

SHORT COMMUNICATION

POTENTIOMETRIC DETERMINATION OF K^+ IONS USING A K^+ -SELECTIVE ELECTRODE WITH MACROCYCLIC LIQUID MEMBRANE

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ABSTRACT. This paper describes analytical applications of K^+ -selective liquid membrane electrode. The membrane is the solution of the active complex formed by the K^+ ions with dibenzo-18-crown-6 ionophore (DB-[18]-C-6) extracted in propylenecarbonate (PC). Successful application of the developed electrode for K^+ ions determination in aqueous solution and samples of commercial mineral water by direct potentiometry is presented.

KEY WORDS: K^+ -selective electrode, Macrocyclic ligand, Potentiometry

INTRODUCTION

Crown ethers have been developed in an attempt to mimic the complexation behavior toward alkali metals of naturally occurring macrocycles such as valinomocine, nonactine and other compounds [1, 2], but the field shortly developed many compound with certain analytical properties.

Macrocyclic ligands are known as efficient and selective ion-carriers through liquid membranes. Due to these properties, the crown ethers have been used in recent years to develop ion-selective electrodes for determination of alkali [3-7] and other transitional metals [8-10].

The response of the ion-selective electrode has been attributed to an exchange process of K^+ ions between the analyzed aqueous solution and organic solution of membrane in propylenecarbonate. This electrode has been successfully used for direct potentiometric determination and potentiometric titrations of K^+ ions in aqueous solutions.

EXPERIMENTAL

Construction of the electrode. The electrode was prepared according to literature method [3]. The internal reference solution was ionic pair formed by the K^+ ions with DB-[18]-C-6 ionophore (10^{-2} M) extracted in a mixture of propylenecarbonate and toluene (9/1 v/v).

The direct measurements of the electromotive force of the electrode were made in solution of K^+ (Merck) at pH = 5.6. The determinations of the electromotive force have been made with a digital FASTECHO 763 pH meter versus a saturated calomel electrode (Radiometer).

RESULTS AND DISCUSSION

Response of the electrode to the concentration of K^+ ions. In Table 1 is presented the variation of the electromotive force of the electrode versus the saturated calomel electrode (SCE) at 25 °C and ionic strength $\mu = 0.3$ provided with (10^{-1} M) $MgCl_2$ (which does not influence the electrode potential) as a function of $-\log[K^+]$ in aqueous solutions for most important coupling anions.

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Table 1. The variation of the electromotive force of the electrode (vs. SCE) at 25 °C and $\mu = 0.3$ M (MgCl_2), as a function of $-\log [\text{K}^+]$.

Log $[\text{K}^+]$	E (mV)							
	CH_3COO^-	Γ^-	Cl^-	SCN^-	NO_3^-	Bp^-	SO_4^{2-}	CO_3^{2-}
$\Delta E/\Delta \log [\text{K}^+]$ (mV)	58.85	58.10	57.21	56.70	50.76	48.97	47.44	45.68

The values of the potential slope $\Delta E/\Delta \log [\text{K}^+]$ presented in Table 1 have been statistically calculated through the linear regression method. The influence of the nature of the coupling anion is also presented in Table 1. The best values of the electrode slope were obtained for CH_3COO^- and Γ^- as coupling anions.

The range of linear response of the electrode is between $10^{-2} - 5 \times 10^{-6}$ M for all the coupling anions.

Influence of the pH. The influence of pH on the response of the K^+ -selective electrode was studied in the 2-9 pH range using solutions of 10^{-2} M citric acid/ Na^+ citrate (for the pH range 2-6.5) and 10^{-2} M boric acid/ Na^+ borate (for the pH range 6.5-9) buffer solutions [11].

It was found that the pH variation between 3.6 and 7 does not affect the electrode potential.

Selectivity of the electrode. The constructed electrode has been tested for a series of cations, which can interfere the K^+ ions in the ionic exchange equilibrium in the membrane. For these cations, the selectivity coefficients have been determined using the mixed solution method and the separate solution method [12]. The characteristics of the electrode and the values of the selectivity coefficients are presented in Table 2. The strong interference of the Pb^{2+} is avoided by the MgCl_2 (10^{-1} M) support electrolyte, which precipitates the Pb^{2+} ions in analyzed aqueous samples

Even if the values of the selectivity coefficients determined through the separate solution method are smaller, the mixed solution method better represent the condition and properties of the real samples.

Table 2. The characteristics of the K^+ -selective electrode at pH = 5.6, temperature = 25 °C, $\mu = 0.3$ M.

Range of linear response		$10^{-2} - 5 \times 10^{-6}$ M	
$\Delta E/\Delta \log [\text{K}^+]$ (mV) (CH_3COOK)		58.85	
Selectivity coefficients to the cations			
Cation	Mixed solution method	Separate solution method	Relative error (%)
Na^+	2.85×10^{-3}	2.79×10^{-3}	2.10
Ag^+	1.42×10^{-3}	1.37×10^{-3}	3.52
Hg^{2+}	2.32×10^{-3}	2.18×10^{-3}	1.72
Ca^{2+}	2.83×10^{-4}	2.77×10^{-4}	2.12
Ba^{2+}	8.33×10^{-4}	7.98×10^{-4}	4.20
Ni^{2+}	7.04×10^{-4}	6.94×10^{-4}	1.42
Zn^{2+}	7.35×10^{-4}	7.08×10^{-4}	3.67
NH_4^+	5.42×10^{-4}	5.31×10^{-4}	2.02
Pb^{2+}	-	1.06	-

Dynamic response and reproducibility of the electrode. The response characteristics of the newly developed K^+ -selective electrode were evaluated during a period of 28 days, after the electrode conditioning in a 10^{-2} M solution of CH_3COOK for 24 hours.

The response time of the electrode in diluted solutions (10^{-4} - 10^{-5} M) were about 1 min, while in more concentrated solutions (10^{-2} - 10^{-3} M) the electrode potential reaches an equilibrium value in a few seconds. A magnetic stirrer was used during all potential measurement. The reproducibility of the electrode response was tested over 4 weeks, when the electrode potential changed only by ± 3 mV, without modifying the electrode slope value.

Analytical applications. The validation of the constructed electrode was checked by determining the K^+ ions in commercial mineral waters samples by direct potentiometry and potentiometric titrations. The samples were selected from the commercial mineral water "Valcele", "Izvorul Minunilor" and "Biborteni Magnesia" because of the different content in potassium and the different ion matrix profile of each of the samples. For direct potentiometric determinations, a calibration curve was used, according to the data presented in Table 1 and Figure 1. From these data, the lower limit of K^+ concentration that can be determined by direct potentiometry with this electrode is 5×10^{-6} mol.M $^{-1}$.

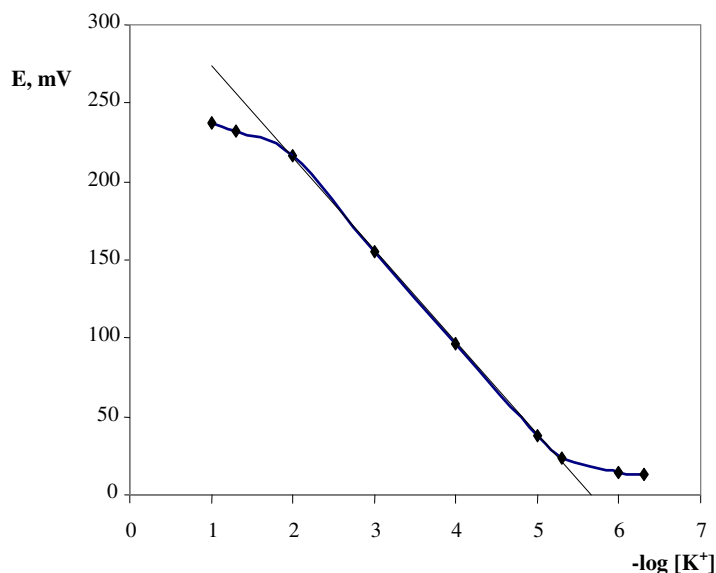


Figure 1. The variation of the electromotive force of the electrode (vs. SCE) as a function of $-\log [K^+]$ for CH_3COOK at $25^\circ C$, $pH = 5.6$, and $\mu = 0.3$ M ($MgCl_2$).

The expression of the regression equation for the calibration graph presented in Figure 1 is $Y = -58.853X + 333.19$, where X represents the function $-\log [K^+]$ and Y represents the value of the electromotive force of the electrode (mV) versus SCE, the value of the correlation coefficient being $R^2 = 0.9996$. This equation can be used for determining the corresponding K^+ ions concentration in any synthetic or real sample. Table 3 presents the result for K^+ ions determination by direct potentiometric determinations in commercial mineral water samples comparison with the AAS method. The results obtained by direct potentiometric measurement with the newly developed K^+ -selective electrode are in accordance with that obtained by the AAS method (using a digital GBC AVANTA PM atomic absorption spectrometer). The validity of direct potentiometric determination of K^+ ions using the new K^+ -selective electrode was checked by the standard addition method. The experimental data are presented in Table 4.

Table 3. The results of the K^+ ion determination in commercial mineral water samples.

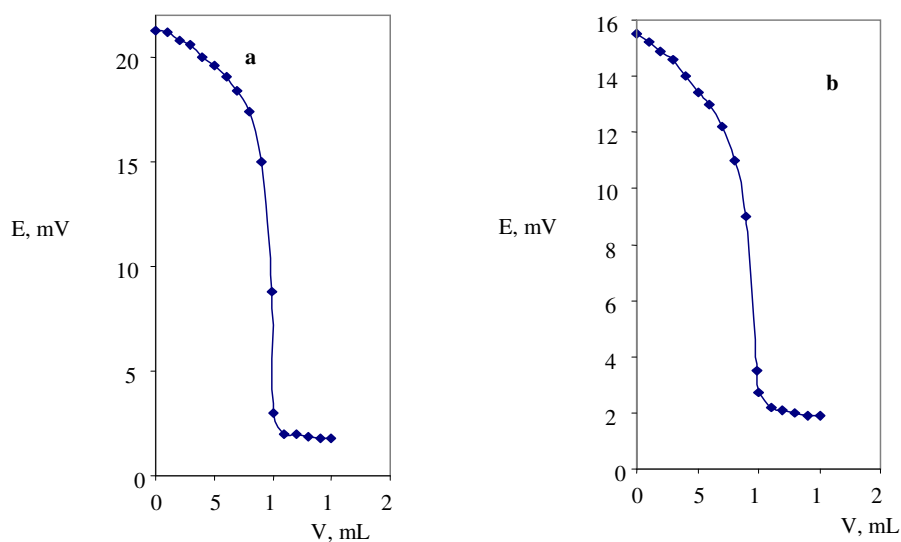
Sample No *	Potentiometric with K^+ -selective electrode (mg.L ⁻¹)	AAS method (mg.L ⁻¹)	RSD (%)
1.	12.81	12.84	0.17
	12.66	12.70	0.22
	12.72	12.70	0.11
2.	4.11	4.13	0.34
	4.06	4.05	0.15
	4.03	4.05	0.35
3.	7.81	7.85	0.36
	7.16	7.13	0.30
	7.53	7.57	0.37

*1 – Valcele; 2 – Izvorul Minunilor; 3 – Biborteni Magnesia.

Table 4. The results of the K^+ ions determination in commercial mineral water samples using the standard additions method

Sample No *	Initial K^+ (AAS) (mg.L ⁻¹)	Addition of K^+ (mg.L ⁻¹)	Theoretical total (mg.L ⁻¹)	Experimental with K^+ -selective electrode (mg.L ⁻¹)	RSD (%)
1.	12.84	1.95	14.79	14.73	0.29
	12.70	1.95	14.65	14.61	0.19
2.	4.13	3.90	8.03	8.05	0.18
	4.05	3.90	7.95	7.94	0.09
3.	7.85	1.95	9.80	9.78	0.14
	7.13	1.95	9.08	9.11	0.23

*1 – Valcele; 2 – Izvorul Minunilor; 3 – Biborteni Magnesia.

Figure 2. Potentiometric titration of 100 mL of CH_3COOK (10^{-2} M curve a and 10^{-3} M curve b with $Na_3[Co(NO_2)_6]$ (5×10^{-2} M curve a and 5×10^{-3} M curve b).

The newly developed sensor was also successfully used as indicator electrode for the titration of K^+ synthetic solutions with $Na_3[Co(NO_2)_6]$. A 100 mL aliquot of 10^{-2} M CH_3COOK was titrated with 5×10^{-2} M $Na_3[Co(NO_2)_6]$ (Figure 2 a) and another 100 mL aliquot of 10^{-3} M CH_3COOK was titrated with 5×10^{-3} M $Na_3[Co(NO_2)_6]$ (Figure 2 b). It can be observed that on the addition of $Na_3[Co(NO_2)_6]$ the concentration of K^+ ions decreases causing a decrease in potential.

Potential rises of 120 mV in the titration curve in Figure 2a and of 63 mV in the titration curve in Figure 2b. However the curves have a sharp break point that corresponds to the stoichiometry of the $K_3[Co(NO_2)_6]$ complex. After the end-point the sensor potential remains almost constant because it is not responding to small changes in K^+ ions concentration. This method proves that the amount of K^+ ions can be accurately determined with the newly developed electrode.

CONCLUSIONS

An inexpensive ion-selective electrode with liquid membrane for K^+ ions has been developed, characterized and used for determination of K^+ ions in mineral water samples. The liquid membrane contains the complex formed by the K^+ ions with the crown ether DB-[18]-C-6 extracted in an organic solvent, supported on a micro porous alumina rod.

The range of linear response and the nearly Nernstian cationic response (58.8 mV) proves good analytical performances for the constructed electrode. The newly developed electrode has shown good performance characteristics with time, stability being checked up in four weeks. The electrode exhibited fairly good selectivity towards the nominated cations over each other. The developed methods have shown to be simple, accurate and precise.

REFERENCES

1. Stefanak, L.; Simon, W. *Microchem J.* **1967**, 12, 125.
2. Pioda, L.; Stankova, V; Simon, W. *Anal. Lett.* **1969**, 2, 665.
3. Isvoranu, M.; Luca, C.; Pleniceanu, M.; Spinu, C. *J. Serb. Chem. Soc.* **2006**, 71, 1345.
4. Mahajan, R.K.; Kumar, M.; Sharma V; Kaur, I. *Talanta* **2002**, 58, 445.
5. Wright, A.J.; Matthews, S.E.; Fischer, W.B.; Beer, P.D. *Chem. Europ. J.* **2001**, 7, 3437.
6. Yamauchi, A.; Hayashita, T.; Kato, A.; Nishizawa, S.; Watanabe, M.; Teramae, N. *Anal. Chem.* **2000**, 72, 5841.
7. Pungor, E. *Talanta* **1997**, 44, 1505.
8. Mahajan, R.K.; Kaur, I.; Kumar, M. *Sensors and Actuators B: Chemical* **2003**, 91, 26.
9. Lu, J.; Chen, R.; He, X. *J. Electroanal. Chem.* **2002**, 528, 33.
10. Mousavi, M.F.; Sahari, S.; Alizadeh, N.; Shamsipur, M. *Anal. Chim. Acta* **2000**, 414, 189.
11. Britton, H.T.S.; Robinson, R.A. *J. Chem. Soc.* **1931**, 1456, 458.
12. Umezawa, Y. *Handbook of Ion Selective Electrodes: Selectivity Coefficients*, CRC Press: Boca Raton; **1990**.