Reactivity towards Electron Transfer of Azide Ion in Metal–Metal Ion-Exchange Reactions

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CATALYSED electron-transfer by azide ion has been reported for some oxidation–reduction reactions in solution[1] but it does not seem to have received attention in metal–metal ion-exchange reactions. We found that azide ion is more effective than chloride ion and almost as effective as bromide ion in catalysing the exchange $Zn^{2+} + 2e \rightleftharpoons Zn^0$ (Hg); also that reactivity could be reconciled with electrocapillary properties. Surprisingly, such properties of azide ion have not previously been examined to any extent.

From faradaic impedance measurements at a dropping-mercury electrode[2] the pseudo-capacity traces in 1M-NaCl, NaN_3, and NaBr solutions containing each $1{\cdot}5 \times 10^{-3}$ M-Zn^{2+}, at 1000 c./sec. and 25°, were as shown in Figure 1. By analysing vectorially the components of impedance[3] following the simple equivalent circuit[4,5] the standard rate constant values were as given in Table 1. In

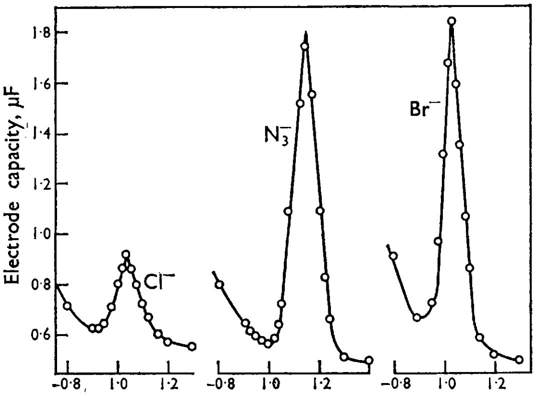

FIGURE 1. *Pseudo-capacity traces.*

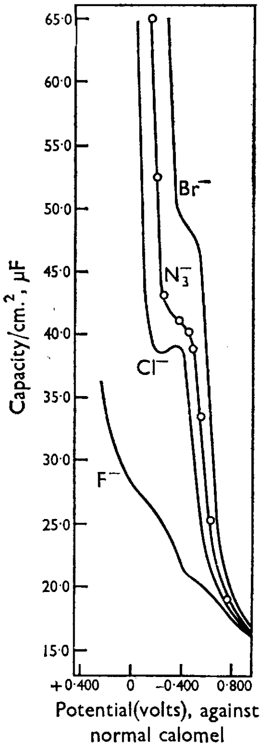

FIGURE 2. *Anodic limb of capacity curves: N_3^- present work; F^-, Cl^-, Br^-, Graham's values.*

TABLE 1

	C_m	R_m	R_s	C_d	A	$K \times 10^3$
Cl^-	0·93	150	32	0·60	0·0390	3·9
N_3^-	1·80	164	36	0·53	0·0333	7·4
Br^-	1·85	152	32	0·57	0·0347	7·7

C_m is peak capacity (μF), R_m peak resistance (ohms), R_s solution resistance (ohms), C_d pure double layer capacity (μF), A electrode area (cm.²), K standard rate constant (cm./sec.).

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chloride and bromide media our values agree reasonably with those previously reported;[6] recently reported values by Hush and Blackledge,[7] however, are exceptionally higher.

with azide concentration as shown in Table 2. (*c*) Rise of the anodic limb of the differential capacity curve in 0·1N-azide solution compared with that observed in halide solutions (Figure 2).

TABLE 2

Molarity ..	0·1	0·5	0·7	1·0	1·3	2·0
γ_{max} (dyne/cm., 25°)..	421·7	420·5	418·8	418·0	417·0	416·5

As suggested for halide ions and irrespective of mechanism,[8] reactivity of azide ion seems also to be consistent with specific adsorption of the ion on mercury, which is preliminarily indicated by: (*a*) Potential of the electrocapillary maximum of mercury, which in 0·1N-sodium azide solution amounts at 25° to $-0{\cdot}540$v with respect to a normal calomel electrode, as compared with $-0{\cdot}506$v and $-0{\cdot}574$v in chloride and bromide solutions respectively.[9] (*b*) Variation of the maximum interfacial tension of mercury γ_{max}

Hydrazoic acid is a weak acid ($k_a = 2{\cdot}8 \times 10^{-5}$) and its salts would be expected to hydrolyse partially. The pH value of a 0·1N-sodium azide solution is approximately 8·2, which is almost the same as that of a 0·1N-sodium fluoride solution. While in sodium fluoride solution specific adsorption of the prevailing hydroxyl ions could possibly account for the rise of capacity limb,[10] in sodium azide this is rather unlikely, and specific adsorption of azide ion would be the primary cause.

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