

CHEMICAL EQUILIBRIA INCLUDING PARTICLES I^- , I_3^- , I_5^- , AND I_2 IN TWO-PHASE WATER-NITROBENZENE EXTRACTION SYSTEM

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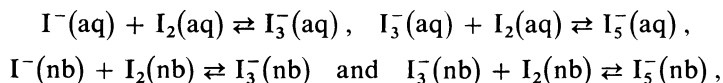
General relations among thermodynamic parameters characterizing chemical equilibria with species I^- , I_3^- , I_5^- and I_2 in the two-phase water-nitrobenzene extraction system have been derived. Furthermore, these relations have been used for calculating equilibrium constants $K_1^{aq}(I_3^-)$ and $K_2^{aq}(I_5^-)$ corresponding to homogeneous reactions $I^-(aq) + I_2(aq) \rightleftharpoons I_3^-(aq)$ and $I_3^-(aq) + I_2(aq) \rightleftharpoons I_5^-(aq)$ proceeding in the aqueous phase of the system under study. Finally, stability of polyiodides I_3^- and I_5^- in both phases has been discussed.

Fundamental chemical and physical properties of interhalogen compounds and polyhalides were summarized together with methods of their preparation and principal reactions in a review by Sharpe¹. Polyiodides were employed as effective agents for the extraction of alkali metals (especially of caesium) from water into nitrobenzene²⁻⁴.

In the present paper, several relations among thermodynamic parameters characterizing chemical equilibria including particles I^- , I_3^- , I_5^- and I_2 have been derived for the case of the water-nitrobenzene extraction system. Then, these relations have been applied for calculating equilibrium constants corresponding to the reactions $I^-(aq) + I_2(aq) \rightleftharpoons I_3^-(aq)$ and $I_3^-(aq) + I_2(aq) \rightleftharpoons I_5^-(aq)$ taking place in the aqueous phase of the system under study.

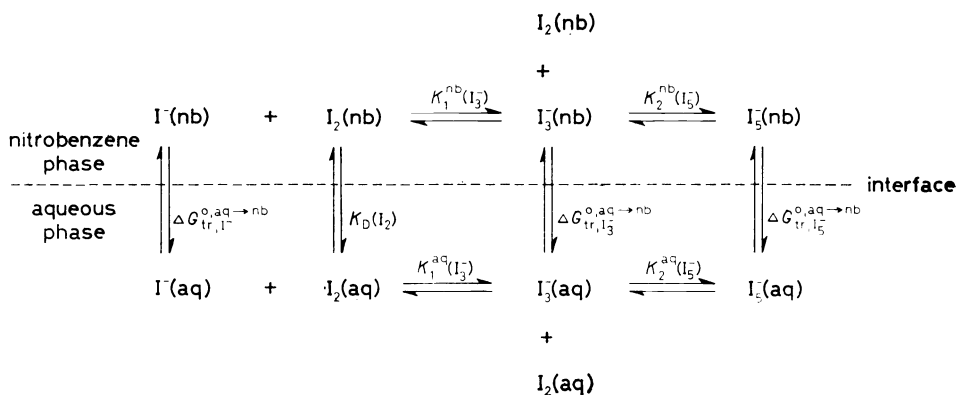
RESULTS AND DISCUSSION

Let us assume an equilibrium system of two immiscible liquid phases consisting of an aqueous (abbrev. aq) phase and a nitrobenzene (nb) phase in which species I^- , I_3^- , I_5^- and I_2 taking part, as may be inferred from literature^{4,5}, in the following homogeneous chemical reactions



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the corresponding equilibrium constants being $K_1^{aq}(I_3^-)$, $K_2^{aq}(I_5^-)$, $K_1^{nb}(I_3^-)$ and $K_2^{nb}(I_5^-)$ (see Scheme 1). The equilibrium distribution constant of iodine I_2 between the nitrobenzene and the aqueous phase is denoted by a symbol $K_D(I_2)$, the standard Gibbs energies corresponding to the transfers of the ions I^- , I_3^- and I_5^- from the aqueous phase into the nitrobenzene one being $\Delta G_{tr,I^-}^{o,aq \rightarrow nb}$, $\Delta G_{tr,I_3^-}^{o,aq \rightarrow nb}$ and $\Delta G_{tr,I_5^-}^{o,aq \rightarrow nb}$.



SCHEME 1

The two-phase extraction system with species I^- , I_3^- , I_5^- , and I_2

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

$$-RT \ln K_1^{nb}(I_3^-) = \mu_{I_3^-}^{o,nb} - \mu_{I^-}^{o,nb} - \mu_{I_2}^{o,nb} \quad (1)$$

$$-RT \ln K_2^{nb}(I_5^-) = \mu_{I_5^-}^{o,nb} - \mu_{I_3^-}^{o,nb} - \mu_{I_2}^{o,nb} \quad (2)$$

$$-RT \ln K_1^{aq}(I_3^-) = \mu_{I_3^-}^{o,aq} - \mu_{I^-}^{o,aq} - \mu_{I_2}^{o,aq} \quad (3)$$

$$-RT \ln K_2^{aq}(I_5^-) = \mu_{I_5^-}^{o,aq} - \mu_{I_3^-}^{o,aq} - \mu_{I_2}^{o,aq} \quad (4)$$

$$-RT \ln K_D(I_2) = \mu_{I_2}^{o,nb} - \mu_{I_2}^{o,aq} \quad (5)$$

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

$$\Delta G_{tr,I_3^-}^{o,aq \rightarrow nb} = \mu_{I_3^-}^{o,nb} - \mu_{I_3^-}^{o,aq} \quad (7)$$

$$\Delta G_{tr,I_5^-}^{o,aq \rightarrow nb} = \mu_{I_5^-}^{o,nb} - \mu_{I_5^-}^{o,aq} \quad (8)$$

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

By combining relations (1), (3), (5), (6) and (7) we obtain the sought equation in the form

$$\Delta G_{\text{tr}, \text{I}_3^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} = \Delta G_{\text{tr}, \text{I}^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} + RT \ln \frac{K_1^{\text{aq}}(\text{I}_3^-)}{K_1^{\text{nb}}(\text{I}_3^-) \cdot K_{\text{D}}(\text{I}_2)}. \quad (9)$$

Analogously, the combination of relationships (2), (4), (5), (7) and (8) yields

$$\Delta G_{\text{tr}, \text{I}_5^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} = \Delta G_{\text{tr}, \text{I}_3^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} + RT \ln \frac{K_2^{\text{aq}}(\text{I}_5^-)}{K_2^{\text{nb}}(\text{I}_5^-) \cdot K_{\text{D}}(\text{I}_2)}. \quad (10)$$

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

$$\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}_3^-}^{\text{o}} = \Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}^-}^{\text{o}} + \frac{RT}{F} \ln \frac{K_1^{\text{aq}}(\text{I}_3^-)}{K_1^{\text{nb}}(\text{I}_3^-) \cdot K_{\text{D}}(\text{I}_2)}, \quad (11)$$

$$\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}_5^-}^{\text{o}} = \Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}_3^-}^{\text{o}} + \frac{RT}{F} \ln \frac{K_2^{\text{aq}}(\text{I}_5^-)}{K_2^{\text{nb}}(\text{I}_5^-) \cdot K_{\text{D}}(\text{I}_2)} \quad (12)$$

because the standard Galvani potential differences of the ions I^- , I_3^- and I_5^- between the nitrobenzene and aqueous phase⁶ denoted by the symbols $\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}^-}^{\text{o}}$, $\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}_3^-}^{\text{o}}$ and $\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}_5^-}^{\text{o}}$ are defined by relationships:

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

$$\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}_3^-}^{\text{o}} = \Delta G_{\text{tr}, \text{I}_3^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} / F \quad (14)$$

$$\Delta_{\text{aq}}^{\text{nb}} \varphi_{\text{I}_5^-}^{\text{o}} = \Delta G_{\text{tr}, \text{I}_5^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} / F. \quad (15)$$

Using the values $\Delta G_{\text{tr}, \text{I}^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} = 18.8 \text{ kJ mol}^{-1}$, $\Delta G_{\text{tr}, \text{I}_3^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} = -23.4 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{tr}, \text{I}_5^-}^{\text{o}, \text{aq} \rightarrow \text{nb}} = -38.8 \text{ kJ mol}^{-1}$ inferred from data on the two-phase water-nitrobenzene extraction system published by Rais⁵, the values $\log K_1^{\text{nb}}(\text{I}_3^-) = 8.0$, $\log K_2^{\text{nb}}(\text{I}_5^-) = 2.7$ and $\log K_{\text{D}}(\text{I}_2) = 2.3$ from a paper by Tribalat and Grall⁴ and applying Eqs (9) and (10) we have

$$\log K_1^{\text{aq}}(\text{I}_3^-) = 2.9 \quad (16)$$

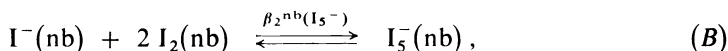
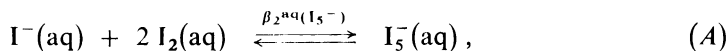
and

$$\log K_2^{\text{aq}}(\text{I}_5^-) = 2.3 \quad (17)$$

at a temperature of 25°C.

In this context it should be noted that the constant $K_1^{\text{aq}}(\text{I}_3^-)$ calculated here is in a fairly good agreement with the value of $K_1^{\text{aq}}(\text{I}_3^-) = 10^{2.85}$ given in ref.³. On the other hand, up to the present time the constant $K_2^{\text{aq}}(\text{I}_5^-)$ has not been probably determined by an experimental method with sufficient accuracy.

If the ionic particles I_3^- and I_5^- are regarded, at least formally, as "complex" anions with a "central" ion I^- and an electroneutral iodine "ligand" I_2 , then the constants $K_1^{aq}(I_3^-)$, $K_1^{nb}(I_3^-)$, $K_2^{aq}(I_5^-)$ and $K_2^{nb}(I_5^-)$ may be understood to be the consecutive stability constants of those anions. From this point of view it is possible to express the total stability of the anion I_5^- in the single phases of the system under study in terms of the constants $\beta_2^{aq}(I_5^-)$ and $\beta_2^{nb}(I_5^-)$ corresponding to the equilibria



where

$$\beta_2^{aq}(I_5^-) = K_1^{aq}(I_3^-) \cdot K_2^{aq}(I_5^-), \quad (18)$$

$$\beta_2^{nb}(I_5^-) = K_1^{nb}(I_3^-) \cdot K_2^{nb}(I_5^-), \quad (19)$$

so that – with regard to Eqs (16)–(19) and taking the results of a paper by Tribalat and Grall⁴ into account (see also the text above) – we can write:

$$\log \beta_2^{aq}(I_5^-) = 5.2 \quad (20)$$

and

$$\log \beta_2^{nb}(I_5^-) = 10.7. \quad (21)$$

The fact that the stability of the polyiodide anions I_3^- and I_5^- is essentially higher in the nitrobenzene phase than in the aqueous one, i.e.,

$$10^{2.9} = K_1^{aq}(I_3^-) \ll K_1^{nb}(I_3^-) = 10^{8.0} \quad (22)$$

and

$$10^{5.2} = \beta_2^{aq}(I_5^-) \ll \beta_2^{nb}(I_5^-) = 10^{10.7}, \quad (23)$$

may be apparently explained by the higher basicity and solvatability of water than those of nitrobenzene.

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