Thermodynamics of Acid–Base and Complex Equilibria

Measurement of pK for Weak Bases with the Aid of Sodium Ion-Selective Electrodes

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A method for obtaining pK_a of weak bases from emf measurements of cells with glass pH electrodes and sodium ion-selective electrodes is described. The Harned–Ehlers method [1] uses hydrogen and Ag/AgCl electrodes; it yields accurate results but requires special apparatus and techniques and numerous data. The present method produces somewhat less accurate data; it retains the advantages of a cell with liquid junction, however, and is both simple and rapid. It is particularly suited to the study of bases where the solubility of AgCl is often of concern.

To determine the equilibrium constant K_a for the process $BH^+ \rightleftharpoons B + H^+$, one measures the emf (E) of cells

$$\begin{array}{c|c|c} \text{pH glass} & & \\ \text{electrode} & BH^+(m_1), B(m_2), NaCl(m_3) & \text{Na ISE} \end{array}$$

The emf of this cell is given by

$$pK_a + \log(\gamma_{Na^+}\gamma_B/\gamma_{BH^+}) = \\ = (E - E^\circ)/k + \log(m_{BH}/m_B m_{Na})$$

where k is the Nernst slope, 2.3026 RT/F. With weak bases ($K_b < 10^{-4}$) and a fixed small molality of Na^+ (*e.g.*, 0.01 *m*), the last term remains constant when the buffer is diluted with NaCl solution. More important, the activity coefficient term is small and varies linearly with ionic strength (I). Thus E is a linear function of I, with a small slope. This is not the case with the Harned method, where this term is log $(\gamma_{BH^+}\gamma_{Cl^-}/\gamma_B)$.

The value of pK_a can be derived from the intercept (E′) at I = 0. Similar measurements of E′ for a reference base of known pK_a (*e.g.*, tris(hydroxymethyl)aminomethane [2]) provide the value of E°. If the buffer ratio and sodium molality are the same for the reference buffer and the unknown buffer, $\Delta pK_a = \Delta E'/k$.

Results are given for several weak bases in water and in 50% methanol/water at temperatures from 15 to 35 °C. The responses of the electrodes were in accord with the Nernst slope. Two or three measurement were sufficient to yield values of pK_a. The results agreed well with accepted constants from the literature.

References

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Formation and Stability of Alkali-Metal Complexes of Some Carboxylic and Hydroxycarboxylic Acids in Aqueous Solution

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Alkali-metal ions form weak complexes with various low-molecular-weight organic ligands [1]. Most of these ligands are of biological interest and are present both in biofluids and in natural waters. Since a large amount of alkali-metal ions is present in all natural fluids (*e.g.* sodium and potassium are the main ionic constituents of all intra- and extracellular liquids and play a fundamental role in electrical communication through membranes), the knowledge of the formation constants of their complexes is quite important. Furthermore, the comparison of the stability constants concerning complexes of other metal ions, determined in different ionic media (in particular K^+ and Na^+), can give rise to some uncertainties if the formation constants of the alkali-metal complexes are unknown.

For the above reasons we thought it useful to study systematically the complexes of alkali-metal ions with carboxylic and hydroxycarboxylic acids. The formation constants have been determined potentiometrically by alkalimetric titrations of the acids using KNO_3, $NaNO_3$, $NaClO_4$, $LiNO_3$, $CsNO_3$ and tetraethylammonium bromide as background in the concentration range 0.03–1.0 mol dm^{-3} at 25° and 37 °C. Citrate, tartrate, malate, oxalate, malonate, phthalate and succinate ligands were investigated. The potentiometric data have been analyzed by using modified versions of ACBA [2] and MINIQUAD [3] least squares computer programs.

All the ligands considered form complexes with alkali-metal ions and the stability constants show the trends citrate > tartrate > malate and oxalate > malonate ~ phthalate > succinate for hydroxycarboxylic and carboxylic acids respectively. As regards the metal ion the trend is $Li > Na > K > Cs$. The hydroxycarboxylic acids form protonated species too.

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Mixed Metal Complexes in Solution. Thermodynamic Study of Heterobinuclear Metal(II)–Citrate Complexes in Aqueous Solution

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Though the formation of mixed ligand ternary complexes is well known in the literature, the study in solution of mixed metal complexes having one ligand and two different metal ions has been very little developed. The formation of this type of ternary species might explain a number of apparently anomalous data and some interferences in analytical procedures.

We have previously reported the stability constants of heterobinuclear copper(II)–L-histidinate complexes with nickel(II), zinc(II) or cadmium(II) in aqueous solution [1]. Such mixed metal complexes are formed by another imidazole derivative too [2]. Now we are extending our investigation to another set of ligands, namely hydroxypolycarboxylic acids, widely used as buffers, which are of relevant importance in the analytical field and also in biofluids. In this work we report the thermodynamic parameters for the formation of heterobinuclear complexes of citrate (cit^{3-}) with Cu(II)–Ni(II), Ni(II)–Zn(II), Cu(II)–Zn(II) ion couples, determined in aqueous solution at 25 °C and 0.1 mol dm^{-3} ($K[NO_3]$). The alkalimetric titration curves of solutions containing citric acid and two different metal ions exhibit two buffer regions, one in the acidic and the other in the neutral–alkaline range. By comparing the experimental curves with those calculated taking into account only the binary species, the existence of heterobinuclear complexes in the acidic region was excluded, whilst it was strongly evident in the neutral–alkaline region. The species present in the latter pH range, when considering the binary systems, are of the type $[M_2(cit)_2H_{-2}]^{4-}$, (M = Cu(II), Ni(II) or Zn(II)); graphical analysis and computer calculations showed the presence of the $[MM'(cit)_2H_{-2}]^{4-}$ for each couple of metal considered. The stability constants corresponding to the equilibrium: $M^{2+} + M'^{2+} + 2\ cit^{3-} \rightleftarrows [MM'(cit)_2H_{-2}]^{+}\ 2H^{+}$ are:

Cu(II)–Ni(II)	$\log\beta = 1.55 \pm 0.05$
Ni(II)–Zn(II)	$\log\beta = -2.92 \pm 0.08$
Cu(II)–Zn(II)	$\log\beta = 1.51 \pm 0.11$

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Theoretical Studies on the Protonation of Diamines in Aqueous Solution

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A considerable amount of thermodynamic work has been carried out on protonation of polyamines