

NOTE

## Contribution to the thermodynamics of 1-(2-thiazolylazo)-2-naphthol in the water–nitrobenzene extraction system

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General relations among thermodynamic parameters characterizing chemical equilibria including species  $H_2A^+$ , HA,  $H^+$  and  $A^-$  in both phases of a two-phase water–nitrobenzene extraction system have been derived. From the extraction measurements, the equilibrium distribution constant of electroneutral 1-(2-thiazolylazo)-2-naphthol (TAN, HA) between the nitrobenzene and aqueous phases has been determined:  $\log K_D(HA) = 3.90 \pm 0.02$ . By using this value and further known constants and applying the mentioned relations, the following values of dissociation constants of TAN in nitrobenzene saturated with water have been calculated for a temperature of 25 °C:  $pK_d^{nb}(H_2A^+) = -\log K_d^{nb}(H_2A^+) = 4.9$  and  $pK_d^{nb}(HA) = -\log K_d^{nb}(HA) = 16.5$ .

*Keywords:* 1-(2-thiazolylazo)-2-naphthol, water–nitrobenzene system, distribution constant, dissociation constants.

Study of electrochemical phenomena at the liquid/liquid interface is a rapidly developing area in electrochemistry. These studies, which were carried out mainly at the water/nitrobenzene interface, are relevant to many problems. Among them, and of particular importance, are a better knowledge of biological systems, liquid extraction processes, and liquid ion-selective electrodes.<sup>1–7</sup>

1-(2-Thiazolylazo)-2-naphthol, TAN, and some other thiazolylazodyes and their derivatives were used as valuable chelatometric indicators and selective reagents for uranium,<sup>8,9</sup> copper,<sup>8,10–12</sup> somewhat later for cobalt, zirconium and thorium.<sup>10,13</sup>

The aim of the present communication is to formulate general relations among thermodynamic parameters which characterize dissociation equilibria including particles  $H_2A^+$ ,  $H^+$ , HA and  $A^-$  in both phases of a water–nitrobenzene extraction system and ion transfers across the interface of this system. Furthermore,

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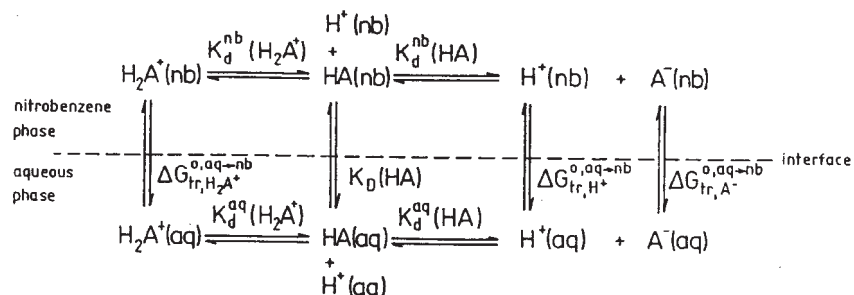
the derived relations have been applied for the case of TAN in the mentioned extraction system.

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

The extraction experiments on a two-phase water–nitrobenzene–TAN system were performed in 25 cm<sup>3</sup> glass test tubes with polyethylene stoppers using 10 cm<sup>3</sup> of each phase. The initial analytical concentrations of TAN in the nitrobenzene phase were in the range of 0.01–0.10 M. The equilibrium in the extraction system at 25±2 °C was achieved approximately in 2 hours, using a laboratory shaker. Then, both phases were separated by centrifugation (10 min, 2500 rpm).

The equilibrium concentration of TAN in the aqueous phase were determined spectrophotometrically.<sup>14</sup> The equilibrium distribution constant of this electro-neutral compound between the nitrobenzene and aqueous phases was calculated as a ratio of the corresponding equilibrium concentrations in the single phases.

The following values of log  $K_D(\text{HA})$  were obtained by the above mentioned method for five various initial concentrations (0.01, 0.03, 0.05, 0.075 and 0.10 M) of TAN in the nitrobenzene phase: 3.87, 3.94, 3.89, 3.86 and 3.95, respectively. From these results it follows that  $\log K_D(\text{HA}) = 3.90 \pm 0.02$ .



Scheme 1. The two-phase extraction system with the species  $\text{H}_2\text{A}^+$ .

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 a cation particle  $\text{H}_2\text{A}^+$  is dissociated in both phases (see Scheme 1), the corresponding dissociation constants being  $K_d^{\text{aq}}(\text{H}_2\text{A}^+)$ ,  $K_d^{\text{aq}}(\text{HA})$ ,  $K_d^{\text{nb}}(\text{H}_2\text{A}^+)$  and  $K_d^{\text{nb}}(\text{HA})$ . The equilibrium distribution constant of an electro-neutral compound HA between the nitrobenzene and aqueous phases is denoted by the standard Gibbs energies corresponding to the transfers of the ions  $\text{H}_2\text{A}^+$ ,  $\text{H}^+$  and  $\text{A}^-$  from the aqueous phase into the nitrobenzene one being  $\Delta G_{\text{tr}, \text{H}_2\text{A}^+}^{0, \text{aq} \rightarrow \text{nb}}$ ,  $\Delta G_{\text{tr}, \text{H}^+}^{0, \text{aq} \rightarrow \text{nb}}$  and  $\Delta G_{\text{tr}, \text{A}^-}^{0, \text{aq} \rightarrow \text{nb}}$ , respectively.

Then, these equilibrium constants and the foresaid Gibbs energies must fulfil the following relations:

$$-RT \ln K_d^{\text{nb}}(\text{H}_2\text{A}^+) = \mu_{\text{H}^+}^{0, \text{nb}} + \mu_{\text{HA}}^{0, \text{nb}} - \mu_{\text{H}_2\text{A}^+}^{0, \text{nb}} \quad (1)$$

$$-RT \ln K_d^{\text{aq}}(\text{H}_2\text{A}^+) = \mu_{\text{H}^+}^{0, \text{aq}} + \mu_{\text{HA}}^{0, \text{aq}} - \mu_{\text{H}_2\text{A}^+}^{0, \text{aq}} \quad (2)$$

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

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

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

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

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

$$\Delta G_{\text{tr}, \text{H}_2\text{A}^+}^{\text{o,aq} \rightarrow \text{nb}} = \mu_{\text{H}_2\text{A}^+}^{\text{o,nb}} - \mu_{\text{H}_2\text{A}^+}^{\text{o,aq}} \quad (8)$$

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

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

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

Analogously, the combination of Eqs. (3) – (7) yields

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

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

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

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

because the standard Galvani potential differences between the nitrobenzene and aqueous phases<sup>15</sup> for the ions  $\text{H}_2\text{A}^+$ ,  $\text{H}^+$  and  $\text{A}^-$ , denoted by the symbols  $\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{H}_2\text{A}^+}^{\text{o}}$ ,  $\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{H}^+}^{\text{o}}$  and  $\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{A}^-}^{\text{o}}$ , respectively, are defined by relations

$$\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{H}_2\text{A}^+}^{\text{o}} = -\Delta G_{\text{tr}, \text{H}_2\text{A}^+}^{\text{o,aq} \rightarrow \text{nb}} / F \quad (13)$$

$$\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{H}^+}^{\text{o}} = -\Delta G_{\text{tr}, \text{H}^+}^{\text{o,aq} \rightarrow \text{nb}} / F \quad (14)$$

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

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

By using the following values  $pK_d^{\text{aq}}(\text{H}_2\text{A}^+) = -\log K_d^{\text{aq}}(\text{H}_2\text{A}^+) = 0.88$ ,<sup>14</sup>  $pK_d^{\text{aq}}(\text{HA}) = -\log K_d^{\text{aq}}(\text{HA}) = 9.10$ ,<sup>14</sup>  $\log K_D(\text{HA}) = 3.90 \pm 0.02$  determined here,  $\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{H}^+}^{\text{o}} = -0.337 \text{ V}$ ,<sup>16</sup> inferred from data on the water–nitrobenzene system pub-

lished by Rais,<sup>17</sup>  $\Delta_{\text{aq}}^{\text{nb}}\varphi_{\text{H}_2\text{A}^+} = 0.130 \text{ V}$ ,<sup>18</sup>  $\Delta_{\text{aq}}^{\text{nb}}\varphi_{\text{A}^-} = -0.130 \text{ V}$ ,<sup>18</sup> and employing Eqs. (11) and (12) we have the values of dissociation constants of TAN in nitrobenzene saturated with water at 25 °C in the forms

$$\text{p}K_{\text{d}}^{\text{nb}}(\text{H}_2\text{A}^+) = -\log K_{\text{d}}^{\text{nb}}(\text{H}_2\text{A}^+) = 4.9 \quad (16)$$

$$\text{p}K_{\text{d}}^{\text{nb}}(\text{HA}) = -\log K_{\text{d}}^{\text{nb}}(\text{HA}) = 16.5 \quad (17)$$

where  $K_{\text{d}}^{\text{nb}}(\text{H}_2\text{A}^+)$  and  $K_{\text{d}}^{\text{nb}}(\text{HA})$  are expressed in  $\text{mol dm}^{-3}$ .

The fact that the dissociation constants of the TAN particles  $\text{H}_2\text{A}^+$  and  $\text{HA}$  are essentially higher in the aqueous phase than in the nitrobenzene one, *i.e.*,  $K_{\text{d}}^{\text{aq}}(\text{H}_2\text{A}^+) \gg K_{\text{d}}^{\text{nb}}(\text{H}_2\text{A}^+)$  and  $K_{\text{d}}^{\text{aq}}(\text{HA}) \gg K_{\text{d}}^{\text{nb}}(\text{HA})$ , can be obviously explained by the higher basicity and solvating power of water compared to those of nitrobenzene.

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#### ИЗВОД

#### ПРИЛОГ ТЕРМОДИНАМИЦИ 1-(2-ТИАЗОЛИЛАЗО)-2-НАФТОЛА У ЕКСТРАКЦИОНОМ СИСТЕМУ ВОДА-НИТРОБЕНЗЕН

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Изведене су опште термодинамичке релације које карактеришу хемијску равнотежу хемијских врста  $\text{H}_2\text{A}^+$ ,  $\text{HA}$ ,  $\text{H}^+$  и  $\text{A}^-$  у обе фазе двофазног екстракционог система вода-нитробензен. На основу екстракционих мерења одређена је равнотежна константа расподеле електронутралног 1-(2-тиазолилазо)-2-нафтола (TAN, HA) као  $\log K_{\text{D}}(\text{HA}) = 3.9 \pm 0.02$ . Користећи ову вредност, као и друге познате константе, као и примењујући поменуте изведене релације, израчунате су следеће вредности константи дисоцијација TAN у нитробензену засићеном водом на 25 °C:  $\text{p}K_{\text{d}}^{\text{nb}}(\text{H}_2\text{A}^+) = -\log K_{\text{d}}^{\text{nb}}(\text{H}_2\text{A}^+) = 4,9$  и  $\text{p}K_{\text{d}}^{\text{nb}}(\text{HA}) = -\log K_{\text{d}}^{\text{nb}}(\text{HA}) = 16,5$ .

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