

A Method of Studying Metal Complex Formation in an Anion Exchanger Phase

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A method is developed for studying the step-wise complex formation within an anion exchanger phase at increasing concentrations of an anionic ligand. The method presupposes the use of a salt medium in the outer solution and a knowledge of the complexity in this phase.

To test the method it is applied to the cadmium bromide system at 20°C and with sodium perchlorate as supporting electrolyte. The ligand number \bar{n}_R in the resin phase is found to attain a limiting value of 4 at increasing ligand concentrations. The stability constants obtained are much higher than the corresponding ones in the outer solution.

In a previous paper (Fronæus¹) a method was developed for studying the formation of anionic complexes in water solutions and in absence of a neutral salt medium. It was based upon the use of an anion exchanger saturated with the ligand. When this method was applied to copper(II) complex systems with glycolate and tartrate ions as ligands, it was found in preliminary measurements that the sorption of copper by the ion exchanger was of a much lower order of magnitude than the sorption of cadmium in the cadmium bromide system though the former systems have a stronger tendency to anionic complex formation in water solutions (*cf.* Ref.²).

In order to explain these differences it is necessary to know how the step-wise complex formation proceeds within the anion exchanger at an increasing ligand concentration. In the present paper a method is developed for the calculation of the complexity constants valid in the anion exchanger phase. The method presupposes the use of a salt medium in the outer solution and a knowledge of the complexity constants in this phase. To test the method it is applied to the cadmium bromide system, because its complexity in water solutions is well known at different ionic strengths.

THEORY OF THE METHOD

The notation used is the same as in previous papers (Fronæus^{1,3}). The central ion is called M and the ligand A without any marking of the ionic charges. An index R indicates the resin phase.

The distribution of the free central ion between the anion exchanger and the water phase is given by the Donnan equation

$$[M]_R \cdot [A]_R^\nu = K[M] \cdot [A]^\nu \quad (1)$$

where ν is the ratio between the absolute values of the ionic charges of the central ion and the ligand. If the ionic strength can be kept constant in the outer solution as well as in the anion exchanger, we can presume that the factor K and the complexity constants in both the phases will be approximately constant when the concentration of A is varied within limited ranges. Generally the total concentrations C_M and C_{MR} of the central ion can be kept so low that variations in these quantities should not influence the constancy of the activity coefficients.

If we presuppose that only mononuclear complexes are formed, we have the following relations

$$C_M = [M](1 + \sum_{j=1}^N \beta_j [A]^j) \quad (2)$$

$$C_{MR} = [M]_R(1 + \sum_{j=1}^N \beta_{jR} [A]_R^j) \quad (3)$$

or
$$C_M = [M] \cdot X \quad (4)$$

$$C_{MR} = [M]_R \cdot X_R \quad (5)$$

Combination of eqns. (1), (4) and (5) yields the following expression for the ratio φ between the equilibrium values of C_{MR} and C_M .

$$\varphi = K \cdot \frac{X_R}{[A]_R^\nu} \cdot \frac{[A]^\nu}{X} \quad (6)$$

Since the value of ν is not restricted to whole numbers it is evident that the deduction of eqn. (6) is *general* and does not presuppose the existence of a neutral complex. (The contrary has been asserted by Kraus and Nelson ⁴).

However, in the case that ν is a whole number and if the uncharged complex MA_ν really exists the following relation holds ¹

$$K = l_\nu \cdot \beta_\nu \cdot \beta_{\nu R}^{-1} \quad (7)$$

where l_ν is the Nernst distribution coefficient for this complex.

Calculation of \bar{n}_R . It is possible to determine $\bar{n}_R = (C_{AR} - [A]_R)/C_{MR}$, *i.e.*, the ligand number in the resin phase, from eqn. (6). Derivation of $\ln \varphi$ with respect to $\ln[A]_R$ yields, if K is constant

$$\frac{d \ln \varphi}{d \ln [A]_R} = \frac{d \ln X_R}{d \ln [A]_R} - \nu + \left(\nu - \frac{d \ln X}{d \ln [A]} \right) \frac{d \ln [A]}{d \ln [A]_R} \quad (8)$$

The definitions of the ligand numbers \bar{n} and \bar{n}_R give the relations $d \ln X / d \ln [A] = \bar{n}$ and $d \ln X_R / d \ln [A]_R = \bar{n}_R$. Hence

$$\bar{n}_R = \nu + \frac{d \ln \varphi}{d \ln [A]_R} + (\bar{n} - \nu) \frac{d \ln [A]}{d \ln [A]_R} \quad (9)$$

φ , $[A]_R$ and $[A]$ are determined experimentally and then from plots of $\ln\varphi$ and $\ln[A]$ against $\ln[A]_R$ the derivatives in eqn. (9) can be obtained. \bar{n} is in this case computed from the known complexity constants in the water phase.

Calculation of the complexity constants β_{jR} . From eqn. (6) the function $K \cdot X_R$ can be calculated for varying ligand concentrations $[A]_R$. Then the constants K and $K\beta_{jR}$ can be obtained, e.g. by extrapolations to $[A]_R = 0$ of this function and of the quantities KX_{jR} defined by the relation

$$KX_{jR} = \frac{KX_{j-1,R} - K\beta_{j-1,R}}{[A]_R} \quad (10)$$

$(X_R = X_{0R}, \beta_{0R} = 1)$

In general it is very difficult to determine φ experimentally with sufficient accuracy at so low values of $[A]_R$ that a safe K -value can be obtained by extrapolation. Consequently, in such cases the complexity constants determined are also rather uncertain. However, the stability constants $b_{jR} = \beta_{jR}/\beta_{j-1,R}$ can be calculated for $j > 1$ even if K is unknown.

Furthermore, in those cases where an uncharged complex MA_ν is formed, the distribution coefficient l_ν can be calculated from eqn. (7) when β_ν and $K\beta_{\nu R}$ are known.

Calculation of \bar{n} and β_j . Under certain conditions it should be possible to use the anion exchange method for an independent determination of the complexity constants in the water phase.

If the ligand is sorbed much more easily than the perchlorate ion the anion exchanger will be almost saturated with respect to A, and thus $[A]_R$ will be approximately constant for varying but not too low values of $[A]$. Then eqn. (9) yields

$$\bar{n} \approx \nu - \frac{d \ln \varphi}{d \ln [A]} \quad (11)$$

and the complexity constants β_j can be computed from the function $[A]^\nu/\varphi$, which in this case is proportional to X according to eqn. (6).

If the complexity is fairly strong and $[A]_R \gg [A]$ it can be expected that \bar{n}_R is approximately equal to the coordination number N for not too low ligand concentrations. Thus, if \bar{n}_R is calculated by the method developed above and is found to be constant and equal to an integer when $[A]$ is varied, it is very probable that the values of \bar{n} used in eqn. (9) are correct, and a confirmation of the complexity constants β_j , taken from another investigation, is obtained.

MEASUREMENTS AND CALCULATIONS

Chemicals used. A known amount of cadmium, containing some ^{115}Cd (from A.E.R.E., Harwell, England), was dissolved in nitric acid and the nitrate was converted into perchlorate by evaporation several times with perchloric acid. The concentration of the stock solution of radioactive cadmium perchlorate was calculated from the weighed amount of cadmium.

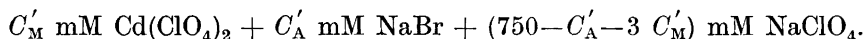
Sodium perchlorate was prepared by neutralizing perchloric acid with sodium carbonate. The crystals formed between 80°C and 135°C, in which region the perchlorate crystallizes without water of crystallization, were separated and dried at 110°C. A stock

solution was prepared, the concentration of which was checked by means of a cation-exchanger column in the hydrogen form.

Sodium bromide was of analytical grade, and the concentration of the stock solution was determined by titration according to Mohr.

The anion-exchanger was Dowex 2 \times 8, containing fixed quaternary ammonium groups. It was converted to the bromide or perchlorate form and air-dried.

Method of investigation. The complex solutions had the initial composition



C'_M was kept constant in the measurement series. v litres of the complex solution were shaken for 20 h in a thermostat at 20.0°C with m grams of the air-dried exchanger. The value of vm^{-1} was always 0.015 lg^{-1} .

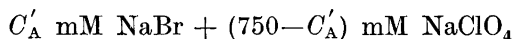
When a distribution equilibrium had been attained, the resin phase was separated from the solution. The remaining cadmium concentration C_M of the outer solution was determined by measurement of the gamma activity on 10 ml of the solution. For these determinations a scintillation detector (type P-20 from Tracerlab) was used. A glass cup containing 10 ml of the solution to be measured was placed in a fixed position in the lead shielding, in the centre of which the scintillation detector was immersed to a fixed depth. A satisfactory reproducibility of geometry was assured. In order to get a relation between counts per minute and cadmium concentration, the gamma activity of some reference solutions with known concentrations was determined. A rectilinear relation between activity and concentration was obtained, and this relation was not perceptibly affected by the presence of varying amounts of sodium bromide and perchlorate.

The load C_{MR} on the exchanger was calculated according to the relation $C_{MR} = vm^{-1} (C'_M - C_M \delta)$.

The equilibrium concentration C_A of the outer solution was determined by titration according to Mohr.

The load C_{AR} was determined by eluting the resin, which had been carefully separated from the solution, with v_1 litres of 2 M NaClO_4 in small portions. The bromide concentration C''_A of this solution was determined by titration, and C_{AR} was calculated from the relation $C_{AR} = v_1 m^{-1} C''_A$. The value of $v_1 m^{-1}$ was here 0.060 lg^{-1} . However, a certain amount of outer solution adhered to the particles of the separated resin, which could not be washed before the elution. But the ratio of surface area and mass of the resin was the same in all the measurements. Then, as the experiments were performed in quite the same manner, we have $C_{AR}^a = k C_A$, where k is a constant and C_{AR}^a is the contribution from the outer solution adherent to the resin particles. The correction term C_{AR}^a is, however, of rather little magnitude in comparison to C_{AR} and may be neglected.

An approximate value of the swelling factor δ was determined by shaking solutions of the composition



with a known amount of the resin until equilibrium was reached. The value

of vm^{-1} was here as before 0.015 lg^{-1} . Then the value of δ was given by the ratio between the initial and the equilibrium sodium ion concentrations, which were determined by titrations with sodium hydroxide after percolating samples through a cation-exchanger column in the hydrogen form.

According to the description above, we will have the concentrations in the resin phase, C_{MR} and C_{AR} , expressed in mmoles per gram of the air-dried resin. In order to express the concentrations in moles per litre, it is necessary to know the water content of the resin in the swelled state. It is composed of two contributions: the water content of the air-dried resin and the water

Table 1. Anion exchange measurements on the cadmium bromide system. The anion exchanger initially in the bromide form. $C'_M = 2.987 \text{ mM}$.

C_M mM	δ	$C_{MR} \times 10^2$ mmole.g ⁻¹	C_{MR} mM	C_A M	C_{AR} mmole.g ⁻¹	C_{AR} M	φ
1.7110	0.986	1.95	71.35	0.180	0.063	0.230	42
0.4780	0.986	3.77	135.0	0.320	0.185	0.665	285
0.3705	0.986	3.93	140.0	0.350	0.225	0.795	380
0.2940	0.986	4.05	144.0	0.390	0.245	0.875	490
0.2625	0.985	4.09	144.5	0.425	0.275	0.975	550
0.1585	0.985	4.25	147.5	0.475	0.350	1.20	930
0.1010	0.985	4.33	148.0	0.570	0.460	1.55	1 450
0.0465	0.984	4.41	145.5	0.655	0.685	2.25	3 100
0.0225	0.983	4.45	142.0	0.695	0.965	3.10	6 350
0.0115	0.982	4.46	135.5	0.725	1.45	4.45	12 000
0.0069	0.981	4.47	130.0	0.740	2.00	5.90	19 000
0.0032	0.981	4.48	127.5	0.745	2.55	7.25	39 500

Table 2. Anion exchange measurements on the cadmium bromide system. The anion exchanger initially in the perchlorate form. $C'_M = 1.513 \text{ mM}$.

C_M mM	δ	$C_{MR} \times 10^2$ mmole.g ⁻¹	C_{MR} mM	C_A M	C_{AR} mmole.g ⁻¹	C_{AR} M	φ
1.5315	0.985	0.0074	0.29	0.007	0.0013	0.005	0.2
1.5215	0.985	0.022	0.87	0.015	0.0035	0.014	0.6
1.5010	0.985	0.052	2.04	0.029	0.0074	0.029	1.4
1.4805	0.985	0.083	3.25	0.042	0.010	0.040	2.2
1.4545	0.985	0.120	4.70	0.054	0.013	0.052	3.2
1.3670	0.984	0.250	9.77	0.081	0.022	0.085	7.1
1.2460	0.984	0.430	16.50	0.105	0.031	0.120	13
0.9620	0.984	0.850	32.00	0.160	0.053	0.200	33
0.6745	0.983	1.28	46.70	0.210	0.083	0.305	69
0.4590	0.983	1.59	57.10	0.265	0.115	0.405	125
0.3075	0.982	1.82	62.60	0.315	0.175	0.595	205
0.1690	0.982	2.02	68.30	0.420	0.225	0.755	405
0.0715	0.981	2.17	69.60	0.515	0.400	1.30	975
0.0240	0.980	2.24	69.30	0.610	0.690	2.15	2 900
0.0065	0.979	2.26	66.65	0.690	1.43	4.20	10 500

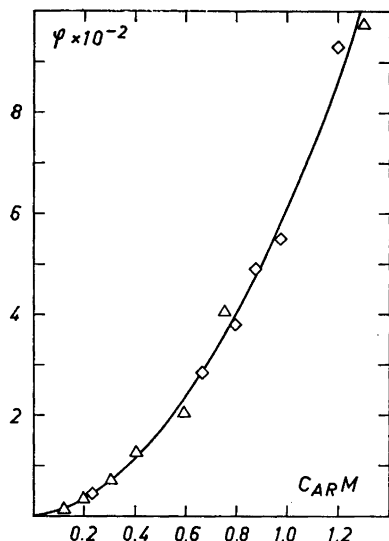


Fig. 1. The distribution φ of the cadmium bromide system as a function of the bromide concentration in the resin phase, C_{AR} . The anion-exchanger was initially either in the bromide form (symbol \diamond) or in the perchlorate form (symbol \triangle).

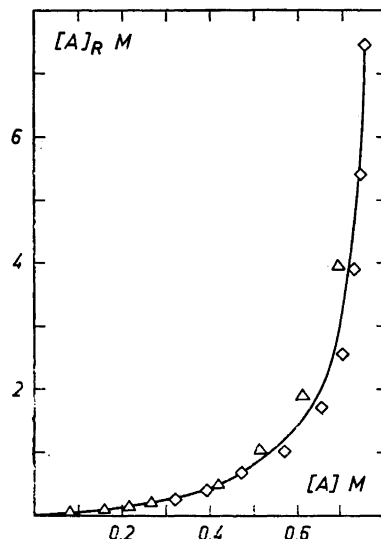


Fig. 2. The bromide ion concentration in the resin phase, $[A]_R$, as a function of the bromide ion concentration in the outer solution, $[A]$. The meaning of the symbols \diamond and \triangle is the same as in Fig. 1.

taken up by the air-dried resin during the swelling procedure. The first quantity can be determined from the loss of weight of the air-dried exchanger, when it is dried further (at about 80°C), until a constant weight is attained. The second quantity can be calculated by means of the swelling factor δ . If v represents the volume of the solution before the resin is added and $v\delta$ the volume of the outer solution at equilibrium, the volume of water taken up by the air-dried resin is $v(1-\delta)$.

The data from the measurements on the cadmium bromide system are collected in Tables 1 and 2. In Table 1 the bromide form of the anion exchanger was used, in Table 2 the anion exchanger was initially in the perchlorate form. The water content of the two forms in the air-dried state was for the first one 0.064 and for the second 0.024 grams water per gram of the air-dried exchanger.

Fig. 1 shows the distribution φ as a function of the ligand concentration C_{AR} for the two series. As seen in the figure, φ is a monotonously and rapidly rising function of C_{AR} .

The ligand numbers in the resin phase, \bar{n}_R , were calculated from eqn. (9). In this case $\nu = 2$. The terms $\text{dln}\varphi/\text{dln}[A]_R$ and $\text{dln}[A]/\text{dln}[A]_R$ were obtained by graphic methods, and \bar{n} was computed from the relation

$$\bar{n} = \frac{C_A - [A]}{C_M} = \frac{X' \cdot [A]}{X}$$
 We mean by X the function $1 + \sum_{j=1}^N \beta_j [A]^j$ (cf. eqns. (2) and (4)) and by X' the derivative of X with respect to $[A]$.

Table 3. Computation of \bar{n}_R for the cadmium bromide system. The anion exchanger initially in the bromide form.

φ	[A] M	[A] _R M	$\frac{d \ln \varphi}{d \ln [A]_R}$	$\frac{d \ln [A]}{d \ln [A]_R}$	\bar{n}	\bar{n}_R
42	0.180				1.44	
285	0.320	0.25	1.10	0.55	1.94	3.1
380	0.350	0.35	1.20	0.55	2.04	3.2
490	0.390	0.40	1.20	0.52	2.14	3.3
550	0.425	0.48	1.30	0.48	2.24	3.4
930	0.475	0.67	1.40	0.42	2.36	3.6
1 450	0.570	1.00	1.60	0.36	2.58	3.8
3 100	0.655	1.70	1.70	0.23	2.80	3.9
6 350	0.695	2.55	1.75	0.15	2.90	3.9
12 000	0.725	3.90	1.80	0.09	2.94	3.9
19 000	0.740	5.40	1.90	0.06	2.98	4.0
39 500	0.745	6.75	2.00	0.04	3.00	4.0

Table 4. Computation of \bar{n}_R for the cadmium bromide system. The anion exchanger initially in the perchlorate form.

φ	[A] M	[A] _R M	$\frac{d \ln \varphi}{d \ln [A]_R}$	$\frac{d \ln [A]}{d \ln [A]_R}$	\bar{n}	\bar{n}_R
0.2	0.007	0.0048	0.80	1.20	0.21	0.7
0.6	0.014	0.013	1.20	1.20	0.38	1.3
1.4	0.028	0.026	1.36	1.18	0.59	1.7
2.2	0.041	0.033	1.50	1.17	0.73	2.0
3.2	0.053	0.042	1.60	1.16	0.83	2.2
7.1	0.080	0.060	1.70	1.14	1.00	2.6
13	0.105	0.074	1.70	1.10	1.14	2.8
33	0.160	0.100	1.70	0.95	1.37	3.1
69	0.210	0.145	1.70	0.75	1.57	3.4
125	0.265	0.205	1.70	0.70	1.76	3.5
205	0.315	0.365	1.70	0.56	1.93	3.7
405	0.420	0.495	1.70	0.40	2.25	3.8
975	0.515	1.05	1.75	0.30	2.49	3.9
2 900	0.610	1.90	1.80	0.20	2.69	3.9
10 500	0.690	3.95	1.87	0.13	2.83	4.0

At the calculation of the X- and X'-functions, the following values of the complexity constants were used for the outer solution, the ionic strength of which was 0.75 M (*cf.* Ref.², Kivalo and Ekari):

$$\beta_1 = 36 \text{ M}^{-1}, \quad \beta_2 = 125 \text{ M}^{-2}, \quad \beta_3 = 145 \text{ M}^{-3}, \quad \beta_4 = 340 \text{ M}^{-4}$$

The results are shown in Tables 3 and 4. In the calculation of \bar{n}_R according to eqn. (9) at first an approximate value of \bar{n}_R has been determined by using C_{AR} and C_A instead of $[A]_R$ and $[A]$, respectively. Then $[A]_R$ and $[A]$ have been computed from the relations

$$[A]_R = C_{AR} - \bar{n}_R \cdot C_{MR} \quad \text{and} \quad [A] = C_A - \bar{n} \cdot C_M$$

Table 5. Calculation of the stability constants of the cadmium bromide system in the resin phase.

$[A]_R$ M	KX_R	KX_{1R} M ⁻¹	$KX_{2R}10^{-3}$ M ⁻²	$KX_{3R}10^{-4}$ M ⁻³	$KX_{4R}10^{-5}$ M ⁻⁴
0	<0.1	25	2.0	10	3.0
0.0048	0.118				
0.013	0.790	55	2.3		
0.026	2.55	95	2.7		
0.033	3.85	115	2.7		
0.042	6.60	155	3.1		
0.060	19.1	320	4.9		
0.074	41.0	550	7.1		
0.100	139	1400	14.0	12	
0.145	530	3700	26	17	
0.205	1770	8600	42	20	
0.365	89×10^2	245×10^2	67	18	
0.495	33×10^3	67×10^3	140	28	3.5
1.05	39×10^4	37×10^4	350	35	2.5
1.90	42×10^5	22×10^5	1200	65	3.0
3.95	72×10^6	18×10^6	4600	120	3.0

The difference between the approximate and the corrected values of \bar{n}_R is rather slight. In the first series, starting with an anion exchanger in the bromide form, the \bar{n}_R -values are almost constant (≈ 4) throughout the greater part of the measurement series, that is the fourth complex is entirely dominating in the resin phase. This is also to be expected at the high ligand concentrations, which are attained in this experiment. The ionic strength of the inner solution is not quite constant through the series. It varies from about 9.5 to 7.4 M, the ionic strength thus decreasing somewhat at increasing C_{AR} , owing to the decreasing δ -values. As the fourth complex is dominating here in the series, it is, of course, impossible to compute any complexity constants from this material.

In the second series, where the anion-exchanger is initially in the perchlorate form, it is possible to reach down to lower C_{AR} values and consequently obtain a variation in the \bar{n}_R values (Table 4). Here the ionic strength of the inner solution varies between 10.4 and 7.7 M (as before the lowest ionic strength is to be found in solutions with the highest C_{AR} -values).

Attempts have also been made to calculate approximate values of the complexity constants in the resin phase for the cadmium bromide system on the basis of these measurements. By successive extrapolations to $[A]_R = 0$ of the functions KX_{jR} the following values of $K\beta_{jR}$ are obtained (Table 5). $K < 0.1$,

$$K\beta_{1R} = 25 \pm 5 \text{ M}^{-1}, \quad K\beta_{2R} = (2.0 \pm 0.5)10^3 \text{ M}^{-2},$$

$$K\beta_{3R} = (1.0 \pm 0.3)10^5 \text{ M}^{-3}, \quad K\beta_{4R} = (3 \pm 1)10^5 \text{ M}^{-4}$$

Owing to the uncertainty in the determination of φ at low $[A]_R$ -values and the rapid decrease of the KX_R -function at decreasing $[A]_R$, only an upper limit of K can be obtained. Thus, only lower limits of the complexity constants

β_{jR} can be determined. However, in spite of the lacking knowledge of the exact value of K , the stability constants of the system, $b_{jR} = \beta_{jR}/\beta_{j-1,R}$, can be calculated for $j > 1$. The following values are obtained:

$$b_{1R} > 200 \text{ M}^{-1}, b_{2R} = 80 \pm 30 \text{ M}^{-1}, b_{3R} = 50 \pm 25 \text{ M}^{-1}, b_{4R} = 3.0 \pm 1.5 \text{ M}^{-1}$$

In the case of the cadmium bromide system ν is a whole number, and the uncharged complex CdBr_ν is formed. The Nernst distribution coefficient l_2 of this complex can be calculated from eqn. (7) when β_2 and $K\beta_{2R}$ are known. Inserting the values of these constants we get $l_2 = 16 \pm 4$.

DISCUSSION

The stability constants valid in the resin phase cannot be determined with any higher degree of accuracy. Especially the ratio b_{3R}/b_{4R} is probably influenced by the fact mentioned above, that the ionic strength of the inner solution decreases somewhat at the higher ligand concentrations. Nevertheless, the values obtained are of great interest in so far as they can give the following information about the complexity of the cadmium bromide system within the anion exchanger phase.

(a) The ligand number \bar{n}_R attains the limiting value 4, and thus there is no steric hindrance to the formation of the higher complexes within the resin phase.

(b) The stability constants b_{1R} , b_{2R} , and b_{3R} are much higher than the corresponding ones in the outer solution, while b_{4R} and b_4 are of the same order of magnitude. This fact is probably connected with the very high ionic strength of the resin phase. Thus, according to an investigation by Kivalo and Ekari (*cf.* Ref.²) on the cadmium bromide system in water solutions the constants b_1 , b_2 , and b_3 increase monotonously, when the ionic strength of the solutions is increased from 1 to 3 M by addition of sodium perchlorate. b_4 , on the other hand, does not increase.

The high values of the constants b_{3R} and $b_{3R}b_{4R}$ and of the distribution coefficient l_2 are obviously responsible for the fairly high sorption of cadmium by an anion exchanger saturated with bromide ions.

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