

## USE OF A FLOW-INJECTION SYSTEM IN THE EVALUATION OF THE CHARACTERISTIC BEHAVIOR OF NEUTRAL CARRIERS IN LITHIUM ION-SELECTIVE ELECTRODES

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### ABSTRACT

A flow-injection system based on microconduits is used to investigate electrode characteristics such as selectivity, detection limit, and response and equilibrium times of the new ionophore, *N,N,N',N'*-tetraisobutyl-5,5-dimethyl-3,7-dioxanonane diamide, in lithium ion-selective electrodes. These characteristics were compared with those of the ionophore *N,N'*-diheptyl-*N,N'*,5,5-tetramethyl-3,7-dioxanone diamide. The new ionophore has superior detection limits and shorter response and equilibrium time, but the other exhibits better selectivity for lithium with respect to sodium. Values of  $K_{LiNa}^{Pot}$  for the new ionophore vary from 0.0450 to 0.566, depending on the methods of measurement and solution conditions. This phenomenon is discussed. Stop-flow experiments effectively demonstrated the response and equilibrium time differences between these two ionophore membranes.

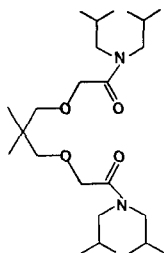
Flow-injection techniques have found wide application in several areas of analytical chemistry. In the area of ion-selective electrodes, they offer advantages of increased sensitivity, decreased chemical and mechanical interferences, fast response time and very good reproducibility of results [1]. Flow-injection techniques with potentiometric detection have been applied to the determination of ions in blood serum [2–4]. Few studies have used this technique to characterize electrode behavior. This paper describes an investigation of the characteristic behavior of a new compound, *N,N,N',N'*-tetraisobutyl-5,5-dimethyl-3,7-dioxanonane diamide (ionophore 1), as the ionophore in a lithium ion-selective electrode. Its behavior is compared to that of the previously reported *N,N'*-diheptyl-*N,N'*,5,5-tetramethyl-3,7-dioxanonane diamide (ionophore 2) by using flow-injection measurements.

Zhukov et al. [5] prepared several lipophilic diamides and investigated

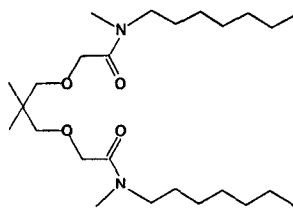
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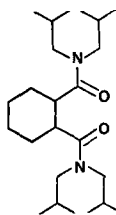
(1)



(2)



(3)



their characteristic behavior as neutral carriers in lithium ion-selective electrodes. The compounds included ionophore 2 and ionophore 3 and it was reported that ionophore 3 showed an improved selectivity for lithium ions [5] compared to ionophore 2 [6]. It was of interest to prepare ionophore 1 which resembles ionophores 2 and 3, combining features of both (backbone or side chains).

Ionophores 1 and 2 were synthesized and their characteristics compared in lithium ion-selective electrodes using a flow-injection system with microconduits. These characteristics include slope, linear range, detection limit, response and equilibrium times, and selectivity coefficients for lithium with respect to sodium,  $K_{LiNa}^{Pot}$ , under different measurement and solution conditions.

## EXPERIMENTAL

### Reagents and syntheses

All solutions were prepared from salts of reagent grade, with deionized water. The chlorides of the metals were used.

**Synthesis of ionophores.** For the synthesis of ionophore 1, a solution of the acid chloride [7] (1.0 g, 0.0039 mol) in benzene (10 ml) was added dropwise with stirring and cooling (ice bath) to a solution of diisobutylamine (1.10 g, 0.0085 mol) in dichloromethane (15 ml) and triethylamine (3 ml). After addition was complete, the reaction mixture was left at room temperature overnight and then dichloromethane (50 ml) was added. The solution was washed twice with water, twice with distilled water, twice with hydrochloric acid (20 ml, 5 M), once with saturated sodium hydrogen carbonate solution, and finally with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum to give the product as a yellow oil (1.8 g; yield ca. 82%). This was purified by column chromatography on silica gel, eluting first with petroleum ether (30–60 fraction; 100 ml), followed by a 2:1 mixture of petroleum ether (30–60) and chloroform to collect the product. The yield was 1.4 g (64%). Elemental content of the product (vs. theoretical) was as follows: 67.5% C (67.8%); 11.5% H (11.4%).

Ionophore 2 was synthesized and characterized as described by Zhukov et al. [5].

**Plasticizer/PVC stock solution.** Poly(vinyl chloride) (0.6 g) was mixed with 1.36 g of tris(2-ethylhexyl)phosphate as described earlier [8]. Cyclohexanone (7.5 ml) was added and the mixture was shaken until all the PVC had dissolved.

**Membrane preparation.** A 10.6-mg portion of ionophore 1 and about 3.6 mg of potassium tetrakis(*p*-chlorophenyl)borate (about 30% mole ratio with respect to ionophore 1) were dissolved in 500  $\mu\text{l}$  of the PVC stock solution and mixed very well using a vortex mixer. For ionophore 2, 9.7 mg of the ionophore and 3.2 mg of potassium tetrakis(*p*-chlorophenyl)borate were dissolved in 500  $\mu\text{l}$  of the stock PVC solution. These solutions were used to prepare the electrodes.

#### Apparatus, sample cell, and electrode preparation

Figure 1 shows the apparatus arrangement. Microconduits made from PVC blocks were used as the sample cell [9]. The channels on the block were engraved with a Dremel drill (model 210). The channel radius was 0.6 mm. A clear plastic sheet was tightly glued on the top of these channels with double-sided adhesive tape inserted between the microconduit and the sheet to seal the microconduit. The carrier solution was pumped via an air-pressurized reservoir which, because of its simplicity, stability and versatility, is superior to a peristaltic pump or chromatographic pump. An attempt to use a peristaltic pump or a chromatographic pump failed, as noise was introduced into the system by the static electricity generated. Unless otherwise stated, a sample of 100  $\mu\text{l}$  was injected into the carrier stream, with a flow rate of 0.9 ml  $\text{min}^{-1}$  easily controlled by adjusting the air pressure. A Beckman model 3500 digital pH meter and a Corning model 146 digital pH meter were used for simultaneous potential measurements with both electrodes on a given injected sample. No significant differences were observed in potential measurements when the two pH meters were used separately with a single

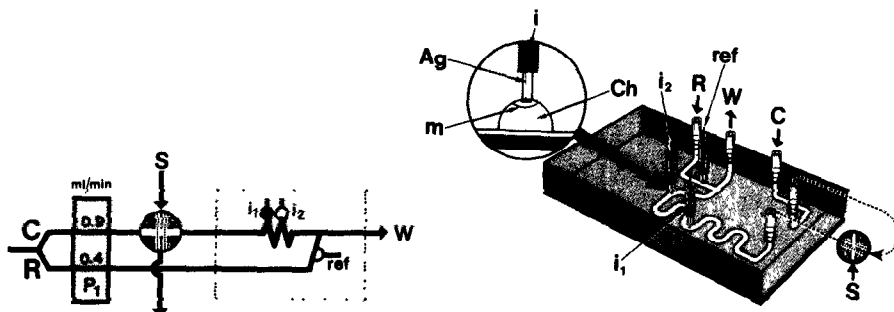


Fig. 1. Manifold and microconduit design: C, carrier stream; P, pump; S, sample solution;  $i_1$ , ion-selective electrode 1;  $i_2$ , ion-selective electrode 2; R, reference stream; ref, reference electrode; W, waste; i, gold pin; Ag, silver wire; m, membrane; Ch, channel of microconduit.

electrode. Responses were recorded on a chart recorder (Linear model 385).

Silver wires were inserted and glued to various positions, as shown in Fig. 1, with tetrahydrofuran, as described by Ružička and Hansen [9]. The ends of the silver wires were next inserted into gold pins for electrical contact. The surface of the silver wire in the conduit was oxidized with a few drops of a solution prepared by dissolving equal amounts of sodium chloride and sodium phosphate (0.3 g) in about 5 ml of bleach solution (Clorox); this deposited a reference layer of silver chloride on the silver surface. The wire was then washed with water and methanol and allowed to dry. The PVC solution containing the neutral carrier was applied to the surface of the silver wire under a microscope. Three layers were applied with drying between applications. Thus, a rugged miniature ion-selective electrode was constructed in the microconduit. The reference electrode was prepared in the same manner except that no PVC solution was applied to the silver wire surface.

#### Selectivity coefficients ( $K_{LiNa}^{Pot}$ )

The selectivity coefficients were determined by following three different methods [10–12]. Potentials were taken from the recorded peaks.

*Method 1 [10].* Equal concentrations of lithium or sodium were separately injected into the carrier stream. The potential changes with respect to the baseline were recorded and the selectivity was calculated from the equation  $\log K_{LiNa}^{Pot} = (E_{Na} - E_{Li})/S$ , where  $S$  is the slope of lithium response.

*Method 2 [11].* A plot of voltage vs. logarithm of the lithium concentration (calibration graph) was first constructed by injecting pure lithium standards. Then a known concentration of pure sodium solution ( $C'_{Na}$ ) was injected into the carrier stream, and the potential response was recorded. The lithium concentration ( $C'_{Li}$ ) corresponding to this potential was obtained from the lithium calibration curve. The selectivity coefficient then is given by  $K_{LiNa}^{Pot} = C'_{Li}/C'_{Na}$ . The reverse approach can be used when a known concentration of lithium is injected.

*Method 3 [12].* Several lithium solutions with known concentrations, prepared in carrier solution, were injected into the carrier stream and the changes in potential were recorded. A known concentration of sodium prepared in the carrier solution was next injected and the potential was recorded. A calibration plot of potential vs. logarithm of the lithium concentration was constructed and from this curve the concentration of lithium corresponding to exactly the potential of the sodium in the carrier solution was determined. In the case of lithium carrier solution, the following two forms of the Nicolsky equation are applied to the potential,  $E_1$ , measured on injection of sodium in lithium carrier solution, and to the potential,  $E_2$ , measured in constructing the calibration ( $C_{Li\ total}$ ) plot:

$$E_1 = \text{const} + RT (zF)^{-1} \ln (C_{Li\ carrier} + K_{LiNa}^{Pot} C_{Na})$$

$$E_2 = \text{const} + RT (zF)^{-1} \ln C_{Li\ total}$$

Because  $E_1$  and  $E_2$  are equal,  $C_{\text{Li total}} = C_{\text{Li carrier}} + K_{\text{LiNa}}^{\text{Pot}} C_{\text{Na}}$ . Thus, the selectivity coefficient,  $K_{\text{LiNa}}^{\text{Pot}}$ , in lithium carrier stream is

$$K_{\text{LiNa}}^{\text{Pot}} = (C_{\text{Li total}} - C_{\text{Li carrier}})/C_{\text{Na}}$$

In the case of sodium carrier solution, the equations are

$$E_3 = \text{const} + RT (zF)^{-1} \ln K_{\text{LiNa}}^{\text{Pot}} C_{\text{Na total}}$$

$$E_4 = \text{const} + RT (zF)^{-1} \ln (C_{\text{Li}} + K_{\text{LiNa}}^{\text{Pot}} C_{\text{Na carrier}})$$

where  $E_3$  is the potential measured for injection of sodium in sodium carrier solution and  $E_4$  is the potential measured in constructing the plot of potential vs. lithium concentration ( $C_{\text{Li}}$ ) in sodium carrier solution. Because  $E_3$  and  $E_4$  are again equal,  $K_{\text{LiNa}}^{\text{Pot}} C_{\text{Na total}} = C_{\text{Li}} + K_{\text{LiNa}}^{\text{Pot}} C_{\text{Na carrier}}$ . Thus, the selectivity coefficient,  $K_{\text{LiNa}}^{\text{Pot}}$ , in the sodium carrier stream is

$$K_{\text{LiNa}}^{\text{Pot}} = C_{\text{Li}}/(C_{\text{Na total}} - C_{\text{Na carrier}}).$$

In these equations,  $R$ ,  $T$ ,  $z$  and  $F$  are defined as in the classical Nicolsky equation;  $C_{\text{Li total}}$  and  $C_{\text{Na total}}$  are the net concentration changes plus carrier solution concentrations of lithium and sodium, respectively;  $C_{\text{Li carrier}}$  and  $C_{\text{Na carrier}}$  are the lithium carrier and sodium carrier solution concentrations, respectively;  $C_{\text{Li}}$  and  $C_{\text{Na}}$  are the lithium concentration in the sodium carrier solution and the sodium concentration in the lithium carrier solution, respectively. This is basically the matched potential method [12]. A major and important difference from method 2 is that the lithium and sodium solutions are prepared in the carrier solution and so the carrier concentration remains constant throughout the response peak.

## RESULTS AND DISCUSSION

### *Measurement conditions*

Fast and very reproducible results were obtained for electrodes containing ionophore 1, with rise times in the order of 6 s. The response dependence on the flow rate and the sample volume was investigated. An optimum response was obtained using a flow rate of 3 ml min<sup>-1</sup>. The response was increased 32% by increasing the flow rate from 0.9 ml min<sup>-1</sup> to 3 ml min<sup>-1</sup>.

To minimize diffusion of the sample plug into the carrier stream, it was necessary to decrease the dispersion as much as possible. This was done by increasing the sample volume from 50  $\mu$ l to 100  $\mu$ l. Further increases in sample volume did not increase the signals. Under these conditions, the electrodes reach the equilibrium potential while the sample plug flows through the electrodes. The flat portion of the responses shown in Fig. 2A corresponds to the equilibrium potential. It is clear that the dispersion,  $D$ , is equal to one and there is no mixing of the sample plug with the carrier solution.

Economy of carrier solution was weighed against the increase in response by the increase of flow rate. It was more economical to use a flow rate of 0.9 ml min<sup>-1</sup> and increase the signal by an increase in sample volume to 100  $\mu$ l.

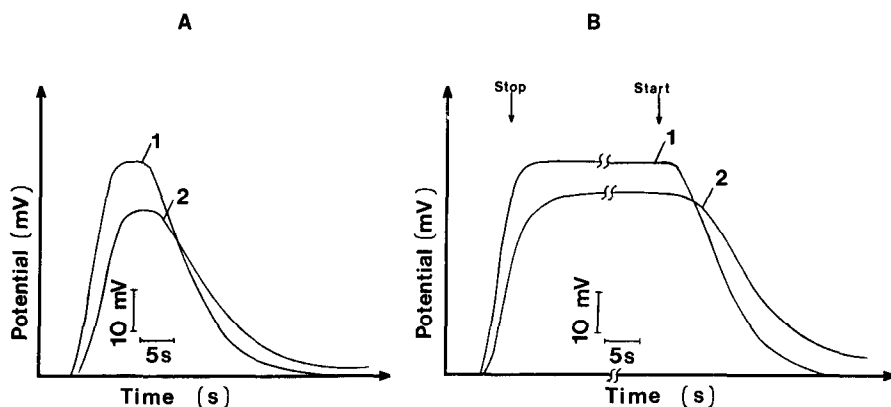


Fig. 2. (A) Flow curves for electrodes 1 and 2; (B) stop-flow curves for electrodes 1 and 2. In both cases, the carrier was 1.4 mM lithium and 10 mM lithium was injected.

Comparison of the relative peak heights for injection of lithium into an aqueous unbuffered 1.4 mM lithium carrier stream revealed substantially higher signals than for injection of the same concentration of sodium. This gives quick quantitative information about the selectivity of the electrode. One advantage in the use of the flow-injection technique with ion-selective electrodes employing microconduits, as described here, is the possibility of having more than one electrode implanted in the cell. Two different ionophore-membrane electrodes can be easily monitored and compared at the same time and with the same sample injection, which eliminates the possibility of error from concentration inaccuracy of the sample solution or previous electrode treatment (history).

#### *Response and equilibrium times*

A stop/flow experiment was used to study the response behaviors of two electrodes. Figure 2B shows the stop/flow curves for injection of 10 mM lithium into a 1.4 mM lithium carrier solution. Although electrode 2 (ionophore 2 membrane) is upstream 0.4 s, under the applied flow rate of 0.9 ml  $\text{min}^{-1}$  with respect to electrode 1 (ionophore 1 membrane), electrode 1 responds first at 4.8 s after injection; electrode 2 responds at 5.2 s after injection, so there is a real difference in their response times of 0.8 s. Differences between equilibrium times for electrodes 1 and 2 can be observed in both the flow curve and stop/flow curves (Fig. 2). As determined from the flow curve, electrode 1 reaches equilibrium potential at 11.8 s after sample injection (10 mM lithium) and electrode 2 appears to do so at 13.9 s, a total real difference of 2.5 s. Note that the maximum response for electrode 2 is only about 90% that of the equilibrium response achieved under stopped-flow conditions, indicating that true equilibrium was not reached under flow conditions; i.e., the true response for electrode 2 is even slower. This is more

evident from the stop/flow curve. Electrode 1 reaches equilibrium potential at 15.6 s after injection and electrode 2 does so at 21.5 s when the flow is stopped at 10 s, a total real difference of 6.4 s. It may be noted that the dynamic flow system does decrease the apparent equilibrium time of the electrodes, demonstrating one of the advantages of the flow-injection method compared to the batch method. When flow is continued after a period of being stopped, electrode 1 returns to the background potential significantly faster than electrode 2 does. Thus, it is concluded that the rate constants ( $\bar{k}$ ,  $\bar{k}$ ) [13] of ion transport from aqueous solution to the membrane phase for electrode 1 are larger than for electrode 2. In addition, the relative membrane permeabilities (permeability  $P = (\bar{k}/\bar{k})C_s$ , where  $C_s$  is the free ionophore concentration in the membrane) of the two electrodes differ in proportion to the difference in  $K_{ij}^{Pot}$  values ( $= P_1/P_2$ ) [13]. Alternatively, one might expect the diffusion coefficient for ionophore 2 and its lithium ion complex to be lower in the membrane phase than for ionophore 1, resulting in longer equilibrium times for electrodes using ionophore 1 [13].

### Figures of merit

Figure 3 illustrates the linear range, sensitivity (slope) and detection limit [14] of electrode 1 in 1.4 mM lithium carrier stream. Table 1 summarizes the linear ranges, slopes and detection limits of electrodes 1 and 2 in 1.4 and 14 mM lithium streams. These three characteristic behaviors of electrodes are all dependent upon the composition of the carrier solution. Higher concentration of lithium in the carrier solution reduces the observed sensitivity of the electrodes, increases the values of observed detection limits, and reduces the observed linear ranges for both electrodes. In 1.4 mM lithium carrier stream, electrode 1 has a larger linear range than that of electrode 2, and its observed detection limit is 40% lower than that of electrode 2.

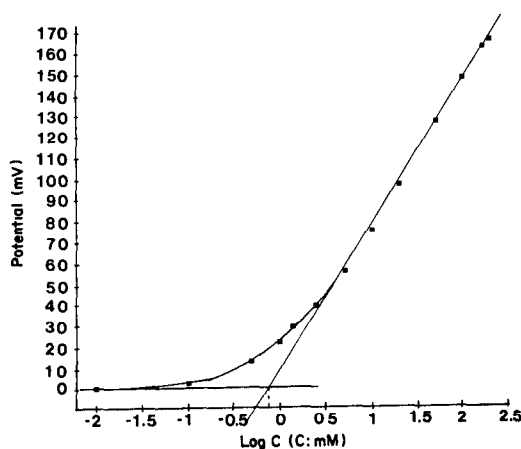


Fig. 3. Logarithmic lithium concentration (mM) vs. millivolt curve for the electrode based on ionophore 1 in unbuffered 1.4 mM Li carrier solution.

TABLE 1

Figures of merit for electrodes

	1.4 mM Li carrier stream		14 mM Li carrier stream	
	Ionophore 1	Ionophore 2	Ionophore 1	Ionophore 2
Range (mM) <sup>a</sup>	2.5–1000	5.0–1000	10–1000	10–1000
Slope ( $\pm$ s.d.)	68.9 ( $\pm$ 0.7)	69.1 ( $\pm$ 0.7)	53.7 ( $\pm$ 1.1)	47.5 ( $\pm$ 1.5)
Standard error of estimate (mV)	1.6	1.3	1.9	2.0
Correlation coefficient	1.000	1.000	0.999	0.994
Detection limit ( $\pm$ s.d.) (mM)	0.74 ( $\pm$ 0.07)	1.2 ( $\pm$ 0.1)	4.5 ( $\pm$ 0.9)	4.7 ( $\pm$ 1.5)

<sup>a</sup>Linear range of potential response vs. logarithm of concentration plot.*Selectivity coefficients*

Table 2 summarizes the  $K_{ij}^{\text{Pot}}$  values calculated by methods 1, 2, and 3, respectively, for electrode 1 and electrode 2 in different carrier streams with a series of lithium or sodium solution injections. Methods 1 and 2 are separate-solution methods, because pure lithium or sodium is injected and  $D = 1$  was deliberately set in the flow system. Method 3, the matched-potential method, is a revised fixed-interference method or a revised fixed primary-ion method, depending on the carrier solution used. When sodium carrier solutions are used, method 3 is experimentally similar to the method recommended by IUPAC and the uncertainty of this method is better than that of the IUPAC method in the present application. Direct comparison of  $K_{ij}^{\text{Pot}}$  values by the three methods may not be appropriate because solution conditions are quite different, and it is impossible to use exactly the same set of concentrations of lithium and sodium to calculate  $K_{ij}^{\text{Pot}}$  values by the three methods. However, the general trend is that method 1 gives the largest range of  $K_{ij}^{\text{Pot}}$  values, methods 2 and 3 give a smaller range of  $K_{ij}^{\text{Pot}}$  values, and similar solution conditions seemed to give similar  $K_{ij}^{\text{Pot}}$  values by the three different methods. In each method, electrode 2 shows a better selectivity for lithium.

*Selectivity and carrier solution composition*

Four different carrier solutions were used in this study, and the choice of 14 mM and 140 mM sodium carrier solutions was based on the practical purpose of application to determination of lithium in blood. In different carrier solutions,  $K_{ij}^{\text{Pot}}$  values for the PVC hydrophobic membrane electrode varied. For a perfect PVC liquid membrane, a bulk membrane model [13] can be used. The membrane potential ( $E_m$ ) is [15]

$$E_m = \text{const.} + RT (zF)^{-1} \ln \left( \sum_n K_{in} a_i + \sum_n K_{jn} a_j \right) \quad (1)$$

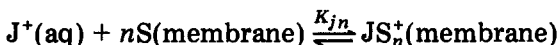
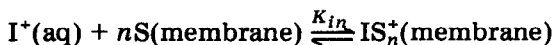


TABLE 2

Values of selectivity coefficients ( $K_{ij}^{\text{Pot}}$ ) calculated by the three methods

Carrier stream	Method 1			Method 2			Method 3									
	Li <sup>+</sup> (mM)	Na <sup>+</sup> (mM)	Ionophore 1	Li <sup>+</sup> (mM)	Na <sup>+</sup> (mM)	Ionophore 1	Li <sup>+</sup> (mM)	Na <sup>+</sup> (mM)	Ionophore 1							
	1/K	K	1/K	1/K	K	1/K	1/K	K	1/K							
<i>1.4 mM Li<sup>+</sup></i>	10	0.302	3.31	0.287	3.48	10	0.254	3.93	0.197	5.07	2	0.319	3.13	0.357	2.80	
	20	0.236	4.23	0.188	5.33	20	0.227	4.40	0.150	6.60	5	0.272	3.68	0.212	4.72	
	100	0.134	7.47	0.0907	11.0	100	0.145	6.90	0.0906	11.03	10	0.235	4.26	0.169	5.90	
	200	0.114	8.77	0.0752	13.3	200	0.113	8.83	0.0815	12.28	—	—	—	—	—	
<i>14 mM Li<sup>+</sup></i>	10	0.566	1.77	0.601	1.66	10	0.334	3.00	0.360	2.78	20	0.268	3.73	0.183	5.46	
	25	0.385	2.60	0.381	2.62	25	0.268	3.74	0.242	4.13	50	0.222	4.51	0.146	6.85	
	100	0.178	5.62	0.163	6.15	100	0.182	5.50	0.162	6.16	100	0.174	5.74	0.166	8.65	
	200	0.145	6.88	0.0982	10.2	200	0.164	6.09	0.112	8.97	—	—	—	—	—	
<i>14 mM Na<sup>+</sup></i>	16	0.283	3.53	0.166	6.01	1.00	—	—	0.193	5.19	2	0.185	5.41	0.136	7.35	
	18	0.290	3.45	0.169	5.90	1.88	—	0.220	4.54	0.171	5.85	4	0.225	4.44	0.162	6.17
	20	0.277	3.61	0.159	6.30	2.50	—	0.219	4.57	—	—	6	0.218	4.59	0.141	7.09
<i>140 mM Na<sup>+</sup></i>	160	0.0450	22.2	0.0219	45.6	5	0.184	5.45	0.117	8.55	20	0.110	9.09	0.0632	15.82	
	180	0.0467	21.4	0.0214	46.7	10	0.174	5.75	0.0986	10.1	40	0.126	7.94	0.0638	15.68	
	200	0.0464	21.5	0.0220	45.3	—	—	—	—	—	60	0.118	8.47	0.0652	15.34	

Here,  $a_i$  and  $a_j$  are single ion activities of ions  $I^+$  and  $J^+$ ,  $n$  is the number of ionophores complexed with  $I^+$  or  $J^+$ , and  $K_{in}$  and  $K_{jn}$  are the equilibrium constants of the reactions



where  $S$  is the ionophore in the membrane phase. It is reasonable to assume that only 1:1 complexes are formed, thus  $n = 1$  in the above chemical equations and from Eqn. 1 the selectivity coefficient compared to the classical Nicolsky equation reads  $K_{ij}^{\text{Pot}} = K_j/K_i$ .

Further consideration shows that  $K_j$  or  $K_i$  are functions of  $\beta_{js}$  or  $\beta_{is}$ ,  $K_{js}$  or  $K_{is}$ , as well as  $a_s$  and  $k_s$ :

$$K_j = \beta_{js}K_{js}(a_s/K_s) \text{ and } K_i = \beta_{is}K_{is}(a_s/K_s)$$

where  $\beta_{js}$  or  $\beta_{is}$  is the stability constant of the complex  $JS^+$  or  $IS^+$  in aqueous solution, and  $K_{js}$  or  $K_{is}$  is the equilibrium constant for transfer of the complex into the membrane;  $K_s$  is an equilibrium constant for transfer of free ligands into the boundary layer and  $a_s$  is the activity of free ionophore,  $S$ , in the membrane. Combining these last three equations yields

$$K_{ij}^{\text{Pot}} = [\beta_{js}K_{js}(a_s/K_s)] / [\beta_{is}K_{is}(a_s/K_s)] \quad (2)$$

Equation 2 can further be reduced to

$$K_{ij}^{\text{Pot}} = \beta_{js}K_{js} / \beta_{is}K_{is} \quad (3)$$

as it can be assumed that the concentration of ionophore in the membrane is not changed.

Equation 3 shows that  $K_{ij}^{\text{Pot}}$  is a constant only when the membrane condition which determines  $K_{js}/K_{is}$  is not altered by any external conditions. However, in many practical cases, the membrane condition is altered by external conditions such as composition of solutions used for activation or storage of electrodes. During use, electrodes are always conditioned by different electrolyte solutions, often in a haphazard way, especially if operated batchwise. In a flow-injection system, when various carrier solutions are passed through the electrode cell, the solution composition can be maintained with a high reproducibility and it is therefore of interest to investigate it in more detail. Thus, for each carrier solution, the membrane is altered such that a different set of  $K_{js}$  and  $K_{is}$  values apply in Eqn. 3. This is evidenced by the changes in  $K_{ij}^{\text{Pot}}$  value in different carrier solutions. Even when the electrodes are exposed to different solutions for a short time, the electrode membrane properties are slightly altered, as evidenced by the variation in  $K_{ij}^{\text{Pot}}$  values observed when different concentrations of lithium and sodium are injected in the same carrier stream. The dependence of  $K_{ij}^{\text{Pot}}$  values on solution conditions has been reported for other ion-selective electrodes, in which a beaker method was employed for measurements [10].

In summary, many factors such as the choice of measurement method (1–3) used, the carrier solution composition and injected solution composition affect the value of the selectivity coefficient. Under the present measurement conditions, the new ionophore *N,N,N',N'*-tetrakisobutyl-5,5-dimethyl-3,7-dioxanonane diamide exhibits selectivity coefficients  $K_{LiNa}^{Pot}$  from 0.566 to 0.0450. It is apparent that the selectivity coefficient should be determined under conditions that are similar to those of analytical measurements. Comparing the selectivities for electrodes with ionophores 1 and 2, the response of ionophore 2 toward lithium ion relative to sodium ion is comparable to that of ionophore 1, but the detection limit and response and equilibrium times of the new ionophore electrode are superior to those with ionophore 2.

#### REFERENCES

- 1 E. Pungor, K. Toth and A. Hrabeczy-Pall, *Trends Anal. Chem.*, 3(1) (1984) 28.
- 2 P. C. Meier, D. Ammann, H. F. Osswald and W. Simon, *Med. Progr. Technol.*, 5 (1977) 1.
- 3 J. Růžička, E. H. Hansen and E. A. G. Zagatto, *Anal. Chim. Acta*, 88 (1977) 1.
- 4 M. E. Meyerhoff and P. M. Kovach, *J. Chem. Educ.*, 60 (1983) 767.
- 5 A. F. Zhukov, D. Erne, D. Amman, M. Guggi, E. Pretsch and W. Simon, *Anal. Chim. Acta*, 131 (1981) 117.
- 6 M. Guggi, U. Fiedler, E. Pretsch and W. Simon, *Anal. Lett.*, 8 (1975) 857.
- 7 N. L. Kirsch, R. J. J. Funck, E. Pretsch and W. Simon, *Helv. Chim. Acta*, 60 (1977) 2326.
- 8 V. P. Y. Gadzekpo and G. D. Christian, *Anal. Lett.*, 16 (1983) 1371.
- 9 J. Růžička and E. H. Hansen, *Anal. Chim. Acta*, 161 (1984) 1.
- 10 K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 41(10) (1969) 1203.
- 11 G. J. Moody and J. D. R. Thomas, *Analyst (London)*, 95 (1970) 919.
- 12 V. P. Y. Gadzekpo and G. D. Christian, *Anal. Chim. Acta*, 164 (1984) 279.
- 13 W. E. Morf, *The Principles of Ion-Selective Electrodes and of Membrane Transport*, Elsevier, Amsterdam, 1981, pp. 113–149 and 375–400.
- 14 IUPAC, *Pure Appl. Chem.*, 48(1) (1976) 1.
- 15 W. R. Morf, *The Principles of Ion-Selective Electrodes and of Membrane Transport*, Elsevier, Amsterdam, 1981, pp. 264–336.