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The Properties of the Liquid Nitron Nitrate Membrane Electrode

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Synopsis. The preparation and properties of the nitron nitrate nitrobenzene liquid membrane electrode, which is responsive to nitrate ions, are described. Special attention is given to the selectivity characteristics. High selectivities for NO_3^- over NO_2^-, $C_2H_3O_2^-$, Cl^-, CrO_4^{2-}, and SO_4^{2-} were observed.

Nitron(1,4-diphenyl-3,5-endanilo-4,5-dihydro-1,2,4-triazole) is a gravimetric analytical reagent specific for nitrate.[1] An electrode using nitron as an ion exchange site in a liquid membrane was prepared, but it showed poor selectivity characteristics.[2] This experiment was undertaken in order to investigate further the properties of the nitron nitrate membrane electrodes responsive to nitrate ions, using nitron nitrate dissolved in nitrobenzene.

Experimental

Reagents. Nitron nitrate was prepared by the usual method.[3] Several recrystallizations from hot dilute surfuric acid were performed until a silky white nitron nitrate precipitate was obtained. The other reagents were of an analytical reagent grade and were used without further purification.

Construction of Nitron Nitrate Membrane Electrodes. Nitron liquid membrane electrodes were constructed by using an Orion calcium electrode barrel (92–20) in which a nitron nitrobenzene solution as a liquid ion exchanger and a reference phase were placed, using an Orion membrane (92–20–04) as a separator. The nitron nitrobenzene solution was prepared by shaking a suspension of excess nitron nitrate in a 10^{-2} M $NaNO_3$ solution with the same volume of nitrobenzene. The nitrobenzene phase was separated and filtered to remove any turbidity from the insoluble nitron nitrate. To determine the concentration of nitron in nitrobenzene, a 50 ml portion of the nitrobenzene solution was evaporated to dryness in a platinum crucible at 180 °C; the weight of the residue was 0.456 g/l. The inner-reference phase comprised an Ag–AgCl electrode immersed in an aqueous solution containing 5×10^{-3} M $NaNO_3$ and 5×10^{-3} M NaCl saturated with AgCl.

The cell assembly for the measurement of the potential was:

$$-\text{SCE}|\text{Test soln.}|\text{Membrane}|\text{Ref. soln.}|\text{Ag–AgCl}+$$

The potential measurements were made relative to a Corning 476109 calomel reference electrode with a ceramic junction using an Orion Model 801 digital pH meter at room temperature (16—18 °C). The individual ion activities were calculated from the extended Debye-Hückel equation.

Results and Discussion

Figure 1 shows typical response curves for the nitron liquid membrane electrode in the $NaNO_3$, $Mg(NO_3)_2$, and $Ce(NO_3)_3$ solutions, respectively. It is clear that the nature and type of charge of the cation present do not substantially influence the potentiometric response of the membrane electrodes to nitrate ions with respect to either the linear response or the slope of the calibration curves. Linear responses to the nitrate ion concentrations are obtained over the range from 10^0 to 10^{-3} M; the slope of the linear plot against $-\log a_{NO_3^-}$ is 53—54 mV per decade for the membrane electrode.

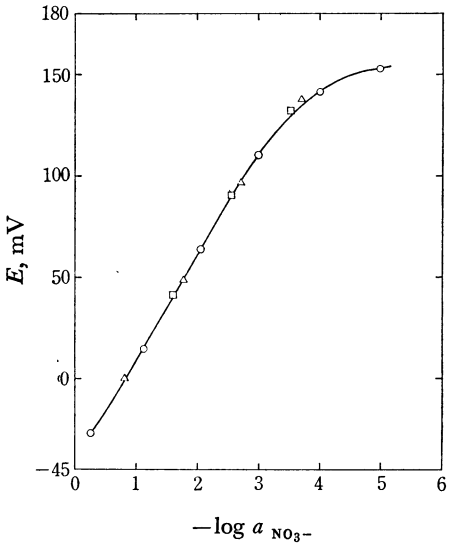

Fig. 1. Response curves for nitron membrane electrode in pure nitrate solutions.
○: $NaNO_3$, △: $Mg(NO_3)_2$, □: $Ce(NO_3)_3$.

Equilibrium potantials (±0.5 mV) are attained within 1—3 min for the membrane electrode.

Figure 2 shows the electrode response to nitrate ions in solutions of various pH values. The pH values of the solutions were adjusted from 2 to 12 by the addition of small amounts of a HCl or NaOH solution. The results show that the electrodes are insensitive to the pH change from 2 to 9 and that, at low concentrations, the pH ranges are somewhat reduced. In alkaline solutions, a sharp potential change in the negative direction is observed because the electrode responds

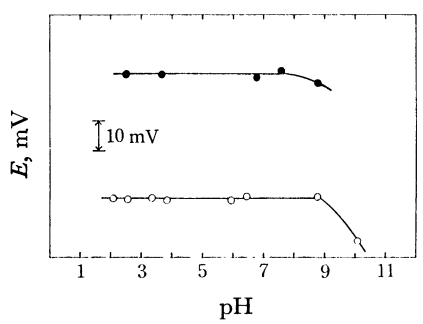

Fig. 2. Electrode response as a function of pH.
○: 0.1 M $NaNO_3$, ●: 1×10^{-3} M $NaNO_3$.

Table 1. Selectivity constants, K_j of nitron liquid membrane electrode

Anion	K_j	
	Method I[a)]	Method III[a)]
ClO_4^-	1.6×10^{2}	1.9×10^{2}
I^-	14	13
ClO_3^-	1.7	2.4
Br^-	0.13	6.8×10^{-2}
NO_2^-	6.4×10^{-2}	3.3×10^{-2}
$C_2H_3O_2^-$	4.8×10^{-2}	6.0×10^{-3}
Cl^-	6.0×10^{-3}	3.3×10^{-3}
CrO_4^{2-}	2.2×10^{-2}	—
SO_4^{2-}	1.4×10^{-3}	—

a) The same method number in Ref. 4.

preferentially to hydroxide ions.

The selectivity constants, K_j were calculated from the electrode potentials measured in 10^{-1} M solutions of pure $NaNO_3$ and a pure interferant (Method I) and from the graphical method (Method III) in the literature[4]; the results are shown in Table 1.

The performance of the nitron nitrobenzene membrane electrode was compared with essentially the same type of electrode in which nitron had been dissolved in benzylalcohol.[2] Both electrodes show a linear response from 10^0 to 10^{-3} M $NaNO_3$ solutions, but the slope of the linear plot of the nitron nitrobenzene membrane (53—54 mV) is larger than that of the nitron benzylalcohol membrane (40 mV). For the anions tested, the nitron nitrobenzene membrane shows considerably less interference than the nitron benzylalcohol membrane ($K_{Cl^-}=0.294$, $K_{C_2H_3O_2^-}=0.095$, $K_{SO_4^{2-}}=0.102$). There is also a significant difference in the numerical values of the selectivity constants for Cl^-. Therefore, the response curve for the present membrane electrode was also constructed in NO_3^- solutions containing 10^{-2} M NaCl; it is shown in Fig. 3. The results support the idea that the selectivity constant for Cl^- is of the order of 10^{-3}. The selectivity constants depend on the concentrations of both the sample solution and the ion exchanger in the membrane, and deteriorate with an increase in the concentration of the ion exchanger in the membrane.[5] In the case of a hydroxylic solvent like alcohol, nearly equal selectivity

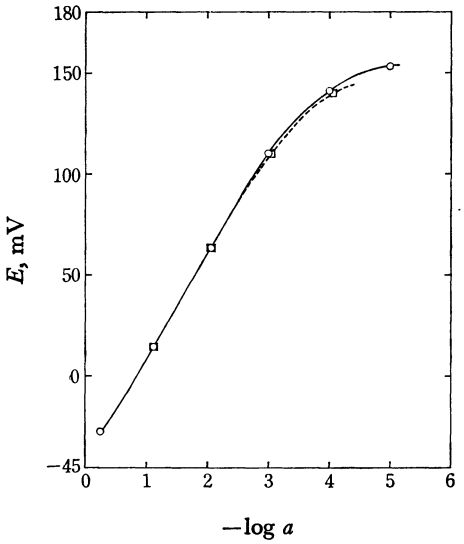

Fig. 3. Response of nitron membrane electrode to NO_3^- and to NO_3^- in 10^{-2} M NaCl.
○: NO_3^-, □: NO_3^- in 10^{-2} M NaCl.

constants are observed because of the solvation of the anions in the organic phase to a degree nearly equal to that of water.[6] From these considerations, the difference of the selectivity constants between the membranes of nitron nitrate in nitrobenzene and in benzylalcohol may be ascribed to the difference in the properties of the solvents, *e.g.* the solubilities of nitron nitrate in the organic phases (0.456 g/l nitrobenzene, 11.5 g/l benzylalcohol[2]).

References

1) A. J. Clear and M. Roth, "Treatise on Analytical Chemistry," Part II, Vol. 5, ed. by I. M. Kolthoff and P. J. Elving, Interscience Publishers, New York (1961), p. 273.
2) A. V. Gordievskii, V. S. Shterman, A. Y. Syrclenkov, N. I. Savvin, and A. F. Zhukov, *Zh. Anal. Khim.*, **27**, 772 (1972).
3) S. W. Dollons, *Analyst*, **32**, 349 (1907).
4) K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, **41**, 1203 (1969).
5) N. Yoshida and N. Ishibashi, *Chem. Lett.*, **1974**, 493.
6) R. E. Reinsfelder and F. A. Schultz, *Anal. Chem. Acta*, **65**, 425 (1973).