

# Potassium Sensing by Using a Newly Synthesized Squaraine Dye in Sol-Gel Matrix

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Squaraines are a group of fluorescent dyes and pigments derived from squaric acid and dialkylanilines well known in applications such as photoreceptors, organic solar cells, optical recording media, and non-linear optics. Their very promising spectral properties, long wavelength absorption and emission, and high absorptivity and quantum yields have not been exploited so far in relation to optical sensor design. They exhibit excellent solubility in sol-gel matrices, and the ligand is an integral part of the fluorophore  $\pi$  system, which makes the molecule a fluoroionophore. In this work, potassium-sensing agent, bis[4-N-(1-aza-4,7,10,13,16-pentaoxacyclooctadecyl)-3,5-dihydroxyphenyl] squaraine has been used for potassium sensing in a sol-gel matrix. The spectrofluorimetric response of dye-doped tetraethyl ortosilicate (TEOS) film after exposure to certain concentrations of  $K^+$  has been investigated, and 62% of relative signal change was achieved. The dynamic working range of the sensor membrane has been found between  $10^{-9}$  and  $10^{-6}$  M  $K^+$ , in other terms from nanomolar to micromolar levels, which is an advantage over flame emission spectroscopy, in view of detection limit. The sensor is fully reversible within the dynamic range and the response time ( $\tau_{90}$ ) is found to be 2 min under batch conditions. The cross-sensitivity of the molecule to  $Na^+$ ,  $Ba^{2+}$ ,  $Ca^{2+}$ , and  $NH_4^+$  was also tested in separate solutions.

**KEY WORDS:** Optical potassium sensing; squaraine structure; sol-gel matrix,

## INTRODUCTION

Crown ether molecules, which are also named as "host molecules" after derivatization, possesses a well-defined cavity and have demonstrated unique ionophoric properties toward many guest molecules, including inorganic and organic species [1]. Probably one of the most important applications of crown ethers in sensor technologies is the sensing of alkali and earth alkali metals. Highly selective ionophores (e.g., valinomycin) in combination with potential sensitive fluorescent dyes (PSD), polarity-

sensitive fluorophores, or lipophilic anionic dyes incorporated into PVC membranes or Langmuir Blodgett films have been used in potassium sensing. The first PSD-based optical sensor for potassium, consisting of valinomycin and rhodamine B octadecyl ester was introduced by Wolfbeis [2]. Wang and co-workers [3] used a combination of valinomycin, nonactine, and a sodium ionophore in plasticized PVC matrix for sensing. Toth *et al.* [4] introduced an optical potassium sensor in which the potassium selective ionophore is incorporated in plasticized polyvinyl chloride film with hydrogen-selective ionophore. The potassium-selective ionophore (BME 44), which is a five heteroatom containing azacrown, facilitates the transport of potassium ions while the chromoionophore ETH 5350 promotes the uptake of proton ions into the membrane phase from the solution. Ambrose and co-workers [5] used a combination of ETH 5350,

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valinomycin, and a tetraphenyl borate derivative in thin decyl methacrylate films on glass substrates. Shortreed and co-workers presented a miniaturized fiber optic sodium sensor based on a highly sodium selective crown ether-calyx [4] arene ionophore and chromoionophore ETH 5294 (9-dimethyl amino-5-octadecanoylimino-5H-benz [a] phenoxazine, ETH 5350, and valinomycin [6].

On the other hand, squaraine derivatives are a group of fluorescent dyes and pigments derived from squaric acid and dialkylanilines well known in applications such as photoreceptors, organic solar cells, optical recording media, and non-linear optics. Their very promising spectral properties, long wavelength absorption and emission, and high absorptivity and quantum yields have not been exploited so far in relation to optical sensor design [7,8]. In the present work, newly synthesized azacrown containing squaraine derivative has been used for sensor preparation in sol-gel matrix. In the squaraine-containing structures, the squaryl moiety is assumed to act as a signal transducer and converts the information (recognition event) into an optical signal. In regard to the recognition moiety, it is responsible for selectivity and efficiency of binding, which depend on the ligand topology, on the characteristics of cation (ionic radius, charge, coordination number, hardness, etc.).

Following the choice of indicator, the next step is the immobilization of the dye in the proper matrix. Sol-gel matrix is believed to be useful for analytical applications because of its optical transparency, simplicity of preparation, and the chemical and mechanical stability of the matrix, which allows spectral measurements from the UV to the near IR, the possibility of giving any desired geometric shape, as well as low temperature studies, without concern for solubility [9,10] and therefore have been chosen as matrix material.

The squaryl moiety containing azacrown structure has been investigated in view of its possible use for optical sensing of  $K^+$  and  $Na^+$ . The sensor characteristics such as dynamic working range, sensitivity, limit of detection, and selectivity have been investigated. In addition the interferences of various cations on the response of potassium also been studied.

## EXPERIMENTAL DETAILS

### Materials

The azacrown containing squaryl dye, 2bis[4-N-(1-aza-4,7,10,13,16-pentaoxacyclooctadecyl)-3,5-dihydroxyphenyl] squaraine, was synthesized and purified as

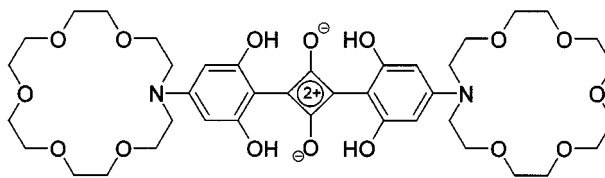
described previously [8] and is shown in Fig. 1. The sol-gel components, tetraethyl orthosilicate (tetraethoxysilane, TEOS) and tetramethyl orthosilicate (tetramethoxysilane, TMOS), were purchased from Merck and Fluka, respectively. Analytical-grade concentrated hydrochloric acid was purchased from Merck. Studies performed in buffered acidic solutions were carried out using *N,N*-bis(2-hydroxyethyl)-2-amino-ethanesulfonic acid (BES) from Sigma. Acid solutions and buffers used for investigating the pH effects were prepared with high-quality pure water obtained from Elga. The surfactant additive Triton X-100 (polyethylene glycol *t*-octylphenyl ether) was obtained from Merck. Absolute ethanol or methanol used throughout the studies was used as received.

The absorption and emission spectra of azacrown dye was identical in both TEOS and TMOS sol-gel matrices. Because there was no visual difference between both the absorption and emission spectra obtained from the TMOS and TEOS precursors, the non-toxic one, TEOS, is used throughout the studies.

### Sol-Gel Matrix and Film Preparation Process

Azacrown dye-doped silica gel glasses were prepared by hydrolyzing of TEOS or TMOS. 2 ml of TEOS and 1 ml of acidic water (pH 2 via addition of HCl) were sonicated for 5 min. After sonification, the pH of the liquid sol was increased with addition of 250  $\mu$ L 0.14 M sodium phosphate (pH 6), and 1 ml, 2-mM dye solution was added. This was then followed by the addition of 1 ml and 20  $\mu$ L of Triton X-100 to improve the homogeneity of the silica sol-gel and to give a crack-free monolith. In all cases the solutions were aged at room temperature in closed glass vials.

Glass slides (11  $\times$  40  $\times$  1 mm) were used as solid support onto which the sol-gel was cast by dip-coating technique. Prior to casting, the glass surface was activated by treatment with concentrated  $HNO_3$  for 24 h and then washed with distilled water, followed by ethanol or methanol. After evaporation of the solvents in a desiccator, the glass slides were fixed diagonally in a quartz sample



**Fig. 1.** Structure of bis[4-N-(1-aza-4,7,10,13,16-pentaoxacyclooctadecyl)-3,5-dihydroxyphenyl] squaraine.

cuvette. The advantage of this kind of a placement was to improve the reproducibility of the measurements.

### Spectroscopic Measurements

The absorption spectra of sol-gel glass slides at approximately  $4\ \mu\text{M}$  thickness were measured using a Jasco V-530 UV-VIS spectrophotometer. The fluorescence emission spectra were recorded using a PTI-QM1 fluorescence spectrophotometer. pH measurements were performed with a pH-meter Jenway 3040 Ion-Analyzer calibrated with Merck pH standards of pH 7.00 (titrisol buffer) and pH 4 at  $20^\circ\text{C}$

## RESULTS AND DISCUSSION

### Matrix Modification and Effect of Surfactant

An important consideration in the preparation of azacrown dye-doped films is the pH of the reaction media. The initial hydrolysis of the sol-gel process requires catalysis of either acidic or basic pH. Direct addition of dye into the acid catalyzed sol-gel composition resulted in a non-functional sensor glass, because the azacrown dye had been pH dependent. Increasing the pH of sol-gel composition just before the addition of the dye by using a pH buffer solved this problem. Before the addition of the pH sensitive dye, sodium phosphate with sufficient buffer capacity ( $250\ \mu\text{L}$ ,  $0.14\ \text{M}$ , pH 6) was added, and the pH of the liquid was increased. We used this buffer modified sol-gel composition for coating.

Because the surfactant-free samples showed cracking, Triton X-100 was added to improve the homogeneity. According to Brinker and Scherer [11], addition of surfactant provides a higher level of homogeneity. Polymerization in the presence of a surfactant increases the molecular mass and the inner tensions in the glass formed during condensation and polycondensation and as a result cracks do not form [11].

### UV-Vis and Fluorescence Emission Spectroscopy Studies

It was observed that general absorption and emission spectra characteristics of azacrown containing squaraine derivative in the sol-gel glass slide remained unchanged compared to the other published spectra (8), a proof of the dye's stability in the sol-gel immobilized phase. The sol-gel glass slides were stored in a dark desiccator and were reusable. The absorption maximum,  $\lambda_{\text{max}}^{\text{ab}}$ , of azacrown dye in the sol-gel matrix is blue-shifted  $7\ \text{nm}$  with

respect to acetonitrile and chloroform solutions [7,8]. A 2-nm parallel blue-shift was also observed in fluorescent emission spectra from 665–657 nm. The absorption spectrum of squaraine derivative in doped sol-gel glass and in acetonitrile is shown in Fig. 2. The absorption band of the squaraine dye in the sol-gel is slightly broader compared to absorption bands recorded in acetonitrile and chloroform, which may be related to enhanced polar interactions between the dye molecule and the sol-gel structure.

As stated by Kessler and Wolfbeis [12], depending on the nature of interaction between the dye and its micro-environment, the dye may undergo not only spectral shifts but also changes in other polarity-dependent parameters such as molar absorptivity changes and fluorescence quantum yield differences.

### Azacrown Dye as a Potassium Sensor

The glass slides were coated with the squaraine dye-doped sol-gel and exposed to different concentrations of BES-buffered potassium solutions, and fluorescence emission spectra between  $10^{-9}\ \text{M}$  and  $10^{-6}\ \text{M}\ \text{K}^+$  were recorded in acid-catalyzed, buffer-modified sol-gel matrix. Potassium chemosensor prepared in solgel matrix has an emission peak with maximum at 657 nm, and the optimal excitation wavelength of 625 nm was determined experimentally (Fig. 3). The calibration plot of potassium-selective composition in the concentration range of  $10^{-9}$  to  $10^{-6}\ \text{M}$  in BES-buffered solutions at pH 6.8 is shown in Fig. 4.

The potassium sensor responds to potassium by a decrease in fluorescence intensity that can be used as the analytical signal. Upon exposure to potassium concentra-

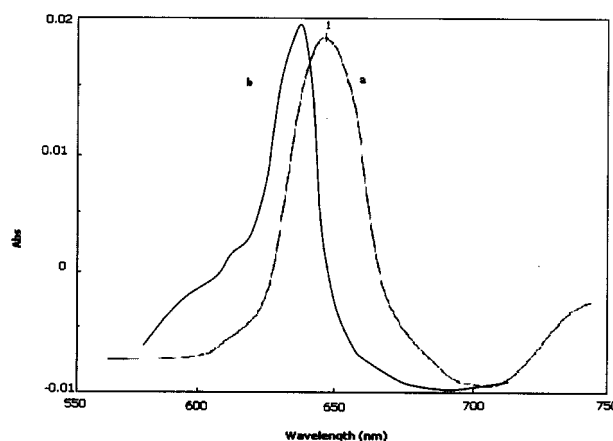


Fig. 2. The absorption spectra of azacrown dye in acetonitrile (a) and dye-doped sol-gel glass (b) ( $\lambda_{\text{max}}^{\text{ACN}} = 640\ \text{nm}$ ,  $\lambda_{\text{max}}^{\text{sol}} = 647\ \text{nm}$ ).

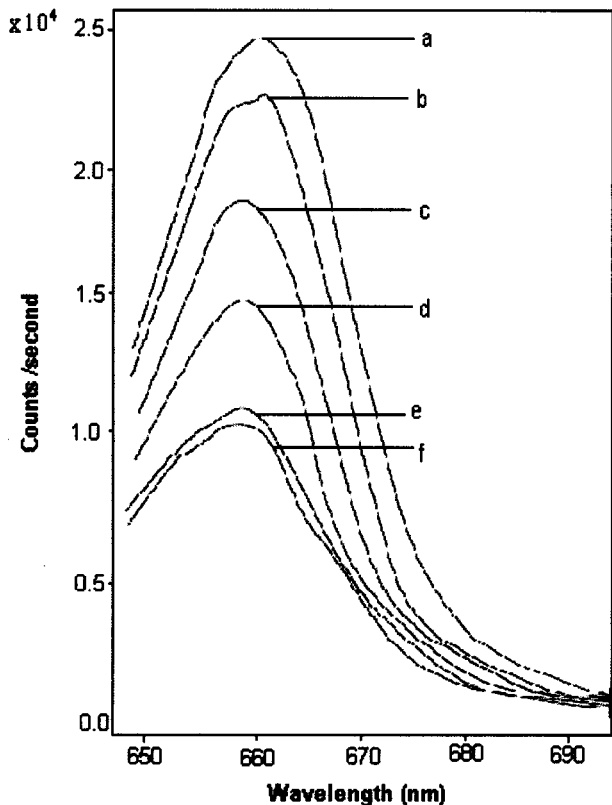


Fig. 3. Emission spectra of potassium-selective composition after exposure to different  $K^+$  concentrations. (a)  $[K^+] = 0$  M; (b)  $10^{-9}$  M; (c)  $5 \cdot 10^{-9}$  M; (d)  $10^{-8}$  M; (e)  $10^{-7}$  M; (f)  $10^{-6}$  M,  $\lambda_{exc} = 625$ ,  $\lambda_{em} = 657$  nm.

tions from 0 M– $10^{-6}$  M, the membrane exhibits a 61% relative signal change in the direction of decrease in fluorescence intensity. The intensity-based response curve of sensor glass for the determination of  $K^+$  in the concentration range from  $10^{-9}$ – $10^{-6}$  M is shown in Fig. 5. Regeneration was accomplished in concentrated (200 mM/L) BES-buffered solutions at pH 5.8. The approximate response time ( $\tau_{90}$ ) in a concentration range of  $10^{-9}$ – $10^{-6}$  M may be concluded as 2 min. The sensor was fully reversible, and a drift of 7.3% of the upper signal level has been observed after the first cycle. After a series of measurements in the range  $10^{-9}$ – $10^{-6}$  M  $K^+$ , the ion binding process was seen to be faster than that of unbinding.

Cross Sensitivity to pH

The pH dependence of the reaction media was investigated both in plain buffer and by recording the signal intensity of a potassium-loaded azacrown structure at various pH values (pH 3–9). The pH dependence of the

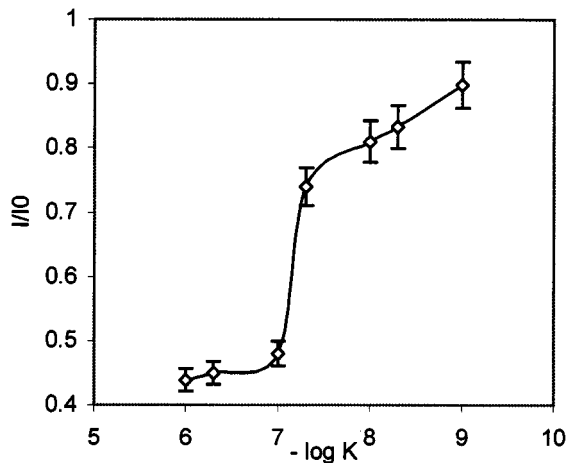


Fig. 4. Calibration plot of potassium-selective composition in the concentration range of  $10^{-9}$ – $10^{-6}$  M in BES-buffered solutions at pH 6.8. Data presented are mean of five sets of measurements all with different fresh sensor glasses.

molecule is probably due to the acid-base transformations of the squaryl moiety. We note that the potassium loaded and unloaded forms of indicator dye exhibit similar spectral characteristics but have different pH dependencies. In the case of potassium-loaded form of indicator, the highest signal intensity was reached at pH 7.2. Above and below pH 7.2, the signal intensity has shown a slight tendency to decrease. In the case of the unloaded form of indicator the pH dependence is more than that of its loaded form. Because a pH of 6.8 has also been appropriate for physiological media, following experiments were realized at pH 6.8 in BES-buffered solutions. Small changes in the pH of the sample had no effect on response. In well-defined and constant pHs, the response is repro-

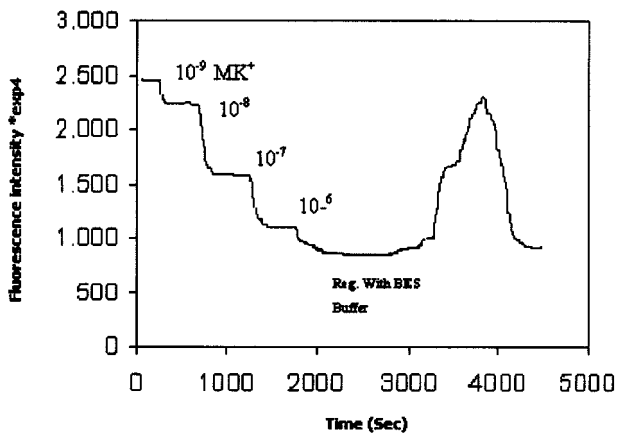


Fig. 5. The intensity-based response curve of dye-doped sol-gel glass for the determination of  $K^+$  in the concentration range from  $10^{-9}$ – $10^{-6}$  M

ducible and promising. pH dependence of the sensor glass in plain buffer and in potassium containing BES buffer is shown in Fig. 6.

*Effect of Ionic Strength*

The potassium concentration-dependent spectral response of sensor glass is affected by the ionic strength of the buffer solution. By making the ionic strength of the buffer solution 135 mM with NaCl, the relative signal change of the potassium-induced emission spectrum of the sensor in contact with this solution increased by around 10%. This effect of ionic strength also caused a change in loading capacity of the sensor slide, which increased 10-fold, from 10<sup>-6</sup> M to 10<sup>-5</sup> M K<sup>+</sup> ion concentration. Emission spectra and calibration curve of potassium-selective composition in BES-buffered and 135 mM NaCl-containing solutions at pH 6.8 has is shown in Fig. 7.

**Cross-Sensitivity to Other Cations**

We have also investigated the cross sensitivity of sensor glass to different test cations such as sodium, barium, calcium, and ammonium. Owing to the fitness-based specific host-guest interaction between the azacrown and potassium ions, the ionic radius has to be considered. The selectivities were calculated in accordance with the following expression [13].

$$\frac{(1 - \alpha)^2}{\alpha^2} = K_{extr} (C_K + \sum K_{Kx}^{opt} C_x \dots)$$

$$K_{Kx}^{opt} = \frac{C_K}{C_x}$$

where the  $K_{extr}$  is the equilibrium constant for sodium/ionophore extraction and  $C_K$  and  $C_x$  are the concentrations

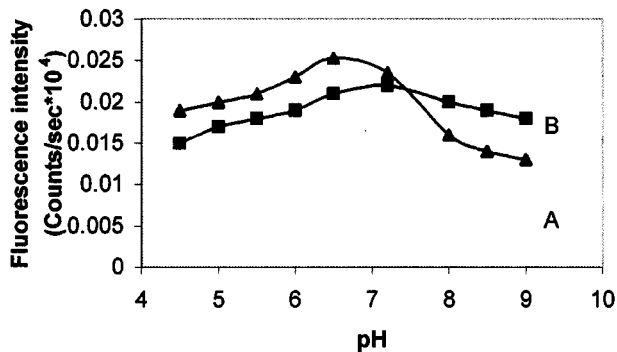


Fig. 6. pH dependence of the fluorescence intensity of sensor glass (A) in plain BES buffer and (B) in BES buffer containing 10<sup>-6</sup> M K<sup>+</sup>.

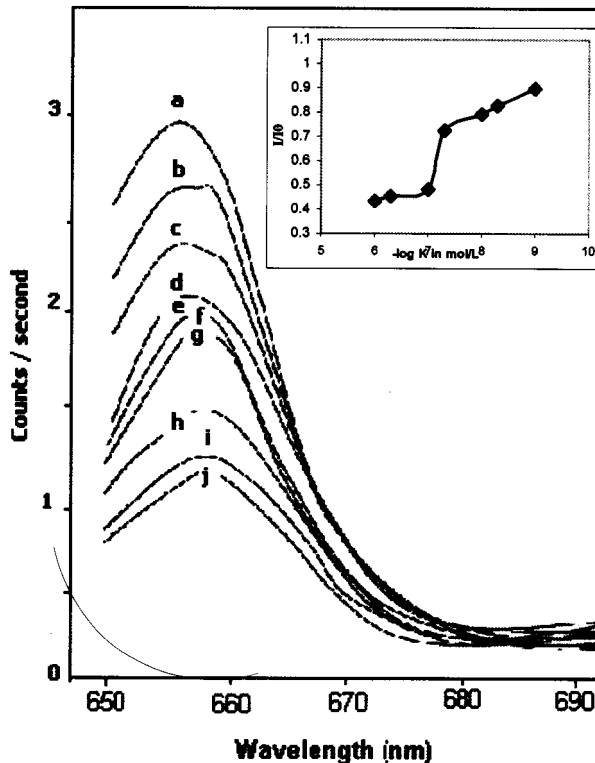


Fig. 7. Emission spectra and calibration curve of potassium-selective composition in BES-buffered and 135 mM NaCl-containing solutions at pH 6.8. After exposure to certain concentrations of K<sup>+</sup> ions. (a) K<sup>+</sup> = 0 M; (b) 10<sup>-9</sup> M; (c) 5.10<sup>-9</sup> M; (d) 10<sup>-8</sup> M; (e) 5.10<sup>-8</sup> M; (f) 10<sup>-7</sup> M; (g) 5 10<sup>-7</sup> M; (h) 10<sup>-6</sup> M; (i) 5.10<sup>-6</sup> M; (j) 10<sup>-5</sup> M.

of potassium and interferant ions, respectively. For simplicity, cation concentrations rather than activities are used to avoid calculating activity coefficients. The apparent selectivity coefficients were calculated by taking the ratio of potassium and interfering cation concentrations that yield the same  $\alpha$  value ( $\alpha = 0,5$ ), as determined graphically from the separate calibration curves. If  $\alpha$  is defined as the ratio of the concentration of potassium ion-loaded fluoroionophore  $[H_2L_{org}K_2]$  relative to the total amount of indicator present in the membrane  $[H_4L_{org}]_{tot}$ , and if the optical signal is dependent on the unloaded form of fluoroionophore within the film,

$$\alpha = \frac{I_0 - I}{I_0 - I_1} = \frac{[H_2L_{org}K_2]}{[H_4L_{org}]_{tot}}$$

where  $I$  is the measured fluorescence intensity at any K<sup>+</sup> concentration and  $I_0$  and  $I_1$  are the fluorescence intensities of the film when the indicator dye in its unloaded and fully loaded forms, respectively. Figure 8 summarizes a selectivity comparison of different test cations. According to Fig. 8, the selectivity of the proposed potassium sensor

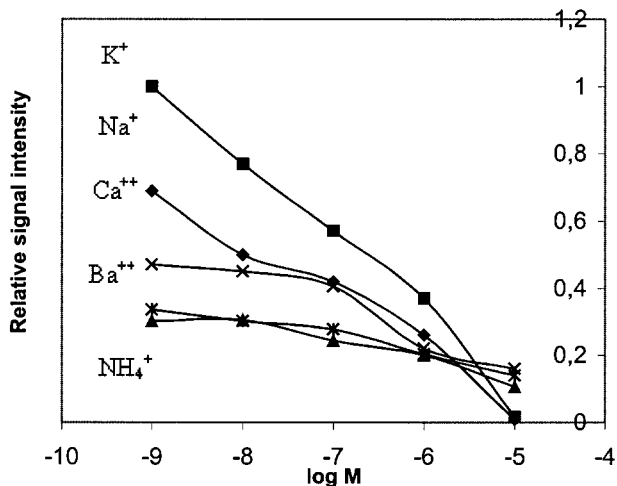


Fig. 8. Work function of sensor glass for potassium and interfering anions.

against sodium was found to be 1.4 ( $\log K_K^{Na}$ ). Because  $\alpha = 0.5$  cannot be reached by  $Ca^{2+}$ ,  $Ba^{2+}$ , and  $NH_4^+$ , it can be concluded that, the azacrown structure was effectual in binding  $K^+$  and  $Na^+$  but ineffectual in binding the  $Ca^{++}$ ,  $Ba^{++}$ , and  $NH_4^+$  in immobilized form. Thus, the responses of azacrown to  $Ca^{++}$ ,  $Ba^{++}$ , and  $NH_4^+$  were negligible

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