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**THE REGULARITIES OF DISTRIBUTION OF THE IONIZED AND
NON-IONIZED FORMS IN THE DILUTE SOLUTIONS OF WEAK
MULTIBASIC ORGANIC ACIDS**

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Pursuant to the conditions of an equality of the concentrations of various ionized and non-ionized forms in the dilute solutions of weak multi-basic organic acids, the areas of dominance of these forms in connection with the values of corresponding usual and "partial" degrees of dissociation have been formulated. Considered are weak dibasic and tri-basic acids, and the general case of a weak multi-basic acid, H_nA .

Keywords: *di-basic acids; tri-basic acids; degrees of dissociation; multi-basic acids; hydrogen ions; anions; equations.*

1. Introduction

The majority of drugs are weak acids and/or bases. Their biopharmaceutical properties are closely connected with the dissociation parameters of these compounds which determine the distribution of the ionized and non-ionized forms of the latter in solution. Ionization state (which is determined by the degree of ionization) is the very factor that affects within physiological systems the rate at which the compound is able to diffuse across membranes and obstacles such as blood-brain barrier, determines the acid-base homeostasis and enzyme kinetics in the cell and in the body. Acid dissociation parameters are also essential in aquatic chemistry and chemical oceanography, where the acidity of water plays a fundamental role.

Dilute solutions of weak multi-basic organic acids with the close values of the dissociation constants of various steps (the case of "overlapping equilibriums") are the complex systems which contain the various anions, hydrogen ions and non-ionized acid molecules. The conditions of an existence of these forms within the various acid concentration bounds, their connection with the dissociation parameters and particularly with the degrees of dissociation of the various dissociation steps have not been established so far. In this paper with the aid of the formerly suggested by us method [1, 2] the regularities of distribution of the various ionized and non-ionized forms in the dilute solutions of weak multi-basic organic acids are described.

2. Di-basic Acids

It was shown in [1,2] that the concentrations of ionized and non-ionized forms in $\text{mol} \cdot \text{dm}^{-3}$ in the dilute solutions of weak

dibasic organic acids with "overlapping equilibriums" may be expressed as follows:

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2') \quad (1)$$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') \quad (2)$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2' \quad (3)$$

$$[H_2A] = c(1 - \alpha_1) \quad (4)$$

were α_1 and α_2 are the usual degrees of dissociation of first and second dissociation steps, α_2' is the "partial" degree of dissociation of second step, c is the total concentration of

acid in $\text{mol} \cdot \text{dm}^{-3}$. Taking into account these equations, we can formulate the conditions of an equality of the concentrations of the ionized and non-ionized forms:

$$[H^+] = [H_2A]: \alpha_1 = \frac{1 - \alpha_2}{2} = \frac{1}{\alpha_2' + 2} \quad (5)$$

$$[HA^-] = [H_2A]: \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha_2'} \quad (6)$$

$$[A^{2-}] = [H_2A]: \alpha_1 = 1 - \alpha_2 = \frac{1}{\alpha_2' + 1} \quad (7)$$

When the equality (7) exists we have:

$$\alpha_1 + \alpha_2 = 1$$

It follows from Eq. (1) that in this case

$$[H^+] = c.$$

$$[HA^-] = [A^{2-}]: \alpha_1 = 2\alpha_2 \quad (8)$$

$$\alpha_2' = 0.5 \quad (9)$$

It is necessary to note that this is very rare case. Taking into account the conditions of an equality of the concentrations of various

The conditions of an equality of the concentrations of mono- and dianions can be also formulated:

ionized and non-ionized forms, we may formulate the areas of dominance of the latter:

$$[H^+] > [H_2A]: \alpha_1 > \frac{1 - \alpha_2}{2} \quad \text{or} \quad \alpha_1 > \frac{1}{\alpha_2' + 2} \quad (10)$$

(and vice versa)

$$[HA^-] > [H_2A]: \alpha_1 > \frac{1 + \alpha_2}{2} \quad \text{or} \quad \alpha_1 > \frac{1}{2 - \alpha_2'} \quad (11)$$

(and vice versa)

$$[A^{2-}] > [H_2A]: \alpha_1 > 1 - \alpha_2 \quad \text{or} \quad \alpha_1 > \frac{1}{\alpha_2' + 1} \quad (12)$$

(and vice versa)

$$[HA^-] > [A^{2-}]: \alpha_1 > 2\alpha_2 \quad \text{or} \quad \alpha_2' < 0.5 \quad (13)$$

The hydrogen ion concentration in all cases exceeds not only the concentrations of

every anion but also the total concentration of all anions which is equal to $\alpha_1 c$.

3. Tri-basic Acids

The concentrations of the ionized and non-ionized forms in this case are connected

with the corresponding dissociation degrees as follows:

$$[H^+] = c(\alpha_1 + \alpha_2 + \alpha_3) = c\alpha_1(1 + \alpha_2' + \alpha_2'\alpha_3') \quad (14)$$

$$[H_2A^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') \quad (15)$$

$$[HA^{2-}] = c(\alpha_2 - \alpha_3) = c\alpha_1\alpha_2'(1 - \alpha_3') \quad (16)$$

$$[A^{3-}] = c\alpha_3 = c\alpha_1\alpha_2'\alpha_3' \quad (17)$$

$$[H_3A] = c(1 - \alpha_1) \quad (18)$$

The conditions of an equality of the concentrations of the ionized and non-ionized forms may be expressed as follows:

$$[H^+] = [H_3A]: \alpha_1 = \frac{1 - \alpha_2 - \alpha_3}{2} = \frac{1}{2 + \alpha_2' + \alpha_2'\alpha_3'} \quad (19)$$

$$[H_2A^-] = [H_3A]: \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha_2'} \quad (20)$$

$$[HA^{2-}] = [H_3A]: \alpha_1 = 1 - \alpha_2 + \alpha_3 = \frac{1}{1 + \alpha_2'(1 - \alpha_3')} \quad (21)$$

$$[A^{3-}] = [H_3A]: \alpha_1 = 1 - \alpha_3 = \frac{1}{1 + \alpha_2'\alpha_3'} \quad (22)$$

$$[H_2A^-] = [HA^{2-}]: \alpha_1 = 2\alpha_2 - \alpha_3 = \frac{1}{2 - \alpha_3'} \quad (23)$$

This latter equality is very rare; it takes place in case of tri-mellitic acid which has the sufficiently high α_2 value.

The areas of dominance of various ionized and non-ionized forms in the dilute solutions of weak tri-basic organic acids are formulated as follows:

$$[H^+] > [H_3A]: \alpha_1 > \frac{1 - \alpha_2 - \alpha_3}{2} \quad \text{or} \quad \alpha_1 > \frac{1}{2 + \alpha_2' + \alpha_2'\alpha_3'} \quad (24)$$

(and vice versa)

$$[H_2A^-] > [H_3A]: \alpha_1 > \frac{1 + \alpha_2}{2} \quad \text{or} \quad \alpha_1 > \frac{1}{2 - \alpha_2'} \quad (25)$$

(and vice versa)

$$[HA^{2-}] > [H_3A]: \alpha_1 > (1 - \alpha_2 + \alpha_3) \quad \text{or} \quad \alpha_1 > \frac{1}{1 + \alpha_2'(1 - \alpha_3')} \quad (26)$$

(and vice versa)

$$[A^{3-}] > [H_3A]: \alpha_1 > 1 - \alpha_3 \quad \text{or} \quad \alpha_1 > \frac{1}{1 + \alpha_2'\alpha_3'} \quad (27)$$

(and vice versa)

$$[H_2A^-] > [HA^{2-}]: \alpha_1 > 2\alpha_2 - \alpha_3 \quad \text{or} \quad \alpha_1 > \frac{1}{2 - \alpha_3'} \quad (28)$$

4. General equations

For weak multi-basic organic acid H_nA ionized forms are connected with the concentrations of the ionized and non- corresponding degrees of dissociation as follows:

$$[H^+] = c \sum_{m=1}^n \alpha_m = c \sum_{m=1}^n \alpha'_m \alpha'_{m-1} \quad (29)$$

$$[H_{n-1}A^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha'_2) \quad (30)$$

$$[H_{n-2}A^{2-}] = c(\alpha_2 - \alpha_3) = c\alpha_1\alpha'_2(1 - \alpha'_3) \quad (31)$$

$$\dots\dots\dots$$

$$[H_{n-m}A^{m-}] = c(\alpha_m - \alpha_{m+1}) = c\alpha_1\alpha'_2\dots\alpha'_m(1 - \alpha'_{m+1}) \quad (32)$$

$$\dots\dots\dots$$

$$[A^{n-}] = c\alpha_n = c\alpha_1\alpha'_2\dots\alpha'_n \quad (33)$$

$$[H_nA] = c(1 - \alpha_1) \quad (34)$$

The conditions of an equality of the concentrations of the ionized and non-ionized forms are presented below:

$$[H^+] = [H_nA]: \alpha_1 = \frac{1 - \sum_{m=2}^n \alpha_m}{2} \quad (35)$$

(the equation connected α_1 with the corresponding "partial" degrees of dissociation is not quoted because of its complexity).

$$[H_{n-1}A^-] = [H_nA]: \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha'_2} \quad (36)$$

$$[H_{n-m}A^{m-}] = [H_nA]: \alpha_1 = 1 - \alpha_m + \alpha_{m+1} = \frac{1}{1 + \alpha'_2\dots\alpha'_m(1 - \alpha'_{m+1})} \quad (37)$$

$$[A^{n-}] = [H_nA]: \alpha_1 = 1 - \alpha_n = \frac{1}{1 + \alpha'_2\dots\alpha'_m} \quad (38)$$

$$[H_{n-m}A^{m-}] = [H_{n-(m+1)}A^{(m+1)-}]: \alpha_m = 2\alpha_{m+1} - \alpha_{m+2} \quad (39)$$

$$\alpha'_{m+1} = \frac{1}{2 - \alpha_{m+2}} \quad (40)$$

The conditions of dominance of the acids (eqs. 11 and 25). For other forms the concentration of mono-anion in comparison with the concentration of non-dissociated acid are the same as in the cases of di- and tri-basic acids (eqs. 11 and 25). For other forms the areas of dominance may be described as follows:

$$[H_{n-m}A^{m-}] > [H_nA]: \alpha_1 > 1 - \alpha_m + \alpha_{m+1} \text{ or } \alpha_1 > \frac{1}{1 + \alpha'_2\dots\alpha'_m(1 - \alpha'_{m+1})} \quad (41)$$

(and vice versa)

$$[A^{n-}] > [H_n A] : \alpha_1 > 1 - \alpha_n \text{ or } \alpha_1 > \frac{1}{1 + \alpha_2 \dots \alpha_m} \quad (42)$$

(and vice versa)

$$[H_{n-m} A^{m-}] > [H_{n-(m+1)} A^{(m+1)-}] : \alpha_m > 2\alpha_{m+1} - \alpha_{m+2} \text{ or}$$

$$\alpha_{m+1} > \frac{1}{2 - \alpha_{m+2}} \quad (43)$$

In general the $[H^+]$ value always exceeds the concentration of every anion and even the total concentration of all anions. If we take into account that this summary anions

concentration $\sum_{m=1}^n [H_{n-m} A^{m-}] = \alpha_1 c$ and the

concentration of non-dissociated acid $[H_n A] = c(1 - \alpha_1)$, the condition of an equality of these two concentrations may be formulated:

$$\alpha_1 = 0.5 \quad (44)$$

Summary

As a further development of the method of an analysis of the complex equilibriums in the processes of electrolytic dissociation of weak multi-basic organic acids the conditions of a dominance of the concentrations of various anions and hydrogen ions in comparison with the concentration of non-

dissociated acid in the dilute acid solutions were formulated. The areas of a dominance of these ionized and non-ionized forms were connected with the values of the corresponding usual and "partial" degrees of dissociation.

References

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ÇOXƏSASLI ZƏİF ÜZVİ TURŞULARIN DURU MƏHLULLARINDA İONLAŞMIŞ VƏ İONLAŞMAMIŞ FORMALARIN PAYLANMA QANUNAUYGUNLUQLARI

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Çoxəsaslı zəif üzvi turşuların duru məhlullarında müxtəlif ionlaşmış və ionlaşmamış formaların qatılıqlarının bərabərliyindən çıxış edərək bu formaların dominant sahələri ceçilib.

Açar sözlər: çoxəsaslı turşular, dissosiasiya dərəcəsi, anionlar

ЗАКОНОМЕРНОСТИ РАСПРЕДЕЛЕНИЯ ИОНИЗИРОВАННЫХ И НЕИОНИЗИРОВАННЫХ ФОРМ В РАЗБАВЛЕННЫХ РАСТВОРАХ СЛАБЫХ МНОГООСНОВНЫХ ОРГАНИЧЕСКИХ КИСЛОТ

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Из условий равенства концентраций различных ионизированных и неионизированных форм в разбавленных растворах слабых многоосновных органических кислот выделены области доминирования этих форм как функции значений соответствующих обычных и «парциальных» степеней различных ступеней диссоциации. Рассмотрены случаи слабых двух- и трехосновных органических кислот, а также общий случай слабой многоосновной кислоты H_nA .

Ключевые слова: *двухосновные кислоты, трехосновные кислоты, степени диссоциации, многоосновные кислоты, ионы водорода, анионы, уравнения.*