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Anion recognition through novel C-thiophenecalix[4]resorcinarene: PVC based sensor for chromate ions

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Abstract

Novel ionophore, C-thiophenecalix[4]resorcinarene (**I**) has been synthesized and characterized by IR, NMR and C, H, N analysis. Poly(vinyl chloride) (PVC) based membranes of ionophore (**I**) using dibutylphthalate (DBP), dioctylphthalate (DOP), 1-chloronapthalene (CN), tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl)sebacate (DOS) as plasticizing solvent mediators were prepared and used as CrO_4^{2-} selective sensors. Of the various sensors prepared, the one with membrane composition 2:66:120 mg (I: PVC: DBP) exhibited the best performance. This sensor works well over a wide concentration range 5.6×10^{-6}–1.0×10^{-1} M (detection limit ∼ 0.30 ppm) with Nernstian compliance (29.0 mV per decade) between pH 6.5–10.0 with a fast response time of ∼13 s. The selectivity coefficient values as determined by fixed interference method (FIM) indicate excellent selectivity for CrO_4^{2-} ions over a large number of anions. The sensor exhibits adequate shelf-life (∼5 months) with good reproducibility (S.D. ± 0.2 mV). The sensor has been used in the potentiometric titration of chromate with Pb(II). Determination of chromium in electroplating waste using the sensor was successfully achieved.

Keywords: Chromium; Sensors; Calixarenes; Chromium-selective electrodes; Chromate ions

1. Introduction

Chromium compounds are extensively used in corrosion control, oxidation processes, leather industry, electroplating, etc. In India, leather manufacturing industries are extensively using chromium compounds for tanning process and a large quantity of aqueous waste containing high chromium concentration is being discharged as such. It is reported that chromium concentration in discharged waste is up to several thousands parts per million causing serious threat to microorganisms of aquatic systems and human life in nearby areas. Cr(III) and Cr(VI) are the predominantly present oxidation states in aqueous systems, of these Cr(VI) is a well known carcinogen with exposure occurring in both occupational and environmental samples [1]. Environmental Protection Agency (EPA) has adopted up to 0.01 ppm of total chromium as maximum contaminant level in community water systems. Presently, sophisticated techniques viz., AAS, ICP, etc. are employed for the determination of trace amount of chromium. However, these methods are disadvantageous in terms of cost and unsuitability for routine analyses of large number of samples [2–5]. Recently, ion-sensors are being used for such quantification, as these provide a convenient, fast and 'on-line' method of analysis.

Extensive efforts have been made to develop a good sensitive sensor for chromium [6–14]. However, most of the developed sensors do not permit chromium estimation at lower concentrations (<1 ppm) [9–12,14], exhibit poor selectivity in the presence of common anions [6,8–11,14], show non-Nernstian response [6,7] and high response time [13,14]. Crown ethers, cryptands, porphyrins, calixarenes, hydrogen-

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bonding ionophores etc. are being employed for ion-sensing because of their selective complexation properties. Among these, calixarenes and resorcinarene receptors have attracted recent attention because of the flexibility in synthesizing the ionophores of desired binding properties. The lower or upper rim and methylene bridge of these compounds can be easily modified to achieve desirable structures to bind specific guest species [15]. Recently, we have prepared a new C-thiophenecalix[4]resorcinarene derivative expected to act as a ionophore showing affinity for anions [16,17]. Therefore, PVC based membranes incorporated with C-thiophenecali [4]resorcinarene as neutral ionophore were prepared and investigated for their response towards anions. The results, reported in present communication, show that these membranes show high selectivity towards chromate ions over large number of anions and could, therefore, be used as a selective sensor for its quantification.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade and used without further purification. Dibutylphthalate (DBP) and dioctylphthalate (DOP), Reidel, India; 1-chloronapthalene (CN) and tris(2-ethylhexyl) phosphate (TEHP), E. Merck, Germany; bis(2-ethylhexyl)sebacate (DOS) and high molecular weight poly(vinyl chloride) (PVC), Aldrich, USA were used as obtained. Analytical reagent-grade tetrahydrofuran (THF), sulfuric acid and sodium hydroxide were obtained from Ranbaxy, India. Solutions of different concentrations were prepared by successive dilution of 0.1 M stock solutions.

2.2. Synthesis of C-thiophenecalix[4]resorcinarene(**I**)

To a solution of resorcinol (18.06 g, 0.164 mol) dissolved in 70 ml of ethanol, was added 20 ml concentrated HCl, maintaining the reaction mixture below 50 °C. Thiophene-2-aldehyde (19.04 g, 0.17 mol) was added drop wise over a period of 30 min to obtain a heterogeneous reaction mixture. The mixture was slowly heated to give a homogenous solution. It was refluxed for 8 h to obtain dark brown coloured precipitates, filtered and washed with water to remove excess HCl [18]. The precipitates of C-thiophenecalix[4]resorcinarene thus obtained were crystallized from hot acetone (Fig. 1).

The yield was 70%, m.p. >320 °C (dec.). IR (KBr): n (–OH str. and C–H str.) 3400–3050 $\mathrm{cm^{-1}}$ (b); ^{1}H NMR ($CDCl_3$): δ4.4 (s, 4H, meso –CH), 6.21 (s, 8H, Ar–H), 6.59 (t, 4H, thiophene–H), 6.84 (d, 8H, thiophene–H) and 7.69 (s, 8H, –OH); analytically calculated for $C_{44}H_{32}O_8S_4$: C, 64.68%; H, 3.95% and S, 15.69%; found: C, 64.48%; H, 3.80% and S, 15.50%.

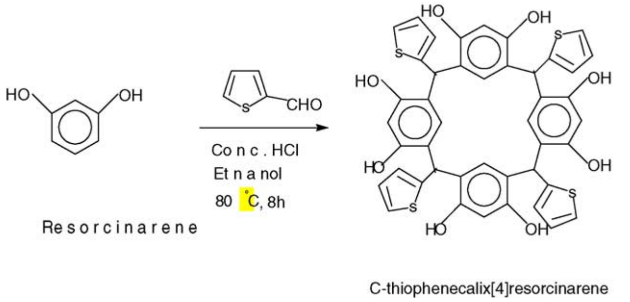

Fig. 1. Synthesis and structure of C-thiophenecalix[4]resorcinarene.

2.3. Potential measurements

The potential measurements were carried out at 25 ± 0.1 °C with a digital potentiometer (Model 5652 A, ECIL, India) and Century Microvoltmeter (Model CVM 301, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrodes.

SCE/internal solution (0.1 M, CrO_4^{2-})/membrane/test solutions/SCE.

2.4. Preparation of membranes

CrO_4^{2-} selective membranes were prepared by dissolving a mixture of ionophore (2 mg), plasticizers (DBP, DOP, TEHP, DOS, or CN) (120 mg) and PVC (66 mg) in THF. The solution was poured into acrylic rings placed on a glass plate and the solvent was then allowed to evaporate at room temperature. The resulting membrane of 0.5 mm thickness was obtained. It was then cut to size and attached to "Pyrex" tube and equilibrated in 0.5 M CrO_4^{2-} solution for 2–3 days. A number of such membranes were prepared and those, which generated stable potentials and exhibited quick response were selected for further studies. The composition of such membranes is given in Table 1.

3. Results and discussion

3.1. Performance characteristics of sensor

The potentiometric response characteristics of a CrO_4^{2-} sensor based on C-thiophenecalix[4]resorcinarene as electroactive material, with various plasticizers (TEHP, DOP, DOS, CN and DBP) in PVC matrix were measured in the concentration range of 1.0×10^{-7}–1.0×10^{-1} M. A perusal of data presented in Table 1 shows that the sensor No.1 without plasticizer exhibited a narrow working concentration range of 7.9×10^{-5}–1.0×10^{-1} M with a slope 30 mV per decade of activity (Fig. 2). Solvent mediators are frequently used to enhance the performance characteristics of plasticized membranes. It is well documented that the addition of the plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement