Monatshefte für Chemie 115, 125—133 (1984)

Monatshefte für Chemie
Chemical Monthly

Study on Heterogeneous Equilibria in Saturated Solutions of Sparingly Soluble Diprotic Acids

Tomislav J. Janjić*, **Lidija B. Pfendt**, and **Mirjana B. Pasulj**

Chemical Institute, Faculty of Sciences, University of Belgrade,
YU-11001 Belgrade, Yugoslavia

(Received 21 February 1983. Accepted 30 August 1983)

Heterogeneous equilibria in saturated solutions of sparingly soluble diprotic acids: 1,2-, 1,3- and 1,4-benzenedicarboxylic acid, and octanedioic acid, respectively, at ionic strength $I = 1$ (NaCl) and the temperature of 25 °C, have been investigated. The corresponding equilibrium constants were determined by the application of three independent methods: the formation function method, the method of protons bound to the acid in the solution and the solubility method. The results obtained by these three different methods are in good agreement.

(Keywords: Heterogeneous equilibria; Diprotic acids)

Untersuchung heterogener Gleichgewichte in gesättigten Lösungen schwerlöslicher diprotischer Säuren

Es wurden die heterogenen Gleichgewichte in gesättigten Lösungen schwerlöslicher diprotischer Säuren (Benzol-1,2-, -1,3- und -1,4-dicarbonsäuren und Oktandisäure) bei einer Ionenstärke $I = 1$ (NaCl) und der Temperatur von 25 °C untersucht. Die entsprechende Gleichgewichtskonstanten wurden mit drei unabhängigen Methoden bestimmt: mit der Methode der Bildungsfunktion, der Methode der an die Säure in Lösung gebundenen Protonen, bzw. mit der Methode der Löslichkeitsbestimmung. Die erhaltenen Ergebnisse stehen in guter Übereinstimmung.

Introduction

In the present paper equilibrium processes in heterogeneous systems consisting of a sparingly soluble diprotic acid and its saturated solution have been studied. For these investigations, which have not been hitherto performed, we have modified the methods described in one of our earlier papers on the investigation of heterogeneous equilibria in systems of some protonated metal(II)—*EDTA*-complexes[1].

Experimental

The *pH*-measurements were made on a Radiometer PHM4c *pH*-meter, equipped with a glass-calomel assembly.

The solutions used were prepared with doubly distilled water and standardized in the usual manner. The ionic strength of all the solutions was kept constant, $I = 1$ (NaCl). The equilibrium concentration of hydronium ions was obtained from measured *pH*-values and the mean activity coefficient, which amounts for this ionic strength to 0.72[2]. The measurements were performed at $25 \pm 0.1\,°C$.

The initial solutions were 0.1000 *M* with respect to the disodium salt of the corresponding diprotic acid. Equal aliquots of these solutions (20 ml) were acidified with 0.1000 *M* hydrochloric acid and thermostated. The equilibrium time was followed *pH*-metrically in the course of 1 h. The solutions were then separated from the precipitate and further investigated. From one part of the separated solutions the concentration of neutralizable protons was determined by *pH*-metric titration with standard sodium hydroxide solution (0.0300 to 0.2000 *M*). The other part of the separated solutions was used for the determination of the stoichiometric solubility of the acids studied. The latter solutions were neutralized with sodium hydroxide and then the actual concentration of the corresponding salt was determined spectrophotometrically. Measurements being made at absorption maxima wavelengths, which in case of 1,2-, 1,3- and 1,4-benzenedicarboxylic acid corresponded to 273 nm, 278 nm, and 240 nm, respectively.

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

Results and Discussion

Heterogeneous systems investigated in this paper consisted of saturated aqueous solutions of 1,2-, 1,3- and 1,4-benzenedicarboxylic acid, and octanedioic acid, respectively. In these systems, between the solid phase $(H_2A)_s$ and the solution, the following equilibria might take place:

$$(H_2A)_s + 2\,H_2O \rightleftarrows 2\,H_3O^+ + A^{2-} \ldots K_{s1} = [H_3O^+]^2 \cdot [A^{2-}] \qquad (1)$$

$$(H_2A)_s + H_2O \rightleftarrows H_3O^+ + HA^- \ldots K_{s2} = [H_3O^+] \cdot [HA^-] \qquad (2)$$

$$(H_2A)_s \rightleftarrows H_2A \ldots K_{s3} = [H_2A] \qquad (3)$$

The corresponding equilibrium constants K_{s1}, K_{s2} and K_{s3} were determined by the application of three independent methods based on the determination of the formation function, the concentration of protons bound to the acid in the solution, and the stoichiometric solubility of the acid, respectively.

Formation Function Method

This method is based on the determination of the average number of protons bound per mole of the acid:

$$\bar{n}_{tot} = \frac{[\mathrm{H}A^-] + 2[\mathrm{H}_2A] + 2[\mathrm{H}_2A]_s}{C_{tot}} \tag{4}$$

In the equation given, $[\mathrm{H}_2A]_s$ corresponds to the number of moles of the acid which are precipitated from 1 l of the solution, and C_{tot} denotes the stoichiometric concentration of the acid which would be present in the solution, if the total amount of the precipitate were dissolved.

From mass-balance it follows that:

$$C_{tot} = [A^{2-}] + [\mathrm{H}A^-] + [\mathrm{H}_2A] + [\mathrm{H}_2A]_s \tag{5}$$

By combining equations (1), (2), (4) and (5), there is obtained the relation:

$$C_{tot}[\mathrm{H}_3\mathrm{O}^+](2 - \bar{n}_{tot}) = \frac{2K_{s1}}{[\mathrm{H}_3\mathrm{O}^+]} + K_{s2} \tag{6}$$

from which the equilibrium constants K_{s1} and K_{s2} can be calculated by linear regression analysis. The value of the expression on the left side of this equation can be determined if the magnitude of $\bar{n}_{tot}$ is known; the latter is calculated from the experimental data in the following way:

$$\bar{n}_{tot} = \frac{[\mathrm{HCl}] - [\mathrm{H}_3\mathrm{O}^+] + [\mathrm{OH}^-]}{C_{tot}} \tag{7}$$

In the above expression [HCl] corresponds to the stoichiometric concentration of hydrochloric acid added to the solution of the neutral salt of the corresponding diprotic acid, and $[\mathrm{H}_3\mathrm{O}^+]$ denotes the equilibrium concentration of hydronium ions. The concentration of hydroxide ions in strongly acid solutions in which the measurements were performed, is negligibly small.

Method of Protons Bound to the Acid in the Solution

The concentration of protons bound to the acid in the solution, $[\mathrm{H}^+]_b$, which is experimentally determined from the difference between the neutralizable protons in the solution, $[\mathrm{H}^+]_{tot}$, and the concentration of hydronium ions, can be expressed as follows:

$$[\mathrm{H}^+]_b = [\mathrm{H}^+]_{tot} - [\mathrm{H}_3\mathrm{O}^+] = [\mathrm{H}A^-] + 2[\mathrm{H}_2A] \tag{8}$$

From the equation (8) and the expression for the corresponding equilibrium constants [eqns. (2) and (3)] there is obtained the relation:

$$[H^+]_b = \frac{K_{s2}}{[H_3O^+]} + 2K_{s3} \tag{9}$$

from which the constants K_{s2} and K_{s3} can be calculated by linear regression analysis.

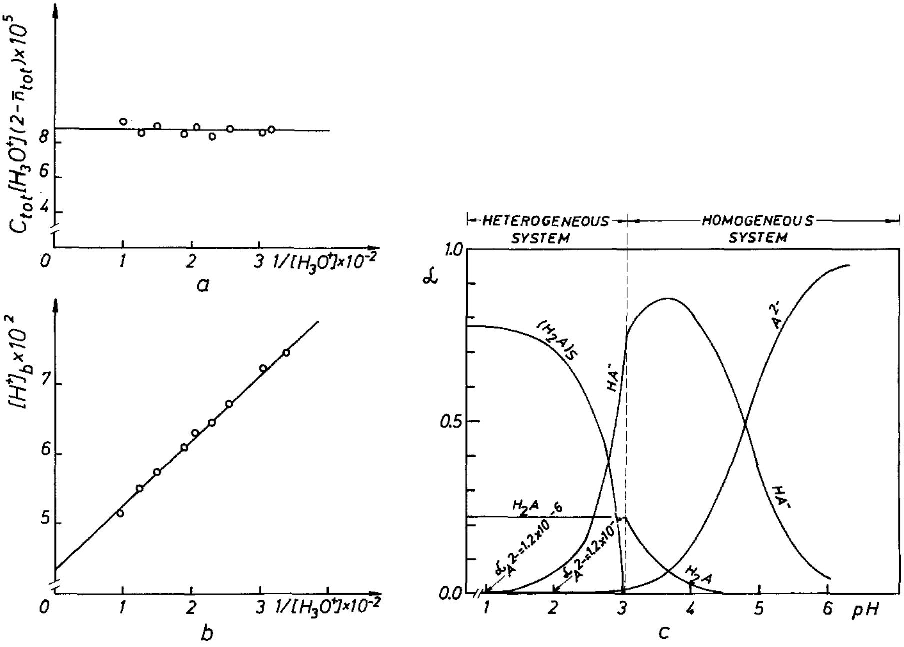

Fig. 1. Diagrams used in the determination of the equilibrium constants in the system of 1,2-benzenedicarboxylic acid: formation function method (*a*); the method of protons bound to the acid in the solution (*b*). The distribution diagram (*c*). $C_{tot} = 0.1\,M$, $I = 1$ (NaCl), $t = 25\,°C$

Solubility Method

This method is based on the determination of the stoichiometric solubility (S) of investigated acids at different pH values:

$$S = [A^{2-}] + [HA^-] + [H_2A] \tag{10}$$

From equations (1)–(3) and the equation (10), we obtain:

$$S[H_3O^+]^2 = K_{s1} + K_{s2}[H_3O^+] + K_{s3}[H_3O^+]^2 \tag{11}$$

By applying the regression analysis to a series of equations of this type, all three equilibrium constants can be calculated[3].

From equations (6), (9) and (11) it follows that the applicability of the methods described for the determination of individual constants, as well as the precision of their estimation, depend on the absolute concentration of individual species in the solution and their relative ratio.

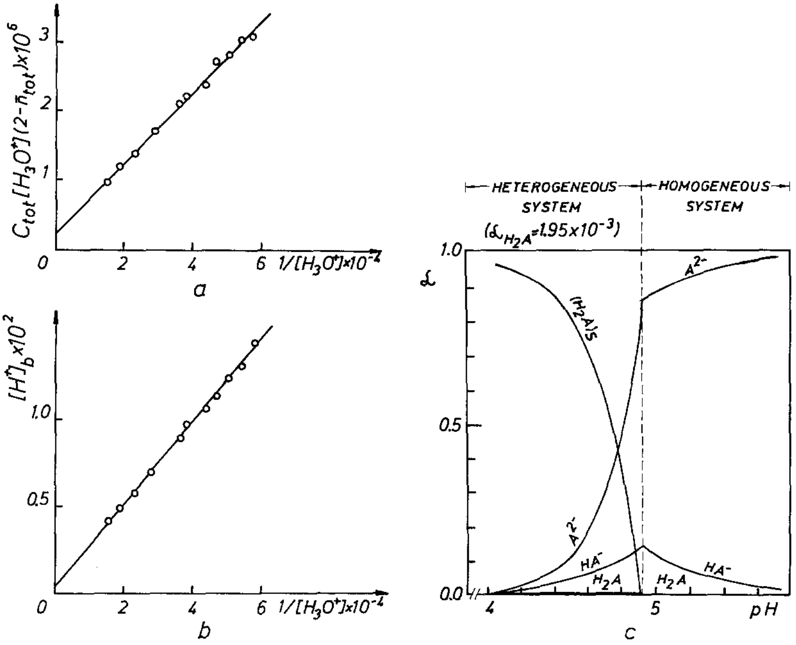

Fig. 2. Diagrams used in the determination of the equilibrium constants in the system of 1,3-benzenedicarboxylic acid: formation function method (*a*); the method of protons bound to the acid in the solution (*b*). The distribution diagram (*c*). $C_{tot} = 0.1\,M$, $I = 1$ (NaCl), $t = 25\,°C$

Equilibrium constants determined in a heterogeneous system offer the possibility for the calculation of acid dissociation constants K_{a1} and K_{a2} ($K_{a1} = [H_3O^+][HA^-]/[H_2A]$; $K_{a2} = [H_3O^+][A^{2-}]/[HA^-]$), by means of the following relations:

$$pK_{a1} = pK_{s2} - pK_{s3} \qquad (12)$$

$$pK_{a2} = pK_{s1} - pK_{s2} \qquad (13)$$

In cases when the solubility of the acid was sufficiently high, the acid dissociation constants were determined by *pH*-metric titration of its homogeneous solution according to *Rossotti-Rossotti*'s method[4].

Figs. 1 to 4 show the diagrams used for the determination of equilibrium constants in heterogeneous systems studied, as well as the distribution diagrams in heterogeneous and homogeneous systems, calculated by the usual procedure[5] on the basis of the evaluated equilibrium constants. All these diagrams relate to $C_{tot} = 0.1\,M$.

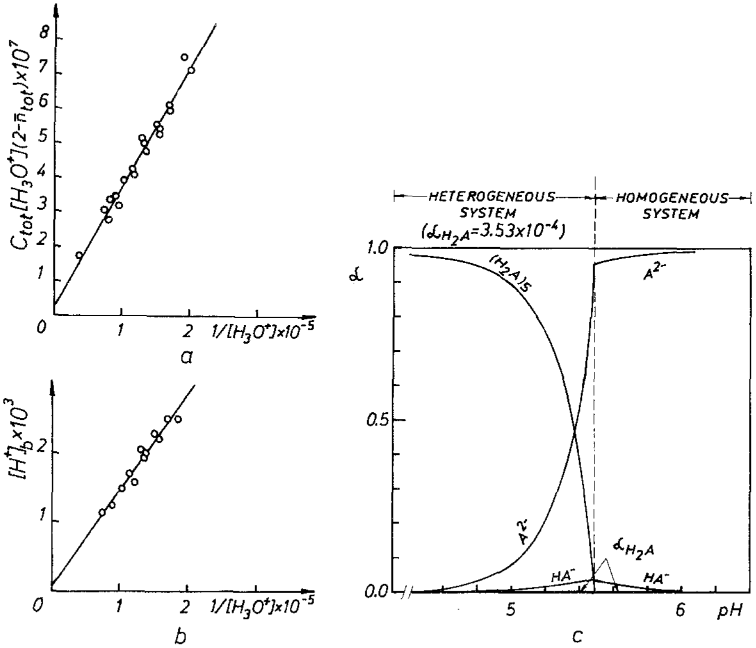

Fig. 3. Diagrams used in the determination of the equilibrium constants in the system of 1,4-benzenedicarboxylic acid: formation function method (*a*); the method of protons bound to the acid in the solution (*b*). The distribution diagram (*c*). $C_{tot} = 0.1\,M$, $I = 1$ (NaCl), $t = 25\,°C$

From Fig. 1 *c* which illustrates the distribution of components in the system of 1,2-benzenedicarboxylic acid, it is seen that the concentration of the species A^{2-} in the solution of the heterogeneous system is very small, and that it decreases continuously with decrease in *pH* value. Therefrom it follows that the corresponding equilibrium constant (K_{s1}) could not be determined by methods described. However, by *pH*-metric titration of the homogeneous solution of 1,2-benzene dicarboxylic acid its acid dissociation constants have been determined, and from them the corresponding equilibrium constant K_{s1} was calculated by the application of equation (13).

On the contrary, in case of 1,3- and 1,4-benzenedicarboxylic acid the concentration of the species H_2A in the solution of the heterogeneous system is relatively small, but constant (Figs. 2 *c* and 3 *c*). Therefore, in case of less soluble 1,4-benzenedicarboxylic acid, the constant K_{s3} could

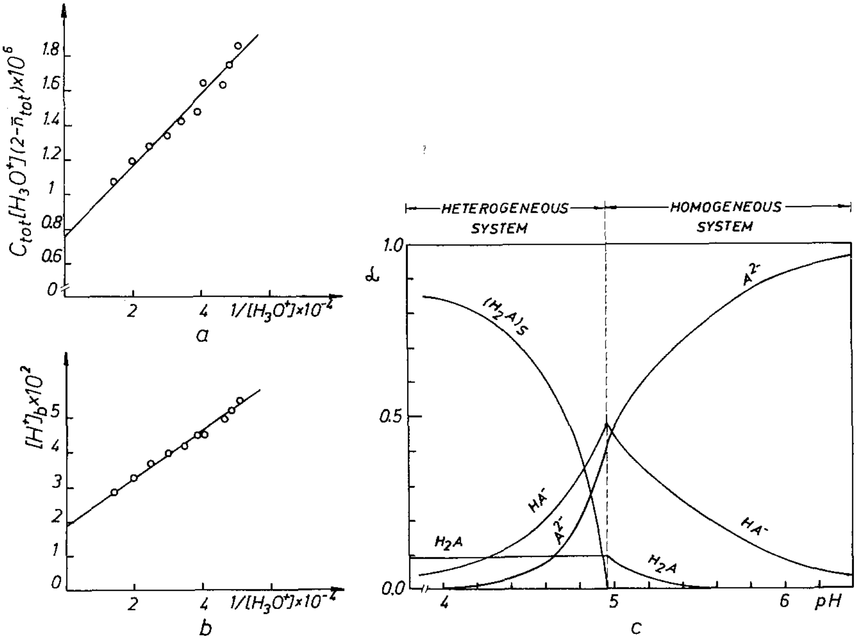

Fig. 4. Diagrams used in the determination of the equilibrium constants in the system of octanedioic acid: formation function method (*a*); the method of protons bound to the acid in the solution (*b*). The distribution diagram (*c*). $C_{tot} = 0.1\,M$, $I = 1$ (NaCl), $t = 25\,°C$

be determined approximately only by the method of bound protons. Low solubility of these acids renders impossible a successful titration of their homogeneous solutions.

From Fig. 4 *c* it is seen that the absolute concentration of individual species and their relative ratio in the solution of the heterogeneous system of octanedioic acid are very suitable for the determination of all the equilibrium constants.

Concentration equilibrium constants and the corresponding standard deviations, determined by the method described in heterogeneous and homogeneous systems studied, are summarized in Table 1.

Table 1. *Concentration equilibrium constants in the heterogeneous and homogeneous systems studied.* $C_{tot} = 0.1\,M, I = 1$ (NaCl), $t = 25\,°C$

Investigated acid	Method applied[a]	Heterogeneous systems			Homogeneous systems			
					Calculated[c]		Obtained[d]	
		pK_{s1}	pK_{s2}	pK_{s3}	pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}
1,2-benzene-dicarboxylic	1.	8.66 ± 0.02[b]	4.05 ± 0.02	—	—	—		
	2.	8.63 ± 0.02[b]	4.02 ± 0.01	1.67 ± 0.01	2.35 ± 0.02	—	2.36 ± 0.02	4.61 ± 0.01
	3.	8.59 ± 0.03[b]	3.98 ± 0.03	1.64 ± 0.02	2.34 ± 0.04	—		
1,3-benzene-dicarboxylic	1.	10.60 ± 0.03	6.6 ± 0.3	—	—	4.0 ± 0.3		
	2.	—	6.63 ± 0.01	3.67 ± 0.09	2.96 ± 0.09	—	—	—
	3.	10.57 ± 0.01	6.63 ± 0.02	3.74 ± 0.05	2.89 ± 0.05	3.94 ± 0.03		
1,4-benzene-dicarboxylic	1.	11.76 ± 0.01	7.7 ± 0.5	—	—	4.1 ± 0.5		
	2.	—	7.85 ± 0.08	4.5	3.4	—	—	—
	3.	11.82 ± 0.02	7.8 ± 0.3	—	—	4.0 ± 0.3		
Octanedioic	1.	11.01 ± 0.03	6.11 ± 0.03	—	—	4.90 ± 0.05		
	2.	—	6.17 ± 0.01	2.02 ± 0.01	4.15 ± 0.03	—	4.12 ± 0.02	4.83 ± 0.01

[a] 1. Formation function method. 2. Method of protons bound to the acid in the solution. 3. Solubility method.

[b] Calculated according to eq. (13) using the corresponding values for pK_{s2} and pK_{a2}.

[c] Calculated by eq. (12) and (13), respectively.

[d] Obtained by pH-metric titration in homogeneous system.

The Table shows that the equilibrium constants in heterogeneous systems, determined by different methods, are in good agreement. Besides, the acid dissotiation constants in homogeneous systems, determined experimentally whenever possible, are consistent with those calculated on the baasis of the equilibrium constant determined in the corresponding heterogeneous systems.

Equilibrium constants determined in this paper, besides other application, are indispensable for the treatment of two-phase buffer systems consisting of a sparingly soluble diprotic acid as the solid phase and its saturated solution (buffered phase), the latter will be subject of our further investigation.

Acknowledgement

The authors are grateful to the Serbian Republic Research Found for financial support.

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