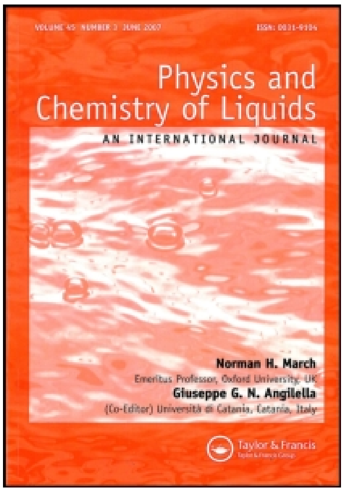

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On the potentiometric investigation of the thermodynamic properties of mixed electrolyte systems: a new mixed solution method for the determination of potentiometric selectivity coefficients of ion-selective electrodes

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With the aim of extending the use of ion-selective electrodes (ISEs) for the thermodynamic investigation of concentrated mixed electrolyte systems based on potentiometry, a mixed solution method (MSM) is reported for the determination of potentiometric selectivity coefficients ($K_{i,j}^{\text{pot}}$) of ISEs. In this new method, the measurements are performed simultaneously in the presence of all relevant interfering ions in mixed electrolyte systems. As a result, the determination of $K_{i,j}^{\text{pot}}$ is carried out in a realistic matrix environment with composition and ionic strength close to that of real mixed electrolyte samples and under experimental conditions where the ISE reveals its real practical mixed ion response behaviour.

Keywords: Mixed electrolyte; Ion-selective electrode (ISE); Potentiometric selectivity coefficient; Ammonium ion-selective electrode; Interfering ions

1. Introduction

Both vapour pressure and potentiometric-based methods are known to be the most used experimental techniques for studying the thermodynamic properties of electrolyte solutions [1–3]. In principle, the advantages offered by potentiometric method are its rapidity and the possibility of measurements in a relatively wide concentration range (particularly in the diluted range), along with its relative simplicity to generate experimental (electromotive force, emf) data. In this respect, considerable efforts have led in the few decades, in the field of sensor technology, particularly to the development of different carrier-based solvent polymeric membrane electrodes that were found to be

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attractive devices for the investigation of the thermodynamic properties of electrolyte systems (see, e.g. [1–12]). Practically, modelling the thermodynamic properties of various electrolyte systems, and essentially of mixed salts, are of interest in many fields such as chemical industry, geochemistry, marine chemistry, atmospheric sciences, and in many application processes such as extraction techniques, desalination, or in various environmental processes. As a result, different types of cation and anion-selective electrodes were designed and used for such purposes. Among these types of electrodes, carrier-based membrane ion-selective electrodes (ISE) were the least used for the determination of activity coefficients of electrolyte solutions [3,6], even though they were in continuous development since they have been first used in as ISE, in 1966–1967 [4]. The survey of literature shows that these kinds of membranes were rarely used in aqueous solvent electrolyte systems. Furthermore, with the exception of our previous works [8–12], it seems, even, to have never been used in mixed (organic–water) solvent electrolyte systems for the determination of activity coefficients. Nevertheless, based on our previous experimental works using this type of ISE for the determination of activity coefficients of electrolytes, particularly in mixed electrolyte systems, it appears clearly that the ability of such ISE could be limited by the value of their potentiometric selectivity coefficients toward the interfering ions. The survey of literature shows that despite the emergence of new procedures for determination of $K_{i,j}^{\mathrm{pot}}$ [13–19], the researchers working in the field of ISE, continue to use mostly the traditional methods (i.e. SSM, FIM and MPM), along with the Nicolsky–Eisenman equation. Particularly, the determination of selectivity coefficients in a mixture of several interfering ions was also investigated, but only in specific limited cases, using Nicolsky–Eisenman equation (e.g. [20–23]). In fact, in most practiced determination methods of selectivity coefficients use simple test solutions containing only one or two (primary and/or interfering) ions. It is now admitted that for polymeric membrane electrodes, interferences by other secondary ions are mainly dictated by a competitive extraction mechanism into the organic phase, and consequently, the response of the ISEs are usually influenced with the related thermodynamic parameters [24,25]. Since in such simple solutions the environment of each ion and the membrane are different compared to that of real samples in which several ion are simultaneously present, therefore, this fact could affect the response of the ISEs.

With the aim of extending the use of such electrodes for the thermodynamic investigation of mixed electrolyte systems, in this work a new mixed solution method is presented, which provides the opportunity of the determination of $K_{i,j}^{\mathrm{pot}}$ of ISEs in the presence of all relevant interfering ions. As a result, the measurements are performed in a realistic matrix environment with composition and ionic strength close to that of real mixed electrolyte samples and in which the ISE shows its real practical response behaviour.

In order to illustrate the principle of this method, the selectivity coefficients of a solvent polymeric ammonium membrane ISE (with nonactin/monactin as ionophore) were determined by the present method and compared to the results obtained by the traditional methods (i.e. SSM, FIM and MPM). The tested interfering ions in this work were Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}, which represent the most biologically important ions. Except for SSM, such data have not yet been reported for this ISE by the other mentioned methods. This ammonium ISE was selected [22] because it presents a relatively high interference with K^+ ions.

2. Experimental

2.1. *Preparation of the membrane electrodes*

Ammonium ISE membranes were prepared using high molecular polyvinyl chloride (PVC), 1% mixture of nonactin (72%) and monactin (28%) as ionophore, 65.7% bis(2-ethylhexyl)sebacate, sodium tetraphenylborate, and tetrahydrofuran (THF), all of Selectophore grade from Fluka (Buchs, Switzerland). Analytical grade chloride salts, from Merck (Germany), were also used for the preparation of the appropriate solutions of primary and/or interfering ions in doubly distilled water. The used ammonium ion-selective master membrane was prepared with the following composition (wt.%) [26]: 1% of the mixture of nonactin (72%) and monactin (28%), 0.6% sodium tetraphenylborate (NaTFPB). A quantity of 65.7% bis(2-ethylhexyl)sebacate and 32.7% PVC were dissolved previously in THF as a solvent. The electrodes were assembled by using disks (6 mm diameter and about 200 µm thicknesses) and PVC bodies (with an outer diameter of 8 mm and inner diameter of 4 mm). The electrodes were then filled with 10^{-3} or 10^{-5} M NH_4Cl internal filling solution and with an Ag/AgCl internal reference electrode. The prepared electrodes were normally conditioned for 48 h in 0.001 M NH_4Cl electrolyte solution, except when mentioned otherwise. The external reference electrode used in this work was a double junction Ag/AgCl reference electrode (Fluka, Switzerland), with 1 M lithium acetate as a bridge electrolyte.

2.2. *Preparation of the test solutions*

For the SSM and MPM, the simple test solutions of only one (NH_4^+ primary or Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} interfering) ions were prepared from their chloride salts in doubly distilled water in the concentration range: 10^{-6} to 10^{-1} M. For the FIM, the determination of each $K_{i,j}^{\mathrm{pot}}$was performed using the corresponding solution containing each time the primary ion ($i = NH_4^+$) and separately one of the desired secondary ion ($j = Li^+$, Na^+, K^+, Mg^{2+} and Ca^{2+}), by dissolving their corresponding chloride salts in doubly distilled water.

Finally, for the determination of each $K_{i,j}^{\mathrm{pot}}$coefficient according to the present method, e.g. for $i = NH_4^+$ and $j = K^+$, two series of solutions (I and II) were prepared. In the first series (solutions I), the desired interfering ion ($j = K^+$) was absent, the concentration of all other interfering ions were fixed (at 1 mM) but the concentration of the primary ion (NH_4^+) was varied. In the second series (solutions II), the primary ion ($i = NH_4^+$) was absent, the concentration of all other interfering ions were fixed as before, but the concentration of the interfering ions (j) was varied.

2.3. *Potentiometric measurements*

The experimental cell potentials were measured using 692 Metrohm (Switzerland) ion-meter, connected to a Topward multimeter (model 1304, Taiwan, Korea) interfaced with a GPIB Bus (1304G), and finally connected to a personal computer (32 MHz) for data acquisition and processing. All measurements were performed under stirring conditions at room temperature (25 ± 1°C) using the following galvanic cell:

Ag(s)/AgCl(s)/4 M KCl//1 M lithium acetate//sample solution/
ISE membrane/0.01 M NH_4Cl/AgCl(s)/Ag(s)

The calibration of the ammonium ISE was checked before and after each series of measurements.

3. Principle of the method

The determination of each selectivity coefficient by the present method was based on the following procedure. Using Nicolsky–Eisenman equation for the first solutions series (solutions I)

$$E_{\mathrm{I}} = E' + \frac{2.303RT}{Z_iF}\log[a_i + D] \tag{1}$$

where

$$D = \sum_l K_{i,l}^{\mathrm{pot}}(a_l)^{z_i/z_l} \tag{2}$$

E_{I} is the experimental potential of the corresponding solutions, E' the cell constant potential, $s = 2.303RT/Z_iF$ the slope of the electrode, a_i the varying activity of the primary ion and a_l is used for the fixed activity of all other interfering ions present, z_i and z_l are integers with sign and magnitude corresponding, respectively, to the charge of the primary (i) ion and other fixed interfering ions present (l). In equation (1), D is related to the contribution of all other interfering ion l, except j ($l \neq j$) to the cell potential.

For the second solutions series (solutions II)

$$E_{\mathrm{II}} = E' + \frac{2.303RT}{Z_iF}\log\left[K_{i,j}^{\mathrm{pot}}(a_j)^{z_i/z_j} + D\right] \tag{3}$$

Subtracting equation (1) from equation (3):

$$\Delta E = E_{\mathrm{II}} - E_{\mathrm{I}} = \frac{2.303RT}{Z_iF}\log\frac{K_{i,j}^{\mathrm{pot}}(a_j)^{z_i/z_j} + D}{a_i + D} \tag{4}$$

For $\Delta E = E_{\mathrm{II}} - E_{\mathrm{I}} = 0$, $K_{i,j}^{\mathrm{Pot}}$ can be determined from the following equation

$$K_{i,j}^{\mathrm{pot}} = \left(\frac{a_i}{(a_j)^{z_i/z_j}}\right)_{\Delta E=0}. \tag{5}$$

However, it is possible to obtain a relation for $K_{i,j}^{\mathrm{pot}}$, mathematically independent [4] from the charge of the interfering ion, as follows. From the intersection of the extrapolated two linear parts of the potential curve E_{I} *versus* $\log a_i$, we have

$$D = a_i'. \tag{6}$$

Now, substituting the obtained a_i' value ($D = a_i'$) in equation (4) and for $a_i = a_j = 1$, $K_{i,j}^{\text{pot}}$ is obtained based on the following equation

$$K_{i,j}^{\text{pot}} = \left[\left(10^{(\Delta E/(2.303RT/Z_iF))}\right)(1 + a_i') - a_i'\right]_{a_i=a_j=1}. \qquad (7)$$

Therefore, using equation (7), $K_{i,j}^{\text{pot}}$ can be determined for primary and each interfering ions (at $a_i = a_j = 1$), by substituting, successively, the corresponding value of a_i' [equation (6)] extracted from the resulting plotted curve.

4. Results and discussion

Standard procedures with corrections for liquid junction potentials [24,27] were performed to determine each log $K_{i,j}^{\text{pot}}$ value by SSM, FIM, MPM, and by proposed method for the fabricated ammonium ISEs, with respect to each interfering ions: $j = \text{Li}^+$, Na^+, K^+, $\text{Mg}^{2+}$and Ca^{2+}. All these results along with the available SSM log $K_{i,j}^{\text{pot}}$ values [24,27] for this ISE are presented in table 1. The reported SSM $K_{i,j}^{\text{pot}}$ values (obtained with the absence of ion-exchanger in the membrane) could only be considered as comparative values and indicating the order of magnitude of the selectivity coefficients for such ISE. The slopes obtained with the fabricated ammonium ISE for the primary ion $i = \text{NH}_4^+$, and for the interfering ions $j = \text{Li}^+$, Na^+, K^+, Mg^{2+} and Ca^{2+} ions were: 57.2, 54.9, 58.9, 57.7, 6.1 and 37.5 (mV/decade activity change), respectively. Although, for this ISE, the only non-Nernstian slope obtained with classical conditioning procedure was for Mg^{2+} (6.1 mV/decade activity change), however, the corresponding slope obtained from the application of the proposed Bakker's SSM (e.g. 30.4 mV/decade activity change) was found for this ion [16]. As a result, the log $K_{i,j}^{\text{pot}}$ values obtained by the conventional SSM, for the interfering ions $j = \text{Li}^+$, Na^+, K^+ (i.e. −3.3, 2.6 and −0.8, respectively, for which $z_i = z_j$) should be acceptable but on the contrary, those obtained for the interfering ions $j = \text{Mg}^{2+}$ and Ca^{2+} (i.e. −3.4 and −3.7, respectively for which $z_i \neq z_j$), should be considered unacceptable.

Table 1. Measured potentiometric selectivity coefficients of the fabricated ammonium ISE by different methods. The reported values[a] correspond to a membrane with different composition.

	log K_{ij} ($i = \text{NH}_4^+$)				
j	SSM[a] $a_i = a_j = 0.1\,\text{M}$	SSM[b] $a_i = a_j = 0.1\,\text{M}$	MPM[b]	FIM[b]	MSM[c] $a_l = 0.001\,\text{M}$ ΔE (at $a_i = a_j = 1\,\text{M}$)
Li^+	−2.7	−3.3	−3.7	−2.5	−3.8
Na^+	−2.7	−2.6	−1.8	−2.0	−2.5
K^+	−0.8	−0.8	−1.0	−0.7	−0.9
Mg^{2+}	−5.0	−3.4	−3.5	−3.9	−3.9
Ca^{2+}	−4.5	−3.7	−3.2	−3.4	−3.8

[a] Reported values for a membrane with the following composition (wt.%) [24,27]: 4.6% of the mixture of nonactin (72%) and monactin (28%), 68.9% tris(2-ethylhexyl)phosphate and 26.5% PVC.

[b] Values obtained in this work.

[c] Values obtained with the presented method.

[b] and [c] correspond to a membrane with the following (wt.%) composition: 1.05% of the mixture of nonactin (72%) and monactin (28%), 67.07% bis(2-ethylhexyl)sebacate and 31.88% PVC.

SSM = Separate solution method; MPM = matched potential method and MSM = mixed solution method (presented method).

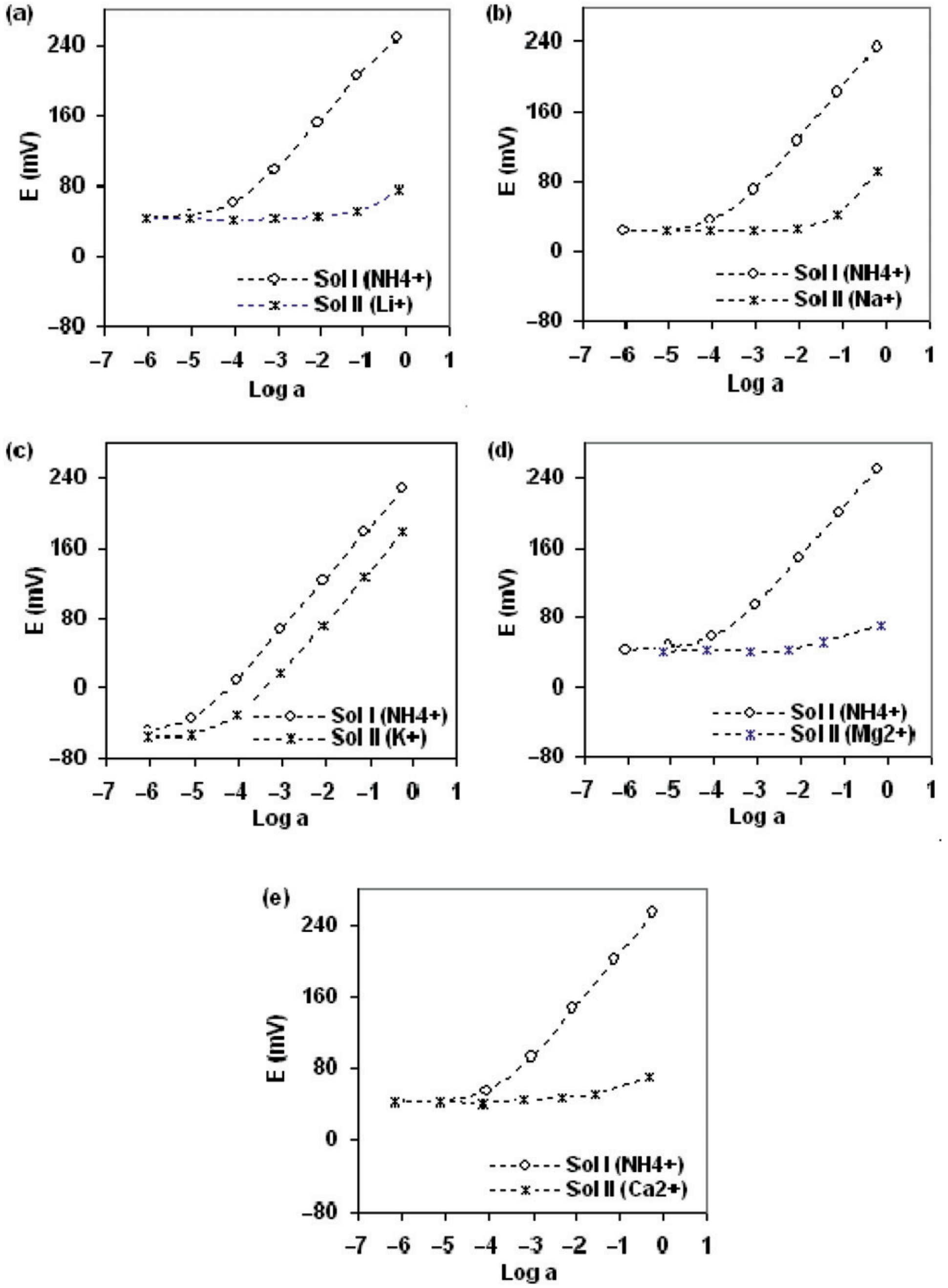

Figure 1. (a)–(e) The experimental potential curves, E (mV) *vs.* $\log a$, generated by the presented method, using solution series (I) and (II) for the determination of each potentiometric selectivity coefficients of the ammonium solvent polymeric ISE membrane (with $i = \mathrm{NH}_4^+$ and $j = \mathrm{Li}^+$, Na^+, K^+, Mg^{2+} and Ca^{2+}).

The experimental results obtained by the present mixed solution method (MSM) are reported in figure 1(a)–(e), and the corresponding potentiometric selectivity coefficients are summarised in table 1. In order to obtain these results, the value of $D = a'_i$ [equation (6)] was first determined, respectively, for each interfering ion by extrapolation from the corresponding curve of E (mV) *versus* log a_i and then by its substitution in equation (7). Table 1 shows that the resulting log $K^{\mathrm{pot}}_{i,j}$ values by the application of the presented method compare well with the values obtained by the other current methods, and show generally more coherent (or more selective) values for the series of used ions.

5. Conclusions

With the aim of extending the use of polymeric membrane ISE for the thermodynamic investigation of mixed electrolyte systems, a new mixed solution method is presented, in which the potentiometric selectivity coefficients of ion-selective electrodes could be measured in the presence of all relevant interfering ions simultaneously. The application of this method has been illustrated using a solvent polymeric ammonium-selective electrode containing a mixture of monactin/nonactin ionophore, in the mixed solutions containing, simultaneously, all the following interfering ions: $j = \mathrm{Li}^+$, Na^+, K^+, Mg^{2+} and Ca^{2+}. Compared to the conventional method, the method here reported presents the particularity that the potentiometric selectivity coefficients of electrode is evaluated in a more realistic electrolytic environment, under which the ISE shows its real practical mixed ions response behaviour. Effectively, in the used mixed electrolyte solutions (where several ion are simultaneously present), the ISE showed its real competitive extraction mechanism from sample solution to the organic (membrane) phase. Compared to the currently used methods, the resulting $\log K$ values generated by the application of the presented method were found to be generally more selective for the series of used interfering ions.

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