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Estimation of diquat from aqueous solution using clay membranes

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Abstract

Studies have been made on the use of montmorillonite and kaolinite clay membranes for estimating the concentration of diquat (1, 1' -ethylene - 2, 2' - dipyridilum dibromide) in aqueous solution. The montmorillonite membrane can be used for estimating diquat ion in the concentration range of 3 x 10^{-7} to 2 X 10^{-4} M while kaolinite membrane cannot be used for the estimation of the diquat in aqueous solutions, as the same were too fragile and did not develop reproducible potentials.

Key words: Diquat, clay membranes, aqueous solutions.

Introduction

Growing urbanization and industrialization continuously leads to an increase in the discharge of pollutants i.e. water contaminated with acids, bases, floated and suspended solids and other obnoxious materials. In regions, where production or use of the synthetic materials of advanced chemical technology is extensive, certain chemicals, especially those which are not biological degradable, lead to persistent deterioration in the quality of water. In contrast with domestic waste of metabolic origin, the major problem with such pollutants arises from their failure to exhibit susceptibility to biochemical oxidation and as a result they persist in water for pretty long time. The discharge of such pollutants is objectionable and damaging to public health and natural waters.

The assessment, development and application of processes for the treatment of wastes depend on a detailed knowledge of the composition of the waste and its treated effluent. This knowledge can be obtained only by the proper application of suitable analytical methods. In order to ensure that the treated effluent conforms to the discharge consent conditions, it is necessary to, carry out many routine analyses each day to ensure the smooth and efficient operation of the treatment plant. For this, it is not essential to apply the standard methods of analysis, which are often time consuming. Instead some rapid methods can be successfully substituted with little, if any, loss in either precision or accuracy. Several reports (Rechnitz and Kugles, 1965), concerning the theory of operation and application of ion-selective electrodes have appeared in literature from time to time. Besides this, periodical reviews, such as that by Srivatsava *et al.* (1985), Qureshi and Varshney (1991), Mittal *et al.* (2005), Patterson and Andrew (1969) mention developments in this field. Botre *et al.* (1972), Oberoi *et al.* (1988), and Shedlovsky *et al.* (1963) used ion- exchange membrane for the investigation of free surfactant activity. As such efforts have been made for the use of montmorillonite membrane electrodes for determining the diquat (1, 1' -ethylene - 2, 2' - dipyridilum dibromide) concentration in solution.

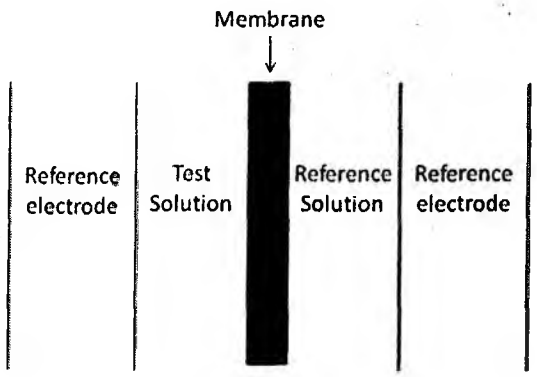
Material and Methods

Clay samples (montmorillonite and kaolinite) were supplied by Ward's natural earth science Est. New York. All other reagents used were of Analytical Reagent grade chemicals. Double distilled water was used for preparing solutions throughout these investigations.

Preparation of membrane: The following procedure was adopted for the preparation of gel membrane: Polystyrene was obtained in the form of a cylindrical rod by heating its granules in a pyrex tube in sulphuric acid bath at 200°C. The molten mass after cooling was ground to fine particles by putting it against a lathe. The powder was finally ground to get 200 mesh (BSS) product. Clays (montmorillonite and kaolinite) (200 mesh powder) and polystyrene (200 mesh powder) in the ratio of 4:1 by weight was homogenized. This homogenized mass was put in a die of diameter 2.5cm. The die was then kept in a specimen mount press and heated to 70 °C. A pressure ranging between 6500-7000 psi was applied. By this method membrane of 0.1 cm thickness was obtained. The membranes prepared by above method were then checked under high resolving microscope for any deformity or cracks. Only those membranes which showed negligible asymmetry were used for investigation.

Potential measurement: The membranes were equilibrated with 10^{-4} M diquat solutions for four

to five days. Equilibrated membranes were washed with water, dried and fixed to one end of a small glass tube with Araldite. This tube contained the reference solution and the whole assembly was immersed in a 50 ml beaker containing the test solution. Saturated calomel electrodes were used as reference and the potential measurements were made on a sensitive potentiometer in conjunction with a suspended coil galvanometer with lamp and scale arrangement. All measurements were made at a constant temperature (25 ± 0.20 °C). The cell arrangement may be represented as follows:



Results and Discussion

Before measuring potentials, the membrane was equilibrated with respective diquat solution (10^{-1} M) for four to five days. The potentials generated across the montmorillonite and kaolinite membranes in contact with diquat solutions are shown in Fig. 1.

A true permselective membrane should normally be permeable to counter-ions and should inhibit the movement of co-ions across the membrane phase. This consequently gives rise to electrical potential known as membrane potential E_m, which is the sum of diffusion and Donnan potentials. For a cation exchange membrane E_m is given by the Nernst equation as:

$$E_m = -\frac{RT}{Z_+ F} \ln \frac{a_+''}{a_+'}$$

where a'' and a' refer to the activities in the two solutions and Z_+ is the charge on the ion under consideration. Since it is almost impossible to have an ideally permselective membrane in practice, due to certain amount of co-ion transference, the expression for E_m for a cation exchange membrane is according to Helfferich (1962).

$$E_m = -\frac{RT}{Z_+ F}\left[\ln \frac{a_+''}{a_+'} - (Z_- - Z_+)\int_{'}^{''} \bar{t}_- \, d\ln a_+\right]$$

where Z_+ and Z- are the charges on counter ion and co-ion, respectively, the transference number of co-ion in the membrane phase and 'a' terms refer to activity in the solutions. The first term on the right hand side gives the thermodynamic limiting value of the concentration potential and the second gives the deviation due to co-ion influx.

In the cell under consideration, the potential measured includes the potential due to reference electrodes, liquid junction potentials and the membrane potential. Liquid junction potentials are negligibly small and the potentials due to reference electrodes cancel each other. Thus the measured potential may be taken as equal to membrane potential. If the activity of the reference solution is fixed (10^{-4} M) the cell potential should change with the changing activity of the test solution. If the membrane potential changes linearly with the concentration of the test solution, calibration plots can be drawn and the membrane can be used for ion-activity measurements.

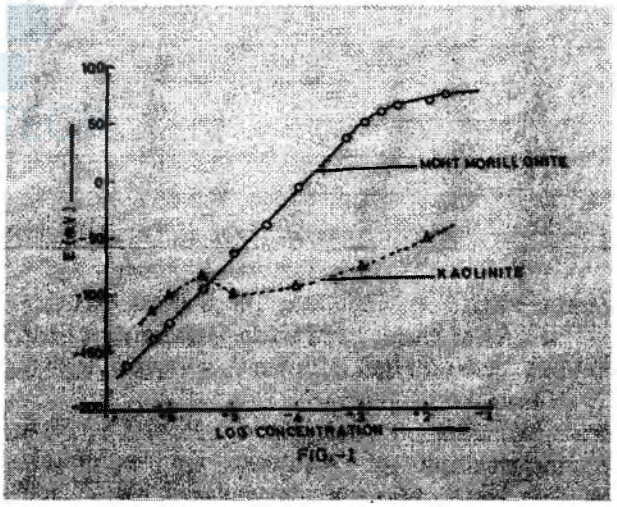


Fig 1. Variation of membrane potential as a function of log concentration

Fig.1 shows the linear nature of the potential *vs* concentration plots of montmorillonite membrane for diquat whereas non linear behavior was observed for kaolinite membrane. Although the slope of the plot indicates a non-Nernstian behavior for montmorillonite membrane yet it can be used for estimating the diquat-ion concentration. It is clear from the plot that montmorillonite membrane can be used to

determine the concentration of diquat in the range of 10^{-7} to 10^{-4} M. However at higher diquat concentrations the membrane response deviates from the linear behavior.

In case of kaolinite membrane non linear behavior was observed for the entire concentration range showing inability of this membrane for the estimation of diquat ion concentration in aqueous solutions.

The selectivity of the montmorillonite membrane for diquat was determined by observing the interference of other cations by the separate solution method (Levin, 1973; Moody 'and Thomas, 1971). In this method potentials are measured in presence of ion 'A' for which the membrane shows selectivity and then in the presence of the interfering ion 'B' of the same concentration. The selectivity co-efficient is calculated by the expression.

$$\ln K_{AB}^{Pot} = \frac{E_B - E_A}{S} + \ln \frac{a_A}{(a_B)^{\frac{Z}{Y}}}$$

Where E_A and E_B are the potentials in the presence of ions 'A' and 'B' respectively, S the experimental value of slope of the potential vs concentration plot of the ion 'A'. If both the ions 'A' and 'B' have same charge and activity, K_{AB}^{Pot} should be less than 1, for the membrane showing no interference by the ion 'B'. If the interfering ion is bivalent, K_{AB}^{Pot} should be less than 0.01 and similarly if the interfering ion is trivalent, K_{AB}^{Pot} should be less than 0.05.

The values of for some interfering ions in case of montmorillonite membrane showing response to diquat are given in table 1. It is apparent from the table that other cations normally do not interfere in the estimation of diquat ion estimation.

From these studies it can be concluded that montmorillonite membrane can be used for estimating diquat-ion concentration with little if any loss in precision or accuracy.

Table 1. Selectivity co-efficient K_{AB}^{Pot} values for interfering cations for montmorillonite

Interfering ion B	K_{AB}^{Pot}
Na^+	4.6×10^{-3}
K^+	3.4×10^{-3}
NH_4^+	2.8×10^{-3}
Ca^{2+}	6.7×10^{-2}
Sr^{2+}	5.2×10^{-2}
Mg^{2+}	5.9×10^{-2}
Zn^{2+}	3.7×10^{-2}
Al^{3+}	1.9×10^{-2}
Fe^{3+}	1.3×10^{-2}

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