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Ultrasonic velocity measurement on EDTA complexes

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Method of calculation of stability constant from ultrasonic velocity measurements are described. The method based on excess compressibility is discussed in detail and the results obtained for Cu-EDTA, Zn-EDTA and Al-EDTA systems are compared with the stability constants determined using the velocity difference. Both the methods are found to lead to the same result, confirming the validity of the new method.

Key words: EDTA complexes, ultrasonics, stability constant

INTRODUCTION

Most of the investigators [1-4] have used ultrasonic velocity measurements for the determination of stoichiometry of the complexes and only a few have used them for the computation of stability constant [4-6].

This paper describes the utility of a new parameter "apparent mole fraction difference", which is defined as the difference in the mole fraction of a binary mixture having the same ultrasonic property (like compressibility or velocity) on the ideal and experimental scales for the determination of stoichiometry and conditional stability constant for copper-EDTA, zinc-EDTA and aluminium-EDTA systems [7].

EXPERIMENTAL

Computation of apparent mole fraction difference due to compressibility under Job's method of continuous variation

The excess compressibility ($\Delta\beta$) is given by

$$\Delta\beta = \beta_{\text{expt}} - \beta_{\text{ideal}} \tag{1}$$

If Φ_1' and Φ_2' are the values of the mole fractions (M.F.) of the components whose adiabatic compressibilities are β_1 and β_2 respectively, then ideal compressibility (β_{ideal}) may be written as

$$\beta_{\text{ideal}} = \Phi_1'\beta_1 + \Phi_2'\beta_2 \tag{2}$$

similarly if Φ_1 and Φ_2 are the mole fraction of the components that corresponds to β_{expt} then

$$\beta_{\text{expt}} = \Phi_1\beta_1 + \Phi_2\beta_2 \tag{3}$$

It is evident from eqns. (2), (3) and (4)

$$\Delta\beta = (\beta_1 - \beta_2)(\Phi_1' - \Phi_1) \tag{4}$$

since the mixtures are prepared under Job's method and $(\Phi_1 + \Phi_2) = (\Phi_1' + \Phi_2') = 1$. Denoting $(\Phi_1' - \Phi_1)$ which also equals to $(\Phi_2 - \Phi_2')$ as $\partial\Phi_\beta$, eqn. (4) will become

$$\Delta\beta = (\beta_1 - \beta_2)\partial\Phi_\beta \tag{5}$$

This equation gives the relation between excess compressibility and $\partial\Phi_\beta$ and hence it is clear wherever $\Delta\beta$ is realisable, $\partial\Phi_\beta$ is also realisable.

Estimation of $\partial\Phi_\beta$

At any mole fraction Φ_1, the experimental value of compressibility β_{expt} is determined and that value is substituted in eqn. (2) as required by the definition. Hence

$$\beta_{\text{expt}} = \Phi_1'\beta_1 + \Phi_2'\beta_2 \tag{6}$$

Remembering $\Phi_2' = 1 - \Phi_1'$ and simplifying one gets

$$\Phi_1' = \frac{\beta_{\text{expt}} - \beta_2}{(\beta_1 - \beta_2)} \tag{7}$$

and

$$\partial\Phi_\beta = (\Phi_1' - \Phi_1) \tag{8}$$

Determination of stoichiometry

It is evident from eqn. (5) that variation of $\partial\Phi_\beta$ is like the variation of $\Delta\beta$ with the mole fraction of any one of the components. The maximum value $\Delta\beta$ corresponds to that of $\partial\Phi_\beta$ at the stoichiometric point similar to the absorbance behaviour in spectrophotometry [8].

Evaluation of conditional stability constant (K) of 1:1 complexes

The method of computation of conditional stability constant is same as in earlier cases [4-6]. The important details alone are considered.

The computation of $\partial\Phi_\beta$ are made in the region nearer to the stoichiometric point, where the ionic strength is nearly constant. The value of $\partial\Phi_\beta$ is proportional to complex concentration, which is p (the extent of complexation) times the metal added when ligand added where the metal

is in excess. The value p/q approaches unity in the case of strong complexes and will have the same value at the stoichiometric point especially in 1:1 complexes.

In the vicinity of the stoichiometric point, the values of $\partial\Phi_\beta$ are estimated from the values of the compressibility which are arrived at by Gregory Newton's Forward Interpolation procedure from the measured compressibility values given for different mole fractions of the metal/ligand.

With the estimated values of $\partial\Phi_\beta$ nearer to the stoichiometric point, a linear point of $\partial\Phi_\beta$ versus metal concentration [B] can be constructed. The slope and intercept are found through least square. The value of $\partial\Phi_{\beta_o}$ corresponding to the stoichiometric point (viz. 0.5 MF)is then determined using the slope and intercept values. The value $\partial\Phi_{\beta_o}$ alongwith the value $\partial\Phi_\beta$ estimated from the experimental value at stoichiometric point [A_o = B_o] is used for computing complex concentrations [x] which is given by

$$[x] = \left(\frac{\partial\Phi_\beta}{\partial\Phi_{\beta_o}}\right)[B_o] \qquad (9)$$

The computation of conditional stability constant (K_c) is straightforward by making use of [x] and [B_o]

$$K_c = \frac{[x]}{\{[B_o] - [x]\}^2} \qquad (10)$$

The above treatment can also be seen to be applicable for apparent mole fraction difference due to velocity.

RESULTS AND DISCUSSION

Table I represents the values of $\partial\Phi_\beta$ computed by the procedure described for copper-EDTA system. It is evident from the Table that $\partial\Phi_\beta$ is maximum at 0.5 MF, thereby establishing the stoichiometry of the complex at 1:1. The values of apparent mole fractions difference due to velocity ($\partial\Phi_u$) so computed also confirms the above results.

Table II gives the values of the conditional stability constant (K_c) obtained through $\partial\Phi_\beta$ and $\partial\Phi_u$. The versatility and usefulness of the proposed approach is seen from the consistency in the values of K_c. Conditional stability constant values are usually reported under constant ionic strength, since this condition is not realisable in this type of work, a direct comparison of K_c values with literature is not possible. It can be seen that $K_cCu > K_cZn > K_cAl$ in agreement with reported trend in literature [9].

TABLE–I: Values of $\partial\Phi_\beta$ and $\partial\Phi_u$ for different MF of copper

System: copper-EDTA; pH: 3.0, Temp: 303K

MF of copper 1	$\partial\Phi_\beta$	$\partial\Phi_u$
0.1	0.19	0.20
0.2	0.30	0.34
0.3	0.39	0.49
0.4	0.48	0.52
0.5	0.49	0.54
0.6	0.44	0.48
0.7	0.34	0.38
0.8	0.21	0.24
0.9	0.13	0.14

TABLE–II: Values of conditional stability constant

Temp: 303K; pH = 3.0

System	log K_c values through	
	$\partial\Phi_\beta$	$\partial\Phi_u$
Copper-EDTA	6.10	6.17
Zinc-EDTA	5.21	5.27
Aluminium-EDTA	4.83	4.75

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