HETEROGENOUS POLYMER BASED LIQUID MEMBRANCE ELECTRODE FOR THE DETERMINATION OF CINCHONINE

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This paper reports for the first time the development of heterogenous polymer based liquid membrane electrode for the determination of cinchonine, a quinoline alkaloid. The parameters that influence the performance of such ion-selective electrode viz. nature of polymer, composition of the membrane and choice of the mediator were optimized. The ion-selective electrode thus developed is useful in the determination of 10^{-6} - 10^{-2} M of cinchonine.

Quinoline alkaloids obtained from the dried root or stem of cinchona had been the potent antimalarial drug since past three centuries. Cinchonine and quinine which can be obtained either by synthesis or isolation from cinchona bark [1] are important of this class of alkaloids. A survey of various analytical procedures so far developed for the determination of cinchonine include indirect titrimetry and gravimetry [2]. These conventional methods, though accurate are time consuming and difficult. On the other hand, ion-selective electrodes [3] offer several advantages in terms of simplicity, rapidity, accuracy and possibility of application to pharmaceutical preparations without prior separation.

Ion-selective electrode (ISE) methodologies reported for the determination of cinchonine are by indirect titration utilizing either sodium tetraphenylborate [4] or fluoborate indicator electrode [5]. Liquid membrane based ISE offer a wide range of compounds as sensors in view of the rapid strides that are taking place in the fields of solvent extraction and co-ordination chemistry. Heterogenous polymer based liquid membrane electrodes (LME) offer several advantages over conventional U-tube assembly and are often preferred. This paper describes for the first time development of heterogenous polymer based liquid membrane electrode for the determination of cinchonine.

EXPERIMENTAL

Apparatus: The potentials of electrodes were measured against a double junction calomel reference electrode (1 M KCl) with high impedance digital pH/mV meter (Chemtrix Model 60 A) having a sensitivity of ± 1 mV. A Remi magnetic stirrer was used for stirring the solution.

Reagents: Cellulose acetate (Koch-Light Laboratories Ltd., England), sodium tetraphenylborate (TPB) (E. Merck A.G., Darmstadt), cinchonine (BDH, England) were used as such. All other chemicals used were BDH AR grade. Double distilled water was used for preparing standard solutions.

Design of Cinchonine Selective ISE

Preparation of cinchonine - TPB sensor compound: The cinchonine - TPB compound is prepared by slow addition of cinchonine hydrochloride (adjusted to pH 3) to sodium tetraphenylborate solution while maintaining the pH during precipitation around 6. The precipitated salt was filtered, washed free of excess of sodium and tetraphenylborate ions and dried in air.

Preparation of Polymeric membranes: The membranes were cast according to a slightly modified procedure to the one described by Moody and Thomas [7]. Acetone solutions of cellulose acetate and cinchonine - TPB were mixed and cast in glass tubes of 10 mm dia as discs by slow evaporation and the entire disc was used as a membrane while assembling the electorde.

Electrode assembly: A 10 mm dia membrane disc was affixed to a teflon holder with silicone adhesive and was allowed and dry. The electrode was assembled (Fig. 1) after incorporating 1 ml of saturated solution of cinchonine - TPB in 2-nitrotoluene and 1 ml of 0.1 M

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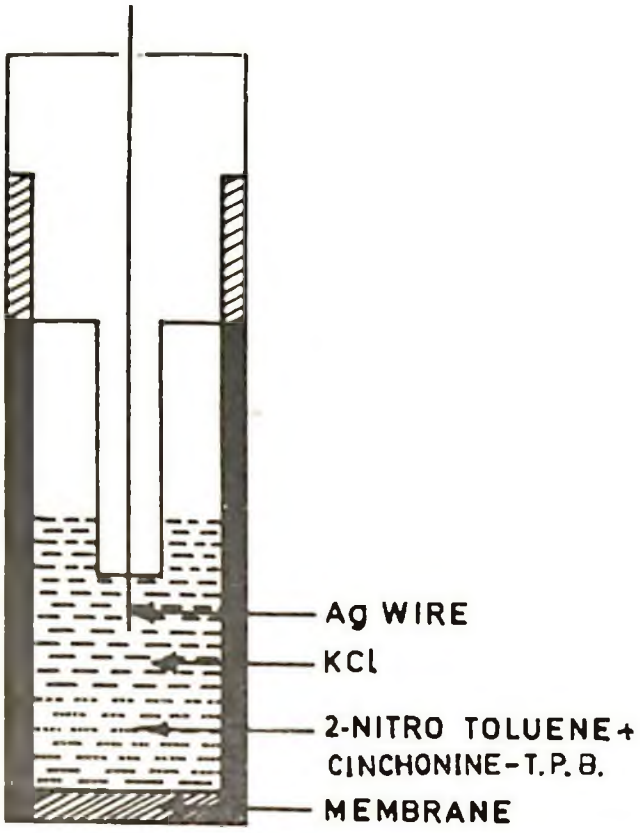


Fig. 1 Electrode assembly.

KCl. The other end of the teflon holder can be screwed on to a teflon rod through which passes a silver wire contact which dips in the internal filling solutions on assembling the electorde.

Evaluation of Electrode Performance

Preparation of cinchonine solutions (0.1 M): Dissolve 2.94 g of cinchonine in minimum amount of HCl and adjust the pH to 3 using dil. NaOH solution and make upto 100 ml. All other solutions were prepared by serial dilution.

Determination of cinchonine: An aliquot of sample solution of cinchonine was made upto 25 ml in a standard volumetric flask. Transfer the solution to 50 ml beaker and measure the response of cinchonine sensing ion-selective electrode. Prepare a calibration graph for cinchonine in the concentration range 10^{-6} - 10^{-2} M. The concentration of unknown is obtained by measuring the response of cinchonine sensing ISE in unknown solution and by referring to the caliberation curve.

RESULTS AND DISCUSSION

Preliminary studies on the choice of polymer indicated that cellulose acetate could be cast as a membrane at room temperature without a need for plasticizer unlike the case of polyvinylchloride [8]. Other polymeric materials like polymethyl methacrylate, polystyrene, nylon etc. are not that successful owing to their glass transition temperature [9].

Evaluation of Optimum Membrane Composition

Variation of cellulose acetate: The membranes 1 to 3 were prepared by casting with varying amounts of cellulose acetate and a fixed amount of the sensing compound cinchonine-TPB (0.2 g) to give membranes of composition 1:1, 1.2 and 2:1 (sensing compound (s): cellulose acetate (CA)). The response characteristics of these membranes are shown in Table 1 from which it is clear that all membranes gave linear response over the concentration range 10^{-4} - 10^{-2} M. Membrane 1 shows better response characteristics at lower concentrations of cinchonine compared to other membranes. Hence, a 1:1 (cinchonine-TPB : CA) is used in subsequent studies.

Choice of mediator: The various mediators investigated include 2-nitrotoluene, nitrobenzene and 1,2-dichloroethane. 0.1 ml of these mediators is incorporated while casting the membrane and saturated solution of cinchonine-TPB in respective mediator is used as internal filling solution. The results of such studies are shown in Table 2 from which it is clear that 2-nitrotoluene is superior to other mediators.

Effect of concentration of internal filling solution: As the solubility of cinchonine-TPB in 2-nitrotoluene is quite low ($\sim 10^{-6}$ M), saturated solution was employed as internal filling solution.

TABLE 1

Response Characteristics of Cinchonine ISE with varying compositions of the membrane

Concentration range of cinchonine (M)	Slope values/decade from E vs log concentration plots		
	1:1	1:2	2:1
10^{-6} - 10^{-5}	8	4	6
10^{-5} - 10^{-4}	20	15	15
10^{-4} - 10^{-3}	41	40	40
10^{-3} - 10^{-2}	41	40	41

TABLE 2

Response characteristics of cinchonine ISE with various mediators

Concentration range of cinchonine (M)	Slope values/decade from E vs log concentration plots		
	2-nitro-toluene	Nitro-benzene	1,2-Dich-loroethane
10^{-1} - 10^{-2}	8	5	4
10^{-2} - 10^{-3}	20	12	8
10^{-3} - 10^{-4}	41	40	25
10^{-4} - 10^{-5}	41	40	28

Performance of ISE with optimum membrane compositions: Of the various heterogenous polymer membranes that were prepared and examined, those containing the sensing compound and cellulose acetate in the weight ratio of 1:1 with incorporation of 0.1 ml of 2-nitrotoluene during casting are best. These membranes showed a linear response over two decades viz. 10^{-4} - 10^{-2} M and are useful in determining cinchonine concentrations down to 10^{-6} M. These membranes have been studied over a period of 2 months and found to provide instantaneous and stable response. This clearly shows that the exchange reactions in the membrane are quite fast and unaltered.

ACKNOWLEDGEMENT

The authors are thankful to Prof. K.I. Vasu, Director, CECRI, for his keen interest and kind permission to publish these results.

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