BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2758—2761 (1973)

A Study of Complex Formation by the Cation Exchange Method. Bivalent Metal Complexes with Univalent Anions

Emiko OHYOSHI*
Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto 860

(Received November 13, 1972)

An attempt was made to estimate the amount of the cationic complex MA^+ adsorbed on a cation exchanger. This method is based on the fact that the ratio of the distribution coefficients of M^{2+} and MA^+ should vary with the ionic strength of the medium. The Ni(II) acetate system studied by Fronaeus has been reexamined. The results show that the distribution coefficient of $NiAc^+$ (Ac=acetate) is negligible compared with that of Ni^{2+} upon the variation of the ionic strength from 0.2 to 1.0. It was found that Fronaeus overestimated the distribution coefficient of $NiAc^+$ and that this caused the value of β_2 to be much greater. In conclusion, the two functions, φ_1 and f, introduced by Fronaeus could not be determined with high accuracy; for the stability constants obtained by Fronaeus's method, they must be confirmed by conducting the experiment at a different ionic strength.

The cation exchange resin has been widely used for the study of complex formation. In cases where the reaction $M^{2+}+A^-=MA^+$ or $M^{3+}+A^-=MA^{2+}$ occurs, it is difficult to estimate the amounts of them adsorbed on the resion. Fronaeus proposed a method to analyze the data under such conditions and used it to study the acetate complexes of Ni(II)[1] and Ce(III)[2] and the thiocyanate complexes of Ni(II).[3] In these investigations, he estimated an appreciable amount of the cationic complex to be adsorbed on the resin. On the other hand, it has been demonstrated, by means of acetate labelled with tritium and with ^{14}C, that the cationic species of Co(II) and Mn(II) acetate complexes are not taken up by the cation exchanger.[4] If Fronaeus overestimated the distribution coefficient of the cationic complex of Ni(II) acetate, the evaluation of the stability constants would also be higher.

In this study, we attempted to ascertain the extent of the adsorption of a cationic complex, MA^+, experimentally. Although M^{2+} and MA^+ were both adsorbed on the resin, the change in the ionic strength of the medium should have different effects on their distribution coefficients depending on the different ionic charges. From this, we can conclude whether the extent of the adsorption of MA^+ is appreciable or negligible. This method was applied to study the Ni(II) acetate system, and the results were compared with those obtained by Fronaeus's method.

Estimation of the Amount of MA^+ Adsorbed on a Cation Exchanger. When a cation exchange resin, NaR, is added to a solution involving a free metal ion, M^{2+}, and the complexes MA^+, MA_2, ⋯, MA_n^{2-n}, the following exchange equilibria are established:

$$M^{2+} + 2NaR = MR_2 + 2Na^+ \tag{1}$$

$$MA^+ + NaR = MAR + Na^+ \tag{2}$$

The distribution coefficients of M^{2+} and MA^+, l_0 and l_1, can be expressed as:

$$l_0 = [MR_2]/[M^{2+}] = k_0[NaR]^2/[Na^+]^2$$

$$l_1 = [MAR]/[MA^+] = k_1[NaR]/[Na^+]$$

where k_0 and k_1 are the equilibrium quotients of Reactions (1) and (2). The distribution of the metal, M(II), between resin and solution is given as:

$$\varphi = \frac{l_0(1+l_1'[A^-])}{1+\sum\beta_j[A^-]^j} \tag{3}$$

where $l_1'=l_1\beta_1/l_0$ and $\beta_j=[MA_j^{2-j}]/([M^{2+}][A^-]^j)$. For the determination of β_j under such conditions, Fronaeus[1] introduced two functions, φ_1 and f:

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* Present address: Kurokami Radioisotope Laboratory, Kumamoto University, Kumamoto.

[1] S. Fronaeus, *Acta Chem. Scand.*, **6**, 1200 (1952).

[2] S. Fronaeus, *Svensk Kem. Tidskr.*, **65**, 19 (1953).

[3] S. Fronaeus, *Acta Chem. Scand.*, **7**, 21 (1953).

[4] N. C. Li, W. M. Westfall, A. Lindenbaum, J. M. White and J. Schubert, *J. Amer. Chem. Soc.*, **79**, 5864 (1957).

$$\varphi_1 = (l_0/\varphi - 1)/[\mathrm{A}^-] \qquad (4)$$

$$\varphi_1{}^0 = \lim_{[\mathrm{A}^-]=0} \varphi_1 = \beta_1 - l_1{}'$$

$$f = [(l_0/\varphi)\{(\beta_1 - l_1{}')[\mathrm{A}^-] - 1\} + 1]/[\mathrm{A}^-]^2$$

$$= \beta_1\varphi_1 - \sum_{j=2}^{n}\beta_j[\mathrm{A}^-]^{j-2} \qquad (5)$$

At relatively small values of $[\mathrm{A}^-]$, the following relation between the differences can be given:

$$\Delta f = \beta_1\Delta\varphi_1 - \beta_3\Delta[\mathrm{A}^-] \qquad (6)$$

β_1 can be obtained graphically from Eq. (6); $\beta_2, \beta_3 \cdots \beta_n$ can also be obtained from Eq. (5).

This method has been widely used in the study of complex formation containing cationic species. However, the evaluation of l_1/l_0 seems to be generally large, considering the differences in the ionic charge and in the size of M^{2+} and MA^+, *e.g.*, $l_1/l_0=0.78$ for the Mn(II) chloride system at $\mu=0.69$.[5] In this case, the value of k_1 is estimated to be greater than that of k_0. If l_1/l_0 is overestimated, all of the formation constants of complexes β_1, β_2, $\cdots$, β_n would also be overestimated. As may be seen from Eq. (4), the function φ_1 comes to involve a large error as $[\mathrm{A}^-]$ approaches 0 where $l_0/\varphi \simeq 1$. The value of $\beta_1 - l_1{}'$ obtained from the extrapolation of φ_1 to $[\mathrm{A}^-]=0$ must also be uncertain. Since this value affects the function f, reliable values for β_1, β_2, $\cdots$, β_n can not be expected by means of the functions φ_1 and f.

The use of the function $1/\varphi$, whose accuracy is much greater than that of φ_1 at small values of $[\mathrm{A}^-]$, may be more feasible for the analysis of the data.

$$\frac{1}{\varphi} = \frac{1}{l_0}\,\frac{1+\sum\beta_j[\mathrm{A}^-]^j}{1+l_1{}'[\mathrm{A}^-]} \qquad (7)$$

Differentiating $1/\varphi$ and assuming that the terms greater than $[\mathrm{A}^-]^2$ can be neglected at small values of $[\mathrm{A}^-]$, we obtain:

$$\frac{\mathrm{d}(1/\varphi)}{\mathrm{d}[\mathrm{A}^-]} \simeq \frac{1}{l_0}\,\frac{(\beta_1 - l_1{}') + 2\beta_2[\mathrm{A}^-]}{1+2l_1{}'[\mathrm{A}^-]} \qquad (8)$$

This equation shows that when $l_1{}'$ can not be neglected, a plot of $1/\varphi$ *vs.* $[\mathrm{A}^-]$ at small values of $[\mathrm{A}^-]$ gives a curve the slope of which decreases ($\beta_2/l_1{}' < \beta_1 - l_1{}'$) or increases ($\beta_2/l_1{}' > \beta_1 - l_1{}'$) with an increase in $[\mathrm{A}^-]$. On the other hand, if the plot gives a straight line and if the intercept agrees with the value of $1/l_0$ obtained experimentally, it can generally be concluded that $l_1{}'$ can be neglected and that the slope corresponds to β_1/l_0. Though it is rare, an apparent linear relation between $1/\varphi$ and $[\mathrm{A}^-]$ will be given when $\beta_2/l_1{}' \simeq \beta_1 - l_1{}'$. In this case, the slope corresponds to $(\beta_1 - l_1{}')/l_0$. However, we can readily distinguish between the two cases. The linear relation can be settled at any concentration of Na^+ in the former case, while it can not be expected in the latter since the value of $\beta_2/l_1{}'$ becomes smaller of greater than that of $\beta_1 - l_1{}'$ at a different Na^+ concentration.

The term $\beta_1 - l_1{}'$, which can be obtained from the slope of the $1/\varphi$ plot *vs.* $[\mathrm{A}^-]$ at $[\mathrm{A}^-]=0$ (see Eq. (8)), is expressed by:

$$\beta_1 - l_1{}' = \beta_1\{(1 - k_1[\mathrm{Na}^+]/(k_0[\mathrm{NaR}])\} \qquad (9)$$

When $[\mathrm{Na}^+] \gg [\mathrm{M}^{2+}]$ and $[\mathrm{NaR}] \gg [\mathrm{MR}]$, we obtain:

$$\beta_1 - l_1{}' = \beta_1(1 - K[\mathrm{Na}^+]) \qquad (10)$$

where K is nearly constant. The β_1 varying with the ionic strength can be estimated by the change in the activity coefficient of M^{2+}, γ. The relation expressed by:

$$\beta_1 = \gamma\beta_{1(\mathrm{a})}/\gamma_{(\mathrm{a})} \qquad (11)$$

where $\beta_{1(\mathrm{a})}$ and $\gamma_{(\mathrm{a})}$ are β_1 and γ at a fixed ionic strength of a. By substituting this equation to Eq. (10), we obtain:

$$\gamma_{(\mathrm{a})}(\beta_1 - l_1{}')/\gamma = \beta_{1(\mathrm{a})}(1 - K[\mathrm{Na}^+]) \qquad (12)$$

When the values of $(\beta_1 - l_1{}')\gamma_{(\mathrm{a})}/\gamma$ decrease with an increase in $[\mathrm{Na}^+]$, a linear relation can be obtained in a range where K is practically constant. From the slope, the magnitude of $K[\mathrm{Na}^+]$, that is, l_1/l_0, can be estimated. On the other hand, the values remain essentially constant; in other words, the decrease in $\beta_1 - l_1{}'$ with an increase in the ionic strength is the same as that caused by the decrease in the activity of M^{2+}, the ratio l_1/l_0 is very small in comparison with unity, and $l_1{}'$ can practically be neglected.

Experimental

Materials. A stock solution of Ni(II) was prepared by dissolving $\mathrm{NiCl_2 \cdot 6H_2O}$ in 1.0 M $\mathrm{NaClO_4}$ to obtain the concentration of 0.01 M. The solution involving 1.0 M $\mathrm{CH_3COONa}$ and 1.0 M $\mathrm{CH_3COOH}$ was diluted with 1.0 M $\mathrm{NaClO_4}$ to produce various acetate concentrations at $\mu=1.0$. In a similar manner, acetate soltuions at other ionic strengths (0.2—0.5) were prepared. All the chemicals used were of a G.R. grade. For the cation exchanger, Dowex 50W-X8 (100—200 mesh) in the sodium form was used.

Procedures. The ion-exchange experiments were carried out as follows. The solutions (10 ml) made up from the stock solution of Ni(II) (1.0 ml) and the solutions in varying acetate concentrations (9.0 ml) were shaken with portions of dry resin (0.2—0.5 g) in 20 ml glass vials with stoppers for 8 hr at 25 °C. Then the amount of Ni(II) in each supernatant was determined by EDTA titration, using murexide as the indicator. The distribution coefficient, φ, was calculated as follows:

$$\varphi = \frac{\text{mmol of Ni(II) in the resin/mass of dry resin (g)}}{\text{mmol of Ni(II) in the soln./vol. of soln. (ml)}}$$

Results and Discussion

Measurements of l_0. Fronaeus reported that the distribution coefficient of Ni(II) is dependent on the concentration of $\mathrm{NiR_2}$, though it is kept very small in comparison with the exchange capacity. He concluded that Ni^{2+} ions are not as free as Na^+ ions in the resin phase, but are partly coordinated to groups fixed at the exchanger. Thus, he corrected the φ values to that at a constant value of [NiR], 10^{-2} mmol/g, for the calculation of the formation constants of Ni(II) acetate complexes. It is important to know whether or not the exchange reaction between the Ni^{2+} ion and NaR is reversible. In the case of a reversible reaction involving a minute amount of M^{2+} compared with $[\mathrm{Na}^+]$ and [NaR], the value of l_0 should remain

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[5] D. F. C. Morris and E. L. Short, *J. Chem. Soc.*, **1961**, 5148.

Table 1. Effect of variation in the mass of resin on l_0 of Ni(II), pH=4.5, μ=1.0, volume of soln.=10.0 ml

Mass of resin (g)	l_0
0.200	15.6
0.300	16.5
0.400	16.0
0.500	15.8

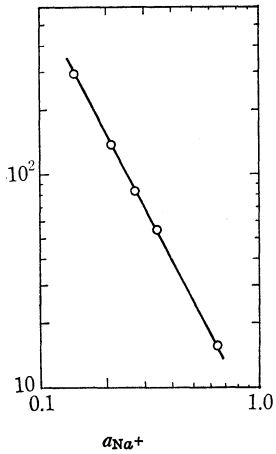

Fig. 1. Relationship between l_0 of Ni(II) and the activity of Na+ ion.

unchanged with a varying mass of resin, and a linear relation whose slope is 2 should be obtained between log l_0 and the log of the activity of Na^+. To examine the reversivility, we measured l_0 as a function of the mass of the resin and the concentration of Na^+ in the solution. As is shown in Table 1 and Fig. 1, the value of l_0 remains practically constant with the variation in the mass of resin from 0.2 to 0.5 g, and the plot of log l_0 *vs.* the log of the activity of Na^+ yields a straight line with the slope of 2. From these results, the reversible exchange reaction between the Ni^{2+} ion and the exchanger, NaR, could be confirmed.

The Ni(II) Acetate System. The Ni(II) acetate complexes were studied by the cation exchange method. Figure 2 shows the realtion between $1/\varphi$ and $[Ac^-]$ at the same ionic strength as that used by Fronaeus (μ=1.0). At the values of $[Ac^-]$ examined, a linear relation is obtained and the intercept of the line agrees well with the value of $1/l_0$ obtained experimentally. This indicates either that l_1' is negligible or that β_1-l_1' is nearly equal to β_2/l_1. To know the magnitude of l_1', the experiments were carried out at the Na^+ concentrations of 0.2, 0.3, 0.4, and 0.5. The results are shown in Fig. 3, where $1/\varphi$ is plotted *vs.* $[Ac^-]$. All of the plots yield a good linearity, and the intercept of each line agrees well with the values of $1/l_0$ obtained at the corresponding concentration of Na^+. From this, we can conclude that l_1' is negligible at an ionic strength of less than 1, since it is unreasonable to say that the relation $\beta_1-l_1'\simeq\beta_2/l_1'$ is settled at any concentration of Na^+. The values for β_1-l_1' are given as 6.5, 5.9, 5.6, and 5.5 from the slopes of the straight lines at μ= 0.2, 0.3, 0.4, and 0.5. In Eq. (12), when we take the fixed ionic strength as 0.2, the values of $\gamma_{(0.2)}$ $(\beta_1-l_1')/\gamma$ at μ=0.2, 0.3, 0.4, 0.5, and 1.0 were calculated to be 6.5, 6.7, 6.7, 6.8, and 6.0 by the estimation of the activity coefficient of Ni^{2+} from the formula of Davies:[6] $\log \gamma_i=-0.5Z_i^2\sqrt{\mu}/(1+\sqrt{\mu})+0.1Z_i^2\mu$, where $Z_i=2$. These values seem to be essentially the same, considering that the γ values were calculated from an approxinate formula. That is, the extent of the decrease in β_1-l_1' with an increase in the ionic strength is nearly equal to that caused by the decrease in the activity of Ni^{2+}. The acetate complex of Ni(II), $NiAc^+$, like those of Co(II) and Mn(II),[4] is not taken up by the cation exchanger to any appreciable extent. Thus, the values of β_1 at μ=0.2, 0.3, 0.4, 0.5, and 1.0 were obtained as 6.5, 5.9, 5.6, 5.5, and 5.2. The values for β_2 could not be determined exactly in the range of low concentrations of Ac^- studied. Fronaeus reported that β_1=4.7 and β_2=18 at μ=1.0. Although the value of β_1 is in fair agreement with our results, the value of β_2 appears to be too large. If such a high value is given for β_2, the slope of the lines in Fig. 3 must be increased with an increase of $[Ac^-]$, even at small values of $[Ac^-]$. This large value of β_2 is caused by the estimation of l_1' as 1.9.

The value of 6.5 at μ=0.2 obtained for β_1 in this study is larger than that of 2.6 determined by polaro-

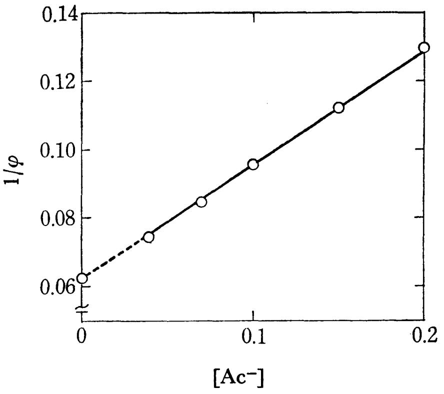

Fig. 2. A plot of $1/\varphi$ *vs.* $[Ac^-]$ for Ni(II) acetate system at μ=1.0.

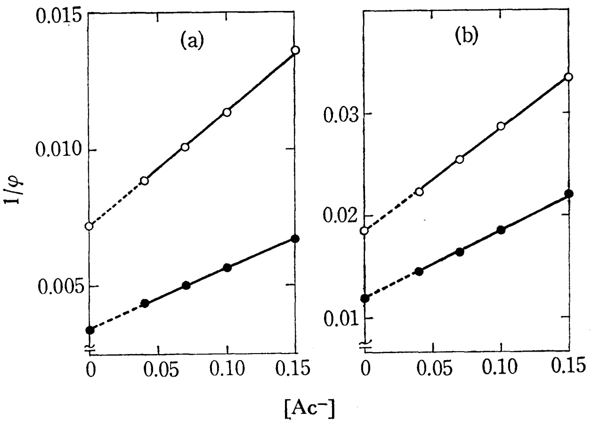

Fig. 3. Plots of $1/\varphi$ *vs.* $[Ac^-]$ for Ni(II) acetate system at various ionic strengths; (a) μ=0.2 —●—, μ=0.3 —○—, (b) μ=0.4 —●—, μ=0.5 —○—.

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[7] N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).

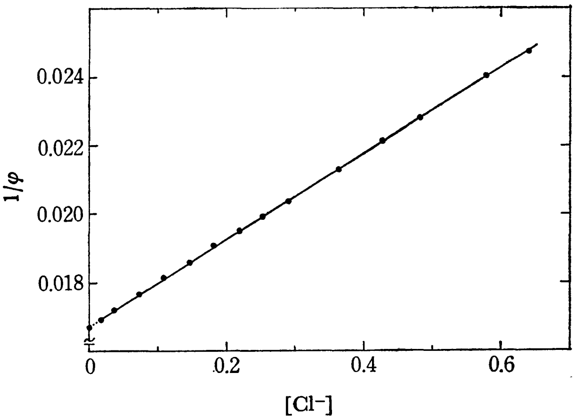

Fig. 4. A plot of $1/\varphi$ *vs.* [Cl⁻] for Mn(II) chloride system.[5]

graphy[7] at the same ionic strength. However, this value of 2.6 seems to be rather small in comparison with the value of 10 determined at $\mu=0.1$ by potentiometry.[8]

Mn(II) Chloride System. The study of Mn(II) chloride complexes by Fronaeus's method[5] appears to be a similar example of overestimating l_1'. Morris and Short estimated l_1' to be 2.98 and determined the formation constants, β_1, β_2, and β_3, to be 3.85, 1.80, and 0.44 at $\mu=0.691$. These values are comparable to those of the Fe(III) chloride complexes.[9] For the calculation of the function, φ_1, from which the value of β_1-l_1' was obtained, they used the value of l_0 obtained experimentally. As is shown in Fig. 4, when we try to plot the function $1/\varphi$ against [Cl⁻], a good linearity is yielded over the range of [Cl⁻] investigated and the intercept of the line agrees with the value of $1/l_0$ within the limits of experimental error ($\pm 0.5\%$). Assuming that $l_1'\simeq 0$, β_1 is obtained as 0.75. This value is close to that of 1.1 obtained by polarography.[10] It is noted that the evaluation of β_1-l_1' by Fronaeus's method is much affected by the value of l_0 adopted; that is, β_1-l_1' is greatly varied with a minute change in l_0.

In conclusion, when l_1' is estimated by Fronaeus's method to be appreciable, it is necessary to confirm the results by an experiment at a different ionic strength.

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9) E. Rabinowitch and W. H. Stockmayer, *J. Amer. Chem. Soc.*, **64**, 345 (1942).

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