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## Methodological Aspects in the Study of Alkali Metal Ion Weak Complexes Using Different ISEs Electrodes

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The detection of alkali metal complex formation with polycarboxylate, hydroxo-polycarboxylate and amino-polycarboxylate ligands has been investigated employing ISE- $\text{Na}^+$  potentiometry. To minimize the effects due to the variation of activity coefficients, a set of measurements were made at constant ionic strength. The formation of alkali metal complexes in solution has been evidenced unequivocally comparing the experimental values of free  $\text{Na}^+$  ions with those of total sodium added for each point of titration curve. There are no doubts about the formation of alkali metal complexes in solution. After detection, the formation constants were determined and their values, compared with those evaluated by pH-metric technique (previously) or by ISE- $\text{Na}^+$  potentiometry at variable ionic strengths (this work), show a good agreement, suggesting that also potentiometric techniques at variable ionic strengths can be used in the study of this topic with a good accuracy. Moreover, our results confirm the low stability of alkali metal complexes (ion pairs) in aqueous solution, which is founded on coulomb interactions. In general, the values of stability constants depend not only on the number of charged oxygen donor groups, but also on the presence of amino donor(s) (NTA, EDTA and EDDS) and hydroxyl group (citrate).

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**Keywords:** sodium, ion pairs, weak complexes, ISE potentiometry, polycarboxylic acids.

### 1. INTRODUCTION

The coordination chemistry in solution of alkali metal ions was relatively little investigated, in particular if compared with the great number of results reported in the literature for complexes of transition metal ions. All the classical experimental techniques were employed in determining the formation constants of weak complexes (ion pairs), so as reported in the review of Marcus and Hefter [1]. Among the other experimental methods, potentiometry, NMR, calorimetry, circular dichroism and

dilatometry were employed to study the formation in solution of alkali metal complexes.

In a recent review [2] we focused the main reasons for the scarce interest in this topic and, in this connection, the weakness of alkali metal ion pairs is certainly an important factor. As well known, the pH-metric classical method for determination of stability constants is based on the competition for the ligand molecule between the cation investigated and the hydrogen ion. In general, for the most of ligands, the alkali metal cations are scarcely competitive towards  $H^+$ , hence their effect on the pH variation may be small. Furthermore, the not great pH variation can be assigned with certainty to the complexation reaction only if the values of the activity coefficients at the ionic strength under investigation are known with a good accuracy. In the last decades we proposed several papers [3-17] dealing with complexes or ion pairs of alkali metal ions, in which the conditional (at a fixed ionic strength) formation constants were calculated from pH-metric data obtained at different ionic strengths, taking rigorously into account the variation of activity coefficients as a function of ionic strength, but avoiding explicit calculations of their values. In the NEA report [18] dealing with the citrate complexes, the determination of formation constants of alkali metal complexes with citrate ion [19] by ISE potentiometric measurements was discussed. According to the NEA authors [18], the existence of citrate complexes with alkali metal ions "should not be considered as completely proven" because the above measurements [19] were carried out at different ionic strengths and therefore the results depend on the model used for activity coefficients.

The results reported in this paper were obtained elaborating ISE potentiometric data at ionic strength values kept, as far as possible, constant over the experiment, in order to compare the formation constants values so calculated with those determined at the same ionic strength, elaborating experimental data from potentiometric measurements at variable ionic strength. From the comparison, extended to the results from some ISE- $Na^+$  measurements at variable ionic strengths, we aim to draw some conclusions about the reliability of our pH-metric based chemical model at variable ionic strength for the evaluation of weak complex formation constants. The investigation regarded the complexes of sodium with some carboxylic and aminocarboxylic ligands, namely acetate, benzoate, malonate, phthalate, citrate, mellitate, nitrilotriacetate, ethylenediaminetetraacetate and ethylenediamine-N,N'-disuccinate.

## 2. EXPERIMENTAL PART

### 2.1. Chemicals

Sodium chloride (purity of 99.5%) was from Sigma-Aldrich and before use was maintained at 120°C for almost 2 hours. Tetrabutylammonium bromide ( $Bu_4NBr$ , purity of 99.0%), tetraethylammonium iodide ( $Et_4NI$ , purity  $\geq 98.5\%$ ), tetrabutylammonium hydroxide (stock solution 1.0 mol  $L^{-1}$ ) and tetraethylammonium hydroxide (stock solution 1.0 mol  $L^{-1}$ ) were from Fluka. Citric (*cit*) and malonic (*mal*) acids were Merck products (purity of 99.5% and 99% respectively). Acetic, Nitrilotriacetic (NTA), ethylenediaminetetraacetic (EDTA), ethylenediamine-N,N'-disuccinic acid (EDDS) and 1,2,3,4-butanetetracarboxylic (*btc*) acids were Sigma-Aldrich products (purity of 99.7%,

99%, 99.995%, 35% in water and 99.5% respectively). Benzoic and Phthalic acid (*phthal*) were from Carlo Erba (purity of 99.5%). Mellitic acid (*mlt*) was from Fluka (purity  $\geq 98\%$ ).

Grade A glassware and deionised and twice distilled water were used for all the solutions.

Tetrabutylammonium hydroxide solution was standardized against potassium hydrogen phthalate (Fluka, puriss.) and the purity of the acids was evaluated by pH-metric titrations.

## 2.2. Potentiometric apparatuses

Two potentiometric apparatus were used in this paper, both of them consisted of a Metrohm potentiometer (resolution of  $\pm 0.1$  mV), used for the measurement of the electromotive force (e.m.f.) of the ISE- $\text{Na}^+$  and ISE- $\text{H}^+$  electrodes.

In the first set up, the ISE- $\text{Na}^+$  electrode was purchased by Metrohm (model 6.0501.000) and was combined with an Ag/AgCl reference electrode (Metrohm, 6.0733.100). The sodium-selective electrode has a selectivity constant of  $2 \cdot 10^{-2}$  with respect to  $\text{H}^+$ . The system was equipped with a combined  $\text{H}^+$  glass electrode (Metrohm, 6.0222.100). Temperature control was achieved by means of water circulation, in the outer chamber of the titration cell from a thermocryostat (model D1-G Haake). The titrant ( $\text{NaCl}$  solution  $0.1 \text{ mol L}^{-1}$ ) was dispensed with a 765 Dosimat (minimum deliverable volume of  $\pm 0.001$  mL) burette by Metrohm.

In the case of the second set up, the Metrohm 713 potentiometer was equipped with a combined sodium-selective electrode (Orion, model 86-11), whereas the pH measurements were performed with a combined  $\text{H}^+$  glass electrode (Metrohm, model 6.0224.100). Temperature control was achieved by means of water circulation, in the outer chamber of the titration cell from a thermocryostat (model D1-G Haake). The titrant ( $\text{NaCl}$  solution  $0.1 \text{ mol L}^{-1}$ ) was delivered with a 665 Dosimat (minimum deliverable volume of  $\pm 0.001$  mL) burette by Metrohm.

## 2.3. Procedure used for potentiometric titrations

Two procedures were used in this paper, to obtain different information on the formation of alkali metal ion weak complexes. In the first case, the choice of the ligand to metal ratios and of the quantities of sodium titrant added was made in order to keep constant the value of the ionic strength during the experiment and obtain the maximum of percentage complex formation with respect to sodium. The procedure adopted is as follows: the ionic strength was adjusted with  $\text{Bu}_4\text{NBr}$ , at  $I = 0.1 \text{ mol L}^{-1}$ , for the NTA and EDTA systems, and  $I = 0.3 \text{ mol L}^{-1}$ , for the *phthal*, *mal*, *cit* and *btc* systems. The concentration of the ligands were: *cit*  $0.0475 \text{ mol L}^{-1}$ , EDTA  $0.0100 \text{ mol L}^{-1}$ , *mal*  $0.100 \text{ mol L}^{-1}$ , NTA  $0.0167 \text{ mol L}^{-1}$ , *phthal*  $0.100 \text{ mol L}^{-1}$ , *btc*  $0.0100 \text{ mol L}^{-1}$ , while the concentration of  $\text{NaCl}$  added as titrant ranged between  $1.00 \cdot 10^{-4}$  to  $4.8 \cdot 10^{-4} \text{ mol L}^{-1}$ .

To evaluate how the variation of ionic strength during titration can affect the experimental results, a second procedure was adopted for *cit* system. In this case, the ionic strength was adjusted with  $\text{Et}_4\text{NI}$  at  $I = 0.3 \text{ mol L}^{-1}$  and *cit* concentration ranged between  $0.015 \leq c_{\text{L}}/\text{mol L}^{-1} \leq 0.030$ . Similar conditions were also adopted for the *mlt* and EDDS systems. The ionic strength was adjusted at  $I = 0.3$

and  $0.4 \text{ mol L}^{-1}$  for the *mlt* system and at  $I = 0.3, 0.4$  and  $0.5 \text{ mol L}^{-1}$  for the EDDS system. The ligand concentration ranged between  $0.010 \leq c_L/\text{mol L}^{-1} \leq 0.021$  (*mlt*) and  $0.010 \leq c_L/\text{mol L}^{-1} \leq 0.040$  (EDDS), whereas the concentration of NaCl added as titrant between  $1.00 \cdot 10^{-4} \leq c_{\text{NaCl}}/\text{mol L}^{-1} \leq 1.5 \cdot 10^{-2}$ . The higher is the ligand concentration, the greater variation of ionic strength during titration. As an example, the ionic strength value due to the presence of *mlt*, when  $c_L = 0.0146 \text{ mol L}^{-1}$ , is  $I = 0.3068 \text{ mol L}^{-1}$ . In our calculations the variation of ionic strength during titration and its effect on activity coefficients were taken into account, so as described below.

In both procedures, the solutions were basified at  $\text{pH} \sim 10\text{-}11$  with tetraalkylammonium hydroxide to maintain the acids in the dissociated form and to avoid the interference of  $\text{H}^+$  ions. The titrations were carried out in a stream of purified nitrogen gently bubbled in the titration cell to avoid  $\text{CO}_2$  contamination, which could acidify the solution interfering with the e.m.f. measurement. The couple was calibrated in  $-\log[\text{Na}^+]$  units (pNa) recording the e.m.f. values obtained adding known volumes of NaCl solution  $0.1 \text{ mol L}^{-1}$  in a tetraalkylammonium halide solution. The  $\text{Na}^+$  concentration of calibrating solutions ranges between  $2 \cdot 10^{-4}$  and  $5 \cdot 10^{-3} \text{ mol L}^{-1}$  and the ionic strength was the same as the solutions being examined, controlled with tetraalkylammonium halide. Even the calibration solutions were basified at  $\text{pH} \sim 10\text{-}11$  with tetraalkylammonium hydroxide. Each titration was repeated in triplicate and, to check the stability of the electrode response, before each titration the calibration procedure was repeated.

#### 2.4. ICP-OES measurements

The sodium impurities in the solution under titration were quantified by ICP measurements, performed by a model Liberty – Series II ICP-OES Varian spectrometer. The contribution of sodium impurities is not negligible ( $2.5 \cdot 10^{-5} \text{ mol L}^{-1}$  as mean value), in particular with low concentrations of sodium titrant added.

#### 2.5. Data analysis and calculations

The non-linear least squares computer program ESAB2M [20] was used for the refinement of all the parameters of the acid-base titrations ( $E^0$ ,  $K_w$ , liquid junction potential coefficient,  $j_a$ , analytical concentration of reagents). The non-linear least squares BSTAC and STACO [21] computer programs were used in the calculation of complex formation constants. Both programs can deal with measurements at different ionic strengths. The ES4ECI [21] program was used to draw the speciation and sequestration diagrams, and to calculate species formation percentages. The linear and non-linear computer program LIANA [22] was used to fit the experimental data by means of the equations reported in the next sections.

The slope of the Nernst equation for the sodium-selective electrode was checked and in all cases resulted equal to  $59.2 \pm 0.1 \text{ mV}$  at  $25^\circ\text{C}$ , therefore the tabulated slope of  $59.16 \text{ mV}$  was used. The same program was used for the elaboration of titration points for each metal-ligand system in order to calculate the stability constant of ion pair Na-acid. The electrode formal potential considered

in the elaboration was the daily mean value. In the calculation both of  $E^0$  values and of formation constants, we took into account the presence of unavoidable impurities of sodium in the reactants. The concentration of sodium impurities was well confirmed by ICP measurements.

The uncertainty budgets are evaluated in accordance with recommended procedures [23-25] using commercial spreadsheets.

As regards the measurements for which the ionic strength is not constant, the variation of activity coefficients has been taken into account by the procedure explained in the below Section *Experimental evidence of weak complexes with measurements at variable ionic strength*.

All species reported in this paper can be expressed according to the following equilibria:



where  $p$  and  $q$  are the stoichiometric coefficients, whereas  $n$  is the charge of the fully deprotonated ligand (*e.g.*, for EDTA  $n = 4$ ).

### 3. RESULTS AND DISCUSSION

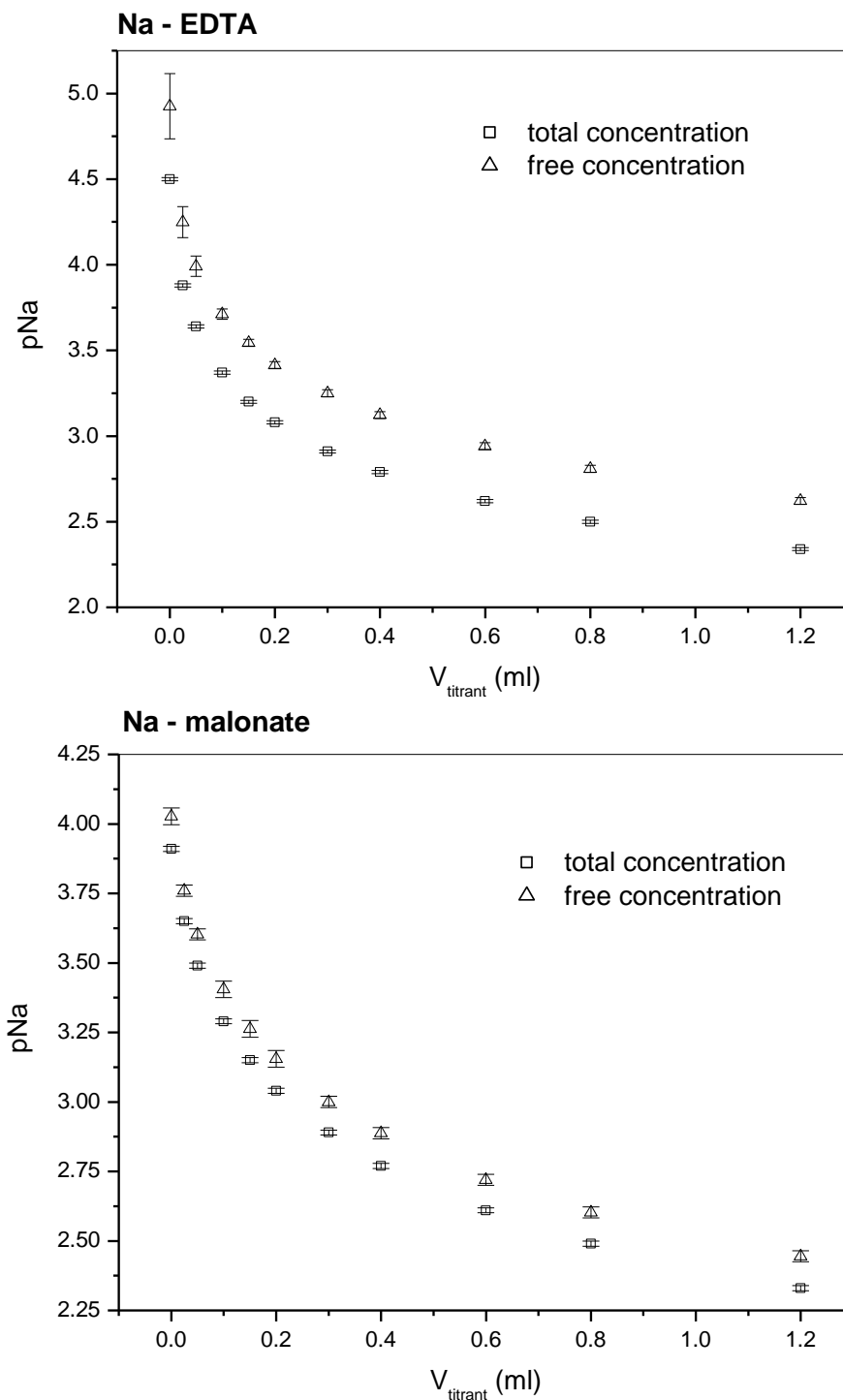
#### 3.1. Experimental evidence of weak complexes with measurements at constant ionic strength

The free sodium concentration in solution is always lowered by the addition of the ligands investigated in this work. As an example, in Fig. 1, we reported a comparison between the measured pNa at different titrant volumes added and the pNa resultant from the total Na concentration in the solution, for Na-EDTA and Na-*mal* systems. Since the value of ionic strength during experiments is kept constant and the values of activity coefficients, with a good approximation, do not vary significantly, this effect, as more significant as the number of potential donor groups involved increases, can only depend on the complexation of sodium ions.

In order to support the experimental evidence of the complex formation, an estimation of pNa combined uncertainty is proposed. The uncertainty budgets are evaluated following the procedure described in ref. [26] for a potentiometric apparatus calibrated according to the concentration scale. The procedure is in accordance with the metrological literature recommendation [23-25]. For pNa uncertainty budget, we must consider the contributions acting on formal potential  $E^0$ , to the potential reading  $E$  and to the junction potential  $E_j$ . The standard uncertainty is:

$$u_c(\text{pNa}) = [(u(E^0) c(E^0))^2 + (u(E) c(E))^2 + (u(E_j) c(E_j))^2]^{0.5} \quad (3)$$

where the terms  $c(x_i) = \partial(\text{pNa})/\partial x_i$  are the sensitivity coefficients of  $E^0$ ,  $E$ , and  $E_j$  all equal to  $1/s$  (as above underlined, we fixed the slope  $s = 59.16$  mV).



**Figure 1** Comparison between the measured pNa at different titrant volumes added (titrant NaCl 0.1 mol L<sup>-1</sup>) and the pNa resultant from the total Na concentration in the solution, for Na-EDTA and Na-malonate systems. The measured pNa are the means of values obtained with 6 replicates and the error bars represent the extended uncertainty  $U(\text{pNa})$  (see *Uncertainty budget* paragraph). Total Na concentration takes into account the concentration of Na at  $V_{\text{titrant}} = 0$  mL.

Evaluation of  $E^0$  is run by means of a refinement procedure based on the treatment of titration data; similarly, the uncertainty estimation must follow the same path. Four quantities contribute to the overall uncertainty of  $E^0$ :

1) the relative standard uncertainty on volume of the calibration solution  $u(V)$  (total volume 25 mL). The estimation of  $u(V)$  has been assessed on 0.08%.

2) The resolution of the automatic burette. The estimation of  $u(V_{\text{tit}})$  (relative uncertainty on volume dispensed by the automatic burette) has been assessed on 0.12%, assuming a triangular distribution on the stated accuracy of the burette.

3) The resolution of the potentiometer. The estimation of  $u(E)$  (relative uncertainty on potential reading) has been assessed on 0.10%, assuming a rectangular distribution on the instrument resolution and considering a value of 55 mV (the first point of the titration considered in the  $E^0$  refinement).

4) The standard deviation on  $E^0$  from the refinement process. The values of standard deviation on  $E^0$  has been evaluated by BSTAC [21] and ranged between 0.005 and 0.16 mV. It accounts for the accordance degree between experimental and calculated titration curves taking into account in the calculation the covariance(s) among the parameters under refinement.

The uncertainty contribution of the concentration of titrant solution,  $u(C_{\text{NaCl}})$ , resulted negligible.

Combining the aforementioned contributions we obtained a relative standard uncertainty of  $E^0$  ranging between 0.19 and 0.24%.

The uncertainty contribution on  $E$  was evaluated considering the potential resolution and the repeatability for each titration point. The uncertainty contribution of the  $E_j$ ,  $u(E_j)$ , resulted negligible.

For each pNa value obtained during the titration we calculated the combined standard uncertainty  $u_c(\text{pNa})$  and the extended  $U(\text{pNa})$ , using a coverage factor  $k = 2$ . The  $U(\text{pNa})$  values range between 0.02 and 0.2 units, and higher values are calculated for the titration points at the beginning of the titration. In the calculation of  $\log\beta$  values low weights are attributed to these points.

The uncertainty of the total Na concentration in the solution -  $u_c(\text{pNa}_{\text{tot}})$  - was also calculated. Three quantities contribute to the overall uncertainty of total Na concentration: i) the relative standard uncertainty on the volume of the solution  $u(V)$  (total volume 25 mL). The estimation of  $u(V)$  has been assessed on 0.33%; ii) the relative standard uncertainty on the concentration of titrant solution,  $u(C_{\text{NaCl}})$ , equal to 0.095%; iii) the resolution of the automatic burette. The estimation of  $u(V_{\text{tit}})$  (relative uncertainty on volume dispensed by the automatic burette) has been assessed on 0.3%, assuming a triangular distribution on the stated accuracy of the burette.

The combined standard uncertainty  $u_c(\text{pNa}_{\text{tot}})$  for pNa = 3 is 0.0046 and the extended  $U(\text{pNa})$ , using a coverage factor  $k = 2$ , is 0.009.

### 3.2. Experimental evidence of weak complexes with measurements at variable ionic strength

As already pointed out in the experimental section, a second set of measurements was made with variable ionic strength (in a small concentration range) during the titration, owing to the high charge of ligands (e.g. for mellitic acid,  $z = 6$ ) as well as their relatively high concentration, up to 20

mmol L<sup>-1</sup>. In this light, together with the uncertainty budget considered in the previous section, we must add a term relative to the variation of the  $E^0$  and  $\log\beta$  with ionic strength during a titration. For example, considering the titration n° 2 of the Na/mlt system, where  $c_{\text{mlt}} = 0.010 \text{ mol L}^{-1}$ , we can note that the ionic strength value is  $I = 0.301 \text{ mol L}^{-1}$  at the beginning of the titration, whereas is  $I = 0.244 \text{ mol L}^{-1}$  at the end of the titration, and the average ionic strength value is  $I = 0.283 \text{ mol L}^{-1}$ . In the refinement process, the computer program BSTAC [21] uses a Debye-Hückel smoothing function for the correction of both  $E^0$  and  $\log\beta$ , such as:

$$\log\beta(I) = \log\beta(I=0.3\text{M}) - z^* \cdot 0.51 \cdot I^{0.5}/(1+1.5 \cdot I^{0.5}) + C \cdot I \quad (4)$$

where  $z^* = \Sigma (\text{charge})_{\text{react}}^2 - \Sigma (\text{charge})_{\text{prod}}^2$  and C is an empirical parameter. Rearranging eq. (4) we obtain:

$$\log\beta(I=0.3\text{M}) = \log\beta(I) + z^* \cdot 0.51 \cdot I^{0.5}/(1+1.5 \cdot I^{0.5}) + C \cdot I \quad (5)$$

therefore, the uncertainty on the  $\log\beta(I = 0.3 \text{ M})$  is given by the error propagation and is:

$$u(\log\beta_{(I=0.3\text{M})}) = (\sigma_{\log\beta_{\text{exp}}}^2 + ((\partial(\log\beta_{(I=0.3\text{M})})/\partial I) \sigma_I)^2 + ((\partial(\log\beta_{(I=0.3\text{M})})/\partial C) \sigma_C)^2)^{0.5} \quad (6)$$

where  $\sigma_{\log\beta_{\text{exp}}}$  is the standard deviation on the stability constant calculated by the computer program, whereas C is the parameter that accounts for the ionic strength dependence in the measurements. Assuming that the ionic strength value is free from error and  $\log\beta_{\text{exp}}$  is constant, we obtain:

$$u(\log\beta_{(I=0.3\text{M})}) = (\sigma_{\log\beta_{\text{exp}}}^2 + ((\partial(\log\beta_{(I=0.3\text{M})})/\partial C) \sigma_C)^2)^{0.5}$$

and calculating the derivative, we have:

$$u(\log\beta_{(I=0.3\text{M})}) = (\sigma_{\log\beta_{\text{exp}}}^2 + (\Delta I \cdot \sigma_C)^2)^{0.5}$$

where  $\Delta I = (I - I_{\text{ref}})$ . Numerically, when  $\Delta I = 0.05$  and  $\sigma_C = 0.03$ ,  $u(\log\beta_{(I=0.3\text{M})}) \sim 0.003$ .

### 3.3. Formation constants

The values of formation constants of 1:1 sodium - ligand complexes obtained in Bu<sub>4</sub>NBr and in Et<sub>4</sub>NI at different ionic strengths, and maintaining or not the same ionic conditions during the titration, are collected in Table 1. The corresponding values calculated at the same ionic strength by employing pH-metric technique [5, 6, 9, 13] starting from the protonation constants determined in different ionic media, are also reported. The agreement may be considered quite good, especially if considering that we deal with weak complexes.



Our investigation also included monocarboxylic acids, such as acetic and benzoic acids, but in this case the very weak complex formation might cause small e.m.f. variation, which falls within the limits of error in  $E^0$  value.

As regards the speciation models, in this paper we can only report the formation of ML species, and only in the case of mellitic acid of the  $M_2L$  complex. This is due to the experimental procedure adopted, in particular we performed measurements at high pH values, therefore we cannot determine the formation of protonated species, such as MHL or successive  $MH_qL$  species, that are reported for many systems. Furthermore, owing to the relative low M:L concentration ratio, the formation percentages of polynuclear  $M_pL$  species is low, hampering their determination. For this purpose, the calculation of weak complexes, by means of protonation measurements in different ionic media is more suitable.

For citrate, in the past, Daniele *et al.* [9] reported the formation of three species, namely *Nacit*, *NaHcit* and *Na<sub>2</sub>cit*, calculating the alkali metal weak complexes determining the protonation of citrate in different ionic media at different ionic strengths. The stability of the *Na<sub>2</sub>cit* species is higher than that of the *Nacit* one by 0.5 logK units almost at any ionic strength values, whereas for the *NaHcit* species they report values of 6.43, 6.45 and 6.75 (expressed as in eq. (1)) at  $I = 0.1, 0.5$  and  $1.0 \text{ mol L}^{-1}$ , respectively.

For mellitate, De Robertis *et al.* [27], reported the formation of twelve species, namely  $M_pL$  (with  $1 \leq p \leq 4$ ),  $M_pHL$  (with  $1 \leq p \leq 3$ ),  $M_pH_2L$  (with  $1 \leq p \leq 2$ ) and  $M_pH_3L$  (with  $1 \leq p \leq 2$ ). Also in this case the stabilities of alkali weak complexes were calculated starting from protonation constants in different ionic media at different ionic strengths. There is a good agreement between the stability of the ML and the  $M_2L$  species found in this paper and in that of De Robertis *et al.*

**Table 1.** Stability constant values of the NaL complexes expressed as  $\log\beta_{NaL} \pm 2\sigma$ . The experimental values were determined for various ligands (L) in  $Bu_4NBr$  or  $Et_4NI$ , at different ionic strengths (expressed as  $\text{mol L}^{-1}$ ) and  $t = 25^\circ\text{C}$ .

L	$\log\beta_{NaL}$							
	$I = 0$	$I = 0.1^f$	$I = 0.1$	$I = 0.3^f$	$I = 0.3^h$	$I = 0.3$	$I = 0.4^h$	$I = 0.5^h$
<i>mlt</i>	3.06 <sup>a)</sup>				1.91 ± 0.01		1.94 ± 0.02	
<i>mlt</i>	4.75 <sup>a1)</sup>				3.48 ± 0.02		3.54 ± 0.02	
EDTA	2.54 <sup>b)</sup>	2.04 ± 0.02	1.84 <sup>g)</sup>					
NTA	1.90 <sup>b)</sup>	1.46 ± 0.03	1.35 <sup>g)</sup>					
<i>btc</i>	1.82 <sup>c)</sup>			1.06 ± 0.06		1.07 <sup>c)</sup>		
<i>cit</i>	1.53 <sup>d)</sup>			1.12 ± 0.02	1.04 ± 0.01	0.98 <sup>d)</sup>		
EDDS					0.940 ± 0.005		0.913 ± 0.004	0.868 ± 0.005
<i>phthal</i>	1.02 <sup>e)</sup>			0.60 ± 0.03		0.75 <sup>e)</sup>		
<i>mal</i>	0.91 <sup>e)</sup>			0.48 ± 0.02		0.58 <sup>e)</sup>		

<sup>a)</sup> calculated from ref. [27]; <sup>a1)</sup>  $\log\beta$  for binuclear complex  $Na_2L$ ; <sup>b)</sup> calculated from ref. [5]; <sup>c)</sup> calculated from ref. [13]; <sup>d)</sup> calculated from ref. [9]; <sup>e)</sup> calculated from ref. [6]; <sup>f)</sup> this work, values measured at constant ionic strength in  $Bu_4NBr$ ; <sup>g)</sup> ref. [5]; <sup>h)</sup> this work, values measured at variable ionic strength in  $Et_4NI$ .

#### 4. CONCLUSIONS

The formation of alkali metal complexes with polycarboxylate ligands is clearly shown by our results and their existence cannot be further questioned.

With the aim of correctly solving analytical problems, in building chemical speciation models for interpretation of natural chemical system behaviour, the formation of alkali metal complexes cannot be neglected.

The determination of formation constants of these species can be made by employing ion-selective electrodes, either at constant or at variable ionic strength, but pH-metric measurements of protonation constants at different ionic strengths can allow to estimate them with a quite good accuracy, particularly if considering the weakness of the chemical species investigated. Furthermore, by employing pH-metric readings, we are allowed to determine the formation of protonated species (important for polyprotic ligands) as well, whose percentage of formation, in the experimental conditions suitable for the use of Na<sup>+</sup>-ISE electrode, is negligible.

As regards the values of stability constants, they depend not only on the number of charged coordinating groups in the ligand molecule but also (i) on the nitrogen donor group(s), as shown by the formation constant values calculated for NTA, EDTA and EDDS, and (ii) on the presence of hydroxyl group as revealed by the citrate ion binding properties.

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