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Some Aspects of the Constant Ionic Medium Principle. Studies on the Iron(III) Fluoride and Tris(propylenediamine)cobalt(III) Iodide Systems

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When a significant part of a monovalent ion of an inert medium is replaced by a polyvalent ion, either the total of ionic equivalents or the formal ionic strength can be kept constant. Determinations of the first stability constant of the $Fe^{3+}-HF$ and $Co\,pn_3^{3+}-I^-$ systems clearly indicate that a constant concentration of equivalents is the better choice. When the ionic strength was constant, the stability constant was dependent on the total metal ion concentration. This can be shown to be due to activity coefficient changes and, on the cobalt-ammine system, also to perchlorate association.

When equilibria are studied in electrolytic solutions, a constant ionic medium is commonly employed with the aim of keeping activity coefficients constant. Activity coefficients are generally found to be effectively independent of the concentrations of the reacting species, as long as these concentrations are low compared to that of the inert electrolyte. On the other hand, if a significant part of one of the medium ions is replaced with some other ion *of the same charge*, it is common experience [1–10] that the activity coefficients change. The studies by Biedermann and Sillén [3] on the effects of exchanging Na^+ by H^+ and by Ginstrup [5] who varied the anion (ClO_4^-, Cl^-, Br^-) as well as the cation (H^+, Na^+) are important in this respect. Occasionally, the activity coefficient variation is quite small, as when H^+ is substituted for Li^+ (Ref. 1) or when I^- is substituted for ClO_4^- (see discussion in Ref. 9).

When a significant amount of the medium is replaced with an ion *of different charge* the question arises of how the concept "constant ionic medium" should be defined. Several workers, including the present author, have successfully used a constant *total concentration of ionic equivalents*:

$$I_{\mathrm{I}} = \tfrac{1}{2}\sum_i c_i|z_i| \qquad (1)$$

c_i and z_i being the concentrations and charges of the ions. Often, however, a constant *formal ionic strength* is preferred:

$$I_{\mathrm{II}} = \tfrac{1}{2}\sum_i c_i z_i^2 \qquad (2)$$

I_{I} and I_{II} differ only when polyvalent ions are present in significant amounts. There is no theoretical ground for the use of the one principle or the other, except at very low concentrations ($I_{\mathrm{II}} \ll 0.1$ M), where activity coefficients should depend on I_{II} only.[11] It is the aim of the present investigation to compare the two principles expressed by eqns. (1) and (2). On two model systems, β_1 for the 1:1 complex has been determined for various total concentrations of the (polyvalent) metal ion. Two series of experiment have been run for each system, one with I_{I} constant, the other with I_{II} constant.

As this question was raised in connexion with studies of outer-sphere cobaltamine halide complexes,[9,12–14] it has been natural to choose one such system for these experiments, namely the tris(propylenediamine)cobalt(III) iodide system.[14] However, the cobaltammine systems are almost certainly complicated by perchlorate complexation,[15] a fact which, as shown below, tends to obscure the present issue. As discussed before,[15] the perchlorate ion is associated to Fe^{3+} to a much smaller degree, if at all. Therefore, the iron(III) fluoride system has been chosen as another model system. Under the conditions chosen, perchlorate association should, in this system, have no influence on the measurements.

Since the concentration of the trivalent ion should be varied as much as possible, some method of ligand measurement has been the natural choice. In the iron(III) fluoride solutions, $[F^-]$ has been measured with a fluoride ion sensitive electrode. The $Copn_3^{3+}-I^-$ system has been studied with the aid of a I^-, I_3^-/Pt electrode, employed previously.[14]

As shown,[14] the measured quantity – an emf difference – is roughly independent of the ligand concentration. The latter can thus be kept low enough to avoid the formation of higher complexes, without any adverse effects on the precision of the measurements. A low ligand concentration has the further advantage that the complex formation does not affect the composition of the medium.

It was felt desirable to perform the measurements over a range of I_I (and I_{II}) values. For the iron system, a lower limit is set by the necessity to suppress the hydrolysis of Fe^{3+}, by keeping the acidity high. The medium concentrations 1 M and 0.5 (acidities 0.4 M and 0.2 M), respectively, were chosen for this system. The ligand is then present mainly as HF. The cobaltammine iodide system was studied at $I_I(I_{II})=0.60$, 0.30, and 0.15 M, in addition to 1.0 M as already reported (I_I only [14]). All measurements have been performed at 25 °C.

EXPERIMENTAL

Chemicals. Analytical grade chemicals were used. Details of the preparation of $Co\,pn_3(ClO_4)_3$ have been given before.[14]

Measurements. For the $Fe^{3+}-HF$ system, the element was constituted as follows

RE	C_H $HClO_4$ $NaClO_4$	C_L HF C_M $Fe(ClO_4)_3$ C_H $HClO_4$ $NaClO_4$	FME	(3)

Ag – AgCl electrodes were used as reference electrodes. $NaClO_4$ was added to give $I_I(I_{II})=0.5$ or 1.0 M throughout the element. When $I_I(I_{II})=0.5$ M, $C_L=0.500\times10^{-3}$ M and 1.000×10^{-3} M, $0\leq C_M\leq0.0500$ M, $C_H=0.2000$ M; when $I_I(I_{II})=1.0$ M, $C_L=0.500\times10^{-3}$ M and 1.000×10^{-3} M, $0\leq C_M\leq0.1000$ M, $C_H=0.400$ M. In the bulk of the experiments, C_M was successively increased in the test solution by titration, all other total concentrations being kept constant. All experiments were repeated at least twice. All acid fluoride solutions were handled and stored using plastic equipment only.

The fluoride membrane electrode (Orion Research Inc.) was shown to conform to Nernst's equation under the prevailing conditions. Stable potentials were normally reached within 10 min. The reproducibility (between titrations) was within 0.5 mV.

For the cobaltammine study, the following element was used

RE	$NaClO_4$	C_L NaI C_T NaI_3 C_M $Co\,pn_3(ClO_4)_3$ $NaClO_4$	Pt	(4)

The measurements have been described in detail earlier.[14] Titrations as well as batch measurements were performed. C_M ranged from 0 to 0.1 M, C_L from 0.01 to 0.1 M. C_T was ca. 2×10^{-3} M in all experiments. Emf's could normally be reproduced within 0.1 mV.

Elements were thermostated to 25 °C. All emf's were measured by a Radiometer PHM 52 potentiometer.

CALCULATIONS, RESULTS

Iron(III) fluoride system

Since F^- is protolyzed to HF in these acidic solutions, the reaction under study is

$$Fe^{3+}+HF\rightleftharpoons FeF^{2+}+H^+ \tag{5}$$

with the stability constant

$$*\beta_1=[MF]h/[M][HF] \tag{6}$$

where h is the free hydrogen ion concentration. Below, small correction terms are introduced to account for the formation of F^-

$$K_F=h[F^-]/[HF] \tag{7}$$

and of $FeOH^{2+}$

$$K_{OH}=[MOH]h/[M] \tag{8}$$

The values [16,17] $K_F=1.11\times10^{-3}$ M ($I=1$ M) and 1.24×10^{-3} ($I=0.5$ M) and $K_{OH}=1.6\times10^{-3}$ M (both ionic strengths [17]) have been used.

The emf of element (3) may be written

$$E = E^\circ - k \log [\mathrm{F}^-] \qquad (9)$$

where E° is constant if activity coefficients and liquid junction potentials are constant, and $k = RTF^{-1} \ln 10$. The difference in emf between a solution with $C_{\mathrm{M}} > 0$ and one with $C_{\mathrm{M}} = 0$ (subscript "0") is then

$$E_{\mathrm{L}} = E - E_0 = k \log[\mathrm{F}^-]_0/[\mathrm{F}^-] \qquad (10)$$

Further

$$C_{\mathrm{L}} = [\mathrm{HF}] + [\mathrm{F}^-] + [\mathrm{MF}] = [\mathrm{HF}]_0 + [\mathrm{F}^-]_0 \qquad (11)$$

$$C_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{MF}] + [\mathrm{MOH}] \qquad (12)$$

$$h = C_{\mathrm{H}} + [\mathrm{MF}] + [\mathrm{F}^-] + [\mathrm{MOH}] \qquad (13)$$

Taking eqn. (11) into account, eqn. (13) may be written

$$h = C_{\mathrm{H}} + C_{\mathrm{L}} - [\mathrm{HF}] + [\mathrm{MOH}] \qquad (14)$$

For the calculation of h, the approximations

$$[\mathrm{HF}] \approx C_{\mathrm{L}}([\mathrm{F}^-]/[\mathrm{F}^-]_0) \qquad (15)$$

and

$$[\mathrm{MOH}] \approx C_{\mathrm{M}} K_{\mathrm{OH}} C_{\mathrm{H}}^{-1} \qquad (16)$$

are completely satisfactory. $([\mathrm{F}]/[\mathrm{F}]_0)$ is obtained from eqn. (10). When $C_{\mathrm{M}} = 0$, $h_0 = C_{\mathrm{H}}$, effectively. To calculate $^*\beta_1$ [eqn. (6)] we further need accurate values of [HF] and of ([HF)] + [F]). The latter quantity may then be subtracted from C_{L} [eqn. (11)] to yield [MF], which in turn may be substratected from C_{M} [eqn. (12)] to yield ([M] + [MOH]).

Eqns. (7) and (11), combined, give

$$([\mathrm{HF}] + [\mathrm{F}^-]) = \frac{C_{\mathrm{L}}\,(K_{\mathrm{F}} + h)}{([\mathrm{F}^-]_0/[\mathrm{F}^-])(K_{\mathrm{F}} + h_0)}$$

However, the error introduced by omitting the K_{F}'s is completely negligible:

$$([\mathrm{HF}] + [\mathrm{F}^-]) = \frac{C_{\mathrm{L}} h}{([\mathrm{F}^-]_0/[\mathrm{F}^-]) h_0} \qquad (17)$$

Further

$$[\mathrm{HF}] = ([\mathrm{HF}] + [\mathrm{F}^-]) h/(K_{\mathrm{F}} + h) \qquad (18)$$

Table 1. Experimental data on the *iron(III) fluoride system*. Series I: constant I_{I}; series II: constant I_{II}. I1 and II1: $C_{\mathrm{L}} = 1.000 \times 10^{-3}$ M; I2 and II2: $C_{\mathrm{L}} = 0.500 \times 10^{-3}$ M.

	Series I1		Series I2		Series II1		Series II2	
$C_{\mathrm{M}} \times 10^2$/M	E_{L}/mV	$^*\beta_1$	E_{L}/mV	$^*\beta_1$	E_{L}/mV	$^*\beta_1$	E_{L}/mV	$^*\beta_1$
$I = 0.5$ M								
6.18	45.0	180.3	46.4	178.9	45.2	182.0	46.7	181.5
10.86	58.9	181.1	59.5	177.9	59.1	182.7	60.2	183.4
14.55	66.1	180.1	66.5	177.2	66.6	183.9	67.6	185.6
19.83	73.9	179.8	74.0	176.2	74.7	185.9	76.5	188.2
23.57	78.2	179.1	78.3	176.2	79.3	187.4	80.1	189.6
26.34	81.1	179.7	81.1	176.4	82.3	188.7	83.1	191.3
28.5	83.0	178.9	83.1	176.5	84.4	189.3	85.5	194.5
31.6	85.6	178.6	85.7	176.6	87.2	190.5	88.0	193.7
45.3	94.7	177.9	94.7	176.0	97.1	195.8	98.0	200.7
$I = 1.0$ M								
12.35	43.4	154.1	43.6	150.3	43.2	152.2	44.1	153.9
21.73	56.4	154.2	56.6	152.3	56.1	152.2	56.8	153.3
29.1	63.4	154.5	63.7	153.7	63.2	153.2	63.6	153.4
39.7	71.0	154.0	71.1	153.1	70.8	153.3	71.1	153.1
47.1	75.2	154.1	75.0	151.3	75.2	154.1	75.4	153.6
52.6	78.0	154.2	77.9	152.5	78.0	154.5	78.0	153.4
57.0	79.9	153.9	78.9	152.0	80.0	154.8	80.0	152.9
63.1	82.4	153.9	81.9	149.4	82.6	154.6	82.6	153.4
90.6	91.5	153.7			91.3	153.0		

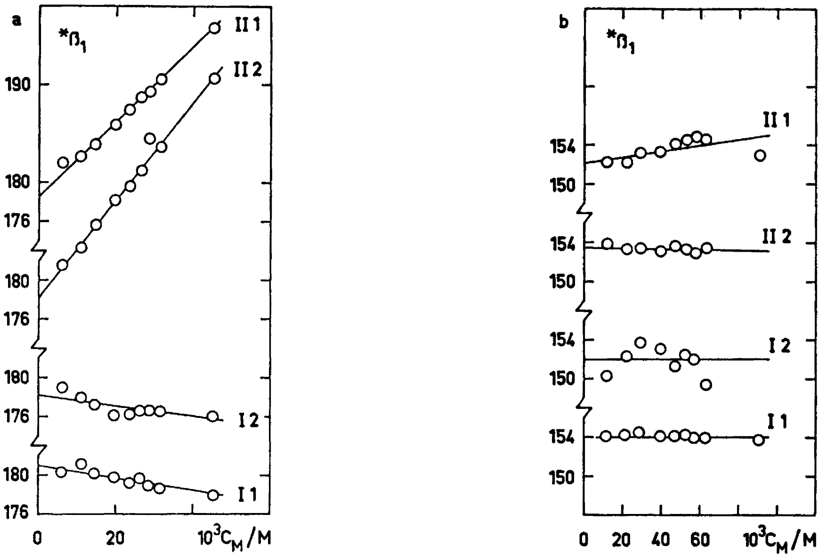

Fig. 1. Iron(III) fluoride system. $*\beta_1$ *vs.* C_M in 0.5 M (*a*) and 1.0 M medium (*b*). The series are labelled as in Table 1. For clarity the curves are successively displaced 10 units vertically, as indicated on the ordinate axes. Straight lines are drawn only to emphasize the trends.

Finally,

$$*\beta_1 = \frac{(C_L - ([HF]+[F^-]))h(1+K_{OH}\,h^{-1})}{(C_M - C_L + ([HF]+[F]))\,[HF]} \qquad (19)$$

These calculations were performed using a programmable desk calculator.

The experimental data are given in Table 1. In Fig. 1, $*\beta_1$ is plotted *vs.* C_M for the various I_I, I_{II}, and C_L.

It should be mentioned that although each experiment was run at least twice, only the mean values are given here, for brevity and clarity. As a consequence, most of the *slopes* of the plots in Fig. 1 appear to be accurate to within $1-2$ units of $*\beta_1$ over the range of C_M. However, between single titrations (of the same experiment) the slopes normally differed $3-4$ units of $*\beta_1$. Therefore, the only difference in Fig. 1 that can be considered significant is that between the $I_{II}=0.5$ experiments, with a positive slope of ca. 20 units, on the hand, and, on the other, all other experiments, which have practically zero slope.

Tris(propylenediamine) cobalt-(III) iodide system

Since the calculations have been described in detail before,[14] only the working equations will be given here. For the emf difference

$$E_L = 1.5k \log \delta C_L/[L] \qquad (20)$$

where δ is a correction for the slight dissociation of I_3^-:

$$\delta = \left(\frac{1-(K_{tri}[L])^{-1}}{1-(K_{tri}\,C_L)^{-1}}\right)^{\frac{1}{3}} \qquad (21)$$

Inspection of the literature [17,18] shows that K_{tri} does not vary much between $I=0$ and $I=1$. In the present context it is satisfactory to use $K_{tri}=725$ M^{-1}. Then

$$\bar{n}/[L] = (C_L/[L]-1)/C_M \qquad (22)$$

Normally, $\boldsymbol{\beta}_1$ is obtained from $\bar{n}/[L]$ by extrapolation [the bold-faced symbol is used to distinguish this observed constant from the "true" β_1; *cf.* eqn. (25) below]

$$\lim_{[L]\to 0} \bar{n}/[L] = \boldsymbol{\beta}_1 \qquad (23)$$

Table 2. Experimental data on the *Co* $pn_3^{3+}-I^-$ *system*. Series 1: $C_L = 28\times10^{-3}$ M ($I = 0.15$ M and 0.30 M), $C_L = 50\times10^{-3}$ M ($I = 0.60$ M); series 2: $C_L = 13\times10^{-3}$ M ($I = 0.15$ M and 0.30 M), $C_L = 25\times10^{-3}$ M ($I = 0.60$ M). The values of $\boldsymbol{\beta}_1$ in the last column are extrapolated values ($I = 0.15$ M and 0.30 M) or averages ($I = 0.60$ M), respectively.

	Series 1		Series 2		$\boldsymbol{\beta}_1$
$C_M\times10^3$ M	E_L mV	$\boldsymbol{\beta}_1$ M^{-1}	E_L mV	$\boldsymbol{\beta}_1$ M^{-1}	$(C_L=0)$ M^{-1}
$I_I = 0.15$ M					
2.50	0.69	9.22	0.70	8.52	7.99
4.71	1.28	9.10	1.31	8.45	7.97
10.00	2.71	9.20	2.74	8.49	7.96
16.00	4.33	9.34	4.38	8.63	8.10
20.00	5.48	9.61	5.49	8.80	8.21
25.00	6.90	9.85	6.89	9.00	8.37
$I_{II} = 0.15$ M					
6.00	1.15	5.97	1.03	4.97	4.34
10.00	2.05	6.53	1.83	5.39	4.68
15.00	3.35	7.33	3.05	6.15	5.55
20.00	5.05	8.65	4.60	7.17	6.23
$I_I = 0.30$ M					
5.00	0.75	4.49	0.77	4.44	4.40
9.41	1.40	4.49	1.47	4.55	4.60
20.00	2.95	4.53	3.09	4.59	4.65
32.0	4.80	4.72	4.85	4.61	4.52
40.0	5.90	4.69	6.00	4.64	4.58
50.0	7.45	4.84	7.50	4.73	4.64
$I_{II} = 0.30$ M					
12.00	1.28	3.11	1.20	2.84	2.64
20.00	2.27	3.36	2.20	3.19	3.06
30.0	3.81	3.88	3.80	3.77	3.68
40.0	5.83	4.63	5.90	4.55	4.48
$I_I = 0.60$ M					
40.0	3.40	2.61	3.45	2.53	2.57
80.0	6.75	2.69	6.70	2.57	2.63
$I_{II} = 0.60$ M					
40.0	2.35	1.72	2.80	2.01	1.87
80.0	6.20	2.43	6.85	2.62	2.52

which eliminates the influence of higher complexes. Since these should be negligible under the present conditions, $\boldsymbol{\beta}_1$ has instead been calculated directly for each data point

$$\boldsymbol{\beta}_1 = 1/([\mathrm{L}]/\bar{n} - [\mathrm{L}]) \tag{24}$$

The results are given in Table 2; Fig. 2 shows $\boldsymbol{\beta}_1$ plotted *vs.* C_M. The values of $\boldsymbol{\beta}_1$ in Fig. 2 are those obtained by extrapolation to $C_L = 0$ according to eqns. (27) or (30) below. When $I = 0.60$ M (and 1.00 M), an extrapolation was not meaningful, since the values for different C_L were equal within the limits of error. Averages have been plotted instead.

Effects of perchlorate association. Since the stability constant has been computed in the same way, in principle, for both systems, the following is valid for the iron system as well.

If ClO_4^- (denoted A) forms a complex MA, stability constant γ_1, it can be readily shown that the apparent $\boldsymbol{\beta}_1$, as computed here, is related to the "true" β_1 by the relation (*cf.* Refs. 12, 15)

$$\boldsymbol{\beta}_1 = \beta_1/(1+\gamma_1[\mathrm{A}]) \tag{25}$$

provided, of course, that activity coefficients are constant. When I_I is constant, we have, as a satisfactory approximation

$$[\mathrm{A}] = I_I - C_L \tag{26}$$

i.e.

$$\boldsymbol{\beta}_1 = \frac{\beta_1}{1+\gamma_1(I_I - C_L)} \quad (I_I \text{ constant}) \tag{27}$$

or, after extrapolation to $C_L = 0$

$$\boldsymbol{\beta}_1 = \beta_1/(1+\gamma_1 I_I) \tag{28}$$

When I_{II} is constant

$$[\mathrm{A}] = I_{II} - C_L - 3C_M \tag{29}$$

hence

$$\boldsymbol{\beta}_1 = \frac{\beta_1}{1+\gamma_1(I_{II} - C_L - 3C_M)} \quad (I_{II} \text{ constant}) \tag{30}$$

or, after extrapolation

$$\boldsymbol{\beta}_1 = \frac{\beta_1}{1+\gamma_1(I_{II} - 3C_M)} \tag{31}$$

Eqn. (31) shows, thus, that when perchlorate association occurs to a significant degree, $\boldsymbol{\beta}_1$ would depend on C_M, even if activity coefficients were constant, when the formal ionic strength I_{II} is held constant.

Combined effect of perchlorate association and activity coefficient changes. In reality, of course,

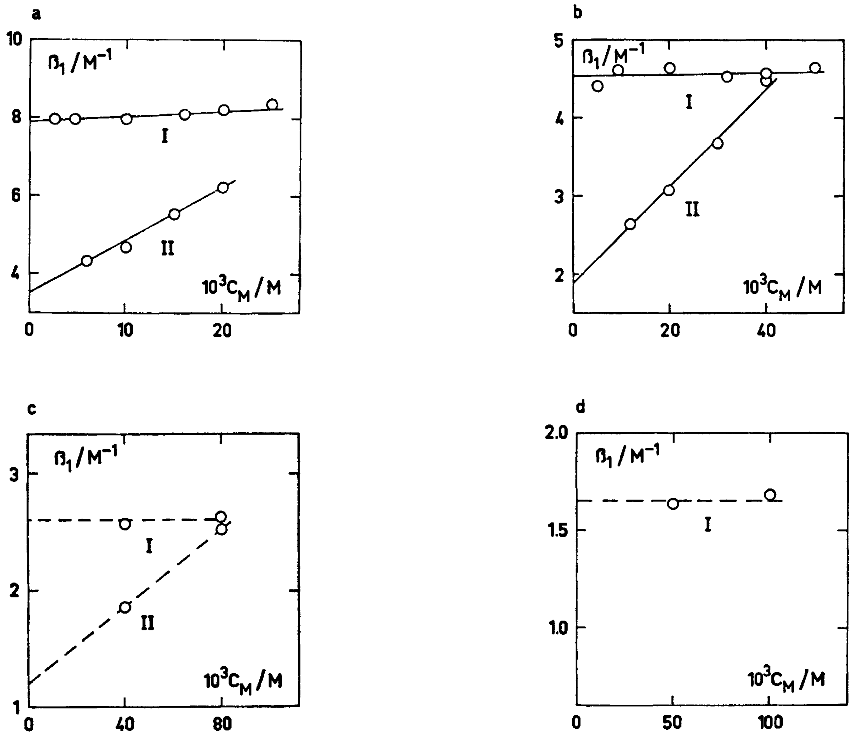

Fig. 2. Co pn$_3^{3+}$ – I$^-$ system. β_1 ($C_L = 0$) *vs.* C_M in the media 0.15 M (*a*), 0.30 M (*b*), 0.60 M (*c*) and 1.00 M (*d*; data taken from Ref. 14).

both these factors should affect the results when I_{II} is constant. At first thought one might expect the effects of both factors to disappear for small C_M, thus giving, on extrapolation to $C_M = 0$, the same value of β_1 as when I_I is constant [*cf.* eqns. (28) and (31)]. However, a closer look reveals that if both factors affect this system one should expect β_1 to start at values *lower* than those obtained at constant I_I, and then increase with increasing C_M. This is exactly what is observed, Fig. 2.

DISCUSSION

In order to explain the variation of the stability constant with C_M in some of the present experiments, a number of factors may be discussed:

1. The formation of higher complexes.
2. Liquid junction potential changes.
3. Perchlorate association.
4. Activity coefficient changes.

As already mentioned, the possibility of keeping C_L low decreases the interference from higher complexes. Estimates based on known [14,17] stabilities of ML_n, $n \geq 2$, show that these can be safely neglected in the ranges of C_L and C_M studied, in both systems.

Estimates according to Henderson's equation,[19] however doubtful, indicate liquid junction potential changes to be very small in both systems when I_I is kept constant, in agreement with the experimental results. They may be of some significance when I_{II} is kept constant. However, regarding the iron system (Fig. 1), the fact that $^*\beta_1$ increases rather rapidly when $I_{II} = 0.5$ M, but hardly at all when $I_{II} = 1.0$ M is difficult to explain with liquid junction potential changes.

As regards perchlorate association, the data on the iron system when $I_{II} = 0.5$ M could indeed be explained using the hypothesis: constant activity factors, and perchlorate association. The required perchlorate association would be of a quite reasonable magnitude. However, when $I_I = 0.5$ M, perchlorate association does not cause a change in $^*\beta_1$ with C_M, according to eqn. (27). On the other hand, if the above hypothesis were correct, since I_{II} is *not* constant when I_I is, activity coefficients – and hence also $^*\beta_1$ – should be expected to vary with C_M. Since no variation is observed, the data when $I_I = 0.5$ M do not support the hypothesis. Moreover, the stability constant of the perchlorate complex is expected to follow the general trend, *i.e.* it should be slightly, but not dramatically, smaller when $I_{II} = 1$ M. Thus, a significant increase of $^*\beta_1$ with increasing C_M should be expected also when $I_{II} = 1$ M. The near constancy observed is strong evidence against perchlorate association as a major factor contributing to the trends found on the iron(III) fluoride system. In fact, from the data when $I_{II} = 1$ M, an upper limit of about 0.1 M^{-1} can be estimated for the stability constant of $FeClO_4^{2+}$.

In this connexion, reference may be made to the study by Olson and Simonson [15,20] on the hydrolysis of iron(III). They found that when Na^+ of the inert medium was exchanged for Ba^{2+} or La^{3+}, the light absorption by the hydrolyzed species was constant if the exchange was performed keeping the perchlorate concentration constant but changed if a constant ionic strength (I_{II}) was applied. The authors assumed that activity coefficients were constant in the former case but varied in the latter. Sykes,[21] however, interpreted the same results assuming constant activity coefficients when I_{II} was constant, the formation of $FeClO_4^{2+}$ being responsible for the observed spectral change. However, Sykes failed to realize that the constancy of the spectra when $[ClO_4^-]$ was constant is very difficult to rationalize from his assumptions. Thus, the best interpretation of these data seems to be that given by Olson and Simonson.[20] This is of special interest, since the ionic strength was very low, < 0.05 M.

In the present study of the $Fe^{3+} - F^-$ system, it may now be concluded that changing activity coefficients are the main cause of the changes of $^*\beta_1$ observed. It may also be concluded, on the other hand, that the activity coefficients are practically constant when I_I is constant. In Fig. 3 the variation with I_I of $^*\beta_1$, as determined by several workers [17,22] is shown. When I_I is decreased below 0.5 M, $^*\beta_1$ increases rather rapidly. Thus, when $I_{II} = 0.5$ M (Fig. 1), an increase of C_M implies a decrease of I_I, and an increase of $^*\beta_1$ should be expected. The observed increase is even of the right order of magnitude. Around $I_I = 1$ M the situation is quite different: $^*\beta_1$ passes through a very flat minimum (Fig. 3). Even a substantial change in the medium will have little effect on $^*\beta_1$, as observed (Fig. 1).

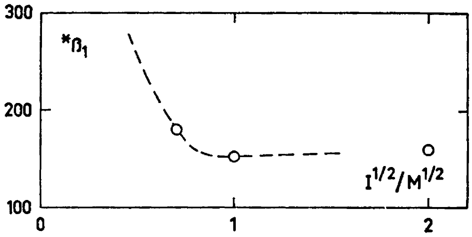

Fig. 3. $^*\beta_1$ for $Fe^{3+} - HF$ *vs.* $I^{\frac{1}{2}}$. Data from the present work and from Refs. 17 and 22. For zero ionic strength, values of $^*\beta_1 \approx 10^3$ are reported.[17]

The trends observed in the series II experiments in the $Co\,pn_3^{3+} - I^-$ system, Fig. 2, can all be rationalized assuming perchlorate association and activity coefficients changes acting together, possibly with some contribution from liquid junction potential changes. It should be noticed, however, that the results cannot be explained by perchlorate association [eqn. (31)] and/or liquid junction potential changes alone. When I_I is constant, β_1 is constant, as expected, except at $I_I = 0.15$ M, where a slight increase occurs. This may be due to a variety of reasons. However, since the trend is more pronounced the higher the value of C_L (Table 2), it probably has its grounds in the slight decrease in the *actual* value of I_I in these solutions caused by the complex formation. The extrapolation according to eqn. (27) performed is probably inadequate in eliminating this trend completely. However, the value of β_1 approached at low C_M should be that valid at $I_I = 0.150$ M.

In conclusion, the present investigation shows quite convincingly that it is not the formal ionic strength I_{II} but rather the total concentration of ionic equivalents I_I that should be held constant. As shown in the cobaltammine system, this is especially important when the medium is not completely inert.

This conclusion is, in a way, a consequence of Brønsted's principle of specific interactions.[23] If the reacting species are predominantly positive [*cf.* eqn. (5)] their activity coefficients depend on the negative part of the medium; the composition of this part should be kept as constant as possible. In the example of the iron(III) fluoride system, $[ClO_4^-]$ should be kept constant. Conversely, with negative reacting species, a constant positive part of the medium is required. However, this is always equivalent to saying that I_I [eqn. (1)] should be constant. That this is true also when species of different charges react is indicated by the results on the Co $pn_3^{3+}-I^-$ system.

Support of this conclusion has been given earlier by Olson and Simonson,[20] as already mentioned, and also, *e.g.*, by Näsänen,[24] who stated that a pentavalent ion had about the same medium effect as five monovalent ions [not 25, as required by eqn. (2)]. Sillén and his coworkers have in fact used a constant medium as defined by eqn. (1) in their numerous studies on hydrolysis and other equilibria.[6,25–28] Leden,[29] studying the silver and cadmium sulfate systems, replaced ClO_4^- with SO_4^- according to eqn. (1) as well as to eqn. (2). The results were significantly different. Although no direct choice could be made from the results, it was inferred from various evidence that the exchange according to eqn. (1) was the better one.

Naturally, medium effects cannot be expected always to be completely eliminated even when I_I is kept constant. As well as when, *e.g.*, ClO_4^- is exchanged with Cl^-,[5] an effect could be expected when Na^+ is replaced by 1/3 M^{3+}, or ClO_4^- by 1/2 SO_4^{2-}, *etc.* This *qualitative* medium effect might be serious only when a substantial part of the medium is exchanged, and when there are reacting species of a charge opposite to that of the exchanging medium ions.

The present study also emphasizes (Fig. 3) the fact that there normally is a region where activity coefficients and hence also equilibrium constants are not very sensitive to the medium concentration (the *quantitative* medium effects are small). Of course it may be an advantage to work in this region. It should be clear, however, that the qualitative medium effects mentioned above are not eliminated in this region.

Finally, some comments will be made on the stability constants observed *per se*. As for $^*\beta_1$ of the $Fe^{3+}-HF$ system, the values 180 ± 2 M^{-1} in 0.5 M medium and 153 ± 2 M^{-1} in 1.0 M medium are in good agreement with earlier determinations.[17] In the Co $pn_3^{3+}-I^-$ system, the observed stability constant β_1 decreases with increasing medium concentration, as expected both from activity coefficient changes and from the perchlorate association, eqn. (28). The constant obtained earlier [14] at $I_I = 1$ M conforms to the same pattern.

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