8\%$.

The QBr compounds were synthesized as described previously [8]. The structure of each was confirmed by proton-NMR, and the purity estimated by Volhard bromide determination.

3. Results

A single well-defined NMR peak was obtained for each QBr tested, and this was true for both aqueous and polybromide phases. The peaks for the two chloro-compounds (CMPB and 2EMC) were much broader than those of the other QBr compounds tested. This is not unexpected since the presence of a chloromethyl group would tend to decrease the symmetry of the electric field surrounding the N nucleus and hence result in the quadrupolar line-broadening which is observed in ^{14}N spectra of most (non-quaternary) nitrogen compounds. In no case did

the NMR spectrum of any of the aged solutions display any signals other than that attributable to the QBr under test.

Chemical shifts relative to the nitromethane standard used are reported in Table 2, for freshly-prepared and aged solutions and for both the polybromide and aqueous phases. Variations in chemical shift for a given QBr were small, averaging 0.2 ± 0.2 ppm over the whole set of samples, with a maximum deviation of 0.5 ppm. These variations are within the precision of the method.

The QBr concentrations in each phase as determined by ^{14}N NMR, and the aqueous phase bromine concentrations, are reported in Table 3. It can be seen that the concentration of QBr in the polybromide phase is not changed by the ageing procedure, nor is the aqueous phase bromine concentration. The QBr concentration in the aqueous phase of the aged solutions, however, shows a consistent increase, averaging 17%.

4. Discussion

The results presented are not consistent with any significant decomposition of any of the QBr compounds tested. The ^{14}N NMR spectra of aged materials contained no new signals and no signifi-

Table 3. Effect of solution ageing on phase composition

QBr	[QBr] in polybromide/M			[QBr] in aqueous/M			[Br ₂] in aqueous/M		
	Fresh	50° C, 4580 h	Aged/fresh	Fresh	50° C, 4580 h	Aged/fresh	Fresh	50° C, 4580 h	Aged/fresh
EMMB	4.13	4.11	1.00	0.338	0.360	1.07	0.088	0.096	0.92
MEPB	4.47	4.05	0.91	0.180	0.227	1.26	0.041	0.043	0.95
CMPB	4.40	4.51	1.03	0.130	0.175	1.35	0.056	0.058	0.97
2MEP	4.31	4.24	0.98	0.118	0.163	1.38	0.042	0.037	1.14
2EMP	3.88	3.96	1.02	0.132	0.150	1.14	0.024	0.027	0.89
3EM	4.09	4.07	1.00	0.234	0.256	1.09	0.038	0.038	1.00
2EMC	4.13	4.12	1.00	0.154	0.175	1.14	0.049	0.051	0.96
2M2E, chg	4.19	4.12	0.98	0.025	0.030	1.2	0.092	0.091	1.01
2M2E, 1/2 chg	4.61	4.47	0.97	0.282	0.287	1.02	0.057	0.062	0.92
2M2E, disch	*	*	-	0.914	0.919	1.01	0.127	0.128	0.99

* Insufficient volume of sample for analysis.

cant changes in peak shape or chemical shift were observed. Further, the QBr concentration in the polybromide remained unaltered over the test period, with the possible exception of the MEPB sample, although even in this instance the difference is approximately twice the precision of the analysis and may therefore be a chance deviation. For all samples the aqueous bromine concentration showed no significant alteration between the initial and aged condition.

There is a consistent difference between the aqueous-phase QBr concentration of the freshly prepared and aged samples. No certain reason can be suggested for this, although there was some difference in the treatment between the aged and fresh samples. However, since the difference in aqueous-phase QBr concentration observed does not affect the conclusions reached, no further work was done to establish the cause of this change in concentration.

5. Conclusions

There is no evidence for decomposition of any of the

quaternary ammonium bromides examined. This is consistent with the observations of Eustace [5], and with the stable battery performance observed by several groups [1–3, 6].

References

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