IONIC PRODUCT OF WATER IN THE NITROBENZENE PHASE OF THE TWO-PHASE WATER–NITROBENZENE EXTRACTION SYSTEM

Emanuel MAKRLÍK*
Motorlet, 158 01 Prague 5-Jinonice

Received July 20, 1990
Accepted September 14, 1990

General relations among thermodynamic parameters, which characterize the transfers of the ions H^+ and OH^- from the aqueous into nitrobenzene phase of the two-phase water–nitrobenzene extraction system and dissociation equilibria of H_2O in both phases of this system, have been derived. Further, using the known parameters ionic product of water in nitrobenzene saturated with water has been evaluated for a temperature of 25°C: $P_{H_2O}^{nb} = 10^{-29.2}$ mol^2 dm^{-6}.

Nitrobenzene, a dipolar aprotic solvent, was frequently used in solution extraction, especially in the separation of cesium, strontium and radium from aqueous solutions.[1-3] In the last years, a considerable attention was paid to the study of charge transfer across the water/nitrobenzene interface.[4-6] Nitrobenzene is also suitable for accurate conductometric measurements[7].

In the present communication, general relations among thermodynamic parameters characterizing the transfers of the ions H^+ and OH^- from the aqueous into nitrobenzene phase of the two-phase water–nitrobenzene extraction system and dissociation equilibria of H_2O in both phases of this system have been derived. Furthermore, ionic product of water in nitrobenzene saturated with water has been calculated.

RESULTS AND DISCUSSION

Let us consider an equilibrium two-phase extraction system consisting of an aqueous (abbrev. aq) phase and a nitrobenzene (nb) phase (see Scheme 1 of the system under study below).

The equilibrium constants $K_{H_2O}^{aq}$ and $K_{H_2O}^{nb}$ can be evidently expressed in the forms

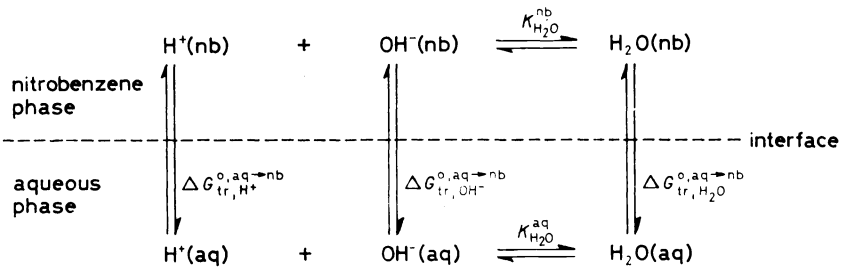
$$K_{H_2O}^{aq} = a_{H_2O}^{aq}/P_{H_2O}^{aq} \qquad (1)$$

and

$$K_{H_2O}^{nb} = a_{H_2O}^{nb}/P_{H_2O}^{nb}\,, \qquad (2)$$

---

[*] Present author's address: 341 42 Kolinec 250.



SCHEME 1

The two-phase water–nitrobenzene extraction system

where the symbols $P^{aq}_{H_2O} = a^{aq}_{H^+} \cdot a^{aq}_{OH^-}$ and $P^{nb}_{H_2O} = a^{nb}_{H^+} \cdot a^{nb}_{OH^-}$ represent ionic products of water in the aqueous and nitrobenzene phase, a^{aq}_i and a^{nb}_i being equilibrium molar activities of species i in the aqueous and nitrobenzene phase, respectively.

The change of Gibbs energy, $\Delta G^{o,aq\to nb}_{tr,H_2O}$, defined by the relation

$$\Delta G^{o,aq\to nb}_{tr,H_2O} = -RT\ln\left(a^{nb}_{H_2O}/a^{aq}_{H_2O}\right) \tag{3}$$

characterizes the nitrobenzene phase saturation with water. At this opportunity it is necessary to add that solubility of water in nitrobenzene at a temperature of 25°C is 0·16 mol dm^{-3} (refs[8,9]).

Finally, $\Delta G^{o,aq\to nb}_{tr,H^+}$ and $\Delta G^{o,aq\to nb}_{tr,OH^-}$ denote the standard Gibbs energies corresponding to the transfers of the ions H^+ and OH^- from the aqueous phase into the nitrobenzene one.

Then, the equilibrium constants $K^{aq}_{H_2O}$ and $K^{nb}_{H_2O}$ and the mentioned Gibbs energies must fulfil the following relations (*4*)–(*8*):

$$-RT\ln K^{aq}_{H_2O} = \mu^{o,aq}_{H_2O} - \mu^{o,aq}_{H^+} - \mu^{o,aq}_{OH^-} \tag{4}$$

$$-RT\ln K^{nb}_{H_2O} = \mu^{o,nb}_{H_2O} - \mu^{o,nb}_{H^+} - \mu^{o,nb}_{OH^-} \tag{5}$$

$$\Delta G^{o,aq\to nb}_{tr,H_2O} = \mu^{o,nb}_{H_2O} - \mu^{o,aq}_{H_2O} \tag{6}$$

$$\Delta G^{o,aq\to nb}_{tr,H^+} = \mu^{o,nb}_{H^+} - \mu^{o,aq}_{H^+} \tag{7}$$

$$\Delta G^{o,aq\to nb}_{tr,OH^-} = \mu^{o,nb}_{OH^-} - \mu^{o,aq}_{OH^-}\,, \tag{8}$$

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

Combining relations (*1*)–(*8*) yields the equation sought in the form

$$\Delta G^{\mathrm{o,aq}\to\mathrm{nb}}_{\mathrm{tr,H^+}} + \Delta G^{\mathrm{o,aq}\to\mathrm{nb}}_{\mathrm{tr,OH^-}} = RT\ln\left(P^{\mathrm{aq}}_{\mathrm{H_2O}}/P^{\mathrm{nb}}_{\mathrm{H_2O}}\right) \qquad (9)$$

which is equivalent to the equation

$$\Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{H^+}} = \Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{OH^-}} + \frac{RT}{F}\ln\left(\frac{P^{\mathrm{nb}}_{\mathrm{H_2O}}}{P^{\mathrm{aq}}_{\mathrm{H_2O}}}\right) \qquad (10)$$

because the standard Galvani potential differences of the ions H^+ and OH^- between the nitrobenzene and aqueous phase[4] denoted by $\Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{H^+}}$ and $\Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{OH^-}}$ are defined by the relations

$$\Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{H^+}} = -\Delta G^{\mathrm{o,aq}\to\mathrm{nb}}_{\mathrm{tr,H^+}}/F \qquad (11)$$

and

$$\Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{OH^-}} = \Delta G^{\mathrm{o,aq}\to\mathrm{nb}}_{\mathrm{tr,OH^-}}/F\,. \qquad (12)$$

By using the following values $\Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{H^+}} = -0.337$ V inferred from data on the two-phase water–nitrobenzene extraction system published by Rais[10], $\Delta^{\mathrm{nb}}_{\mathrm{aq}}\varphi^{\mathrm{o}}_{\mathrm{OH^-}} = 0.562$ V (ref.[11]) and $pP^{\mathrm{aq}}_{\mathrm{H_2O}} = -\log P^{\mathrm{aq}}_{\mathrm{H_2O}} = 14.0$ (ref.[12]; for purposes of the present communication, the preceding value of $pP^{\mathrm{aq}}_{\mathrm{H_2O}}$ is given with one decimal place accuracy) and applying Eq. (*10*) we have the value of ionic product of water in nitrobenzene saturated with water at a temperature of 25°C in the form

$$pP^{\mathrm{nb}}_{\mathrm{H_2O}} = -\log P^{\mathrm{nb}}_{\mathrm{H_2O}} = 29.2\,, \qquad (13)$$

where $P^{\mathrm{nb}}_{\mathrm{H_2O}}$ is expressed in $\mathrm{mol^2\,dm^{-6}}$.

The fact that ionic product of water is substantially higher in the aqueous phase than in the nitrobenzene one, i.e.,

$$10^{-14.0}\,\mathrm{mol^2\,dm^{-6}} = P^{\mathrm{aq}}_{\mathrm{H_2O}} \gg P^{\mathrm{nb}}_{\mathrm{H_2O}} = 10^{-29.2}\,\mathrm{mol^2\,dm^{-6}}\,, \qquad (14)$$

can be apparently explained by the higher basicity of water than that of nitrobenzene.

REFERENCES

1. Rais J., Selucký P.: Czech. 149 403.
2. Rais J., Kyrš M., Heřmánek S.: Czech. 153 933.
3. Šebesta F., Jirásek V., Sedláček J., Rais J.: Czech. 180 850.
4. Koryta J.: Electrochim. Acta *24*, 293 (1979).
5. Koryta J.: Electrochim. Acta *29*, 445 (1984).
6. Koryta J.: Electrochim. Acta *33*, 189 (1988).

7. Škarda V., Rais J., Kyrš M.: J. Inorg. Nucl. Chem. *41*, 1443 (1979).
8. Rais J., Selucký P., Kyrš M.: J. Inorg. Nucl. Chem. *38*, 1346 (1976).
9. Vaňura P., Makrlík E., Rais J., Kyrš M.: Collect. Czech. Chem. Commun. *47*, 1444 (1982).
10. Rais J.: Collect. Czech. Chem. Commun. *36*, 3253 (1971).
11. Makrlík E.: Unpublished results.
12. Koryta J., Dvořák J.: *Principles of Electrochemistry*. Wiley, Chichester 1987.

Translated by the author.