

## Arbeitsvorschriften und Meßwerte · Procedures and Data

## Contribution to the Bromocresol Green Transfer across the Water/Nitrobenzene Interface

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Received October 2nd, 1996

Studies on the electrochemical phenomena at the liquid/liquid interface are a rapidly developing area in interfacial chemistry [1–3].

Organic dyes are a large group of reagents which are employed widely in analytical chemistry.

Transfer phenomena of the acidic dye bromocresol green, which is a typical indicator, at the interface between water and some organic solvents were studied in detail by electrochemical methods and UV-VIS spectroscopy [4]. A study of the transfer of dyes is attractive and of interest as it will enlarge the area of research and application of ion transfers across the liquid/liquid interfaces, provide information on such ion transfers including the mechanism of ion transfer across the mentioned interfaces and help in the development of a new way of dye analysis.

In the present communication, the dissociation constants of bromocresol green in nitrobenzene saturated with water have been evaluated using general thermodynamic relations and some known thermodynamic and electrochemical parameters.

## Experimental

Nitrobenzene, bromocresol green and all other chemicals of analytical grade purity were supplied by Lachema, Brno, Czech Republic.

The extraction experiments concerning a two-phase water- $\text{H}_2\text{SO}_4$ -nitrobenzene-bromocresol green (abbrev.  $\text{H}_2\text{A}$ ) system were performed in 25 cm<sup>3</sup> volume glass test-tubes with polyethylene stoppers using 10 cm<sup>3</sup> of each phase. The initial analytical concentrations of bromocresol green in the nitrobenzene phase were in the range of 0.02–0.06 mol dm<sup>-3</sup>. The initial analytical concentration of  $\text{H}_2\text{SO}_4$  in the aqueous phase suppressing the dissociation of bromocresol green in the system was always 1 mol dm<sup>-3</sup>.

The equilibrium in the extraction system at a temperature of  $25 \pm 1$  °C was achieved approximately in 10 minutes using a laboratory shaking apparatus. Then, both phases were separated by centrifugation.

The equilibrium concentrations of bromocresol green in the aqueous phase were determined spectrophotometrically (Spe-

kol 11, Carl Zeiss, Jena, Germany) at 445 nm. The concentration of bromocresol green in the equilibrium nitrobenzene phase was calculated from the mass balance of this compound in the system under study.

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

## Results and Discussion

Let us consider an equilibrium system of two immiscible liquid phases consisting of an aqueous (abbrev. aq) phase and a nitrobenzene (nb) phase in which an acid  $\text{H}_2\text{A}$  is dissociated in both phases (see Scheme 1), the corresponding dissociation constants being

$$K_d^{\text{aq}}(\text{H}_2\text{A}), K_d^{\text{aq}}(\text{HA}^-), K_d^{\text{nb}}(\text{H}_2\text{A}) \text{ and } K_d^{\text{nb}}(\text{HA}^-).$$

The equilibrium distribution constant of the electroneutral acid  $\text{H}_2\text{A}$  between the nitrobenzene and aqueous phases is denoted by  $K_D(\text{H}_2\text{A})$ , 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 nitrobenzene one being

$$\Delta G_{\text{tr,HA}^-}^{\text{o, aq} \rightarrow \text{nb}}, \Delta G_{\text{tr,A}^{2-}}^{\text{o, aq} \rightarrow \text{nb}} \text{ and } \Delta G_{\text{tr,H}^+}^{\text{o, aq} \rightarrow \text{nb}}, \text{ respectively.}$$

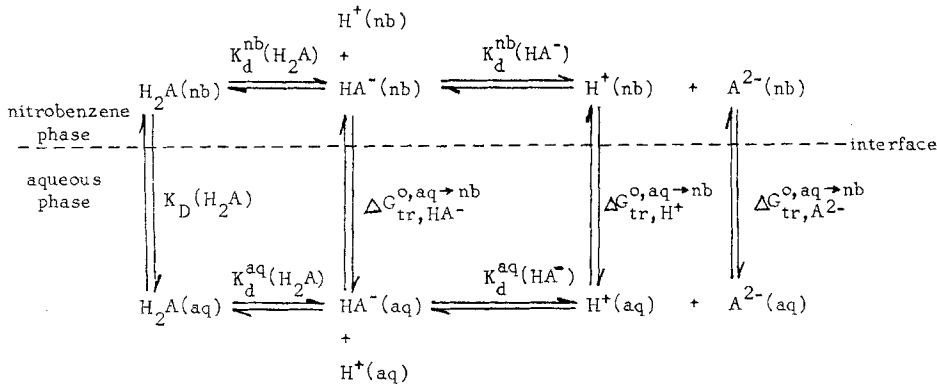
Then, these equilibrium constants and the mentioned Gibbs energies must fulfil the following relations (1)–(8):

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

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

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

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



**Scheme 1** The two-phase water-nitrobenzene extraction system with the acid  $H_2A$

$$-RT \ln K_D(H_2A) = \mu_{H_2A}^{o, nb} - \mu_{H_2A}^{o, aq} \quad (5)$$

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

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

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

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

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

$$\Delta G_{tr, H^+}^{o, aq \rightarrow nb} + \Delta G_{tr, A^{2-}}^{o, aq \rightarrow nb} = RT \ln \frac{K_d^{aq}(H_2A)}{K_d^{nb}(H_2A)K_D(H_2A)} \quad (9)$$

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

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

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

$$\Delta_{aq}^{nb} \Phi_{HA^-}^o = \Delta_{aq}^{nb} \Phi_{H^+}^o + \frac{RT}{F} \ln \frac{K_d^{aq}(H_2A)}{K_d^{nb}(H_2A)K_D(H_2A)} \quad (11)$$

$$\Delta_{aq}^{nb} \Phi_{A^{2-}}^o = \frac{\Delta_{aq}^{nb} \Phi_{H^+}^o + \Delta_{aq}^{nb} \Phi_{HA^-}^o}{2} + \frac{RT}{2F} \ln \frac{K_d^{aq}(HA^-)}{K_d^{nb}(HA^-)} \quad (12)$$

because the standard Galvani potential differences between the nitrobenzene and aqueous phases [5] for the ions  $H^+$ ,  $HA^-$  and  $A^{2-}$  denoted by the symbols

$\Delta_{aq}^{nb} \Phi_{H^+}^o$ ,  $\Delta_{aq}^{nb} \Phi_{HA^-}^o$  and  $\Delta_{aq}^{nb} \Phi_{A^{2-}}^o$  are defined by relations

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

$$\Delta_{aq}^{nb} \Phi_{HA^-}^o = \Delta G_{tr, HA^-}^{o, aq \rightarrow nb} / F \quad (14)$$

$$\Delta_{aq}^{nb} \Phi_{A^{2-}}^o = \Delta G_{tr, A^{2-}}^{o, aq \rightarrow nb} / 2F \quad (15)$$

It is obvious that each of equations (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

$$\Delta_{aq}^{nb} \Phi_{HA^-}^o = -0.102 \text{ V} [4], \Delta_{aq}^{nb} \Phi_{A^{2-}}^o = 0.086 \text{ V} [6],$$

$$pK_d^{aq}(H_2A) = -\log K_d^{aq}(H_2A) = 3.1 [4], pK_d^{aq}(HA^-) = -\log K_d^{aq}(HA^-) = 4.5 [4], \Delta_{aq}^{nb} \Phi_{H^+}^o = -0.337 \text{ V}$$

inferred from data on the two-phase water-nitrobenzene extraction system published by Rais [7] and  $\log K_D(H_2A) = 3.60 \pm 0.01$  determined here (see Experimental section) and employing equations (11) and (12) we have the values of the dissociation constants of bromocresol green in nitrobenzene saturated with water at a temperature of 25 °C:

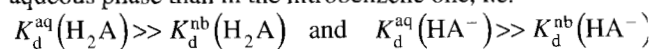
$$pK_d^{nb}(H_2A) = -\log K_d^{nb}(H_2A) = 10.7 \quad (16)$$

and

$$pK_d^{nb}(HA^-) = -\log K_d^{nb}(HA^-) = 14.8 \quad (17)$$

where  $K_d^{nb}(H_2A)$  and  $K_d^{nb}(HA^-)$  are expressed in  $\text{mol dm}^{-3}$ .

The fact that the dissociation constants of the bromocresol green particles  $H_2A$  and  $HA^-$  are essentially higher in the aqueous phase than in the nitrobenzene one, i.e.



can be obviously explained by the higher basicity and ability to solvate of water than those of nitrobenzene.

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## References

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