Evaluation of Equilibrium Constants  
- A New Approach†

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A criterion of adequacy of physicochemical data: stability constants ($K_{ijk}$) of complexes, dissociation constants, activity coefficient ($f$) of hydrogen ion is presented. The data obtained from repeated titrations made in titrand + titrant systems of high ionic strength provide linear relationships between $\log K_{ijk}$ and $f$, and relative error ($\% e$) of determination of weak acid (H$_a$L) concentration. The relationships enable to evaluate the $\log K_{ijk}$ and $f$ values corresponding to $\% e = 0$, preferably according to the interpolation procedure. The accuracy depends on the degree of linearity between the variables considered. This idea was employed in the determination of $K_{ijk}$ for complexes Na$_3$K$_2$H$_4$L formed by anions of tartaric acid and was found to be promising.

Zaprezentowano nowe kryterium poprawności otrzymywanych danych fizykochemicznych takich jak: stałe trwałości kompleksów $K_{ijk}$, stałe dysojacji i współczynnik aktywności $f$. Nowa metoda wykorzystuje fakt liniowej zależności między $\log K_{ijk}$ i $f$, a $\% e$. Metodę przetestowano na przykładzie kompleksu Na$_3$K$_2$H$_4$L.

† Dedicated to Professor Adam Hulanicki on the occasion of his 70th birthday.
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It is a well-recognised opinion that potentiometric titration has been used extensively as an indispensable tool applicable for analytical and physicochemical studies. Furthermore, this realm provides the possibility of applying more sophisticated math than in many other areas of chemical analysis. The accurately formulated models applied in potentiometric titrations are based on semi-empirical relationships obtained on the basis of the material balances assumed. And, last but not least, the method ensures one particular attribute which deserves mentioning: it is the greatest possible informative content (efficiency) available. Namely, \( n \) physicochemical data due to the system tested are evaluated on the basis of \( N \geq n + 1 \) experimental points \((V_j,Y_j), j = 1, ..., N; Y_j - \text{value of variable } Y (\text{e.g., } \text{pH}) \text{measured at volume } V = V_j \text{[ml]} \) of titrant added. Moreover, some complementary procedures are not required here, as was already inferred \(\text{e.g.} \) in determination of equilibrium constants related to liquid-liquid extraction systems \([1]\).

Another problem is the figures of merit, particularly relevant to the precision and accuracy of the physicochemical data thus evaluated. Precision, defined by standard deviation \((s)\), expresses the dispersion of a series of replicate measurements around a central location \(x^*\), whereas a bias expresses deviation of \(x^*\) from the true value \((x_0)\) of variable \(x\) \([2]\). Some sources of the bias \(\text{e.g.,} \) calibration, interference and drift) can be assessed and corrected but most often cannot be removed entirely and explained clearly. Therefore, it is useful to consider the reliability of analytical results comprising both bias and precision. This could be used as a criterion for evaluating results obtained from measurements \([2]\). An example of such an approach was provided by Michałowski \([3]\) who introduced, as the criterion of reliability, the \(z\) value defined as follows:

\[
z = \frac{1}{N} \cdot \sum_{j=1}^{N} (x_j - x_0)^2 = \left( \bar{x} - x_0 \right)^2 + \left( 1 - \frac{1}{N} \right) \cdot s^2
\]

where: \(x_j (j = 1, ..., N)\) is the value of \(j\)-th measurement, \(N\) is number of measurements, \(x^* = \bar{x} = 1/N \cdot \Sigma x_j\) is the mean value, \(x_0\) is the true value, \(s^2\) is the variance; the bias and the standard deviation are nearly of equal rights (weights). Another approach is based on the concept of negentropy \([4]\). Obviously, such criteria would not be suitable for determination of the physicochemical data made according to iteration procedure applied to the regression equation, expressed by a function \(Y = f(V)\), related to the system in question. The degree of fit of the function to experimental points \((V_j, Y_j)\) cannot be considered as a sufficient criterion of validity of the parameters involved.

In this respect, very few attempts have been made previously to enhance the case that the data can be loaded by systematic errors affected by the analytical procedure applied. In order to obtain the correct values of the data, it is necessary to apply a criterion separating accurate and inaccurate data. An approach of this kind, applicable for the systems where a reaction \(A + B = AB\), defined by equilibrium constant \(K = [A][B]\), occurs during titration, was formerly reported by Fortuin \([5]\); \(K\) is the solubility prod-
uct \((K_w)\) or the ionic product of water \((K_w)\). The value for \(K\) was considered as a criterion of correctness of the analyte content found from the nomogram constructed for this purpose \([5–7]\). Such an approach is in reverse relation to the one suggested by Michałowski et al. \([6–8]\) who found the linearity between log\(K\) (or p\(K\)) and % e. This linearity enables \(K = (K)_{pK - 0}\) to be evaluated by perpendicular projection (at % e = 0) to the ordinate axis. A similar approach was subsequently applied to some conditional equilibrium constants \(K\) (of the kind defined in the paper \([1]\)) generated from replicated titrations \([9,10]\) made in the complex systems containing polybasic organic acids in concentrated titrand + titrant isomolar systems of high ionic strength. The values for linear correlation coefficients between the variables assumed were usually close to +1 or -1; it is a prerequisite of the approach done there.

Another problem concerns the evaluation of the activity coefficient \((f)\) for hydrogen ions at high ionic strength values of electrolytic solutions. Application of empirical extensions of Debye-Hückel and Davies equations reliant on the ionic strength \((I)\), temperature and dielectric permeability make the calculations of the \(f\) value incorrect at high \((ca 2 \text{ mol l}^{-1})\) ionic strength values; an example of such an approach was recently provided in reference \([11]\) where the modified Bromley equation was applied for the study of nickel(II) complexes with ethanolamine at high \((up to 3 \text{ mol l}^{-1})\) ionic strength media \((\text{NaClO}_4)\). One should hint that an indubitable effect of a basic form of a weak acid on the activity coefficient \((f)\) of hydrogen ions is not considered. The problems encountered provide arguments for the application of an aligning approach, similar to that used for evaluation of other physicochemical data, e.g. equilibrium constants of complexes. In the present paper, the \(f\) value is one of the parameters evaluated in the optimisation procedure, while the value of pH measured is defined as \(-\log h\), where \(h\) is the activity of the hydrogen ion.

Determination of stability constants of weak complexes in concentrated solutions of electrolytes seems to be an important activity considering the fact that measurements in different electrochemical studies are customarily made at constant and rather high ionic strength of basal solution. Possible complexes formed between cations of alkali metals and basic forms of acids (particularly organic) are usually omitted in the calculations. This assumption enables maintain an exceedingly simple form of the related regression equations. Nevertheless, it provides a bad assessment of physicochemical data.

More recently, pH-metric titration was also applied for the determination of stability constants of the complexes of \(M_nL_pH\) type \([12]\) and for studies of some mixed complexes formed by some divalent cations with pyruvate, oxalate and citrate ions \([13]\). Tartaric acid complexes were also tested using ion-chromatographic method \([14]\).

The present paper provides an unconventional method of validating stability constants through the determination of a set of stability constants \(K_{jk}\) of mixed complexes \(M_jK_nL\) formed by non-hydrolysable cations \(M^+\), \(K^+\) with basal forms \(H_kL^{+k-n}\) of a weak acid \(H_nL\). This method is tested with tartaric acid (i.e. acid of \(H_2L (n = 2)\) type) complexes with the sodium and potassium ions.
As it is stated below, the function derived from the corresponding balances enables us to evaluate both physicochemical ($K_{ijk}$, activity coefficient ($f$) of hydrogen ions) and analytical (concentration ($s$)) data. The stability constants are defined by the relation [1]

$$[M,K_j H_k L] = K_{ijk}[M][K][H]^k[L]$$

(2)

where $0 < i + j + k \leq 2$, $K_{000} = 1$; charges of the corresponding species are omitted for simplicity.

Theoretical part

The substances present in the titrand (D) + titrant (T) system, together with primary molar concentrations and volumes of the solutions added, are given in Table 1. In setting up the experiment, D and T were prepared according to an unconventional manner [1] in flasks of equal volumes ($V_r$) and filled up to the mark with distilled water. $V_0$ ml of D ($V_0 \leq V_i$) was titrated with $V$ ml of T and the points ($V_j$, $pH_j$), $j = 1, ..., N$, were recorded.

Table 1. Composition of titrand (D) and titrant (T)

<table>
<thead>
<tr>
<th>Substance</th>
<th>D ($V_o$)</th>
<th>T ($V$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_n$L ($C_0$)</td>
<td>$V_t$</td>
<td>$V_t$</td>
</tr>
<tr>
<td>MOH ($C$)</td>
<td>$-$</td>
<td>$V_M$</td>
</tr>
<tr>
<td>MB ($C_1$)</td>
<td>$V_{MB}$</td>
<td>$V_{MB}'$</td>
</tr>
<tr>
<td>KB ($C_2$)</td>
<td>$V_{KB}'$</td>
<td>$V_{KB}'$</td>
</tr>
</tbody>
</table>

Assuming (a) the conceivable complexes of $M_i K_j H_k L$ type for $n = 2$ (diprotic acid, $H_2L$), (b) the pH interval where $[H] >> [OH]$ and (c) the isomolarity condition expressed by the formula $C_j V_{MB}^* = C V_M + C_j V_{KB}^*$, where: $V_{MB}^* = V_{MB} - V_{MB}'$, $V_{KB}^* = V_{KB} - V_{KB}'$, we get the function [15–17]

$$pH = -\log \{2 \cdot p^{1/2} \cdot \cos(\Phi/3) - a\}$$

(4)

where: $pH = -\log h$, $f = h/[H]$, $h$ and $f$ stand for activity and the activity coefficient of hydrogen ions, respectively, and:

$$\Phi = \arccos\left(\frac{-q/2 \cdot p^{-3/2}}{p}\right)$$

(4a)

$$p = a^2 - b/3$$

(4b)

$$q = 2 \cdot a^3 - a \cdot b + c$$

(4c)

$$a = f(x_1 + b_{bd}/V_0 - b_{bd}/W)/3$$

(5a)

$$b = f^2 \cdot (x_0 - (d \cdot C_0 - b_{bd}/V_0 + b_{bd}/W) \cdot x_1)$$

(5b)
Evaluation of equilibrium constants

\[ c = f^3 \cdot x_0 \cdot (b_m/V_0 - b_m/W - 2 \cdot d \cdot C_0) \]  
\[ W = V_0 + V; \quad d = V/V_t; \quad b_m = CV_mV_0/V_t \]  
\[ x_1 = a_0 + a_1[M] + a_2[K] \]  
\[ x_0 = b_0 + b_1[M] + b_2[K] + b_3[M]^2 + b_4[K]^2 + b_5[M][K] \]  
\[ a_0 = K_{001}/K_{002}, \quad a_1 = K_{101}/K_{002}, \quad a_2 = K_{011}/K_{002} \]  
\[ b_0 = 1/K_{002}, \quad b_1 = K_{100}/K_{002}, \quad b_2 = K_{010}/K_{002} \]  
\[ b_3 = K_{200}/K_{002}, \quad b_4 = K_{020}/K_{002}, \quad b_5 = K_{110}/K_{002} \]  

At great excess of M and K, i.e. for

\[ [M] \gg \Sigma_i[M_iK_jH_kL] \quad \text{and} \quad [K] \gg \Sigma_j[M_iK_jH_kL] \]  

one can assume that

\[ [M] = z_1 + y/W, \quad [K] = z_2 - y/W \]  

where:

\[ z_1 = (C_1V_{MB} - C_2V_{KB}^*)/V_t, \quad z_2 = C_2V_{KB}^*/V_t, \quad y = C_2V_{KB}^* V_0/V_t \]  

Equation (3), together with the related defining expressions (4–8) for the parameters and variables involved, is the basis for calculations made according to an iterative computer program. The sum of unweighted squares

\[ SS = \sum_{j=1}^{N} (\text{pH}_j - \text{pH}(V_j))^2 \]  

was chosen as the criterion of optimisation, where \( \text{pH}(V_j) \) is the pH-value calculated for \( j \)-th experimental point \( (V_j, \text{pH}_j; \quad j = 1, ..., N) \), at defined stage of optimisation procedure, and \( W_j = V_0 + V_j \) is the total volume of the system at this point.

A set of parameters under optimisation, consisting of \( C_0, f \) and nine stability constants of complexes \( (K_{ijk}) \), was found by employing an iterative computer program MINUIT 96.03 (Function Minimization and Error Analysis) taken from CERN Program Library (entry D506). The program uses the Davidon-Fletcher-Powell variable-metric algorithm, with the sum of squares (10) chosen as the criterion of optimisation. In order to fulfil the requirement of positive values due to \( K_{ijk} \) optimised and avoid deleterious application of the constraints put on them, \( K_{ijk} \) were expressed by \( \log K_{ijk} \), taken as the quantities optimised, \( K_{ijk} = 10^{\log K_{ijk}} \).

EXPERIMENTAL

Materials and equipment

Solutions of NaNO₃ and KNO₃ were prepared by dissolving the corresponding salts (Merck, p.a.) in water. Tartaric acid (H₂L) solution was obtained by dissolving the preparation (Merck, purity > 99%) in water and standardising it against the NaOH solution, which was previously standardised against potas-
sium hydrogen phthalate (POCh Gliwice, anal. grade). Doubly distilled water, boiled to remove CO₂, was applied for preparation of stock solutions, titrand (D) and titrant (T).

pH-metric titrations were performed with an automatic titrator (Mettler-Toledo DL 25) equipped with DG 11-SC (Mettler-Toledo electrode) and interfaced with a Pentium 90 computer where the results were stored. The titrations were made at 20°C. The electrode was calibrated against standard buffer solutions with pH equal to 4.00 and 7.00 (POCh Gliwice).

**Procedure**

Four series of mixtures (D and T) were prepared in Vf = 200 ml flasks in accordance with Table 1. The composition (concentrations [mol L⁻¹] and volumes [ml] of stock solutions) of D and T is shown in Table 2. In all series, 15 titrations were made; V₀ = 50 ml of titrand (D) was titrated up to pH ca 6. The number (N) of titration points (Vj, pHj) taken for the evaluation was equal to 60. The overdetermined set of experimental points covers the pH-interval where a relatively high level of concentrations of particular forms is available.

**Table 2. Preparation of D and T in series 1, 2, 3 and 4; volumes in ml, concentrations in mol L⁻¹**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Series 1</th>
<th>Series 2</th>
<th>Series 3</th>
<th>Series 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L (C₀ = 0.1013)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>NaOH (C = 0.1170)</td>
<td>–</td>
<td>25</td>
<td>–</td>
<td>25</td>
</tr>
<tr>
<td>NaN₃ (C₁ = 2.5)</td>
<td>100</td>
<td>30</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>KNO₃ (C₂ = 2.5)</td>
<td>31.17</td>
<td>100</td>
<td>101.17</td>
<td>30</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

Full (eq.7a, b) and simplified models were applied. The simplified model does not involve the mixed complex NaKL.

A good degree of fit, within the range 10⁻²–10⁻³ attained for SS (10), was achieved for a number of titration points assumed in both models. The convergence was generally accomplished after about 500 calls to the function in the full model, and after about 300 calls in the simplified one. The optimised values were than used to plot the linear relationships between logKᵢjk and % e, where

\[
\% e = 100 \cdot \left( C₀ - C₀₀ \right) / C₀₀ \quad \text{%}
\]

and C₀₀ is the C₀ value found from independent, preliminary titrations of tartaric acid with the standardised NaOH solution.

The values of logKᵢjk evaluated from the corresponding plots of logKᵢjk vs % e dependencies (Fig.1a, b) at % e = 0 are specified in Table 3 (full model) and in Table 4 (simplified model). The values Kᵢjk = (Kᵢjk)ᵛe=0 thus obtained are considered as unbiased ones.
Figure 1. (a, b) The points (%$e$, log$K_{ijk}$) related to different sets (ijk) of the series 4.
Table 3. Values of \( \log K_{ijk} \) and \( f \) found at \( \% e = 0 \) for the series 1, 2, 3 and 4 (together with the related standard deviations) when all complexes were considered; \( I = 1.645 \text{ mol L}^{-1} \)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Series 1</th>
<th>Series 2</th>
<th>Series 3</th>
<th>Series 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log K_{002} ) (H(_2)L)</td>
<td>7.46 ± 0.25</td>
<td>7.30 ± 0.15</td>
<td>7.34 ± 0.08</td>
<td>7.35 ± 0.02</td>
</tr>
<tr>
<td>( \log K_{001} ) (HL)</td>
<td>4.06 ± 0.14</td>
<td>4.10 ± 0.16</td>
<td>4.12 ± 0.03</td>
<td>4.23 ± 0.05</td>
</tr>
<tr>
<td>( \log K_{100} ) (NaL)</td>
<td>0.63 ± 0.04</td>
<td>0.68 ± 0.14</td>
<td>0.59 ± 0.04</td>
<td>0.70 ± 0.02</td>
</tr>
<tr>
<td>( \log K_{010} ) (KL)</td>
<td>0.61 ± 0.14</td>
<td>0.63 ± 0.13</td>
<td>0.42 ± 0.04</td>
<td>0.54 ± 0.02</td>
</tr>
<tr>
<td>( \log K_{011} ) (NaHL)</td>
<td>4.65 ± 0.05</td>
<td>4.10 ± 0.29</td>
<td>4.19 ± 0.05</td>
<td>4.27 ± 0.06</td>
</tr>
<tr>
<td>( \log K_{011} ) (KHL)</td>
<td>4.46 ± 0.20</td>
<td>4.52 ± 0.08</td>
<td>4.51 ± 0.02</td>
<td>4.54 ± 0.02</td>
</tr>
<tr>
<td>( \log K_{200} ) (Na(_2)L)</td>
<td>0.57 ± 0.18</td>
<td>0.65 ± 0.30</td>
<td>0.44 ± 0.05</td>
<td>0.62 ± 0.04</td>
</tr>
<tr>
<td>( \log K_{020} ) (K(_2)L)</td>
<td>0.92 ± 0.20</td>
<td>0.45 ± 0.16</td>
<td>0.48 ± 0.12</td>
<td>0.55 ± 0.02</td>
</tr>
<tr>
<td>( \log K_{110} ) (NaKL)</td>
<td>0.29 ± 0.11</td>
<td>0.16 ± 0.16</td>
<td>-0.11 ± 0.10</td>
<td>0.24 ± 0.13</td>
</tr>
<tr>
<td>( f )</td>
<td>1.24 ± 0.20</td>
<td>1.04 ± 0.08</td>
<td>1.22 ± 0.05</td>
<td>1.06 ± 0.01</td>
</tr>
</tbody>
</table>

Table 4. Values of \( \log K_{ijk} \) and \( f \) found at \( \% e = 0 \) for the series 1, 2, 3 and 4 (together with the related standard deviations) when mixed complex is not taken into consideration; \( I = 1.645 \text{ mol L}^{-1} \)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Series 1</th>
<th>Series 2</th>
<th>Series 3</th>
<th>Series 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log K_{002} ) (H(_2)L)</td>
<td>7.43 ± 0.25</td>
<td>7.51 ± 0.10</td>
<td>7.31 ± 0.03</td>
<td>7.25 ± 0.05</td>
</tr>
<tr>
<td>( \log K_{001} ) (HL)</td>
<td>4.13 ± 0.21</td>
<td>4.14 ± 0.22</td>
<td>4.21 ± 0.03</td>
<td>4.15 ± 0.06</td>
</tr>
<tr>
<td>( \log K_{100} ) (NaL)</td>
<td>0.45 ± 0.18</td>
<td>0.41 ± 0.14</td>
<td>0.56 ± 0.02</td>
<td>0.57 ± 0.02</td>
</tr>
<tr>
<td>( \log K_{010} ) (KL)</td>
<td>0.50 ± 0.22</td>
<td>0.46 ± 0.04</td>
<td>0.44 ± 0.03</td>
<td>0.50 ± 0.02</td>
</tr>
<tr>
<td>( \log K_{011} ) (NaHL)</td>
<td>4.49 ± 0.12</td>
<td>4.51 ± 0.30</td>
<td>4.28 ± 0.03</td>
<td>4.27 ± 0.08</td>
</tr>
<tr>
<td>( \log K_{011} ) (KHL)</td>
<td>4.37 ± 0.26</td>
<td>3.99 ± 0.14</td>
<td>4.23 ± 0.08</td>
<td>4.29 ± 0.14</td>
</tr>
<tr>
<td>( \log K_{200} ) (Na(_2)L)</td>
<td>0.54 ± 0.31</td>
<td>0.36 ± 0.14</td>
<td>0.44 ± 0.04</td>
<td>0.48 ± 0.04</td>
</tr>
<tr>
<td>( \log K_{020} ) (K(_2)L)</td>
<td>0.87 ± 0.19</td>
<td>0.52 ± 0.04</td>
<td>0.42 ± 0.04</td>
<td>0.55 ± 0.02</td>
</tr>
<tr>
<td>( f )</td>
<td>1.28 ± 0.16</td>
<td>1.16 ± 0.11</td>
<td>1.23 ± 0.03</td>
<td>1.08 ± 0.04</td>
</tr>
</tbody>
</table>

The numbers obtained for the dissociation constants of tartaric acid are the following:

\[
\begin{align*}
\text{pk}_1 &= 3.40, 3.20, 3.22 \text{ and } 3.12; \\
\text{pk}_2 &= 4.06, 4.10, 4.12 \text{ and } 4.23 - \text{full model} \\
\text{pk}_1 &= 3.30, 3.37, 3.10 \text{ and } 3.10; \\
\text{pk}_2 &= 4.13, 4.14, 4.21 \text{ and } 4.15 - \text{simplified model}
\end{align*}
\]

They are comparable with those found in the literature [18]: \( \text{pk}_1 = 3.03 \) and \( \text{pk}_2 = 4.12 \) (at \( I = 1.00 \text{ mol L}^{-1} \) and \( T = 37^\circ C \); \( k_1 = K_{001}/K_{002}, k_2 = 1/K_{001} \). The protonation constants of dicarboxylic acids, obtained under assumption that no complexes are formed by HL and L and cations of basal (background) electrolyte (e.g. Na\(^+\)), are somewhat smaller than those found from the more complex models under similar conditions [18, 19] (ionic strength, temperature). For this reason, tetraethylammonium iodide (NE\(_4\)I) was considered as the electrolyte providing the species do not form the complexes in aqueous media. The comparative studies were made in order to find the influence of cations: Na\(^+\) and NE\(_4\)\(^+\) on the \( K_{001} \) and \( K_{002} \) values [19]. The NaHL and NaL complexes were assumed in the model formulated for this purpose; NE\(_4\)\(^+\) was considered \( (a \text{ priori}) \) as unable to form similar complexes. Likewise, the protonation constants of tartaric acid found from our models (full and simplified) provide similar regularities. Thus the data found for \( K_{110} \), although comparable with their standard deviations, seem to be a useful information about the system [20].
Evaluation of equilibrium constants

**Full Model.** The values found for $K_{101}$ and $K_{011}$ (for NaHL and KHL) are similar although KHL seems to be stronger in most cases, except Series 1 (with Na⁺ predominating over K⁺) where NaHL appears to be stronger. The precipitate KHL was not formed under the conditions assumed. A better inspection of the strength of the complexes of MHL type provides the value $K^\text{HL}_M$, $[\text{MHL}] = K^\text{HL}_M [\text{M}] [\text{HL}]$. The formation constants found are:

$$
\log K^\text{HL}_{\text{Na}} = 0.59, 0.00, 0.07, 0.04 \text{ for NaHL (} K^\text{HL}_{\text{Na}} = K_{101}/K_{001}) $$

$$
\log K^\text{HL}_K = 0.4, 0.42, 0.39, 0.31 \text{ for KHL (} K^\text{HL}_K = K_{011}/K_{001})
$$

Apparently, potassium hydrotartrate complexes are more stable. According to these data, it can be assumed that the stability of sodium complexes depends on concentration of Na⁺ in the solution and, on the other hand, potassium complexes do not show this dependency.

The values for NaL and KL are: $\log K_{100} = 0.65 \pm 0.04$ and $\log K_{010} = 0.55 \pm 0.09$. Referring to double and mixed complexes we have: $\log K_{200} = 0.57 \pm 0.09$ for Na₂L, $\log K_{020} = 0.60 \pm 0.21$ for K₂L and $\log K_{110} = 0.15 \pm 0.18$ for NaKL.

The $f = (f)_{\%e=0}$ values found for the series were 1.24, 1.04, 1.22 and 1.06 (Fig. 2). It seems that $f$ is affected by composition of the solution considered. High concentration of Na⁺ affects the activity coefficient as well [11]. The $f$ value found for series 1 and 3 was higher although the ionic strength was the same ($I = 1.645 \text{ mol l}^{-1}$) in all series. It should be stressed that the activity coefficient was considered as one of the

![Figure 2](image.png)

*Figure 2. The points (% e, f) related to all series*
equilibrium constants of the system in question, i.e. the related calculations were not aided by the doubtful empirical formulae for \( f \) value.

**Simplified Model.** The decision of omitting the mixed complex NaKL in the model resulted from the fact that \( K_{110} \) value appeared to be low and comparable with its standard deviation [20].

The differences between stability constants for NaL and KL (\( \log K_{100} = 0.50 \pm 0.08 \) and \( \log K_{010} = 0.48 \pm 0.03 \), respectively) are insignificant within confidence limits and comparable with ones found in full model. Analogous remark refers to the double complexes: \( \log K_{200} = 0.46 \pm 0.08 \) for Na2L, \( \log K_{020} = 0.59 \pm 0.20 \) for K2L.

Omission of NaKL in the model affects more distinctly the \( K_{101} \) and \( K_{011} \) values; the stabilities of NaHL and KHL are still comparable although the sodium complexes appear to be more stable this time. The related constants are: \( \log K_{Na}^{HL} = 0.36, 0.37, 0.07, 0.12 \) for NaHL and: \( \log K_{K}^{HL} = 0.24, -0.15, 0.02, 0.14 \) for KHL.

The simplification of the model affected the \( f \) value only in a slight degree. In compliance with the full model, the results in series 1 and 3 were higher then in series 2 and 4. According to these results it can be inferred that the \( f \) values are not affected by the model applied as much as by the composition of the solution [19].

**CONCLUSIONS**

The methodology applied in this paper is applicable to solving different problems involved with handling the results obtained from potentiometric (pH-metric) titration, particularly the ones carried out in solutions of high ionic strength (\( I = 1.645 \) mol \( \text{L}^{-1} \)). The constancy of ionic strength and total concentration of the acid in the system is possible if the D+T system is prepared according to the unconventional procedure described in reference [8], being a substantial improvement upon the conventional one. In addition, the similarity between D and T provides the assumptions concerning both constancy of dielectric permeability, and additivity of volumes valid in the titration process.

Omission of the NaKL in the set of complexes does not improve significantly the data for the remaining parameters of the system and makes the omission of the incriminated complex doubtful.

**REFERENCES**

Evaluation of equilibrium constants


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