The OECD/NEA TDB review of selected organic ligands

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Summary. Within the scope of the OECD Nuclear Energy Agency (NEA) Thermochemical Data Base Project (TDB) a comprehensive review of selected organic ligands has been carried out by the authors. The selected ligands are oxalate, citrate, ethylenediaminetetraacetate (edta) and α-isosaccharinate (isa), and the elements considered in the review are U, Np, Pu, Am, Tc, Ni, Se and Zr, as well as the necessary basic data concerning protonation of the ligands and interactions with the major competing elements Na, K, Mg and Ca. This review on organic ligands showed that the pragmatic ionic strength correction procedure, the Specific Interaction Theory (SIT), chosen as the default method for all NEA TDB reviews, can be applied successfully also to organic ligands. The SIT interaction parameters derived from ligand protonation data for different media, e.g. NaCl and KCl, pass the consistency test when applied to other systems evaluated in the organics review, e.g. solubility data. Hence, the thermodynamic constants selected in this NEA TDB organics review can be used with some confidence in real world applications, provided that SIT is used in the speciation calculations.

1. Introduction

The modelling of the behaviour of hazardous materials under environmental conditions is among the most important applications of natural and technical sciences for the protection of the environment. In order to assess, for example, the safety of a waste deposit, it is essential to be able to predict the eventual dispersion of its hazardous components in the environment (geosphere, biosphere). For hazardous materials stored in the ground or in geological formations, the most probable transport medium is the aqueous phase. An important factor is therefore the quantitative prediction of the reactions that are likely to occur between hazardous waste dissolved or suspended in ground water, and the surrounding rock material, in order to estimate the quantities of waste that can be transported in the aqueous phase. It is thus essential to know the relative stabilities of the compounds and complexes that may form under the relevant conditions. This information is often provided by speciation calculations using chemical thermodynamic data. The local conditions, such as ground water and rock composition or temperature, may not be constant along the migration paths of hazardous materials, and fundamental thermodynamic data are the indispensable basis for dynamic modelling of the chemical behaviour of hazardous waste components.

In the field of radioactive waste management, the hazardous material consists to a large extent of actinides and fission products from electronuclear reactors, in addition to lesser amounts from other sources such as waste from medicine, industry and research facilities. The scientific literature on thermodynamic data, mainly on equilibrium constants and redox potentials in aqueous solution, has been contradictory in a number of cases, especially in actinide chemistry. A critical and comprehensive review of the available literature is necessary in order to establish a reliable thermochemical database that fulfils the requirements for rigorous modelling of the behaviour of the actinide and fission products in the environment.

The Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency recognised the need for an internationally acknowledged, high-quality thermochemical database for application in the safety assessment of radioactive waste disposal, and initiated the development of the NEA Thermochemical Data Base (TDB) project in 1984 [1]. The RWMC assigned a high priority to the critical review of relevant chemical thermodynamic data of compounds and complexes for this area containing the actinides uranium, neptunium, plutonium and americium, as well as the fission product technetium. The first four books in the series on the chemical thermodynamics of uranium [2], americium [3], technetium [4] and neptunium and plutonium [5] originated from this initiative.

In 1998, Phase II of the TDB Project (TDB-II) was started [1] to provide for the further needs of the radioactive waste management programs by updating the existing database [6] and applying the TDB review methodology to other elements (nickel, selenium, zirconium) and to simple organic compounds and complexes. The latter review work, referred to as the “NEA organics review” [7] in this paper, is
summarised in the following sections, and the special topic of ionic strength corrections in the case of organic ligands is elucidated with some examples. Detailed discussions and calculations, and all numerical values with their references are reported in [7].

2. Focus of the NEA organics review

The NEA organics review is within the scope and the spirit of the previous reviews aimed at helping to model the chemical behaviour of actinides and fission products in the near and far field of a radioactive waste repository using consistent data.

A prerequisite for a successful widely recognised critical evaluation of thermodynamic data is the sensible decision which organic ligands the evaluation should comprise. This decision has two aspects, namely the importance of the ligands in radioactive waste problems, and the availability of experimental data. In the beginning of the project it was decided that the evaluation of organic ligands should be limited to oxalate, citrate, ethylenediaminetetraacetate (edta) and α-isosaccharinate (isa).

From the viewpoint of importance for radioactive waste problems this set of ligands is very well posed. Oxalate is, with respect to its complexation strength, the major product of radiolytic degradation of bitumen, sometimes used for waste conditioning, and ion exchange resins used in decontamination procedures. In addition, oxalate is one of the strong complexing natural organic ligands (besides humic substances). Citrate and edta are used in decontamination processes and thus, they become part of the radioactive waste inventory. In terms of complexation strength, oxalate, citrate and edta cover a wide range of complex stability, and they may be used in model calculations as representatives of dicarboxylic acids (oxalate), hydroxy-polycarboxylic acids (citrate) and polyamino-polycarboxylic acids (edta). Finally, from the viewpoint of complexation strength, isa is the most important product of alkaline degradation of cellulose in cement pore waters. Thus, isa is of major concern in many performance assessments of planned radioactive waste repositories.

Regarding the availability of experimental data, the situation is less clear. In the case of oxalate, citrate and edta a large body of experimental studies has been published and the NEA organics review provides, based on the critical discussion of several hundreds of publications, a considerable set of selected thermodynamic values. However, in the case of isa the number of experimental studies is very limited and, despite of the importance of isa for performance assessments, only a few thermodynamic values could be selected. The critical review of experimental studies concerning isa mainly is a status report pointing out gaps in our present knowledge and further research needs.

As the task of the NEA organics review is to complement the other reviews of the NEA TDB project, which are restricted to inorganic compounds and complexes of actinides and fission products, a natural choice of elements comprises U, Np, Pu, Am, Tc, Ni, Se and Zr. However, the NEA organics review cannot be restricted to these elements as it aims at a thermodynamic data set useful for practical application. In addition to the above mentioned actinides and fission products the review considers also the major constituents of ground and surface waters which may interact with the selected organic ligands, i.e. H, Na, K, Mg and Ca. Any geochemical model including organic ligands should take into account these competing interactions and therefore, the NEA organics review provides a selected consistent set of these auxiliary constants.

The situation is more complicated for Na and K interactions. Here, we are in the realm of ambiguity characterised by the question: “Weak complexation or strong specific ion interaction?”. The answer is different for different ligands. In the case of oxalate, Na and K interactions are treated solely as specific ion interactions. In the case of edta, Na and K complexation constants had to be included in the speciation models. Na and K interactions with citrate are in between these two extremes. In the course of the review process both variants have been evaluated and compared, and finally the review team decided to treat the effects of Na and K on citrate solely as rather strong specific ion interactions.

The elements Ca and Mg are included in the NEA organics review because complexation of the organic ligands with these competing cations is of importance in geochemical models concerning the complexation of actinides and fission products in common ground and surface waters.

3. Review procedure and results

The literature has been surveyed up to the end of 2001 for all ligands. For oxalate a few more recent references are included, and for isa the aim had been to consider all relevant literature up to 2004. Experimental measurements published in the scientific literature are the main source for the selection of recommended data. Previous reviews are not neglected. They have been primarily used as sources for original scientific literature, but they also form a valuable source of critical information on the quality of primary publications.

In the realm of metal–organic complexes a plethora of experimental studies is found in the literature dealing with mixed complexes, i.e. complexes containing a common metal ion and two or more different ligands. In the NEA organics review mixed complexes, in general, were considered if they contain combinations of oxalate, citrate, edta and isa with or without additional inorganic ligands. Mixed complexes comprising other organic ligands are mentioned occasionally for qualitative comparison only. From the viewpoint of application, by far the most important class of mixed complexes are ternary metal–hydroxide–organic ligand complexes. These hydrolysed organic complexes may predominate in alkaline ground and surface waters and in high pH cement pore waters and thus, they are important in assessing the influence of organic ligands on element complexation in cementitious repositories.
eration about such complexes is discussed in the NEA organics review, but only in a few cases reliable thermodynamic constants could be selected. Also of importance in many ground and surface waters would be the class of metal–carbonate–organic ligand complexes. However, the NEA organics review can only state the almost complete lack of such data.

The detailed discussion of organic compounds has been restricted in the NEA organics review to the so-called “sparingly soluble” solids. These are mainly metal oxalates, which are discussed in some detail, and a few thermodynamic constants could be selected, mainly related to calcium oxalate solids. The generally rather soluble citrate and edta compounds are discussed in qualitative terms. From the viewpoint of model application in performance assessments the most important solid is calcium oxalate, because the possible precipitation of this solid in many ground and surface waters can limit the concentration of dissolved oxalate to rather low levels.

When necessary, experimental source data were re-evaluated by using chemical models that are either found or are consistent with side-reactions discussed in another section of the review (for example, data on metal complex formation might need to be re-interpreted to take into account consistent values for ligand protonation reactions). Re-evaluation of literature values might also be necessary to correct for known systematic effects (for example, if chloride complexation has been neglected in the original literature) or to make extrapolations to standard state conditions (I = 0) by using the Specific Ion Interaction Theory (SIT).

Once the critical review process in the NEA TDB project is completed, the resulting manuscript is reviewed independently by qualified experts nominated by the NEA. The purpose of the additional peer review is to receive an independent view of the judgments and assessments made by the primary reviewers, to verify assumptions, results and conclusions, and to check whether the relevant literature has been exhaustively considered. The independent peer review is performed by persons having technical expertise in the subject matter to be reviewed, to a degree at least equivalent to that needed for the original review.

The thermodynamic data selected in the NEA organics review are provided with uncertainties representing the 95% confidence level. There is no unique way to assign uncertainties, and the assignments made in the review are to a large extent based on the subjective choice by the reviewers, supported by their scientific and technical experience in the corresponding area.

The quality of thermodynamic models cannot be better than the quality of the data on which they are based. The quality aspect includes both the numerical values of the thermodynamic data used in the model and the “completeness” of the chemical model used, e.g., the inclusion of all relevant dissolved chemical species and solid phases. For the user it is important to consider that the selected data set presented in the NEA organics review is certainly not “complete” with respect to all the conceivable systems and conditions; there are gaps in the information. The gaps are pointed out in the various sections of the review, and this information may be used as a basis for the assignment of research priorities.

4. The specific ion interaction theory (SIT) applied to organic ligands

The selected thermodynamic data in the NEA database refer to standard state conditions, i.e., infinite dilution (I = 0) for aqueous species. Equilibrium constants studied in the laboratory are usually determined in an ionic medium. However, there is no “standard” ionic medium, or ionic strength, preferred in experimental determinations of equilibrium constants. The most “popular” media are NaCl, NaClO₄, and KNO₃ at high concentrations. The latter two media are of no relevance for environmental modeling. Hence, all experimental data have to be extrapolated to zero ionic strength as part of the data review procedure. The approach chosen in the NEA TDB project is the Specific Ion Interaction Theory (SIT)

\[
\log_{10} \gamma_i = -z_i^+ \cdot D + \sum \varepsilon(i,k) \cdot m_k
\]

where \( \gamma_i \) is the activity coefficient of species \( i \) with charge \( z_i \), \( D \) is the Debye–Hückel term, \( D = A \cdot \sqrt{I_m}/(1 + B \cdot a_i \cdot \sqrt{I}) \), with a temperature dependent parameter \( A = 0.509 \text{ (kg mol}^{-1})^{1/2} \) at 25°C, \( B \cdot a_i = 1.5 \text{ (kg mol}^{-1})^{1/2} \) at 25°C, the ionic strength \( I_m \) on the molal scale, and \( \varepsilon(i,k) \) is an aqueous species interaction coefficient which describes the specific short-range interactions between aqueous species \( i \) and \( k \). The sum extends over all species in solution. An important feature of the SIT model is that in the summation the \( \varepsilon(i,k) \) values are in general negligible if \( z_i \cdot z_k > 0 \), i.e. if the ions have electrical charges of the same sign. In the case of a laboratory system with high concentration of an ionic medium (1 : 1 salt MX), the SIT equation simplifies to

\[
\log_{10} \gamma_M = -z_M^2 \cdot D + \varepsilon(M,X) \cdot m_X
\]

for a cation \( M \), and likewise for an anion \( Y \) using the interaction coefficient \( \varepsilon(Y,N) \). The question in the organics review project was whether the SIT approach, which has been applied successfully to inorganic complexation, would also work in the case of metal–organic complexation.

4.1 Oxalate protonation constants

Experimentally determined values for the first protonation equilibrium of oxalate in NaCl media,

\[
ox_2^- + H^+ \Leftrightarrow H_2O_2^-,
\]

can be analysed by SIT using the following formula

\[
\log_{10} K_1 + 4D = \log_{10} K_1^* - \Delta \varepsilon \cdot m_{NaCl}
\]

where \( \log_{10} K_1 \) is a measured equilibrium constant on the molal scale. In the case of pure NaCl media \( m_{NaCl} = I_m \). If the term \( \log_{10} K_1 + 4D \) is plotted as a function of \( m_{NaCl} \), the molal NaCl concentration, the data should follow a straight line characterised by two parameters, the abscissa \( \log_{10} K_1^* \).
which is the stability constant at zero ionic strength, and the slope $-\Delta \varepsilon$, where $\Delta \varepsilon$ is the sum of SIT interaction parameters for this reaction.

$$\Delta \varepsilon = \varepsilon(\text{Hox}^-, \text{Na}^+) - \varepsilon(\text{H}^+, \text{Cl}^-) - \varepsilon(\text{ox}^2-, \text{Na}^+)$$

As can be seen in Fig. 1, all NaCl data considered as reliable in the NEA organics review essentially follow the expected linear behaviour, up to 5 m NaCl, and the parameters $\log_{10} K_1^\ast$ and $\Delta \varepsilon$ can be obtained, e.g. by a weighted linear least squares regression analysis.

An analogous procedure could be applied to data measured in NaClO$_4$ media with a resulting parameter $\Delta \varepsilon = \varepsilon(\text{Hox}^-, \text{Na}^+) - \varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{ox}^2-, \text{Na}^+)$. The observed differences between equilibrium data measured in NaCl and NaClO$_4$ media are solely ascribed to the SIT interaction parameters $\varepsilon(\text{H}^+, \text{Cl}^-)$ and $\varepsilon(\text{H}^+, \text{ClO}_4^-)$, respectively. However, these parameters have been determined independently from mean activity data of HCl and HClO$_4$, and they are used as constants in SIT analyses. Hence, the parameters $\varepsilon(\text{H}^+, \text{X}^-)$ with $\text{X}^- = \text{ClO}_4^-$, Cl$^-$, NO$_3^-$ can be included explicitly in the SIT regression analysis for all data measured in NaCl, NaClO$_4$ and NaNO$_3$ media using the following formula

$$\log_{10} K_1 + 4D - \varepsilon(\text{H}^+, \text{X}^-) \cdot m_{\text{X}^-} = \log_{10} K_1^\ast - \Delta \varepsilon^\ast(\text{Na}^+) \cdot m_{\text{Na}^+}$$

where

$$\Delta \varepsilon^\ast(\text{Na}^+) = \varepsilon(\text{Hox}^-, \text{Na}^+) - \varepsilon(\text{ox}^2-, \text{Na}^+).$$

As is shown in Fig. 2, all data measured in Na media and considered as reliable in the NEA organics review plot in the same data range and they essentially follow the expected linear behaviour. Consequently, the common parameters $\log_{10} K_1^\ast$ and $\Delta \varepsilon^\ast(\text{Na}^+)$ can be obtained by a weighted linear least squares regression analysis of all data measured in Na media.

In the NEA organics review [7] 120 experimental data measured in LiClO$_4$, LiNO$_3$, NaClO$_4$, NaCl, NaNO$_3$, KCl, KNO$_3$, and Et$_4$NI (tetraethylammonium iodide) media have been identified as reliable, and a multi-dimensional least squares SIT regression has been applied to all these data. This procedure takes care of the fact that a common value of $\log_{10} K_1^\ast$ should fit all the experimental data according to the formula

$$\log_{10} K_1 + 4D - \varepsilon(\text{H}^+, \text{Cl}^-) \cdot m_{\text{Cl}^-} - \varepsilon(\text{H}^+, \text{NO}_3^-) \cdot m_{\text{NO}_3^-} - \varepsilon(\text{H}^+, \Gamma^-) \cdot m_{\Gamma^-} = \log_{10} K_1^\ast - \Delta \varepsilon^\ast(\text{Li}^+) \cdot m_{\text{Li}^+} - \Delta \varepsilon^\ast(\text{Na}^+) \cdot m_{\text{Na}^+} - \Delta \varepsilon^\ast(\text{Et}_4\text{N}^+) \cdot m_{\text{Et}_4\text{N}^+}$$

In this equation the SIT interaction parameters $\varepsilon(\text{H}^+, \text{Cl}^-) = 0.14 \pm 0.02$, $\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.12 \pm 0.01$, $\varepsilon(\text{H}^+, \text{NO}_3^-) = 0.07 \pm 0.01$ and $\varepsilon(\text{H}^+, \Gamma^-) = 0.19 \pm 0.01$ have been used, and $\Delta \varepsilon^\ast(M^+) = \varepsilon(\text{Hox}^-, M^+) - \varepsilon(\text{ox}^2-, M^+)$ are fit parameters, where $M^+$ is the cation of the background electrolyte, i.e. Li$^+$, Na$^+$, K$^+$ or Et$_4$N$^+$. When applying the SIT model to the activity coefficients of tetraethylammonium halides, it appeared that the specific ion-interaction coefficient, $\varepsilon(\text{Et}_4\text{N}^+, \text{X}^-)$, depends on the ionic strength. A proper representation of the data is achieved by setting:

$$\varepsilon(\text{Et}_4\text{N}^+, \text{X}^-) = \varepsilon_1(\text{Et}_4\text{N}^+, \text{X}^-) + \varepsilon_2(\text{Et}_4\text{N}^+, \text{X}^-) \cdot \log_{10}[\text{Et}_4\text{N}^+].$$

As shown in detail in the NEA organics review [7], a pronounced ionic strength dependence is found in $\log_{10} K_1^\ast$ data (Fig. 3) but not in $\log_{10} K_1^\ast$ data referring to the second oxalate protonation equilibrium. Because of this, the protonation constant of oxalate in tetraethylammonium salts was
\[ \varepsilon(\text{Li}^+) = -(0.51 \pm 0.09) \text{ kg mol}^{-1} \]

\[ \varepsilon(\text{ox}^2-, \text{Na}^+) = -(0.08 \pm 0.01) \text{ kg mol}^{-1} \]

\[ \varepsilon(\text{ox}^2-, \text{K}^+) = (0.07 \pm 0.08) \text{ kg mol}^{-1} \]

### 4.2 Calcium oxalate solubility

A large number of studies has been published within the last 100 years reporting solubility data for calcium oxalate hydrates in pure water and various ternary and higher systems. All the papers have been scrutinised in the NEA organics review [7]. For the final data analysis only studies carried out in NaCl and KCl media with proper characterization of the solids in equilibrium with the solutions have been considered [8–15].

In all the above cases analytical equilibrium concentration data of dissolved calcium, oxalate, NaCl or KCl have been reported, and the aqueous speciation was recalculated in the NEA organics review [7] as follows.

The complexes Ca(ox)(aq) and Ca(ox)\(_3^2-\) are included in the speciation calculations using equilibrium constants derived from reliable experimental data not involving solubility measurements. In order to adjust these constants to the actual ionic strength of a particular equilibrium experiment the SIT has been used with the following interaction coefficients: \(\varepsilon(\text{Ca}^2+, \text{Cl}^-) = (0.14 \pm 0.01)\), \(\varepsilon(\text{ox}^2-, \text{Na}^+) = -(0.08 \pm 0.01)\) and \(\varepsilon(\text{ox}^2-, \text{K}^+) = (0.07 \pm 0.08)\), and it has been assumed that \(\varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl}) \approx \varepsilon(\text{Ca}(\text{ox})(\text{aq}), \text{NaCl}) = \varepsilon(\text{Ca}(\text{ox})(\text{aq}), \text{KCl}) = (0.0 \pm 0.1)\), and \(\varepsilon(\text{Mg}(\text{ox})_2^2-, \text{Na}^+) \approx \varepsilon(\text{Ca}(\text{ox})_2^2-, \text{Na}^+) = \varepsilon(\text{Ca}(\text{ox})_2^2-, \text{K}^+) = -(0.15 \pm 0.10).\) The parameters \(\varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})\) and \(\varepsilon(\text{Mg}(\text{ox})_2^2-, \text{Na}^+)\) have been derived in the NEA organics review from Mg oxalate complexation data determined in NaCl media.

As the speciation calculations showed, the complex Ca(ox)\(_3^2-\) is unimportant (\(< 0.04\%\) of total oxalate in all cases) in the calcium oxalate equilibrium experiments considered in the review, and hence the uncertainties of its stability constant and related SIT interaction coefficient have no influence on the results. However, the complex stability of Ca(ox)(aq) turned out to be a critical parameter in a consistent re-evaluation of calcium oxalate solubility experiments (1 to 10\% of total oxalate, depending on ionic strength and temperature).

The results of the speciation calculations, i.e. the calculated concentrations of [Ca\(^{2+}\)] and [\(\text{ox}^2-\)], have been used to determine the solubility product of the reaction

\[
\text{Ca(ox)} \cdot \text{H}_2\text{O}(cr) \Leftrightarrow \text{Ca}^{2+} + \text{ox}^2- + \text{H}_2\text{O}
\]

and to extrapolate it to zero ionic strength with the same SIT interaction parameters as used in the speciation calculations according to the formula

\[
\log_{10} K_{s,0} = \log_{10} K_{s,0}^* - 8D \\
+ (\varepsilon(\text{Ca}^{2+}, \text{Cl}^-) + \varepsilon(\text{ox}^2-, \text{M}^+)) \cdot I_s
\]
where

\[ M^+ = \text{Na}^+ \text{ or } K^+ . \]

Fig. 4 (at 25°C) and 5 (at 37°C) reveal that the re-evaluated solubility products, \( \log_{10} K'_{\text{edta}} \), extrapolated to zero ionic strength with parameters selected and estimated in the NEA review, do not show any systematic ionic strength dependence, which is a strong indication of the internal consistency of the speciation model derived in this review.

### 4.3 Application of the SIT to metal–edta complexation

In the data evaluation for metal–edta complexation the effect of Na(edta)\(^{3-}\) and Kedta\(^{3-}\) complexation has to be considered explicitly. For example, equilibrium data reported for the reaction

\[ \text{Mg}^{2+} + \text{edta}^{4-} \Leftrightarrow \text{Mg(edta)}^{2-} \]

in NaCl media [16] have been corrected for Na(edta)\(^{3-}\) complexation according to the formula

\[ \log_{10} K_{\text{corr}} = \log_{10} K + \log_{10}(1 + K_{\text{Na}} \cdot \text{[Na]}^+) \]

where \( K_{\text{Na}} \) is the equilibrium constant of the reaction

\[ \text{Na}^+ + \text{edta}^{3-} \Leftrightarrow \text{Na(edta)}^{3-} \]

corrected with SIT to the appropriate ionic strength, given by the NaCl concentration. The corrected data exhibit a linear behaviour in a SIT plot (Fig. 6) up to 5 m NaCl. Together with the data of [17], measured in Me4NCl media, a consistent picture of ionic strength dependence arises, resulting in a two-dimensional SIT analysis (Fig. 6). The results are \( \log_{10} K'_{i} = (10.90 \pm 0.10), \quad \Delta \varepsilon(\text{Me}_4\text{NCl}) = -(1.02 \pm 0.20) \text{ kg mol}^{-1}, \quad \Delta \varepsilon(\text{NaCl}) = -(0.52 \pm 0.04) \text{ kg mol}^{-1} \). The SIT interaction coefficient for NaCl media allows an estimate of \( \varepsilon(\text{Na(edta)}^{2-}, \text{Na}^+) = \Delta \varepsilon(\text{NaCl}) + \varepsilon(\text{Mg}^{2+}, \text{Cl}^-) + \varepsilon(\text{Na}^{+}, \text{Cl}^-) \)

Those stability constants, valid at \( I = 0 \), together with their \( \Delta \varepsilon \) values have been used to calculate \( K \) at the appropriate ionic strength, given by the NaCl concentration, and subsequently to correct the experimental \( \log_{10} K \) values of Am\(^{3+}\)–edta\(^{4-}\) for complexation effects according to the following formula:

\[ \log_{10} K_{\text{corr}} = \log_{10} K + \log_{10}(1 + K_{\text{Na}} \cdot \text{[Na]}^+) \]

Fig. 6. Weighted two-dimensional least squares SIT regression plots for the reaction Mg\(^{2+}\)–edta\(^{4-}\) ↔ Mg(edta)\(^{2-}\). The data measured in NaCl [16] and Me\(_4\)NCl [17] have been considered as two data sets linked by a common \( \log_{10} K'_{i} \) value in the regression analysis. The results are \( \log_{10} K'_{i} = (10.90 \pm 0.10), \quad \Delta \varepsilon(\text{Me}_4\text{NCl}) = -(1.02 \pm 0.20) \text{ kg mol}^{-1}, \quad \Delta \varepsilon(\text{NaCl}) = -(0.52 \pm 0.04) \text{ kg mol}^{-1} \).
have been found. Considering these differences, an over-organics review [7] and differences up to 0.14 log units interpreted in terms of the reaction

$$\text{NaClO}_4 \rightleftharpoons \text{Uedta}^{(aq)} + 5\text{H}^+$$

involving equilibrium constants for $\text{H}_2\text{edta}^{2+}$ and $\text{H}_6\text{edta}^{4+}$ determined by the authors [19]. The edta protonation constants reported by [19] have been re-analysed in the NEA organics review [7] and differences up to 0.14 log units have been found. Considering these differences, an overall uncertainty of ±0.2 has been assigned to the experimental data [19]. A weighted least squares SIT regression analysis gives $\log_{10} K^\circ = 4.80 \pm 0.19$ and $\Delta \varepsilon = -(0.02 \pm 0.09)$ kg mol$^{-1}$. Again, the linear behaviour of the data in the SIT plot in the range 1 to 3.5 m NaClO$_4$ corroborates the applicability of SIT for organic ligands (Fig. 8).

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