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A. M. ROZEN, L. M. GINDIN, and I. F. KOPP

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Abstract

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THERMODYNAMICS OF EXTRACTION EQUILIBRIA OF STRONG ELECTROLYTES DISSOCIATED IN THE ORGANIC PHASE

EXTRACTION OF HYDROCHLORIC ACID AND COBALT AND CALCIUM CHLORIDES BY ISOAMYL ALCOHOL

(Presented by Academician A. N. Frumkin, July 2, 1959)

A number of extraction equilibria of electrolytes are characterized by the fact that in the aqueous phase the salt is dissociated, while in the organic phase it is not, i.e., it behaves as a nonelectrolyte. A detailed consideration of such equilibria is given in a paper by one of the authors ([1]). However, when solvents of high dielectric constant are used—for example, in the extraction of chlorides by alcohols—such an explanation is clearly incorrect, as follows from the comparatively high electrical conductivity of the organic phase (see Table 1).

Table 1

Composition of aq. phase, x_{CaCl2}, g/l	–	–	–	–	–	120	240
Composition of aq. phase, x_{HCl}, mol/l	2.6	3.9	5.5	6.3	6.6	1.2	1.75

Composition of org. phase (isoamyl alcohol), y_{HCl}, mol/l	0.01	0.75	1.16	2.34	3.3	3.9	1.3	5.5
Electrical conductivity $\chi \cdot 10^2$, $ohm^{-1} \cdot cm^{-1}$	10^{-3}	0.53	1.06	2.6	5.0	8.5	0.6	0.8
Viscosity, centipoise	3.5	5.0	5.9	6.3	6.6	6.1	7.5	12.0

As is seen from Table 1, the HCl solution in alcohol obtained on extraction has an electrical conductivity typical of electrolyte solutions; i.e., dissociation of HCl occurs in the organic phase. Let us determine how this affects the extraction equilibria. We shall use the distribution law

$$a_o/a_{\text{w}} = k; \qquad a_o = ka_{\text{w}}, \tag{1}$$

where a_{w} and a_o are the activities of the extracted substance in the aqueous and organic phases, and k is the distribution constant. For hydrochloric acid,

$$a_{\text{w}} = (\text{H}^+)_{\text{w}}(\text{Cl}^-)_{\text{w}}\gamma^2_{\pm\text{w}},$$

where $\gamma_{\pm\text{w}}$ is the mean activity coefficient, and the parentheses denote molal concentrations. In the organic phase, in the absence of dissociation,

$$a_o = (\text{HCl})_o\gamma_o;$$

in the presence of dissociation,

$$a_o = (\mathrm{H}^+)_o(\mathrm{Cl}^-)_o\gamma_{\pm o}^2.$$

If extraction is accompanied by hydration with m molecules of water and solvation with n molecules of solvent S, then, in the absence of dissociation,

$$a_o = a_o/S^n a_{\mathrm{H_2O}}^m,$$

and, in the presence of dissociation,

$$a_o = a_o/a_{\mathrm{H_2O}}^m.$$

Substituting into equation (1), denoting $(\mathrm{HCl})_{\mathrm{w}} = x$, $(\mathrm{HCl})_o = y$, and noting that in the absence of salting-out agents $(\mathrm{H}^+)_{\mathrm{w}} = (\mathrm{Cl}^-)_{\mathrm{w}} = x$, $(\mathrm{H}^+)_o = (\mathrm{Cl}^-)_o = y$, we find that, when dissociation is present in the organic phase,

$$(\mathrm{H}^+)_o(\mathrm{Cl}^-)_o = k(\mathrm{H}^+)_{\mathrm{w}}(\mathrm{Cl}^-)_{\mathrm{w}}\gamma_{\pm\mathrm{w}}^2 a_{\mathrm{H_2O}}^m/\gamma_{\pm o}^2; \qquad y = \sqrt{k}\, x\gamma_{\pm\mathrm{w}} a_{\mathrm{H_2O}}^{m/2}/\gamma_{\pm o}. \quad (2)$$

If dissociation in the organic phase is absent, then

$$(\mathrm{HCl})_o = k(\mathrm{H}^+)_{\mathrm{w}}(\mathrm{Cl}^-)_{\mathrm{w}}\gamma_{\pm\mathrm{w}}^2 S^n a_{\mathrm{H_2O}}^m/\gamma_o; \qquad y = kx^2\gamma_{\pm\mathrm{w}}^2 S^n a_{\mathrm{H_2O}}^m/\gamma_o. \quad (3)$$

Let us compare equation (2) with experiment (2). The activity coefficient $\gamma_{\pm o}$ of an HCl solution in isoamyl alcohol, according to the data of (4), decreases sharply in the concentration range from 0 to 0.1 mole/l, and for $x > 0.2$ mole/l changes only slightly, so that one may take $\gamma_{\pm o} = 0.05 = \mathrm{const}$. Then, if hydration is absent, $m = 0$, equation (2) predicts a linear dependence of y on $x\gamma_{\pm v}$, which, however, is not in full agreement with experiment (Figs. 1, 2; $\gamma_{\pm v}$ and $a_{\mathrm{H_2O}}$ are taken from (3)). If hydration is taken into account by putting $m = 4$ (from the change in phase volumes $m = 4$ was found; by Fischer titration $m = 3.5$), then equation (2) represents the experimental data well (Figs. 1, 3); at $\gamma_{\pm o} = 0.05$ and x in moles per

[Figure 1 and Figure 2 graphs]

Fig. 1. Distribution of hydrochloric acid between water and isoamyl alcohol. 1—dependence of y on x; 2—dependence of y on $x\gamma_{\pm v}$; 3—dependence of y on $x\gamma_{\pm v}a_{\mathrm{H_2O}}^2$

Fig. 2. Dependence of the distribution coefficients of HCl $(1, 2, 3)$ and $\mathrm{CaCl_2}$ (4) on the concentration of isoamyl alcohol S upon dilution with benzene. 1—$x_{\mathrm{HCl}} = 4.2$ mole/l; 2—2.6 mole/l; 3—0.75 mole/l. $S = S_0 - 2y_{\mathrm{HCl}}$, or $S = S_0 - 4y_{\mathrm{Ca}}$; S_0 in mole/l

kilogram we find $k = 2.5 \cdot 10^{-4}$*. Thus, the extraction equilibria of hydrochloric acid are satisfactorily explained on the assumption that it is dissociated in the organic phase and is extracted together with 4 molecules of water ($m = 4$).

However, equation (3), based on the assumption of extraction of undissociated acid, can also be brought into approximate agreement with the experimental data if it is assumed that HCl molecules are solvated by 2 molecules of alcohol. A direct test of the dependence of the distribution coefficient α_{HCl} on the concentration of free alcohol by the method of dilution with benzene (Fig. 2) showed that at strong dilution indeed $\alpha \sim S^2$ (for $CaCl_2$, $\alpha \sim S^4$, $n = 4$). Thus, the principal objection to this mechanism—the high electrical conductivity of the organic phase—is removed. However, at large dilutions it disappears, since $\varkappa$ falls sharply with dilution (at $x_{\mathrm{HCl}} = 150$ g/l

* This value should be compared with that calculated from the zero ion activity coefficient γ_0 (4), which brings the nonaqueous solution to the same standard state as the aqueous one, so that $a_o\gamma_o^2 = a_v$ and $k = 1/\gamma_o^2$. We find $\lg k = -3.6$ instead of $-2\lg\gamma_o = -6$ according to (4). The difference is probably connected with the extraction of HCl together with water and with the decrease in ΔG_{solv} (equation (6)).

and alcohol contents of 100, 70, 40, and 30%, we obtain, respectively, $\varkappa \cdot 10^2 =$ 1.34; 0.27; 0.016; 0.008 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$. Thus, upon sufficient dilution of the alcohol with benzene (dielectric constant $\simeq 2$), the dielectric constant decreases and undissociated acid is extracted. This mechanism is also possible in extraction with pure alcohol (if the fraction of HCl extracted in the form of undissociated molecules is roughly estimated by extrapolating the distribution coefficients at large dilutions to high alcohol concentrations, we find that this fraction is $\sim \alpha_{\mathrm{extr}}/\alpha$ ($\simeq$ 20-25%)); however, in equation (2) it is automatically taken into account by the activity coefficients $\gamma_{\pm o}$.

The distribution of calcium, cobalt, and nickel chlorides can also be interpreted on the assumption of dissociation in the organic phase, i.e., by setting

$$\{\mathrm{Me}^{2+} + 2\mathrm{Cl}^-\}_{\mathrm{B}} \rightleftharpoons \{\mathrm{Me}^{2+} + 2\mathrm{Cl}^-\}_{\mathrm{o}}.$$

$$\frac{(\mathrm{Me}^{2+})_{\mathrm{o}}(\mathrm{Cl}^-)_{\mathrm{o}}^2\gamma_{\pm o}^3}{(\mathrm{Me}^{2+})_{\mathrm{B}}(\mathrm{Cl}^-)_{\mathrm{B}}^2\gamma_{\pm \mathrm{B}}^3} = k_{\mathrm{Me}}. \tag{4}$$

Fig. 3. Distribution of $CaCl_2$ between water and alcohols. The dashed line is the dependence of y on x; solid lines are the dependence of y on $x\gamma_{\pm \mathrm{B}}$; 1 — isoamyl alcohol, 2 —butyl alcohol.

If only one salt is distributed, with concentration x in the aqueous phase and y in the organic phase, then $(\mathrm{Me}^{2+})_{\mathrm{o}} = (\mathrm{Cl}^-)_{\mathrm{o}} = y$, and

Fig. 3. Distribution of $CaCl_2$ between water and alcohols. The dashed line is the dependence of y on x; solid lines are the dependence of y on $x\gamma_{\pm B}$; 1 – isoamyl alcohol, 2 –butyl alcohol

Figure 1: Fig. 3. Distribution of $CaCl_2$ between water and alcohols. The dashed line is the dependence of y on x; solid lines are the dependence of y on $x\gamma_{\pm B}$; 1 –isoamyl alcohol, 2 –butyl alcohol

$$y = k_{Me}^{1/3} x\gamma_{\pm B}/\gamma_{\pm o}; \qquad \alpha = y/x = k^{1/3}\gamma_{\pm B}/\gamma_{\pm o}. \tag{5}$$

Verification of equation (5) for calcium chloride using the data of [2] is shown in Fig. 3. As is seen from Fig. 3, there is a considerable deviation from equation (5); possibly a decreasing factor should be introduced into the equation to take hydration into account (it is sufficient to take $m = 6$). Figure 3 also gives data on the extraction of $CaCl_2$ by butyl alcohol. As is seen from comparison of the curves, butyl alcohol, having a larger oxygen-to-carbon ratio and a higher dielectric constant, is the more effective extractant. This follows from the theoretical equation for the electrolyte–electrolyte equilibrium constant, which can be derived using the calculation of hydration energy according to [5]*.

$$RT\ln k = -\Delta G_{hydr} \simeq 0.5e^2N\left(1/D_{H_2O} - 1/D_{alc}\right)\sum z_i^2/r_i + \Delta G_{solv}, \tag{6}$$

where D is the dielectric constant; z_i and r_i are the charge and radius of the solvated ions. For two alcohols,

$$\ln k_{but}/k_{am} \sim (1/D_{am} - 1/D_{but}) > 0$$

and $k_{am} < k_{but}$. On going to higher alcohols the dielectric constant and, consequently, k_{alc} decrease, i.e., the extraction properties deteriorate.

Let us now verify equation (5) for cobalt and nickel. According to the data of [6] (extraction of $CoCl_2$ and $NiCl_2$ by caprylic alcohol), $\lg\alpha_{Co,Ni} = ax - b$, where $a = 0.088$, $b = 5.8$, and x is in weight percent. It can be shown that for $CoCl_2$ and $NiCl_2$, at high concentrations, the logarithm of the activity coefficient depends linearly on concentration, $\lg\gamma_{\pm B} = a_1x - b_1$, and from (5) it follows that $\lg\alpha = a_1x - b_1 + \lg k^{1/3}/\gamma_0$, which agrees qualitatively with the data–

* G_{solv} is the free energy of formation of the solvate shell

$$(\Delta G_{solv} \simeq zeN(n_{alc}\mu_{alc} - n_{H_2O}\mu_{H_2O})/r^2) - T\Delta S_{solv}.$$

···([6]). However, the quantitative agreement is insufficient (from the slope of the curve $\lg\gamma_{NiCl_2} = f(x)$, $a_1 = 0.04$ was found instead of $a_1 = 0.088$). It is possible

that, owing to the low dielectric constant of caprylic alcohol, $CoCl_2$ dissociates only into $CoCl^+$ and Cl^-, so that $a_o = y^2\gamma^2_{\pm oef}$. Then $y = k^{1/2}(x\gamma_{\pm B})^{3/2}/\gamma_o$ and $\lg\alpha = (1.5a_1x + 0.5\lg x) + \lg k^{1/2}\gamma_o - 1.5b_1$. At $x > 20\%$, the term in parentheses is $\simeq 0.08x$, i.e., $a = 0.08$, which is close to the results of ([6]).

In the extraction of HCl by isoamyl alcohol in the presence of large amounts of $CaCl_2$, it was found ([2]) that $y_{HCl} = k_1\sqrt{x_{HCl}}$. We shall show that this follows from equation (2). Let us take into account that $CaCl_2$ is extracted much more weakly than HCl, and it may be assumed that the concentration of chloride ion in the organic phase is determined only by extraction of HCl, i.e., $(H^+)_o = (Cl^-)_o = y_{HCl}$. In the aqueous phase, $(H^+)_B = x_{HCl}$, $(Cl^-)_B = x_{HCl} + 2x_{Ca}$. Substituting the ion concentrations into (2), we obtain

$$y_{HCl} = \sqrt{k}\left(\sqrt{x_{HCl} + 2x_{Ca}\gamma_{\pm B}a^{m/2}_{H_2O}/\gamma_{\pm o}}\right)\sqrt{x_{HCl}} = \sqrt{k}B\sqrt{x_{HCl}} \simeq k_1\sqrt{x_{HCl}}, \tag{7}$$

since $x_{Ca} = \text{const} \simeq 5$ mol/l $\gg x_{HCl}$, and consequently $B \simeq \text{const}$. In the case of distribution of cobalt chloride in the presence of $CaCl_2$, it is necessary to solve jointly the distribution equations (4) for Co and Ca; dividing the first by the second, we obtain

$$\beta_{Co/Ca} = \alpha_{Co}/\alpha_{Ca} = k_{Co}/k_{Ca} = \text{const}. \tag{8}$$

As indicated in our work ([7]), $\beta_{Co/Ca} = 5 = \text{const}$. Thus, this result is explained very simply, with $k_{Co} = 5k_{Ca}$ ($k_{Co} > k_{Ca}$, probably because $r_{Co} < r_{Ca}$). In the case of extraction of $CoCl_2$ from an aqueous phase containing HCl, it is necessary to solve equations (4) and (2) jointly. Dividing the first by the square of the second, we find*

$$k^2_{HCl}/k_{Co}\gamma_o = \alpha^2_{HCl}/\alpha_{Co}\gamma_{\pm B} = a^{2m}_{H_2O} = A = \text{const}. \tag{9}$$

A check showed that at $x_{HCl} = 0.16 \div 7$ mol/l, $x_{Co} = 19 \div 50$ g/l, $A = 20 \pm 2 = \text{const}$.

The considerable increase in the distribution coefficient of cobalt and in the separation factor $\beta_{Co/Ni}$ upon simultaneous introduction of HCl and $CaCl_2$ ([7]) can be explained by the transition to extraction of the anionic complex $CoCl^{2-}_4$, responsible for coloring the solution blue. In conclusion we note that the class of equilibria considered is limited to solvents with high dielectric constants. At low dielectric constants, dissociation in the organic phase is impossible, since $k_{acc} \sim D^{-3}$.

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Norilsk Mining and Metallurgical Combine
named after A. P. Zavenyagin

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REFERENCES CITED

[1] A. M. Rozen, *Atomic Energy*, **2**, no. 5, 445 (1957). [2] L. M. Gindin, A. M. Rozen et al., *Zhurn. neorg. khim.*, no. 1 (1960). [3] R. Robinson, R. Stokes, *Electrolyte Solutions*, London, 1956. [4] N. A. Izmailov, *ZhFKh*, **30**, 2164 (1956); **31**, 2169 (1957). [5] D. Bernal, R. Fowler, *UFN*, **14**, 586 (1934). [6] L. Garwin, A. Hixon, *Ind. Eng. Chem.*, **41**, 2298 (1949). [7] L. M. Gindin, I. F. Kopp et al., *Zhurn. neorg. khim.*, no. 1 (1960).

* Expressions (8), (9) are also obtained when dissociation is incomplete or absent.

Note: Figure translations are in progress. See original paper for figures.