
STABILITY OF NH_4^+ AND $[\text{Zn}(\text{NH}_3)_4]^{2+}$ IN NITROBENZENE SATURATED WITH WATER

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General relations among thermodynamic parameters characterizing complex-formation equilibria in both phases of a two-phase extraction system and ion transfers across the interface of this system have been derived. Using the mentioned relations and known parameters stability constant of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and protonization constant of NH_3 in nitrobenzene saturated with water have been calculated for a temperature of 25°C.

Some ions, especially transition metal cations, form complex particles with an ammonia ligand. Stability constants of these complexes were determined by various methods in many papers — see, e.g., refs¹⁻⁸. Solvent extraction of ammine complexes of Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} and Co^{2+} from water into nitrobenzene were studied by Kyrš and Pivoňková^{9,10}.

In the present communication, general relations among thermodynamic parameters characterizing complex-formation equilibria in both phases of a two-phase extraction system and ion transfers through the interface of this system have been derived. Further, stability constant of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and protonization constant of NH_3 in nitrobenzene saturated with water have been calculated.

EXPERIMENTAL

Nitrobenzene and all other chemicals used of analytical grade purity were supplied by Lachema, Brno, Czechoslovakia. The extraction experiments on a two-phase water-nitrobenzene- NH_3 system have been performed in 25 cm³ volume glass test-tubes with polyethylene stoppers using 10 cm³ of each phase. The analytical concentrations of NH_3 in the aqueous phase have been in the range of 0.2–1.0 mol dm⁻³. The equilibrium in the extraction system at a temperature of 25 ± 1°C has been achieved approximately in 10 minutes using a laboratory shaking apparatus. Then, both phases have been separated by centrifugation. The equilibrium aqueous phase has been removed from this system and distilled water of the same volume (10 cm³) has been added to the remaining nitrobenzene phase. Practically all NH_3 (>99%) has been reextracted by subsequent 10 minutes shaking in the test-tube used earlier from the original equilibrium

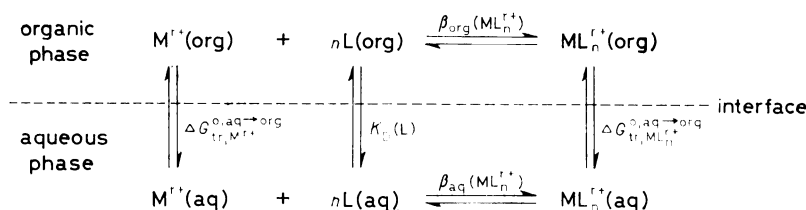
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nitrobenzene phase into water. The NH_3 content in this aqueous medium has been determined in the absence of the corresponding nitrobenzene phase by neutralization titration using an aqueous solution of HCl (0.01 mol dm^{-3}) as an agent and methyl red as an indicator. The NH_3 concentration in water thus determined is equal, within a range of experimental errors, to that in the equilibrium nitrobenzene phase of the system under study.

The concentration of NH_3 in the equilibrium aqueous phase has been calculated from the mass balance of this compound in the system under consideration. Finally, the equilibrium distribution constant of NH_3 between the nitrobenzene and aqueous phase has been calculated as a ratio of the corresponding equilibrium concentrations of this species in the single phases.

RESULTS AND DISCUSSION

Let us consider a system of two immiscible liquid phases consisting of an aqueous (abbrev. aq) phase and an organic (org) phase in which a cation M^{r+} forms a complex ion particle ML_n^{r+} with an electroneutral ligand L in both phases (see Scheme 1 of the system under study below), the corresponding stability constants being $\beta_{\text{aq}}(\text{ML}_n^{r+})$ and $\beta_{\text{org}}(\text{ML}_n^{r+})$. The equilibrium distribution constant of the ligand L between the organic and aqueous phase is denoted by a symbol $K_D(\text{L})$, the standard Gibbs energies corresponding to the transfers of the cations M^{r+} and ML_n^{r+} from the aqueous phase into the organic one being $\Delta G_{\text{tr},\text{M}^{r+}}^{\text{o, aq} \rightarrow \text{org}}$ and $\Delta G_{\text{tr},\text{ML}_n^{r+}}^{\text{o, aq} \rightarrow \text{org}}$.



SCHEME 1

The two-phase extraction system with the complex ML_n^{r+}

Then, these equilibrium constants and the mentioned Gibbs energies must fulfil the following relations (1)–(5):

$$-RT \ln \beta_{\text{org}}(\text{ML}_n^{r+}) = \mu_{\text{ML}_n^{r+}}^{\text{o, org}} - \mu_{\text{M}^{r+}}^{\text{o, org}} - n\mu_{\text{L}}^{\text{o, org}} \quad (1)$$

$$-RT \ln \beta_{\text{aq}}(\text{ML}_n^{r+}) = \mu_{\text{ML}_n^{r+}}^{\text{o, aq}} - \mu_{\text{M}^{r+}}^{\text{o, aq}} - n\mu_{\text{L}}^{\text{o, aq}} \quad (2)$$

$$-RT \ln K_D(\text{L}) = \mu_{\text{L}}^{\text{o, org}} - \mu_{\text{L}}^{\text{o, aq}} \quad (3)$$

$$\Delta G_{\text{tr},\text{M}^{r+}}^{\text{o, aq} \rightarrow \text{org}} = \mu_{\text{M}^{r+}}^{\text{o, org}} - \mu_{\text{M}^{r+}}^{\text{o, aq}} \quad (4)$$

$$\Delta G_{\text{tr},\text{ML}_n^{r+}}^{\text{o, aq} \rightarrow \text{org}} = \mu_{\text{ML}_n^{r+}}^{\text{o, org}} - \mu_{\text{ML}_n^{r+}}^{\text{o, aq}} \quad (5)$$

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

The combination of relations (1)–(5) yields the sought equation in the form

$$\Delta G_{\text{tr}, \text{ML}_n^{r+}}^{o, \text{aq} \rightarrow \text{org}} = \Delta G_{\text{tr}, \text{M}^{r+}}^{o, \text{aq} \rightarrow \text{org}} + RT \ln \frac{\beta_{\text{aq}}(\text{ML}_n^{r+})}{\beta_{\text{org}}(\text{ML}_n^{r+}) \cdot [K_D(\text{L})]^n} \quad (6)$$

which is equivalent to the equation

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{ML}_n^{r+}}^o = \Delta_{\text{aq}}^{\text{org}} \varphi_{\text{M}^{r+}}^o + \frac{RT}{rF} \ln \frac{\beta_{\text{org}}(\text{ML}_n^{r+}) \cdot [K_D(\text{L})]^n}{\beta_{\text{aq}}(\text{ML}_n^{r+})} \quad (7)$$

because the standard Galvani potential differences of the ions M^{r+} and ML_n^{r+} between the organic and aqueous phase¹¹ denoted by $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{M}^{r+}}^o$ and $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{ML}_n^{r+}}^o$ are defined by relations (8) and (9):

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{M}^{r+}}^o = -\Delta G_{\text{tr}, \text{M}^{r+}}^{o, \text{aq} \rightarrow \text{org}} / rF, \quad (8)$$

$$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{ML}_n^{r+}}^o = -\Delta G_{\text{tr}, \text{ML}_n^{r+}}^{o, \text{aq} \rightarrow \text{org}} / rF. \quad (9)$$

It is obvious that Eq. (6) or (7) derived in this paper can be employed for calculating one constant when the values of all the remaining constants are known.

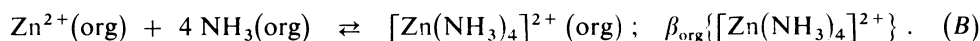
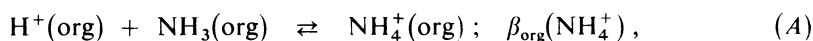
By using the values $\log \beta_{\text{aq}}(\text{NH}_4^+) = 9.54$ (ref.⁸), $\log \beta_{\text{aq}}\{[\text{Zn}(\text{NH}_3)_4]^{2+}\} = 9.32$ (ref.⁸), $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{Zn}^{2+}}^o = -0.343$ V (ref.¹²; org. = nitrobenzene saturated with water), $\Delta_{\text{aq}}^{\text{org}} \varphi_{[\text{Zn}(\text{NH}_3)_4]^{2+}}^o = -0.163$ V (ref.¹³) evaluated previously from "classical" extraction measurements in the water–nitrobenzene system, $\log K_D(\text{L}) = -2.20 \pm 0.01$ ($\text{L} = \text{NH}_3$) determined here (see Experimental) and the values $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{H}^+}^o = -0.337$ V and $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{NH}_4^+}^o = -0.278$ V inferred from data on the mentioned two-phase system published by Rais¹⁴ and applying Eq. (7) we have the following values of the equilibrium constants

$$\log \beta_{\text{org}}(\text{NH}_4^+) = 12.74 \quad (10)$$

and

$$\log \beta_{\text{org}}\{[\text{Zn}(\text{NH}_3)_4]^{2+}\} = 24.20 \quad (11)$$

which correspond to the equilibria proceeding in nitrobenzene saturated with water at a temperature of 25°C:



From the equilibrium (A) point of view it is evident that the protonization constant $\beta_{\text{org}}(\text{NH}_4^+)$ may be regarded as a quantitative expression of the stability of the "complex" particle NH_4^+ in nitrobenzene saturated with water.

From the results given above it follows that the protonization constant of NH_3 and the stability constant of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ are substantially higher in the nitrobenzene phase than in the aqueous one, i.e.,

$$10^{9.54} = \beta_{\text{aq}}(\text{NH}_4^+) \ll \beta_{\text{org}}(\text{NH}_4^+) = 10^{12.74} \quad (12)$$

and

$$10^{9.32} = \beta_{\text{aq}}\{[\text{Zn}(\text{NH}_3)_4]^{2+}\} \ll \beta_{\text{org}}\{[\text{Zn}(\text{NH}_3)_4]^{2+}\} = 10^{24.20}. \quad (13)$$

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

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