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# Poly(vinyl chloride) Membrane Electrode on a Graphite Substrate for the Potentiometric Titration of Tetramethylammonium Bromide With Sodium Tetraphenylborate

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A poly(vinyl chloride) membrane electrode, based on the ion-pair complex of tetramethylammonium bromide (TMAB) with sodium tetraphenylborate, is described. The electrode exhibits a linear response with a slope of 49 mV per decade of concentration at 20 °C within the range  $1 \times 10^{-4}$ –0.1 M TMAB, at an ionic strength of 0.1 M NaBr. The effect of the pH of the test solution and the interference of other cations and  $\text{SiO}_4^{4-}$  (or silicate ions of lower charge such as  $\text{HSiO}_4^{3-}$  or  $\text{H}_2\text{SiO}_4^{2-}$ ) were studied. Potentiometric titration was used to determine TMAB, in the presence of  $\text{SiO}_4^{4-}$ , with satisfactory results.

**Keywords:** Tetramethylammonium bromide; potentiometric titration; poly(vinyl chloride) membrane on graphite

Quaternary ammonium salts are important analytical, pharmaceutical and industrial chemicals, e.g., in the synthesis of zeolites.<sup>1</sup> Many analytical methods, such as titrimetry,<sup>2</sup> gravimetry<sup>3</sup> and spectrophotometry,<sup>4</sup> are available for the determination of quaternary ammonium salts. Most of these methods are tedious, non-selective and difficult to apply to quaternary ammonium compounds with short hydrocarbon chains. Such compounds are normally used in low concentrations and are then difficult to determine with high precision and reproducibility.

In the present paper, a poly(vinyl chloride) (PVC) membrane supported on a graphite electrode, similar to those previously reported by Dowle *et al.*,<sup>5</sup> is described for the determination of tetramethylammonium bromide (TMAB). An electrode based on the ion pair of TMAB with sodium tetraphenylborate (TPB) in a PVC membrane was prepared.

We were particularly interested in the possible interference from  $\text{SiO}_4^{4-}$ , because the aim was to apply this electrode to the study of solutions used for the synthesis of zeolites, which contain silicate ions.

## Experimental

### Apparatus

For the addition of the titrant solution a Radiometer ABU 1<sup>a</sup> Auto-Burette was used (Radiometer, Copenhagen, Denmark). The pH and e.m.f. values were measured with an Orion (Cambridge, MA, USA) Model 701 pH meter and a Corning (Halstead, Essex, UK) 113 pH and millivoltmeter, respectively. The reference electrode was an Orion 90-02-00 double-junction electrode with an Orion 90-00-02 inner filling solution, the outer filling solution being 0.10 M  $\text{NH}_4\text{F}$ . Subsequently, the Orion 960 autochemistry system was used.

### Reagents

**Sodium tetraphenylborate solution.** Analytical-reagent grade (Aldrich, Brussels, Belgium). The solution was standardised with 0.1 M  $\text{AgNO}_3$ .

**Silver nitrate solution.** Titrisol ampoule (Merck).

**Tetramethylammonium bromide.** Recrystallised from water shortly before use and dried over  $\text{P}_2\text{O}_5$ , pro analysi (Merck, Darmstadt, FRG).

**Tetrahydrofuran.** Pro analysi (Merck).

**Chemicals for selectivity tests.** Pro analysi (Merck).

**Tetraethylammonium hydroxide (TEAOH), 20% solution** (Janssen Chimica, Beerse, Belgium).

**Sodium bromide.** Pro analysi (Merck).

**Buffer solutions.** Titrisol ampoules (Merck).

**Tritolyl phosphate.** From UCB (Brussels, Belgium).

**Poly(vinyl chloride) powder.** From Solvic (Brussels, Belgium).

**Hexadecyltrimethylammonium bromide [cetyltrimethylammonium bromide (CTAB)].** From Sigma (St Louis, MO, USA). Doubly distilled water was used to prepare all the solutions.

### Sensing Material

The compound was prepared by reacting equivalent amounts of solutions of TMAB and TPB. The salt that precipitated was filtered on a glass filter and washed three times with water. The compound was then dispersed in water and dialysed with Dialysis tubing—Visking, 5-24/32 in (Medicell International, London, UK) for 48 h; it was then free of bromide (tested with  $\text{AgNO}_3$  plus  $\text{HNO}_3$ ). The material was air dried at 80 °C, ground in a glass pestle and stored in a dark-glass vessel.

### Coating Solution

A mixture of 75 ml of tetrahydrofuran and 6.0 g of tritolyl phosphate was stirred in a closed dark-glass vessel, and 4 g of PVC powder were added slowly until complete dissolution was achieved.

A study of the membrane composition with various concentrations of sensing material showed no significant differences in the *E* versus  $\log[\text{TMAB}]$  slopes from 0.4 to 20% m/m. Potential readings were carried out after 5 min in stirred solutions of TMAB [the ionic strength was not adjusted to a constant value (Fig. 1)]. The lowest concentration of active reagent, down to  $\log[\text{TMAB}] = -5$ , containing 0.4% m/m of the sensing material, was chosen, because larger amounts are increasingly difficult to keep in suspension. In addition, economic reasons advocate the lowest concentration compatible with a reliable operation.

A similarly low concentration was reported by Dowle *et al.*<sup>5</sup> These workers also used tritolyl phosphate as a plasticiser. Previous investigations<sup>6,7</sup> had shown this to be an excellent compound for this application.

Additionally, 40 mg of the sensing material were added to the coating solution and stirred continuously until a finely dispersed suspension was obtained. This could take typically 1 h.

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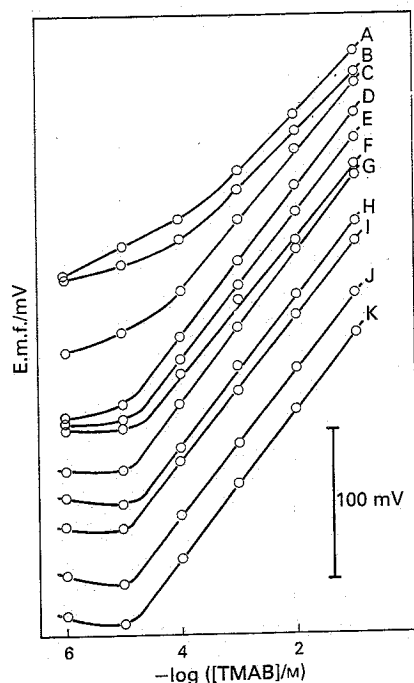


Fig. 1. Calibration graphs for TMAB electrodes. Sensing material concentration: A, 0.1; B, 0.2; C, 0.3; D, 0.4; E, 0.7; F, 1.1; G, 1.6; H, 2.5; I, 5.0; J, 10; and K, 20% m/m

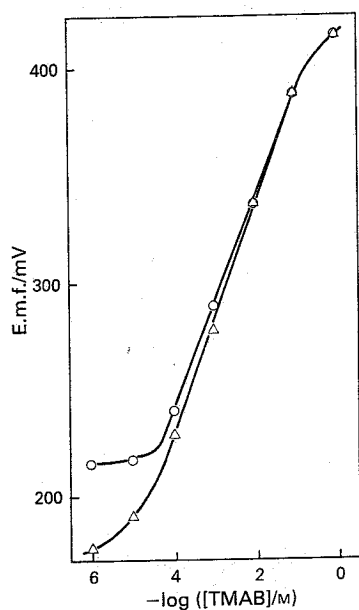


Fig. 2. Calibration graph for the TMAB electrode:  $\Delta$ , solutions of TMAB without NaBr; and  $\circ$ , solutions of TMAB with NaBr and total ionic strength 0.10 M

#### Electrode Preparation

As the substrate for the PVC membrane, a graphite rod ( $40 \times 8$  mm) was used, which was ignited in a colourless flame before use. A brass cap, to which a co-axial cable was soldered, was clamped to the rod. The rod was fixed in a PTFE tube ( $110 \times 12$  mm) and sealed with a silicone-rubber O-ring. About 30 mm of the rod protruded through the end of the Teflon tube. A co-axial cable was fixed on to the thicker end of the tube with a nylon screw. The electrode was immersed in the coating solution until 1 cm of the PTFE tube was wetted. The coated electrode was allowed to dry in air, and the coating procedure was repeated twice.

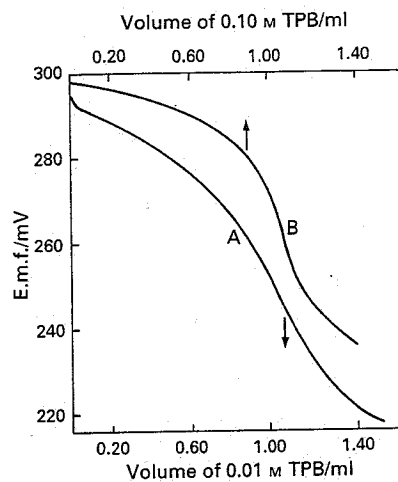


Fig. 3. Representative titration curves for the titration of A, 1.00 ml of 0.01 M TMAB; and B, 1.00 ml 0.10 M TMAB with 0.01 and 0.10 M TPB, respectively, in a total starting volume of 40.0 ml

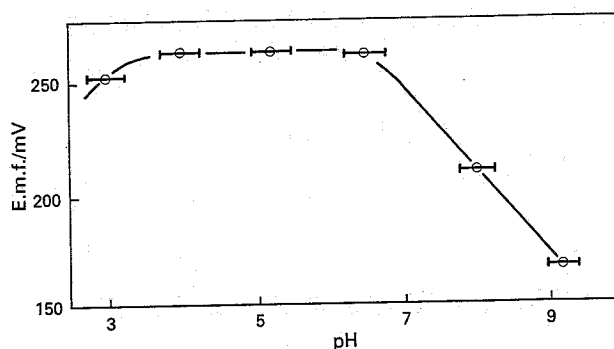


Fig. 4. Effect of pH on the TMAB electrode potential in a 0.001 M TMAB solution

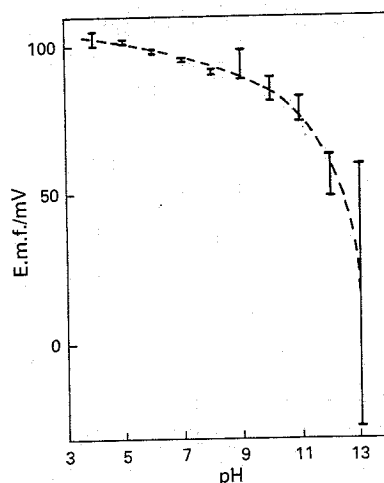


Fig. 5. Response (maximum time 5 min) of a TMAB electrode (0.4% m/m) in buffered 0.001 M TMAB solutions. The potential is drifting to more negative values

#### Preparation and Standardisation of a 0.01 M TPB Solution

A 3.42-g amount of TPB was weighed into a 1-l calibrated flask and the volume adjusted with distilled water. After 1 d, this solution was passed through a filter-paper (Schleicher & Schull No. 589/3). The concentration of this solution was determined with freshly prepared 0.1 M  $\text{AgNO}_3$  by potentiometric titration, using the TMAB - TPB electrode and a double-junction electrode. A 25.00-ml portion of the filtered

**Table 1.** Selectivity coefficients for the TMA - TPB electrode

Interferent		Log $k_{TMA}^{pot} + z_j^{z+}$
Cation	Anion	
Li <sup>+</sup>	Cl <sup>-</sup>	-1.4
NH <sub>4</sub> <sup>+</sup>	Br <sup>-</sup>	-1.1
Na <sup>+</sup>	Cl <sup>-</sup>	-1.3
K <sup>+</sup>	Cl <sup>-</sup>	-1.3
Ag <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	4.5
Ba <sup>2+</sup>	Cl <sup>-</sup>	-1.4
Ca <sup>2+</sup>	Cl <sup>-</sup>	-1.3
Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	-1.4
Cu <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	-1.2
Mn <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	-1.3
Zn <sup>2+</sup>	Cl <sup>-</sup>	-1.3
Fe <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	-1.5
Cd <sup>2+</sup>	Cl <sup>-</sup>	-0.9
Co <sup>2+</sup>	Cl <sup>-</sup>	-1.1
Al <sup>3+</sup>	NO <sub>3</sub> <sup>-</sup>	-1.3
Fe <sup>3+</sup>	Cl <sup>-</sup>	0.5
CTA <sup>+</sup>	Br <sup>-</sup>	6.2

TPB solution and 15 ml of water were transferred into a 50-ml beaker. This sample was titrated with the standard AgNO<sub>3</sub> solution. The concentration was calculated by the second-derivative method as  $0.00995 \pm 0.00001$  M ( $n = 4$ ).

#### Preparation and Standardisation of a 0.01 M TMAB Solution

A 1.5983-g amount of dried and recrystallised TMAB was weighed into a 1-l calibrated flask and the volume adjusted with distilled water. A 1-ml aliquot of this solution and 39 ml of water were transferred into a 50-ml beaker and titrated potentiometrically with a 0.00995 M TPB solution by means of the TMAB electrode and a double-junction electrode. The titre of the TMAB solution was calculated as  $0.01035 \pm 0.00001$  M ( $n = 4$ ) corresponding to 1.5945 g of TMAB.

The potentiometric titration method of determining TMAB described here was not compared with the two-phase titration<sup>2</sup> or gravimetric<sup>3</sup> methods, because these last two methods were considered too inaccurate, particularly in the dilute solutions in which the TMAB-TPB electrode functions. It was not possible to use the spectrophotometric method<sup>4</sup> because no colour was developed in the TMAB solution on addition of the reagent dithiazone in a suitable pH range. Apparently, the chain length of TMAB is too short for this reaction, because the spectrophotometric method works well for quaternary ammonium salts such as TEAOH.

## Results

### Construction of the Calibration Graph

To construct the calibration graph (Fig. 2) suitable increments of standard 0.01 M TMAB were diluted in a 100-ml calibrated flask, sufficient to cover the concentration range  $1 \times 10^{-6}$ – $1 \times 10^{-3}$  M, for subsequent titration.

The total ionic strength of each solution was 0.1 M (except at the highest concentration) and NaBr was used as the supporting electrolyte. The highest concentrations were prepared from a standard solution of 1 M TMAB. A freshly prepared TMAB electrode and the reference electrode were immersed in these solutions, stirred at a constant rate and the e.m.f. values were recorded when stable readings were obtained, usually after 20 s, at ambient temperature (20 °C). These data were plotted *versus*  $-\log[\text{TMAB}]$  (Fig. 2).

An electrode response of 49 mV per decade of concentra-

tion was determined over the linear range ( $7 \times 10^{-5} < \text{concentration} < 1 \times 10^{-1}$  M). The effect of the addition of NaBr to TMAB solutions, to equalise the ionic strength ( $\mu = \frac{1}{2} \sum c_i z_i^2$ , with  $c_i = \text{concentration of ion type } i$ ,  $z_i = \text{charge of the ion}$ ) at 0.1 M, is to cause a rise in electrode potentials below  $\mu = 0.1$  M. In a calibration graph for solutions without additional electrolyte the slope in the linear region is 53 mV per decade of concentration (Fig. 2). The response is sub-Nernstian.

### Electrode Stability

Electrode potentials were stable to within 1 mV in 1 min at pH 5 and with  $1 \times 10^{-3}$  M TMAB. In addition, electrode stability is not a critical factor when the electrode is applied to potentiometric titrations.<sup>8</sup>

### Standard Procedure for Potentiometric Titrations

An aliquot of a solution containing TMAB was transferred into a 50-ml beaker, water was added and the pH was fixed at a suitable value (see later) with very small volumes of HCl and/or NaOH; the total volume was adjusted to 40 ml with distilled water. The resulting solution was titrated with 0.01 M TPB, with constant magnetic stirring, using the TMAB electrode as the sensor and a double-junction electrode as the reference electrode.

In the titration curve for dilute TMAB ( $2.5 \times 10^{-4}$  M) solution with  $1 \times 10^{-2}$  M TPB, the electrode potential dropped initially because the TPB added was not precipitated instantaneously. An example is given in Fig. 3, where two curves are shown for  $2.5 \times 10^{-4}$  and  $2.5 \times 10^{-3}$  M TMAB titrated with 0.01 and 0.10 M TPB, respectively.

### Interference by Other Agents

#### Effect of pH

The object was to determine TMAB in solutions with pH values of *ca.* 13, in order to ascertain whether solutions at these pH levels interfered in the determination of TMAB. Therefore, the pH of a  $1 \times 10^{-3}$  M test solution was adjusted by the addition of very small volumes of NaOH and/or HCl. The respective electrode potential was monitored as a function of pH. From the graph (Fig. 4) obtained it is clear that pH has a negligible effect within the range 3.0–7.0, and in this range the electrode can be used for the determination of TMAB.

In a study of the influence of pH on the response of the electrode with buffered TMAB solutions, the potentials in stirred solutions ( $1 \times 10^{-3}$  M TMAB) were monitored until the electrode potential was constant to within 1 mV in 5 min (maximum time: 5 min).

The total potential drop is shown in Fig. 5. Initially, the potential drifted to more negative values. It should be noted that a comparison of electrode responses to various buffer solutions can include the influence of ions other than H<sup>+</sup> or OH<sup>-</sup>, as the buffers differ in chemical composition and ionic strength.

#### Effect of SiO<sub>4</sub><sup>4-</sup> as an interfering agent on the volume of titrant at the equivalence point

For a cation-selective electrode positive ions, particularly, are suspected to interfere; interference by SiO<sub>4</sub><sup>4-</sup> (or ions of lower charge such as HSiO<sub>4</sub><sup>3-</sup> or H<sub>2</sub>SiO<sub>4</sub><sup>2-</sup>) is not likely. Nevertheless, this was checked by adding 100 μl of 0.1 M Na<sub>4</sub>SiO<sub>4</sub> to 1.00 ml of 0.01035 M TMAB and titrating with 0.00995 M TPB. In three experiments the following values for the volume of titrant at the equivalence point were obtained: 1.042, 1.039 and 1.040 ml. The mean value is 1.040 ml with a standard deviation of 0.0015 ml, which is in good agreement with results for experiments without SiO<sub>4</sub><sup>4-</sup>.

*Determination of selectivity coefficients*

A method for the examination of interference is the determination of the selectivity of the electrode, obtained by using the separate solution method<sup>9</sup> and the equation:

$$\text{Log } k_{\text{TMA}^+, j^{z+}}^{\text{pot}} = (E_2 - E_1)/S + \log[\text{TMA}^+] - \log[j^{z+}]^{1/z}$$

where  $E_1$  is the potential of the electrode in a TMA<sup>+</sup> solution of 0.01 M and  $\mu = 0.1$  M (adjusted with KCl, except at Ag<sup>+</sup>), and  $E_2$  is the potential of the same electrode in a solution with [TMA<sup>+</sup>] = 0 and [j<sup>z+</sup>] = 0.01 M at the same ionic strength;  $j$  represents the interferent and  $S$  is the electrode slope (49 mV). Results are given in Table 1.

**Conclusions**

The electrode described here is easy to construct and was used successfully as a sensor in the potentiometric titration, with TPB of substances such as TMAB and TEAOH, even in the presence of SiO<sub>4</sub><sup>4-</sup>, after adjusting to an appropriate pH. The low cost and ease of operation of potentiometric instrumentation make the potentiometric titration of TMAB a highly desirable alternative to many other methods.

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