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Acid–Base Equilibriums in Solutions of Polybases (Model and Experiment): II.[1] Thermodynamic Dissociation Constants of Protonated Trifunctional Bases

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Abstract—A procedure for estimation of dissociation constants of protonated tribasic species is developed distinguished by a new approach to evaluation of concentrations of all moieties in the equilibrium and accounting for it in the calculation of the solution ionic strength.

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Thermodynamic dissociation constants of a protonated base are defined by the following relations [1]:

$$K_{a1} = a_{H^+}\frac{[B]f_0}{[BH^+]f_1}\,,\ K_{a2} = a_{H^+}\frac{[BH^+]f_1}{[BH_2^{2+}]f_2}\,,\ K_{a3} = a_{H^+}\frac{[BH_2^{2+}]f_2}{[BH_3^{3+}]f_3}\,. \quad (1)$$

In the equation (1) $a(H^+)$ is activity of lionium ions, that is, of the solvated hydrogen ions, hereinafter denoted as *a*(lionium), at any point of the potentiometric titration curve; [B], $[BH^+]$, $[BH_2^{2+}]$, and $[BH_3^{3+}]$ are equilibrium concentrations of neutral and protonated tribasic species in the process of titration with a strong acid; f_0, f_1, f_2, and f_3 are the activity coefficients of the neutral and protonated forms of the polybase.

It has been noted earlier [2] that the known methods for estimating the ionic strength in an acid–base equilibrium [3–5] proceed from the concentration of the first ionized species, e.g., $[BH^+]$ for a bifunctional base. However, it has been shown [1, 2, 6, 7] that at the calculation of dissociation constants the equilibrium concentrations of remaining ions should not be omitted because they are comparable by the value with the concentrations of the first protonated ion, and from the data depicted in Fig. 1 is seen that in the process of neutralization the concentrations of next ions (e.g., $[BH_3^{3+}]$) are even higher than the concentration of the ion $[BH^+]$.

The most acceptable method for the estimation of ionic strenght with accounting for equilibrium concentrations of all charged moieties is plotting the titration curve in logarithmic coordinates [1, 2, 7]. Then the equilibrium concentrations of all the species [B], $[BH^+]$, $[BH_2^{2+}]$, and $[BH_3^{3+}]$ formed at the titration of trifunctional base with a strong monoprotic *para*-toluenesulfonic acid can be evaluated from the plots log *a*(lionium)–log *C*. Estimation of the values of activity coefficients f_0, f_1, f_2, and f_3 is carried out using the advanced (as compared with the Debye method) Davis method [8]:

$$\log f_1 = \frac{Az_i^2\sqrt{I}}{1+\sqrt{I}} + 0.1I. \quad (2)$$

The results of measuring electromotive force in chain (I) in acetone medium as a dependence of molal concentration of perchloric acid allowed the estimation of the degree of $HClO_4$ dissociation and initial values for the calculation of the chain standard potential.

The perchloric acid dissociation degree can be estimated with Eq. (3) [1, 2, 7, 12].

$$\log(1-\alpha) = (E_0^* - E_{measured} + \theta\log m)/\theta. \quad (3)$$

The value of E_0^* that equals the difference $E^0 - \theta pK_a(HClO_4) = E_0^*$ ($\theta = 2.3RT/F$), is calculated using

[1] For communication XXI, see [1].

the least-squares method from the dependence $E_{measured} = f(\log m)$ at $\log m = 0$. The value obtained is $E_0^* = 0.5515$, with the regression coefficient $r = 0.9936$.

The value of the chain (I) standard potential is calculated using the author's own computer program "cubic" from the approximation of the function $E' = f(m\alpha)^{0.5}$ at $(m\alpha) = 0$, where $E' = E_{measured} + \theta\log(m\alpha)$.

$$E' = -14.876(m\alpha)^{3/2} + 6.8269(m\alpha) - 1.3006(m\alpha)^{0.5} + 0.7127,$$
$$r\ 0.9999.$$

Thus, we obtained the standard potential of the chain (I) in the acetone medium, $E_0 = 0.7127$ V. Meanwhile, the index of dissociation constants of perchloric acid in acetone is: $pK_a(HClO_4) = (0.7127 - 0.5515)/0.0595 = 2.71$

The chain (I) standard potential with the equilibrium concentrations of neutral molecule of base and charged species [B], $[BH^+]$, $[BH_2^{2+}]$, and $[BH_3^{3+}]$ formed in the process of titration of 0.03904 N solution of 3,4,4'-triaminodiphenyl oxide with 0.1541 N solution of perchloric acid in acetone medium (Fig. 1), and their activity coefficients f_0, f_1, f_2, and f_3 allow calculation of thermodynamic acidity constants of the protonated trifunctional bases in the medium of an organic solvent by the above formulas (1) and (2).

Activity of lionium ions in the process of titration of a base can be estimated using the Nernst equation:

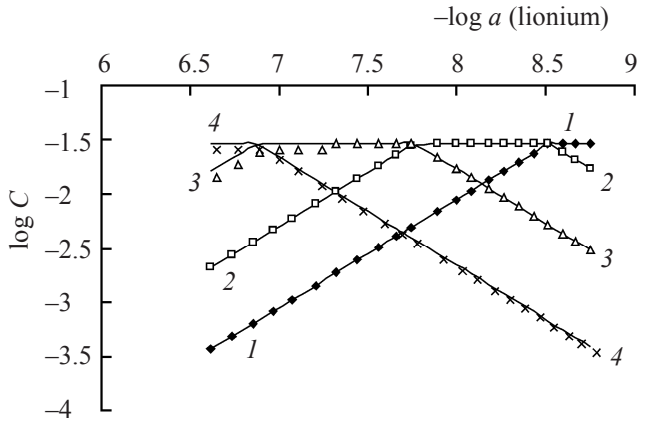
$$-\log a(\text{lionium}) = (E_0 - E_{measured})/0.0595.$$

The proposed procedure that, as shown in preceding publications, differed from the known ones by application of logarithmic plots at the estimation of ionic strength and activity coefficient, was tested on an example of 1,3-diphenylguanidine (DPhG) in DMF medium. The value of pK_a(DPhG/DMFA) = 9.1 has been published [13]. We obtained [1] the value pK_a(DPHG/DMFA) = 9.15±0.03, that attested the reliability and reproductivity of the proposed method.

As seen from Fig. 1, the equilibrium concentrations of various species in the titrate are quite comparable. Therefore at the pK_a calculations all the concentrations should be accounted for.

The protonated trifunctional bases are characterized by the similarity of acidity constants confirmed by the existence of a single jump of potential on the potentiometric titration curve (omitted here).

The values of thermodynamic dissociation constants of protonated 3,4,4'-triaminodiphenylmethane in acetone calculated in the respective buffer regions areas follows: $pK_1 = 7.99±0.11$, $pK_2 = 6.94±0.11$, $pK_3 = 5.82±0.09$.



Logarithmic diagram of the titration process of 0.03904 N solution of 3,4,4'-triaminodiphenyloxide with 0.1541 N solution of perchloric acid in acetone that allows estimation of concentrations of moieties in equilibrium: (*1*) log [B], (*2*) log $[BH^+]$, (*3*) lgo$[BH_2^{2+}]$, and (*4*) log $[BH_3^{3+}]$.

The developed procedure of determining thermodynamic acidity constants of protonated bases in the medium of an organic solvent is quite acceptable for experimental measuring pK_a values of any trifunctional bases at the simultaneous neutralization of these functional groups.

EXPERIMENTAL

Measuring of electromotive force and potentiometric titration was carried out in acetone at 25.0±0.2ºC with a pH meter–millivoltmeter METROHM-632 (Switzerland). The solvent was purified and dried from water by common procedures [9, 10]. The water content in the acetone measured by modified K. Fisher method [11] was 0.01 wt % or less.

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