

Short Communication

CONSTRUCTION AND ANALYTICAL APPLICATIONS OF AN IMPROVED LIQUID-MEMBRANE ELECTRODE FOR SALICYLATE

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Summary. The construction and analytical applications of an improved liquid-membrane electrode for salicylate are described. Tests of various combinations of symmetrical tetraalkylammonium salicylates and solvents showed that the best liquid ion-exchanger was tetraoctylammonium salicylate in *p*-nitrocumene. Electrode response is Nernstian down to 2×10^{-5} M. Major interferences are perchlorate and periodate; the working pH range is 6–9. The electrode is useful for direct potentiometric determinations of salicylate in pharmaceutical preparations.

The construction and analytical applications of electrodes sensitive to salicylate ion have already been reported [1–5]. Although there is a need for salicylate electrodes with good response characteristics for application in pharmaceutical analysis, most of the reported electrodes are not very sensitive or selective.

In this communication, the performance characteristics of a new liquid-membrane salicylate-sensitive electrode are described. The best liquid ion-exchanger for the electrode was found to be tetraoctylammonium salicylate dissolved in *p*-nitrocumene; other compounds tested were tetraheptylammonium, tetraoctylammonium, tetradecylammonium, tetradodecylammonium or tetraoctadecylammonium salicylate dissolved in 4-nitro-*m*-xylene, 2-nitro-*m*-xylene, *p*-nitrocumene, 3-nitrotoluene or 2-nitrotoluene. The electrode response is Nernstian down to 2.00×10^{-5} M and the selectivity in presence of various common anions is satisfactory.

Experimental

Instrumentation. The reference electrode was an Orion 90-01-00 Ag/AgCl single-junction electrode, filled with Orion 90-00-01 solution. The e.m.f. values were measured with a Corning Model 12 Research pH/mV meter, at ambient temperature with constant magnetic stirring.

Reagents. All solutions were prepared with deionized-distilled water from reagent-grade materials, unless otherwise stated. Pharmaceutical preparations were obtained from local drugstores. Standard 0.1000 M sodium salicylate solution was prepared by dissolving 1.381 g of salicylic acid in 45 ml of

0.2 M sodium hydroxide, adjusting the pH to 7.0 with 0.1 M sodium hydroxide and diluting to 100.0 ml. The purity of the salicylic acid used was checked by potentiometric titration with standard sodium hydroxide solution. Salicylate solutions were stored in amber bottles. All other salicylate solutions were prepared by dilution with water.

Preparation of the liquid ion-exchangers. An appropriate amount of tetraoctylammonium bromide (or tetraheptylammonium, tetradecylammonium, tetradodecylammonium or tetraoctadecylammonium bromide) was dissolved in 5.0 ml of *p*-nitrocumene (or 2-nitrotoluene, 3-nitrotoluene, 4-nitro-*m*-xylene or 2-nitro-*m*-xylene) to give a 0.01 M solution (or 5×10^{-3} M for the last two bromide salts). After extraction with three 10-ml portions of aqueous 0.10 M sodium salicylate (to exchange bromide with salicylate), the organic phase was dried thoroughly with anhydrous sodium sulfate and used for preparation of the electrode.

Construction of the electrodes. An Orion liquid-membrane electrode body (model 92) was used with Orion perchlorate membranes and the above ion-exchange solution. The internal reference solution was 0.01 M sodium salicylate/0.1 M sodium chloride. The electrodes were conditioned for 24 h before use in 0.01 M sodium salicylate and stored in this solution when not in use.

Calibration graphs. Phosphate buffer (30 ml, 0.50 M, pH 7.0) was pipetted into a 100-ml beaker, the electrodes were immersed, constant stirring was started, and 0.001 ml of 0.1 M sodium salicylate standard solution was added. The reading was recorded after stabilization to ± 0.1 mV. Further increments of 0.1 M standard solution were added to cover the 3.3×10^{-6} – 1.2×10^{-2} M range and the calibration graphs were plotted in the usual way.

Determination of salicylate in pharmaceutical preparations. Locacorten Tar ointment (10 g), Locasalen ointment (5 g), Olamyc tincture (10 ml), Volog tincture (10 ml) or Pyralvex solution (4 ml) was dissolved in chloroform (120 ml). The chloroform solution was centrifuged at 4000 rpm for 5 min, transferred to a separatory funnel and extracted with four 40-ml portions of 0.1 M sodium hydroxide. The aqueous solution was neutralized with 1 M hydrochloric acid and transferred to a 250-ml volumetric flask. Phosphate buffer (50 ml, 0.50 M, pH 7.0) was added and the solution was diluted to the mark; 30.00 ml of this solution was pipetted into the measuring cell for e.m.f. recording. The salicylate concentration was found from the above calibration graph. Collodion BAG (2 ml), a Greek product, was dissolved in 100 ml of water, the solution was mixed with buffer and the e.m.f. was measured, as described before.

Results and discussion

Characteristics of the electrodes. Twenty-one electrodes were constructed with the salicylates of various symmetric tetraalkylammonium cations dissolved in different organic solvents. The slopes of the calibration graphs and the lower limits of linear response for these electrodes are summarized in

TABLE 1

Slope and lower limit of linear response for various salicylate electrodes at 25°C

Quaternary ammonium ion	Slope and lower limit ^a in different solvents				
	2-Nitro- <i>m</i> -xylene	4-Nitro- <i>m</i> -xylene	2-Nitro-toluene	3-Nitro-toluene	<i>p</i> -Nitro-cumene
Tetraheptyl	—	—	59(3.7)	—	—
Tetraoctyl	58(4.3) ^a	54(4.4)	53(4.2)	58(4.5)	59(4.7)
Tetradecyl	52(4.3)	53(4.4)	53(4.4)	51(4.7)	53(4.7)
Tetradodecyl	54(4.4)	60(4.4)	54(4.2)	57(4.7)	56(4.7)
Tetraoctadecyl	52(4.2)	23(4.4)	53(4.6)	53(4.7)	47(4.7)

^aThe first number indicates the slope of the linear response plot in mV, with the $p[\text{salicylate}]$ corresponding to the lower limit of linear response in parenthesis.

Table 1. The results show that the limit of linear response is affected markedly when tetraheptylammonium is replaced by tetraoctylammonium in the liquid ion-exchanger but remains practically unchanged when tetraoctylammonium is replaced by bulkier quaternary compounds up to tetraoctadecylammonium. In terms of sensitivity, slightly better results were obtained when 3-nitrotoluene or *p*-nitrocumene was used as solvent. The combination of tetraoctylammonium salicylate in *p*-nitrocumene was chosen for further studies. A typical calibration graph for this electrode is shown in Fig. 1.

The pH dependence of the electrode response was checked at three salicylate concentrations (Fig. 2). At pH 6–9, the potentials are practically stable,

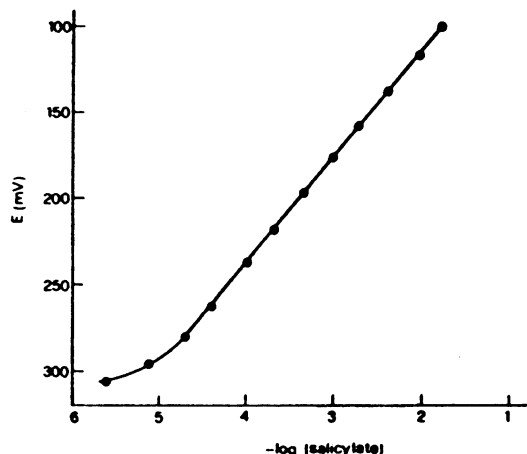


Fig. 1. Calibration graph for the electrode based on tetraoctylammonium salicylate in *p*-nitrocumene.

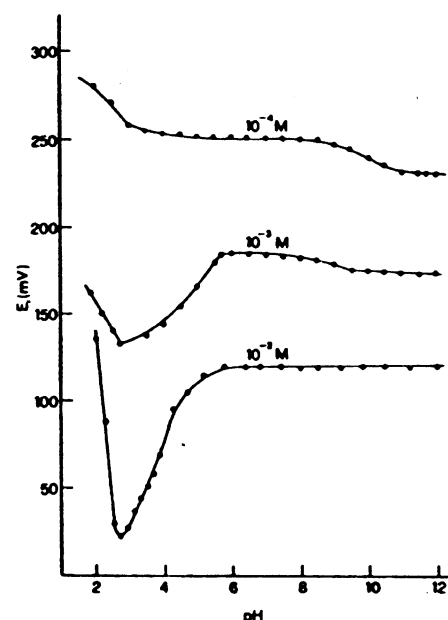


Fig. 2. The pH dependence of the response to 10^{-2} – 10^{-4} M salicylate.

but change slightly up to pH 12; at pH < 6, the potential changes markedly with pH especially at high concentrations, in an unpredictable way. For direct potentiometric measurements, a pH of 7 (phosphate buffer) was selected as the optimum.

Potentiometric selectivity coefficients for the salicylate electrode were measured by the mixed solution method and calculated as described previously [6]. The results are presented in Table 2.

Analytical applications. The salicylate electrode was applied in the direct potentiometric determination of salicylic acid in some pharmaceutical preparations. The salicylic acid was isolated by extractions and measured directly in the aqueous extract after pH adjustment. The results (with the nominal values in parentheses) were: Locacorten Tar ointment, 1.20 g/100 g (1.0); locazalen ointment, 2.9 g/100 g (3.0); Olamyc tincture, 22.3 mg ml⁻¹ (20.0); Volog tincture, 22.1 mg ml⁻¹ (20.0); Pyralvex solution, 12.9 mg ml⁻¹ (10.0); BAG, 8.4 g/100 g (8.4). Thus the electrode seems suitable for application in pharmaceutical analysis.

TABLE 2

Potentiometric selectivity coefficients for the salicylate electrode^a

Ion _j	α'_{sal} ($\times 10^{-4}$ M)	$K_{sal,j}^{pot}$	Ion _j	α'_{sal} ($\times 10^{-4}$ M)	$K_{sal,j}^{pot}$
NO ₃ ⁻	7.5	3.8×10^{-2}	SO ₄ ^{2-b}	6.6	<10 ⁻⁴
Cl ⁻	7.5	<10 ⁻⁴	CO ₃ ^{2-b}	6.6	<10 ⁻⁴
Br ⁻	7.5	4.4×10^{-3}	C ₆ H ₅ COO ⁻	7.5	4.5×10^{-3}
I ⁻	7.5	5.6×10^{-1}	ClO ₄ ⁻	7.5	20
CH ₃ COO ⁻	7.5	<10 ⁻⁴	IO ₄ ⁻	7.5	28

^aExcept where mentioned, the activity of ion j (present as the sodium salt) was 7.5×10^{-3} M. The activity of salicylate in pure solutions was 10^{-3} M in all cases, α'_{sal} is the activity of salicylate in mixed salicylate/interferent solutions. ^bAt an activity of 1.9×10^{-2} M.

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