

THE EXTRACTION TRANSFER OF H^+ -18-CROWN-6 SPECIES ACROSS THE WATER-NITROBENZENE PHASE BOUNDARY IN THE EXTRACTION OF AQUEOUS SOLUTIONS OF PERCHLORIC ACID BY NITROBENZENE IN THE PRESENCE OF 18-CROWN-6

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A study was made of the extraction of perchloric acid in water-nitrobenzene and water-nitrobenzene-18-crown-6 (hereafter L) systems. The experimental data was interpreted on the basis of the assumption that the extraction occurs according to the equations $\text{H}_{\text{aq}}^+ + \text{ClO}_4^-_{\text{aq}} \rightleftharpoons \text{H}_{\text{org}}^+ + \text{ClO}_4^-_{\text{org}}$ and $\text{H}_{\text{aq}}^+ + \text{L}_{\text{aq}} + \text{ClO}_4^-_{\text{aq}} \rightleftharpoons \text{HL}_{\text{org}}^+ + \text{ClO}_4^-_{\text{org}}$. Crown is also protonated in the aqueous phase according to the equation $\text{H}_{\text{aq}}^+ + \text{L}_{\text{aq}} \rightleftharpoons \text{HL}_{\text{aq}}^+$. The values of the corresponding extraction constants, the protonation constants of 18-crown-6 in nitrobenzene and water and the individual extraction constants of the HL_{org}^+ species in the water-nitrobenzene system were determined, along with the magnitude of the molar free enthalpy for the transfer of these species across the given phase boundary.

Since the discovery of the extraction and complexing properties of cyclic polyethers (crowns) by Pedersen, a great deal of effort has been expended on the study of these systems and a number of reviews have been published¹⁻⁴. Crowns are used especially in the extraction of heavy metals of the alkali metal and alkaline earth subgroups and can also be utilized for the extraction of lanthanoids and actinoids⁵.

In the quantitative description of these systems, it is also often necessary to know the extraction behaviour of the H^+ ion. While a great deal of work has been devoted to the determination of the values of extraction constants and stability constants of the complexes of alkali metals and alkaline earths with crowns in water and various organic solvents, far less work has been published on the complexes of H^+ ions.

Nonetheless, it was possible to prepare and isolate a compound with the composition $[\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}] [\text{Cl}-\text{H}-\text{Cl}^-]$ (ref.⁶), as well as the associate species $\text{H}_3\text{O}^+ \cdot 18\text{-crown-6}$ with the PF_6^- , ClO_4^- , BF_4^- and I^- anions (see ref.⁷). Analogous compounds were also prepared from substituted crowns (e.g. ref.⁷). The extraction behaviour of the protonated crowns has been studied in systems of aqueous solutions of acids and dichloroethane^{8,9}, chloroform¹⁰, and dodecane¹¹ as organic solvents. In accordance with the fact that these solvents have low polarity, the authors found ion associates of the type $\text{H}^+\text{-crown} \cdot \text{X}^-$ in the organic phase, where X^- is an inorganic ion.

The values of the protonation constants of some crowns in chloroform¹² and 1,2-dichloroethane¹³ were determined by Shchori, Nae and Jagur-Grodzinski on the basis of conductometric and spectrophotometric measurements. Makrlík et al.¹⁴ determined the protonation constant value for 18-crown-6 in nitrobenzene by the cyclic voltammetry method ($\log K(\text{HL}_{\text{org}}^+) = 5.9$), but did not consider the possible formation of HL^+ species in the aqueous phase.

In previous works^{15,16} we determined the value of the protonation constant of linear polyethers and poly(ethylene glycols) from the distribution of the Ba^{2+} and Sr^{2+} ions in systems consisting of an aqueous solution of a mineral acid and solution of Co(III)-dicarbolide in nitrobenzene in the presence of the test ligand. However, this procedure does not yield results that are even of the correct order of magnitude when the product of the given protonation constant and distribution constant of the ligand in the water-nitrobenzene system (hereafter K_D) is so large that, at ligand concentrations below the concentration of Co(III)-dicarbolide, practically all the ligand passes into the organic phase. This situation occurs in systems containing 18-crown-6 (refs^{17,18}).

In contrast, the high value of the extraction constant of the H^+ -18-crown-6 species ($K_{\text{ex}}(\text{HL}^+) = K_D K(\text{HL}_{\text{org}}^+)$) permits its value to be determined from the distribution of a strong mineral acid in the presence and absence of the ligand. Perchloric acid seems most suitable because of its complete dissociation and the relatively high hydrophobicity of the perchlorate anion¹⁹.

This work was carried out to study the extraction of perchloric acid by itself and in the presence of 18-crown-6 in the water-nitrobenzene system, and to determine the values of the corresponding extraction constants and protonation constants of 18-crown-6 in water and nitrobenzene, and then to employ these values to calculate the values of the individual extraction constants of the HL^+ species and magnitude of the free enthalpy for the transfer of these species across the water-nitrobenzene phase boundary.

EXPERIMENTAL

Chemicals

18-crown-6 (Fluka, Switzerland) was >98% pure. The purity was checked by the mass spectrometric method in the Central Laboratories of the Prague Institute of Chemical Technology. Because of its high hygroscopicity, crown was dried in a desiccator over P_2O_5 prior to weighing. The remaining chemicals were of p.a. purity from Lachema Brno.

Procedure

The extraction was carried out by shaking the water and organic phases (7 ml water + 7 ml organic phase in systems not containing crown, or 3 + 3 ml for systems containing crown) in ground-glass bottles (or test-tubes) with polyethylene stoppers. The time of contact of the phase was selected as 1 h on the basis of

preliminary experiments; this is sufficiently long for attainment of equilibrium. The phases were separated by centrifuging (2 000 r. p. m.).

The concentration of perchloric acid in the aqueous phase was determined by titration with carbonate-free sodium hydroxide using bromocresol green as an indicator. The concentration of acid in the nitrobenzene phase was determined by two-phase potentiometric titration with carbonate-free sodium hydroxide in a nitrogen atmosphere using the RTS-822 titrator (Radiometer, Denmark). Preliminary experiments indicated that $2 \cdot 10^{-5}$ mmol of acid can still be determined under these conditions.

The pH values were determined using a combined OP-0808 P electrode (Radelkis, Hungary) in combination with a Radelkis OP 211 pH meter. The electrode was calibrated using two buffers (pH 2.12 and 7.01).

All the experiments were carried out at a temperature of 23 °C.

RESULTS AND DISCUSSION

A study was made of the extraction of perchloric acid into nitrobenzene from aqueous solutions with a concentration of $c_{\text{HClO}_4} = 0.593 - 7.086 \text{ mol l}^{-1}$. The dependence of $\log c_{\text{HClO}_4, \text{org}}$ on $\log a_{\text{HClO}_4, \text{aq}}$, where a denotes the activity, is given in Table I, together with some literature data²¹. Activity coefficients needed for $a_{\text{HClO}_4, \text{aq}}$ calculation have been taken from ref.²⁰.

In the extraction of perchloric acid in the presence of 18-crown-6, the dependence of the concentration of perchloric acid in the organic phase on the concentration in the aqueous phase ($c_{\text{HClO}_4, \text{aq}} = 0.06 - 1.1 \text{ mol l}^{-1}$) was measured for a total concentration of crown in the system, related to one phase, of $c_L = 0.010 \text{ mol l}^{-1}$ and the dependence of the extraction of perchloric acid on the crown concentration ($c_L = 0.003 - 0.100 \text{ mol l}^{-1}$) was found for a concentration of acid in the aqueous phase of $c_{\text{HClO}_4, \text{aq}} = 0.10$ and 1.0 mol l^{-1} . The results are given in Table II.

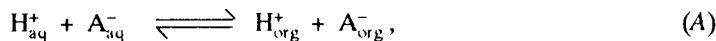
TABLE I
Dependence of $\log c_{\text{HClO}_4, \text{org}}$ on $\log a_{\text{HClO}_4, \text{aq}}$ for the extraction of perchloric acid from water into nitrobenzene

$\log a_{\text{HClO}_4, \text{aq}}$	$\log c_{\text{HClO}_4, \text{org}}$	$\log a_{\text{HClO}_4, \text{aq}}$	$\log c_{\text{HClO}_4, \text{org}}$
-0.336	-4.403	1.253	-2.630
-0.253	-3.955	1.411	-2.589
-0.251	-4.039	1.579	-2.523 ^a
0.018	-3.741	1.624	-2.406
0.019	-3.878	1.898	-2.258
0.021	-3.717	2.026	-2.143 ^a
0.436	-3.194	2.414	-1.930
0.501	-3.228	2.508	-1.796 ^a
0.863	-3.000	2.767	-1.678 ^a
0.958	-2.902	3.027	-1.523 ^a
1.166	-2.854 ^a	3.306	-1.387

^a Ref.²¹.

The dependence of the change in the acidity of the aqueous phase on the concentration of crown ($c_L = 0.01 - 0.10 \text{ mol l}^{-1}$) was measured for two concentrations of perchloric acid, 0.003 and 0.01 mol l^{-1} . The results are given in Table III.

The extraction of a strong acid, e.g. perchloric acid, (hereafter HA) from aqueous solution into nitrobenzene, assuming complete dissociation in the organic phase, which is true at least for low concentrations of the extracted component¹⁰, can be described by the equation



whose equilibrium constant can be expressed as

$$K_{\text{ex. 0}} = \{\text{H}_{\text{org}}^+\} \{\text{A}_{\text{org}}^-\} / \{\text{H}_{\text{aq}}^+\} \{\text{A}_{\text{aq}}^-\}, \quad (I)$$

where { } denotes the activity of the given species.

If the concentration of acid in the organic phase is low, then the activities can be approximated by the concentrations, so that Eq. (I) becomes

$$K_{\text{ex. 0}} = [\text{H}_{\text{org}}^+] [\text{A}_{\text{org}}^-] / [\text{H}_{\text{aq}}^+] [\text{A}_{\text{aq}}^-]. \quad (2)$$

In the presence of a neutral ligand (hereafter L), e.g. crown, the protonated species HL_n^+ is extracted according to the equation

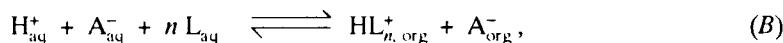


TABLE II

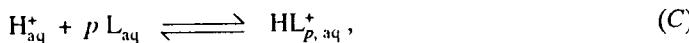
Extraction of perchloric acid from water into nitrobenzene in the presence of 18-crown-6

$c_{\text{HClO}_4, \text{aq}}$ mol l^{-1}	γ_{\pm}	c_L mol l^{-1}	$c_{\text{HClO}_4, \text{org}}$ mol l^{-1}
0.0658	0.870	0.010	0.00180
0.117	0.799	0.030	0.00418
0.120	0.798	0.003	0.00136
0.121	0.798	0.100	0.00861
0.122	0.797	0.010	0.00245
0.225	0.775	0.010	0.00341
0.689	0.786	0.010	0.00599
0.776	0.798	0.010	0.00635
1.054	0.845	0.030	0.0165
1.069	0.848	0.003	0.00240
1.073	0.849	0.010	0.00692

where

$$K_{\text{ex}, n} = [\text{HL}_{n, \text{org}}^+] [\text{A}_{\text{org}}^-] / \{\text{H}_{\text{aq}}^+\} \{\text{A}_{\text{aq}}^-\} [\text{L}_{\text{aq}}]^n. \quad (3)$$

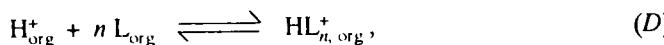
In addition to reaction (B), protonated species can also be formed in the aqueous phase



where

$$K(\text{HL}_{p, \text{aq}}) = \{\text{HL}_{p, \text{aq}}^+\} / \{\text{H}_{\text{aq}}^+\} [\text{L}_{\text{aq}}]^p. \quad (4)$$

An analogous equilibrium is present in the organic phase



where

$$K(\text{HL}_{n, \text{org}}) = [\text{HL}_{n, \text{org}}^+] / [\text{H}_{\text{org}}^+] [\text{L}_{\text{org}}]^n. \quad (5)$$

Assuming complete dissociation of the extracted perchloric acid in both the aqueous and organic phases, then it holds for the system not containing crown that

$$[\text{H}_{\text{org}}^+] = [\text{ClO}_4^-] = c_{\text{HClO}_4, \text{org}} \quad (6)$$

$$[\text{H}_{\text{aq}}^+] = [\text{ClO}_4^-] = c_{\text{HClO}_4, \text{aq}} \quad (7)$$

TABLE III
Dependence of the pH of aqueous solutions of perchloric acid on the concentration of 18-crown-6

c_{HClO_4} mol l ⁻¹	c_{L} mol l ⁻¹	pH	$\log K(\text{HL}_{\text{aq}})$
0.003	—	2.53	—
0.003	0.0101	2.55	0.67
0.003	0.0101	2.56	0.86
0.003	0.0500	2.64	0.77
0.003	0.100	2.62	0.36
0.010	—	1.90	—
0.010	0.0500	2.04	0.91
0.010	0.100	2.12	0.84

and also

$$\{H_{\text{aq}}^+\} \{ClO_4^-_{\text{aq}}\} = \gamma_{\pm}^2 c_{HClO_4 \text{org}}^2 = a_{HClO_4 \text{aq}}^2, \quad (8)$$

where symbol γ_{\pm} denotes the mean activity coefficient of perchloric acid in water and a_{HClO_4} is the corresponding activity.

Substitution into Eq. (2) yields

$$K_{\text{ex},0} = c_{HClO_4 \text{org}}^2 / a_{HClO_4 \text{aq}}^2, \quad (9)$$

which, on taking logarithms and rearrangement, yields

$$\log c_{HClO_4 \text{org}} = \frac{1}{2} \log K_{\text{ex},0} + \log a_{HClO_4 \text{aq}}. \quad (10)$$

The dependence of $\log c_{HClO_4 \text{org}}$ on $\log a_{HClO_4 \text{aq}}$ is a straight line with a slope of unity and intercept on the y-axis equal to $0.5 K_{\text{ex},0}$. Linear regression analysis of the data in Table I yielded the slope value $\text{tg} \gamma = 0.75$, standard deviation $s(\text{tg} \gamma) = 0.02$ and intercept on the y-axis = -3.711 ($s = 0.034$). The deviation of the slope from the theoretical value of 1.0 can be at least partly attributed²¹ to the decrease in the water activity in the aqueous phase with increasing acid concentrations. When the calculation was carried out using only acid values below 2.0 mol l⁻¹, then the slope value approached unity with no substantial change in the intercept on the y-axis. The scatter of the values of the slope and intercept on the y-axis was, however, greater.

The final value $\log K_{\text{ex},0} = -7.42 \pm 0.2$, where the error is given²² as three times the standard deviation. If constant $K_{\text{ex},0}$ is calculated from the values of the individual extraction constants of the H^+ and ClO_4^- ions in the water-nitrobenzene system, published by Rais¹⁹, i.e. $\log K_i(H^+) = -5.7$ and $\log K_i(ClO_4^-) = -1.4$, then it follows that

$$\log K_{\text{ex},0} = \log K_i(H^+) + \log K_i(ClO_4^-) = -7.1. \quad (11)$$

This is relatively good agreement, considering that these values were measured in systems containing various ions.

In the mathematical description of the extraction of perchloric acid into nitrobenzene in the presence of crown, it is necessary to consider not only Eqs (B) and (C), but also the distribution of 18-crown-6 between water and nitrobenzene, i.e. the reaction



whose distribution constant $K_D = 0.1$ is given in the literature².

Assuming that the extraction of perchloric acid as H_{org}^+ species is negligible, which is true here, then the $K_{\text{ex},1}$ value can be calculated to a first approximation by numerical substitution into Eq. (3). In addition to this equation, however, it is also necessary to consider the electroneutrality condition for both phases

$$[\text{A}_{\text{aq}}^-] = [\text{H}_{\text{aq}}^+] + [\text{HL}_{\text{aq}}^+] = c_{\text{HClO}_4 \text{ aq}} \quad (12)$$

$$[\text{HL}_{\text{org}}^+] = [\text{A}_{\text{org}}^-] = c_{\text{HClO}_4 \text{ org}} \quad (13)$$

together with the mass balance for 18-crown-6,

$$c_L = [\text{L}_{\text{aq}}] + [\text{L}_{\text{org}}] + [\text{HL}_{\text{aq}}^+] + [\text{HL}_{\text{org}}^+] \quad (14)$$

After substitution, Eq. (14) becomes

$$c_L = [\text{L}_{\text{aq}}] (1 + K_D) + c_{\text{HClO}_4 \text{ org}} + K (\text{HL}_{\text{aq}}) [\text{L}_{\text{aq}}] [\text{H}_{\text{aq}}^+] \quad (15)$$

and Eq. (12) becomes

$$c_{\text{HClO}_4 \text{ aq}} = [\text{H}_{\text{aq}}^+] + K (\text{HL}_{\text{aq}}) [\text{L}_{\text{aq}}] [\text{H}_{\text{aq}}^+] \quad (16)$$

It is justifiable to replace the activities by the concentrations in Eq. (4) if the activity coefficients are at least approximately equal, i.e. $\gamma(\text{H}_{\text{aq}}^+) = \gamma(\text{HL}_{\text{aq}}^+)$, which is a reasonable assumption in the investigated region; in addition, the value of the equilibrium constant $K (\text{HL}_{\text{aq}})$ employed was determined under the same assumptions (see below), so that any deviations would partly compensate one another.

If $K_{\text{ex},1}$ was calculated assuming that protonated species HL_{aq}^+ are not formed in the aqueous phase, then the scatter in the calculated values was approximately one order of magnitude. If, on the other hand, it was assumed that all the crown in the aqueous phase is converted to HL_{aq}^+ species, then a significant dependence of the calculated constant values $K_{\text{ex},1}$ on the acidity was found. On the other hand, if the calculation was carried out using the value $K (\text{HL}_{\text{aq}}) = 5.83$, measured potentiometrically (see below), then the calculated value of constant $K_{\text{ex},1}$ is truly independent of the crown concentration and of the acidity. The calculated value $K_{\text{ex},1} = 0.138$, with a standard deviation of $s(K_{\text{ex},1}) = 0.034$.

The protonation constant of 18-crown-6 in water was found by measuring the dependence of the pH of aqueous solutions of perchloric acid ($c_{\text{HClO}_4} = 0.003$ and 0.01 mol l^{-1}) on the concentration of added 18-crown-6 ($c_L = 0.01 - 0.10 \text{ mol l}^{-1}$) – see Table III.

It follows from the definition of the pH that

$$\text{pH} = -\log (\gamma(\text{H}_{\text{aq}}^+) [\text{H}_{\text{aq}}^+]) \quad (17)$$

It then holds for the protonation constant of 18-crown-6 in water that

$$K (\text{HL}_{\text{aq}}) = \gamma(\text{HL}_{\text{aq}}^+) [\text{HL}_{\text{aq}}^+]/\gamma(\text{H}_{\text{aq}}^+) [\text{H}_{\text{aq}}^+] [\text{L}_{\text{aq}}] \quad (18)$$

which, assuming at least approximate equality of the activity coefficients $\gamma(\text{HL}_{\text{aq}}^+)$ and $\gamma(\text{H}_{\text{aq}}^+)$ yields

$$K(\text{HL}_{\text{aq}}) = [\text{HL}_{\text{aq}}^+]/[\text{H}_{\text{aq}}^+] [\text{L}_{\text{aq}}]. \quad (19)$$

If the acidity of a perchloric acid solution of a given concentration is denoted as pH_0 , then

$$\text{pH}_0 = -\log(\gamma(\text{H}_{\text{aq}}^+) c_{\text{HClO}_4\text{,aq}}). \quad (20)$$

If it is assumed that the $\gamma(\text{H}_{\text{aq}}^+)$ value does not change much after addition of crown, then it follows that

$$\log[\text{H}_{\text{aq}}^+] - \log c_{\text{HClO}_4} = \text{pH}_0 - \text{pH} \quad (21)$$

and introduction of $\Delta\text{pH} = \text{pH}_0 - \text{pH}$, then

$$[\text{H}_{\text{aq}}^+] = c_{\text{HClO}_4\text{,aq}} \cdot 10^{\Delta\text{pH}}. \quad (22)$$

It follows for the mass balance of perchloric acid and crown that

$$[\text{H}_{\text{aq}}^+] + [\text{HL}_{\text{aq}}^+] = c_{\text{HClO}_4\text{,aq}} \quad (23)$$

$$[\text{L}_{\text{aq}}] + [\text{HL}_{\text{aq}}^+] = c_{\text{L}} \quad (24)$$

and, after rearrangement,

$$[\text{HL}_{\text{aq}}^+] = c_{\text{HClO}_4\text{,aq}} (1 - 10^{\Delta\text{pH}}) \quad (25)$$

$$[\text{L}_{\text{aq}}] = c_{\text{L}} - c_{\text{HClO}_4\text{,aq}} (1 - 10^{\Delta\text{pH}}). \quad (26)$$

Substitution into Eq. (18) yields the relationship for the $K(\text{HL}_{\text{aq}})$ value:

$$K(\text{HL}_{\text{aq}}) = (1 - 10^{\Delta\text{pH}})/10^{\Delta\text{pH}} \{c_{\text{L}} - c_{\text{HClO}_4\text{,aq}} (1 - 10^{\Delta\text{pH}})\}. \quad (27)$$

This calculation method has the advantage that it eliminates any possible error resulting from the calibration of the glass electrode, as the only condition here is a linear dependence of the potential on the logarithm of the concentration of hydrogen ions which, taking into consideration the calibration method using two buffers, need not even have the theoretical value 2.303 RT/F .

The calculated value is then $K(\text{HL}_{\text{aq}}) = 5.83$, with standard deviation $s(K(\text{HL}_{\text{aq}})) = 2.1$.

In general form, the equilibrium in the extraction system can be described by Eqs (A), (B), (C) and (E) together with the extraction of the protonated crown as an associate with the acid anion, i.e. the reaction



where

$$K_{\text{ex}, m}^{\text{as}} = [\text{HL}_m \text{A}_{\text{org}}] / \{\text{H}_{\text{aq}}^+\} \{\text{A}_{\text{aq}}^-\} [\text{L}_{\text{aq}}]^m, \quad (28)$$

so that it holds that

$$c_{\text{L}} = [\text{L}_{\text{aq}}] + [\text{L}_{\text{org}}] + \sum_1^N n K_{\text{ex}, n} \{\text{H}_{\text{aq}}^+\} \{\text{A}_{\text{aq}}^-\} [\text{L}_{\text{aq}}]^n / [\text{A}_{\text{org}}] + \\ + \sum_1^M m K_{\text{ex}, m}^{\text{as}} \{\text{H}_{\text{aq}}^+\} \{\text{A}_{\text{aq}}^-\} [\text{L}_{\text{aq}}]^m + \sum_1^P p K (\text{HL}_{p, \text{aq}}) \{\text{H}_{\text{aq}}^+\} [\text{L}_{\text{aq}}]^p \quad (29)$$

$$[\text{A}_{\text{org}}^-] = \sum_0^N [\text{HL}_{n, \text{org}}^+] \quad (30)$$

$$[\text{A}_{\text{org}}^-] = \sum_0^N K_{\text{ex}, n} \{\text{H}_{\text{aq}}^+\} \{\text{A}_{\text{aq}}^-\} [\text{L}_{\text{aq}}]^n / [\text{A}_{\text{org}}^-] \quad (31)$$

$$[\text{A}_{\text{org}}^-] = \left(\sum_0^N K_{\text{ex}, n} \{\text{H}_{\text{aq}}^+\} \{\text{A}_{\text{aq}}^-\} [\text{L}_{\text{aq}}]^n \right)^{0.5} \quad (32)$$

Assuming at least approximate equality of the activity coefficients $\gamma(\text{H}_{\text{aq}}^+)$ and $\gamma(\text{HL}_{p, \text{aq}}^+)$, Eq. (5) becomes

$$K (\text{HL}_p) = [\text{HL}_p^+] / [\text{H}_{\text{aq}}^+] [\text{L}_{\text{aq}}]^p, \quad (33)$$

so that it follows from

$$c_{\text{HA, aq}} = c_{\text{A, aq}} = c_{\text{H, aq}} = [\text{H}_{\text{aq}}^+] + \sum_1^P [\text{HL}_{p, \text{aq}}^+] \quad (34)$$

that

$$[\text{H}_{\text{aq}}^+] = c_{\text{A, aq}} / (1 + \sum_1^P K (\text{HL}_{p, \text{aq}}) [\text{L}_{\text{aq}}]^p) \quad (35)$$

because

$$\{H_{aq}^+\} \{A_{aq}^-\} = a_{H\Lambda, aq}^2 = [H_{aq}^+] c_{\Lambda, aq} \gamma_x^2 \quad (36)$$

is the concentration of extracted acid in the organic phase,

$$c_{H\Lambda, org} = a_{H\Lambda, aq}^2 \left(\sum_0^N K_{ex, n} [L_{aq}]^n / [A_{org}] + \sum_0^M K_{ex, m}^a [L_{aq}]^m \right). \quad (37)$$

On the basis of these relationships, a special block "UBBE" was set up for general least squares minimizing in the LETAGROP program²²⁻²⁴. The sum of the squares of the relative deviations of the calculated and experimental concentrations of extracted acid in the organic phase was minimized so that

$$U = \sum \{(c_{HClO_4, org}^{\text{exp}} - c_{HClO_4, org}^{\text{calc}}) / c_{HClO_4, org}^{\text{calc}}\}^2, \quad (38)$$

where indices exp and calc refer to the experimental values of the concentration of extracted acid in the organic phase and those calculated on the basis of the minimized constants.

The results are given in Table IV. It can be seen from the table that the simplest model including the presence of the species H_{aq}^+ , HL_{aq}^+ , H_{org}^+ and HL_{org}^+ describes the experimental data with sufficient precision. The addition of the species $HL_{2, aq}^+$, $HL_{2, org}^+$ and $HL\Lambda_{org}$ to the model did not lead to any substantial decrease in the value of function U or to any decrease in the value of the standard deviation σ defined as $\sigma = \{U/(n - N)\}^{0.5}$, where n is the number of experimental values and N is the number of unknown equilibrium constants determined in the calculation. It seems that, as the concentration of the extracted acid increases in the organic phase, there is an increase in the association of species HL_{org}^+ and A_{org}^- to form the uncharged associate $HL\Lambda_{org}$; however, in contrast to the HL_{org}^+ and HL_{aq}^+ species, the existence of this associate cannot be considered as proven as a consequence of the fact that other effects may occur at higher acid concentrations in the organic phase, e.g. a change in the activity coefficient values in nitrobenzene. Considering that the protonated crown is present in the organic phase only as the associate leads to a greater deterioration in the agreement between the experimental and theoretical values of $c_{H\Lambda, org}$ than when complete dissociation is assumed. The participation of hydrated H_{org}^+ ions in the overall acidity of the organic phase is practically negligible in the studied concentration interval. Thus, it can be concluded that, in the given concentration range, the organic phase contains practically only one positively charged species, protonated crown HL_{org}^+ apparently in the hydrated form. The agreement between the values of the protonation constants of 18-crown-6 in water, determined independently by potentiometric measurement, $\log K(HL_{aq}) = 0.765$, and calculation by the LETAGROP program from the extraction data, $\log K(HL_{aq}) = 0.88$,

TABLE IV
Comparison of various models for the extraction of perchloric acid into nitrobenzene in the presence of 18-crown-6

Model	Equilibrium constants ^a			U	σ
	$\log K(\text{HL}_{\text{aq}})$	$\log K(\text{HL}_{2\text{-aq}})$	$\log K_{\text{ex.} 1}$		
$\text{HL}_{\text{aq}}^+ \text{HL}_{\text{org}}^+$	0.765 ^b	—	-0.773 ± 0.07	—	0.06191
$\text{HL}_{\text{aq}}^+ \text{HLA}_{\text{org}}$	0.765 ^b	—	—	1.922(2.158)	1.5478
$\text{HL}_{\text{aq}}^+ \text{HL}_{\text{org}}^+$	0.880(1.149)	-0.714 ± 0.22	—	—	0.03521
$\text{HL}_{\text{aq}}^+ \text{HLA}_{\text{org}}$	2.055(3.161)	—	—	2.785(3.863)	1.2810
$\text{HL}_{\text{aq}}^+ \text{HL}_{\text{org}}$	0.861(1.142)	-0.732 ± 0.24	-0.511(0.332)	—	0.03407
$\text{HL}_{\text{aq}}^+ \text{HL}_{\text{org}}^+ \text{HL}_{2\text{-org}}$	0.984(1.307)	-0.695(0.250)	—	0.298(0.947)	0.03136
$\text{HL}_{\text{aq}}^+ \text{HL}_{\text{org}}^+ \text{HL}_{2\text{-aq}}^+ \text{HL}_{2\text{-org}}$	0.844(1.184)	2.243(3.365)	-0.727(-0.506)	0.610(1.692)	0.03389
			—	—	0.06862

^a The error in the constant is given as three times the standard deviation²² and is converted to the logarithmic scale using the approximate relationship $\log K \pm \{ \log (K + 1.5s(K)) - \log (K - 1.5s(K)) \}$, where $s(K)$ is the standard deviation of constant K . For $s(K) > 0.2 K$, where this relationship is not longer valid, only the upper limit is given in parenthesis in the form $\log K(\log (K + 3s(K))$; ^b calculation carried out for $\log K(\text{HL}_{\text{aq}}) = 0.765$ measured potentiometrically – see Table III; ^c reaction (F), Eq. (28).

can be considered very good for these two very different methods. This agreement indicates the correctness of the selected model.

If values $K_{\text{ex},0}$, $K_{\text{ex},1}$, $K(\text{HL}_{\text{aq}})$ and K_D are known, then the magnitude of the protonation constant of 18-crown-6 in nitrobenzene $K(\text{HL}_{\text{org}})$ can be calculated using the formula

$$K(\text{HL}_{\text{org}}) = K_{\text{ex},1} / K_{\text{ex},0} K_D, \quad (39)$$

where $\log K(\text{HL}_{\text{org}}) = 7.71$ (LETAGROP) or $\log K(\text{HL}_{\text{org}}) = 7.56$ (combination of independent potentiometric determination of the $K(\text{HL}_{\text{aq}})$ and numerical calculation of $K_{\text{ex},1}$).

Knowledge of the individual extraction constants of the H^+ ion in the given system $\log K_i(\text{H}^+) = -5.7$, see ref.¹⁹, permits determination of the individual extraction constants of species HL^+ , where

$$\log K_i(\text{HL}^+) = \log K_i(\text{H}^+) + \log K(\text{HL}_{\text{org}}) - \log K(\text{HL}_{\text{aq}}) + \log K_D \quad (40)$$

yielding $\log K_i(\text{HL}^+) = 0.126$ (LETAGROP) or $\log K_i(\text{HL}^+) = 0.098$.

As the molar free enthalpy for transfer across the water–nitrobenzene phase boundary is given by the relationship²⁵

$$\Delta G_{\text{tr}}^0 = -RT \ln K_i \quad (41)$$

then the magnitude of $\Delta G_{\text{tr}}^0(\text{HL}^+)$ can be calculated and was found to be $\Delta G_{\text{tr}}^0(\text{HL}^+) = -714 \text{ J mol}^{-1}$ (LETAGROP) or $\Delta G_{\text{tr}}^0(\text{HL}^+) = -556 \text{ J mol}^{-1}$ at 296 K.

As the difference in the standard galvanic potentials between water and nitrobenzene is given by the relationship²⁶

$$\text{org}_{\text{aq}} \varphi^0 = -\Delta G_{\text{tr}}^0 / F, \quad (42)$$

where F is the Faraday constant, then the measured data can also be used to calculate this value $\text{org}_{\text{aq}} \varphi^0 = 7.4 \text{ mV}$ (LETAGROP) or 5.8 mV (combination of potentiometric and extraction data).

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