J. Chem. Eng. Data 1995, 40, 1091−1093

Determination of the Thermodynamic Stability Constant of the Magnesium Complex of Malonic Acid by Using an Ion-Exchange/Inductively Coupled Plasma Atomic Emission Spectroscopy Method

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An ion-exchange column/inductively coupled plasma atomic emission spectroscopy method was employed to measure the thermodynamic stability constant of the 1:1 magnesium−malonate complex. The method involves pumping buffered solutions containing magnesium and malonate ions through a microcolumn of strong-acid-type cation exchange resin until equilibrium between the solution and resin phases is attained. After an air purge and water wash the sorbed magnesium ions, which are present in an amount related to the free magnesium in solution, are eluted with nitric acid and measured by inductively coupled plasma atomic emission spectroscopy. Although nonlinear calibration curves are obtained under the nontrace ion-exchange conditions used, precise and accurate free magnesium concentrations are obtained. The method is straightforward and easy to use, and is applicable to a variety of systems that are not easily measured by other methods.

Background of Method

For the reaction between magnesium(II) and malonic acid (H_2L) in water at a pH sufficiently high to ensure the malonate is all in the L^{2-} form, the single equilibrium involved is

$$\mathrm{Mg^{2+} + L^{2-} \overset{K}{\leftrightarrow} MgL}$$

In the presence of a strong-acid-type cation exchange resin in the potassium form, RK, the potassium ion also takes part in the equilibrium

$$\mathrm{Mg^{2+} + 2RK \overset{K_{IE}}{\leftrightarrow} R_2Mg + 2K^+}$$

with K_{IE} equal to $[R_2Mg][K^+]^2/([Mg^{2+}][RK]^2)$. The distribution ratio λ for $[Mg^{2+}]$ between the resin and solution phase can be defined as $\lambda = [R_2Mg]/[Mg^{2+}] = K_{IE}[RK]^2/[K^+]^2$. Rearrangement gives $[Mg^{2+}] = [R_2Mg]/\lambda$, which shows that the concentration of free, unhydrated, magnesium ion in solution is proportional to the quantity of magnesium ions sorbed on the resin if [RK] and $[K^+]$ remain constant. This is defined as trace conditions. Concentrations are used rather than activities because the calibration plots are run under the same conditions as the samples.

When levels of $[Mg^{2+}]$ in solution become high relative to $[K^+]$, such that more than 1% of the resin exchange sites become occupied by magnesium ions, [RK] does not remain constant and the calibration plots become curved. These nontrace conditions do not, however, preclude application of the method (Ren and Kratochvil, 1995).

Experimental Section

Reagents and Solutions. A 0.1 M solution of magnesium nitrate was prepared by dissolving the appropriate amount of $Mg(NO_3)_2{\cdot}6H_2O$ in water and diluting to 500 mL in a volumetric flask. The composition of the salt was taken as $Mg(NO_3)_2{\cdot}5.9H_2O$ on the basis of titration of the magnesium with EDTA. A 1 M solution of potassium nitrate was prepared by dissolving the required amount of KNO_3 in water and diluting to 1 L. One pH 9.15 buffer solution, 0.2 M in NH_4NO_3 and 0.1 M in NH_3, was prepared by diluting 10 mL of concentrated ammonia and 50 mL of 2 M nitric acid to 500 mL (buffer solution 1), and another, 0.1 M in $(NH_4)_2C_3H_2O_4$ and 0.1 M in NH_3, by weighing the required amount of malonic acid ($HOOCCH_2COOH$), transferring it quantitatively to a 500-mL volumetric flask containing 10 mL of concentrated ammonia, and diluting the solution to volume with water (buffer solution 2). All chemicals were reagent grade or better. Distilled water was passed through a Barnstead NANOpure water purification system before use.

Apparatus. The ion-exchange column was constructed following the design of Cantwell et al. (1982), using 14.4 mg of 200−400 mesh Dowex 50Wx8 strongly acidic cation-exchange resin. The procedure for its use in a pumped flow system has been previously described (Ren and Kratochvil, 1995). A thermostated circulating water bath (Lauda Model K2) was used to maintain the temperature of the column and the samples at (25.0 ± 0.2) °C. Measurements of magnesium eluted from the resin column were made with an ARL Model 34000 direct reader inductively coupled plasma atomic emission spectrometer using standard operating conditions for the determination of magnesium. A Fisher ACCUMET Model 520 digital pH/ion meter with a Fisher combination glass electrode (model 13-620-92) was used to measure the pH values of the solutions.

Procedure. Operation of the flow system involves five steps: (1) The solution being analyzed for free magnesium is pumped through the resin column until equilibrium between the resin and fresh solution is achieved (i.e., effluent from the column has the same concentration as the influent). (2) Air is pumped through the column to clear most of the sample solution from the column and connecting tubing. (3) Water is passed through the column to flush all traces of remaining sample solution from the column. (4) 2 M HNO_3 is passed through the column to elute all cations from the resin. (5) Pure water is passed through the column to flush nitric acid from the system and prepare it for the next sample. The eluent from steps 4 and 5 is collected in a 10-mL volumetric flask and analyzed for magnesium by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

0021-9568/95/1740-1091$09.00/0 © 1995 American Chemical Society

Experiments were carried out at ionic strengths of 0.10, 0.15, and 0.20 mol L^{-1} by preparing three sets of standards and samples with differing amounts of KNO_3. The standards were prepared by mixing varying amounts of magnesium nitrate solution with 2.5 mL of buffer solution 1 and sufficient potassium nitrate solution to provide the desired ionic strength and diluting to 25 mL with water in volumetric flasks. The samples were prepared by mixing varying amounts of magnesium nitrate solution with 2.5 mL of buffer solution 2 (giving the same concentration of ammonium ion as for the standards) and the same amount of potassium nitrate as in the standards at each ionic strength and diluting to 25 mL with water in volumetric flasks. The total magnesium ion concentration in the standards ranged from 0.8 to 4 mM; free magnesium concentrations in the samples also fell within this range.

Each solution was put into the water bath for at least 10 min to bring the temperature to 25 °C before it was equilibrated with the resin in the column. Approximately 10 mL of each solution was required for equilibration with the resin; the remaining solution was used to check the pH. For all of the solutions the pH values were found to be in the range 9.10−9.20. The column eluent for each solution was analyzed for magnesium, and the free magnesium concentration was obtained by comparing the intensity of the ICP-AES signal for magnesium in the column eluent with a calibration curve obtained from standards at each ionic strength. The difference between the total and free magnesium concentrations in each sample was taken to correspond to magnesium bound as a 1:1 malonate complex, and the difference between the total and the magnesium-complexed malonate concentrations was taken to be free malonate. These assumptions may be considered valid if (1) the formation of a magnesium complex with ammonia is negligible at the ammonia concentration of 1 mM used in the standards and samples and (2) malonic acid (H_2L) is essentially all in the L^{2-} form at pH 9.15. The only reported study of an ammonia complex with magnesium was by Szymaszek and Biernat (1973), who gave a K_1 of 0.19 at 0 °C in 2.4 M Na_2SO_4 by polarography. Application of their K value to the conditions of this study indicates the concentration of $Mg(NH_3)^{2-}$ is small enough to be neglected. Assumption 2 is applicable on the basis of consideration of the malonic acid pK_a values {2.65 for pK_{a1} ($[H_2L]/([HL^-][H^-])$) and 5.28 for pK_{a2} ($[HL^-]/([H^-][L^{2-}])$)} at an ionic strength of 0.1 and 25 °C (Martell and Smith, 1977). The conditional stability constant of the magnesium−malonate complex was calculated from the relation $K_{cond} = [MgL]/([Mg^{2+}][L^{2-}])$ where $[Mg^{2+}]$ and $[L^{2-}]$ are the free magnesium and free malonate concentrations for each sample.

Results and Discussion

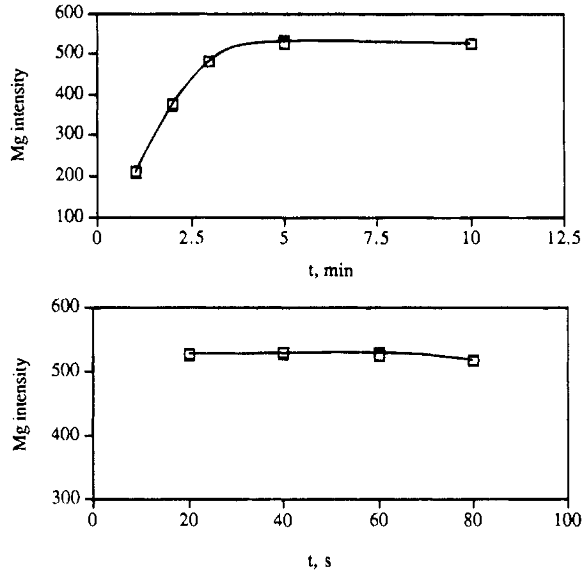

Figure 1. Magnesium concentration, as ICP-AES signal intensity, in eluent from equilibrated strong-acid resin column as a function of column−solution equilibration time t in minutes (elution time of 1 min) (top) and as a function of column elution time t in seconds (equilibration time of 5 min) (bottom). The equilibration solution contained 0.8 mM Mg^{2+} buffered at pH 9.15 and adjusted to an ionic strength of 0.1 mol L^{-1} with KNO_3. All points were run in triplicate.

Column Equilibration and Elution Study. A standard solution containing the lowest magnesium concentration was used to find the time required for equilibrium between the resin and solution phases and to determine the time needed to elute all the magnesium from the resin phase. To obtain the minimum equilibration time, the standard solution was pumped through the column for 1, 2, 3, 5, or 10 min, while the elution time was held at 1 min. The magnesium signal intensity for each eluent was measured by ICP-AES on the eluted sample following dilution to 10 mL with water. The upper plot in Figure 1 shows how the magnesium signal intensity plateaus once equilibration between the resin and solution phases has been achieved. At this point the composition of the solution leaving the column is the same as that entering it, and the resin is in equilibrium with unperturbed solution. On the basis of this study a minimum time of 5 min was chosen as the column equilibration time for subsequent work.

The time required for complete elution of magnesium from the column was determined by equilibrating the column with sample solution for 5 min and then eluting the cations with 2 M HNO_3 for 20, 40, 60, or 80 s, collecting the eluent, and analyzing it for magnesium as above. From the results, shown in the lower plot in Figure 1, all magnesium was eluted from the column within 20 s. We used 1 min as the elution time for all the studies reported here.

Use of Nonlinear Calibration Curves. Traditional ion-exchange methods for stability constant measurements require that equilibration between the resin and the solution phases be made under trace ion-exchange conditions (Rossetti and Rossotti, 1961; Schubert, 1954; Schubert and Lindenbaum, 1952) because only then is the amount of metal ion of interest in the resin phase directly proportional to its free concentration in the solution phase. In this study we found it necessary to make the measurements under nontrace conditions because of drawbacks to using the ion-exchange/ICP-AES method under trace conditions. One drawback is that at the ionic strengths used here the magnesium concentration must be below 5×10^{-5} M to maintain trace ion-exchange conditions (Hewavitharana and Kratochvil, 1993). At this level a minimum of 10 min is required to achieve equilibration between the resin and solution phases with a 14.4 mg column, which doubles the experimental time. The alternative of using a smaller column was not feasible because the small amounts of magnesium obtained on elution approached the limit of detection of the ICP-AES method measurements. A second drawback is that at very low overall concentrations of magnesium even traces of the metal in the KNO_3 used for ionic strength adjustment or in the buffer solution contribute significantly to the overall amount measured, resulting in calibration plots that, though linear, give nonzero intercepts.

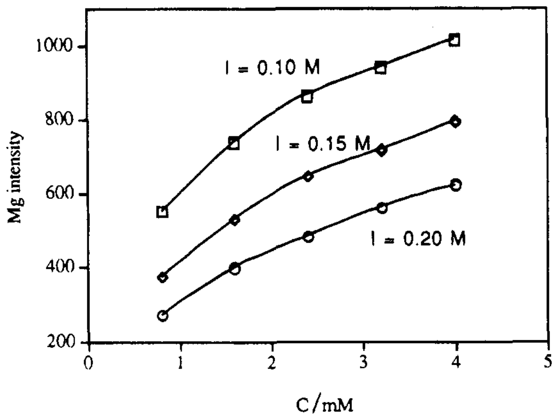

Figure 2. Calibration curves for magnesium eluted from an ion-exchange column, as determined by ICP-AES, at various ionic strengths. All points were run in triplicate.

These problems were overcome by using millimolar level magnesium concentrations and carrying out the ion exchange under nontrace conditions. Figure 2 shows the calibration curves obtained at the three ionic strengths studied. Even though the plots are nonlinear, the relationship between magnesium intensity and free magnesium concentration can be established with good accuracy and precision. Note that these curved plots can only be used to calculate free magnesium concentrations when the concentrations of other cations are held constant in all standards and samples.

Calculation of the Thermodynamic Stability Constant. Three sample solutions were prepared, each containing a fixed amount of malonic acid but different amounts of magnesium at an ionic strength adjusted to 0.1 with KNO_3. The eluent from the column for each sample was measured three times by ICP-AES. A free magnesium concentration was determined for each magnesium signal intensity, and then a conditional stability constant value was calculated as described above. In this way three values for the conditional stability constant were obtained. The experiment was then repeated at ionic strengths of 0.15 and 0.2. The average conditional stability constants at the three ionic strengths, with their standard deviations, were for $I = 0.10$, $\log K = 2.045 \pm 0.006$, for $I = 0.15$, $\log K = 1.970 \pm 0.012$, and for $I = 0.20$, $\log K = 1.918 \pm 0.014$. These results compare well with literature values in this ionic strength range: 2.05 at ionic strength 0.1 (Ostacoli et al., 1968) and 1.91 at ionic strength 0.2 (Cannan and Kibrick, 1938).

The thermodynamic stability constant for magnesium malonate, defined as $K_{\mathrm{th}} = a_{\mathrm{MgL}}/(a_{\mathrm{Mg}^{2}}\text{-}a_{\mathrm{L}^{2-}})$, was calculated using the Davies equation in the form $-\log \gamma_c = Az^2[(\sqrt{I}/(1 + \sqrt{I})) - 0.3I]$ (Davies, 1962), with $A = 0.511$ at 25 °C. Values of 2.90, 2.93, and 2.94 were obtained for data collected at ionic strengths of 0.1, 0.15, and 0.2. The log K_{th} values reported in the literature, almost all of which were calculated from measurements at lower ionic strengths, are 2.86 (Burger et al., 1988; Jones and Stock, 1962; Klaning and Osterby, 1976), 2.84 (Evans and Monk, 1952), and 2.80 (Money and Davies, 1932). For the experimental reasons described earlier it was not feasible for us to measure equilibrium constant values at ionic strengths below 0.1. Note that a slight ionic strength difference exists between the standards and the samples in that the malonate anion, which possesses a −2 charge, is replaced by singly charged nitrate ion in the standards. The difference can, however, be considered negligible owing to the small amount of malonate present compared to nitrate.

Overall, the method described here is straightforward and easy to use, and can be applied to a variety of metal−ligand systems that cannot be readily measured by other techniques. Results in good agreement with literature values were obtained for the magnesium−malonate system. As mentioned earlier, it is assumed that only free, hydrated, metal ions are sorbed on the resin phase; this has been shown to be so for related systems (Cantwell et al., 1982; Ren and Kratochvil, 1995). It is possible that metal complexes with small neutral ligands, in which the metal ligand complex has the same charge as the free metal ion, may be bound by the resin phase in addition to the free metal. This would invalidate the method for such species. The technique is, however, clearly applicable to systems with large or negatively charged ligands.

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Received for review March 2, 1995. Accepted June 3, 1995.[⊗] Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada and by the Department of Chemistry, University of Alberta.

JE9500542

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1995.