

EFFECTS OF SALT CONCENTRATION AND COUNTERION ON STABILITY OF ALKALI ION-18-CROWN-6 COMPLEXES IN AQUEOUS AND METHANOLIC SOLUTION: A CONFLICTING EVIDENCE FROM POTENTIOMETRIC AND SODIUM-23 NMR STUDIES*

Jiří ZÁVADA, Václav PECHANEC, Jaroslav ZAJÍČEK, Ivan STIBOR and Antonín VÍTEK

*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6*

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Contrary to expectation, the title effects observed concurrently by potentiometry with ion-selective electrode and by sodium-23 NMR spectroscopy are completely different. The potentiometric stability constants for the sodium ion-18-crown-6 complex (K_{ISE}) exhibit a very pronounced variation with the counterion, $K_{ISE}^{NaSCN} > K_{ISE}^{NaCl} > K_{ISE}^{NaOH}$, as well as with the sodium salt concentration, the $K_{ISE}^{NaSCN}/K_{ISE}^{NaOH}$ ratio being about 1.5, 2.0, 5.0 and 20 in the 0.01, 0.1, 0.5 and 1.0 mol l⁻¹ aqueous and about 2.0, 12, 600 and 2 500 in the 0.01, 0.1, 0.5 and 1.0 mol l⁻¹ methanolic solution, respectively. Whereas, the corresponding spectroscopic stability constants, K_{NMR} , are virtually insensitive to the changes of counterion as well as to the salt concentration, the overall spread of the K_{NMR} values being less than 3. Resolution for the conflicting evidence is provided in terms of the activity coefficients γ_{ML+} , γ_{M+} , γ_L differentiating between the concentration (K_{conc}) and thermodynamic (K_{th}) stability constants in the relation $K_{conc} = (\gamma_{M+}\gamma_L : \gamma_{ML+}) K_{th}$. At variance with the current opinion it is shown that only K_{ISE} are clean concentration constants subjected to the $\gamma_{ML+}/\gamma_{M+}\gamma_L$ variation, while K_{NMR} are hybrids between the concentration and thermodynamic constant leaning assumedly to the latter (K_{th}). Concerning the powerful effect of counterion and salt concentration of K_{ISE} , it is attributed to a large variation of γ_{ML+} . No satisfactory explanation can be, however, offered in customary terms of the Debye-Hückel theory.

Recently, we have investigated ebullioscopically alkali cation-crown complexation in hydroxylic solutions^{1,2}. Unexpectedly, a powerful effect of counterion has been discovered^{2,3} in course of the study. In ethanol² and methanol³, e.g., titration of alkali thiocyanate (KSCN or NaSCN) solution with 18-crown-6 (18C6) gave ebullioscopic curves that were almost identical with the theoretical trace calculated for a quantitative 1 : 1 complex formation. Whereas, titration of the corresponding alkali alkoxide solution with the same crown gave ebullioscopic curves that fitted with the calculated trace for a complete absence of the crown complex formation. Qualitatively similar counterion effects have been found² also in aqueous solution.

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No definite explanation could be given for these observation on basis of the ebullioscopic evidence. Although examples are known from literature^{4,5} that counterion can affect stability of cation-crown complexes in homogeneous solution, all the reported cases concern poorly solvating media and are thus explicable by differences in ion-pairing. In strongly solvating media, as are ethanol, methanol and in particular water, ion-pairing is assumed to be only of a minor importance and cannot thus account for the pronounced effect of counterion. Some other, as yet unidentified, interaction must be therefore involved.

In order to shed light on the unresolved problem, we have investigated the effect of counterion and salt concentration on alkali ion-18C6 complex formation by independent physico-chemical procedures. In this paper we report results obtained by potentiometry with sodium selective electrode and by sodium-23 NMR measurements.

EXPERIMENTAL

Materials: The sodium salts were of analytical grade quality (Lachema). 18-Crown-6 was prepared by the described procedure⁶ and recrystallized from hexane. Solvents were distilled before use.

Potentiometric Measurements

Apparatus: The concentration of the uncomplexed cation was measured with Crytur sodium ion selective electrode (Monokrystal, Turnov). In methanol the electrode was conditioned analogously as described by Frensdorff⁷. A saturated calomel electrode was used as reference; an additional salt bridge (0.3 mol l^{-1} aqueous solution of tetramethylammonium chloride) was employed in methanolic solutions. The emf was measured with a precision digital OP-208/1 PH-meter (Radelkis, Budapest) in a closed glass cell (30 ml volume) equipped with a magnetic stirrer and inlets for the two electrodes.

Procedure: The electrode system was calibrated for each alkali salt-solvent combination in $0.001-1.0 \text{ mol l}^{-1}$ concentration region. In water the calibration plots (mV vs $\log C$) were practically linear. Almost identical slopes were obtained for all the three investigated salts NaSCN, NaCl, NaOH ($56 \pm 5 \text{ mV}/\log C$ unit). In methanol the calibration plot was linear with NaSCN ($45 \text{ mV}/\log C$ unit), whereas a marked curvature was obtained with NaOH, the slope increasing gradually from $50 \text{ mV}/\log C$ unit in $0.01-0.1 \text{ mol l}^{-1}$ solution over $60 \text{ mV}/\log C$ unit in 0.1 to 0.5 mol l^{-1} solution to about $95 \text{ mV}/\log C$ unit in $0.5-1.0 \text{ mol l}^{-1}$ solution.

Each complexation run was started with measuring the emf of the salt solution. The 18C6 ligand was then added in 10-15 increments totalling in most instances at least a twofold stoichiometric excess. The crown was added either as a weighed solid (in case of 0.1 mol l^{-1} , 0.5 mol l^{-1} and 1.0 mol l^{-1} salt solutions) or from a micrometer buret (1.0 mol l^{-1} solution of 18C6 was added to 0.01 mol l^{-1} solution of the sodium salt).

Calculation of stability constants: The potentiometric stability constants, K_{ISE} , were calculated from the experimental data using the simplified* Frensdorff equation⁷

* Dilution factor has been neglected in the calculation.

$$K_{\text{ISE}} = \frac{(1-u)}{u[C_{\text{L}}^{\text{tot}} - C_{\text{M}^+}^{\text{tot}}(1-u)]}, \quad (1)$$

where u is the fraction of the sodium ion left uncomplexed, $C_{\text{L}}^{\text{tot}}$ is analytical (total) concentration of 18C6, and $C_{\text{M}^+}^{\text{tot}}$ is total concentration of sodium ion in the solution. The fraction u was calculated from the equation

$$u = 10^{-\Delta V/k}, \quad (2)$$

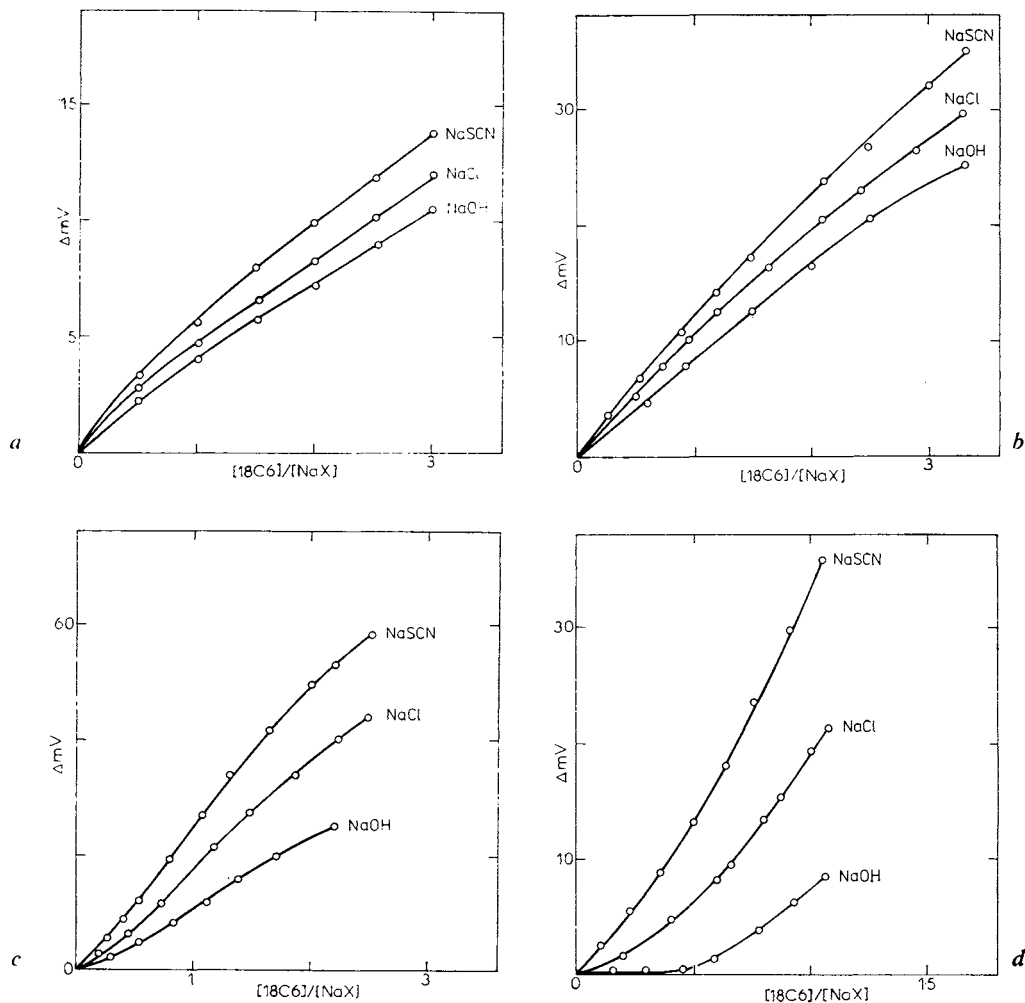


FIG. 1

Potentiometric titration of three different sodium salts (NaX) with 18-crown-6. Initial NaX concentrations: 0.01 mol l^{-1} (a); 0.1 mol l^{-1} (b); 0.5 mol l^{-1} (c); 1.0 mol l^{-1} (d)

where ΔV is the difference between the emf of the salt solution in the absence and in the presence of 18C6 in millivolts and k is the slope in the corresponding calibration plot. In methanolic NaOH solution the calibration plot was non-linear (*vide supra*); to minimize error, the slopes of the corresponding concentration sectors in the calibration plot were used in the calculation.

Sodium-23 NMR Measurements

Apparatus: The measurements were performed with Varian XL-200 spectrometer operating at a magnetic field of 4.7 T in the pulsed Fourier transform mode. The spectrometer was equipped with a 5 mm wide band probe capable of multinuclear operation and with an internal deuterium lock. The solvent contained 2% of deuterium label (D_2O). A 3.0 mol l^{-1} aqueous solution of sodium chloride in sealed capillary was used as an external reference and the reported sodium-23 chemical shifts are referred to this solution. The paramagnetic (downfield) shifts from the reference are designated as positive.

Procedure and calculation of stability constants: Under experimental conditions employed in this study only one population-averaged sodium-23 signal has been invariantly observed whose chemical shift (δ_{obs}) is given by

$$\delta_{obs} = P_f \delta_f + P_c \delta_c, \quad (3)$$

where P_f and P_c are the populations of the cation in the free and in the complexed state, respectively, while δ_f and δ_c are the corresponding chemical shifts. Assuming that only 1:1 complex is formed, the spectroscopic stability constant, K_{NMR} , has been calculated from the experimental parameter using the Popov^{8,9} equation

$$\delta_{obs} = \{ [K_{NMR} C_{M^+}^{tot} - K_{NMR} C_L^{tot} - 1] + [K_{NMR}^2 (C_{M^+}^{tot})^2 + K_{NMR}^2 (C_L^{tot})^2 - 2K_{NMR}^2 C_{M^+}^{tot} C_L^{tot} + 2K_{NMR} C_L^{tot} + 2K_{NMR} C_{M^+}^{tot} + 1] \}^{1/2} \left[\frac{\delta_f - \delta_c}{2K_{NMR} C_{M^+}^{tot}} \right] + \delta_c, \quad (4)$$

where $C_{M^+}^{tot}$ and C_L^{tot} are again the total concentrations of the sodium ion and of the macrocyclic ligand, respectively. In order to solve the Eq. (4), δ_{obs} has been measured as a function of 18C6 sodium ion mole ratio and δ_f has been obtained from the measurement of the sodium salt in absence of the ligand. Using the experimental parameters, the unknown quantities K_{NMR} and δ_c have been adjusted with a non-linear least-squares program.

RESULTS AND DISCUSSION

Effects of Counterion and Salt Concentration Observed with Ion Selective Electrode

The 0.01, 0.1, 0.5 and 1.0 mol l^{-1} aqueous solutions of three different sodium salts (NaOH, NaCl and NaSCN) were titrated with 18C6 and the process was monitored with sodium ion selective electrode. The potentiometric titration curves are given in Fig. 1a–d.

Marked differences due to the sodium counterion are immediately apparent from the titration curves. As a comparison of Fig. 1a–d shows, the differences increase

with increasing overall salt concentration in the solution. Since the calibration potentiometric plots determined from the three salts in the absence of 18C6 are almost identical in the investigated region, the observed differences in the titration curves from Fig. 1a–d are assumed to result from the influences of counterion and salt concentration on the crown complex formation. Stability constants for the complex have been accordingly calculated from the individual titration curves and the results have been summarized in Table I.

Inspection of the horizontal lines in Table I shows the effect of counterion on the sodium complex stability, with the K_{ISE} values decreasing in the order NaSCN > NaCl > NaOH over the full range of the examined salt concentration. The counterion effect is relatively small in the 0.01 mol l⁻¹ solution ($K_{\text{ISE}}^{\text{NaSCN}}/K_{\text{ISE}}^{\text{NaOH}} \sim 1.5$) but it increases gradually on going to the more concentrated solutions; in 1.0 mol l⁻¹ solution the $K_{\text{ISE}}^{\text{NaSCN}}/K_{\text{ISE}}^{\text{NaOH}}$ ratio already approaches the value of about 20.

The vertical columns in Table I allow to assess the effect of salt concentration. A gradual decrease of K_{ISE} values is found on going from 0.01 to 1.0 mol l⁻¹ solution, regardless of anion. However, magnitude of the decrease depends strongly on the counterion, the $K_{\text{ISE}}^{0.01\text{M}}/K_{\text{ISE}}^{1.0\text{M}}$ ratio being about 3 for the thiocyanate, about 10 for the chloride, and about 40 for the hydroxide anion. A close relationship thus exists between the effects of counterion and salt concentration in the crown complex formation.

As a supplement, we have performed an analogous potentiometric study of sodium ion–18C6 complexation in methanolic solution. As the results summarized in Table II show, a quite similar but even more pronounced effects of counterion and salt

TABLE I

Potentiometric stability constants, K_{ISE} , for sodium ion–18C6 complexes determined in aqueous solution: The effect of counterion and salt concentration

[NaX] mol/l	$K_{\text{ISE}}^{a,b}$		
	X = OH	X = Cl	X = SCN
0.01	19.1 ± 0.3	23.8 ± 0.8	27.6 ± 1.1
0.1	6.0 ± 0.2	7.9 ± 0.2	10.3 ± 0.6
0.5	1.9 ± 0.2	4.8 ± 0.4	9.7 ± 1.2
1.0	0.5 ± 0.2	2.5 ± 0.1	9.7 ± 1.0

^a Mean values and standard deviations. ^b Only experimental points for Na⁺/18C6 mol ratios higher than unity were used in the calculation.

concentration have been found. It suggests a more general occurrence* of such effects, at least in hydroxylic media.

In this way, the potentiometric study appears to be in a full accord with the ebullioscopic evidence outlined in the Introductory Part.

A Near-Absence of the Effect of Counterion and Salt Concentration Found in Sodium-23 NMR Study

In order to get another insight into the role of counterion and salt concentration in the sodium ion-18C6 complex formation, sodium-23 resonance frequency was measured in 0.01, 0.1, 0.5 and 1.0 mol l⁻¹ aqueous solution of two different sodium salts (NaOH and NaSCN) as a function of Na⁺/18C6 molar ratio. Stability constants (K_{NMR}) and limiting shifts (δ_c) for the 1:1 Na⁺-18C6 complex have been calculated from the experimental data using the Popov equation (Eq. (4)); the results are summarized in Table III.

A near-independence of K_{NMR} values on the nature of counterion as well as on salt concentration is apparent from Table III. Within limits of experimental error, $K_{\text{NMR}}^{\text{NaOH}}$ and $K_{\text{NMR}}^{\text{NaSCN}}$ values are almost identical and do not vary with salt concentration in 0.01–0.5 mol l⁻¹ region; a significant deviation is found only in 1.0 mol l⁻¹ solution.

Thus an astounding discord exists between the corresponding sodium-23 NMR (Table III) and the potentiometric (Table I) results.

TABLE II

Logarithms of potentiometric stability constants, K_{ISE} , for sodium ion-18C6 complexes determined in methanolic solution: The effect of counterion and salt concentration

[NaX] mol/l	log $K_{\text{ISE}}^{a,b}$	
	X = OH	X = SCN
0.01	4.5 ± 0.2	4.8 ± 0.2
0.1	3.9 ± 0.2	5.0 ± 0.2
0.5	2.5 ± 0.2	5.3 ± 0.3
1.0	2.1 ± 0.2	5.5 ± 0.2

^a Mean values and standard deviations. ^b Only experimental points for Na⁺/18C6 ratios higher than unity were used in the calculation.

* Frensdorff⁷ noted a decrease of K_{ISE} value for potassium ion-dicyclohexyl-18-crown-6 complex by a factor of about 3 on going from 0.001 to 0.008 mol l⁻¹ aqueous solution. No detectable effect of counterion (KOH vs KCl) was however found in the investigated region.

The discord makes it appropriate to compare the present data with relevant literature values. Popov⁸ in a recent sodium-23 NMR study reports the K_{NMR} value for the Na^+ -18C6 complex (determined in 0.05 mol l^{-1} aqueous sodium tetraphenylboronate solution) to be 6.6 ± 1.2 , in a very reasonable accord with our K_{NMR} values of 5.6 ± 0.3 and 4.3 ± 0.4 (determined in 0.01 and 0.1 mol l^{-1} aqueous sodium thiocyanate solution, respectively). Dishong and Gokel¹⁰, on the other hand, report the potentiometric K_{ISE} value for the Na^+ -18C6 complex (determined in a unspecified but presumably very diluted aqueous solution) to be 63. This value agrees reasonably with the K_{ISE} values determined by us in 0.01 mol l^{-1} solution (Table I) but it disagrees with the above values of K_{NMR} . A conflict between K_{NMR} and K_{ISE} is thus apparent also from the scattered literature evidence.

On the Conflicting Evidence

The thermodynamic stability constant, K_{th} , for the 1 : 1 metal ion-ligand complex formation



is defined by

$$K_{\text{th}} = \frac{a_{\text{ML}^+}}{a_{\text{M}^+} a_{\text{L}}} = \frac{[\text{ML}^+] \gamma_{\text{ML}^+}}{[\text{M}^+][\text{L}] \gamma_{\text{M}^+} \gamma_{\text{L}}} \quad (5)$$

Because values of activity coefficients γ_{ML^+} and γ_{L} are unknown, calculation of K_{th} poses a difficult problem of the activity correction. It is therefore a common practice

TABLE III

Sodium-23 NMR stability constants, K_{NMR} , for sodium ion-18C6 complexes determined in aqueous solution: The effect of counterion and salt concentration

[NaX] mol/l	$K_{\text{NMR}}^{a,b}$	
	X = OH	X = SCN
0.01	4.9 ± 0.2	5.6 ± 0.3
0.1	3.5 ± 0.4	4.3 ± 0.4
0.5	4.4 ± 0.3	5.5 ± 0.3
1.0	8.5 ± 2.4	17.0 ± 1.3

^a Mean values and standard deviations. ^b The following δ_{Ijm} values have been calculated: -11.1 ± 0.1 (0.01M-NaOH); -10.9 ± 0.2 (0.01M-NaSCN); -12.2 ± 0.5 (0.1M-NaOH); -12.1 ± 0.5 (0.1M-NaSCN); -11.2 ± 0.2 (0.5M-NaOH); -11.3 ± 0.2 (0.5M-NaSCN); -10.2 ± 0.4 (1.0M-NaOH); -10.2 ± 0.1 (1.0M-NaSCN).

to replace the thermodynamic constant K_{th} by the concentration constant (pseudo-constant), K_{conc} , defined by

$$K_{conc} = \frac{[ML^+]}{[M^+][L]} = K_{th} \frac{\gamma_{M^+}\gamma_L}{\gamma_{ML^+}} \quad (6)$$

Since consideration of the Eqs (1) and (2) shows (*cf. ref.*⁷) that the potentiometric stability constants K_{ISE} we determined for the Na^+-18C6 complex comply with the definition of K_{conc} in the Eq. (6), the observed variation of the K_{ISE} values in Table I and II can be attributed to the variation of the $\gamma_{M^+}\gamma_L/\gamma_{ML^+}$ term.

From literature it is known that activity coefficients of non-complexed sodium salts (γ_{M^+}) in aqueous solution vary¹¹⁻¹³ with the salt concentration as well as with identity of the anion. However, the actual differences found in $0.01-1.0 \text{ mol l}^{-1}$ region are only small¹² ($\gamma_{NaSCN}^{0.1M} = 0.787$; $\gamma_{NaCl}^{0.1M} = 0.78$; $\gamma_{NaOH}^{0.1M} = 0.766$; $\gamma_{NaSCN}^{1.0M} = 0.712$; $\gamma_{NaCl}^{1.0M} = 0.658$; $\gamma_{NaOH}^{1.0M} = 0.679$) and thus cannot explain the pronounced K_{ISE} variation in Table I.

As it concerns the potential γ_L variation, it is known from literature that strong electrolytes affect activity coefficients of neutral solutes in a manner depending also on the salt concentration and identity of the anion. Examination of literature however shows^{14,15}, that the effect of the sodium salts now under study is relatively small and operates moreover in the opposite direction than it would be required for explanation of Table I.

By exclusion of the alternatives it follows that a very large variation of γ_{ML^+} must be the main factor responsible for the large variation of K_{ISE} in Table I and (by analogy) II. While no explicit evidence along these lines exists in literature, it may be shown¹⁶ that ebullioscopic behaviour of Na^+-18C6 complexes² is indeed in accord with this conclusion.

A question rises in this context concerning the striking difference between the stability data from the potentiometric and sodium-23 NMR measurements (Table I and III, respectively). In the Popov's original derivation⁸ of the Eq. (4), K_{NMR} is regarded to be a simple product of concentration, in accord with the definition of K_{conc} in the Eq. (6). Other things being equal, K_{NMR} should thus be subjected to the same pattern of variation as K_{ISE} , in apparent discord with facts.

Re-examination of the Eqs (3) and (4) provides explanation for the apparent paradoxon. In the original derivation⁹ of K_{NMR} , the populations of the free and complexed sodium ions (P_f and P_c , respectively) were put equal to the corresponding molar fractions

$$P_f = C_{M^+}/C_{M^+}^{tot} \quad (7)$$

and

$$P_c = C_{ML^+}/C_{M^+}^{tot}, \quad (8)$$

where C_{M^+} and C_{ML^+} are the concentrations of the free and complexed sodium ions, and $C_{M^+}^{tot}$ is the sum of the two. This, however, is an oversimplification of the actual situation, because the populations P_f and P_c express the distribution of the two alternative metal species (M^+ and ML^+) in a thermodynamic equilibrium necessitating thus activity corrections

$$P_f = \frac{C_{M^+}\gamma_{M^+}}{C_{M^+}^{tot}\gamma_{M^+}^{tot}} = \frac{a_{M^+}}{a_{M^+}^{tot}} \quad (9)$$

and

$$P_c = \frac{C_{ML^+}\gamma_{ML^+}}{C_{M^+}^{tot}\gamma_{M^+}^{tot}} = \frac{a_{ML^+}}{a_{M^+}^{tot}} \quad (10)$$

Substituting P_f and P_c in Eq. (3) from Eqs (9) and (10) gives

$$\hat{c}_{obs} = \frac{a_{M^+}}{a_{M^+}^{tot}} \hat{c}_f + \frac{a_{ML^+}}{a_{M^+}^{tot}} \hat{c}_c \quad (11)$$

which may be rewritten as

$$\hat{c}_{obs} = \frac{a_{M^+}}{a_{M^+}^{tot}} (\partial_t - \partial_c) + \partial_c \quad (12)$$

since

$$a_{M^+}^{tot} = a_{M^+} + a_{ML^+} \quad (13)$$

Solving now the Eq. (5) for a_{M^+} and substituting the result into the Eq. (12) we obtain

$$\begin{aligned} \partial_{obs} = & \{ [K_{NMR}a_{M^+}^{tot} - K_{NMR}a_L^{tot} - 1] + [K_{NMR}^2(a_{M^+}^{tot})^2 + K_{NMR}^2(a_L^{tot})^2 - \\ & - 2K_{NMR}^2a_{M^+}^{tot}a_L^{tot} + 2K_{NMR}a_L^{tot} + 2K_{NMR}a_{M^+}^{tot} + 1] \}^{1/2} \left[\frac{\partial_t - \partial_c}{2K_{NMR}a_{M^+}^{tot}} \right] + \partial_c, \quad (14) \end{aligned}$$

where K_{NMR} means K_{th} from the Eq. (5). Since $a_{M^+}^{tot}$ and a_L^{tot} are unknowns, the Eq. (14) does not allow exact solution. As an inevitable approximation, the unknowns have to be replaced by the known total concentrations ($C_{M^+}^{tot}$ and C_L^{tot} , respectively) yielding thus the original Popov equation (Eq. (4)). In spite of the apparent ubiquity of the concentration terms in the equation (4), it follows clearly from the present derivation that K_{NMR} does not fit with definition of concentration stability constant K_c in Eq. (6), since the experimental parameter ∂_{obs} still involves activity terms (Eq. (12)). Thus K_{NMR} is in actual fact a hybrid between the concentration (K_c) and thermodynamic (K_{th}) constants. From invariability of K_{NMR} in Table III it may be inferred that the hybrid must be close to the latter (K_{th}).

Once the disagreement between K_{NMR} and K_{ISE} is in this way resolved, the origin of the elusive effect of counterion and salt concentration on γ_{ML^+} urges comment. Considering magnitude of the effect, it does not seem viable to invoke customary interactions known from the Debye-Hückel theory¹¹⁻¹³ for its explanation. As we already suggested², some other interaction which was absent or escaped notice in earlier studies of non-complexed strong electrolytes must be therefore considered.

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