

STUDY OF COMPETITIVE REACTIONS BY SOLVENT EXTRACTION: DETERMINATION OF STABILITY CONSTANTS

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ABSTRACT

The methods available for the determination of the stability constants of non-extractable complexes by solvent extraction are reviewed. The method proposed by Connick and McVey is valid only when no complexes of the auxiliary-ligand exist in the aqueous phase. This is applicable only at very low concentrations of the auxiliary-ligand. Hence, the stability constants calculated by this method decrease with increasing concentration and approach the theoretical values only at low concentrations of the auxiliary-ligand. It is essential, therefore, to apply the rigorous method incorporating the constants for the metal-auxiliary-ligand to calculate the stability constants which are independent of the changes in the experimental conditions. This is illustrated by few typical calculations.

INTRODUCTION

SOLVENT extraction, developed as a powerful tool for studying equilibria in solution, has been utilised for the determination of the stability constants in systems containing one ligand. This technique has been extended to study competitive complex formation in systems containing a central metal, M, and two ligands, A and X, in which only the complex of the auxiliary-ligand, MA_c, is extracted in the organic solvent. The stability constants of the complexes, MX_n, can be evaluated by measuring the distribution ratios in the presence and absence of the ligand, as has been pointed out by Connick and McVey.¹

The distribution ratio, D_o, in the presence of only the auxiliary-ligand can be written as

$$D_o = \frac{[MA_c]_{org}}{[M] + [MA_1] + [MA_2] + \dots} = \frac{P_c \beta_c [A]^c}{\sum_0^N \beta_n [A]^n} \quad (1)$$

and that in the presence of both the ligands, A and X, is given by

$$D = \frac{[MA_c]_{org}}{[M] + [MA_1] + [MA_2] + \dots + [MX_1] + [MX_2] + \dots}$$

$$= \frac{P_c \beta_c [A]^c}{\sum_0^N \beta_n [A]^n + \sum_1^N \beta'_n [X]^n} \quad (2)$$

where β and β' represent the overall stability constants with the auxiliary-ligand and the complexing-ligand respectively and P_c is the partition coefficient of the species, MA_c . Equations (1) and (2) can be rearranged to obtain

$$F_o = P_c \beta_c [A]^c [D^{-1} - D_o^{-1}] = \sum_1^N \beta'_n [X]^n. \quad (3)$$

This is the familiar form of Fronaeus function and can be solved either by algebraic or graphical methods for the individual stability constants.

Equations (1) and (2) can also be rearranged as

$$D_o D^{-1} = \frac{\sum_0^N \beta_n [A]^n + \sum_1^N \beta'_n [X]^n}{\sum_0^N \beta_n [A]^n}. \quad (4)$$

If the term $\sum_1^N \beta'_n [X]^n$ is negligible, *i.e.*, if no complexes of the auxiliary-ligand exist in the aqueous phase, Eq. (4) becomes

$$F_o = D_o D^{-1} - 1 = \sum_1^N \beta'_n [X]^n. \quad (5)$$

Equation (5) has been used invariably to determine the stability constants of a number of systems. It is the purpose of the present paper to check the conditions under which this method is applicable.

RESULTS

The relative accuracy of the methods has been tested by a few typical calculations. The distribution ratios, D_o and D have been calculated from Eqs. (1) and (2) from known values of the stability constants at different concentrations of the two ligands. The functions, \bar{F}_o and F_o can then be

obtained from Eqs. (3) and (5). The stability constants are calculated by a generalised least square method using a Fortran Program with CDC-3600 computer and have been compared with the theoretical values.

The data calculated for the stability constants corresponding to Indium-TTA-lactic acid system² are presented in Table I. The values of F_0 calculated from Eq. (5) decrease with increasing concentration of the auxiliary-ligand. Consequently, the stability constants are correspondingly lower and only at very low concentrations of the auxiliary-ligand, the stability constants agree with the assumed values. Experiments are generally carried out at a higher concentration of the auxiliary-ligand to obtain the distribution ratio, D_0 , of measurable precision. A limitation is set in the application of this method by the accuracy in the measurement of such low values of the distribution

TABLE I

Values of \bar{F}_0 , F_0 and stability constants at various concentrations of auxiliary-ligand

$$\beta_1 = 10^6; \quad \beta_2 = 10^{12}; \quad \beta_3 = 10^{17}; \quad P_c = 10^8*$$

$$\beta_1' = 10^8; \quad \beta_2' = 10^6; \quad \beta_3' = 10^8$$

[X] M	\bar{F}_0 Eq. (3)	F_0 [Eq. (5)] at [A] M			
		10^{-8}	10^{-7}	10^{-6}	10^{-5}
10^{-6}	0.001001	0.00099	0.0009017	0.000323	0.00000478
10^{-5}	0.0101001	0.0099	0.009098	0.003258	0.0000478
10^{-4}	0.1101	0.1089	0.0992	0.03552	0.000522
10^{-3}	2.1	2.079	1.8917	0.6774	0.00995
10^{-2}	210	207.9	189.172	67.7419	0.9953
10^{-1}	110100	109000.09	99181.25	35516.12	521.8009
D_0	\approx	10^{-4}	0.09	32	474
$\beta_1' \times 10^{-3}$	0.996	0.98	0.897	0.32	0.0047
$\beta_2' \times 10^{-6}$	1.00	0.99	0.90	0.32	0.0048
$\beta_3' \times 10^{-8}$	1.00	0.99	0.90	0.32	0.0047

* In - TTA-Lactic Acid System

$$\beta_1 = 3.2 \times 10^6; \quad \beta_2 = 9.3 \times 10^{11}; \quad \beta_3 = 1.5 \times 10^{17}; \quad P_c = 1.6 \times 10^8.$$

$$\beta_1' = 1.49 \times 10^8; \quad \beta_2' = 1.86 \times 10^6; \quad \beta_3' = 1.79 \times 10^8.$$

ratio. The method is, therefore, not applicable under normal experimental conditions and the stability constants calculated from Eq. (5) will be lower compared to the theoretical values.

Similar results (Tables II and III) have been obtained from data calculated for different constants. Stry³ suggests that this method 'requires a direct determination of a D_0 value which should be very large and thus difficultly determinable'. It can be seen from Tables II and III that the stability constants calculated from the function obtained in the region of large values of D_0 would be considerably lower. He further recommends the calculation of D_0 from the extraction constant, K , given by

$$D_0 = K \frac{[\text{HA}]_{\text{org}}^N}{[\text{H}^+]^N} \quad (6)$$

TABLE II

Values of \bar{F}_0 , F_0 and stability constants at various concentrations of auxiliary ligand

$$\beta_1 = 10^3; \beta_2 = 10^5; \beta_3 = 10^7; P_0 = 10^3$$

$$\beta_1' = 10^3; \beta_2' = 10^5; \beta_3' = 10^7$$

[X]	F_0	F_0 [Eq. (5)] at [A] M				
		Eq. (3)	10^{-5}	10^{-4}	10^{-3}	10^{-2}
M						
0.005	8.75	8.66	7.95	4.15	..	
0.01	30	29.70	27.2	14.2	0.97	
0.03	390	386	354	185	..	
0.05	1550	1534	1408	736	..	
0.1	11,100	10990	10091	5261	...	
D_0	\approx	10^{-5}	9×10^{-3}	4.74	322	
$\beta_1' \cdot 10^{-3}$	1.00	1.003	0.91	0.44		
$\beta_2' \cdot 10^{-5}$	1.00	0.986	0.90	0.47		
$\beta_3' \cdot 10^{-7}$	1.00	0.99	0.91	0.47		

This would also require the determination of the extraction constant at sufficiently low pH to ensure that the metal in the aqueous phase is present mainly as free metal.

TABLE III

Values of \bar{F}_0 , F_0 and stability constants at various concentrations of auxiliary ligand

$$\beta_1 = 10; \quad \beta_2 = 10^2; \quad \beta_3 = 10^3; \quad P_c = 10^3$$

$$\beta_1' = 5; \quad \beta_2' = 50; \quad \beta_3' = 500$$

[X] M	\bar{F}_0	F_0 [Eq. (5)] at [A] M			
	Eq. (3)	10^{-3}	5×10^{-3}	10^{-2}	10^{-1}
0.01	0.0555	..	0.052	0.05	0.0139
0.02	0.124	0.123	..	0.111	..
0.03	0.2085	..	0.198	0.188	0.052
0.05	0.4375	0.433	0.415	0.394	0.109
0.1	1.5	1.49	1.43	1.35	0.375
0.3	19.5	19.31	18.53	17.55	4.88
0.5	77.5	76.37	73.63	69.8	19.38
D_0	\simeq	10^{-4}	10^{-2}	10^{-1}	25
β_1'	5.0	4.995	4.78	4.53	1.24
β_2'	50	49.38	47.4	44.54	12.69
β_3'	500	495.1	475.0	451.2	124.7

It is, therefore, preferable to take into account the constants, $P_c\beta_c$, for the metal-auxiliary-ligand system. This is readily obtained from the available data and by rearranging Eq. (1) as

$$D_0^{-1} [A]^c = \frac{1}{P_c\beta_c} \sum_0^N \beta_n [A]_n \quad (7)$$

The value of $(P_c\beta_c)^{-1}$ obtained at the intercept of a plot of $D_o^{-1} [A]^c$ vs. $[A]$ can be utilised to calculate the function F_o from Eq. (3) which can then be solved for the individual stability constants. This method of determining the stability constants of competitive reactions is more accurate and the experimental conditions, viz., the changes in the auxiliary-ligand concentration do not affect the final values of the constants.

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