# Short Communication

## Formal Potentials of Importance for Iodometry in 3 M NaCl and 4 M HBr Media

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New methods for iodine analysis, involving the coulometric formation of $IBr_2^-$ and $HgICl_3^{2-}$, have been described in Refs. 1 and 2.

In order to optimize our experimental conditions we constructed redox diagrams of different types in the ionic media 3 M NaCl and 4M HBr.

The reliable calculation of these diagrams required the evaluation of several formal (standard) potentials ($E^{0\prime}$) in the actual media.

The formal redox potentials and the corresponding equilibrium constants, $K$, which were determined, are collected in Tables 1 and 2.

We have assumed that each of the reacting species occurs entirely in the form written in Tables 1 and 2. The uncertainty thus arising was one of the reasons to not provide lg $K$ values more accurately than 0.1 units.

The reference states have been chosen so that the activity coefficients tend to unity as the composition of the test solutions, TS, approaches 4 M HBr and 3 M NaCl, respectively. Hence our two $pE$ scales are different.

To convert the data to a common scale, it is required to estimate the trace activity coefficient of $H^+$, and of the other reacting species, and the mean activity coefficient of 4 M HBr.

The emf measurements were carried out with the equipment and the reagents that were used in the iodine analyses.[1,2]

The reversible emf data are presented in Tables 1 and 2. They may be regarded as correct first estimates of the standard potentials but with wide limits of uncertainty (typically 5 mV).

Each $E^{0\prime}$, determination started with a calibration step. The glass electrode, or the external reference half-cell, was compared with the hydrogen electrode using the cell arrangements shown in Tables 1 and 2.

*Table 1.* Survey of formal redox potentials in 4M HBr medium at 25 °C.

Calibration step: $H_2$ (1atm) | Pt(Platinized) | 4 M HBr | Glass electrode +
Measuring cell: Glass electrode | TS | Ir +.

| Cell reaction, No. | lg $K$, | $E^{0\prime}$ V, | $E^{0\prime}$ V, (est.[a]) | Comments |
|---|---|---|---|---|
| $Br_3^-+H_2(1\ atm) \rightleftharpoons 3\ Br^-(4\ M)$ $+2\ H^+$ (4 M), (1) | 33.0 | 0.976 | 0.99 | Coulometric oxidation of bromide. $[Br_3^-]$=0.02–0.5 mM |
| $I_2Br^-+H_2(1\ atm) \rightleftharpoons 2I^-+Br^-(4\ M)$ $+2H^+$(4 M), (2) | 17.4 | 0.514 | 0.52 | Potentiometric titration |
| $2\ IBr_2^-+H_2(1\ atm) \rightleftharpoons I_2Br^-$ $+3\ Br^-(4\ M)+2H^+$(4 M), (3) | 26.2 | 0.776 | 0.75 | Coulometric oxidation and potentiometric titration |
| $IBr_2^-+H_2(1\ atm) \rightleftharpoons I^-+2\ Br^-(4\ M)$ $+2H^+$(4 M), (4) | 21.8 | 0.645 | 0.64 | Dilution of an iodine solution |

[a] See text and Tables 3 and 4.

*Table 2.* Survey of formal redox potentials in 3 M NaCl medium at 25 °C.

Calibration step:
$H_2$ (1 atm) | Pt(Platinized) (and glass electrode) | TS | RE+ TS: 3 M $Cl^-$, (3 M–$h$) $Na^+$, $h=[H^+]$ ($h=1.7$–7.7 mM)
RE= ⫶ 3M NaCl ⫶ 3 M NaCl saturated with AgCl ($s$) | AgCl($s$) | Ag
The calibration was made with coulometric alkalification of the test solution.
Measuring cell: RE | TS | Ir+(and glass electrode)

| Cell reaction, No. | lg $K$, | $E^{0\prime}$ V | $E^{0\prime}$ V, (est.[a]) | Comments |
|---|---|---|---|---|
| $Cu(II)+\frac{1}{2} H_2(1\ atm)\rightleftharpoons Cu(I)+H^+$, (5) | $8._64$ | $0.51_1$ | —, | Coulometric reduction [Cu(I)]=0.3–1.3 mM, [Cu(II)]=66.7–65.7 mM |
| $2\ ICl_2^-+H_2$ (1 atm)$\rightleftharpoons I_2Cl^-+3\ Cl^-$ (3 M)$+2\ H^+$, (6) | $32._8$ | $0.97_1$ | 0.97 | Potentiometric titration |
| $I_2Cl^-+2\ HgCl_4^{2-}+H_2$ (1 atm)$\rightleftharpoons 2\ HgICl_3^{2-}+3\ Cl^-(3\ M)+2\ H^+$, (7) | $28._9$ | $0.85_4$ | 0.88 | Potentiometric titration |
| $ICl_2^-+HgCl_4^{2-}+H_2$ (1 atm)$\rightleftharpoons HgICl_3^{2-}+3\ Cl^-(3M)+2\ H^+$, (8) | $30._8$ | $0.91_1$ | 0.93 | Dilution of an iodine solution |

[a] See text and Tables 3 and 4.

*Table 3.* Data needed to estimate the equilibrium constants of Table 1 and 2. The superscript zero denotes a value valid at low ionic strengths.

| Reaction | | lg $K^0$ | Ref. |
|---|---|---|---|
| $I_2(s)\rightleftharpoons I_2$ $(aq)$ | (9) | –2.9 | 4–6 (S.C.) |
| $\frac{1}{2}\ I_2(s)+e\rightleftharpoons I^-$ | (10) | 9.05 | 3 (Latimer) |
| $\frac{1}{2}\ Br_2(aq)+e\rightleftharpoons Br^-$ | (11) | 18.35 | 3 |
| $Br_2(aq)+Br^-\rightleftharpoons Br_3^-$ | (12) | 1.2 | 4–6 |
| $I_2(aq)+Br^-\rightleftharpoons I_2Br^-$ | (13) | 1.1 | 4–6 |
| $I_2(aq)+I^-\rightleftharpoons I_3^-$ | (14) | 2.9 | 4–6 |
| $IBr_2^-+e\rightleftharpoons\frac{1}{2}\ I_2(s)+2\ Br^-$ | (15) | 14.7 | 3 |
| $ICl_2^-+e\rightleftharpoons\frac{1}{2}\ I_2(s)+2Cl^-$ | (16) | 17.8 | 3 |
| $I_2(s)+Cl^-\rightleftharpoons I_2Cl^-$ | (17) | –2.69 | 17 |
| lg $K$ (3M NaCl) | | –3.05 | 17 |
| $I_2(s)+I^-\rightleftharpoons I_3^-$ 1 g $K$ (3M $Na^+$ ($ClO_4^-$, $I^-$)) | (18) | –0.3 | Present work |
| $HgCl_4^{2-}+nI^-\rightleftharpoons HgI_nCl_{4-n}^{2-}+n\ Cl^-$ lg $K_n$ (3M) | (19) | 4.3 $n=1$ | Present work |
| | | 8.2 $n=2$ | |
| | | 11.7 $n=3$ | |
| | | 14.8 $n=4$ | |

After the calibration step, the platinum electrode was removed from the vessel and the hydrogen gas was expelled overnight by nitrogen or argon. The redox potential measurements were then undertaken with an iridium electrode. This technique was used throughout.

Tribromide ions (reaction 1), $IBr_2^-$ (3) and Cu(I) (5), were generated by coulometry with

iridium electrodes.

Equilibria involving I(+I) and I(–I), (4) and (8), could conveniently be studied by preparing an iodine solution and diluting it stepwise with the ionic medium. The remaining reactions were investigated by potentiometric titrations of iodine with $I^-$ or $ICl_2^-$.

The validity of our assumptions concerning equilibrium concentrations and of our experimental approach in general, may be tested by the thermodynamic criteria:

$$2\ E^{0\prime}(4)=1.29=E^{0\prime}(2)+E^{0\prime}(3)=0.51+0.78\ V$$

$$2E^{0\prime}(8)=1.82=E^{0\prime}(6)+E^{0\prime}(7)=0.97+0.85\ V$$

*Comparison with previous results.* Many equilibrium constants and standard potentials involving iodine and bromine are available in dilute aqueous solutions. These may be combined to estimate the equilibrium constants of Tables 1 and 2. Most of the information required is easily available in Latimer's treatise,[3] and in the volumes of Stability Constants.[4,5,6]

The data needed for our purpose are gathered in Table 3.

The triiodide formation constant at 3 M $[Na^+]$ level, represents our preliminary result. The mixed formation constants ($K_n$ of (19)) were estimated by using Sillén's,[7] Arnek's[8] and Ciavatta's[9] results concerning tetrachloro and tetraiodo complexes at different ionic strengths. We introduced the hypothesis that the medium

effect on $\beta(HgCl_4^{2-})$ equals that of $\beta(HgI_4^{2-})$, *i.e.* that the activity coefficient quotient

$$y^4(I^-)\times y(HgCl_4^{2-})/[y^4(Cl^-)\times y(HgI_4^{2-})]$$

remains uninfluenced by the medium.

Further, we assumed according to Spiro and Hume[10] (*cf.* also Ref. 11), that the equilibrium constants for the formation of mixed complexes can be calculated assuming a statistical distribution of the ligands.

Hence,

$$\lg\ K_n=n/4\times(\lg\ \beta(HgI_4^{2-}) - \lg\ \beta(HgCl_4^{2-}))$$

$$+\lg 4! - \lg ((4-n)!n!) \tag{i}$$

Spiro and Hume showed that this hypothesis explained both their own spectroscopic and Marcus'[12] distribution data.

The chemical significance of our $\lg K_n$ calculation is visualized in Fig. 1 . It is clear from this figure, that at the low $[I^-]/[Cl^-]$ ratios chosen for analysis, it is permissible to set $[I^-]_{tot}$ equal to $[HgICl_3^{2-}]$ as was done in Table 2.

The activity coefficient data and the estimates necessary to calculate the constants of Tables 1 and 2 from those of Table 3 are summarized in Table 4.

The medium effect estimates were carried out by employing the specific interaction theory essentially in the form developed by Scatchard.[13–15]

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*Table 4.* Activity coefficient data and estimates needed to calculate the $E^{0\prime}$ values of Tables 1 and 2. $y^0$ denotes the activity coefficient of an electrolyte in its own solution in volume concentration terms.

| | | |
|---|---|---|
| (1) | 4M (4.5m) hydrogen bromide medium | |
| | $y^0(4M\ HBr)=3.39$ | (Ref. 18) |
| | $y^0(4M\ HI)=4.31$ | (Ref. 18) |
| | postulates: | |
| | $y(I_2Br^-)=y(Br^-)$ | |
| | $y(IBr_2^-)=y(Br^-)$ | |
| | $y(Br_3^-)=y(Br^-)$ | |
| | (these postulates are not likely to be far from the truth as the | |
| | salting out by HBr is small [a]) | |
| | | |
| (2) | 3M (3.2m) sodium chloride medium | |
| | $y^0(3M\ NaCl)=0.77$ | (Ref. 19) |
| | $y^0(3M\ HCl)=1.48$ | (Ref. 19) |
| | $y(I_2Cl^-)/y(Cl^-)=2.31$ | (Ref. 17) |
| | postulates: | |
| | $y(I_2Cl^-)=y(ICl_2^-)$ | |
| | $y(HgICl_3^{2-})=y(HgCl_4^{2-})$ | |

[a] The salting out by HBr is generally small as it may be estimated by considering solubility data for nonpolar gases and approximating its Setschenow parameter $k_{HBr}$ with $k_{HBr}=k_{HCl}+k_{MeBr}-k_{MeCl}$.[13,20]
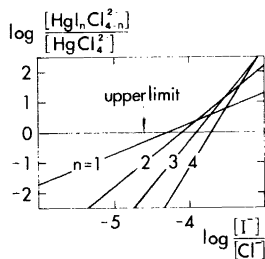
*Fig. 1.* Concentration ratio diagram for the formation of mixed iodide- and chloride-bearing mercury complex species in 3 M $Na^+$ ($Cl^-$, $I^-$) medium. The lines have been calculated with equation (i) using the formation constant data discussed in the text. The arrow indicates the maximum $[I^-]/[Cl^-]$ ratio reached in the titrations.

The activity coefficients reported in the literature have been recalculated to the volume molarity scale by using density data recommended by the Gmelins Handbook of Inorganic Chemistry.[16]

Comparison of $E^{0'}$ and $E^{0'}$(estimated) in Tables 1 and 2, demonstrates that the deviation between the values hardly exceeds the experimental uncertainty. As the distributions of copper(I) and copper(II) ions over different complexes are not known with certainty, we have not been able to estimate lg $K$ (5).

The triiodide formation constants (reactions 14 and 18), also included in Table 3, are needed for the estimates of the $[I_3^-]$ in the redox diagrams shown in Refs. 1 and 2.

In the light of the close agreement generally obtained, we may have little doubt that our experiments may be regarded to be consistent with the numerous results of the classical investigators.

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