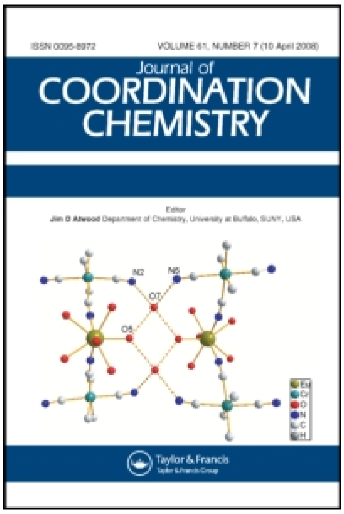

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

EBULLIOMETRIC DETERMINATION OF STEP STABILITY CONSTANTS

A. Walace[a]; Oliveira[a]
[a] Instituto de Quimica, Universidade Estadual de Campinas, Campinas, S.P., Brazil

To cite this Article Walace, A. and Oliveira(1979) 'EBULLIOMETRIC DETERMINATION OF STEP STABILITY CONSTANTS', Journal of Coordination Chemistry, 9: 1, 7 — 11

To link to this Article: DOI: 10.1080/00958977908073095

URL: http://dx.doi.org/10.1080/00958977908073095

J. Coord. Chem.
1979, Vol. 9, pp. 7–11

EBULLIOMETRIC DETERMINATION OF STEP STABILITY CONSTANTS

WALACE A. de OLIVEIRA

Instituto de Quimica, Universidade Estadual de Campinas, CP 1170, Campinas, S.P., Brazil

(Received March 10, 1978; in final form June 14, 1978)

A new technique for the determination of step stability constants is described, which is based on changes in boiling temperatures due to the addition of a titrant. A general theory relating the temperature changes to the several equilibrium constants is discussed. Stability constants of the cadmium (II) halide systems at 100°C and ionic strength 1.00 *m* are determined and show good agreement with values calculated from literature data at 25°C.

INTRODUCTION

The determination of equilibrium constants from changes in boiling temperatures has been done since half century ago,[1,2] but not many reports exist in the literature.[3–5] The technique is outlined by Swietoslawski[6] and is discussed by Rossotti and Rossotti.[7] It has the advantage that the dependence of the equilibrium constant on the temperature can be established. The ebulliometric methods that have been described are restricted to a single equilibrium, which usually involves dimerization, dissociation or esterification reactions. Nevertheless, the method could be an useful tool in the study of multiple equilibria such as the step formation of complexes, provided that a simple and reliable procedure of acquiring and handling the data is developed.

This report describes a new method for the ebulliometric determination of step equilibrium constants. It is called "ebulliometric titration" and consists in monitoring the changes in the boiling temperature of a solution due to the addition of a titrant. In order to test the technique, the several stability constants of cadmium (II) halides, at 100°C, were determined.

EXPERIMENTAL

Apparatus

A twin-thermistor ebullioscope similar to that recently described[8] was used. The apparatus consists of a pair of identical ebulliometers where the solution is brought to boiling and equilibrium is attained between the boiling solution and the vapor of the solvent. Boiling-temperature changes are sensed by means of a pair of matched thermistors, connected to a Wheatstone bridge, whose unbalance voltage is presented to a strip-chart recorder. Temperature elevations were obtained according with a method recently outlined.[9] The uncertainty in the measurements of boiling temperatures was about 50 μdeg.

Reagents

A standard cadmium (II) perchlorate solution was prepared by dissolving cadmium (II) carbonate in perchloric acid; when no more cadmium (II) carbonate would dissolve, the solution was boiled, filtered and standardized against EDTA, according to standard procedures. Sodium perchlorate was prepared by treating sodium carbonate and perchloric acid, filtering as a slightly alkaline solution, acidifying slightly and crystalizing; a concentrated solution was prepared and its concentration was determined gravimetrically. Small pellets of sodium chloride, bromide and iodide, used as titrants, were made by applying a slight pressure to the powder of these salts and were stored in a vacuum dessicator.

Procedure

An experiment begun by charging both ebulliometers with a solution of cadmium (II) perchlorate 0.100 *m*, of ionic strength 1.00 *m*, adjusted with sodium perchlorate. The amount of water corresponding to the solvent hold-up was then added. After boiling equilibrium was attained, pellets of the titrant were added, separately, to both ebulliometers, while recording the temperature changes. All computations were performed on a PDP-10 computer (Digital

Equipment Corp., Maynard, Mass., USA) operating in a multi-user configuration.

THEORY

Since ebulliometric methods have not yet been applied to solutions where multiple equilibria take place in the presence of a supporting electrolyte, it was necessary to develop a theory which relates the boiling-temperature changes to the stability constants of interest. During the titration of a boiling solution of the metal M^{z+} with a salt of the ligand A^- the following equilibria take place

$$MA_{j-1}^{z-j+1} + A^- \rightleftharpoons MA_j^{z-j} \qquad (1)$$

where j = 1, 2, 3, . . . N. The solution contains several species, namely, the ions of the titrant and titrand, the complexes formed and the ions of the supporting electrolyte. Applying the Gibbs-Duhem equation to the system, gives

$$n_{M^{z+}}\,\mathrm{dln}(M^{z+}) + n_A\,\mathrm{dln}(A^-) + \sum_{j=1}^{N} n_{MA^{z-j}}\,\mathrm{dln}\,(MA_j^{z-j})$$

$$+ n_{Na^+}\,\mathrm{dln}(Na^+) + n_{ClO_4^-}\,\mathrm{dln}(ClO_4^-) + n_S\,\mathrm{dln}(S) = 0 \qquad (2)$$

where n denotes the number of moles, S refers to the solvent and the curved brackets represent activities. The activity of the solvent is related to the boiling-point elevation, θ, through the equation[10,11]

$$\ln(S) = -\frac{\Delta H_0 \theta}{RT_0^2}\,(1 - b\theta + c\theta^2 + \ldots) \qquad (3)$$

where ΔH_0 is the heat of vaporization of the solvent at its boiling point T_0; R is the gas constant and b, c, . . . are constants for a given solvent. The numerical values[12] of b and c for boiling water permit the conclusion that the term inside the parenthesis of Eq. (3) can be neglected without affecting the accuracy of our calculations. Introducing the ebullioscopic constant, Kb, defined as

$$Kb = \frac{M_s R T_0{}^2}{1000\Delta H_0} \qquad (4)$$

where M_S is the molecular weight of the solvent; differentiating Eq. (3) and substituting it in Eq. (2); introducing the definition of molality, m, and of the molal activity coefficient γ; and rearranging, gives

$$\frac{\mathrm{d}\theta}{Kb} = \frac{m_{M^{z+}}\mathrm{d}\gamma_{M^{z+}}}{\gamma_{M^{z+}}} + \frac{m_{A^-}\mathrm{d}\gamma_{A^-}}{\gamma_{A^-}} + \frac{m_{Na^+}\mathrm{d}\gamma_{Na^+}}{\gamma_{Na^+}}$$

$$+ \frac{m_{ClO_4}\mathrm{d}\gamma_{ClO_4^-}}{\gamma_{ClO_4^-}} + \sum_{j=1}^{N} \frac{m_{MA_j^{z-j}}\,\mathrm{d}\gamma_{MA_j^{z-j}}}{\gamma_{MA_j^{z-j}}}$$

$$+ \mathrm{d}m_{M^{z+}}$$

$$+ \mathrm{d}m_{A^-} + \mathrm{d}m_{Na^+} + \mathrm{d}m_{ClO_4^-} + \sum_{j=1}^{N} \mathrm{d}m_{MA_j^{z-j}} \qquad (5)$$

It is assumed at this point that the activity coefficients do not vary substantially during the titration. There are two arguments in favour of this assumption. First, the titration is performed in a medium of high ionic strength and relatively small amounts of titrant are added. Second, the addition of titrant will cause a slight decrease in the ionic strength in the beginning of the titration, due to the formation of less charged complexes (assuming z > 1); further addition of titrant will increase the ionic strength. Therefore, we neglect all terms containing dγ in Eq. (5). Remembering that

$$\mathrm{d}m_{ClO_4^-} = 0 \qquad (6)$$

and

$$\mathrm{d}m_{Na^+} = \mathrm{d}m_{NaA} \qquad (7)$$

where m_{NaA} is the analytical concentration of the titrant added to the solution; then Eq. (5) becomes

$$\frac{\mathrm{d}\theta}{Kb} = \mathrm{d}m_{M^{z+}} + \mathrm{d}m_{A^-} + \mathrm{d}m_{NaA} + \sum_{j=1}^{N} \mathrm{d}m_{MA_j^{z-j}} \qquad (8)$$

Integration of this equation within the limits of the titration yields

$$\frac{\Delta\theta}{Kb} + mi_{M^{z+}} = m_{M^{z+}} + m_{A^-} + m_{NaA} + \sum_{j=1}^{N} m_{MA_j^{z-j}} \qquad (9)$$

where $\Delta\theta$ is the change in the boiling temperature of the solution after the beginning of the titration and $mi_{M^{z+}}$ is the initial concentration of the metal. Conservation of mass requires the following relationships

$$m_{NaA} = m_{A^-} + \sum_{j=1}^{N} j m_{MA_j^{z-j}} \qquad (10)$$

$$mi_{M^{z+}} = m_{M^{z+}} + \sum_{j=1}^{N} m_{MA_j^{z-j}} \qquad (11)$$

The stoichiometric stability constants are defined as

$$K_j = \frac{m_{MA_j^{z-j}}}{m_{MA_{j-1}^{z-j+1}} \, m_{A^-}} \qquad (12)$$

Attempts to calculate all K_j at once by simultaneous solution of Eqs. (9)–(12) leads to unwieldy expressions. For this reason the following stepwise approach is adopted. The value of K_1 is calculated first, using only data from the very beginning of the titration, where it is possible to neglect the concentrations of all complexes with $j > 1$. With this simplification, Eqs. (9), (10) and (11) are solved simultaneously and the results substituted in Eq. (12), giving Eq. (13) below. Once the value of K_1 is obtained, a larger portion of the titration curve is used for the calculation of K_2, assuming that $m_{MA_3^{z-3}}$, $m_{MA_4^{z-4}}$ ... are negligible. Following this procedure, equations for the successive calculation of all K_j are easily derived as follows.

$$K_1 = \frac{2m_{NaA} - \dfrac{\Delta\theta}{Kb}}{b_1 a} \qquad (13)$$

$$K_2 = \frac{mi_M z+(2+K_1 a) - b_2(1+K_1 a)}{K_1 b_2 a^2} \qquad (14)$$

$$K_3 = \frac{mi_M z+(3+2K_1 a+K_1K_2a^2) - b_3(1+K_1 a+K_1K_2a^2)}{K_1K_2b_3a^3} \qquad (15)$$

$$K_4 = \frac{mi_M z+(4+3K_1 a+2K_1K_2a^2+K_1K_2K_3a^3) - b_4(1+K_1 a+K_1K_2a^2+K_1K_2K_3a^3)}{K_1K_2K_3b_4a^4} \qquad (16)$$

where

$$a = \frac{\Delta\theta}{Kb} - m_{NaA} \qquad (17)$$

$$b_j = \frac{\Delta\theta}{Kb} + j\,mi_M z+ - 2m_{NaA} \qquad (18)$$

RESULTS

Typical titration curves are shown in Figure 1. These data were used for the calculation of the several stability constants, by introducing them in Eqs. (13)–(16). As the method entails an approximate procedure, correct values are obtained only when using data from the portion of the curve where the approximations hold. Then, one is faced with the problem of choosing the proper regions of the curve for the consecutive calculations of K_j. The behaviour

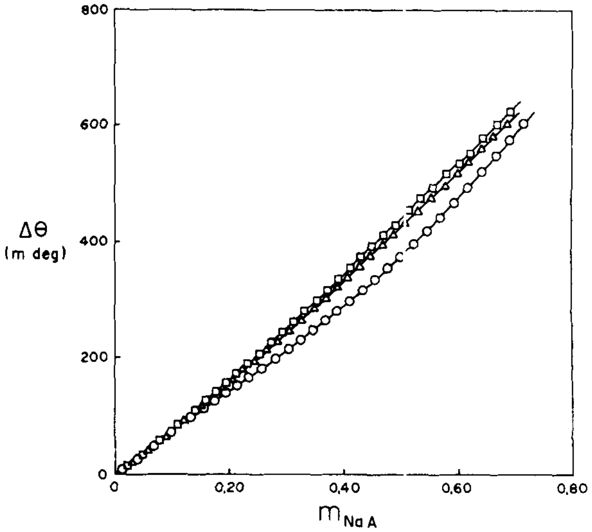

FIGURE 1 Ebulliometric titrations of 0.100 m Cd^{2+} solution, of ionic strength 1.00 m with sodium chloride (□), sodium bromide (△) and sodium iodide (○).

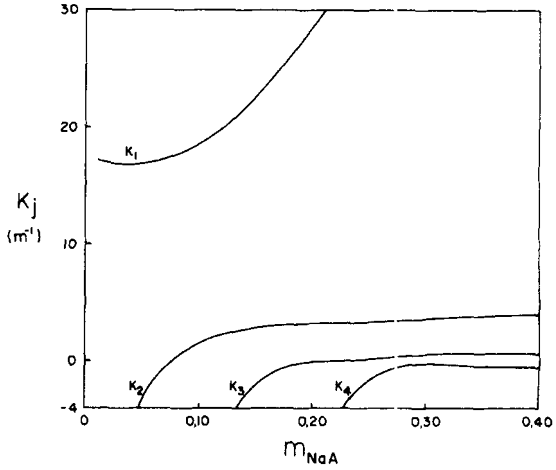

FIGURE 2 Behaviour of the calculated values of K_j as a function of titrant concentration, for the cadmium (II) chloride system.

TABLE I
The stability constants at 100°C and ionic strength 1.00 *m* obtained in this work compared with values calculated from literature data at 25°C

Ligand	j	This work	Calculated
Cl	1	17 ±5	23
	2	3 ±1	3
	3	0.5 ±0.2	0.7
Br	1	26 ±6	27
	2	2 ±1	3
	3	5 ±4	3
	4	0.4 ±0.3	1
I	1	21 ±4	33
	2	4 ±1	12
	3	25 ±9	36
	4	2 ±1	8

of the calculated values as a function of titrant concentration can help in this decision as shown in Figure 2, for the cadmium(II) chloride system. The values of K_1 are reasonably constant in the beginning of the titration, where only the species $CdCl^+$ exists in appreciable concentration. As titration proceeds, the concentration of $CdCl_2$ becomes also important and a relatively larger number of particles are present in solution. Since the approximate treatment (Eq. 13) does not account for this second equilibrium, higher values of K_1 are resulted, as shown in Figure 2.

The behaviour of K_2 may be understood with similar arguments, as follows. The concentration of $CdCl_2$ is so small in the beginning of the titration, that assumption of its existence leads to negative values of K_2. In the concentration range of about 0.18 to 0.28 *m* the calculated K_2 values are invariable and they increase slightly as titration goes on, probably reflecting the formation of $CdCl_3^-$. This apparent increase of K_2 with concentration is small because the value of K_3 is also small. Steeper increases were shown in the profiles of K_2 of the cadmium (II) iodide and bromide systems. The behaviour of K_3 is alike to that of K_2 and indicates that the contribution of the third equilibrium to the total number of particles in solution is a modest one. Figure 2 also shows that attempts to calculate K_4 yielded only negative values. Even at higher titrant concentrations (up to 0.70 *m*) no positive value of K_4 for the cadmium (II) chloride system could be accurately obtained. Most workers[13] who studied this system have also been unable to secure a value for K_4.

It was assumed in the calculations of all K_j that the correct values were those from the plateau of the curves (see Figure 2). Distribution diagrams[14] were also calculated using these K_j to certify that the chosen regions were those where the relative concentration of a given species was more significant. Four or five titrations were done for each ligand and the average values of K_j, with their standard deviations, are listed in Table I.

DISCUSSION

Precision

The approximation technique found necessary in order to calculate the consecutive constants is likely to fail when several complexes strongly coexist. In view of this, the results given in Table I are surprisingly good. The uncertainty in the values of K_1 is of the order of 24%. This error is also due to the fact that the determination of the first stability constant requires the addition of very small amounts of titrant, resulting in smaller and less precise boiling-temperature elevations. The relative error is higher for K_2, K_3 and K_4 because each K_j is affected by uncertainty in the preceeding constants. This is a drawback also encountered in other methods.[7]

The precision of our results was decreased by the fact that the stability constants of the cadmium (II) halides are too close to each other. Complex systems having more different values of constants should give better precision.

Accuracy

The results obtained in this work are compared in Table I with values calculated from literature data at 25°C. In these calculations, Eq. (19) was used

$$\ln(K_j)_{100} = \ln(K_j)_{25} + \frac{\Delta H_j}{R}\left(\frac{1}{298.15} - \frac{1}{373.15}\right) \qquad (19)$$

where R is the gas constant and ΔH_j is the enthalpy change for the stepwise reaction, which was assumed to be constant. The values of $(K_j)_{25}$ were taken from Gerding;[15] ΔH_j for the cadmium (II) chloride and iodide systems were those reported by Gerding and Jönsson;[16] and ΔH_j for the cadmium (II) bromide complexes were those given recently by Fedorov *et al.*,[17] all data at ionic strength 1.0 *M*. The uncertainty in these calculated values of $(K_j)_{100}$ is probably large because it includes the errors in $(K_j)_{25}$ and ΔH_j, plus those due to the assumption that ΔH_j is constant over the temperature range from

25 up to 100°C. The inaccuracy in the values of the enthalpy changes presumably introduces the most serious error. No attempt was made to express $(K_j)_{100}$ in the molal scale because this correction would be comparatively negligible.

Table I shows good agreement between the experimental and the calculated values of the stability constants for the ligands chloride and bromide. For iodide the calculated values are a little higher than the measured ones and this may be due to the uncertainties mentioned in the preceding paragraph or may be caused to some extent by air oxidation of I^- to I_2. This reaction produces a decrease in the total number of particles in solution, resulting, consequently, lower values of stability constants. The conclusions regarding the accuracy of our results are impaired by the great scatter existing in the thermodynamic data available[13] for cadmium (II) halide systems and also because some of these data are at best semi-quantitative as pointed out by Reilly and Stokes.[18]

Convenience

The technique described in the present paper requires simple and inexpensive equipment. A complete experiment can be done in a few hours and since additions of titrant are made in two ebulliometers, two sets of data can be obtained, or two different systems may be studied, with a single experiment. Also, values of stability constants at different temperatures may be secured by varying the barometric pressure in the ebulliometers. The major requirement of the method is that all solutes must be non-volatile at the boiling point of the solvent.

It appears possible to conclude that ebulliometric titration is a convenient technique for the determination of stability constants at the boiling point of the solvent. However, since the response of the solvent activity on the solute concentrations is of low sensitivity, the technique will only be used to some complex systems where the more efficient methods (such as potentiometric, thermometric and optical) are not applicable.

ACKNOWLEDGEMENT

The author is indebted to Dr. O. E. S. Godinho for valuable discussions during the course of this work.

REFERENCES

1. F. Bourion and E. Rouyer, *Ann. Chim.* (Paris), **10**, 254 (1928).
2. E. Rouyer, *Ann. Chim.* (Paris), **13**, 477 (1930).
3. G. Allen and E. F. Caldin, *Trans. Far. Soc.*, **49**, 895 (1953).
4. A. D. Adler, J. A. O'Malley and A. J. Herr, Jr., *J. Phys. Chem.*, **71**, 2896 (1967).
5. R. S. Rodgers and L. M. Mukhergee *J. Chem. Phys.*, **52**, 4550 (1970).
6. W. Swietoslawski, *Ebulliometric Measurements* (Reinhold, New York, 1945), chapter 17.
7. F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants* (McGraw Hill Book Company, New York, 1961).
8. W. A. de Oliveira and L. Meites, *Anal. Chim. Acta*, **93**, 3 (1977).
9. W. A. de Oliveira, *Rev. Sci. Instrum.*, **48**, 1278 (1977).
10. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Reinhold, New York, 1955), p. 181.
11. R. S. Lehrle, Ebulliometry applied to polymer solutions, in *Progress in High Polymers*, Vol. 1, ed. By J. C. Roble and F. W. Peaker, Academic Press Inc., New York, 1961.
12. R. P. Smith, *J. Am. Chem. Soc.*, **61** 500 (1939).
13. L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes* (The Chemical Society, London, 1971) Pt. 1, Spec. Publ. No. 25.
14. J. N. Butler, *Ionic Equilibrium – A Mathematical Approach* (Addison-Wesley Publishing Company, Reading, 1964), p. 367.
15. P. Gerding, *Acta. Chem. Scand.*, **22**, 1283 (1968).
16. P. Gerding and I. Jönsson, *Acta Chem. Scand.*, **22**, 2247 (1968).
17. V. A. Fedorov, L. I. Kiprin, N. S. Shchekina, N. P. Samsonova, M. Ya. Kutuzova and V. E. Mironov, *Zhur. Neorg. Khim.*, **19**, 872 (1974) [*Russ. J. Inorg. Chem.*, **19**, 474 (1974)].
18. P. J. Reilly and R. H. Stokes, *Aust. J. Chem.*, **23**, 1397 (1970).