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# Advantage of the medium factor in relation to the ionic strength

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Studies on metal ion hydrolysis indicated that the supporting electrolytes are not inert and that the effect of the ionic medium on chemical reactions is not negligible. The effect might be determined by the linear free energy relationship that correlates the equilibrium constants with properties of the ionic medium. Data on metal ion hydrolysis show that the medium factor, as a characteristic of the medium, reflects much better the properties of the supporting electrolyte than does the ionic strength. Literature data concerning dissociation of acetic acid and the heat of dissociation of water confirm the advantage of the medium factor.

## Introduction

In investigations of chemical reactions in solutions the activity coefficients of the reacting species have been kept constant by using a constant ionic strength $I_s$ or a constant concentration of the ionic medium $I_{CA}$. The latter mostly involves a constant concentration of an anion of the medium $I_A$, although in some cases the concentration of the medium cation $I_C$ was kept constant. It was expected that the presence of the ions of the supporting electrolyte would not influence the principal chemical reaction. However, a number of works[1] have shown that data obtained at the same ionic strength adjusted by various electrolytes differ, indicating that the supporting electrolytes are not inert and that the effect of the ionic medium on chemical reaction is not negligible. This fact indicates that the constant ionic strength principle, as well as the constant ionic medium principle, does not reflect interactions between the supporting electrolyte and reactants.

The expression for the constant ionic strength principle ($I_s = \frac{1}{2}\Sigma c_i z_i^2$) contains two parameters: the concentration and charge of the ions of the reacting species and supporting electrolyte. The expression for the constant ionic medium principle [$I_{CA} = c_{CA}$ or $I_A = (c_C)c_A$ or $I_C = c_C(c_A)$] contains only one parameter, the concentration of the supporting electrolyte, which may include the concentration of an anion of the reactant (the concentration of the ion given in parentheses is a little lower than that of the non-bracketed ion and might be slightly changeable). It is unreasonable to expect that these two parameters (concentration and the charge) would be sufficient to express the properties of the supporting electrolytes and interactions of their ions with reacting species and solvent molecules. Therefore it is necessary to find some additional parameters that might reflect the properties of the medium ions a little better than the ionic strength.

First, the ionic strength does not reflect hydration of the ions of the supporting electrolyte in spite of the fact that this can not be neglected in investigations of chemical reactions in water solutions. Since the hydration of ions of various electrolytes is different the concentration of the free water molecules is not the same at the same ionic strength adjusted by various electrolytes. As a consequence, the extents of reactions in which water is a reactant (hydrolysis, dissociation, anation) should not be the same. As a parameter which determines hydration one can use the hydration energy because there are accurate data for almost all cations and many anions.[2] By including the hydration energy in the ionic strength expression or other similar expression one might expect better to describe the properties of the medium. The expression for the ionic strength also does not include parameters that reflect the effect of complex formation of the metal ion (as reactant) with an anion of the medium. In reactions of the transition metals this effect might be significant. Thus, one can expect that increasing the complexation ability of the medium anion should lead to stronger interaction between the metal ion and the medium anion and consequently the extent of the studied reaction might decrease. However, for this kind of interaction we have no suitable parameter. Therefore it is necessary to use several of them: size and charge of the medium anion, the electronegativity of the donor atom, *etc.* The interaction between the metal ion and the medium cation is less pronounced and probably can be neglected.

Although the ionic strength includes the charge of the medium ions, as well as that of the reactant ions, it does not differentiate between the sign of the charge of the medium cation and anion in spite of the fact that different electrostatic interactions occur between the metal ion (as reactant) and the medium cation and anion. Therefore, it is useful to check the contribution of these interactions to the extent of reaction.

In order to investigate the effect of the mentioned parameters thorium(IV) ion was chosen as model ion and its hydrolysis (eqn. 1) was studied in various ionic media[3–7] because the

$$p\,\mathrm{Th}^{4+} + q\,\mathrm{H_2O} \rightleftharpoons \mathrm{Th}_p(\mathrm{OH})_q^{(4p-q)+} + q\,\mathrm{H}^+ \quad (1)$$

water molecules are reactants and one could expect a medium effect.

## Experimental

Investigations of metal ion hydrolysis are very complex due to the formation of polynuclear species. Therefore all the present experiments (potentiometric and potentiometric–coulometric) were carried out very carefully:[3–7] (a) chemicals were analytical grade and the most additionally purified by recrystallisation; (b) all experiments were carried out in a thermostatted room 25.0 ± 0.5 °C and thermostatted bath at 25.00 ± 0.02 °C; (c) titrations were carried out in an inert (nitrogen) atmosphere with additional purification of nitrogen; (d) the establishment of the equilibrium was achieved by leaving the system overnight or by drawing the dependence $\Delta E = f(\text{time})$; (e) in order to check the reversibility of the hydrolytic reactions, a lot of forward titrations were followed by back titrations; (f) in order to determine the concentration of the free acid and $E_0$ of the glass electrode with high accuracy, the computer program GEZ was developed enabling automatic control of these parameters.[8]

## Results and discussion

The obtained data show that the ionic medium is not inert and that the medium effect could not be neglected. Even more, as a result of these studies the linear free energy relationship[5,9] (2)

$$\log K_\mathrm{w} - \log K_\mathrm{m} - \chi\eta \qquad (2)$$

was established which correlates the equilibrium constants (or the hydrolysis extent) with properties of the ionic medium. $K_\mathrm{w}$ and $K_\mathrm{m}$ denote equilibrium constants of the hydrolytic reaction in pure water and in the presence of an ionic medium, respectively. The medium factor (or the medium constant) $\chi$ [eqn. (3)] is

$$\chi = c_{(\mathrm{a})}E_{\mathrm{h(a)}}z_{(\mathrm{a})} + c_{(\mathrm{c})}E_{\mathrm{h(c)}}z_{(\mathrm{c})}{}^{-1} \qquad (3)$$

a characteristic of the medium reflecting the interactions of the medium ions with water molecules, whereas the complex formation factor $\eta$ [eqn. (4)] is determined by the reaction of

$$\eta = c_{(\mathrm{a})}z_{(\mathrm{a})}/r_{(\mathrm{a})}\varepsilon_\mathrm{DA} \qquad (4)$$

the metal ions with the medium anion. In eqns. (3) and (4) $c$ denotes concentration, $E_\mathrm{h}$ the hydration energy, $z$ the charge of the medium anion (a) and cation (c), $r_{(\mathrm{a})}$ the radius of the donor atom and $\varepsilon_\mathrm{DA}$ the electronegativity of the donor atom.

Since the hydrolytic reactions are accompanied by interaction of the medium ions with water molecules (expressed by $\chi$) and of the medium anion with the metal ion (expressed by $\eta$), the metal ion hydrolysis (1) should be considered as a complex reaction (5) which includes both side reactions: the hydration ($\chi$) and complex formation ($\eta$). Upon hydrolysis of the thorium(IV) ion, as well of the other metal ions, polynuclear complexes of various composition are formed. The composition depends on the nature and concentration of the metal ion, as well as on the nature and concentration of the ionic medium. In addition the main complex of the thorium(IV) ion $Th_2(OH)_2{}^{6+}$ is formed in all studied media.[3–7] Therefore it is more convenient to consider the medium effect through the stability constant of the main complex $\beta_{2,2}$ than through the equilibrium constant $K_\mathrm{m}$ or the cumulative constant $\beta_{n,m}$. Thus there is a linear correlation between $\log \beta_{(2,2)\mathrm{Th}}$ and the medium factor $\chi$. However there is no correlation between $\log \beta_{(2,2)\mathrm{Th}}$ and the ionic strength $I_\mathrm{s}$ if values of $\log \beta_{(2,2)\mathrm{Th}}$ are obtained at the same ionic strength adjusted by various electrolytes. As an illustration of this, the ionic strength, the corresponding medium factor and $\log \beta_{(2,2)\mathrm{Th}}$ are given in Table 1. In addition to $Th_2(OH)_2{}^{6+}$, complexes $Th_3(OH)_5{}^{7+}$ and $Th_2(OH)_3{}^{5+}$ are formed in nitrate and chloride media, respectively. Therefore Table 1 contains also values of $\log \beta_{q,p}$ of these two complexes.

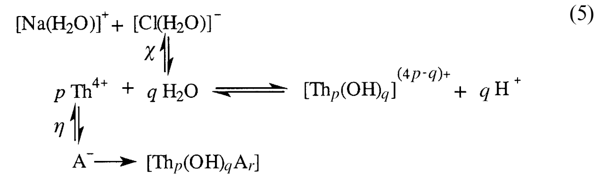
(5)

Table 1 shows that at the same ionic strength (adjusted by various electrolytes) the stability constants of the hydrolytic complexes of the thorium(IV) ion ($\log \beta_{(2,2)\mathrm{Th}}$, $\log \beta_{(5,3)\mathrm{Th}}$, $\log \beta_{(3,2)\mathrm{Th}}$) have different values. For instance, in 3.0 M (K)$NO_3$, 3.0 M (Na)$NO_3$ and 3.0 M (Li)$NO_3$ media † the ionic strength is the same ($I_\mathrm{s}$ = 3 M), but values of $\log \beta_{(2,2)\mathrm{Th,Nit}}$ (or $\log \beta_{(5,3)\mathrm{Th,Nit}}$) are not the same [Fig. 1(upper)]. In contrast representation of these data in the form $\log \beta_{(2,2)\mathrm{Th,Nit}} = f(\chi)$ shows that these $\log \beta_{(2,2)\mathrm{Th,Nit}}$ values follow linearly the values of the medium factor $\chi$ [Fig. 1(lower)]. Application of linear regression analysis to these data confirms the linearity between $\log \beta_{(2,2)\mathrm{Th,Nit}}$ and the medium factor ($R^2 = 0.92$, obtained by program MS Excel 2000). The observed correlation between $\log \beta_{(2,2)\mathrm{Th,Nit}}$ (in general $\log \beta_{q,p}$) and $\chi$ indicates the advantage of the medium factor over the ionic strength. A great number of other and literature data support this, as well as the linear free energy relationship [eqn. (2)] which contains the medium factor $\chi$. For instance, besides data obtained in nitrate media, Table 1 contains two sets of stability constants ($\log \beta_{(2,2)\mathrm{Th,Chlo}}$, $\log \beta_{(3,2)\mathrm{Th,Chlo}}$) of the hydrolytic complexes $Th_2(OH)_2{}^{6+}$ and $Th_2(OH)_3{}^{5+}$ formed in chloride media. These data also show that values of $\log \beta_{(2,2)\mathrm{Th,Chlo}}$ (or $\log \beta_{(3,2)\mathrm{Th,Chlo}}$) obtained at the same ionic strength ($I_\mathrm{s}$ = 1.5 or 4.5 M, adjusted by various chloride salts) are different indicating the absence of a correlation between the ionic strength and $\log \beta_{q,p}$ [Fig. 2 (upper) and Fig. 3 (upper), $I_\mathrm{s}$ = 1.5 M]. In contrast Fig. 2 (lower) and Fig. 3 (lower) show that all these $\log \beta_{q,p}$ values follow linearly the values of the corresponding medium factor $\chi$. (All parts of figures in this paper denoted by "upper" and "lower" represent the same system and the same $\log \beta_{q,p}$ values. The difference is only in the abscissa axis.) A similar linearity is observed for values of $\log \beta_{q,p}$ obtained at $I_\mathrm{s}$ = 4.5 M (Table 1). The correlation coefficient for $\log \beta_{(2,2)\mathrm{Th,Chlo}}$ and $\log \beta_{(3,2)\mathrm{Th,Chlo}}$ ($I_\mathrm{s}$ = 4.5 M) is 0.80 and 0.98, respectively.

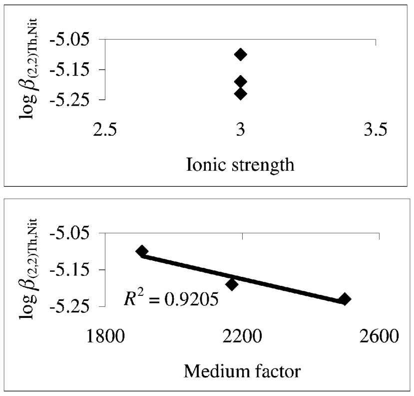

**Fig. 1** Values of $\log \beta_{(2,2)\mathrm{Th,Nit}}$ of the hydrolytic complex (2,2) of $Th^{IV}$ obtained at ionic strength 3.0 M adjusted by various nitrate salts and dependence of $\log \beta_{(2,2)\mathrm{Th,Nit}}$ on the medium factor.

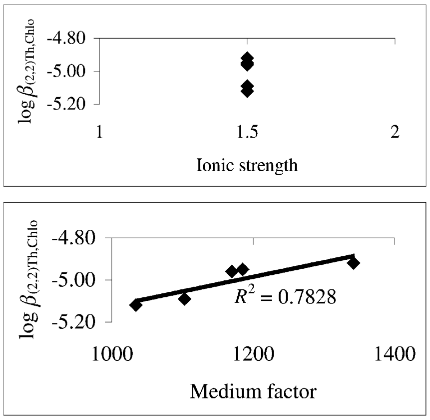

**Fig. 2** Values of $\log \beta_{(2,2)\mathrm{Th,Chlo}}$ of the hydrolytic complex (2,2) of $Th^{IV}$ obtained at ionic strength 1.5 M adjusted by various chloride salts and dependence of $\log \beta_{(2,2)\mathrm{Th,Chlo}}$ on the medium factor.

The absence of correlation between $\log \beta_{q,p}$ and the ionic strength and the excellent correlation with the medium factor might be explained by the fact that the latter contains one parameter more than the ionic strength; the hydration energy $E_\mathrm{h}$ of the medium ions. (There is one parameter more, $z_{(\mathrm{c})}{}^{-1}$,

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† M denotes mol $dm^{-3}$. The symbolism for the medium is in accordance with ref. 1: *e.g.* in the case of 3.0 M (K)$NO_3$ it means that the concentration of nitrate ion is 3.0 M, while that of $K^+$ is lower depending on the concentration of the reactant metal ion.

**Table 1** The values of the ionic strength $I_s$, the medium factor $\chi$ and the stability constant log $\beta_{q,p}$ of the hydrolytic complexes of thorium(IV) ion

| Medium | $I_s$/M | $\chi$ | log $\beta_{(2,2)\mathrm{Th,Nit}}$ | log $\beta_{(5,3)\mathrm{Th,Nit}}$ | log $\beta_{(3,2)\mathrm{Th,Nit}}$ | Ref. |
|---|---|---|---|---|---|---|
| 3.0 M (K)$NO_3$ | 3.0 | 1908 | −5.10 | — | −8.79 | 3 |
| 3.0 M (Na)$NO_3$ | 3.0 | 2169 | −5.19 | −14.23 | — | 6 |
| 3.0 M (Li)$NO_3$ | 3.0 | 2499 | −5.23[a] | −14.24 | — | 3 |
| 0.5 M (Na)$NO_3$ | 0.5 | 362 | −5.06 | −12.59 | — | 6 |
| 1.0 M (Na)$NO_3$ | 1.0 | 723 | −5.08 | −13.04 | — | 6 |
| 1.5 M (Na)$NO_3$ | 1.5 | 1084 | −5.14 | −13.30 | — | 6 |
| 2.0 M (Na)$NO_3$ | 2.0 | 1446 | −5.16 | −13.61 | — | 6 |
| 2.5 M (Na)$NO_3$ | 2.5 | 1808 | −5.18 | −13.79 | — | 6 |
| 3.0 M (Mg)$NO_3$ | 4.5 | 3824 | −5.25 | −14.26 | — | 3 |
| | | | log $\beta_{(2,2)\mathrm{Th,Chlo}}$ | | log $\beta_{(3,2)\mathrm{Th,Chlo}}$ | |
| 1.0 M (Ba)Cl | 1.5 | 1034 | −5.12 | — | −7.92 | 7 |
| 1.0 M (Sr)Cl | 1.5 | 1103 | −5.09[a] | — | −7.95 | 7 |
| 1.0 M (Ca)Cl | 1.5 | 1170 | −4.96 | — | −7.97 | 7 |
| 1.5 M (Na)Cl | 1.5 | 1185 | −4.95 | — | −8.01 | 5 |
| 1.0 M (Mg)Cl | 1.5 | 1342 | −4.92[a] | — | −7.91 | 7 |
| 3.0 M (Ba)Cl | 4.5 | 3101 | −4.96 | — | −8.50 | 7 |
| 3.0 M (Sr)Cl | 4.5 | 3308 | −4.97 | — | −8.52 | 7 |
| 3.0 M (Ca)Cl | 4.5 | 3509 | −4.92 | — | −8.53 | 7 |
| 3.0 M (Mg)Cl | 4.5 | 4025 | −4.90 | — | −8.56 | 7 |

[a] Recalculated value using the computer program GEZ[8] for calculation of the concentration of the free acid and $E_0$ of the glass electrode because values given in corresponding references deviate from the straight lines. In calculation of the ionic strength given the contribution of the metal ion (which hydrolyses) is not included because (a) most stability constants are calculated using data which cover a wide concentration range of the studied metal ion (the concentration of the medium anion was kept constant during all titrations, while that of the thorium(IV) ion was kept constant only during each titration) and (b) the metal ion concentration was much lower than that of the ionic medium and its contribution to the ionic strength is rather small, particularly at high concentration of medium ions. As a consequence some values of the ionic strength are a little lower than experimental ones. For instance, at 3.0 M (Na)$NO_3$ instead of $I_s = 3$, it should say 3.06 M because in these experiments the concentration of thorium(IV) ion was 10 mM, and the concentration of the medium cation, $Na^+$, was 2960 mM (instead of 3000 mM) and that of the medium anion, $NO_3^-$, was 3000 mM.

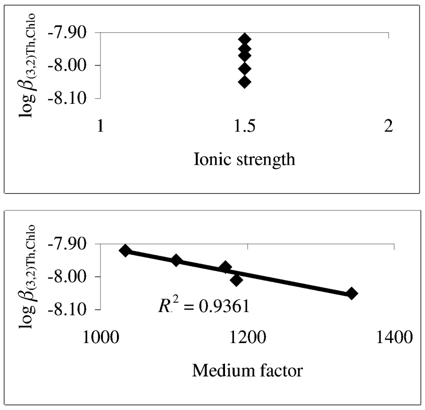

**Fig. 3** Values of log $\beta_{(3,2)\mathrm{Th,Chlo}}$ of the hydrolytic complex (3,2) of $Th^{IV}$ obtained at ionic strength 1.5 M adjusted by various chloride salts and dependence of log $\beta_{(3,2)\mathrm{Th,Chlo}}$ on the medium factor.

which became important only for ionic media that contained polyvalent ions.) Therefore the medium factor reflects the properties of the medium much better than does the ionic strength. Namely, the ions (a cation and an anion) of various electrolytes have different hydration energies.[2] As a consequence of that the systems with different ionic media contain different concentrations of free water molecules. For instance, the hydration energy of the $Li^+$ ion is 542 kJ mol$^{-1}$, the $Na^+$ ion 433 kJ mol$^{-1}$ and the $K^+$ ion 348 kJ mol$^{-1}$.[2] Owing to different $E_h$, the concentration of free water molecules in these three nitrate media decreases in the order: $w_{\mathrm{free,Li}} < w_{\mathrm{free,Na}} < w_{\mathrm{free,K}}$. Since the water molecules are reactants the hydrolysis extent (or log $\beta_{qp}$ value) should decrease in the same order. The slopes of Fig. 1 (lower) and Fig. 3 (lower) confirm this: the stability constants of the hydrolytic complexes decreases with increasing medium factor because the concentration of the free water molecules decreases in the same direction. This statement supports also values of log $\beta_{(2,2)\mathrm{Th,Nit}}$ and log $\beta_{(5,3)\mathrm{Th,Nit}}$ obtained in nitrate media of various ionic strengths (Figs. 4 and 5, $I_s = 0.5$–4.5 M).[3,6]

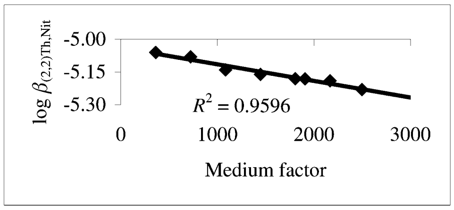

**Fig. 4** Dependence of log $\beta_{(2,2)\mathrm{Th,Nit}}$ values of the hydrolytic complex (2,2) of $Th^{IV}$ on the medium factor ($I_s = 0.5$–4.5 M). The point log $\beta = -5.17$, $\chi = 3824$ [3.0 M (Mg)$NO_3$] is omitted because it deviates from the straight line, reducing $R^2$ to 0.89.

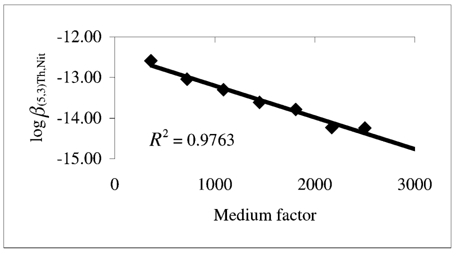

**Fig. 5** Dependence of log $\beta_{(5,3)\mathrm{Th,Nit}}$ of the hydrolytic complex (5,3) of $Th^{IV}$ on the medium factor ($I_s = 0.5$–4.5 M). The point log $\beta = -14.29$, $\chi = 3824$ [3.0 M (Mg)$NO_3$] is omitted because it deviates from straight line, reducing $R^2$ to 0.82.

If in the hydrolytic system competition in complex formation occurs the slopes might have the opposite trend. This kind of competition was observed between complexes $Th_2(OH)_2^{6+}$ and $Th_2(OH)_3^{5+}$ formed in chloride media at a constant [$I_s = 1.5$ M, Figs. 2 (lower) and 3 (lower)] and various ionic strength ($I_s = 0.5$–4.5 M, Figs. 6 and 7).[5,7] At low concentration of the medium (0.5 or 1.0 M $Cl^-$) the hydrolysis of thorium(IV) starts with formation of complex (3,2), while formation of (2,2)

**Table 2** The values of the ionic strength $I_s$, the medium factor $\chi$ and the stability constant log $\beta_{q,p}$ of the hydrolytic complexes of uranyl, nickel(II) and zinc(II) ion

| Medium | $I_s$/M | $\chi$ | $\chi\eta$ | log $\beta_{(2,2)U}$ | log $\beta_{(5,3)U}$ | Ref. |
|---|---|---|---|---|---|---|
| 3.0 M (Na)ClO$_4$ | 3.0 | 1914 | 5505 | −6.04 | −16.54 | 10 |
| 3.0 M (Na)NO$_3$ | 3.0 | 2169 | 10563 | −6.13 | −16.65 | 11 |
| 3.0 M (Na)Cl | 3.0 | 2370 | 13094 | −6.64[a] | −18.07[a] | 12 |
| 3.0 M (Ca)ClO$_4$ | 3.0 | 3053 | 8780 | −6.20 | −16.91 | 10 |
| 3.0 M (Mg)ClO$_4$ | 3.0 | 3569 | 10264 | −6.25 | −17.18 | 10 |
| 3.0 M (Mg)NO$_3$ | 3.0 | 3824 | 18621 | −6.34 | −17.37 | 13 |
| | | | | log $\beta_{(4,4)Ni}$ | — | |
| 1.5 M (Na)ClO$_4$ | 1.5 | 957 | 1376 | −27.03 | — | 1(*c*) p. 245 |
| 3.0 M (Na)ClO$_4$ | 3.0 | 1914 | 5505 | −27.37 | — | 14 |
| 3.0 M (Li)ClO$_4$ | 3.0 | 2244 | 6455 | −27.32 | — | 15 |
| 3.0 M (Na)Cl | 3.0 | 2370 | 13094 | −28.42 | — | 16 |
| 3.0 M (Na)Cl | 3.0 | 2370 | 13094 | −28.55 | — | 17 |
| | | | | log $\beta_{(1,1)Zn}$ | — | |
| 0.5 M (Na)ClO$_4$ | 0.5 | 319 | 153 | −7.77 | — | 9 |
| 0.5 M (Na)NO$_3$ | 0.5 | 362 | 293 | −8.76 | — | 9 |
| 0.5 M (Na)Cl | 0.5 | 395 | 364 | −8.57 | — | 9 |
| 2.0 M (K)Cl | 2.0 | 1406 | 5179 | −9.01 | — | 18 |
| 2.0 M (Na)NO$_3$ | 2.0 | 1446 | 4695 | −8.91 | — | 8 |
| 2.0 M (Na)Cl | 2.0 | 1580 | 5820 | −9.12 | — | 19 |

[a] Omitted from Fig. 8 because it deviates from the straight line. Inserting log $\beta_{(2,2)} = -6.64$ in Fig. 8 the correlation coefficient *R* decreases from 0.9348 to 0.0176, similarly with log $\beta_{(5,3)} = -18.07$.

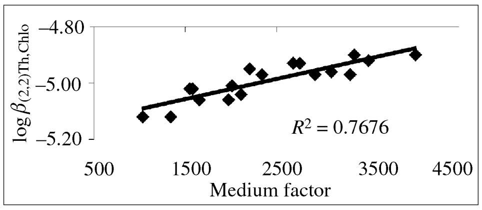

**Fig. 6** Dependence of log $\beta_{(2,2)Th,Chlo}$ of the hydrolytic complex (2,2) of Th$^{IV}$ on the medium factor ($I_s$ = 0.5–4.5 M).

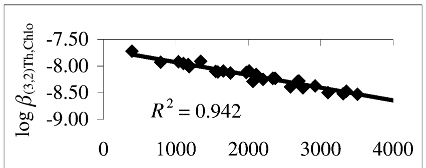

**Fig. 7** Dependence of log $\beta_{(3,2)Th,Chlo}$ of the hydrolytic complex (3,2) of Th$^{IV}$ on the medium factor ($I_s$ = 0.5–4.5 M).

begins at a little higher pH. With increasing concentration of complex (2,2) the concentration of (3,2) decreases. At high concentration of the medium (2.5 or 3.0 M Cl$^-$) the opposite order of complex formation was observed. The hydrolysis begins with formation of (2,2), while formation of (3,2) starts at a little higher pH. As a consequence of that at the same pH, say 3, the concentrations of these two complexes are different: at low concentration of the medium the concentration of (3,2) is higher than of (2,2), while at high concentration of the medium the complex (2,2) is dominant. Therefore, the trend of the linearity of the dependences log $\beta_{(2,2)Th,Chlo} = f(\chi)$ and log $\beta_{(3,2)Th,Chlo} = f(\chi)$ is opposite (Figs. 6 and 7). As a consequence presentation of data obtained in nitrate and chloride media on the same graph [log $\beta_{(2,2)\text{nitrate and chloride}} = f(\chi)$] did not show the effect of the medium. Therefore the dependences log $\beta_{(2,2)Th,Nit} = f(\chi)$ and log $\beta_{(2,2)Th,Chlo} = f(\chi)$ should be represented separately as it was done in Figs. 1 (lower) and 2 (lower), as well as in Figs. 4 and 6.

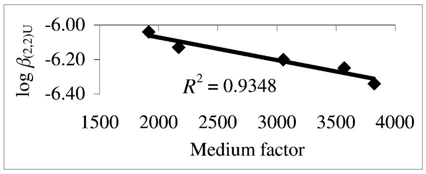

**Fig. 8** Dependence of log $\beta_{(2,2)U}$ values of the hydrolytic complex (2,2) of the uranyl ion on the medium factor ($I_s$ = 3.0 M).

The hydrolysis data of other metal ions are in good agreement with the thorium data and confirm the advantage of the medium factor. As an illustration values of the ionic strength, the medium factor and the stability constants of the hydrolytic complexes of the uranyl ion $(UO_2)_2(OH)_2^{2+}$ (log $\beta_{(2,2)U}$) and $(UO_2)_3(OH)_5^{+}$ (log $\beta_{(5,3)U}$), the nickel(II) ion $Ni_4(OH)_4^{4+}$ (log $\beta_{(4,4)Ni}$) and zinc(II) ion $Zn(OH)^+$ (log $\beta_{(1,1)Zn}$) are given in Table 2. The data show that at the same ionic strength (adjusted by various electrolytes) the stability constants of the hydrolytic complexes of uranyl, nickel(II) and zinc(II) ion have different values. However all these log $\beta_{q,p}$ values follow (linearly) the changes of the medium factor $\chi$. As illustration Fig. 8 shows the dependence log $\beta_{(2,2)U} = f(\chi)$ ($R^2 = 0.93$). For other data the following values of the correlation coefficients are obtained: log $\beta_{(5,3)U}$, $R^2 = 0.98$; log $\beta_{(4,4)Ni}$, $R^2 = 0.57$; log $\beta_{(1,1)Zn}$, $R^2 = 0.65$. In all cases the linearity has the same trend: *the stability constants decrease with increasing medium factor*. This is quite understandable because with increasing medium factor the concentration of the free water molecule decreases. As a consequence the hydrolysis extent (or log $\beta_{q,p}$) decreases.

Calorimetric measurements[5] confirm the advantage of the medium factor. Table 2 given in ref. 5 shows that the enthalpy of formation of the hydrolytic complexes (2,2) and (3,2) [$\Delta H_{(2,2)Th,Chlo}$ and $\Delta H_{(3,2)Th,Chlo}$] has different values on going from 3.0 M (K)Cl, 3.0 M (Na)Cl to 3.0 M (Li)Cl media in spite of the fact that the ionic strength has the same value ($I_s$ = 3 M). The correlation coefficient for the dependence $\Delta H_{(2,2)Th,Chlo} = f(\chi)$ is 0.98, while for $\Delta H_{(3,2)Th,Chlo} = f(\chi)$ it is 0.56. The linearity trend is opposite: the enthalpy of complex (2,2) increases, while that of (3,2) decreases with increasing medium

**Table 3** The values of the ionic strength $I_s$, the medium factor $\chi$ and p$K_a$ of acetic acid obtained in various media

| Medium | $I_s$ | $\chi$ | p$K_a$ | Ref. |
|---|---|---|---|---|
| $KNO_3$ | 1.0 | 623 | 4.5680 | 20 |
| KBr | 1.0 | 669 | 4.5950 | 20 |
| KCl | 1.0 | 690 | 4.5590 | 20 |
| $NaNO_3$ | 1.0 | 723 | 4.5305 | 20 |
| $LiClO_4$ | 1.0 | 748 | 4.5250 | 20 |
| NaCl | 1.0 | 790 | 4.5275 | 20 |
| $LiNO_3$ | 1.0 | 833 | 4.4495 | 20 |
| LiBr | 1.0 | 866 | 4.4760 | 20 |
| LiCl | 1.0 | 900 | 4.4445 | 20 |
| $Ba(ClO_4)_2$ | 1.5 | 882 | 4.4390 | 21 |
| $Sr(ClO_4)_2$ | 1.5 | 951 | 4.4140 | 21 |
| $Ca(ClO_4)_2$ | 1.5 | 1018 | 4.3500 | 21 |
| $Sr(NO_3)_2$ | 1.5 | 1036 | 4.3770 | 21 |
| $Ca(NO_3)_2$ | 1.5 | 1103 | 4.3040 | 21 |
| $SrCl_2$ | 1.5 | 1103 | 4.3590 | 21 |
| $CaCl_2$ | 1.5 | 1170 | 4.3000 | 21 |
| $KNO_3$ | 2.7 | 1717 | 4.7850 | 20 |
| $NaClO_4$ | 2.7 | 1723 | 4.9565 | 20 |
| KBr | 2.7 | 1806 | 4.9355 | 20 |
| KCl | 2.7 | 1898 | 4.8285 | 20 |
| $NaNO_3$ | 2.7 | 1952 | 4.7130 | 20 |
| $LiClO_4$ | 2.7 | 2019 | 4.7885 | 20 |
| NaBr | 2.7 | 2041 | 4.8655 | 20 |
| LiBr | 2.7 | 2095 | 4.6785 | 20 |
| NaCl | 2.7 | 2133 | 4.7555 | 20 |
| $LiNO_3$ | 2.7 | 2249 | 4.5500 | 20 |
| LiCl | 2.7 | 2326 | 4.5850 | 20 |
| $Ba(ClO_4)_2$ | 4.05 | 2380 | 4.6520 | 21 |
| $Sr(ClO_4)_2$ | 4.05 | 2566 | 4.6140 | 21 |
| $Ca(ClO_4)_2$ | 4.05 | 2747 | 4.4730 | 21 |
| $Sr(NO_3)_2$ | 4.05 | 2796 | 4.4420 | 21 |
| $Ca(NO_3)_2$ | 4.05 | 2977 | 4.3110 | 21 |
| $SrCl_2$ | 4.05 | 2977 | 4.4770 | 21 |
| $CaCl_2$ | 4.05 | 3158 | 4.3330 | 21 |

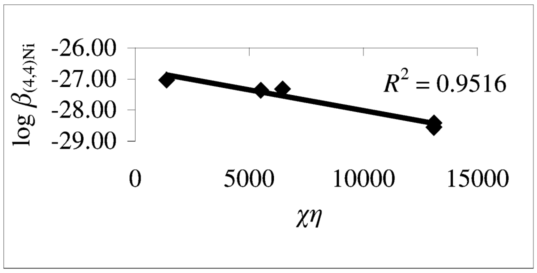

**Fig. 9** Dependence of log $\beta_{(4,4)Ni}$ values of the hydrolytic complex (4,4) of nickel(II) ion on the medium product $\chi\eta$.

factor.[5] This is in agreement with linearity trend of data (log $\beta_{(2,2)Th,Chlo}$ and log $\beta_{(3,2)Th,Chlo}$) obtained by the emf method [Figs. 2 (lower) and 3 (lower)].

A statistical analysis of the hydrolysis data has been carried out using non-linear regression analysis (Microcal Origin 6.0) but we shall not consider the obtained results here for the following reasons: (a) only two sets of data might be explained by non-linear correlation; (b) this kind of analysis might give only a new value for constant *A* or *B* in the ionic strength expression given by Debye and Hückel (1923), Pitzer and Brewer (1961) or similar expressions; and (c) the LFER (linear free energy relation) approach is more powerful because it is possible to find parameters of the ionic medium which cause the effect. At the same time it is possible to determine the contribution of each of them. Thus these parameters help us to understand interactions in water solutions, while constant *A* or *B* completely masks them. For instance, in order to determine the complex formation effect the electronegativity of the donor atom and size of the anion were introduced in the complex formation factor $\eta$ [eqn. (4)] (the hardness and softness of the donor atom also might be useful). As a result for some systems the medium product $\chi\eta$ gives a better correlation with log $\beta_{q,p}$ than does the medium factor $\chi$ indicating that complex formation is significant. As an illustration Fig. 9 shows the dependence log $\beta_{(4,4)Ni} = f(\eta\chi)$ (Table 2). For this dependence the correlation coefficient is 0.95, while for log $\beta_{(4,4)Ni} = f(\chi)$ $R^2 = 0.54$ (Table 2). However, we shall not consider this effect here because it is not the subject of this paper.

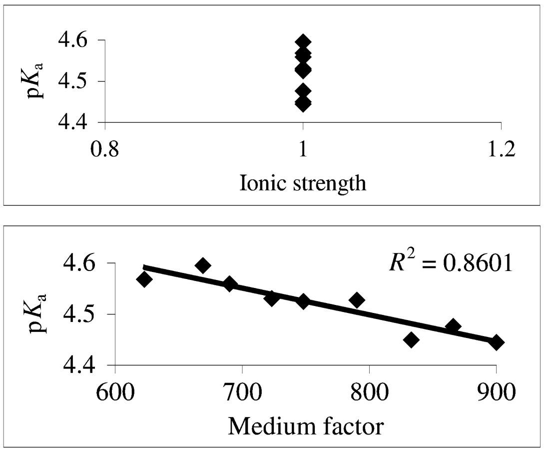

**Fig. 10** Values of p$K_a$ of acetic acid obtained at ionic strength 1.0 M adjusted by various electrolytes and dependence of p$K_a$ on the medium factor.

Since the hydrolysis data indicate the advantage of the medium factor in relation to the ionic strength it was interesting to check the possibility of applying the linear free energy relationship [eqn. (2)] to dissociation reactions (6) because the

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (6)$$

water molecules are reactants in these reactions. For this purpose one might used Ellilä's[20,21] data concerning dissociation of acetic acid in various ionic media (Table 3). Table 3 shows that p$K_a$ values of acetic acid determined at the same ionic strength adjusted by various electrolytes ($I_s$ =1.0 or 1.5 or 2.7 or 4.05 M) are different. As an illustration in [Fig. 10 (upper)] only p$K_a$ values determined at $I_s$ = 1.0 M are shown. Therefore the corresponding medium factor for all electrolytes used to keep the ionic strengths constant (Table 3) was calculated and represented in the form p$K_a = f(\chi)$. The linearity obtained indicates excellent correlation between p$K_a$ values and the medium factor $\chi$. As an illustration in [Fig. 10 (lower)] only the dependence p$K_{a,I_s1.0} = f(\chi)$ is shown ($R^2$ = 0.86). p$K_a$ values determined at $I_s$ = 1.5, 2.7 and 4.05 M gave similar linearity: $R^2$ = 0.86, 0.74 and 0.83.

However the linearity trend is opposite to that observed for hydrolysis: p$K_a$ *values decrease with increasing medium factor*. This unexpected trend might be explained by the fact that for dissociation of acetic acid in the presence of an ionic medium two reactions take place: dissociation [eqn. (7)] and substitution

$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+ \qquad (7)$$

[eqn. (8)]. [In eqn. (8) M denotes the medium cation, while A is

$$\begin{aligned} &CH_3CO_2H + MA + H_2O \rightleftharpoons CH_3CO_2M + HA + \\ &\qquad H_2O \rightleftharpoons CH_3CO_2 + M^+ + H_3O^+ + A^- \qquad (8) \end{aligned}$$

the medium anion. Its hydration is omitted.] In both reactions the hydrogen ions are set free. Therefore competition between these two reactions take place. In the dissociation the medium effect (as the hydration effect) suppresses release of hydrogen ions because with increasing medium factor the concentration of the free water molecules decreases and consequently the dis-

**Table 4** The values of the ionic strength $I_s$, the medium factor $\chi$ and p$K_a$ of glycine (gly) and 3-hydropropanoic acid (hyp) in various media

| Acid | Medium | $I_s$/M | $\chi$ | $T$/°C | p$K_{a1}$ | p$K_{a2}$ | Ref. |
|---|---|---|---|---|---|---|---|
| gly | $KNO_3$ | 0.1 | 318 | 25 | 9.70 | 2.51 | 22 |
| gly | $KNO_3$ | 0.1 | 318 | 25 | 9.69 | — | 23 |
| gly | $NaClO_4$ | 0.1 | 319 | 25 | 9.62 | 2.43 | 24 |
| gly | $NaClO_4$ | 0.1 | 319 | 25 | 9.68 | 2.33 | 25 |
| gly | KCl | 0.1 | 351 | 25 | 9.60 | 2.34 | 26 |
| hyp | $NaClO_4$ | 0.1 | 319 | 30 | 4.52 | — | 27 |
| htp | KCl | 0.1 | 351 | 30 | 4.49 | — | 28 |

**Table 5** The heat of discussion of water in various ionic media

| Medium | $I_s$/M | $\chi$ | $\Delta H_w$/kJ mol$^{-1}$ | Ref. |
|---|---|---|---|---|
| $LiNO_3$ | 3 | 2499 | 59.31 | 29 |
| NaCl | 3 | 2370 | 58.35 | 29 |
| $NaNO_3$ | 3 | 2169 | 56.93 | 30 |
| $NaClO_4$ | 3 | 1914 | 54.76 | 29 |
| $KNO_3$ | 3 | 1908 | 56.51 | 29 |

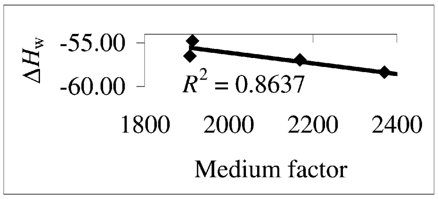

**Fig. 11** Dependence of the heat of dissociation of water $\Delta H$/kJ mol$^{-1}$ on the medium factor ($I_s$ = 3.0 M).

sociation extent also decreases. In the substitution reaction the medium effect (as the acidity effect of the medium cations) supports release of hydrogen ions. The fact that p$K_a$ decreases with increasing of medium factor indicates that the acidity effect is more pronounced than the hydration effect. For simplicity the acidity effect might be explained by the effect of the same concentration of LiCl, NaCl and KCl media. The $Li^+$ ion is a stronger acid than $Na^+$ or $K^+$ ion. Therefore the interaction between acetate ion and lithium ion will be more pronounced. Consequently in the LiCl medium, hydrogen ions will be set free more readily than in KCl media. Thus in the presence of LiCl p$K_a$ values will be lower than in the presence of NaCl or KCl media.

Data concerning dissociation of glycine and 3-hydroxypropanoic acid also indicate the medium effect and the advantage of the medium factor in relation to the ionic strength (Table 4).

Data concerning the heat of dissociation of water in various ionic media also indicate the advantage of the medium factor (Table 5). At the same ionic strength the heat of dissociation has different values. However these values follow linearly the values of the medium factor (Fig. 11).

The medium effect might also be expected in anation reactions (9) because the water molecule is a product. However there are

$$[MX_5(H_2O)]^{n+} + Y^- \rightleftharpoons [MX_5Y]^{(n+1)+} + H_2O \quad (9)$$

not enough data that might be used for consideration of the medium effect in these reactions.

It might be useful to point out an additional advantage of the medium factor. Using the linear dependences log $\beta_{q,p} = f(\chi)$ or p$K_a = f(\chi)$ one might estimate log $\beta_{p,q}$ or p$K_a$ at any value of the medium factor of the corresponding systems.

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