

Coated-wire Lithium Ion-selective Electrodes Based on Polyalkoxylate Complexes

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Barium and lithium adducts of polyalkoxylates have been investigated as sensors in lithium ion-selective electrodes using a microconduit flow injection analysis system. Dioctyl phenylphosphonate (DOPP) and dioctyl 3-nitrophenylphosphonate (N-DOPP) were employed as solvent mediators. Selectivity coefficients, $k_{Li, M}^{pot}$, for the $Ba(PPG\ 1025)_{0.69} \cdot (TPB)_2$ -DOPP-based lithium electrode in 0.14 M sodium chloride solution are as follows: Na^+ 3.7×10^{-2} , K^+ 4.4×10^{-3} , Ca^{2+} 4.1×10^{-1} and Mg^{2+} 8.0×10^{-2} . The selectivity coefficients are compared with those for two other previously reported lithium electrodes. The barium polyalkoxylate adduct is a better sensor for lithium than its lithium analogue.

Keywords: Polyalkoxylate adducts; lithium ion-selective electrodes; matched potential method; microconduit flow injection analysis

Metal ion adducts of polyalkoxylates, together with suitable mediator solvents, have been used as sensors in ion-selective electrodes.¹⁻⁴ Effective linear calibration ranges of 5×10^{-5} – 1×10^{-1} M were obtained for these electrodes with respect to alkaline earth metal cations. Electrodes with polypropoxylate adducts plus dioctyl phenylphosphonate (DOPP) or dioctyl 3-nitrophenylphosphonate (N-DOPP) as solvent mediator showed high interference by lithium ions.³ In fact, in 5.0×10^{-3} M Li^+ , the electrodes were completely insensitive to changes in the respective primary cation levels. This interference effect led to this investigation of the prospects of some polypropoxylate adducts as lithium ion-selective electrodes set up in a flow injection analysis (FIA) mode.

This study is important in view of the possibility of the potentiometric monitoring of lithium during therapeutic treatment of manic psychosis. In this respect, a wide range of materials has been used in the development of lithium electrodes,⁵⁻¹⁵ but their selectivities are frequently unsuitable for the clinical assay of lithium in blood serum.

was obtained from BDH Chemicals, Poole, and sodium tetraphenylborate (NaTPB) from Aldrich Chemical Co. Dioctyl 3-nitrophenylphosphonate was synthesised according to the procedure of Craggs *et al.*¹⁷ Dodecylmethyl-14-crown-4 (6-dodecyl-6-methyl-1,4,8,11-tetraoxacyclotetradecane) was a gift from Professor T. Shono (Osaka University, Japan).

All solutions were prepared from analytical-reagent grade materials using doubly de-ionised water. The chlorides of the metals were used.

Experimental

Apparatus and Materials

Microconduits made from PVC blocks were used as a sample cell and incorporated into a microconduit FIA assembly of the type previously described by Růžička and Hansen¹⁶ (Fig. 1). The indicator electrode contained sensor membranes as described below and the reference electrode consisted of a silver wire coated with silver chloride in contact with 0.14 M sodium chloride solution [Fig. 1(b)]. For preparing the silver-silver chloride electrode, silver wire is treated with a solution of sodium chloride (0.3 g) and disodium hydrogen phosphate (0.3 g) in 5 cm³ of bleach solution (Formula 77 Bleach from Robert McBride Group, Manchester, was used but other ordinary household bleach solutions are also suitable). Compressed air was used to propel the carrier solution (either 0.1 M barium chloride or 0.14 M sodium chloride) at 1.2 cm³ min⁻¹ through the microconduit.

A Radiometer PHM 64 millivoltmeter was used for e.m.f. measurements and the response was recorded on a Linear Instrument Corp. Model 0555-0000 chart recorder. Sample volumes of 100 mm³ were used throughout.

Reagents and Chemicals

Dioctyl phenylphosphonate and potassium tetra-*p*-chlorophenylborate (KTPCIPB) were obtained from Lancaster Synthesis, Morecambe; polypropylene glycol (PPG 1025)

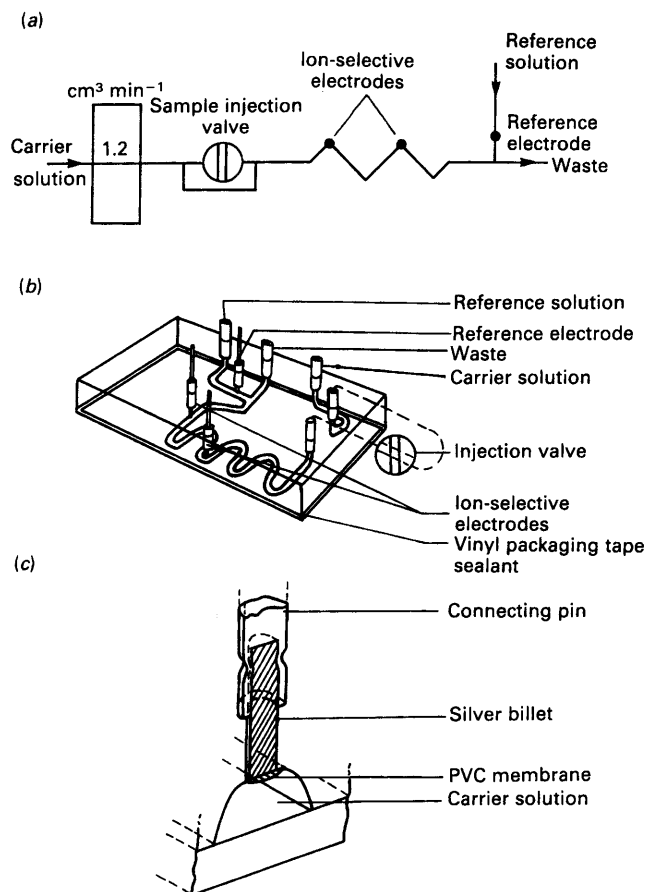


Fig. 1. (a) Manifold design; (b) microconduit; and (c) sectional view of the ion-selective electrode

Preparation of Barium and Lithium (PPG 1025.TPB) Complexes

The barium - PPG complex, $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$, was prepared as reported by Jaber *et al.*³ The lithium complex, $\text{Li}(\text{PPG } 1025)_{0.49}(\text{TPB})_2$, was similarly prepared by adding 10 cm^3 of 1.0 M lithium chloride solution to 100 cm^3 of $1.0 \times 10^{-3} \text{ M}$ PPG 1025 and the oxonium ion was precipitated with sodium tetraphenylborate. The mixture was centrifuged at $35\,000 \text{ rev min}^{-1}$ for 20 min and the supernatant decanted. The precipitate was washed well with water and vacuum dried overnight at 30°C .

Membrane Fabrication

The cation - PPG 1025 - TPB complex (0.04 g) was dissolved in 0.36 g of the chosen solvent mediator and the sensor cocktail completed by adding 0.17 g of PVC in 6 cm^3 of tetrahydrofuran. Electrodes were fabricated according to the procedure of Růžička and Hansen¹⁶ and Gadzekpo *et al.*¹⁸ by placing three successive drops (25 mm^3 each) of sensor cocktail on the surface of silver wire re-coated with silver chloride as described above for the reference electrode. The silver - silver chloride surface was washed with water and methanol and dried before applying the coating. Each successive drop of cocktail was allowed to dry before placing the next drop on the electrode surface. The complete electrode [$\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$ - PVC - DOPP (or N-DOPP)] was conditioned by pumping 0.1 M barium chloride solution through the microconduit for 6 h, and then allowing the electrode to remain in contact with the solution for a further 12 h. With the lithium polypropoxylate membrane electrode, 0.1 M lithium chloride solution was used.

For some of the barium polypropoxylate membranes, potassium tetra-*p*-chlorophenylborate was incorporated in the ratio of 1 part of KTpCIPB to 2 parts of $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$.

The indicator electrodes were assembled into the manifold and microconduit FIA system as depicted in Fig. 1. When not in use, the barium polypropoxylate electrode was kept in contact with 0.1 M barium chloride solution and the lithium polypropoxylate electrode was kept in 0.1 M lithium chloride solution.

Selectivity Coefficients ($k_{\text{Li}, \text{B}}^{\text{pot}}$)

The selectivity coefficients were determined by a variation of the matched potential technique.^{18,19} Thus, a series of lithium standards (0.1 – 10 mM) made up in sodium chloride solution (0.14 M) were injected into the carrier FIA stream of sodium chloride solution (0.14 M). This was followed by injection of the interfering ion, *e.g.*, 0.1 M potassium as potassium chloride in 0.14 M sodium chloride solution. The concentration of lithium ions corresponding to the change in potential of the potassium interferent was determined from a graph of e.m.f. versus $\log[\text{Li}]$. The selectivity coefficient, $k_{\text{Li}, \text{K}}^{\text{pot}}$, is simply given by $[\text{Li}]/[\text{K}]$. It should be noted that 0.16 M sodium chloride solution was injected for determining $k_{\text{Li}, \text{Na}}^{\text{pot}}$ so that the potential change relates to 0.02 M added sodium chloride.

Another series of lithium standards (0.1 – 10 mM) made up in barium chloride solution (0.1 M) was also injected into the FIA stream of 0.1 M barium chloride solution. This was followed by injection of three standard solutions of sodium chloride interferent (0.01 , 0.05 and 0.1 M), also in 0.1 M barium chloride solution. Selectivities were then evaluated as described above.

In order to compare these selectivities with some of the electrodes reported elsewhere, selectivity values for the lithium ion-selective electrode based on $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$ sensor were determined by the separate and mixed solution methods employed by Zhukov *et al.*⁵ and Kitazawa *et al.*⁶ respectively. Also, the same separate and mixed solution methods were used for determining the

selectivity coefficients of the lithium ion-selective electrode based on the sensor of Kitazawa *et al.*,⁶ namely dodecylmethyl-14-crown-4.

Results and Discussion

In this study, a lithium response was obtained for the $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$ - PVC membrane electrode (DOPP as solvent mediator) with a linear slope of $57 \text{ mV decade}^{-1}$. The life of this electrode was 1 month and the FIA response is fast, reproducible and low in noise and drift (Figs. 2 and 3). Lithium levels of 0.1 mM are detectable (*ca.* 0.4 mV from the background) by this electrode in the FIA mode using 0.1 M barium chloride as carrier solution. A similar response was obtained for lithium using a $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$ - PVC membrane electrode with N-DOPP as solvent mediator.

Selectivity coefficients for the lithium response of the two barium-based sensor electrodes are given in Table 1. The electrode containing DOPP shows better selectivity for lithium over sodium than the electrode containing N-DOPP. At higher sodium concentrations, it can be seen that the selectivity worsens. This is expected, as interference generally increases with increasing interferent ion concentrations. Attempts to obtain a lithium response at lower barium chloride concentrations, *e.g.*, $1.0 \times 10^{-3} \text{ M}$, were futile. The electrodes were noisy owing to the low ionic strength of the carrier solution.

The concentration of sodium in blood lies around 0.14 M and it is therefore important that the electrodes are assessed under similar conditions. The response of the electrodes was studied using 0.14 M sodium chloride as carrier solution (Fig. 3). Again, lithium can be measured at levels down to 0.1 mM . In this medium, a linear calibration graph of limited range and a slope of $56 \text{ mV decade}^{-1}$ were observed in more concentrated solution for the electrode containing DOPP as solvent mediator (Fig. 4). Selectivity coefficients in a high sodium background (Table 2) are comparable to those in 0.1 M barium chloride solution.

The best selectivity coefficient data quoted in the literature for the neutral carrier-type lithium sensors range from 10^{-2} to

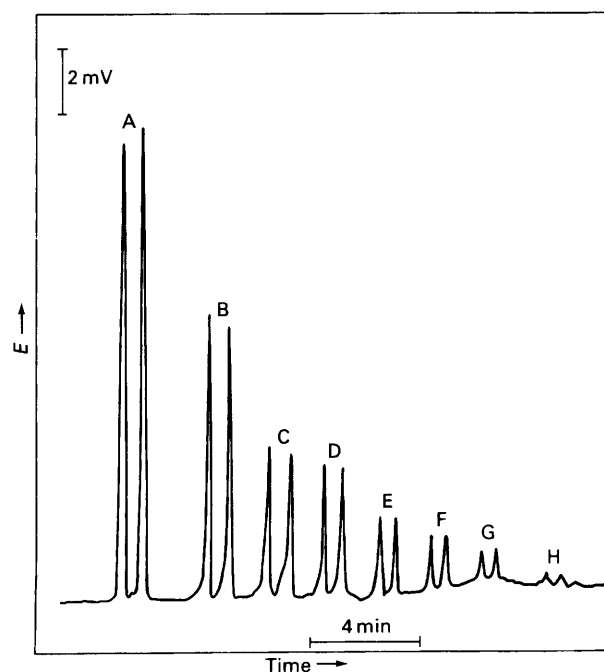


Fig. 2. Lithium response in 0.1 M barium chloride solution. Electrode, $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$ - DOPP. Concentration of LiCl in 0.1 M BaCl_2 : A, 10.0 ; B, 5.0 ; C, 2.5 ; D, 2.0 ; E, 1.0 ; F, 0.5 ; G, 0.25 ; and H, 0.1 mM

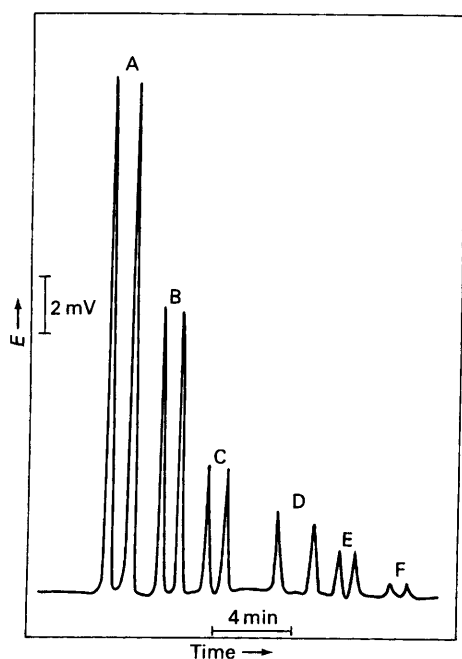


Fig. 3. Lithium response in 0.14 M sodium chloride solution. Electrode, $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$ - DOPP. Concentration of LiCl in 0.14 M NaCl: A, 10.0; B, 5.0; C, 2.0; D, 1.0; E, 0.5; and F, 0.1 mM

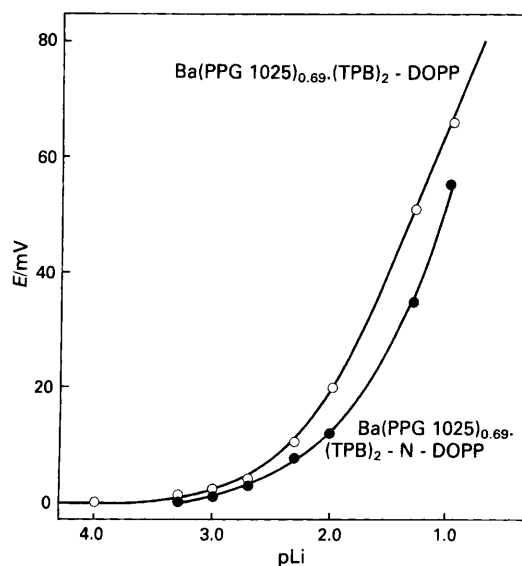


Fig. 4. Calibration of $\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$ electrodes based on DOPP and N-DOPP solvent mediators, respectively, with lithium standards in 0.14 M sodium chloride solution. Carrier solution, 0.14 M sodium chloride

Table 1. Selectivity coefficients, $k_{\text{Li}, \text{Na}}^{\text{pot}}$, for PVC electrodes. Carrier solution: 0.1 M barium chloride. Standards of lithium and sodium were prepared in 0.1 M barium chloride solution

Interferent Na^+/M	Membrane system					
	$\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$		$\text{Li}(\text{PPG } 1025)_{0.49}\text{-TPB}$		$\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2\text{-KTPCIPB}$	
	DOPP	N-DOPP	DOPP	N-DOPP	DOPP	N-DOPP
0.1	4.4×10^{-2}	7.1×10^{-2}	5.0×10^{-2}	1.0×10^{-1}	5.4×10^{-2}	8.6×10^{-2}
0.05	3.3×10^{-2}	6.0×10^{-2}	—	1.0×10^{-1}	4.7×10^{-2}	7.8×10^{-2}
0.01	1.0×10^{-2}	5.0×10^{-2}	—	—	—	9.1×10^{-2}

Table 2. Selectivity coefficients, $k_{\text{Li}, \text{Na}}^{\text{pot}}$, for PVC electrodes. Carrier solution: 0.14 M sodium chloride. Lithium and other standards were prepared in 0.14 M sodium chloride solution.

Interferent		Membrane system					
		$\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2$		$\text{Li}(\text{PPG } 1025)_{0.49}\text{-TPB}$		$\text{Ba}(\text{PPG } 1025)_{0.69}(\text{TPB})_2\text{-KTPCIPB}$	
Ion	Concentration/M	DOPP	N-DOPP	DOPP	N-DOPP	DOPP	N-DOPP
Na^+	0.02	3.7×10^{-2}	9.1×10^{-2}	1.0×10^{-1}	1.3×10^{-1}	3.6×10^{-2}	8.8×10^{-2}
		$(3.9 \times 10^{-2})^*$	$(9.5 \times 10^{-2})^*$				
K^+	0.10	4.4×10^{-3}	2.5×10^{-2}	2.0×10^{-2}	3.2×10^{-2}	1.1×10^{-2}	2.4×10^{-2}
		$(5.1 \times 10^{-3})^*$	$(6.5 \times 10^{-3})^*$				
Ca^{2+}	0.14	4.1×10^{-1}	1.4×10^{-1}	1.7×10^{-1}	1.2×10^{-1}	7.1×10^{-1}	1.7×10^{-1}
		$(4.3 \times 10^{-1})^*$	$(4.3 \times 10^{-1})^*$				
Mg^{2+}	0.10	8.0×10^{-2}	4.5×10^{-2}	6.5×10^{-2}	5.6×10^{-2}	1.3×10^{-1}	5.7×10^{-2}
		$(8.4 \times 10^{-2})^*$	$(1.0 \times 10^{-2})^*$				

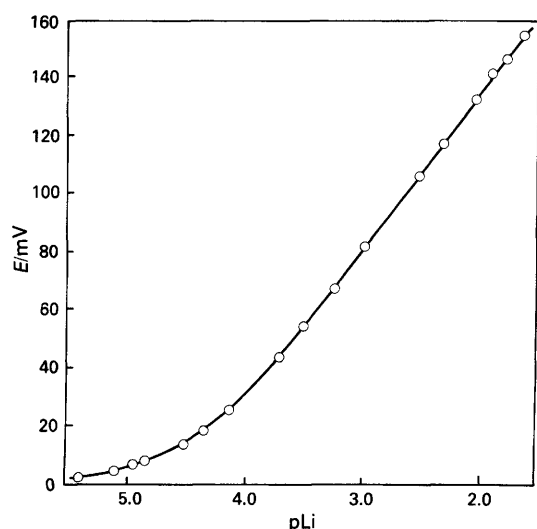
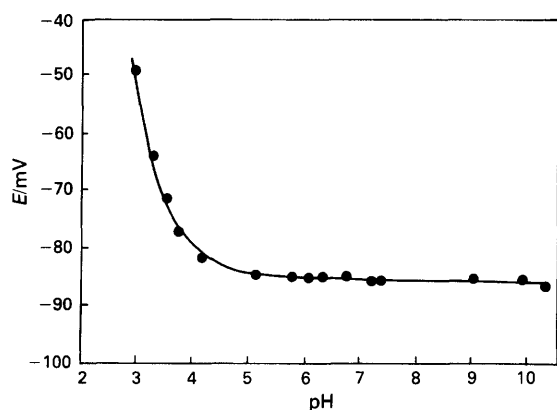
* Values in parentheses were obtained after pre-soaking the electrodes in 1.0 M lithium chloride solution for 24 h and then in 1.0×10^{-3} M lithium chloride solution for 2 h.

2.0×10^{-3} for $k_{\text{Li}, \text{Na}}^{\text{pot}}$, as quoted by Zhukov *et al.*⁵ and Kitazawa *et al.*,⁶ respectively (Table 3). Some values in this work are comparable, *e.g.*, *ca.* 10^{-2} for the DOPP-based barium sensor (Table 1), but it is difficult to make meaningful comparisons of the present pseudo lithium electrode with the other models.^{5,6} Indeed, when using identical techniques (Table 3) the selectivity values are obviously different, and considering all the data the dodecylmethyl-14-crown-4 electrode seems advantageous.

Some barium electrodes were exposed to 0.1 M lithium chloride solution for 24 h and then to 1.0 mM lithium chloride solution for 2 h in order to exchange barium ions for lithium ions. With few exceptions, the resulting selectivity coefficients of the pseudo lithium electrodes were not improved relative to those evaluated without such treatment (Table 2). Selectivities of electrodes based on actual $\text{Li}(\text{PPG } 1025)\text{-TPB}$ complexes are also less favourable than their $\text{Ba}(\text{PPG } 1025)\text{-TPB}$ counterparts (Tables 1 and 2). The minimum concentration of

Table 3. Selectivity coefficients, $k_{Li, Na}^{pot}$, of three different PVC ion-selective electrodes

Sensor material	PVC electrode		$k_{Li, Na}^{pot}$			
	Solvent mediator, %	PVC, %	Sensor, %	Separate solution method	Mixed solution method	Matched potential method
Ba(PPG 1025) _{0.69} .(TPB) ₂	Dioctyl phenylphosphonate (63)	30	7	4.4×10^{-2} (this work)	1.7×10^{-2} (this work)	3.7×10^{-2} (this work)
Dodecylmethyl-14-crown-4 (6-dodecyl-6-methyl-1,4,8,11-tetraoxacyclotetradecane)	<i>o</i> -Nitrophenyl octyl ether (70)	28	1 (+0.5% KTpClPB + 1% TOPO)	9.4×10^{-3} (this work)	6.6×10^{-3} (this work)	3.2×10^{-2} (this work)
<i>N,N,N',N'</i> -Tetraisobutyl-cyclohexane- <i>cis</i> -1,2,-dicarboxylic diamine	<i>o</i> -Nitrophenyl octyl ether (65-66)	33	1-2	1.0×10^{-2} (ref. 5)	—	—

**Fig. 5.** Calibration of Ba(PPG 1025)_{0.69}.(TPB)₂ - DOPP electrode with lithium standards**Fig. 6.** Effect of pH on the lithium response using the Ba(PPG 1025)_{0.69}.(TPB)₂ - DOPP ion-selective electrode. Concentration of Li⁺ in solution, 1.0×10^{-3} M.

lithium detectable by the DOPP-based electrode in 0.14 M sodium chloride solution is 2.0×10^{-3} M, compared with 10^{-3} M for the N-DOPP-based model.

Lipophilic salts, such as KTpClPB, incorporated into PVC membranes are reported to reduce electrical membrane resistance and interferences by lipophilic sample anions.²⁰ Therefore, KTpClPB was incorporated into the PVC barium electrode membranes in a ratio of 1 part of KTpClPB to 2 parts of Ba(PPG 1025)_{0.69}.(TPB)₂. The results were disappointing

in that the selectivity was either essentially unaltered or indeed considerably impaired (Tables 1 and 2). Poor results were also obtained on incorporating KTpClPB into the PVC membrane containing Li(PPG 1025)_{0.69}.TPB.

In the absence of any interfering ion, the linear calibration region of the Ba(PPG 1025)_{0.69}.(TPB)₂ - DOPP electrode is extended to 10^{-4} M Li⁺ (Fig. 5). This compares very favourably with that reported by Zhukov *et al.*⁵

The effect of pH on the Ba(PPG 1025)_{0.69}.(TPB)₂ - DOPP-based electrode response reveals little interference between pH 5 and 10 (Fig. 6).

The inability of the lithium polypropoxylyte adduct to enhance the selectivity parameters could be due to its formation constant being greater than that of the barium analogue and, hence, its inability to exchange lithium ions efficiently. Solvent mediators other than the two investigated may enhance the lithium response and selectivity.

Conclusion

Although the best of the new electrodes described here for lithium response is not as selective as the electrodes previously described by Zhukov *et al.*⁵ and Kitazawa *et al.*,⁶ the response of the Ba(PPG 1025)_{0.69}.(TPB) - DOPP electrode towards lithium ions is of sufficiently high quality for it to be a realistically useful ion-selective electrode. Further, there is the added advantage that the barium propoxylyte sensor is much more easily prepared in the laboratory than are the other neutral carrier sensors.

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