

The Equilibria between Nickel and Acetate Ions

An Ion Exchange and Potentiometric Investigation

STURE FRONÆUS

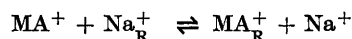
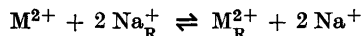
*Department of Inorganic and Physical Chemistry, Chemical Institute,
University of Lund, Lund, Sweden*

In a previous paper¹ the present author has developed and tested a method to investigate the complex equilibria between a bivalent cation M^{2+} as the central group and a univalent anion A^- as the ligand quantitatively by means of a cation exchanger. Within systems of this kind the free central group M^{2+} and the first complex MA^+ can be sorbed by the cation exchanger. For the quotient φ between the total concentrations of the central group in the ion exchanger (C_{MR}) and in the solution (C_M) at equilibrium the following relation was deduced^{1, p. 861}

$$\varphi = \frac{l_0 + l_1 \beta_1 [A^-]}{X} \quad (1)$$

The notations used are explained in the previous paper. Eq. (1) is *general* with regard to the composition of the complex system, provided C_{MR} and C_M are kept sufficiently small^{1, p. 862}.

Generally, the mass law products k_0 and k_1 of the two exchange equilibria*:



of the ion exchanger in the sodium form are no constants, even if C_{MR} and C_M are kept small in comparison with the ionic strengths in the two phases. Thus, under such conditions the distribution coefficients $l_0 = [M^{2+}]_R \cdot [M^{2+}]^{-1}$ and $l_1 = [MA^+]_R \cdot [MA^+]^{-1}$ are no constants either but depend upon the

* In this paper the ions in the ion exchanger phase are denoted M_R^{2+} , MA_R^+ , Na_R^+ and their concentrations $[M^{2+}]_R$, $[MA^+]_R$, $[Na^+]_R$.

composition of the ion exchanger phase. This fact complicates the calculation of the complexity constants of the system.

If the free central group M^{2+} could solely enter the resin phase, then at a fixed value of C_{MR} the coefficient l_0 would have the same value at all measurements, and this would be valid at every appearance of the sorption isotherm of M^{2+} .

For systems of the type $M^{2+} - A^-$ we have as a rule $l_1 > 0$. However, from the result of the preceding investigation we arrive at the conclusion that also when the complex MA^+ is taken up by the ion exchanger, l_0 and l_1 are, at small values of C_{MR} , dependent practically *solely* upon C_{MR} and not upon the ligand number $\bar{n}_R = [MA^+]_R \cdot C_{MR}^{-1}$ in the ion exchanger phase. The theoretical background of this behaviour will be developed in a subsequent paper. Thus, if the measurements are carried out at a fixed value of C_{MR} , the coefficients l_0 and l_1 can be treated as constants at the calculations.

In the present investigation this ion exchange method was applied on the nickel acetate system. Furthermore, to get a check on the results obtained a potentiometric investigation was also performed. Both investigations were carried out at a constant ionic strength, $I = 1$ C, with sodium perchlorate as a supplementary salt in the solutions.

The complex formation between nickel and acetate ions has very seldom been studied quantitatively. The investigations that are reported in the literature are essentially of a qualitative nature and scarcely give any information about the composition of the complex system or the strength of the complexes formed. Cryoscopic measurements by Calame² and an extinction investigation by Major³ are of this kind.

THE ION EXCHANGE INVESTIGATION

On the calculation of the complexity constants

The calculation of the complexity constants of the system is not performed in exactly the same way as in the previous paper¹, but has been somewhat modified. From corresponding values of φ and $[A^-]$, determined at a fixed value of C_{MR} (see p. 1204), the constants are calculated as follows. The function φ is extrapolated graphically to $[A^-] = 0$, and this can be performed with great accuracy owing to the weak complexity of the present system. At the extrapolation we obtain:

$$l_0 = \lim_{[A^-] \rightarrow 0} \varphi$$

When l_0 has been determined, we can form the function φ_1^* :

$$\varphi_1 = (l_0 \varphi^{-1} - 1) \cdot [A^-]^{-1} \quad (2)$$

* The same as $l_0 \varphi_1$ in the preceding paper.

If we put $l_1\beta_1l_0^{-1} = l$ in eq. (1) we find that an extrapolation of φ_1 to $[A^-] = 0$ gives:

$$\beta_1 - l = \lim_{[A^-] \rightarrow 0} \varphi_1$$

Now, for the sake of convenience we introduce a new function f containing the two quantities l_0 and $\beta_1 - l$:

$$f = \frac{l_0\varphi^{-1}\{(\beta_1 - l)[A^-] - 1\} + 1}{[A^-]^2} \quad (3)$$

It is easy to verify that eq. (1) can be written:

$$f = \beta_1\varphi_1 - \sum_{j=2}^N \beta_j[A^-]^{j-2} \quad (4)$$

If the complexity is slight and at not very great $[A^-]$ -values we can with sufficient accuracy put $N = 3$. Then, if f and φ_1 are determined at different $[A^-]$, we get the following relation between the differences:

$$\Delta f = \beta_1 \cdot \Delta\varphi_1 - \beta_3 \cdot \Delta[A^-] \quad (5)$$

It must be possible to represent graphically the connection between $\Delta f/\Delta[A^-]$ and $\Delta\varphi_1/\Delta[A^-]$ by a straight line, from the slope of which β_1 is obtained. After β_1 has been determined, the constants of the other mononuclear complexes can easily be computed according to eq. (4) from corresponding values of $[A^-]$ and $f - \beta_1\varphi_1$.

M e a s u r e m e n t s

Chemicals used. Nickel perchlorate was prepared from nickel carbonate, p.a., and perchloric acid, p.a., and was recrystallized from water to be released from the excess of perchloric acid. A stock solution was used and its concentration of nickel was checked by electroanalysis in ammoniacal solution according to Okáč⁴.

Potassium dithio-oxalate was prepared from diphenyl oxalate and potassium hydro-sulphide according to Auger and Billy⁵. As water solutions of the salt are not stable, they were made up just prior to use.

The *cation exchanger* was Amberlite IR-105 transferred into the sodium form and air-dried at room temperature. It was stored in a closed vessel, so that the content of water was constant during all the measurements. The exchange capacity was 2.30 meq. per gram of the dried exchanger in the sodium form.

The *other chemicals* used were prepared in the same way as in a previous treatise⁶. All stock solutions had the ionic strength 1 C.

The measurements were performed in the same manner as before¹, p. 864, v liters of the solution:

$$\begin{cases} C'_M \text{ mC Ni(ClO}_4)_2 \\ C'_A \text{ mC NaAc} \\ 0.5 C'_A \text{ mC HAc} \\ (1000 - 3 C'_M - C'_A) \text{ mC NaClO}_4 \end{cases}$$

were shaken in a thermostat at 20.0° C with m grams of the dried ion exchanger, until an equilibrium was attained. Then the solution was separated and the equilibrium concentrations C_M and C_A of nickel and acetate were ascertained.

The nickel concentration was extinctionmetrically determined. Potassium dithio-oxalate solution was added in excess, and the extinction was measured with a Beckman Quartz Spectrophotometer (Model DU) at the wave length 5 000 Å, where the extinction curve has a relative maximum. As the nickel dithio-oxalate complex formed is very strong, the molar extinction, obtained from solutions with known nickel concentration, is independent of the acetate ion concentration. The molar extinction at the wave length used is great, so even very low nickel concentrations can be ascertained with great accuracy.

The acetate concentration C_A at equilibrium was determined by extinctionmetric titration in the way described before¹, p. 865. Cupric perchlorate was added and the extinction measurements were carried out at the wave length 3 000 Å.

The nickel concentration C_{MR} in the resin phase was calculated from the relation:

$$C_{MR} = \frac{v}{m} (C'_M - C_M \cdot \delta) \quad (6)$$

As the value of m/v was kept constant (40.0 g · l⁻¹) at all measurements, the relative volume decrease of the solutions, caused by the swelling of the ion exchanger, was also the same for all solutions measured. Thus δ had a constant value and was obtained from the relation $\delta = C'_A/C_A$ at $C_M = 0$. The value of δ was 0.993.

It should be emphasized here that C_{MR} cannot be determined by analysis of the resin phase, for if the exchanger is washed with water to be released from adherent outer solution, then all of the acetate disappears from the resin phase because of the dissociation of the complex NiAc^+ , taken up by the exchanger. As at the same time an equivalent amount of cations must leave the resin phase, part of the nickel concentration C_{MR} could be lost.

The concentration values obtained at the measurements and the calculated values of C_{MR} and φ are collected in Table 1. In Fig. 1 the function $\varphi(C_A)$ is

Table 1. Ion exchange measurements on the nickel acetate system.



C'_M mC	C_A mC	C_M mC	$C_{MR} \cdot 10^3$ mmole \cdot g $^{-1}$	$\varphi \cdot 10^3$ l \cdot g $^{-1}$
1.000	21.1	0.492	12.80	26.0
1.000	41.7	0.508	12.40	24.4
1.000	68.7	0.525	11.95	22.8
1.000	101.1	0.545	11.45	21.0
1.000	153.9	0.589	10.40	17.6
1.000	201	0.624	9.50	15.2
1.000	251	0.657	8.70	13.2
1.000	304	0.688	7.93	11.5
1.000	404	0.733	6.80	9.30
1.000	504	0.770	5.88	7.65
2.50	23.5	1.38	28.3	20.5
2.50	41.7	1.41	27.5	19.5
2.50	68.1	1.46	26.3	18.0
2.50	99.9	1.52	24.8	16.3
2.50	150.7	1.61	22.5	14.0
2.50	201	1.69	20.5	12.1
2.50	252	1.77	18.5	10.5
2.50	302	1.82	17.3	9.50
2.50	403	1.90	15.3	8.05
2.50	503	1.98	13.3	6.70
5.00	23.0	2.99	50.7	16.9
5.00	40.7	3.06	49.0	16.0
5.00	66.8	3.16	46.5	14.7
5.00	101.1	3.29	43.3	13.2
5.00	154.4	3.48	38.5	11.1
5.00	201	3.61	35.5	9.85
5.00	252	3.72	32.8	8.80
5.00	302	3.85	29.5	7.65
5.00	403	3.99	26.0	6.50
5.00	504	4.18	21.3	5.10

represented and in Fig. 2 the function $C_{MR}(C_A)$, in both cases at the three given values of C'_M . From these curves three pairs of values (C_{MR}, φ) are obtained at every given C_A . If the function $\varphi(C_{MR})$ is graphically represented at different C_A , it is very easy to determine by interpolation or extrapolation the function $\varphi(C_A)$ at a constant value of C_{MR} (Table 2, last column). The value $C_{MR} = 10^{-2}$

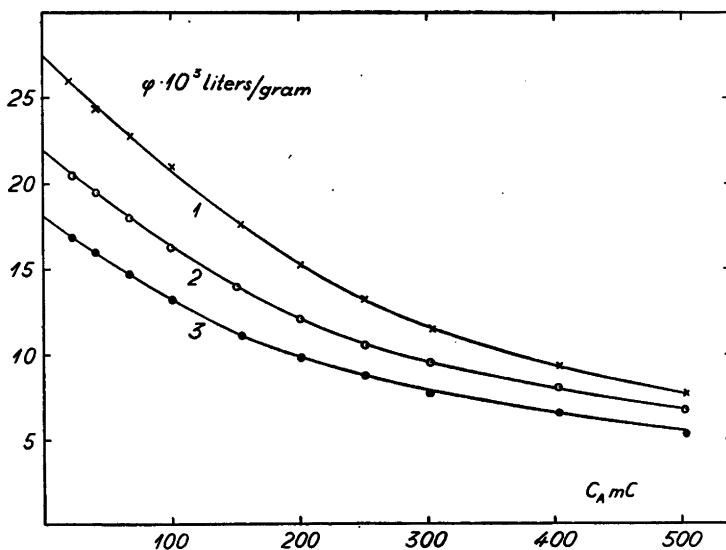


Fig. 1. The function $\varphi(C_A)$ at given values of C'_M . 1. $C'_M = 1.000$ mC; 2. $C'_M = 2.50$ mC; 3. $C'_M = 5.00$ mC.

mmoles.g⁻¹ was selected. As this corresponds to very low equilibrium concentrations C_M , we can put $[A^-] = C_A$. Then $[H^+]$ and $[H^+]_R$ are constant, and this is important, as the affinity of Ni^{2+} for the ion exchanger used is dependent on $[H^+]_R$ and thus on $[H^+]$. In the outer solution $p[H^+]$ was potentiometrically determined and had the value 4.90.

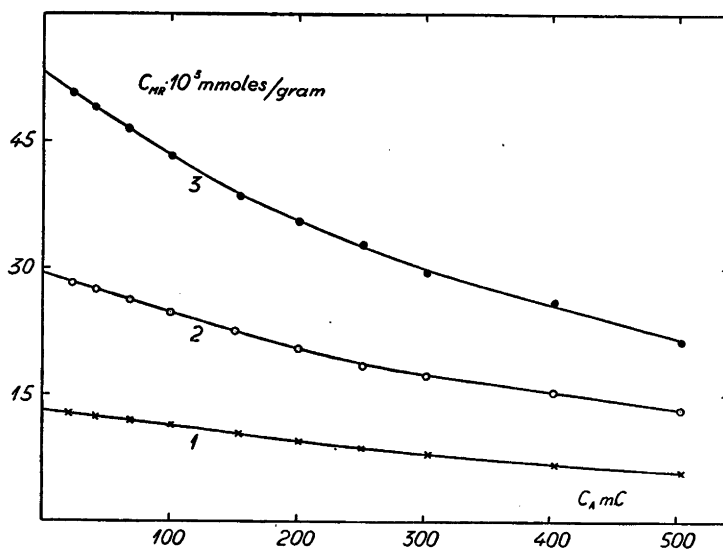


Fig. 2. The function $C_{MR}(C_A)$ at given values of C'_M . 1. $C'_M = 1.000$ mC; 2. $C'_M = 2.50$ mC; 3. $C'_M = 5.00$ mC.

Table 2. Determination of corresponding values of C_A , C_M , and φ at a constant value of C_{MR} .

C_A mC	$C'_M = 1.000$ mC		$C'_M = 2.50$ mC		$C'_M = 5.00$ mC		$C_{MR} = 10^{-2}$ mmole·g ⁻¹
	$C_{MR} \cdot 10^3$ mmole·g ⁻¹	$\varphi \cdot 10^3$ l·g ⁻¹	$C_{MR} \cdot 10^3$ mmole·g ⁻¹	$\varphi \cdot 10^3$ l·g ⁻¹	$C_{MR} \cdot 10^3$ mmole·g ⁻¹	$\varphi \cdot 10^3$ l·g ⁻¹	$\varphi \cdot 10^3$ l·g ⁻¹
0	13.20	27.6	29.4	22.0	53.1	18.1	29.0
20.0	12.80	26.1	28.5	20.7	51.1	17.0	27.3
40.0	12.50	24.7	27.6	19.6	49.1	16.0	25.7
70.0	11.95	22.6	26.2	17.9	46.2	14.6	23.4
100.0	11.40	20.7	24.8	16.3	43.4	13.2	21.2
150.0	10.45	17.8	22.6	14.1	39.0	11.3	18.0
200	9.50	15.2	20.5	12.1	35.6	9.85	15.0
250	8.75	13.3	18.8	10.6	32.6	8.70	12.9
300	8.01	11.6	17.5	9.50	29.9	7.70	11.1
400	6.90	9.40	15.4	8.05	25.7	6.45	8.85
500	5.91	7.65	13.4	6.70	21.8	5.15	7.15

When the function $\varphi([A^-])$ at $C_{MR} = 10^{-2}$ mmoles·g⁻¹ is extrapolated to $[A^-] = 0$ we get $l_0 = 29.0 \cdot 10^{-3}$ l·g⁻¹. In Table 3, column 2 the function φ_1 has been calculated according to eq. (2) and by graphic extrapolation to $[A^-] = 0$ we obtain $\beta_1 - l = 2.80$ C⁻¹. With the two limit values determined the function f has been calculated from eq. (3). When calculating only such $[A^-]$ -values have been used, at which the experimental random errors do not affect the f -values too much. In Table 3 the differences $\Delta[A^-]$, $\Delta\varphi_1$, and Δf have the following meaning:

$$\Delta[A^-] = [A^-] - 0.200 \text{ C}, \quad \Delta\varphi_1 = \varphi_1 - 4.67 \text{ C}^{-1}, \quad \Delta f = f - 3.7 \text{ C}^{-2}$$

The relation between $\Delta\varphi_1/\Delta[A^-]$ and $\Delta f/\Delta[A^-]$ can be represented by a straight line, the slope of which gives us the first complexity constant

$$\beta_1 = 4.7 \pm 0.6 \text{ C}^{-1}$$

Then we have $l = 1.9 \pm 0.6 \text{ C}^{-1}$. In the last column of Table 3 the polynomial $X_2 = \sum_{j=2}^N \beta_j [A^-]^{j-2}$ has been calculated at the higher $[A^-]$ -values. According to eq. (4) we have the following expression: $X_2 = \beta_1 \varphi_1 - f$. The values of X_2 in Table 3 are constant within the limits of experimental errors and we get

$$\beta_2 = 18 \pm 3 \text{ C}^{-2}$$

Table 3. Determination of corresponding values of φ_1 , f , and the polynomial X_2 at different values of $[A^-]$ and at $C_{MR} = 10^{-2}$ mmoles \cdot g $^{-1}$.

$[A^-]$ mC	φ_1 C $^{-1}$	f C $^{-2}$	$\frac{\Delta\varphi_1}{\Delta[A^-]}$ C $^{-2}$	$\frac{\Delta f}{\Delta[A^-]}$ C $^{-3}$	X_2 C $^{-2}$
0	2.80				
40.0	3.20				
70.0	3.41				
100.0	3.68				
150.0	4.07				
200	4.67	3.7			18.2
250	4.99	5.2	6.4	30	18.3
300	5.30	6.5	6.3	28	18.4
400	5.70	8.7	5.2	25	18.1
500	6.11	10.5	4.8	22.5	18.2

Owing to the weak complexity of the system no formation of $NiAc_3^-$ or higher complexes can be detected at the acetate ion concentrations used.

With the constants obtained at the ion exchange measurements the ligand numbers in the outer solution and in the resin phase and the composition of the complex system have been calculated. In Table 4 α_j means the fraction $[MA_j^{2-j}] \cdot C_M^{-1}$.

On the mass law products k_0 and k_1

From the intercepts on the φ — and C_{MR} — axes in Figs. 1 and 2 corresponding values of l_0 and C_{MR} are obtained. These values are collected in Table 5. For

Table 4. The ligand numbers \bar{n} and \bar{n}_R and the composition of the nickel acetate system at different $[A^-]$.

$[A^-]$ mC	\bar{n}	\bar{n}_R	$100 \cdot \alpha_0$	$100 \cdot \alpha_1$	$100 \cdot \alpha_2$
10	0.050	0.020	95.3	4.5	0.2
50	0.255	0.085	78.1	18.4	3.5
100	0.505	0.160	60.6	28.5	10.9
200	0.895	0.28	37.6	35.3	27.1
300	1.155	0.36	24.8	35.0	40.2
500	1.445	0.49	12.7	29.9	57.4

Table 5. The mass law product k_0 as a function of C_{MR} at $p[H^+] = 4.90$.

$C_{MR} \cdot 10^3$ mmole \cdot g $^{-1}$	$l_0 \cdot 10^3$ l \cdot g $^{-1}$	C_M mC	$k_0 \cdot 10^{-3}$ l $^{-1}$ \cdot g
13.2	27.6	0.478	5.34
29.4	22.0	1.34	4.34
53.1	18.1	2.93	3.69

the calculation of k_0 we have the relation: $k_0 = l_0 \cdot [Na^+]^2 \cdot [Na^+]_R^{-2}$. Because of the low nickel concentrations $[Na^+]$ and $[Na^+]_R$ are nearly constant and are given by the following connections, valid at $C_A = 0$:

$$[Na^+] = 1000 - 3 C'_M + 2 (C'_M - C_M) \text{ mC}$$

$$[Na^+]_R = 2.30 - 2 C_{MR} \text{ mmoles} \cdot \text{g}^{-1}$$

From Table 5 it is obvious that k_0 at $p[H^+] = 4.90$ is dependent on the value of C_{MR} , though this quantity is kept very small in comparison with the exchange capacity. This fact will be discussed in a following paper, and here mention will only be made that the variation of k_0 indicates that the nickel ions are not free in the same way as the sodium ions in the resin phase, but are partly coordinated to groups, fixed at the exchanger and in minute concentration.

For l_1 we have only the value that corresponds to $C_{MR} = 10^{-2}$ mmoles \cdot g $^{-1}$. It is calculated from the relation $l_1 = l_0 \beta_1^{-1}$ and then k_1 from $k_1 = l_1 \cdot [Na^+] \cdot [Na^+]_R^{-1}$. For $[Na^+]$ and $[Na^+]_R$ the approximate values 1000 mC and 2.30 mmoles \cdot g $^{-1}$ can be used, and we obtain $k_1 = 5.0$. The value of k_1 shows that the sorption affinity of the ion $NiAc^+$ for the exchanger is much greater than that of Na^+ . This fact again indicates that at the $p[H^+]$ used all the ions $NiAc^+$ are not free in the resin phase.

THE POTENTIOMETRIC INVESTIGATION

In order to get some check on the results obtained a potentiometric investigation of the nickel acetate system was also performed. The measurements for the determination of $[Ac^-]$ were carried out with the quinhydrone electrode, and the cells were of the same type as in a previous paper^{7, p. 78}. The solution of the one half-cell had the composition:

$$\left\{ \begin{array}{l} C_M \text{ mC Ni(ClO}_4)_2 \\ C_A \text{ mC NaAc} \\ 0.5 C_A \text{ mC HAc} \\ (1000 - 3 C_M - C_A) \text{ mC NaClO}_4 \end{array} \right.$$

Table 6. Determination of $\bar{n}/[A^-]$ as a function of $[A^-]$ from emf measurements.

C_M mC	C_A mC	E_A mV	$-\vartheta$ mC	$[A^-]$ mC	$\bar{n}/[A^-]$ C ⁻¹
101.0	12.99	13.6	0.32	7.95	5.89
101.0	19.23	12.7	0.32	12.02	5.68
101.0	31.3	12.1	0.32	19.8	5.60
101.0	45.5	11.7	0.3	29.0	5.53
101.0	58.8	11.3	0.3	38.0	5.34
101.0	83.3	10.9	0.3	54.5	5.09
101.0	125.0	10.2	0.3	83.8	4.83
101.0	159.1	9.9	0.3	108	4.67
101.0	200	9.5		137	4.57
101.0	250	9.0		175	4.24
101.0	313	8.4		224	3.94
101.0	400	7.7		295	3.52
50.0	12.99	7.2	0.16	10.01	5.64
50.0	19.23	6.8	0.16	14.94	5.53
50.0	31.3	6.4	0.16	24.5	5.39
50.0	45.5	6.1	0.2	36.0	5.17
50.0	58.8	5.9	0.2	46.8	5.04
50.0	83.3	5.7	0.2	66.8	4.88
50.0	125.0	5.4	0.2	101.5	4.65
50.0	159.1	5.1	0.2	130	4.46
50.0	200	4.8		165	4.24
50.0	250	4.6		209	3.92
50.0	313	4.3		264	3.71
50.0	400	3.8		344	3.26

Measurements were performed with $C_M = 0, 50,$ and 101 mC and with varying values of C_A . At $C_M = 0$ the emf of the cell is independent of C_A and denoted E_0 . The difference between E_0 and the emf at the other C_M -values is called E_A . The values obtained of E_A are collected in Table 6. The quantities $[A^-]$ and $\bar{n}/[A^-]$ have been calculated from the eq. (19–21) of the previous paper^{7, p. 79}. In these equations we have only to replace $[B]$, C_B , and E_B by $[A^-]$, C_A , and E_A and put $\vartheta_0 = 0$. In the present case the correction term ϑ is equal to the difference between $[H^+]$ in the complex solution and $[H^+]$ in the solution with $C_A = 0$ but with the same C_M -value.

From Fig. 3 it is obvious that the function $\bar{n}/[A^-]$ at small values of the variable $[A^-]$ is not entirely independent of C_M , but the dependence is very slight, proving that practically only mononuclear complexes are formed,

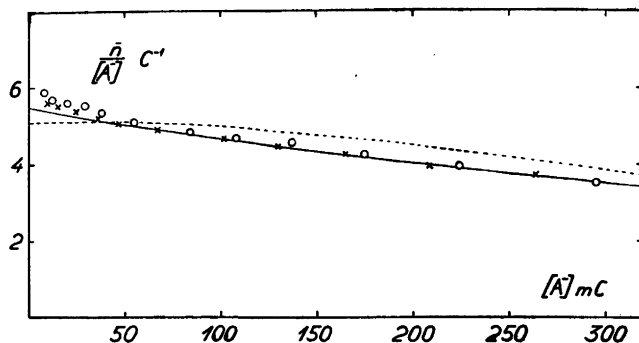


Fig. 3. $\bar{n}/[A^-]$ as a function of $[A^-]$. — Circles and crosses relate to the emf measurements at $C_M = 101$ and 50 mC respectively, and the full drawn curve represents the limiting function at $C_M = 0$. — The dashed curve is the same limiting function calculated from the ion exchange measurements.

and the limiting function valid at $C_M = 0$ can be obtained at once. From its value at $[A^-] = 0$ we get $\beta_1 = 5.5 \pm 0.3 C^{-1}$.

For the sake of comparison in Fig. 3 the same limiting function has been calculated from the values of \bar{n} and $[A^-]$ in Table 4. The agreement between the two curves of the same function is quite satisfactory, if we take into consideration that the potentiometric measurement of $[A^-]$, which is the only potentiometric method available in this case, is not very suitable for an accurate determination of β_2 and higher complexity constants, if the complexity is as slight as that of the nickel acetate system.

Thus, as the polynomial X and the complexity constants are uniquely determined ^{7, eq. (12)} by the limiting function mentioned above, the results from the ion exchange investigation are confirmed.

SUMMARY

The complex equilibria of the nickel acetate system are investigated by the use of a cation exchanger and potentiometrically.

The results from the two investigations are consistent and prove the existence of two mononuclear complexes, *viz.* $NiAc^+$ and $NiAc_2$, at acetate ion concentrations ≤ 500 mC. From the emf measurements it can be concluded that practically no polynuclear complexes are formed. At the temperature $20^\circ C$ and the ionic strength $I = 1$ C the complexity constants of the complexes formed are:

$$\beta_1 = 4.7 \pm 0.6 C^{-1}, \beta_2 = 18 \pm 3 C^{-2}$$

The sorption of NiAc^+ by the ion exchanger is studied. The fraction of the total nickel concentration in the resin phase that consists of the complex mentioned, is obtained as a known function of $[\text{Ac}^-]$ in the outer solution.

My thanks are due to Professor S. Bodfors for kindly putting an assistant at my disposal and for his interest in this work.

REFERENCES

1. Fronæus, S. *Acta Chem. Scand.* **5** (1951) 859.
2. Calame, P. *Z. physik. Chem.* **27** (1898) 401.
3. Major, E. *Acta Univ. Szegediensis, Acta Chem. et Phys.* [N.S.] **1** (1942) 17; *C. A.* **41** (1947) 7257c.
4. Okác. A. *Z. anal. Chem.* **88** (1932) 189.
5. Auger, V., and Billy, M. *Compt. rend.* **136** (1903) 555.
6. Fronæus, S. *Komplexsystem hos koppar.* (1948). Lund.
7. Fronæus, S. *Acta Chem. Scand.* **4** (1950) 72.

Received November 20, 1951.