

## CONTRIBUTION TO THE THERMODYNAMICS OF BROMOPHENOL BLUE IN THE TWO-PHASE WATER-NITROBENZENE EXTRACTION SYSTEM

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General relations among thermodynamic parameters characterizing dissociation equilibria with species  $H_2A$ ,  $HA^-$  and  $A^{2-}$  ( $H_2A$  is a symbol for an electroneutral undissociated acid) in a two-phase extraction system have been derived. From the extraction measurements, the equilibrium distribution constant of electroneutral bromophenol blue between the nitrobenzene phase and the aqueous one has been determined:  $\log K_D(H_2A) = 3.60 \pm 0.01$ . By using this value and further known constants and applying the mentioned relations the following values of dissociation constants of bromophenol blue in nitrobenzene saturated with water have been calculated for a temperature of 25°C:  $pK_a^{org}(H_2A) = -\log K_a^{org}(H_2A) = 10.1$  and  $pK_a^{org}(HA^-) = -\log K_a^{org}(HA^-) = 14.5$ .

Studies on the electrochemical phenomena at the liquid/liquid interface are a new rapidly developing area in electrochemistry<sup>1-4</sup>.

Organic dyes are a large group of reagents which are used widely in analytical chemistry. Transfer phenomena of acidic organic dye bromophenol blue at the interface between water and some organic solvents (nitrobenzene, 1,2-dichloroethane and nitrobenzene + chlorobenzene) were reported<sup>5</sup>.

In this communication, general relations among thermodynamic parameters that characterize dissociation equilibria of an acid  $H_2A$  in both phases of a two-phase system and ion transfers across the interface of this system have been derived. Further, the derived relations have been applied for the distribution of bromophenol blue in the water-nitrobenzene extraction system.

### EXPERIMENTAL

Nitrobenzene, bromophenol blue and all other chemicals of analytical grade purity were supplied by Lachema, Brno, Czechoslovakia.

The extraction experiments concerning a two-phase water- $H_2SO_4$ -nitrobenzene-bromophenol blue (abbrev.  $H_2A$ ) system have been performed in 25 cm<sup>3</sup> volume glass test-tubes with polyethylene stoppers using 10 cm<sup>3</sup> of each phase. The analytical concentrations of bromo-

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phenol blue in the nitrobenzene phase have been in the range of  $0.01\text{--}0.04\text{ mol dm}^{-3}$ . The analytical concentration of  $\text{H}_2\text{SO}_4$  in the aqueous phase suppressing the dissociation of bromophenol blue in the system has been always  $1\text{ mol dm}^{-3}$ .

The equilibrium in the extraction system at a temperature of  $25 \pm 1^\circ\text{C}$  has been achieved approximately in 10 min using a laboratory shaking apparatus. Then, both phases have been separated by centrifugation.

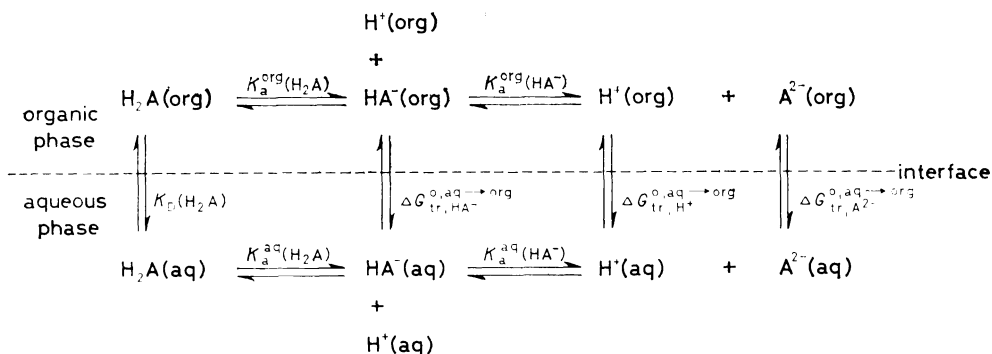
The equilibrium concentration of bromophenol blue in the aqueous phase has been determined spectrophotometrically (Spekol 11, Carl Zeiss, Jena, G.D.R.) at 440 nm. The concentration of bromophenol blue in the equilibrium nitrobenzene phase has been calculated from the mass balance of this compound in the system under study.

The equilibrium distribution constant of an electroneutral undissociated bromophenol blue ( $\text{H}_2\text{A}$ ) between the nitrobenzene and aqueous phase has been calculated as a ratio of the corresponding equilibrium concentrations of this species in the single phases.

The following values of  $K_D(\text{H}_2\text{A})$  have been obtained by the above method for four various analytical concentrations ( $0.01, 0.02, 0.03,$  and  $0.04\text{ mol dm}^{-3}$ ) of bromophenol blue in the nitrobenzene phase: 4 020, 3 910, 4 080, and 3 970. From these results it follows that  $\log K_D(\text{H}_2\text{A}) = 3.60 \pm 0.01$ .

## RESULTS AND DISCUSSION

Let us consider an equilibrium system of two immiscible liquid phases consisting of an aqueous (shortly aq) phase and an organic (org) phase in which an acid  $\text{H}_2\text{A}$  is dissociated in both phases (see Scheme 1 of the system under study below), the corresponding dissociation constants being  $K_a^{\text{aq}}(\text{H}_2\text{A})$ ,  $K_a^{\text{aq}}(\text{HA}^-)$ ,  $K_a^{\text{org}}(\text{H}_2\text{A})$  and  $K_a^{\text{org}}(\text{HA}^-)$ . The distribution constant of the electroneutral acid  $\text{H}_2\text{A}$  between the organic and aqueous phase is denoted by a symbol  $K_D(\text{H}_2\text{A})$ , the standard Gibbs energies corresponding to the transfers of the ions  $\text{HA}^-$ ,  $\text{A}^{2-}$  and  $\text{H}^+$  from the aqueous phase into the organic one being  $\Delta G_{\text{tr},\text{HA}^-}^{\text{org,aq}}$ ,  $\Delta G_{\text{tr},\text{A}^{2-}}^{\text{org,aq}}$  and  $\Delta G_{\text{tr},\text{H}^+}^{\text{org,aq}}$ .



SCHEME 1

The two-phase extraction system with the acid  $\text{H}_2\text{A}$

Then, these equilibrium constants and the mentioned Gibbs energies must fulfil the following relations (1)–(8):

$$-RT \ln K_a^{\text{aq}}(\text{H}_2\text{A}) = \mu_{\text{HA}^-}^{\text{o, aq}} + \mu_{\text{H}^+}^{\text{o, aq}} - \mu_{\text{H}_2\text{A}}^{\text{o, aq}} \quad (1)$$

$$-RT \ln K_a^{\text{org}}(\text{H}_2\text{A}) = \mu_{\text{HA}^-}^{\text{o, org}} + \mu_{\text{H}^+}^{\text{o, org}} - \mu_{\text{H}_2\text{A}}^{\text{o, org}} \quad (2)$$

$$-RT \ln K_a^{\text{aq}}(\text{HA}^-) = \mu_{\text{A}^{2-}}^{\text{o, aq}} + \mu_{\text{H}^+}^{\text{o, aq}} - \mu_{\text{HA}^-}^{\text{o, aq}} \quad (3)$$

$$-RT \ln K_a^{\text{org}}(\text{HA}^-) = \mu_{\text{A}^{2-}}^{\text{o, org}} + \mu_{\text{H}^+}^{\text{o, org}} - \mu_{\text{HA}^-}^{\text{o, org}} \quad (4)$$

$$-RT \ln K_D(\text{H}_2\text{A}) = \mu_{\text{H}_2\text{A}}^{\text{o, org}} - \mu_{\text{H}_2\text{A}}^{\text{o, aq}} \quad (5)$$

$$\Delta G_{\text{tr, HA}^-}^{\text{o, aq} \rightarrow \text{org}} = \mu_{\text{HA}^-}^{\text{o, org}} - \mu_{\text{HA}^-}^{\text{o, aq}} \quad (6)$$

$$\Delta G_{\text{tr, A}^{2-}}^{\text{o, aq} \rightarrow \text{org}} = \mu_{\text{A}^{2-}}^{\text{o, org}} - \mu_{\text{A}^{2-}}^{\text{o, aq}} \quad (7)$$

$$\Delta G_{\text{tr, H}^+}^{\text{o, aq} \rightarrow \text{org}} = \mu_{\text{H}^+}^{\text{o, org}} - \mu_{\text{H}^+}^{\text{o, aq}}, \quad (8)$$

where  $\mu_i^{\text{o, aq}}$  and  $\mu_i^{\text{o, org}}$  are the standard chemical potentials of species  $i$  in the aqueous and organic phase, respectively.

By combining relations (1), (2), (5), (6), and (8) we obtain the sought equation in the form

$$\Delta G_{\text{tr, H}^+}^{\text{o, aq} \rightarrow \text{org}} + \Delta G_{\text{tr, HA}^-}^{\text{o, aq} \rightarrow \text{org}} = RT \ln \frac{K_a^{\text{aq}}(\text{H}_2\text{A})}{K_a^{\text{org}}(\text{H}_2\text{A}) \cdot K_D(\text{H}_2\text{A})}. \quad (9)$$

Analogously, the combination of Eqs (3), (4), and (6)–(8) yields

$$\Delta G_{\text{tr, H}^+}^{\text{o, aq} \rightarrow \text{org}} + \Delta G_{\text{tr, A}^{2-}}^{\text{o, aq} \rightarrow \text{org}} = \Delta G_{\text{tr, HA}^-}^{\text{o, aq} \rightarrow \text{org}} + RT \ln \frac{K_a^{\text{aq}}(\text{HA}^-)}{K_a^{\text{org}}(\text{HA}^-)}. \quad (10)$$

Equations (11) and (12) given below are equivalent to previous relations (9) and (10)

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{HA}^-}^{\text{o}} = \Delta_{\text{aq}}^{\text{org}} \varphi_{\text{H}^+}^{\text{o}} + \frac{RT}{F} \ln \frac{K_a^{\text{aq}}(\text{H}_2\text{A})}{K_a^{\text{org}}(\text{H}_2\text{A}) \cdot K_D(\text{H}_2\text{A})} \quad (11)$$

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{A}^{2-}}^{\text{o}} = \frac{\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{H}^+}^{\text{o}} + \Delta_{\text{aq}}^{\text{org}} \varphi_{\text{HA}^-}^{\text{o}}}{2} + \frac{RT}{2F} \ln \frac{K_a^{\text{aq}}(\text{HA}^-)}{K_a^{\text{org}}(\text{HA}^-)} \quad (12)$$

because the standard Galvani potential differences of the ions  $\text{H}^+$ ,  $\text{HA}^-$  and  $\text{A}^{2-}$  between the organic and aqueous phase<sup>1</sup> denoted by the symbols  $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{H}^+}^{\text{o}}$ ,  $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{HA}^-}^{\text{o}}$  and  $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{A}^{2-}}^{\text{o}}$  are defined by relations

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{H}^+}^{\text{o}} = -\Delta G_{\text{tr, H}^+}^{\text{o, aq} \rightarrow \text{org}} / F \quad (13)$$

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{HA}^-}^{\circ} = \Delta G_{\text{tr,HA}^-}^{\text{org,org}} / F \quad (14)$$

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{A}^{2-}}^{\circ} = \Delta G_{\text{tr,A}^{2-}}^{\text{org,org}} / 2F. \quad (15)$$

It is obvious that each of Eqs (9)–(12) derived in this communication can be applied for calculating one constant when the values of all the remaining constants in these equations are known.

By using the following values  $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{HA}^-}^{\circ} = -0.105 \text{ V}$  (ref.<sup>5</sup>),  $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{A}^{2-}}^{\circ} = 0.077 \text{ V}$  (ref.<sup>6</sup>; org = nitrobenzene saturated with water),  $\text{p}K_{\text{a}}^{\text{aq}}(\text{H}_2\text{A}) = -\log K_{\text{a}}^{\text{aq}}(\text{H}_2\text{A}) = 2.6$  (ref.<sup>5</sup>),  $\text{p}K_{\text{a}}^{\text{aq}}(\text{HA}^-) = -\log K_{\text{a}}^{\text{aq}}(\text{HA}^-) = 4.4$  (ref.<sup>5</sup>),  $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{H}^+}^{\circ} = -0.337 \text{ V}$  inferred from data on the two-phase water–nitrobenzene extraction system published by Rais<sup>7</sup> and  $\log K_{\text{D}}(\text{H}_2\text{A}) = 3.60$  determined here (see Experimental) and employing Eqs (11) and (12) we have the values of the dissociation constants of bromophenol blue in nitrobenzene saturated with water at a temperature of 25°C in the forms

$$\text{p}K_{\text{a}}^{\text{org}}(\text{H}_2\text{A}) = -\log K_{\text{a}}^{\text{org}}(\text{H}_2\text{A}) = 10.1 \quad (16)$$

and

$$\text{p}K_{\text{a}}^{\text{org}}(\text{HA}^-) = -\log K_{\text{a}}^{\text{org}}(\text{HA}^-) = 14.5. \quad (17)$$

From the results given above it follows that the dissociation constants of the bromophenol blue particles  $\text{H}_2\text{A}$  and  $\text{HA}^-$  are essentially higher in the aqueous phase than in the nitrobenzene one, i.e.,

$$10^{-10.1} = K_{\text{a}}^{\text{org}}(\text{H}_2\text{A}) \ll K_{\text{a}}^{\text{aq}}(\text{H}_2\text{A}) = 10^{-2.6} \quad (18)$$

and

$$10^{-14.5} = K_{\text{a}}^{\text{org}}(\text{HA}^-) \ll K_{\text{a}}^{\text{aq}}(\text{HA}^-) = 10^{-4.4}. \quad (19)$$

These facts can be apparently explained by the higher basicity and solvatability of water than those of nitrobenzene.

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