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Determination of Formation Quotients by a Flow Injection Procedure

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A method is described for determining equilibrium constants for reactions of 1 : 1 stoichiometry in which a flow injection procedure is used to generate absorbance–time data that are analysed by two iterative computational procedures. A two-line manifold was used with a well stirred mixing chamber downstream of the confluence point. The physical dispersion of the system was characterized first by the passage of an absorbing solution through the manifold in the absence of chemical reaction. Three chemical systems were then studied at controlled pH and ionic strength in which a metal ion was injected into a carrier and merged with a stream of ligand. These systems were the reaction of iron(III) with salicylic acid, the reaction of iron(III) with thiocyanate and the reaction of lanthanum(III) with Methyl Thymol Blue. Absorbance–time data were taken from the trailing edge of the peak profile between dispersion coefficient values of 5 and 25. Results for the formation quotients in agreement with previously reported values were obtained, except that iron(III) thiocyanate would appear to be more stable when formed in a flow injection (FI) manifold than when formed in a static batch procedure. The flow injection method greatly simplifies the experimental procedure compared with that of Job's method or the method of continuous variation, and the iterative computational methods account for absorbance by the ligand at the wavelength monitored. The educational aspects of this approach are critically evaluated and it is proposed that the FI method would form the basis of a set of teaching experiments.

Keywords: Formation quotients; equilibrium constants; flow injection; spectrophotometry

Introduction

The equilibrium expression for an ML-type complexometric reaction includes activity coefficients. For a reaction of the general form

the formation constant (K_f) is

$$K_f = \frac{[ML]f_{ML}}{[M][L]f_M f_L} \quad (2)$$

for which $[M]$, $[L]$ and $[ML]$ are the respective equilibrium concentrations of the metal, ligand and complex and f_M , f_L and f_{ML} are the respective activity coefficients of the metal, ligand and complex.

Only rarely are true formation constants reported in the literature. It is common practice to report the ratio of concentrations of products to reactants at certain ionic strengths rather than to calculate activity coefficients and report a true K_f at infinite dilution.^{1–3} This is a reasonable

practice considering the experimental difficulties encountered in determining formation constants. The issue is further complicated when side reactions are ignored. To avoid confusion over the definition and to define precisely the constant being determined, the term formation quotient (Q) will be used in this paper:⁴

$$Q = \frac{[ML]}{[M][L]} \quad (3)$$

The most widely used method for determining formation constants (K_f) of metal–ligand complexes is the method of continuous variation, or Job's method.^{5,6} The Job's plot procedure is simple, but requires several solutions over a range of mole fractions. The absorbance of the complex is plotted *versus* mole fraction of the metal species (x_M). The formation quotient is determined by drawing tangents to the curves (low and high x_M); extrapolation of these lines to the point of intersection provides an absorbance for the condition of all metal converted to the complex.⁶

An experimental procedure that uses a flow injection (FI) system to generate data from ML-type reactions is presented. Two iterative methods of data treatment^{4,7} are used to process the data. These methods are used because they allow the determination of Q values from several data points and accommodate the common situation in which both the free ligand and complex absorb at the wavelength of interest. Use of the FI method to generate the data removes the need for the preparation of a large number of discrete solutions.

Experimental Methods of Data-Handling

The iterative methods of determining formation quotients from absorbance–time data from an FI peak profile are based on a model for which the reaction stoichiometry is a 1 : 1 complexometric reaction model and for which the molar absorptivity of the complex (ϵ_{ML}) is unknown; the model accounts for the common situation of the free ligand absorbing at the wavelength at which the formation of the complex is monitored (Fig. 1). At the wavelength of interest (λ), the contribution of the absorbance due to the ligand to the overall absorbance is not negligible. Often the free ligand does not have a chromophore in the visible spectrum, or the absorbance maximum of the complex is red shifted sufficiently that ϵ_L is negligible. The two methods used for the determination of Q in this work are similar in that an initial guess is required to begin the process. The analytical (total) concentration of metal and ligand and the absorbance of the product are required at each data point (time on the FI peak profile).

Long and Drago Method

The method of Long and Drago⁷ is based on minimizing the sum of the squared deviations (χ^2) between experimentally obtained absorbance (A^{exp}) and calculated absorbance (A^{calc}). The method requires an initial guess of Q , from which the

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equilibrium concentration of the complex, [ML], is calculated [eqn. (3)]. The difference ($\Delta\epsilon$) in molar absorptivity between the complex (ϵ_{ML}) and the free ligand (ϵ_L) is calculated from the complete data set of A^{exp} and [ML], based on the initial guess of Q :

$$\Delta\epsilon = \frac{\sum_{i=1}^n \{(\Delta A_i^{\text{exp}})[ML]_i\}}{\sum_{i=1}^n [ML]_i^2} \quad (4)$$

The corresponding sum of squared deviations,

$$\chi^2 = \sum_{i=1}^n \left(\Delta A_i^{\text{exp}} - \Delta A_i^{\text{calc}} \right)^2 \quad (5)$$

for which $\Delta A^{\text{calc}} = \Delta\epsilon [ML]$ and $\Delta A^{\text{exp}} = A^{\text{exp}} - A^0$ (absorbance of free ligand) is calculated for each Q and $\Delta\epsilon$. The formation quotient is varied stepwise until a minimum χ^2 is obtained. The computer program allows for the size of the step to be varied by any amount.

Ramette Method

The method proposed by Ramette^{4,8} follows the model chemical system (Fig. 1) in which the free ligand and the complex absorb at the wavelength of interest (*i.e.*, $\epsilon_L \neq 0$). An apparent molar absorptivity (ϵ) is established with the assumption that all of the ligand is unbound,

$$\epsilon = \frac{A}{bc_L} \quad (6)$$

where A is absorbance, b is pathlength and c_L is the analytical concentration of the ligand. The following mathematical relationship can be established:

$$A^{\text{exp}} = \epsilon c_L = \epsilon_L [L] + \epsilon_{ML} [ML] \quad (7)$$

with the assumption that $b = 1$ cm. Substitution and rearrangement of eqn. (7) leads to the ratio of the two forms of the ligand:

$$\frac{[ML]}{[L]} = \frac{\epsilon - \epsilon_L}{\epsilon_{ML} - \epsilon} \quad (8)$$

Substitution of eqn. (8) into eqn. (3) leads to the working equation for the method:

$$Q = \frac{1}{[M]} \times \frac{\epsilon - \epsilon_L}{\epsilon_{ML} - \epsilon} \quad (9)$$

Eqn. (9) can be rearranged for the general situation in which [M] and ϵ_{ML} are unknown:

$$\epsilon = -\epsilon_{ML} - \frac{1}{Q} \times \frac{\epsilon - \epsilon_L}{[M]} \quad (10)$$

An initial guess of ϵ_{ML} is used to calculate initial metal equilibrium concentrations ([M]); the intercept of a plot of ϵ

Fig. 1 Spectra of the model chemical system. A, Spectrum of the free ligand (MTB); B, spectrum of the complex (La^{III} -MTB).

versus $\epsilon - \epsilon_L/[M]$ provides the subsequent value of ϵ_{ML} , from which the second [M] are calculated. The iteration is continued until the slope ($= -1/Q$) does not change. Linear regression equations are included in the computer program; the program continues until stopped by the user.

Several methods for determining acid dissociation constants by flow injection techniques have been described.⁹⁻¹⁴ A limited number of previous publications show the feasibility of determining formation constants for metal-ligand complexes.¹⁴⁻¹⁶ Yoza *et al.*¹⁵ designed a method for determining K_f of Mg and Ca complexes that relied on an empirical relationship between peak height and known K_f values for the displacement reaction of Methyl Thymol Blue (MTB) from the metals. The ligand of interest was injected into a carrier stream, which was merged with a metal-MTB reagent stream. The decrease in absorbance (from the competitive equilibrium) was plotted versus known formation constants to construct a calibration graph that could be used for unknowns. Tyson¹⁶ proposed determining formation constants from FI data obtained from FI doublet peaks; formation constants were calculated from the peak maximum absorbance and the initial concentrations of reagent and sample.

The method described by Vithanage and Dasgupta¹⁴ is of most relevance to this work. A modified Job's plot was used for determining K_f for two chemical systems: Fe^{II} -1,10-phenanthroline and Mg^{II} -methyl thymol blue. Data on dispersion and the product were obtained simultaneously in a single injection by monitoring the progress of the reaction by means of a diode-array spectrometer at a wavelength at which the product absorbs and at the isosbestic wavelength.

Experimental

Apparatus

A double-line FI manifold was used for all experiments (Fig. 2). Components of the system included a variable-speed peristaltic pump (Ismatec), a six-port injection valve (Rheodyne) and a UV/VIS photodiode-array spectrophotometer (Hewlett-Packard Model 8451A), equipped with an 8 μl flow cell (Hellma). Absorbance-time data for reactions was collected using the Hewlett-Packard Kinetics program. Flow tubing and injection loops were constructed from 0.8 mm i.d. flow tubing. Injection volumes and flow rates for the experiments are listed in Table 1.

A well stirred tank was employed as the mixing chamber in these experiments. The two parts of the approximately 1.2 ml tank were machined from Perspex.^{17,18} The cylindrical part of the chamber, 10 mm in diameter and 20 mm deep, housed a standard cuvette magnetic follower (stir bar); the upper part was conical with a height of approximately 4 mm and a base of 10 mm. An inlet was bored into the lower section and an outlet into the upper section. The well stirred tank was chosen as the mixing device because of the broad concentration gradients it produces. Other mixing devices can be used in lieu of this mixing device: single-bead string reactors, packed-bed reactors, knotted tubular reactors^{19,20} or alternating helical reactors.²¹

Fig. 2 Double-line flow injection system. CS-1 and CS-2 = carrier streams; P = pump; S = sample injection valve; C = confluence point; MC = well stirred mixing chamber; and D = UV/VIS detector.

Chemical Systems and Reagents

Three chemical systems were chosen for studying the FI procedure for determining formation quotients. The only rigorous criteria for choosing the reactions was whether they fit the 1:1 model. The reactions between iron(III) and salicylic acid and between iron(III) and thiocyanate were used to test the FI method for a reaction for which $\varepsilon_L = 0$. The Fe^{III}-salicylic acid complex is a violet complex that has a λ_{max} of 510 nm and the Fe^{III}-thiocyanate complex is a red complex that has a λ_{max} of 546 nm. The reaction between lanthanum(III) and MTB was used to test the method for the situation for which $\varepsilon_L \neq 0$. The blue complex was monitored at 610 nm; the yellow free ligand also absorbs at that wavelength ($\varepsilon_{\text{MTB}} = 2069$). Metal solutions were prepared from iron(III) nitrate and lanthanum chloride analytical-reagent grade salts. Analytical-reagent grade salicylic acid (dry acid) and potassium thiocyanate were used; methyl thymol blue sodium salt (Aldrich) was of 95% technical grade. Metal and ligand solutions were prepared in the appropriate ionic strength and pH buffer. Solution concentrations and buffers are listed in Table 1, along with values of some experimental parameters.

Procedure

The three steps of the experimental procedure are summarized in Table 2 and are discussed briefly below. In a typical FI experiment an inert dye is used to characterize dispersion by means of the dispersion coefficient (D). To simplify solution preparation, it is recommended that the metal or ligand solution be used in steps 1 and 2 rather than prepare an additional dye solution. The absorbance of the undiluted solution at some wavelength (λ_1) should be determined prior to beginning the experiments. A second wavelength (λ_2) at which the metal-ligand complex absorbs is selected for step 3.

The following procedure was followed (refer to Table 2 and Fig. 2). (1) The dispersion of CS-1 (*i.e.*, the dilution due to the merging at the confluence point) was established by determining the steady-state absorbance (at λ_1) of the metal or ligand solution after dilution with CS-2. In the examples discussed below, D for CS-1 was approximately 2.5. (2) The concentration gradient of S was determined by monitoring (at λ_1) the injection of metal or ligand solution into two buffered carrier streams. (3) The absorbance-time profile of the product was established by monitoring (at λ_2) the reaction between the metal and ligand; metal solution (S) was injected into buffer (CS-2), which was merged with ligand carrier (CS-1).

Injections had to be timed with reasonable precision such that the data from the first injection could be correlated with that of the second. After data collection was begun, a mental count of 1 s was made and the valve turned. Slow flow rates of 0.6–0.8 ml min⁻¹ were used in order to ensure that peaks were broad and that the reactions had time to come to equilibrium. Absorbance-time data in the region in which $D = 5$ –25 were collected from the trailing edge of the FI peaks. Data analysis was performed using the methods outlined above. Iterations were performed using BASIC programs that read data from text

files of total metal concentration, total ligand concentration and absorbance of complex. Listings of the QuickBASIC (Microsoft) programs are available from the authors on request.

Results and Discussions

Chemical Systems

The results for steps 2 and 3 from the procedure described above are shown in Fig. 3 for the iron(III)-salicylic acid system. Results from the experiments to determine Q are listed in Table 3. Confidence intervals were obtained through repeating step 3 of the experimental procedure. Thus, the uncertainty in Q values include the imprecision in the manual timing procedure and the normal variations in pump tubing that are inherent in FI experiments. The confidence intervals are large in relation to those typically seen for analytical determinations, but are similar to other formation constant confidence intervals reported in the literature. Literature values for each reaction are discussed below.

Table 2 Summary of experimental procedure

Step	CS-1*	CS-2*	S	Wavelength monitored
1	Metal or ligand	Buffer	No injection	λ_1
2	Buffer	Buffer	Metal or ligand	λ_1
3	Ligand	Buffer	Metal	λ_2

* Carrier streams of the FI system (see Fig. 1).

Fig. 3 Plots of absorbance against time for the iron(III)-salicylic acid system. A, when iron(III) solution was injected into buffered carrier streams (this was used to establish the dispersion profile for the injected solution) and B, when the iron(III) was injected into buffered carrier and merged with the ligand solution at the confluence point.

Table 3 Results from determination of formation quotients by the flow injection procedure

Chemical system	Long and Drago method*	Ramette method*	Mean log Q
Fe ^{III} -salicylic acid	2 045 ± 276	2 074 ± 258	3.31
La ^{III} -MTB	37 560 ± 5300	37 010 ± 5140	4.57
Fe ^{III} -SCN ⁻	553 ± 60	565 ± 56	2.74

* The $\pm$ terms are 95% confidence intervals ($n = 4$).

Table 1 Experimental parameters and solution concentrations of chemical systems

Chemical system	Concentration of solutions/mol l ⁻¹		Buffer solution (ionic strength, pH)	Injection volume/ μ l	Flow rate/ml min ⁻¹	Wavelength/nm	
	Metal	Ligand				λ_1	λ_2
Fe ^{III} -salicylic acid	9.136×10^{-3}	6.111×10^{-4}	NaClO ₄ -HNO ₃ ($I = 0.25 \text{ mol l}^{-1}$, pH = 1.66)	852	0.6	350	510
La ^{III} -MTB	8.460×10^{-5}	5.9×10^{-4}	Acetate-acetic acid ($I = 0.1 \text{ mol l}^{-1}$, pH = 6.20)	852	0.6	458	600
Fe ^{III} -SCN	3.009×10^{-2}	6.972×10^{-4}	NaClO ₄ -HNO ₃ ($I = 0.2 \text{ mol l}^{-1}$, pH = 1.35)	783	0.8	372	460

Iron(III)–salicylic acid

Eight data points were collected from the trailing edge of the absorbance–time profile in the region from $D = 4$ to 13. The calculated mean formation quotient of 2060 ($\log Q = 3.31$) is in reasonable agreement with literature conditional formation constants. Colleter²² reported a $\log K$ of 16.48 for the Fe^{III} –salicylic acid reaction at $I = 0.25 \text{ mol l}^{-1}$. Consideration of the hydrolysis of Fe^{III} and the protonation of the acid ($\alpha_{\text{Fe}} = 0.774$, $\log \alpha_{\text{SA}} = -13.07$) yields a conditional formation constant (K') of 1989. Other reported values for $\log K$ are 16.4 ($I = 0.1$)²³ and 15.8 ($I = 3.0$).²⁴ There was a slight curvature in the plot of data obtained using the Ramette method. It is thought that this is the result of formation of the 1:2 product.

Lanthanum(III)–Methyl Thymol Blue

Nine data points over the range of $D = 3.5$ –25 were used in computing the formation quotient of the La–MTB complex. It is difficult to compare the mean $\log Q$ of 4.57 with literature values of K for this reaction. A $\log K$ of 6.1 (at pH 6.0) was reported for the 1:1 reaction²⁵ and a $\log K$ of 35.8 has been reported for a 2:2 La^{III}–MTB complex ($\log K = 7.4$ at pH 5.84).²⁶ In the latter study, the side reaction coefficients of all six protons were used to determine K at various pH. This approach neglects the conclusions of other researchers that MTB forms complexes as a protonated ligand (H_3L^{3-} , for example).²⁷ In the absence of a reliable reference value, $\log Q = 4.57$ is reasonable, considering both the fit of the data to the 1:1 model (Fig. 4) and the La^{III}–acetate side reaction, which would decrease the conditional formation constant.

Iron(III)–thiocyanate

The reaction between Fe^{III} and SCN^- can form several species depending on the concentration of the ligand; the formation of the 1:2 and 1:3 products is negligible only if the SCN^- concentration is maintained below $1 \times 10^{-3} \text{ mol l}^{-1}$. Calculated Q values were consistently high for the FI method. A mean Q of 559 ($\log Q = 2.74$) was computed for the conditions noted in Table 1. Literature values of $\log Q$ for the 1:1 reaction at similar ionic strength are lower: 2.37 for $I = 0.128$ and 2.14 for $I = 0.5$.²⁸ When the experiment was performed in the batch mode using the same solutions, the results were in agreement with the literature values: $\log Q = 2.37$. The kinetic aspect of the FI method is illustrated by the difference between the results of the batch and FI methods: equilibrium is not established on the time scale of the FI experiment. Although the FI method cannot be used to determine accurately formation quotients for this reaction,

Fig. 4 Plot of eqn. (10) for the determination of Q for the La–MTB system. Slope = $-1/Q$; intercept = ϵ_{ML} . Scatter of the data from the straight-line fit illustrates the uncertainty that gives rise to the large confidence intervals (Table 3).

the linearity of the data shows that the 1:1 complex is being formed in a ratio described by the experimental value of Q . It is an interesting facet of the chemistry that the complex is slightly more stable under the regime of continuous flow than the conventional methods that employ calibrated glassware.

Features of the FI method

The proposed FI method for determining formation quotients simplifies the generation of experimental data such that the more complicated iterative methods of data handling can be more readily used in computing Q values. The iterative methods proposed by Long and Drago⁷ and Ramette^{4,8} can account for the situation of a free ligand that absorbs at the wavelength of interest; metals generally do not absorb in the UV/VIS region of the spectrum, but many common complexometric reagents absorb in the spectral regions of interest to chemists. The iterative methods also provide a measure of the precision of the determination and a measure of the fit of the data to the model.

The FI experiment provides the data required for the iterative methods of determining Q with a minimum of two injections. Absorbance data can be readily imported into computer programs through text files. Thus, the focus of the experiment is shifted from the preparation of a series of experiments to the collection of data obtained from an experiment that requires three solutions: metal, ligand and buffer solutions. In contrast, the Job's plot method requires several data points that must be obtained from the same number of solutions.

Educational Aspects

Equilibrium data on most chemical systems of interest have been tabulated in well known and widely available reference books.^{1–3} The need to determine K_f values from a research standpoint has diminished, but experimental methods for determining K_f and acid dissociation constants (K_a) are useful teaching experiments, usually conducted by students in quantitative analysis classes. An experiment to determine an equilibrium constant helps students acquire a good understanding of the fundamental concepts of chemical equilibrium and many subtopics such as side reactions (metal hydrolysis and ligand protonation), successive or competing equilibria (α -plots), buffer action and the effect of ionic strength. It is advantageous to use an FI system for this experiment to shift the focus of the laboratory work from solution preparation to handling of the data and understanding of the chemistry. This type of experiment, in which the amounts of reagents consumed are minimized, is part of the general trend in chemical education to 'miniaturize' experiments.

The simplification of the procedure for determining formation quotients makes the experiment attractive for use in a teaching laboratory. Traditional methods have the aforementioned problem of being too solution intensive. In the FI method, data for one injection is collected in 5–6 min. A student should be able to conduct the experiment with the FI system and obtain eight or more data points in 15–20 min. Only 3–4 ml of metal solution are required for each injection, the extra solution being required to wash the injection loop; thus, less than 20 ml of buffered carrier and 10 ml of ligand solution are required for steps 1–3. The experimental procedure can be simplified further by characterizing the dispersion of metal in the FI system (step 2) prior to the beginning of the experiment (step 3).

Monographs on complexometric or titrimetric analysis are sources of reactions that can be studied with the FI system.^{6,29} The 1:1 stoichiometry condition is a limitation of the

experiment, but there are ways to establish conditions such that only the first complex is formed. Setting the pH and ligand concentration to appropriate values are two important ways to accomplish this. The use of α -plots (fraction of complex formed *versus* concentration of ligand) can be incorporated into the experiment to establish proper conditions. The rate of the reaction must be considered in order to avoid kinetic effects although, as in the case of the Fe^{III} -SCN reaction, a formation quotient can be calculated from the data. Although the FI method cannot be used to determine formation constants accurately for this reaction, the use of the proposed method as a teaching experiment is not prohibited because a 1:1 complex is formed and good linearity is obtained when the data are plotted (Ramette method).

The FI system can be used to demonstrate other aspects of chemical equilibrium such as the effect of ionic strength. The reaction of a series of Fe^{III} solutions of increasing ionic strengths with salicylic acid or thiocyanate will result in absorbance-time profiles of different shapes and data from which Q values can be determined. The FI peaks can be plotted on a common time axis to illustrate the effect in a quantitative manner.

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References

- Martell, A. E., and Smith, R. M., *Critical Stability Constants*, Plenum Press, New York, 1977.
- Sillen, L. G., and Martell, A. E., *Stability Constants of Metal-Ion Complexes*, Chemical Society, London, 1964.
- Sillen, L. G., and Martell, A. E., *Stability Constants of Metal-Ion Complexes, Supplement No. 1*, Chemical Society, London, 1971.
- Ramette, R. W., *Chemical Equilibrium and Analysis*, Addison-Wesley, Reading, MA, 1981.
- Job, P., *Ann. Chim. Phys.*, 1928, **9**, 113.
- Incze, J., *Analytical Applications of Complex Equilibria*, Ellis Horwood, Chichester, 1976.
- Long, J. R., and Drago, R. S., *J. Chem. Educ.*, 1982, **59**, 1037.
- Ramette, R. W., *J. Chem. Educ.*, 1967, **44**, 647.
- Turner, D. R., Knox, S., Whitfield, M., dos Santos, M., Pescada, C., and Goncalves, M. L., *Anal. Chim. Acta*, 1989, **226**, 239.
- Brooks, S. H., and Rullo, G., *Anal. Chem.*, 1990, **62**, 2059.
- Marcos, J., Rios, A., and Valcarcel, M., *Anal. Chem.*, 1990, **62**, 2237.
- Norgaard, L., *Anal. Chim. Acta*, 1991, **255**, 143.
- Turner, D. R., Dossantos, M. M. C., Coutinho, P., Goncalves, M. D., and Knox, S., *Anal. Chim. Acta*, 1992, **258**, 259.
- Vithanage, R. S., and Dasgupta, P. K., *Anal. Chem.*, 1986, **58**, 326.
- Yoza, N., Shuto, T., Baba, Y., Tanaka, A., and Ohashi, S., *J. Chromatogr.*, 1984, **298**, 89.
- Tyson, J. F., *Analyst*, 1987, **112**, 527.
- Růžicka, J., Hansen, E. H., and Mosback, H., *Anal. Chem.*, 1977, **92**, 235.
- Tyson, J. F., *Analyst*, 1987, **112**, 523.
- Valcarcel, M., and Luque de Castro, M. D., *Flow Injection Analysis: Principles and Applications*, Ellis Horwood, Chichester, 1987.
- Růžicka, J., and Hansen, E. H., *Flow Injection Analysis*, Wiley, New York, 2nd edn., 1988.
- Echols, R. T., and Tyson, J. F., *Anal. Chim. Acta*, 1994, **286**, 169.
- Colleter, J., *Ann. Chim.*, 1960, **5**, 415.
- Babko, A. K., *Zh. Obshch. Khim.*, 1945, **15**, 745.
- Agren, A., *Acta Chem. Scand.*, 1954, **8**, 1059.
- Serdyuk, L. S., and Smirnaya, V. S., *Zh. Anal. Khim.*, 1965, **20**, 161.
- Budesinsky, B., and Antonescu, E., *Collect. Czech. Chem. Commun.*, 1963, **28**, 3264.
- Yoshino, T., Imada, H., Murakami, S., and Kagawa, M., *Talanta*, 1974, **21**, 211.
- Frank, H. S., and Ostwald, R. L., *J. Am. Chem. Soc.*, 1947, **69**, 1321.
- Ringbom, A., *Complexation in Analytical Chemistry*, Robert E. Kreiger, Huntington, NY, 1979.