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A rapid, automated gradient flow injection–spectrophotometric technique for study of metal complexation reactions

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ABSTRACT

Controlled dispersion as generated in flow injection analysis (FIA) essentially permits an infinite variety of known compositional gradients. Using this unique advantage of FIA, the stability constants of metal complexation are calculated by injecting an aliquot of metal solution into the flow of ligand solution in a single-line manifold. While the ligand dilution is negligible, the concentration gradient of injected metal ion can be calculated from the dispersion pattern which is calibrated previously using a dye solution. To show the simplicity, versatility and ease of instrumental setup over approaches based on the classical titration, the method was applied to determine stability constants of murexide with several metal ions. The SQUAD computer program was used for fitting the predefined complexation model to the spectral-mole ratio data. The proper selection of the chemical model was verified by the determination of the number of absorbing species by using a singular value decomposition of each data set. The stability constants obtained for murexide and metals including Cu^{2+},Cd^{2+}, Pb^{2+}, Ca^{2+} and Co^{2+} are 4.35, 4.27, 4.50, 2.55 and 2.57, respectively. The formation constants determined here are in good agreement with those previously reported and with those obtained from conventional batch titrations. The main advantage over the classical batch titration method is that by utilizing just one injection per sample, the proposed method reduces experimental error by reducing the experimental steps needed to obtain the required spectral-mole ratio data. The details of the proposed method are discussed.

1. Introduction

The use of stability constants of metal complex formation as an effective measure of affinity of a ligand for metal ion in solution have a long history, and are an excellent and quantitative index for the success or failure of ligand design [1,2]. In three recent decades, three important developments in the solution coordination chemistry provide a major role for stability constant determinations and further developments of the field [3]. These are, first, the development of the chemistry of macrocyclic and macrobiocyclic complexes [4], with the accompanying opportunities to ligand design and synthesis of new ligands with novel properties and applications; second, the develpomet of the new fields in bioinorganic and inorganic envirmonmental chemistry [5–7], which require a careful study of the complexes formed in multicomponent systems containing more than one ligand and one metal ion; and at last, the development of computers and computer programs for processing equilibrium data to provide rapid determination of stability constants with higher accuracy, and the potential for studying multidentate ligands and systems of many metal ions and ligands, that are too complex to have been investigated by classical methods [8–13]. Nowadays, the calculated stability constants using computer programs, are used for the elucidation of molecular and ionic species present in complex biological and enviromental systems [5].

Among the various methods for studying the complexation equilibria in solution, manipulation of spectrophotometric data with computer programs is a powerful method under extensive experimental conditions [14]. Generally, spectrophotometric methods are highly sensitive and suitable for studying chemical equilibria in solutions. When the spectral profiles of the components involved in the chemical equilibrium are distinct and not overlapped, their concentrations can be measured directly, and the calculation of equilibrium constants can be made with a blink an eye. However, in many cases, the spectral profiles of components are overlapped and analysis is not straightforward [15]. There are several advantages of using multiwavelength data (as compared to selecting single wavelengths) including [16] (a) appropriate analysis results in determination of the pure spectra and concentration profiles for all reacting species. (b) Multivariate data allow the application of a wide range of model free analyses. (c) The need to determine a “good” wavelength to follow the reaction is eliminated. (d) The analysis of multiwavelength data is often significantly more robust. The disadvantages of multiwavelength data

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include the large number of data that are acquired in a short time and the large number of parameters that need to be fitted. Readily available personal computers with large memory solve the first problem and appropriate algorithms solve the second. Keeping the above mentioned advantages, there are several reports in literature trying to use multivariate approaches in determination of stability constants [17–22] and hence, there are monographs for calculation of stability constants from multivariate data [23,24].

In the conventional methods of complexometric titrations, the preparation of a series of mixtures, with constant concentration of one of the components (usually ligand) and varying concentrations of the other (usually metal), is required. These mixtures may be prepared and measured in a batch mode or a manual stepwise titration mode [25–27] and the complete study of the complexation phenomenon requires a wide range of concentration ratios and manipulation is necessary in each step of titration.

Flow analysis has experienced amazing developments in recent decades and continues to evolve [28]. Developments of FIA have been further stimulated by the additional advantages of automation, such as increased precision, decreased cost of individual assay, and the satisfactory reliability of automated equipment [29]. One of the important features of the flow injection method is the possibility of adapting the flow pattern to the requirements of a particular determination [30] and hence, continuous flow titration methods have been reported by many investigators [31–40].

In the present work, we wish to report the utility of FIA in conjunction with a photodiode array UV–vis spectrophotometer and a whole-domain spectral processing computer program, SQUAD, in the study of complexation reactions between murexide and some transition metal ions. The unique and reproducible controlled dispersion aspect of FIA [32] is used for generation of required absorption spectral-mole ratio data to follow the complexation reactions. In the conventional techniques for determination of stability constants, manipulation in every step of titration is mandatory, but in the current method only three and one injections are required before and after dispersion calibration of the reactants, respectively. Other advantages include automation and absolutely no manipulation, skillfulness and carefulness during the titration. By injection of a desired volume of a metal ion solution with proper concentration into flow of ligand, all of the required absorption spectral-mole ratio data are collected to determine the stability constants of the resulting metal:ligand complexes.

2. Experimental section

2.1. Material and chemical reagents

All reagents used were of analytical grade. Murexide, acetic acid (glacial) and sodium acetate were purchased from Merck. Cu $(NO_3)_2 \cdot 3H_2O$, Cd $(NO_3)_2 \cdot 4H_2O$, Pb $(NO_3)_2$, fluorescein, Co $(ClO_4)_2 \cdot 4H_2O$ and Ca $(NO_3)_2 \cdot 4H_2O$ were purchased from Fluka. The stock 1.00×10^{-1} mol L^{-1} acetic acid/acetate buffer solution was made in distilled water and was further diluted to 1.00×10^{-2} mol L^{-1} for use in the preparation of metal and ligand solution. The 1.00×10^{-1} mol L^{-1} stock solutions of Ca^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} were prepared in 1.00×10^{-2} M acetate buffer. The fresh solutions of murexide were prepared daily in the 1.00×10^{-2} mol L^{-1} of acetate buffer. The 1.00×10^{-4} mol L^{-1} standard stock solutions of fluorescein sodium salt were made in 1.00×10^{-2} mol L^{-1} acetate buffer for further dilutions.

2.2. Apparatus, instrumentation and software

The FIA manifold used in all experiments is shown schematically in Fig. 1 and the inset of Fig. 1 shows the scheme of the flow

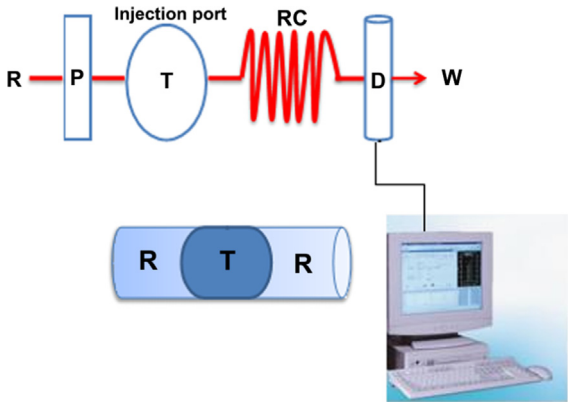

Fig. 1. FIA manifold used for complexometric titration. *R*=Reagent stream (ligand solution in 0.01 mol L^{-1} Acetate buffer), pH=4.72, pumped at 0.75 ml/min rate; *P*=peristaltic pump, *T*=Titrant (Metal in 0.01 mol L^{-1} acetate solution, Injection volume=50 μl); RC=Reaction coil (250.0 cm); *D*=Photodiode array spectrophotometer. *W*=Waste. The inset shows the scheme of the flow segments of titrant and reagent (ligand).

segments of sample and reagent. All tubes employed were silicon (0.80 mm internal diameter and 250.0 cm length). Injection is carried out by using a six-way Rheodyne injection port. In the dispersion calibration step, the carrier stream was a 0.01 mol L^{-1} acetate buffer with a pH of 4.76 and the injected reagent was a murexide solution prepared in the same acetate buffer. In the titration step, carrier stream was a ligand solution prepared in the acetate buffer and the injected sample was a metal solution prepared in the same acetate buffer. For evaluating the dilution effect of metal solution injection into carrier stream of ligand, a blank solution (acetate buffer solution) injected into carrier stream of ligand. A multi-channel Heidolph peristaltic pump (Heidolph PD 5001) was used. The absorption spectra with 1 nm spectral bandpass were recorded using an Agilent-8453 UV–vis diode-array spectrophotometer. Agilent UV–Visible Chem-Station software for data acquisition was used throughout. A 10 μl flow cell with 2.0 mm path length was used. All absorption spectra were recorded in the wavelength range 350–650 nm. The absorption spectra recorded after a single injection of 50 μl of desired solution into carrier stream (both solutions prepared in 1.00×10^{-2} mol L^{-1} acetate buffer solution at pH=4.72). The spectrophotometer starts scanning 200 s after injection, and continues scanning every 6 s for the next 500 s assuring the injected metal solution passes completely through the flow cell. The injected metal passes through the flow cell in the range of 250–655 s and the range analytically adequate for formation constants calculations was in the range of 420–590 s. The pH values were measured and adjusted by an AMTAST pH-meter equipped with combined Ag/AgCl electrode. Home-written Excel-VBA macro was used for preparing required input file format by SQUAD computer program. Further data treatments were done using MATLAB ver. 7.11 [41].

3. Results and discussion

3.1. Theory

Concentration profiles of contributing species in a successive complexation system are calculated by solving a polynomial equation:

$$[L]^{n+1}\beta_n + [L]^n\{\beta_n(nC_{t,M} - C_{t,L}) + \beta_{n-1}\} + [L]^{n-1}\{\beta_{n-1}((n-1)C_{t,M} - C_{t,L}) + \beta_{n-1}\} + \ldots - C_{t,L} \quad (1)$$

where n is the maximum number of successive mononuclear complexes, β_1, β_2,..., β_n are overall formation constants, $C_{t,M}$ and