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Two-Phase Buffer Systems Containing a Sparingly Soluble Diprotic Acid as the Solid Phase

Tomislav J. Janjić[a,*], **Lidija B. Pfendt**[a], and **Mirjana B. Pasulj**[b]

[a] Chemical Institute, Faculty of Sciences, University of Belgrade,
YU-11001 Belgrade, Yugoslavia
[b] Faculty of Farmacy, University of Belgrade, YU-11001 Belgrade, Yugoslavia

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Two-phase buffer systems consisting of a sparingly soluble diprotic acid and its saturated aqueous solution (buffered phase) are investigated. The equations for the dependence of buffer capacity on *pH* and for evaluation of dilution effects in two-phase buffers of this type are derived. Theoretical considerations are experimentally verified on four buffer systems containing 1,2-, 1,3-, 1,4-benzenedicarboxylic and octanedioic acid. The main characteristic of the buffers of this type is a very high buffer capacity within a narrow *pH* range.

(Keywords: Two-phase buffers; Heterogeneous equilibria; Diprotic acids)

Zweiphasen-Puffersysteme mit einer schwerlöslichen diprotischen Säure als feste Phase

Zweiphasen-Puffersysteme, bestehend aus einer schwerlöslichen diprotischen Säure und ihrer gesättigten wäßrigen Lösung (gepufferte Phase), wurden untersucht. Die Gleichungen für die Abhängigkeit der Pufferkapazität vom *pH* und für die Berechnung der Verdünnungseffekte in derartigen Zweiphasen-Puffersystemen wurden aufgestellt. Dabei wurden die theoretischen Betrachtungen an vier Puffersystemen, die Benzol-1,2-, -1,3- und -1,4-dikarbonsäuren bzw. Oktandisäure enthielten, experimentell geprüft. Die wichtigste Eigenschaft solcher Puffer ist ihre sehr hohe Pufferkapazität innerhalb eines engen *pH*-Bereiches.

Introduction

In one of our earlier papers[1] two-phase buffer systems consisting of a sparingly soluble monoprotic acid as the solid phase and its saturated aqueous solution (buffered phase), have been investigated. It has been established that the buffers of this type, contrary to classical (monophase) buffers, possess a very high buffer capacity over a narrow *pH* range. Continuing these investigations in this paper we have studied two-phase buffer systems consisting of a sparingly soluble diprotic acid and its saturated aqueous solution.

Experimental

All apparatus used and the experimental conditions applied in this paper were analogous to those described in our previous paper[2]. All experiments were performed in solutions of constant ionic strength, $I = 1$ (NaCl), at 25 ± 0.1 °C.

In direct titrations of sparingly soluble diprotic acids, a suspension containing $2 \cdot 10^{-3}$ mole of corresponding acid in 20 ml of sodium chloride, was titrated with a standard 1 *M* sodium hydroxide solution. The equilibration time in vigorously stirred systems was from 2 to 3 minutes. In reverse titration, 20 ml of 0.1 *M* solution of disodium salt of the corresponding diprotic acid in sodium chloride was titrated with a standard 1 *M* hydrochloric acid solution. The equilibration was almost instantaneous except in case of 1,2-benzenedicarboxylic acid, due to the formation of a supersaturated solution.

For determination of dilution effects, a suspension containing $2 \cdot 10^{-3}$ mole of corresponding acid in 20 ml of sodium chloride was partially neutralized with a standard sodium hydroxide solution, and after equilibration *pH* was measured. The solution was then diluted with an equal volume of 1 *M* sodium chloride and the *pH* value was measured again after equilibration.

Experimental data were processed by means of suitable programs with a Texas Instruments TI-58 programmable calculator.

Results and Discussion

Mathematical Considerations

In two-phase buffer systems containing a sparingly soluble diprotic acid (H_2A) as the solid phase, the following equilibria are possible:

$$(H_2A)_s + 2\,H_2O \rightleftarrows 2\,H_3O^+ + A^{2-} \qquad K_{s1}^M = a_{H_3O^+}^2 \cdot c_{A^{2-}} \qquad (1)^*$$

$$(H_2A)_s + H_2O \rightleftarrows H_3O^+ + HA^- \qquad K_{s2}^M = a_{H_3O^+} \cdot c_{HA^-} \qquad (2)$$

$$(H_2A)_s \rightleftarrows H_2A \qquad K_{s3} = c_{H_2A} \qquad (3)$$

According to the definition, buffer capacity is given by the following expression:

$$\beta = \frac{\mathrm{d}c_b}{\mathrm{d}pH} \qquad (4)$$

The stoichiometric concentration of the strong base in the solution of such a heterogeneous system is given by the equation:

$$c_b = 2\,c_{A^{2-}} + c_{HA^-} + c_{OH^-} - c_{H_3O^+} \qquad (5)$$

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* $a_{H_3O^+} = 1.10^{-pH}$.

By making the corresponding replacement from eqs. (1)–(2), the eq. (5) becomes:

$$c_b = \frac{2\,K^M_{s1}}{a^2_{\mathrm{H_3O^+}}} + \frac{K^M_{s2}}{a_{\mathrm{H_3O^+}}} + \frac{K_w}{y\,a_{\mathrm{H_3O^+}}} - \frac{a_{\mathrm{H_3O^+}}}{y} \tag{6}$$

In this equation y denotes the mean activity coefficient. Differentiation of eq. (6) gives the expression:

$$\frac{\mathrm{d}c_b}{\mathrm{d}a_{\mathrm{H_3O^+}}} = -\frac{4\,K^M_{s1}}{a^3_{\mathrm{H_3O^+}}} - \frac{K^M_{s2}}{a^2_{\mathrm{H_3O^+}}} - \frac{c_{\mathrm{OH^-}}}{a_{\mathrm{H_3O^+}}} - \frac{1}{y} \tag{7}$$

In view of eqs.:

$$\frac{\mathrm{d}c_b}{\mathrm{d}pH} = \frac{\mathrm{d}c_b}{\mathrm{d}a_{\mathrm{H_3O^+}}} \cdot \frac{\mathrm{d}a_{\mathrm{H_3O^+}}}{\mathrm{d}pH} \tag{8}$$

$$\frac{\mathrm{d}c_b}{\mathrm{d}pH} = \frac{\mathrm{d}c_b}{\mathrm{d}a_{\mathrm{H_3O^+}}}\,(-\,2\cdot 3\,a_{\mathrm{H_3O^+}}) \tag{9}$$

after the corresponding replacements, the eq. (7) gives the expression for the calculation of the total buffer capacity in investigated heterogeneous systems:

$$\beta = \frac{\mathrm{d}c_b}{\mathrm{d}pH} = \underbrace{2.3\left(\frac{4\,K^M_{s1}}{a^2_{\mathrm{H_3O^+}}} + \frac{K^M_{s2}}{a_{\mathrm{H_3O^+}}}\right)}_{\beta_{\mathrm{H_2}A}} + \underbrace{2.3\left(\frac{a_{\mathrm{OH^-}}}{y} + \frac{a_{\mathrm{H_3O^+}}}{y}\right)}_{\beta_{\mathrm{H_2O}}} \tag{10}$$

The first term of the eq. (10), ($\beta_{\mathrm{H_2}A}$), represents the contribution of the investigated acid-base pair, and the second term, ($\beta_{\mathrm{H_2O}}$), the contribution of water ions to the total buffer capacity of the solution. Since the investigation deals with acid buffers, except for very acid solution ($pH < 3$), $\beta_{\mathrm{H_2O}} \ll \beta_{\mathrm{H_2}A}$ and therefore the second term of the eq. (10) can be neglected with respect to the first one.

The first term of eq. (10) can be written in the following form:

$$\beta_{\mathrm{H_2}A} = 2.3\,(4\,K^M_{s1}\,10^{2pH} + K^M_{s2}\,10^{pH}) \tag{11}$$

From eq. (11) it is seen that the buffer capacity of the investigated two-phase buffers, in contrast to analogous monophase ones, increases exponentially with increasing pH value. However, this increasing is limited by the transition of a heterogeneous into a homogeneous system which is accompanied with an abrupt decrease in buffer capacity.

Therefore, maximum buffer capacity is to be expected just before the transition of a heterogeneous into a homogeneous system. Since then the quantity of diprotic acid in the precipitate is negligibly small, the following may be written:

$$C_{tot} = C_{H_2A} + c_{HA^-} + c_{A^{2-}} \tag{12}$$

In a homogeneous system C_{tot} denotes the stoichiometric concentration of diprotic acid, and in a heterogeneous system C_{tot} denotes the apparent stoichiometric concentration of diprotic acid, i.e. the stoichiometric concentration which would be present if the total precipitate is dissolved.

By combining eq. (12) with eqs. (1)–(3) we get the expression for the calculation of the pH value at which the transition of a heterogeneous into a homogeneous system will occur:

$$\begin{aligned} pH = & -\log \left[K^M_{s2}/2\,(C_{tot} - K_{s3}) + \right. \\ & \left. + \sqrt{(K^M_{s2})^2/4\,(C_{tot} - K_{s3})^2 + K^M_{s1}/(C_{tot} - K_{s3})}\right] \end{aligned} \tag{13}$$

The calculation of the buffer capacity in homogeneous systems is carried out in the usual manner as for classical (monophase) buffers with diprotic acids[3].

The dilution effect of investigated two-phase buffer systems is defined in the following way:

$$\Delta pH_{1/2} = pH_{AD} - pH_{BD} \tag{14}$$

where pH_{BD} represents the pH value before dilution, and pH_{AD} that after twofold dilution of the buffer, the ionic strength of the solution being not changed. Theoretical calculation of the dilution effect is based on the fact that a twofold dilution of the solution decrease the base concentration (c_b) to one half of its initial value, i.e. $c_{b(AD)} = 0.5\,c_{b(BD)}$, whereas the concentration of the molecular acid remains constant as long as the system is heterogeneous.

The base concentration before dilution can be calculated from the measured pH value by means of the following equation:

$$c_{b\,(BD)} = 2\,K^M_{s1}/a^2_{H_3O^+} + K^M_{s2}/a^2_{H_3O^+} - a_{H_3O^+}/y \tag{15}$$

which is obtained from eq. (6) by neglecting the third term relating to the concentration of hydroxide ions. Since $c_{b(BD)} = 2\,c_{b(AD)}$, by replacing this value in eq. (15) and by iterative procedure one can calculate the activity of hydronium ions, namely the pH value after dilution. The dilution effect, $\Delta pH_{1/2}$, is calculated then from the known pH value before and after dilution by means of eq. (14).

Experimental Confirmations

The validity of equations derived above has been verified by investigation of four buffer systems consisting of 1,2-, 1,3-, 1,4-benzenedicarboxylic acid and octanedioic acid, respectively, and their saturated aqueous solutions, at constant ionic strength, $I = 1$ (NaCl).

Functional dependence of the buffer capacity on the *pH* value has been experimentally determined by an analysis of the corresponding direct and reverse titration curves, respectively. However, due to a small change of the solution volume in the course of the titration a slight dilution effect affects the measured *pH* values which are therefore somewhat lower. This effect is corrected for each titration point by the corresponding ΔpH value which is calculated by means of eq. (15) which can be applied for any dilution. The corrected experimental data are given in Fig. 1.

For the evalution of the theoretical buffer curves, on the basis of the derived equations, the concentration equilibrium constants, determined in our previous work[2], have been used. From these values the corresponding mixed constants (K_{s1}^{M} and K_{s2}^{M}), have been calculated

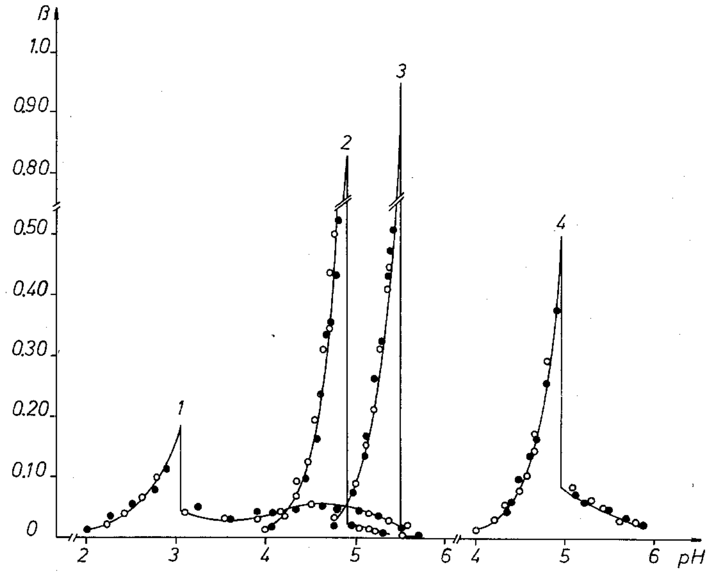

Fig. 1. Dependance of buffer capacity on the *pH* value in two-phase buffer systems containing a sparingly soluble diprotic acid: 1,2-benzenedicarboxylic acid (*1*), 1,3-benzenedicarboxylic acid (*2*), 1,4-benzenedicarboxylic acid (*3*), and octanedioic acid (*4*). Experimental data: direct (○○○) and reverse (●●●) titrations; theoretical buffer curves: unbroken line. $C_{tot} = 0.1\,M$, $I = 1$ (NaCl)

Table 1. *pH and dilution effect, $\Delta pH_{1/2}$, in two-phase buffer systems containing a sparingly soluble diprotic acid as the solid phase; $C_{tot} = 0.1\,M$, $I = 1$ (NaCl), $t = 25\,°C$*

Diprotic Acid	% of Neutralization	*pH*	$\Delta pH_{1/2}$ Found	Calculated
1,2-Benzenedicarboxylic	10	2.60	−0.20	−0.20
1,3-Benzenedicarboxylic	10	4.31	−0.17	−0.17
	30	4.59	−0.17	−0.16
	50	4.74	−0.17	−0.16
1,4-Benzenedicarboxylic	10	5.02	−0.15	−0.15
	30	5.30	−0.16	−0.15
	50	5.41	−0.16	−0.15
	70	5.50	−0.16	−0.15
Octanedioic	10	4.41	−0.22	−0.23
	30	4.70	−0.20	−0.20
	50	4.85	−0.18	−0.19

using the value of 0.72 as the mean activity coefficient[4]. Theoretical buffer curves are presented in Fig. 1 along with experimental data points. Fig. 1 shows that there is a good agreement between them. Besides, from Fig. 1 it may be seen that the transition of a heterogeneous into a homogeneous system is accompanied by an abrupt drop in buffer capacity.

Results obtained for the dilution effect in all four two-phase buffer systems studied are given in Table 1. Along with the experimentally determined dilution effect for different neutralization percentages, Table 1 shows also the theoretical dilution effects, calculated from eqs. (14) and (15); a good agreement between them is evident. Besides, the results show that the dilution effect in two-phase buffers of this type lowers the *pH* value of the solution.

Two-phase buffer systems described in this paper possess very high buffer capacity in a definite *pH* range. With respect to the corresponding two-phase buffers with sparingly soluble monoprotic acids these systems are advantageous due to considerably higher values for the maximum buffer capacity and significantly lower dilution effects. An important advantage of these buffers with respect to classical (monophase) ones is the fact that the disappearance of the solid phase is a visual indication of an abrupt decrease of the buffer capacity.

For the practical application of the described two-phase buffer systems it is noteworthy that they are easily prepared by partial neutralization of the sparingly soluble diprotic acid with sodium hydroxide. On account of their properties these buffers can be recommended for use in cases when the equilibration time is of less importance, and a high buffer capacity is required.

Finally, it has been shown that the investigated sparingly soluble diprotic acids can be determined by the *pH* titration of the two-phase system consisting of the corresponding diprotic acid in the precipitate and its saturated solution.

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