

## Thermodynamic Stability Constant of Metal-Chelates

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CALVIN and MARTELL<sup>1</sup> have discussed the different ways in which one could possibly calculate the thermodynamic stability constant of a metal-chelate. To get the thermodynamic constant from the mass action constant, the activity coefficient term may be estimated by some theoretical equations. This, however, is limited by the DEBYE-HÜCKEL relationship being valid only at low ionic strength and for simple ions.

The other way of getting the thermodynamic equilibrium constant is to work near infinite dilution when all the activity coefficients are equal to unity; but this is limited, as working in infinitely dilute solutions would mean more error and is often very difficult from the experimental point of view. The commonly used method has been to determine  $K_c$ , the mass action constant, at different ionic strengths and then to extrapolate to zero ionic strength to get the thermodynamic stability constant. The problem arises as to which function of ionic strength is to be used in the extrapolation.

In the determination of the thermodynamic stability constant of  $Pb-Cit^-$ , KETY<sup>2</sup> extrapolated  $\log K_{stab}$  after plotting against ionic strength. CALVIN and ZEBROSKI<sup>2a</sup>, for the stability constant of various metal ions with thenoyltrifluoroacetone, plotted  $\log K$  against the square-root of ionic strength. None of these gave linear plots. This is what one would expect because, in the plot of  $\log K$  against ionic strength, no account is taken of the inter-ionic attraction and in the latter, namely, in case of  $\log K$  against the square-root of ionic strength, the proportionality of the activity coefficient with the square-root of the ionic strength is valid only in very dilute solution and even that only in case of small and simple ions.

<sup>1</sup> A. E. MARTELL and M. CALVIN, Chemistry of the metal chelate compounds p. 131–133, Prentice-Hall Inc. 1956.

<sup>2, 2a</sup>. Same as '1', p. 133.

Table 1

*Thermodynamic stability constant (log K<sub>stab</sub>) by different types of extrapolation*

	I	II	III	IV	V**
<i>Al</i> -sulphosalicylate <sup>3</sup>					
at pH 2.4	3.35	3.73	3.60	3.82	3.64
3.0	4.07	4.37	4.28	4.52	4.29
4.0	5.07	5.55	5.32	5.46	5.33
<i>Al</i> -salicylate <sup>4</sup>					
at pH 3.0	3.04	3.34	3.16	3.38	3.26
4.5	4.62	4.84	4.78	4.90	4.82
<i>Ga</i> -sulphosalicylate <sup>5</sup>					
at pH 3.0	4.83	5.35	5.16	5.30	5.18
3.5	5.57	6.23	5.76	6.01	5.90
<i>Ga</i> -salicylate <sup>6</sup>					
at pH 3.0	3.91	4.08	4.15	4.32	4.19
3.5	4.70	5.09	4.68	4.99	4.94
<i>Be</i> -sulphosalicylate <sup>7</sup>					
at pH 4.0	4.07	4.16	4.21	4.20	4.14
4.5	4.60	4.66	4.74	4.69	4.60
<i>Be</i> -salicylate <sup>7</sup>					
at pH 4.0	3.72	3.78	3.79	3.92	3.83
4.5	4.13	4.19	4.12	4.34	4.21
<i>Cu</i> -salicylate <sup>8</sup>					
at pH 4.0	1.97	2.00	2.03	2.23	2.11
4.5	2.35	2.39	2.41	2.59	2.47
<i>Cu</i> -sulphosalicylate <sup>9</sup>					
at pH 4.5	2.71	2.69	2.75	2.85	2.84
<i>Fe</i> (III)- <i>p</i> aminosalicylate <sup>10</sup>					
at pH 2.5	4.57	4.67	4.70	4.84	4.70

\*\* The significance of I, II, III, IV, and V is given in the text.

<sup>3</sup> R. K. NANDA and S. ADITYA, *J. Indian chem. Soc.* **34** (1957) 577; **40** (1963) 660.

<sup>4</sup> R. K. NANDA, Ph. D. Thesis, Utkal University, 1961.

<sup>5</sup> R. K. NANDA and S. ADITYA, *J. Indian Chem. Soc.* **40** (1963) 755.

<sup>6</sup> R. C. DAS, R. K. NANDA and S. ADITYA, *J. Indian Chem. Soc.* **40** (1963) 739.

<sup>7</sup> R. C. DAS and S. ADITYA, *J. Indian Chem. Soc.* **38** (1961) 19; **41** (1964) 765.

<sup>8</sup> R. C. DAS and S. ADITYA, *J. Indian Chem. Soc.* **42** (1965) 15.

<sup>9</sup> R. C. DAS, R. K. NANDA, and S. ADITYA, *J. Indian Chem. Soc.* **42** (1965) 307.

<sup>10</sup> R. C. DAS and S. ADITYA, *J. Indian Chem. Soc.* **37** (1960) 557.

Because of lack of knowledge about the ionic radius parameter the HITCHCOCK<sup>11</sup> type of extrapolation cannot be adopted. However, if one uses the semi-empirical equation of DAVIES<sup>12</sup>:

$$\log f_{\pm} = -0.50 z_+ z_- \frac{\mu^{1/2}}{1 + \mu^{1/2}} - C\mu$$

one can probably use an extrapolation of the HITCHCOCK type. For  $C$ , DAVIES used a value of 0.2, but in view of the points raised by GUGGENHEIM<sup>13</sup>, we have not used any particular value of  $C$  but tried to plot  $\log K + C'A \frac{\mu^{1/2}}{1 + \mu^{1/2}}$  against  $\mu$ ,  $C'$  depending on the valence of the metal ion and that of the ligand. In no case the plot was linear. Following SCATCHARD<sup>14</sup> we have also tried with some success  $\log K + C'A \frac{\mu^{1/2}}{1 + \mu^{1/2}}$  against a different function of  $\mu$ , namely, the square-root of the ionic strength.

Recently FRANK and THOMPSON<sup>15</sup> have pointed out the limitations of the DEBYE-HÜCKEL theory in light of the radius of the ion-cloud. Even in case of simple ions, the upper limit of validity of the theory is about 0.001 M. For higher concentrations,  $\log f_{\pm}$  is proportional to  $C^{1/3}$ .

We have plotted  $\log K$  against  $\mu$  (I),  $\mu^{1/2}$  (II) and  $\mu^{1/3}$  (III) and  $\log K + C'A \frac{\mu^{1/2}}{1 + \mu^{1/2}}$  against  $\mu$  (IV) and also  $\mu^{1/2}$  (V) and obtained  $\log K$  at zero ionic strength for a number of metal chelates we have studied in the last few years. Methods III and V gave linear extrapolations with some scatter. It is difficult to say which of these two is better. The unfortunate fact is that two methods of extrapolation do not give the same value at zero ionic strength. The constants obtained by different extrapolations are presented in the table to give an idea about the uncertainty (even when one gets linear extrapolation, *vide* methods III and V) in getting the thermodynamic stability constants in case of metal chelates.

In view of this, we feel that it is preferable to work in infinitely dilute solution wherever that is feasible. Otherwise, if the thermodynamic constant is reported, it is desirable to determine the stability constants at known ionic strengths and to mention the type of extrapolation used.

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<sup>11</sup> D. I. HITCHCOCK, J. Amer. chem. Soc. **50** (1928) 2076.

<sup>12</sup> C. W. DAVIES, J. chem. Soc. [London] **1938**, 2093.

<sup>13</sup> E. A. GUGGENHEIM and J. C. TURGEON, Trans. Faraday Soc. **51** (1955) 747.

<sup>14</sup> G. SCATCHARD, The Structure of Electrolytic Solutions, p.9., New York, John Wiley & Sons 1959.

<sup>15</sup> Same as ref. <sup>6</sup>, p. 113.