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The Stability of Metal Halide Complexes in Aqueous Solution

IV. The Fluoride and Chloride Complexes of the Vanadyl Ion, VO^{2+}

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The stability constants of the fluoride and chloride complexes of the vanadyl ion, VO^{2+}, have been determined. As could be predicted from the position of vanadium in the Periodic Table, the fluoride complexes are much stronger than the chloride ones which are very weak. They are also much stronger than the fluoride complexes formed by divalent ions of similar size but higher symmetry. This is due to the increase of effective charge on the metal atom induced by the strongly electronegative oxygen. On the other hand they are perceptibly weaker than the fluoride complexes of the uranyl ion, UO_2^{2+}, where two oxygen atoms co-operate in increasing the charge on the central uranium atom.

Vanadium is one of the few elements outside the actinide series forming well-established "yl"-ions in acid solutions, *i. e.* ions where a central metal atom is linked to one or two oxygen atoms by strong bonds of a pronouncedly covalent character (*cf.* Refs.[1,2] and refs. quoted therein). Vanadium(IV) thus forms the vanadyl ion, VO^{2+}, and vanadium(V) the vanidol[1] ion, VO_2^+. In connexion with the work on metal halide complexes at present in progress in this laboratory, it seemed worth-while to investigate the tendency of these ions towards halide complex formation, in order to compare them in this respect with the actinide "yl"-ions and also with di- and monovalent ions of higher symmetry.

From the general trends found for the formation of halide complexes by central ions of different positions in the Periodic Table [3], it can be predicted that the stability of the complexes of VO^{2+} and VO_2^+ will decrease in the sequence $F^- \gg Cl^- > Br^- > I^-$. Moreover the complexes formed by the three heavier halides are expected to be very weak, and therefore it might only be possible to determine very approximate values of their stability constants. The fluoride systems therefore seemed to present the most profitable task.

As to experimental methods, the obvious one for the system VO^{2+}—F^- was measurement of $[H^+]$ in acid fluoride solutions by means of the quinhydrone electrode, provided that the electrode functions satisfactorily in the presence of VO^{2+}. This method has been used before for the investigation of several fluoride systems, and a full description of the calculation of stability constants from such data is given in the work[4] on the rather similar system of UO_2^{2+}, *cf.* also Ref.[5] As stated there, the conditions might be complicated by the existence of hydroxo[2] and/or polynuclear complexes in solution besides the postulated simple series of mononuclear fluoride complexes of VO^{2+}; complexes containing HF_2^- as ligand are also conceivable. Such complexes will, however, cause the ligand number $\bar{n}_M$ to be a function not only of the free ligand concentration*, [A], but also of $[H^+]$ and/or the free central ion concentration, [M]. By varying $[H^+]$ and [M], which is brought about by varying the total concentrations of acid and central ion, C_H and C_M, it is therefore possible to decide whether such complexes exist or not[4].

As to VO_2^+, its fluoride complexes cannot be investigated by measurements involving the quinhydrone electrode, as quinhydrone is certainly oxidized by vanadium (V).

Once the constants of the fluoride system of VO^{2+} are known, the weaker complexes of the heavier halides can be investigated by the method of ligand displacement[6]. This has been carried out in the case of chloride.

The measurements were performed at 20°C in a medium of ionic strength 1 M, with $NaClO_4$ as the supplementary salt.

EXPERIMENTAL

Chemicals. Vanadium(IV)perchlorate solutions were prepared in a way similar to that described in Ref.[2] Vanadium(IV) was determined by titration with cerium(IV). The titration was carried out both potentiometrically and with ferroin as indicator. Provided the concentration of sulphuric acid in the solution was kept as low as about 0.5 M, the indication with ferroin was acceptable and gave the same result as was found potentiometrically (*cf.* Ref.[7]). The concentration of V(IV) in the stock solution was 471 mM. In the preparation of the perchlorate solution a slight oxidation to V(V) occurred the amount of which was determined in two ways. First it was calculated from the difference of emf measured in the potentiometric titrations between the solution which was half oxidized and the original solution, before any Ce(IV) had been added. Secondly it was determined by titrating a solution which had previously been completely reduced by SO_2 (the excess of which was removed by boiling the solution). Both methods gave the same value of the amount of V(V), ≈ 0.4 % of that of V(IV). This contamination was considered to be of no importance.

In order to avoid hydrolysis the stock solution was prepared with an excess of free perchloric acid (*cf.* Ref.[2]). The concentration of free acid was determined potentiometrically in the way described for uranyl perchlorate[4]. As certain difficulties (discussed below) were encountered when quinhydrone electrodes were used in vanadium perchlorate solution of low $[H^+]$, glass electrodes were used in this determination. The concentration of perchloric acid in the stock solution was 143 mM.

Sodium fluoride. A stock solution with C_A = 600 mM was prepared from "Merck" *p. a.* material, and sodium perchlorate was added to bring the total ionic strength to 1 M. In order to determine the small amount of foreign basic impurity usually found in fluoride

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* Unless stated otherwise, the same symbols are used as in the paper on uranyl fluoride[4].

solutions [4], a small amount of perchloric acid was added to the stock solution which was then titrated with alkali. The present preparation also contained this impurity, buffering around pH = 7 where the hydrofluoric acid was practically neutralized. Its concentration was estimated to about 0.2 % of that of the fluoride. From earlier experience [4] it was evident that this foreign base would have to be suppressed before the fluoride solution could be used in the measurements on complex halides. This was achieved by adjustment of the pH of the solution from the original value of 7.2 to about 6.3. At this lower pH the basic impurity is converted into the corresponding acid while the fluoride ion is still practically unaffected.

Stock solutions close to 1 M were prepared from analytical grade *perchloric acid* and *sodium chloride*. *Sodium perchlorate* was prepared by neutralization of perchloric acid as described before [8].

The behaviour of the quinhydrone electrode in solutions of vanadyl perchlorate. The function of the quinhydrone electrode in the presence of vanadium was checked by measuring the emfs of cells of the type

+ Au	C_H mM $HClO_4$ $I = 1$ M ($NaClO_4$) quinhydrone(s.)	1 M $NaClO_4$	C_H mM $HClO_4$ C_M mM $VO(ClO_4)_2$ $I = 1$ M ($NaClO_4$) quinhydrone (s.)	Au —

The measurements were arranged as titrations where C_M was varied and C_H kept constant within a certain series. Series were carried out with $C_H = 10$, 30 and 100 mM. In this range of pH the hydrolysis of V(IV) is negligible for all values of C_M used [2] and thus $C_H = [H^+]$. If the electrode is working ideally the emf measured should therefore always be = 0. As seen from Table 1, this is very nearly the case for $C_H = 30$ mM, at least up to $C_M = 50$ mM. The deviation is also slight for $C_H = 100$ mM. Its direction and order of magnitude resembles that found for the quinhydrone electrode in uranyl perchlorate solution [9] and the cause might be the same in both cases. For $C_H = 10$ mM on the other hand, the deviation is much greater and, moreover, goes in the other direction. The potentials at $C_H = 10$ mM are also much less reproducible than those measured at higher C_H.

Thus, in order to secure an acceptable measurement of $[H^+]$ in vanadyl perchlorate solutions up to a value of $C_M = 50$ mM by means of the quinhydrone electrode, C_H must be at least 25 mM. The question then arises if the electrode gives the right response for $C_H \geqq 25$ mM also in the presence of fluoride. This was tested by performing the fluoride measurements with several different values of C_H and C_M, *i. e.* by varying those quantities which evidently determine the behaviour of the electrode. The calculation of identical complex formation functions (and hence identical stability constants) from all the experimental values of C_H and C_M implies that the underlying determination of $[H^+]$ was correct and the electrode thus functioning normally.

Table 1. The behaviour of the quinhydrone electrode in vanadyl perchlorate solutions.

$[H^+] \rightarrow$ mM	100	30	10
C_M mM	E mV		
2	0	0	0.7
5	−0.1	0	1.3
10	−0.2	0.2	2.2
20	−0.8	0.3	3.5
30	−1.5	0.4	
50	−3.0	0.4	

As pointed out above such a variation of C_H and C_M was also necessary in order to reveal if the solution contains other complexes than the simple mononuclear series $VOF_n^{(n-2)-}$. Therefore, if no variation with C_H or C_M is found for the complex formation function, this means not only that those other complexes do not exist but also that the determination of the constants of the complexes $VOF_n^{(n-2)-}$ is not impaired by faulty electrode function.

Procedure of the main measurements. The measurements were all arranged as titrations. A cell similar to that written above was connected. The specially prepared fluoride stock solution and an acid perchlorate solution were then added from individual burettes to the right-hand solution so that C_H and C_M were both kept constant during each titration. A plastic vessel was used for this half-cell which had to accomodate acid fluoride solutions. The left hand half-cell, serving as a reference electrode, always had $C_H = 10$ mM in the halide measurements.

In the chloride measurements, the solution of the right-hand cell also contained a certain total chloride concentration C_{Cl} which was also kept constant during a titration.

In the halide titrations, the value of E_H could as a rule be reproduced within ±0.2 mV. The potentials attained equilibrium practically at once and were stable for hours.

RESULTS

The fluoride system. Corresponding values of [A] and the ligand number $\bar{n}_M$ were calculated according to the equations listed as (1) and (2) of Ref.[5], *i. e.* by using the constants δ_1 and δ_2 of the hydrogen fluoride system. In particular the value of δ_2 is fairly sensitive to the presence of basic impurities in the sodium fluoride solution [4]. As a new stock solution of fluoride, prepared from salt of another source, was used in the present measurements, it seemed advisable to redetermine the constants δ_1 and δ_2. This was done by titrations similar to those described in Ref.[4] Higher values of C_H were however chosen, *viz.* $C_H = 25$, 50 and 100 mM, because the measurements on vanadyl solutions had to be performed at these values of C_H. The present titrations gave $\delta_1 = 850 \pm 30$ M^{-1}, $\delta_2 = 2\,300 \pm 300$ M^{-2}, in good agreement with the values found for the second fluoride preparation used previously.

In order to find E_H of eqn. (1), Ref.[5], it is necessary to know the liquid junctions potentials of the cells used (*cf.* Ref.[4], eqns. (1) and (2). On the reasonable assumption that these potentials depend only on $[H^+]$ they have been previously determined in separate experiments up to $[H^+] = 35$ mM, with reference to the usual quinhydrone electrode of $[H^+]_0 = 10$ mM and $I = 1$ M (Ref.[4], Table 1). For the present investigation the determination of E_d had to be extended to $[H^+] = 100$ mM, Table 2. At such high values of $[H^+]$, E_d is a very substantial correction to the measured values of E.

Table 2. The liquid junction potential E_d as a function of E (and $[H^+]$). $[H^+]_0 = 10$ mM.

E mV	−35	−40	−45	−50	−55
E_d mV	2.3	3.0	4.0	5.3	6.9
$[H^+]$ mM	44	55	70	90	115

Table 3. Determination of $\bar{n}_M$ as a function of [A] for C_H = 25 mM, C_M = 25 mM.

C_A mM	E_H mV	[A] mM	$\bar{n}_M$
22.9	8.6	0.48	0.60
43.6	22.4	1.70	1.09
62.6	39.3	4.40	1.52
80.0	55.9	9.43	1.91
96.0	69.2	16.5	2.20
110.9	79.6	24.8	2.42
137.1	93.8	42.2	2.71
160.0	103.6	60.0	2.86
180.0	110.0	74.8	3.04
206.0	118.0	97.8	3.11

In the measurements on vanadyl solutions, titrations with C_H = 100 and 50 mM were performed with two different values of C_M, *viz.* 50 and 25 mM, while only one value of C_M, 25 mM, was used with C_H = 25 mM. The results are given in Tables 3—5, and the complex formation functions giving $\bar{n}_M$ as a function of log [A] are plotted in Fig. 1. Evidently all the combinations of C_H and C_M give identical functions. Thus neither polynuclear complexes nor complexes with HF_2^- as ligand seem to exist in these solutions. Above all no hydrolysis occurs, in spite of the fact that values of pH are reached where the hydrolysis is quite substantial in non-complex perchlorate solutions[2]. Evidently the complex formation with fluoride effectively prevents the formation of soluble hydroxo complexes of V (IV) (*cf.* Ref.[4], p. 706; Ref.[10]). On the other hand the absence of hydrolytic reactions also means that fluoride ions do not displace the oxygen of VO^{2+} within the present range of pH contrary to what

Table 4. Determination of $\bar{n}_M$ as a function of [A] for C_H = 50 mM, C_M = 25 and 50 mM.

C_A mM	25			50		
	E_H mV	[A] mM	$\bar{n}_M$	E_H mV	[A] mM	$\bar{n}_M$
22.9	6.2	0.33	0.46	3.9	0.20	0.31
43.6	14.6	0.93	0.81	8.4	0.47	0.57
62.6	25.4	2.06	1.14	14.3	0.91	0.79
80.0	38.0	4.12	1.44	20.8	1.52	1.01
96.0	51.2	7.67	1.75	28.1	2.43	1.19
110.9	63.6	13.08	2.01	35.7	3.67	1.33
137.1	80.8	26.0	2.38	50.4	7.40	1.70
160.0	92.7	40.6	2.62	63.5	13.04	1.99
180.0	101.2	55.2	2.76	74.1	19.98	2.20
206.0	110.0	74.8	2.91	86.0	31.7	2.44
240.0	118.9	100.6	3.12	99.2	51.4	2.65
266.2				107.7	69.0	2.78
288.0				113.4	84.0	2.89

Table 5. Determination of $\bar{n}_M$ as a function of [A] for C_H = 100 mM, C_M = 25 and 50 mM.

25				50			
C_A mM	E_H mV	[A] mM	$\bar{n}_M$	C_A mM	E_H mV	[A] mM	$\bar{n}_M$
22.9	4.0	0.20	0.32	17.3	2.4	0.12	0.16
43.6	8.7	0.49	0.52	33.4	4.9	0.26	0.31
62.6	13.8	0.87	0.75	48.2	7.5	0.41	0.42
80.0	19.6	1.40	0.95	62.0	10.1	0.59	0.55
96.0	26.0	2.14	1.16	75.0	13.0	0.80	0.66
110.9	33.3	3.23	1.31	87.2	16.0	1.05	0.76
137.1	48.4	6.77	1.69	109.0	21.9	1.64	0.97
160.0	62.6	12.54	2.10	128.6	28.6	2.50	1.14
180.0	74.7	20.48	2.34	145.8	35.1	3.55	1.30
206.0	87.8	33.9	2.65	168.8	44.5	5.65	1.54
240.0	101.1	55.0	2.92	200.0	59.3	10.92	1.92
266.4	109.4	73.3	3.04	225.0	70.8	17.67	2.17
288.0	115.1	88.8	3.17	245.5	79.9	25.1	2.37
				276.7	91.9	39.4	2.59
				300.0	99.5	52.0	2.72
				317.8	104.6	62.0	2.84

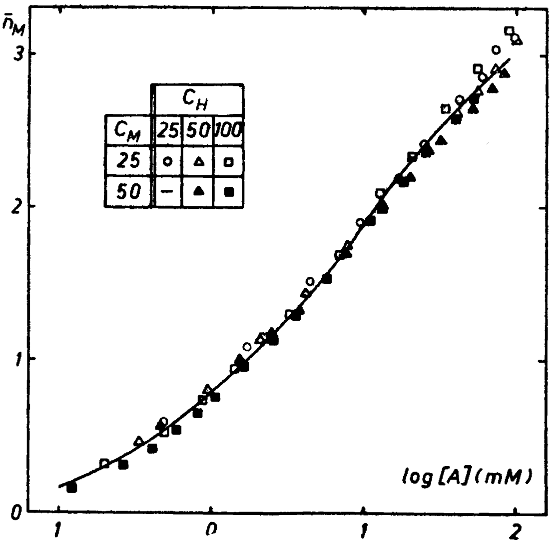

Fig. 1. The complex formation function of the vanadyl fluoride system. The points refer to titrations with different values of C_M and C_H, as indicated by the scheme given in the figure. The curve is calculated from the constants β_n finally found.

has recently * been believed [11]. It might finally also be concluded that the quinhydrone electrode works satisfactorily under the prevailing conditions.

As pointed out in the paper [4] on uranyl fluoride the way of calculating [A] and $\bar{n}_M$ from δ_1 and δ_2 might produce figures at high values of C_A, which are too low for [A] and hence too high for $\bar{n}_M$. A method giving better values of [A] and $\bar{n}_M$ in this region was given and it has also been tried in the present case. However it does not work quite satisfactorily here as $[H^+]$ is so large relative to [HA] and $[HA_2]$ that eqn. (18) of Ref.[4] is no longer a sufficiently close approximation. It can be estimated however that the complex formation curve will only be slightly displaced downwards if calculated according to this method. For the uppermost points at [A] = 100 mM, the difference would be about 0.2 units in $\bar{n}_M$ and it would then decrease rapidly with [A], completely disappearing at [A] $\approx$ 20 mM.

When [A] reached a value of $\approx$100 mM at $C_M = 25$ mM and $\approx$80 mM at $C_M = 50$ mM, a precipitate was formed and simultaneously the emf started drifting. The titration series had then to be interrupted. Unfortunately the complex formation curve (Fig. 1) is still steeply rising at these values of [A] and therefore the present measurements could give no reliable information about the coordination number, N, of the vanadyl ion.

For analysis, a larger quantity of the precipitate was prepared in a separate experiment. The filtered substance was washed with small portions of cold water (it is perceptibly soluble) and then dried at 105°C. It could then be heated for 5 h at 180°C without changing its weight. For the determination of vanadium, samples were dissolved in 2 M sulphuric acid and titrated potentiometrically as described above. For the determination of fluorine, another sample was dissolved in 0.05 M hydrochloric acid and the fluoride then precipitated as PbClF (*cf.* Vogel [12], p. 261). In order to achieve a complete precipitation, pH must be kept between 3 and 4. In such a solution, however, the hydrolysis of vanadium(IV) is quite marked, resulting in a coprecipitation of hydrolysed vanadium species. The filtered and washed precipitate therefore cannot be weighed as PbClF. Instead it was dissolved in nitric acid and titrated according to Volhard. At this procedure, no disturbance was observed from the slight amount of vanadium present. Found: V 22.3, 22.0 %, F 40.8 %. Calc. for Na_3VOF_5: V 22.1 %, F 41.1 % (Calc. for Na_2VOF_4: V 27.0 %, F 40.2 %; for Na_4VOF_6: V 18.7 %; F 41.8 %). From the vanadium analysis it thus seems certain that the compound is Na_3VOF_5. The fluorine analysis is in accordance with this, although it cannot decide between several conceivable alternatives with almost the same fluorine content. The ammonium analogue of Na_3VOF_5 has been known since long ago [13]. Unfortunately, neither the structure of this compound, nor that of any other complex vanadyl fluoride seems ever to have been determined. From these solid phases no evidence can therefore be derived about the co-ordination number of the vanadyl ion in its fluoride complexes. As stated above, the complex formation function, valid for aqueous solution, was also inconclusive on this point. The question must therefore be left open for the present.

From the experimental complex formation function the stability constants β_1, β_2 and β_3 of the first three complexes $VOF_n^{(n-2)-}$ are calculated in the usual

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* The findings of Ducret [11] might be explained by his use of glass electrodes (and probably glass vessels) for acid fluoride solutions.

Table 6. Computation of the stability constants of the vanadyl fluoride system.

$\beta_1 = 2\,000 \pm 100$ M^{-1} $\beta_2 = (2.9 \pm 0.3) \times 10^5$ M^{-2} $\beta_3 = (1.4 \pm 0.2) \times 10^7$ M^{-3}
$\beta_4 = 3 \times 10^7$ M^{-4}
$b_1 = \beta_1$ $b_2 = 150$ M^{-1} $b_3 = 50$ M^{-1}
$b_1/b_2 = 13$ $b_2/b_3 = 3$

[A] mM	$X([A])/X(10^{-4})$	$X_{1M} \times 10^{-3}$ M^{-1}	$X_{2M} \times 10^{-5}$ M^{-2}	$X_{3M} \times 10^{-7}$ M^{-3}	$X_{4M} \times 10^{-7}$ M^{-4}
0	*0.827*	*2.0*	*2.9*	*1.4*	*3*
0.1	1.000	2.10			
0.2	1.174	2.10			
0.3	1.349	2.10			
0.4	1.522	2.10			
0.5	1.699	2.11			
0.6	1.881	2.12			
0.8	2.256	2.18			
1	2.654	2.21			
2	5.032	2.54	2.72		
3	8.114	2.94	3.12		
4	11.93	3.36	3.39		
5	16.54	3.80	3.60	1.4	
6	22.06	4.28	3.80	1.5	
8	36.09	5.33	4.17	1.59	
10	54.21	6.46	4.46	1.56	
15	120.1	9.61	5.07	1.45	
20	223.6	13.47	5.73	1.42	
30	585	23.55	7.19	1.43	
40	1 220	36.85	8.72	1.46	
50	2 221	53.7	10.34	1.49	
60	3 707	74.7	12.11	1.54	
80	8 656	130.9	16.11	1.65	3.1
100	17 160	207.5	20.55	1.77	3.7

way [14], with a lower integration limit $[A]_0 = 0.1$ mM, Table 6. A very tentative value of β_4 is also given. From these constants the complex formation curve and the composition of the system is calculated according to eqns. (2) and (8) of Ref.[14] The formation curve, fulldrawn in Fig. 1, fits the experimental points well. The composition is presented graphically in Fig. 3.

The Chloride System. As the chloride system could be expected to be weak, a high concentration of chloride $C_{Cl} = 400$ mM was used. The values of δ_1 and δ_2 are however likely to change when such a large amount of the perchlorate is exchanged for chloride. These constants must therefore be determined in the chloride medium also. This was done by titrations at $C_H = 50$ and 100 mM and resulted in $\delta_1 = 800 \pm 30$ M^{-1}; $\delta_2 = 3\,100 \pm 300$ M^{-2}.

Fluoride titrations were then performed with a solution having a vanadium(IV) concentration $C_M = 30$ mM, $C_H = 50$ mM and $C_{Cl} = 400$ mM. The function $\bar{n}_M/[A]$ of the fluoride system obtained from these measurements was very close to that found above for pure fluoride solutions, Fig. 2. An addition of $C_{Cl} = 400$ mM was thus able to repress the complex formation of fluoride only very little, on account of the extreme weakness of the chloride complexes. In fact it was no use to try lower values of C_{Cl}, as these would have

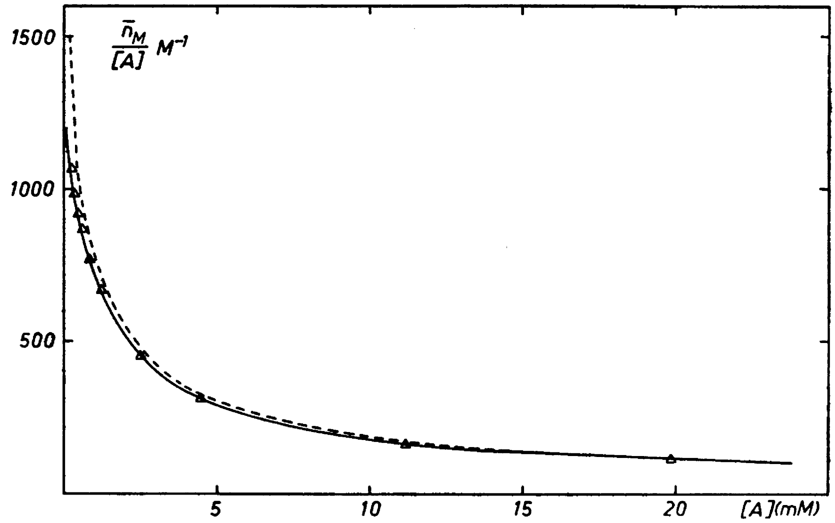

Fig. 2. The function $\bar{n}_M/[A]$ for the vanadyl fluoride system at $I = 1$ M a) in pure perchlorate medium: dashed curve, and b) in the presence of a chloride concentration $C_{Cl} = 400$ mM: triangles, fulldrawn curve.

given functions not significantly separated from the function of $C_{Cl} = 0$. The constant, β_1, of the first chloride complex is therefore calculated from this single value of C_{Cl} under the reasonable assumption that no higher complexes have yet been formed. Using[6] a value of $b = 0.018$ M, the integral $\ln X\ (0.4) = \int\limits_0^b \frac{\bar{n}_M}{[A]} \cdot d[A]$ is graphically found to be $= 0.3625$ giving $\beta_1 = 1.1$ M^{-1}. On account of the possible influence of medium effects *etc.* on the slight difference found between the $\bar{n}_M/[A]$-curves, this value of β_1 can only be considered as showing the order of magnitude. In Fig. 3, the partition of vanadium between VO^{2+} and $VOCl^+$ is shown graphically.

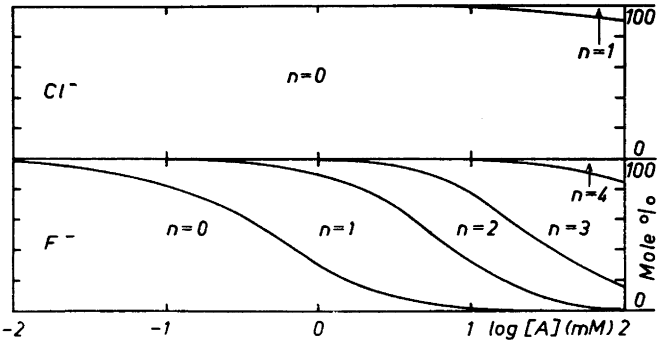

Fig. 3. The distribution of vanadium between the different complexes as a function of log [A].

DISCUSSION

As could be predicted from the position of vanadium in the Periodic Table, the fluoride complexes of VO^{2+} are much stronger than the chloride ones. VO^{2+} is a typical class (a) acceptor [15] and its complex formation with halide ions is thus governed essentially by electrostatic forces [3].

The fluoride complexes of VO^{2+} are much stronger than those of divalent central ions of a similar size, possessing higher symmetry [5], *e. g.* Ni^{2+}, Cu^{2+}, Zn^{2+}. Obviously the effective charge on vanadium in VO^{2+} is greater than $+2$ due to the high electronegativity of the attached oxygen. On the other hand the fluoride complexes of VO^{2+} is markedly weaker than those [4] of UO_2^{2+}. Certainly two oxygen atoms induce a higher effective charge on uranium in UO_2^{2+} than does one oxygen on vanadium in VO^{2+}. This increase of charge is evidently only partly compensated by the increase of ionic size and the result is a net increase of electrostatic attraction.

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