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A PHENOL-FORMALDEHYDE POLYMER MEMBRANE RESPONSIVE TO ANIONS

by

Thomas Norman Dobbelstein

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Dean of Graduate College

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INTRODUCTION

The extraordinary specificity of the glass electrode and the remarkable convenience and speed with which it is used to measure hydrogen ion concentration prompts the hope that similar electrodes can be found to measure the concentration, or more strictly the activity, of other ions. Actually the glass electrode is not an electrode at all but simply a glass membrane across which an electrical potential develops when solutions touching the opposite faces of the membrane differ in hydrogen ion concentration. The electrodes used are two reference electrodes, usually two identical saturated calomel electrodes, one dipping into each solution; the potential between the reference electrodes is that developed across the membrane, the assumption being made that the junction potentials arising where the reference elctrodes touch the solutions are negligible or cancel each other.

The electrical resistance of the glass electrode is very high and the difficulty of measuring small potentials (60 millivolts for each 10-fold difference in the molar concentrations of the hydrogen ion) delayed the introduction of the glass electrode as a working tool for twenty years. The advent of modern electronics made the measurement relatively easy and for the past twenty years, hydrogen ion concentration has been measured exclusively in academic, industrial, and clinical practice with the glass electrode.

The hydrogen ion concentrations measured are all very small and for convenience the designation pH has been adopted, p meaning the negative logarithm of. Hence also the term pH meter. Hence also pNa, meaning the negative logarithm of the concentration of the sodium ion. Hence, also by further generalization, the terms pMetal problem and pAnion problem, the problem with which this dissertation is concerned.

The heart of the membrane electrode is obviously the membrane and the selectivity of the potential developed across it will depend on the nature of either the transport of ions through the membrane or more likely the nature of the exchange of ions between the membrane and the solutions in contact with it. It is precisely these characteristics of membrane phenomenon about which the least is known and which offer the greatest scope for imaginative chemical work, for the overall electrical response, that is, potential as a function of difference in concentration, is well understood.

The electrical phenomena which occur when solutions containing electrolytes are separated by a membrane which is impermeable to at least one of the ions and freely permeable to the other ions was first reported by Wilhelm Ostwald[7] in 1890. However, it was not until 1911 that F. G. Donnan[2] took note of the ionic equilibrium across a semi-permeable membrane and found that equilibrium equations resulting from the second law of thermodynamics could be used to describe the potential differences which develop across such a membrane. The equations were simplified by assuming that the electrolytes present were completely ionized, that the ions behaved as ideal solutes, and that concentrations were identical to activities.

One of the simplest systems is the one having a common diffusible ion, $a^+, b^-, \mid a^+, a^-$, where b^- represents the non-diffusible ion, a^+ and a^- represent the diffusible cation and anion respectively, and the vertical line represents the membrane. At equilibrium the system is (1) $a^+, a^-, b^- \mid a^+, a^-$ (2). Because the system is in equilibrium, if an infinitesimal change is made reversibly at constant temperature and pressure, the Gibbs free energy will remain unchanged. Assuming the change to be the transfer of n moles of a^+ and n moles of a^- from (2) to (1), equivalent quantities of positive and negative charges will have been transferred. Therefore, the electrical work terms cancel and the work is $nRT \ln \frac{a_2^+}{a_1^+} + nRT \ln \frac{a_2^-}{a_1^-} = 0$, where R is the ideal gas constant and T the absolute temperature. From this, $\frac{a_1^+}{a_2^+} = \frac{a_2^-}{a_1^-}$ or

$$a_1^+ a_1^- = a_2^+ a_2^- \quad . \tag{A}$$

To maintain electrical neutrality, at equilibrium

$$a_2^+ = a_2^- \quad \text{and} \quad a_1^+ = a_1^- + b^- \quad . \tag{B}$$

According to equations (A) and (B), as long as the non-diffusible ion, b^-, is present, a_1^+ cannot equal a_2^+ and a_1^-

cannot equal a_2^- and there will, therefore, be an unequal distribution of ions across the membrane.

Assuming equal and constant volumes of solvent on both sides of the membrane gives:

Initial state

c_1	a^+	a^+	c_2
c_1	b^-	a^-	c_2
(1)		(2)	

Equilibrium state

c_1	b^-		
$c_1 + x$	a^+	a^+	$c_2 - x$
x	a^-	a^-	$c_2 - x$
(1)		(2)	

where c_1 and c_2 are the initial concentrations of a^+b^- and a^+a^-. According to equation (A), at equilibrium $(c_1 + x)\,x = (c_2 - x)^2$ which can be rearranged to

$$\frac{c_2 - x}{x} = \frac{c_1 + c_2}{c_2} \qquad \text{(C)}$$

Because there is an unequal distribution of ions across the membrane, there is a potential difference between the two solutions separated by the membrane. This potential difference is called a membrane potential. Let e_1 be the positive potential of (1) and e_2 that of (2). Allow an extremely small quantity, nF where F is the Faraday constant, of current to flow from (2) to (1). This will give the decrease in electrical free energy, $nF(e_1 - e_2)$, and the work obtained from the transfer of pn moles of a^+ from (2) to (1) and qn moles of a^- from (1) to (2), where p and q are the transport numbers of the ions and $p + q = 1$.

This work is

$$pnRT \ln \frac{a_2^+}{a_1^+} + qnRT \ln \frac{a_1^-}{a_2^-} .$$

At Equilibrium,

$$nF(e_1 - e_2) = pnRT \ln \frac{a_2^+}{a_1^+} + qnRT \ln \frac{a_1^-}{a_2^-} .$$

From (A), $\frac{a_2^+}{a_1^+} = \frac{a_1^-}{a_2^-}$ and letting $(e_2 - e_1) = E$,

$$E = \frac{RT}{F} \ln \frac{a_1^+}{a_2^+} = \frac{RT}{F} \ln \frac{a_2^-}{a_1^-} . \qquad (D)$$

According to (C), $\frac{a_2^-}{a_1^-} = 1 + \frac{c_1}{c_2}$.

Therefore, $E = \frac{RT}{F} \ln (1 + \frac{c_1}{c_2})$.

If c_1 is small compared to c_2, the potential difference, E, approaches zero. This is to be expected, because if a^+b^- were completely absent, the a^+a^- would be distributed such that the concentration would become the same in both solutions.

Equation (D) can be applied to systems containing multivalent ions. Consider the system:

Initial state				Equilibrium state			
c_1	a^{+z}	a^{+z}	c_2	$c_1 + \frac{x}{z}$	a^{+z}	a^{+z}	$c_2 - \frac{x}{z}$
c_1	b^-	a^-	c_2	x	a^-	a^-	$c_2 - x$
				c_1	b^-		
(1)		(2)		(1)		(2)	

where a^{+z} is a diffusible multivalent ion. Again, let the decrease in electrical free energy be $nF(e_1 - e_2)$. The work obtained from the transfer of $p\frac{n}{z}$ moles of a^{+z} from (2) to (1) and qn moles of a^- from (1) to (2) is

$$p\frac{n}{z}\, RT \ln \frac{a_2^{+z}}{a_1^{+z}} + qn\, RT \ln \frac{a_1^-}{a_2^-} \ .$$

At equilibrium

$$nF(e_1 - e_2) = p\frac{n}{z}\, RT \ln \frac{a_2^{+z}}{a_1^{+z}} + qn\, RT \ln \frac{a_1^-}{a_2^-} \ .$$

In a derivation analogous to the derivation of equation (A), it can be shown that $\frac{a_2^{+z}}{a_1^{+z}} = \frac{(a_1^-)^z}{(a_2^-)^z}$ and because $p + q = 1$ and $(e_1 - e_2) = E$,

$$E = \frac{RT}{zF} \ln \frac{a_1^{+z}}{a_2^{+z}} = \frac{RT}{F} \ln \frac{a_2^-}{a_1^-}$$

or in general

$$E = \frac{RT}{zF} \ln \frac{a_1^{+z}}{a_2^{+z}} = \frac{RT}{zF} \ln \frac{a_2^{-z}}{a_1^{-z}} \ .$$

The original theory of membrane equilibrium was based on two assumptions: the existence of equilibrium and the existence of constraints which restrict the free diffusion of one or more electrically charged constituents. Thus, the equations derived according to the theory apply equally well to charged colloid units and to ions. The necessary constraint to free diffusion results in unequal distribution across the membrane, thus giving rise to a membrane potential.

E. A. Guggenheim developed the concept of electrochemical potential[5], (μ), and applied this concept in conjunction with the concept of chemical potential, μ, and the thermodynamics of J. Willard Gibbs to provide a more rigorous treatment to the Donnan equilibrium[3]. The difference of the potential of a given ionic species between two phases of different bulk composition is determined by the difference in the chemical composition in the bulk and by the distribution of electric charges at the surfaces. This is expressed as

$$(\mu_i)_1 - (\mu_i)_2 = (\mu_{i1} - \mu_{i2}) + z_i F\ (e_1 - e_2) \quad ,$$

where (μ_i) is the potential of the ionic species, μ_i the potential due to the chemical composition of the phase and $z_i Fe$ the potential due to the distribution of electric charge at its surface, with z_i the charge on the i^{th} species. Because μ_i, the potential due to the chemical composition of the phase, cannot be determined independently, it is generally considered as part of e. This gives the expression

$$(\mu_i)_1 - (\mu_i)_2 = z_i F\ (e_1 - e_2)$$

or in terms of activities where $(\mu_i) = (\mu_i)^o + RT \ln a_i$,

$$E = e_1 - e_2 = \frac{RT}{z_i F} \ln \frac{a_{i1}}{a_{i2}} \quad .$$

This was the state of development of the Donnan theory until it could no longer adequately be used to exactly describe experimental findings. At that time

T. Teorell[12, 13, 14, 15] presented an interpretation of membrane equilibrium which has since become the basis for the interpretation of membrane potentials.

According to the Teorell theory, the overall membrane potential consists of three potential jumps: two Donnan potentials, e_1 and e_2 at each solution-membrane interface and an internal potential, $d_2 - d_1$, resulting from a diffusion process. The overall potential, E, is the sum

$$E = (e_2 - e_1) + (d_2 - d_1) \quad .$$

The Donnan potentials are given by $e = \frac{RT}{F} \ln r$, where r is the Donnan distribution ratio; $r = \frac{c^-}{a^-} = \frac{a^+}{c^+}$ with c the membrane interface concentration, a the ion concentration in the external solution and (+) and (-) indicating cation and anion respectively. For a single I-I valent salt, the extended Planck formula[14] gives

$$d_2 - d_1 = \frac{u-v}{u+v} \frac{RT}{F} \ln \frac{a_1(r_1u + v/r_1)}{a_2(r_2u + v/r_2)} \quad ,$$

where u = cation mobility within the membrane and v = anion mobility within the membrane. This gives the overall membrane potential as

$$E = \frac{RT}{F} \ln \frac{r_2}{r_1} + \frac{u-v}{u+v} \frac{RT}{F} \ln \frac{a_1(r_1u + v/r_1)}{a_2(r_2u + v/r_2)} \quad .$$

As the number of exchange sites approaches infinity, the internal potential of the membrane, $(d_2 - d_1)$, decreases and becomes insignificant with respect to $(e_2 - e_1)$. As a result, the overall potential becomes

$$E = \frac{RT}{F} \ln \frac{r_2}{r_1} = \pm \frac{RT}{F} \ln \frac{a_2 c_1}{a_1 c_2}$$

and in general c_1 becomes equal to c_2. Therefore,

$$E = \pm \frac{RT}{F} \ln \frac{a_2}{a_1} \text{ .}$$

The Donnan theory of membrane equilibrium was developed to explain the equilibrium arising when a membrane, impermeable to at least one species in a solution and permeable to the others, is used as a partition between two solutions. A more rigorous treatment was applied to the theory using the concepts of chemical potential and electrochemical potential. This treatment provided a stronger basis for the Donnan theory with the resulting equation describing the membrane potential being of the same form as the equation proposed by Donnan.

The development of the vacuum-tube voltmeter provided a means for studying membranes having very high resistance. Such membranes are, in general, not permeable and, therefore, the membrane potential is not a result of a diffusion process. There is, however, a penetration of the ions into the surface of the membrane to a depth of 50 to 500 Å at equilibrium[10]. This led to the theory that the membrane potential is a result of a Donnan exchange equilibrium being established at both membrane-solution interfaces. The equation describing the membrane potential according to this theory is essentially of the same form as the equations of Donnan and Guggenheim which describe the membrane potential developed across permeable membranes.

Thus, the membrane potential is presently considered to be caused by the difference between the boundary potentials at the membrane-solution interfaces, these boundary potentials arising from the establishment of a Donnan exchange equilibrium at each membrane-solution interface. The potential across the membrane is then described by the equation

$$E = \frac{RT}{zF} \ln \frac{a_1}{a_2} \quad . \qquad (E)$$

If the activity of the reference solution, say a_2, is maintained constant, equation (E) becomes

$$E = \frac{RT}{zF} \ln a_1 - \frac{RT}{zF} \ln a_2 = \frac{RT}{zF} \ln a_1 + K \quad .$$

where K is a constant. At 25°C. and letting $K = E^o$,

$$E = E^o + \frac{0.060}{z} \log a_1 \quad .$$

Therefore, the potential response will be linear to $\log a_1$ with a slope of $\frac{0.060}{z}$.

Most of the experimental work done in the past has been on the response of systems having only one kind of cation or anion present or at most on cation- or anion-selective systems. However, the recent interest in the development of an ion-specific probe has led to work on the development of ion-selective membranes. That is, on membranes which respond to a given ion and are not affected by the presence of other ions.

According to the exchange theory, a Donnan equilibrium is established between ions in sites in the membrane and ions in the solution. To obtain selectivity, the sites in the membrane must be made to only accommodate an ion having a given charge-to-size ratio. Thus, a membrane-solution equilibrium can only be established for a given kind of ion and the membrane gives a selective potential response to that kind of ion.

This treatment is an oversimplification of the problem because what constitutes a selective exchange site has, to this time, not been determined. Ion-selective membranes have thus far been developed through a process of constructing several series of membranes, altering only one variable in each series, and determining the response characteristics for each membrane. The best value for each variable is then used in an attempt to construct a membrane having the desired response. The initial selection of the range of conditions and materials to be used is based upon the choice of the membrane matrix, the ion to which a selective response is desired and the conditions yielding selectivity in previously prepared membranes.

Ion-selective membranes have been prepared by building into the membrane matrix an insoluble compound containing the ion to which response is desired[9]. On this basis it was thought that a membrane containing nickel dimethylglyoxime should selectively respond to the nickel ion. In an attempt to prepare a nickel-selective membrane, several membrane materials were tried with no success[1]. The final preparation was an attempt to copolymerize nickel bis(4,4'-dihydroxybenzildioxime) with phenol and formaldehyde into a resin, just as bakelite is prepared from phenol and formaldehyde. The resistance of the resulting membrane was as high as that of bakelite itself and there was no potential response to differences in the concentration of nickel across the membrane.

In an attempt to lower the resistance of the phenol-formaldehyde membrane, nickel nitrate was added to the resin before the final polymerization. It was found that the resistance of the phenol-formaldehyde membrane containing nickel nitrate was indeed lower but that the membrane did not respond to nickel. However, it did respond to differences in nitrate concentration. Obviously this membrane was worthy of further investigation.

DEVELOPMENTAL WORK

General Approach

Obviously, if an ion-selective membrane is to be prepared, the basic resin to be used must be itself inert chemically and electrically. Bakelite, the condensation product of phenol with formaldehyde, certainly meets these conditions. It was found that thin films of bakelite, 50 to 180 μ thick, could be easily prepared, that these films had a high resistance, even when soaked in water for several weeks, and that there was no potential response when the film was used as the partition in a concentration cell. Bakelite is relatively easy to work with and chemical modifications of the resin are easily made.

The polymerization of bakelite takes place in three stages forming successively bakelite A, bakelite B, and bakelite C. Bakelite A, the low temperature (50 to 70°C.) polymerization product of phenol and formaldehyde, is a viscous liquid which is soluble in solvents such as ethanol and acetone. Bakelite B is obtained upon heating bakelite A above 70°C. and is a soft elastic material which is insoluble. The bakelite B stage is difficult to isolate because the transformation from bakelite A to bakelite C through the B stage is very rapid, comparable to an explosion in gas-phase reactions[11]. Bakelite C is hard, brittle and insoluble and is formed using polymerization temperatures ranging from 100 to 200°C.

The membranes were generally prepared in the following manner. To a weighed amount of bakelite A in ethanol was added an ethanol-soluble nickel salt, usually nickel nitrate hexahydrate. The mixture was stirred well and poured into a petri dish. It was then placed in an oven at 65°C. for at least 10 hours. The temperature of the oven was then increased at a rate of 10 degrees per hour until the temperature reached 130°C. The temperature was then maintained at 130°C. for at least 12 hours. The resulting membrane was slowly cooled to room temperature and the petri dish containing the membrane then filled with water, covered with a glass plate, and placed in an oven at 65°C. for 20 hours. This soaking facilitated the removal of the membrane from the dish. After this soaking, the membrane was mounted in an apparatus consisting of two L-shaped tubes held together with two number 12 pinch clamps, Figure 1.

A reference solution of 0.10 M potassium nitrate was placed in the left arm of the cell and the test solutions were in turn placed in the right arm. Beckman 39170 fiber-junction saturated calomel reference electrodes were inserted into the test and reference solutions and the potential difference between the two electrodes was measured using a Cary Model 31 vibrating reed electrometer. When the cells were not in use, the saturated calomel reference electrodes were removed, water was placed in the right arm

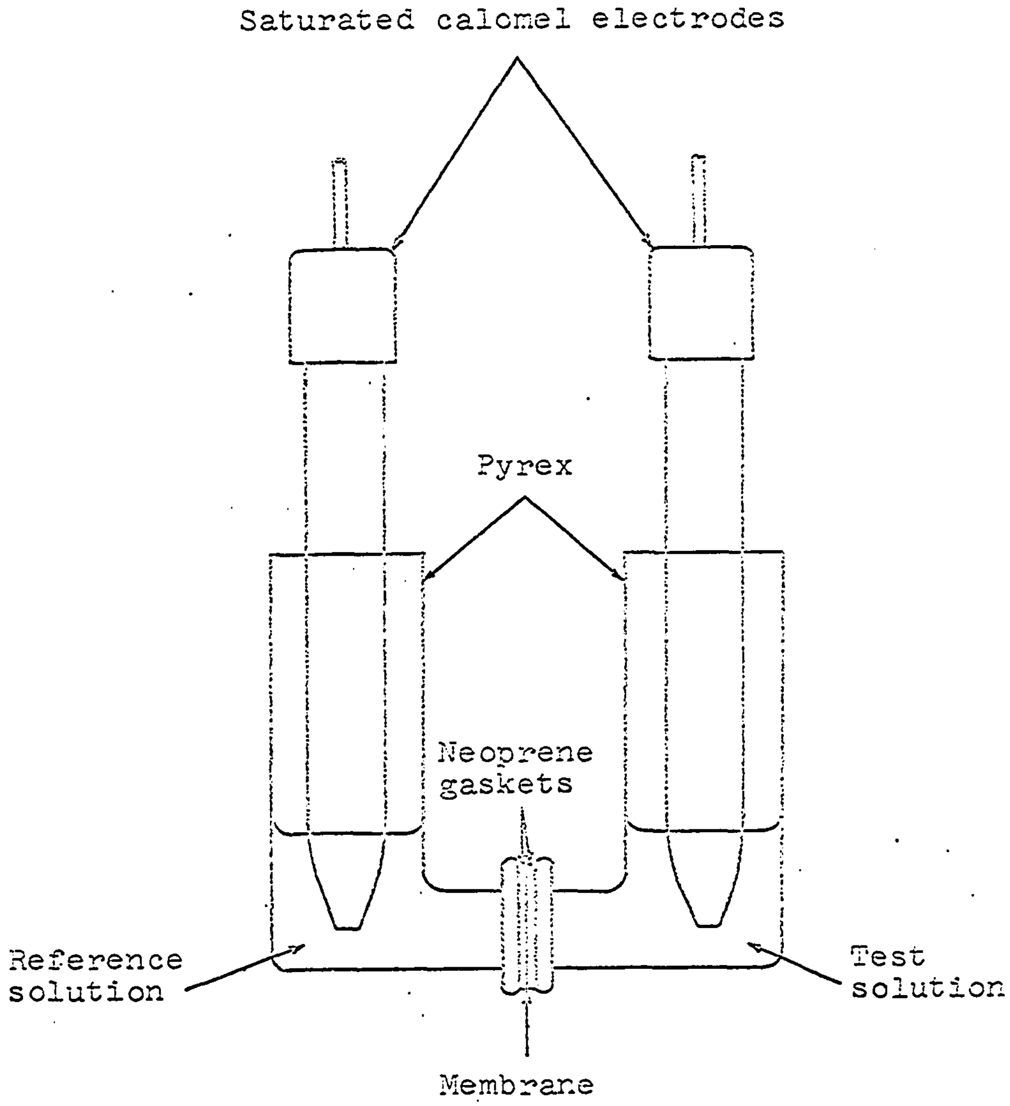

Figure 1. Apparatus for testing membranes

of the cell, the reference solution left in the left arm, and each arm was stoppered to prevent evaporation.

In the first membranes prepared, a bakelite A, prepared from an ammoniacal condensation of phenol with formaldehyde, and nickel nitrate hexahydrate were dissolved in ethanol, the solution poured into a petri dish, and the polymerization carried out as described previously. These first membranes did not respond to changes in concentration of nickel or other cations; they did respond to changes in the concentration of nitrate, Figure 2*. The response to nitrate was linear over the range 10^{-1} to 10^{-3} M, the potentials for 10^{-4} and 10^{-5} M nitrate being equal.

Difficulty was experienced in reproducing the membranes and this led to an investigation of the conditions which affect the preparation of the membrane. Membranes were prepared from phenols other than phenol. The ratio of phenol to formaldehyde, the polymerization temperature, and the time of polymerization for the preparation of bakelite A were investigated. The type and amount of base used to effect polymerization, the temperature, the variation of the amount of nickel nitrate added to the resin, and the addition of compounds other than nickel nitrate to the resin were also investigated.

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*The conventions used in describing the experimental set-up are: 1) reference solution / membrane / test solution. 2) the sign of the potential is arbitrarily defined as the polarity of the electrode dipping into the reference solution.

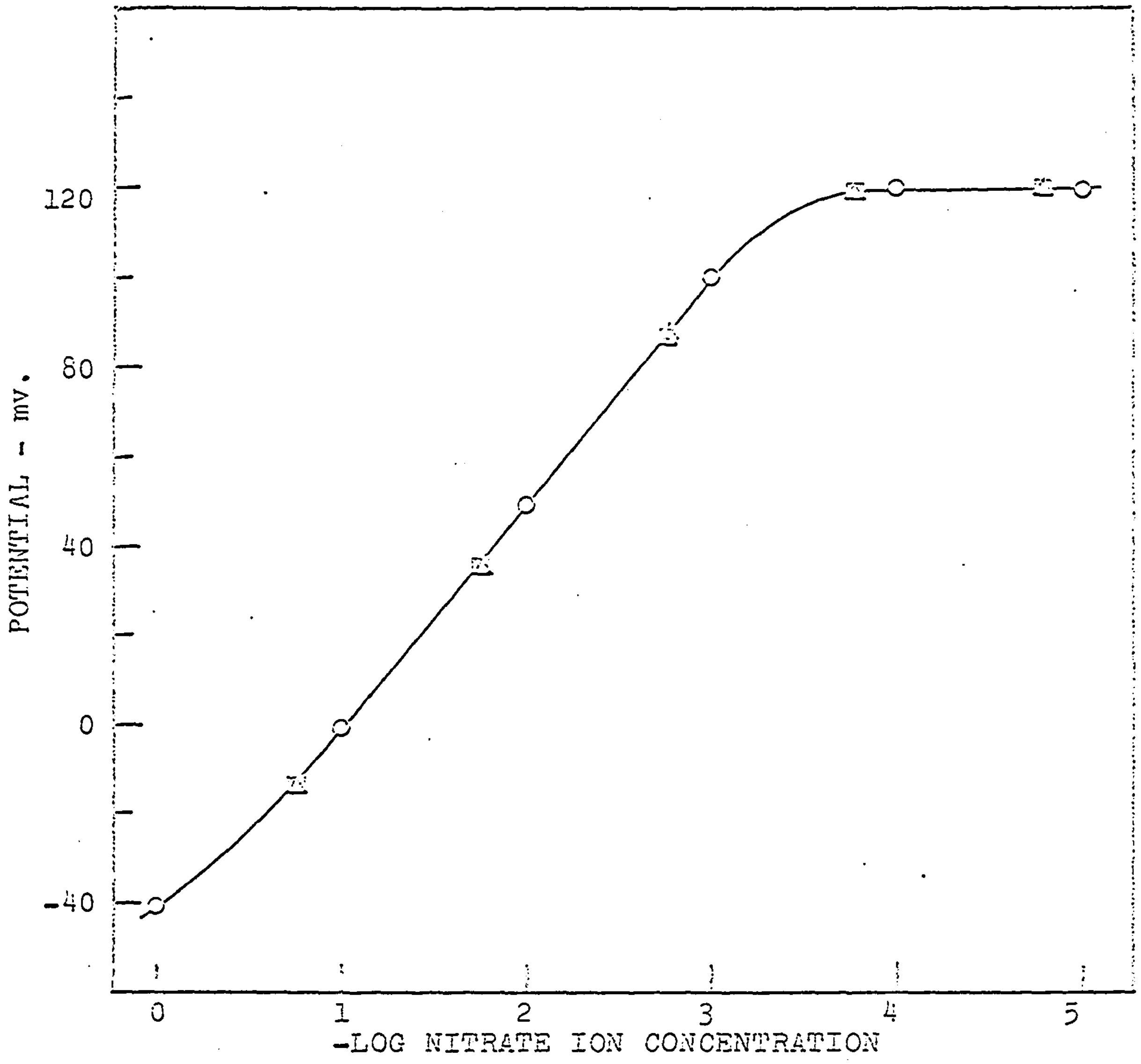


Figure 2. The effect of varying the nature of the cation on the response of a phenol-formaldehyde-nickel nitrate membrane to changes in concentration of nitrate of the solutions on opposite sides of the membrane

○ 0.10 M potassium nitrate // varying concentrations of potassium nitrate

□ 0.10 M potassium nitrate // varying concentrations of copper(II) nitrate

△ 0.10 M potassium nitrate // varying concentrations of nickel nitrate

Membranes Prepared from Phenols Other Than Phenol and from Mixtures of Phenols

The linkage between the aromatic entities of the phenol-formaldehyde resin are generally considered to be methylene groups attached to the aromatic ring at the positions ortho and para to the hydroxyl group, the polymer chains being tied together through occasional cross linking, that is with two methylene groups attached to some of the aromatic rings. Obviously substituents in the aromatic ring will affect the nature of the cross linkage and the presence in the polymer of voids through which ions can move. The possibilities for modification in this direction are numerous but experimental work was confined to resorcinol, hydroquinone, m-cresol, and 3,5-dimethylphenol as representing variations in the number and position of hydroxyl groups and in providing an inert substituent group.

Resorcinol proved too reactive and insoluble material formed within a few minutes on mixing with formaldehyde and heating to 65°C.; the same intractable material formed also with mixtures of resorcinol and phenol, even with as little as 10 per cent resorcinol. Because of this great reactivity, membranes containing resorcinol could not be prepared and tested.

Hydroquinone could not be polymerized without the addition of phenol. A bakelite A prepared from 90 per cent phenol plus 10 per cent hydroquinone was prepared and membranes prepared from it. These membranes did not differ in response characteristics from those prepared from phenol only. In Figure 3 is shown a comparison of the response to nitrate of membranes prepared from a phenol-hydroquinone mixture and from phenol alone. The membranes prepared with 10 per cent hydroquinone were not as mechanically strong as membranes prepared with phenol only. Incorporation of hydroquinone was therefore abandoned.

Meta-cresol was found to polymerize nicely with formaldehyde and membranes were prepared from the resulting polymer. The initial response of these membranes developed rapidly and was identical to the response of membranes prepared from phenol alone. However, the potentials observed were not stable. After a period of 24 hours with 0.10 M potassium nitrate and water on opposite sides of the membrane, the cut-off potential became progressively smaller, to less than 100 mv. as is shown in Figure 4.

Because the initial response of all membranes prepared with the m-cresol resin was good and the membranes reproducible, and because membranes prepared from phenol alone were not uniformly reproducible and responsive, a series of membranes was made from mixtures of various amounts of m-cresol and phenol. To 10 g. of the mixture of m-cresol and phenol, was added 10 g. of 37 per cent formaldehyde solution, and 1 ml. of 27 per cent ammonia. This mixture was placed in an oven at 65°C. and stirred every 30 minutes.

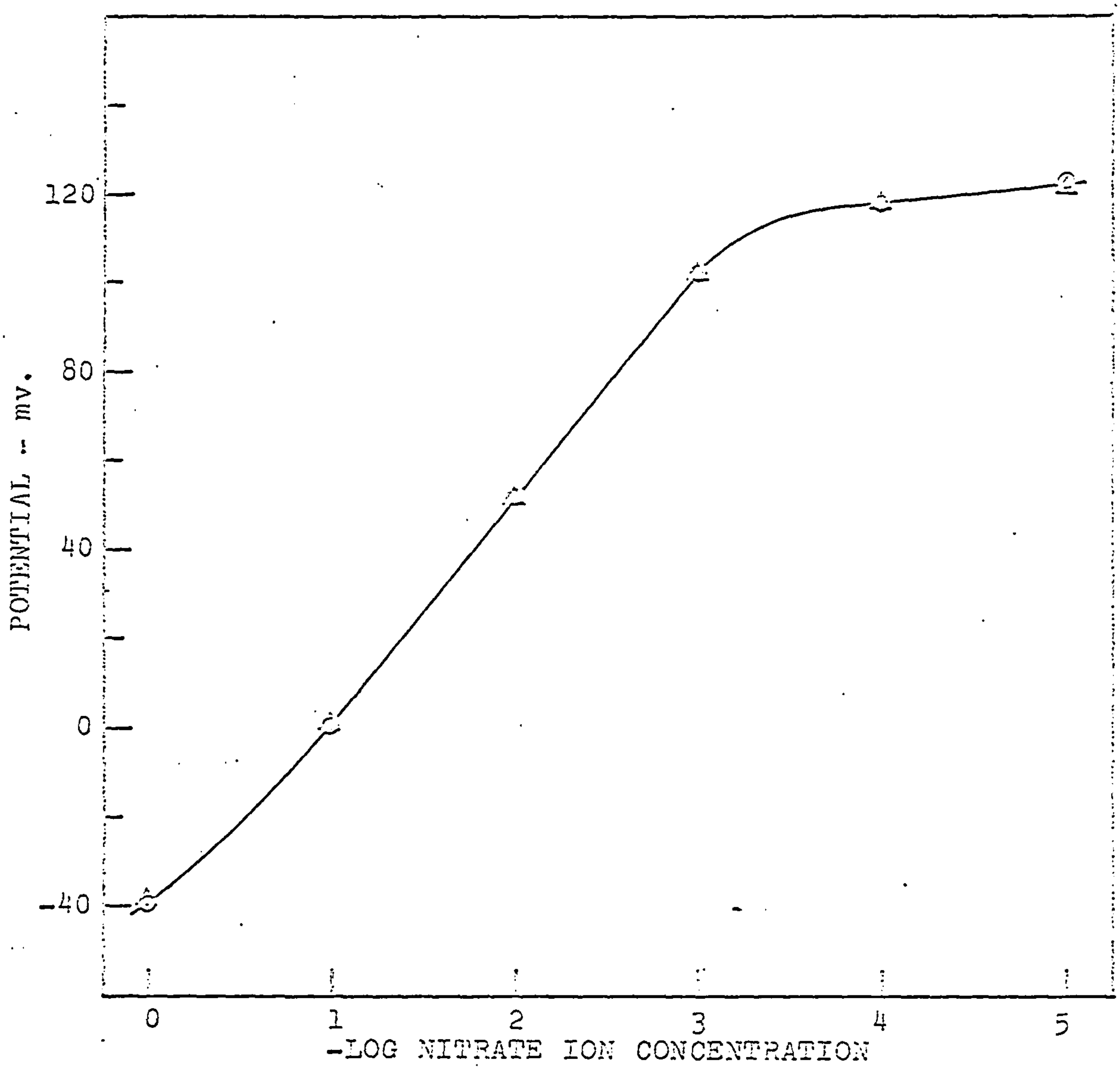


Figure 3. The effect of incorporating hydroquinone in the phenol-formaldehyde-nickel nitrate polymerization mixture

○ no hydroquinone

△ .10 per cent hydroquinone

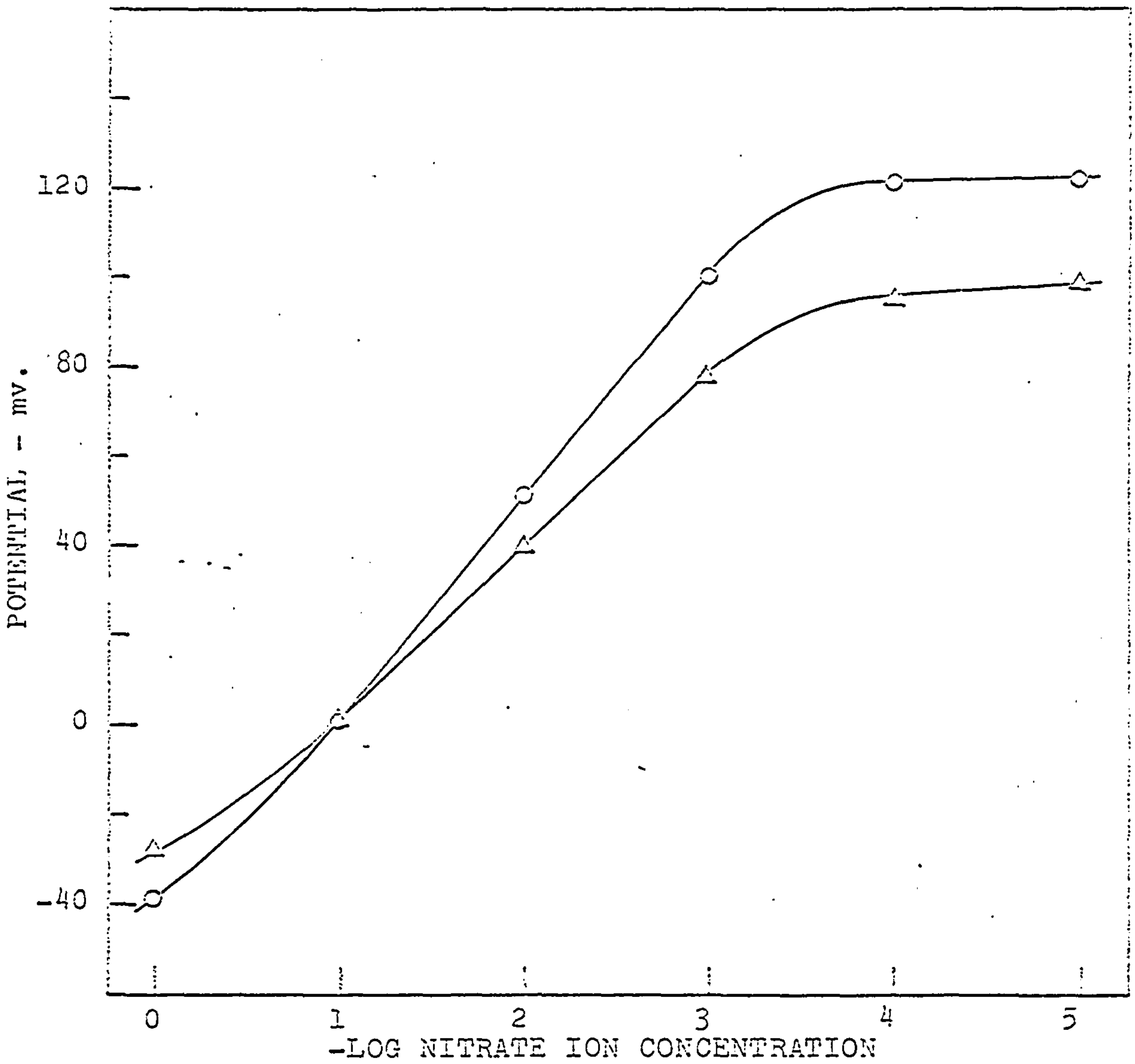


Figure 4. The response of a m-cresol-formaldehyde membrane containing nickel nitrate

○ initial response

△ response after 24 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

A cover was left in place until after two phases were formed. The upper, aqueous phase was then allowed to evaporate with occasional stirring. An additional 2 g. of 37 per cent formaldehyde was then added and mixed in, the resin being viscous at this stage. The mixture was again covered, heated at 65°C. for 30 minutes, uncovered, heated at 65°C. until the aqueous phase no longer remained, removed from the oven, and after cooling to room temperature, used for membrane preparation.

The membranes were prepared by dissolving 1.6 g. of this bakelite A in 20 ml. of ethanol, adding 0.40 g. of nickel nitrate hexahydrate and 1 ml. of ethylene glycol. The resulting solutions were poured into 10 cm. petri dishes, placed in an oven at 65°C. for at least 10 hours, and the temperature then slowly increased to 130°C. and maintained at 130°C. for 12 hours. The membranes were then slowly cooled to room temperature, soaked in water at 65°C. for 20 hours, and mounted as shown in Figure 1.

The response to nitrate of membranes prepared from various mixtures of m-cresol and phenol are shown in Figures 4 through 9. The response of the membranes prepared from phenol bakelite A was reproducible and stable with respect to time, Figure 9. The data of Figures 4 through 8 show that the response to nitrate was not reproducible with respect to time and further work with m-cresol was not attempted.

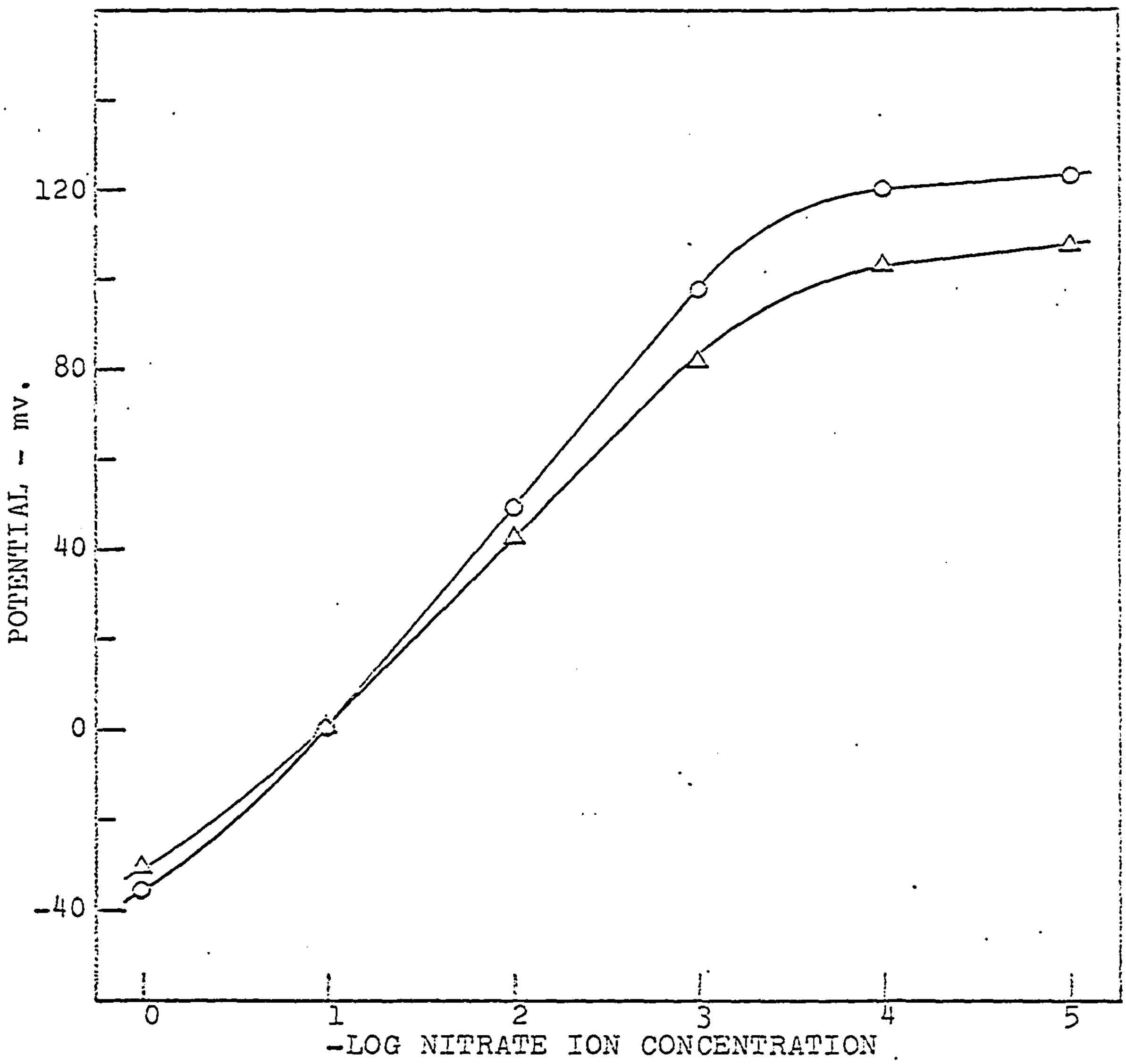


Figure 5. The response of a m-cresol-phenol-formaldehyde-nickel nitrate membrane to nitrate; cresol, 90 per cent; phenol, 10 per cent

○ initial response

△ response after 24 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

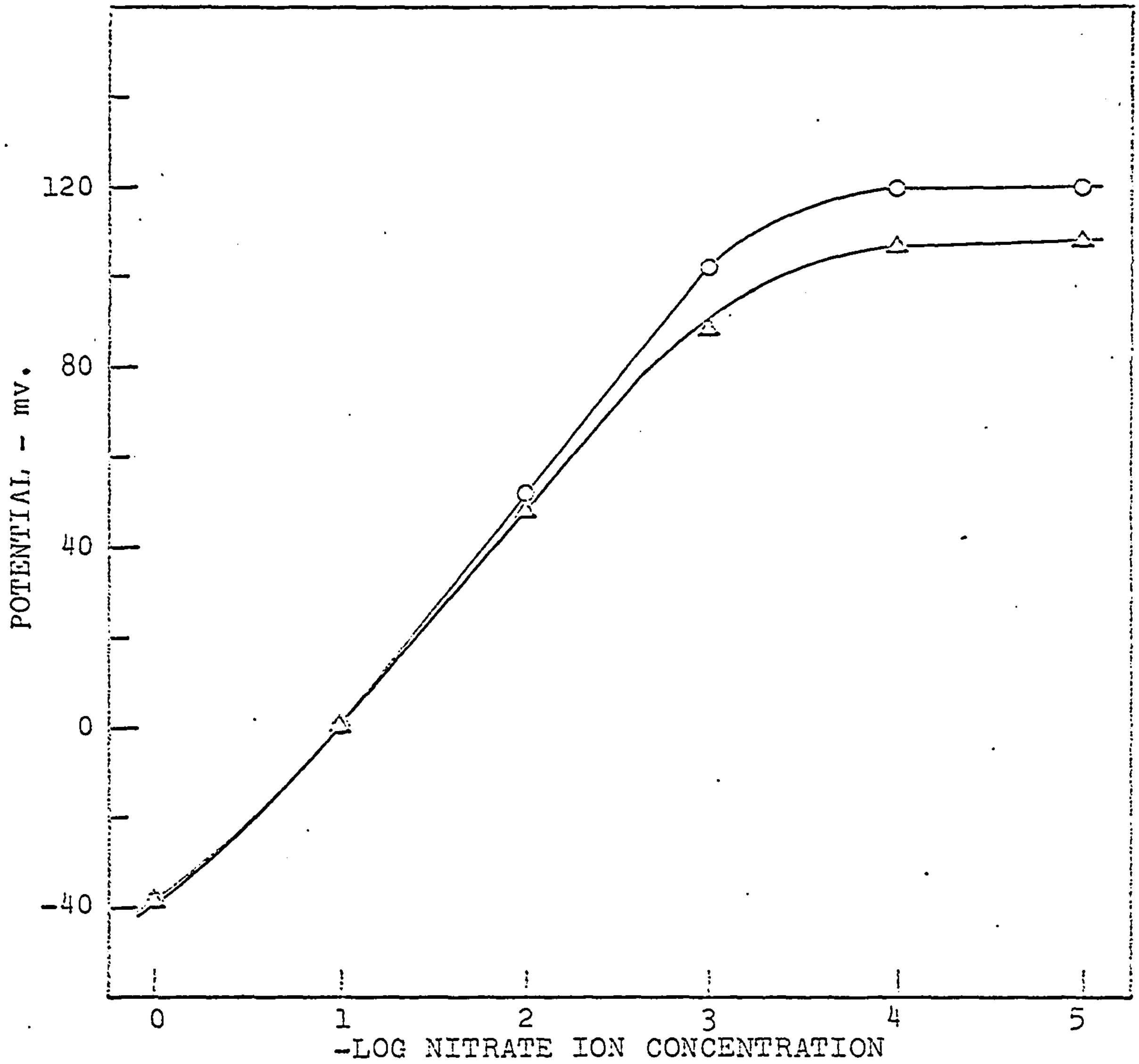


Figure 6. The response of a m-cresol-phenol-formaldehyde-nickel nitrate membrane to nitrate: cresol, 50 per cent; phenol, 10 per cent

○ initial response

△ response after 24 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

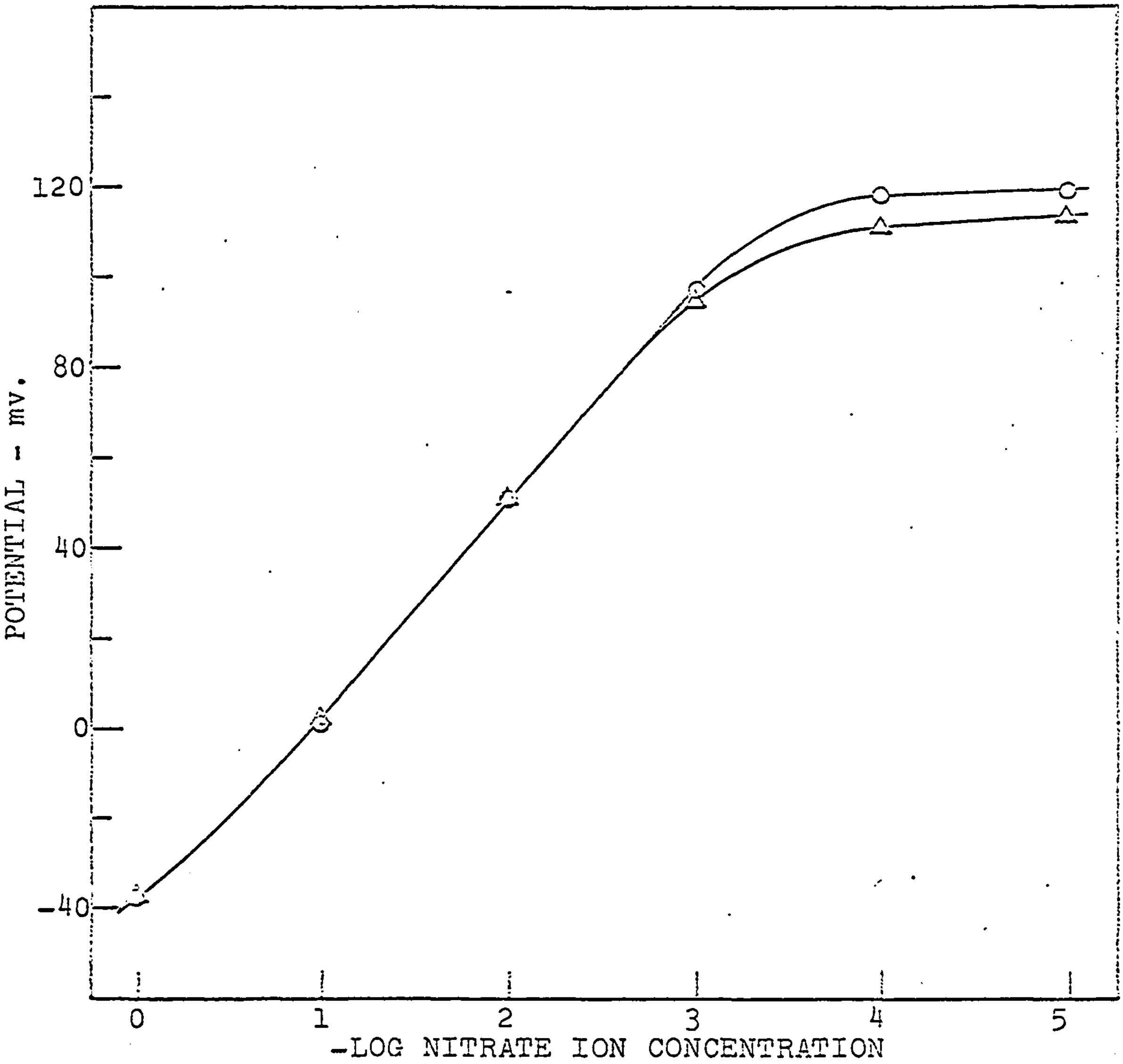


Figure 7. The response of a m-cresol-phenol-formaldehyde-nickel nitrate membrane to nitrate: cresol, 30 per cent; phenol, 70 per cent

○ initial response

△ response after 24 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

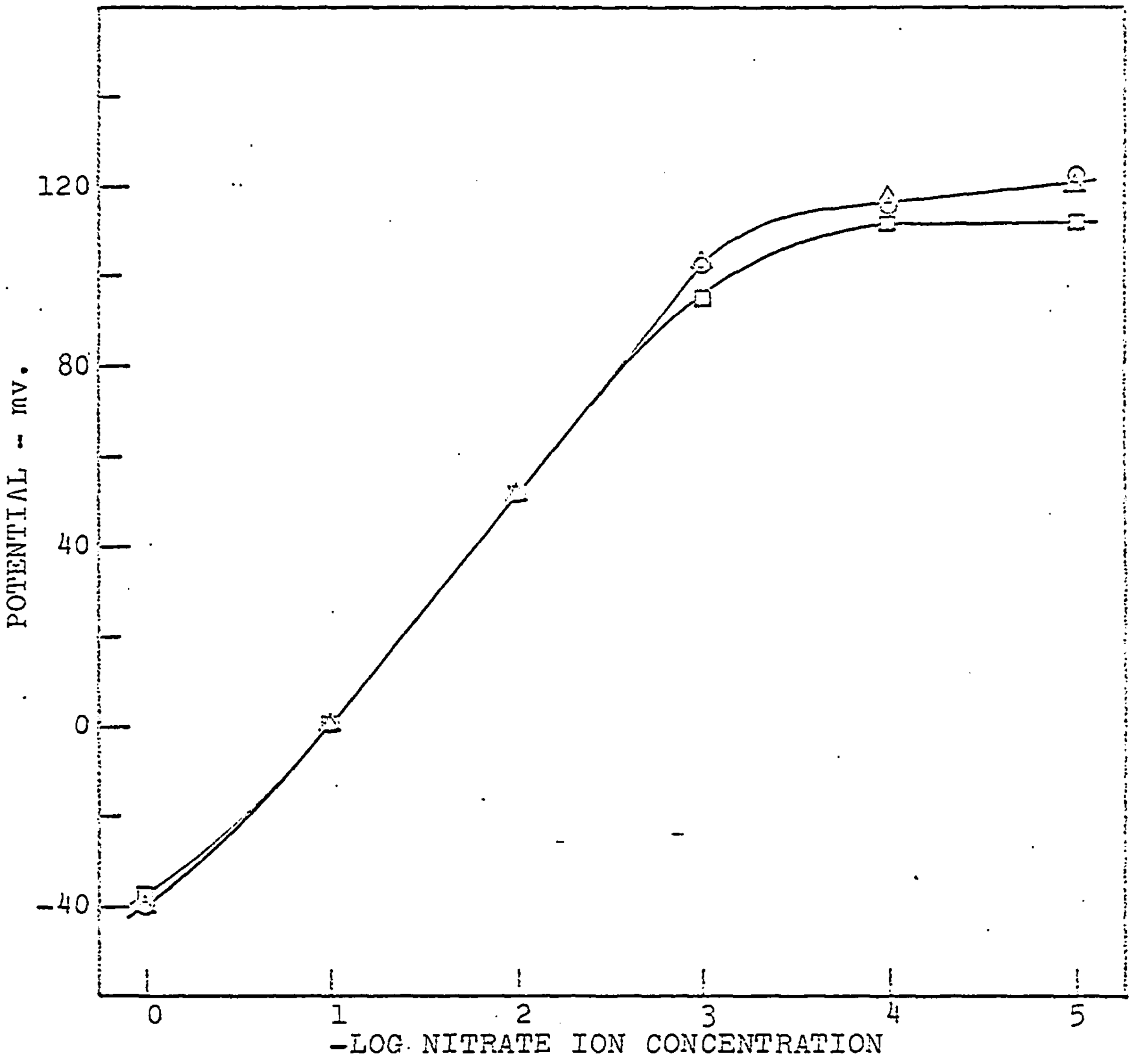


Figure 8. The response of a m-cresol-phenol-formaldehyde-nickel nitrate membrane to nitrate: cresol, 10 per cent; phenol, 90 per cent

○ initial response

△ response after 24 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

☐ response after 240 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

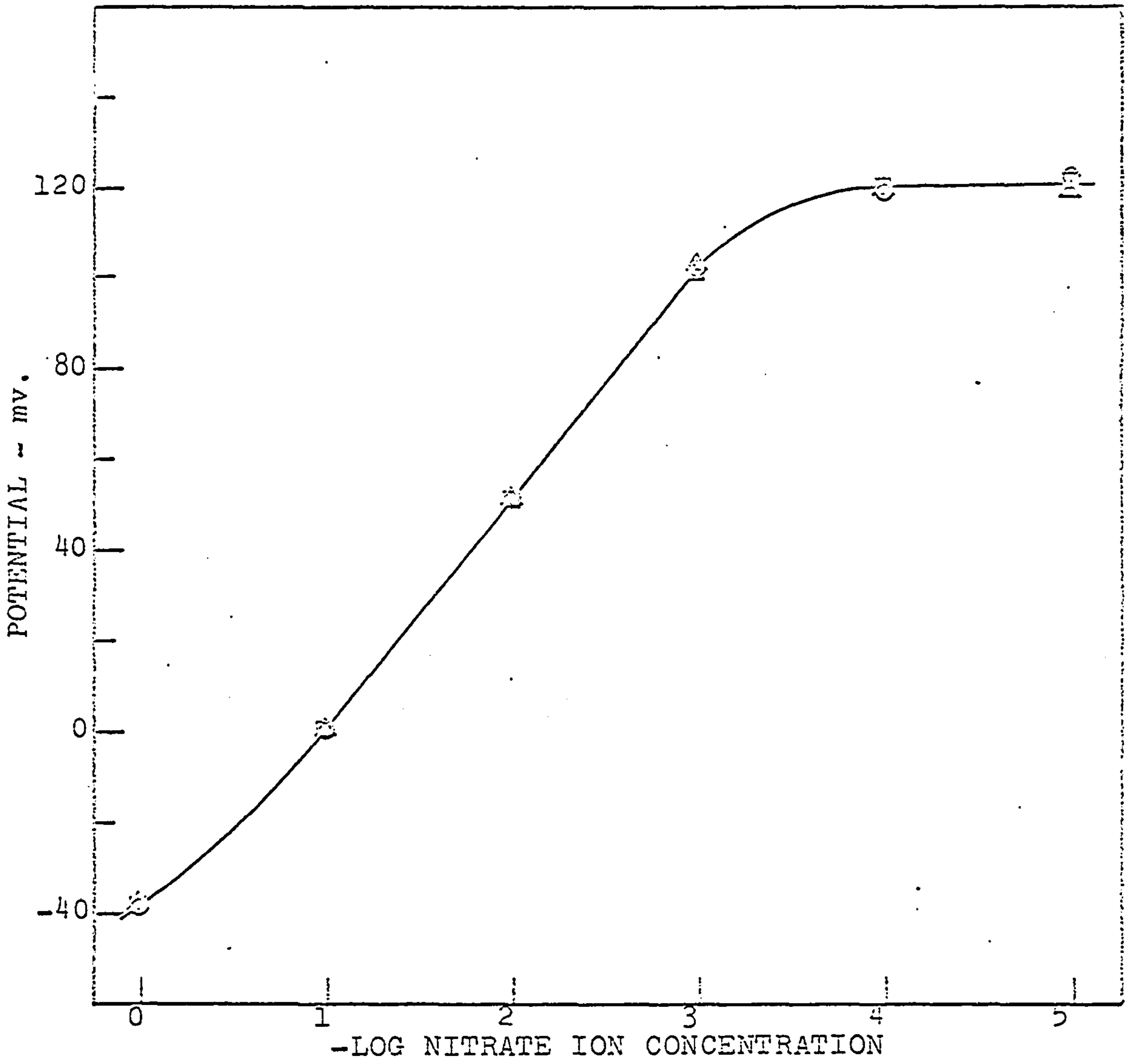


Figure 9. The response of a phenol-formaldehyde-nickel nitrate membrane: cresol, none; phenol, 100 per cent

○ initial response

△ response after 24 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

□ response after 240 hours of standing with 10^{-1} M potassium nitrate and water on opposite sides of the membrane

Membranes prepared from 3,5-dimethylphenol proved extremely brittle and did not respond well to change in nitrate concentration.

Thus, it was found that membranes could not be prepared from resorcinol, that membranes prepared from 10 per cent hydroquinone and 90 per cent phenol were not as mechanically strong as membranes prepared from phenol alone, that the response of membranes prepared from m-cresol and from mixtures of m-cresol and phenol were not stable with time, and that the response of membranes prepared from 3,5-dimethylphenol was poor and the membranes extremely brittle.

Conditions Affecting the Polymerization of Bakelite A

Inasmuch as the best obtainable membrane, in terms of mechanical strength and stability of response, was prepared from phenol alone, and because considerable variations were found from membrane to membrane, a thorough study was made of the variables involved in the preparation of bakelite A: the ratio of phenol to formaldehyde, the catalyst, the polymerization temperature, and the time of polymerization.

It was found that at temperatures of 70°C. or greater the formation of an insoluble polymerization product was enhanced and that if temperatures of 60°C. or less were used, the time required was too great. A temperature of 65°C. was, therefore, used for all polymerizations.

Responsive membranes could not be obtained from bakelite A preparations prepared using acid catalysts. Likewise, the strong bases, sodium hydroxide and potassium hydroxide, could not be used owing to the deposition of sodium or potassium salts of the phenol in the membrane; membranes containing such salts were no longer inert but responded to differences in concentration of numerous ions. Ammonia was finally adopted as catalyst. Membranes prepared using ammonia proved non-responsive and provided a suitable basis for the preparation of selective membranes.

Phenol-formaldehyde ratio and polymerization time were studied simultaneously by varying the polymerization time for each phenol-formaldehyde ratio studied. Ratios of 33, 50 and 66 per cent by weight of phenol to 37 per cent formaldehyde were studied using polymerization times of 5 to 12 hours in a covered container at 65°C. and an additional 3 to 8 hours uncovered at 65°C. The mixture was heated uncovered until it became clear at 65°C. or for some preparations, until it remained clear when cooled to room temperature. It was found that an initial ratio of 50 per cent by weight of phenol to the 37 per cent formaldehyde solution and an addition of more formaldehyde solution, in an amount of 20 per cent of the initial amount taken, after the mixture had become clear upon heating uncovered, gave the best results. After adding the formaldehyde solution to the clear mixture, the mixture was again covered and placed in an oven at 65°C. for 30 minutes, with stirring every 10 minutes. The cover was then removed and the mixture heated at 65°C., with stirring every 30 minutes, until clear or until clear at room temperature. This heating required from 1 to 3 hours. The resulting bakelite A could be dissolved in ethanol, mixed with ethanol-soluble nitrates and ethylene glycol, poured into a petri dish and made into a membrane as previously described.

Although this thorough study of the preliminary polymerization process resulted in learning how to make a good bakelite A, there were still slight variations in the response of membranes subsequently prepared. By adding a little formaldehyde solution to the ethanol solution containing the bakelite A, nitrate salt, and ethylene glycol, thus providing an excess of formaldehyde during the final polymerization to bakelite C, reproducible membranes were obtained in successive preparations.

The Effect of the Amount of Ammonia Used to Effect Polymerization

The response of membranes prepared using acids or strong bases as polymerization catalysts was extremely poor. The response of membranes prepared using ammonia as the catalyst was good. When acids and strong bases were used as catalysts, the resulting linkage between the phenol groups of the resin was entirely the methylene group. Using ammonia as the catalyst, some of the linking groups involve nitrogen, presumably as the dimethyleneamine group. Obviously the amount of ammonia incorporated is a matter of importance.

In the following work, the amount of ammonia used to effect the polymerization to bakelite A was varied and the response of membranes prepared from the resulting bakelite A preparations was determined.

Using no ammonia

To prepare the resin with no ammonia present, 5.0 g. of phenol and 5.0 g. of 37 per cent formaldehyde solution were mixed in a one-ounce screw-cap jar, the jar was covered with a watch glass and placed in an oven at 65°C. for 58 hours, additional formaldehyde was added and the mixture heated at 65°C. for 30 minutes. Nickel nitrate membranes prepared from this bakelite A were cloudy and crumbled so easily that they could not be mounted and tested. This bakelite A when polymerized without nickel nitrate formed a clear, brittle non-responsive membrane.

Using varying amounts of ammonia

To mixtures of 5.0 g. of phenol and 5.0 g. of 37 per cent formaldehyde solution in one-ounce screw-cap jars were added in a series of preparations 0.5, 1.0, 2.0 and 4.0 ml. of 27 per cent ammonia solution. Each jar was covered with a watch glass and placed in an oven at 65°C. for 26, 8, 3, and 1 3/4 hours for the preparations containing 0.5, 1.0, 2.0 and 4.0 ml. of 27 per cent ammonia solution respectively.

They were then uncovered and heated until the resin became clear at 65°C., additional formaldehyde solution was added and the jars were again covered and heated for 30 minutes at 65°C. The covers were removed and heating was continued until the resin again became clear at 65°C. Nickel nitrate membranes were prepared from these bakelite A preparations. A precipitate formed when nickel nitrate hexahydrate was added to a solution of the resin preparation containing 4.0 ml. of 27 per cent ammonia solution in ethanol. After evaporating the solvent from the mixture, a clear film remained which was polymerized at 130°C. However, the membrane cracked excessively as it was cooled to room temperature and, as a result, could not be mounted and tested. The response for the three remaining membranes is shown in Figure 10.

Thus, it was found that there is a minimum amount of ammonia that is necessary to obtain a responsive membrane and that the response does not improve with the addition of ammonia in excess of the minimum.

The Effect of Varying the Amine Used to Effect Polymerization

Inasmuch as nitrogen enters the polymer, it became of interest to learn if improvement in the membranes could be made by replacing the ammonia used to effect the polymerization by other amines. The bases, 2-aminoethanol, isopropylamine, ethylamine and ethylenediamine, were tried

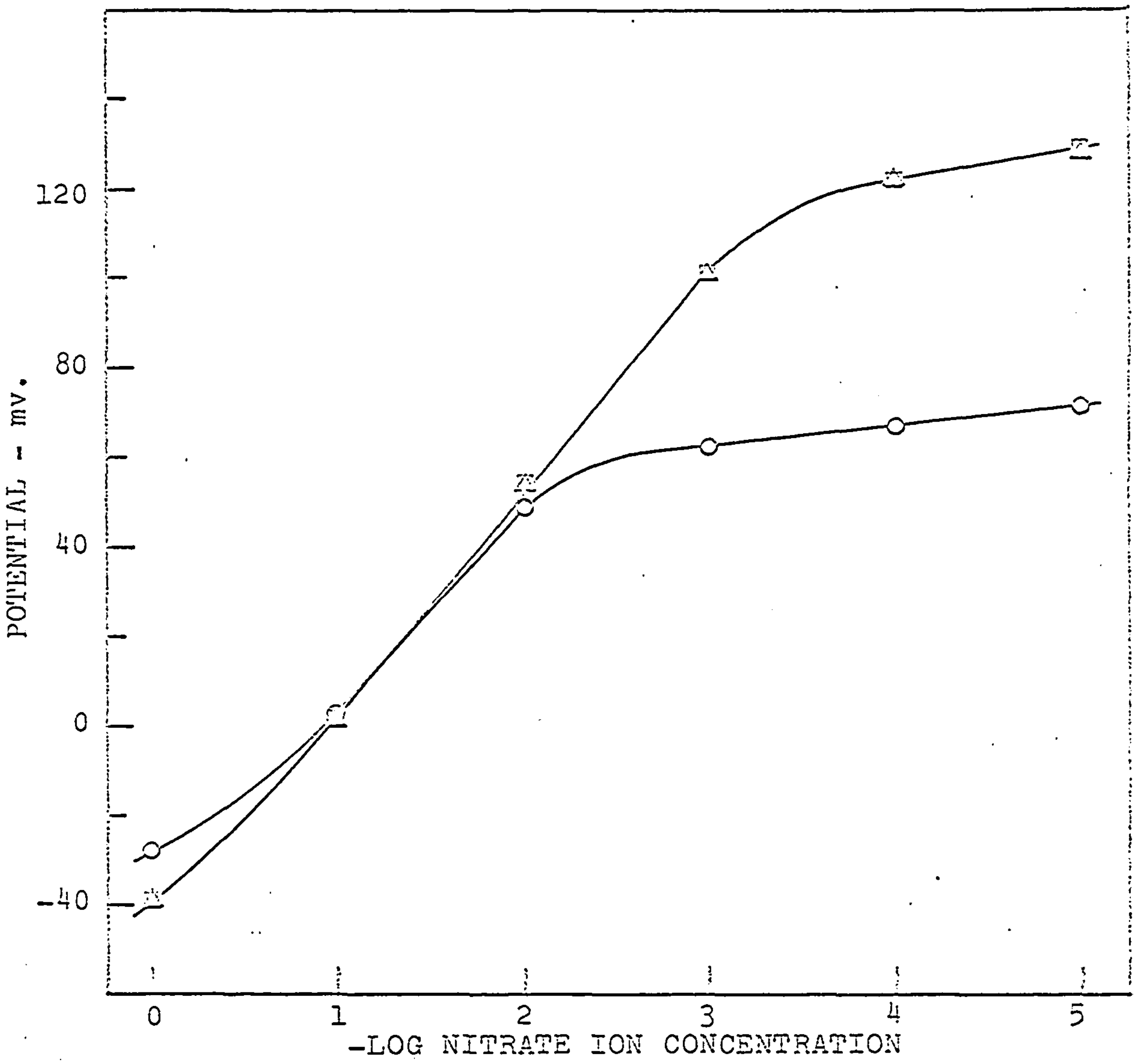


Figure 10. The effect of varying the amount of ammonia used to effect the polymerization on the response of a phenol-formaldehyde-nickel nitrate resin membrane to nitrate. Resin prepared from 5.0 g. phenol and 5.0 g. 37% formaldehyde. Ammonia added:

○ 0.5 ml. of 27% ammonia

△ 1.0 ml. of 27% ammonia

□ 2.0 ml. of 27% ammonia

and the resulting bakelite A preparations treated with nickel nitrate and the further polymerization effected. The response curves found for these membranes are shown in Figure 11. The response of membranes prepared using 2-aminoethanol was good. However, the response was not stable and was affected by the presence of sulfate in 10^{-3} M and greater concentrations. The response of membranes prepared using isopropylamine, ethylamine and ethylenediamine as the condensing agent was not good.

Methylamine, dimethylamine and trimethylamine were also tried as polymerization agents. The response of the resulting membranes is shown in Figure 12. The response to nitrate of membranes prepared using methylamine as condensing agent was good, whereas the response to nitrate of membranes prepared using dimethylamine and trimethylamine as condensing agent was poor. Because a dimethyleneamine linkage cannot be formed from a secondary or tertiary amine and can be formed from a primary amine, it is concluded from the results of this study that the potential response is a function of the formation of dimethyleneamine linkages within the membrane.

The Effect of Temperature on the Polymerization to Bakelite C

The character of the membrane finally formed depends not only on the nature of the bakelite A used and the metal salt incorporated but also on the temperature at which the final polymerization is effected.

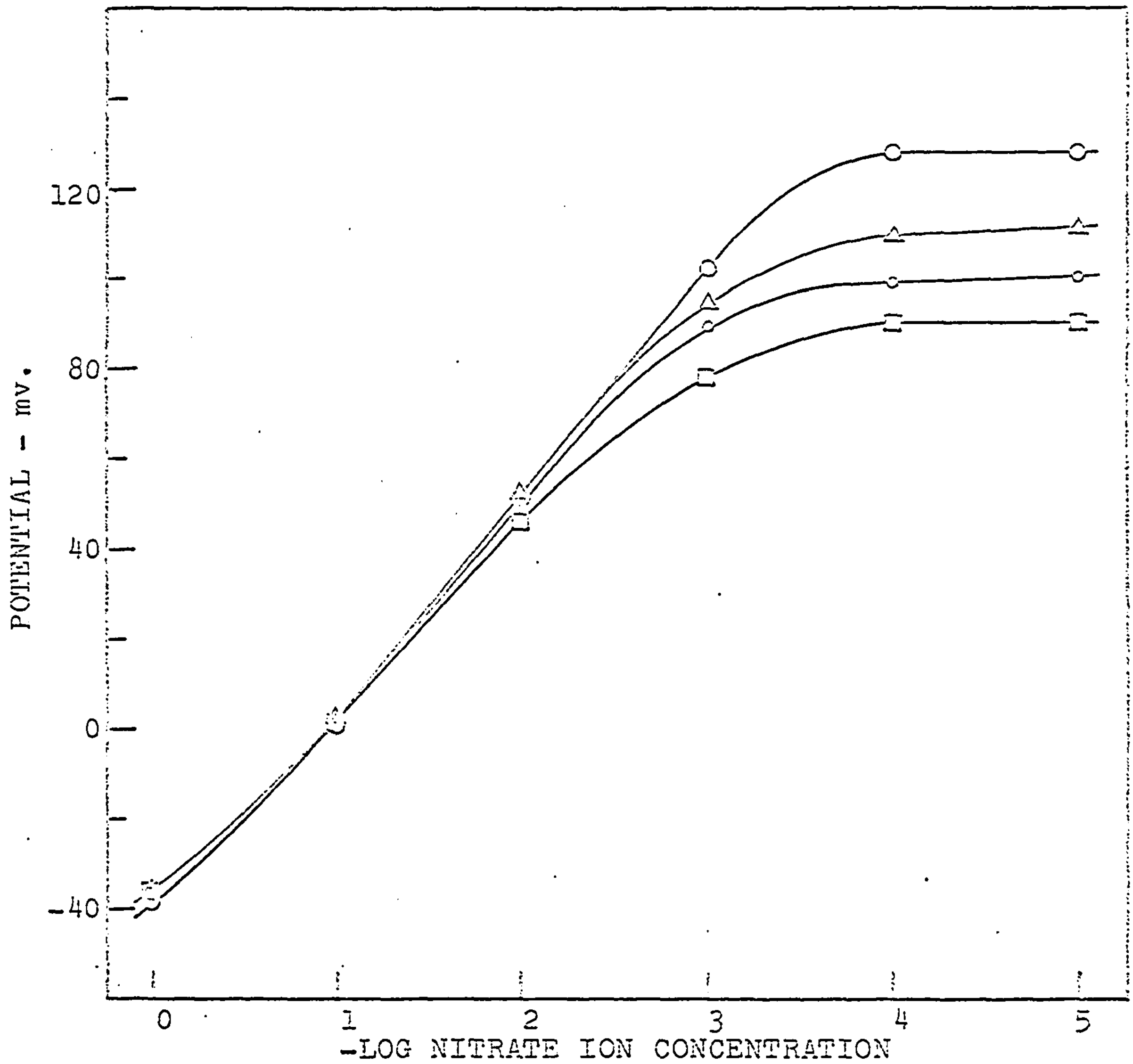


Figure 11. The effect of varying the amine used to prepare a phenol-formaldehyde resin membrane on the response to nitrate. Amine used:

- ○ 2-aminoethanol
- △ isopropylamine
- ∘ ethylamine
- □ ethylenediamine

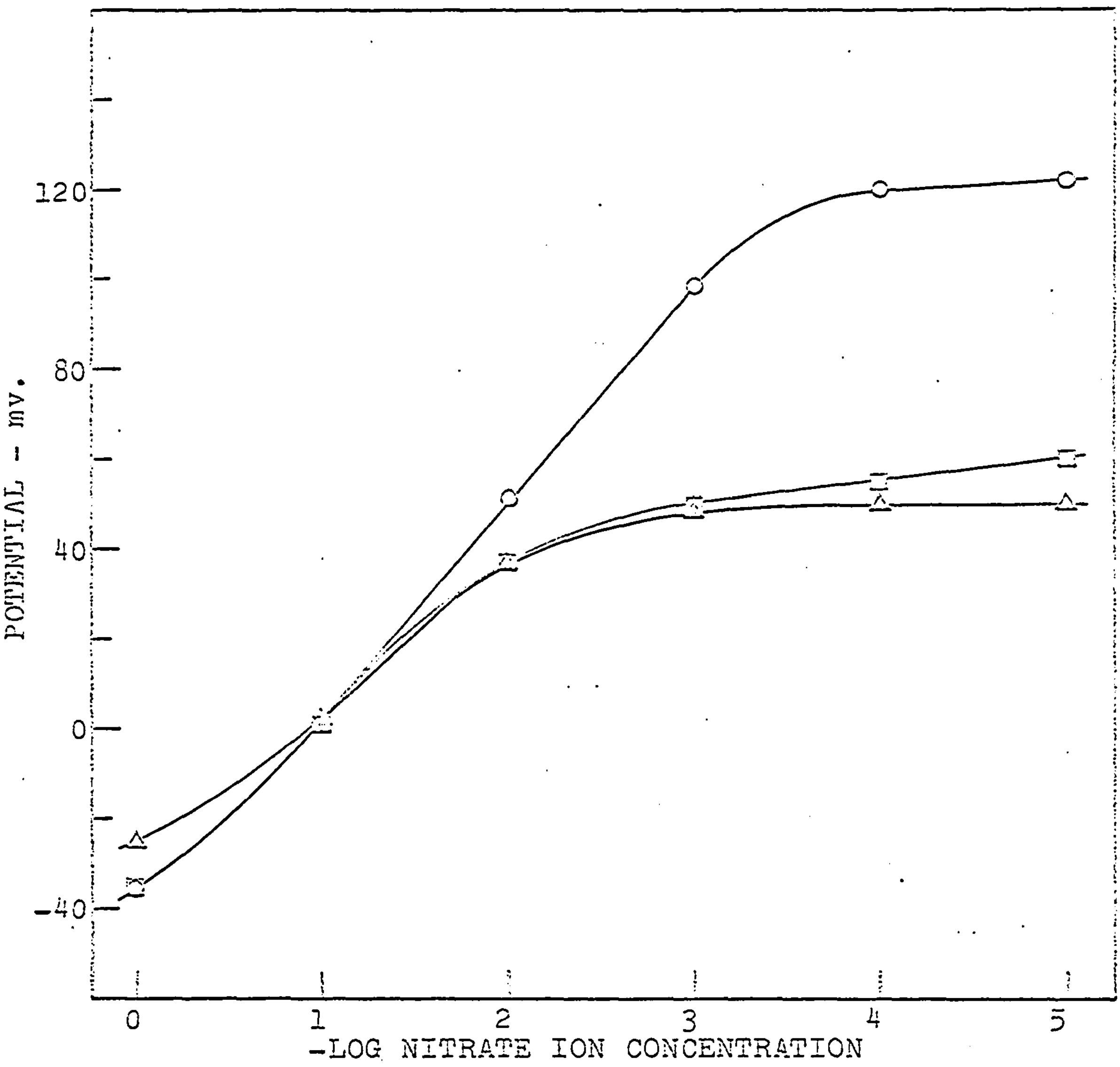


Figure 12. The effect of varying the amine used to prepare a phenol-formaldehyde resin membrane on the response to nitrate. Amine used:

○ methylamine

△ dimethylamine

□ trimethylamine

Membranes prepared from the same bakelite A preparation and having the same nickel nitrate content, after being kept at 65°C. for at least 10 hours, were slowly heated to 110, 130, 140, and 150°C. and kept at these temperatures for 15 hours. The membranes were then slowly cooled to room temperature, soaked in water at 65°C. for 20 hours, mounted, and tested for response to nitrate. The results of this series of tests are shown in Figure 13.

It was found that the response to nitrate of membranes prepared using polymerization temperatures ranging from 110 to 130°C. was good; temperatures of 140 and 150°C. resulted in membranes which did not respond well. The membranes obtained using a temperature of 130°C. were mechanically stronger than those polymerized at 110°C. In all subsequent work a temperature of 130°C. was used for the final polymerization.

Establishing the Optimum Amount of Nickel Nitrate to be Incorporated in the Membrane

A series of membranes was prepared with the initial content of nickel nitrate hexahydrate ranging from 10 to 25 per cent by weight of the polymerization mixture. A constant amount of bakelite A and the various amounts of nickel nitrate hexahydrate were dissolved in ethanol. The polymerization was effected as described previously, the membranes were mounted in the apparatus shown in Figure 1, and the potential response determined. The results of these tests are shown

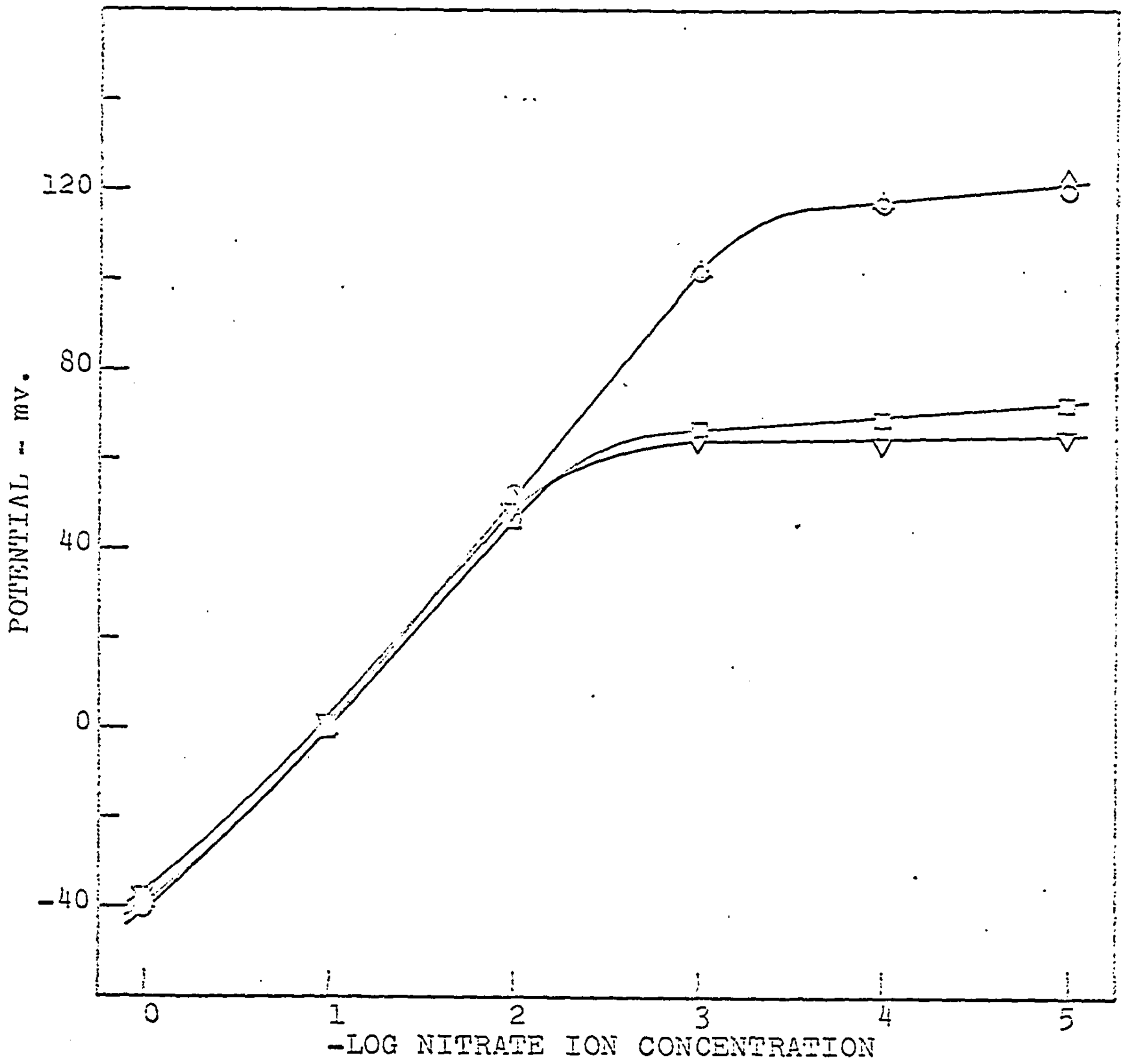


Figure 13. The effect of final polymerization temperature on the response of a phenol-formaldehyde-nickel nitrate membrane to nitrate

○ 110°C.

△ 130°C.

▽ 140°C.

□ 150°C.

in Figure 14. The response to nitrate of membranes prepared starting with initial amounts of 16 to 22 per cent nickel nitrate hexahydrate was good; below 16 per cent and above 22 per cent the response was unsatisfactory.

Thus, the range of nickel content over which satisfactory membranes can be prepared is rather broad. In subsequent work the amount of nickel nitrate hexahydrate added was always in the range 17 to 20 per cent.

The Effect of Incorporating Salts Other Than Nickel Nitrate on the Response of a Phenol-Formaldehyde Membrane to Nitrate

The effect of different cations within the membrane on the potential response of a phenol-formaldehyde membrane was studied by preparing membranes containing various ethanol-soluble nitrates. The amounts of the nitrate added were chosen so as to be equivalent to the amount of nickel nitrate hexahydrate found to be optimum. The response of these membranes to nitrate is shown in Figures 15 and 16.

The membranes prepared from iron(III) nitrate and copper(II) nitrate became opaque and black in color during the polymerization. Oxidation-reduction is probably involved here forming mixtures of iron(III) and iron(II) and copper(II) and copper(I), such mixed-valence compounds being often black in color. The resulting membranes were extremely brittle and the response to nitrate was poor.

The response of the aluminum, calcium, cobalt, hydrogen,

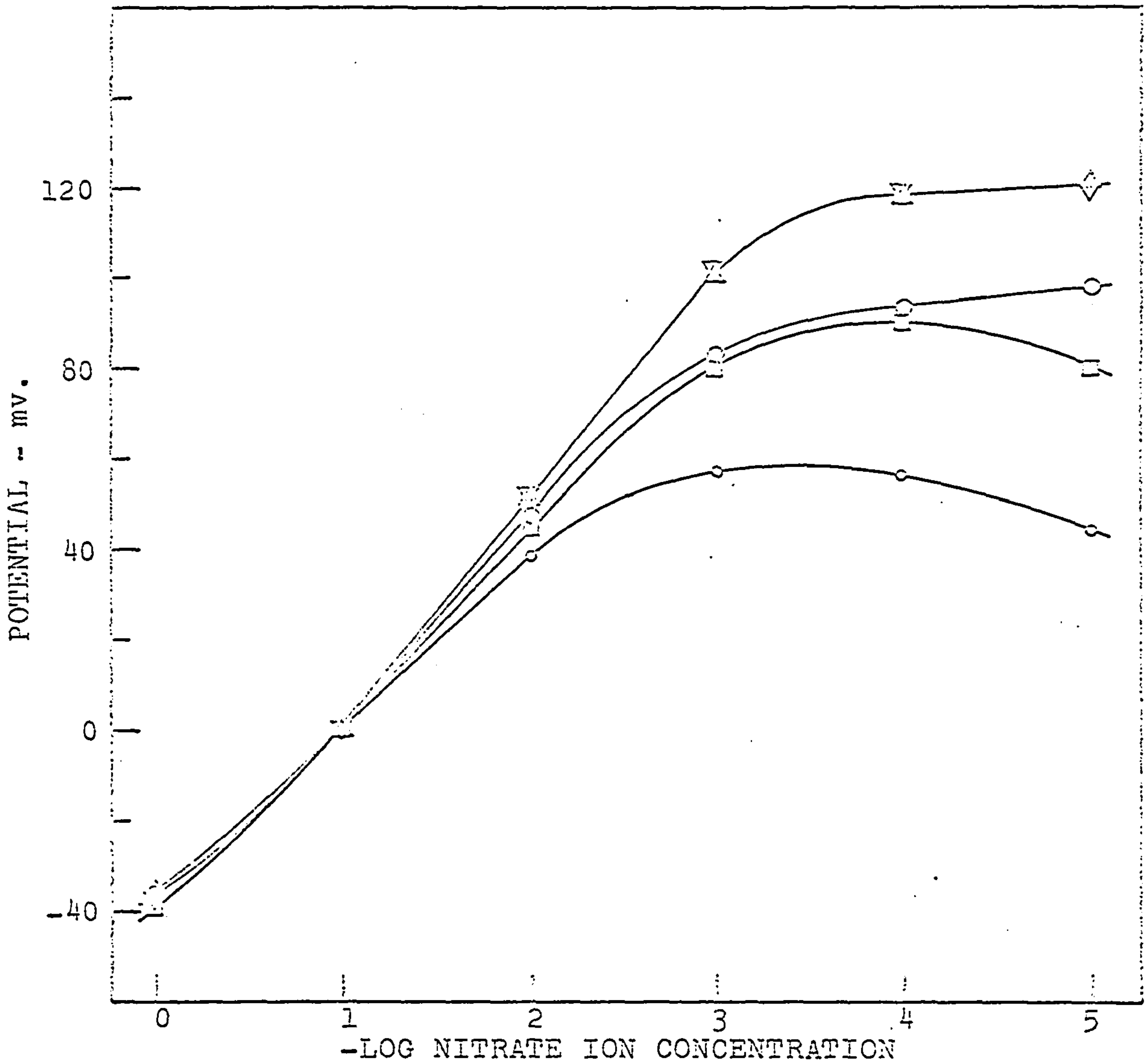


Figure 14. The effect of varying the amount of nickel nitrate hexahydrate incorporated into a phenol-formaldehyde polymer membrane

○ 25 per cent

△ 22 per cent

▽ 19 and 16 per cent

□ 13 per cent

∘ 10 per cent

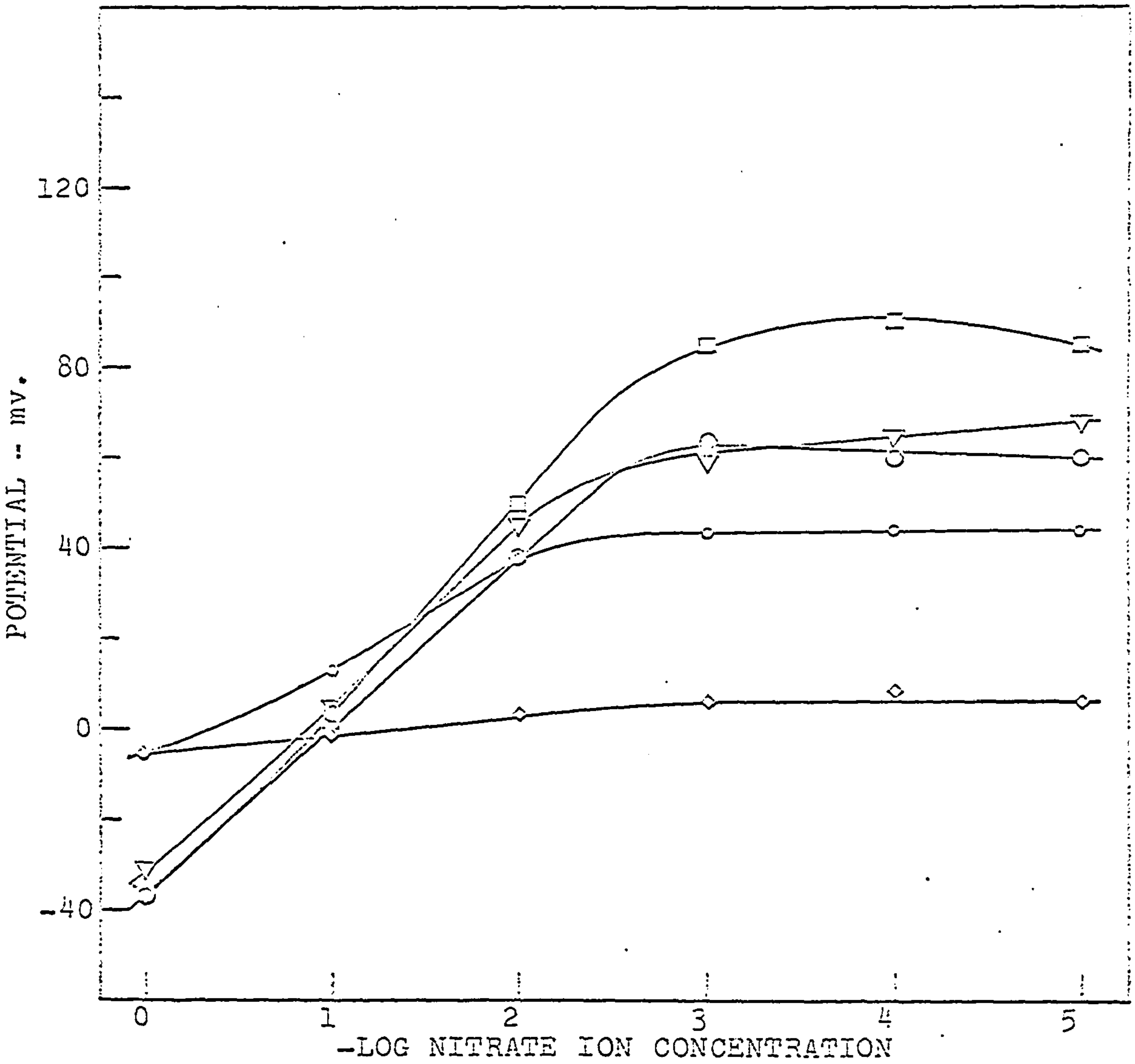


Figure 15. The effect of incorporating various nitrates into a phenol-formaldehyde-ammonium hydroxide membrane

- ○ aluminum nitrate
- ▽ calcium nitrate
- ☐ cobalt nitrate
- ◦ lithium nitrate
- ◇ iron(III) nitrate

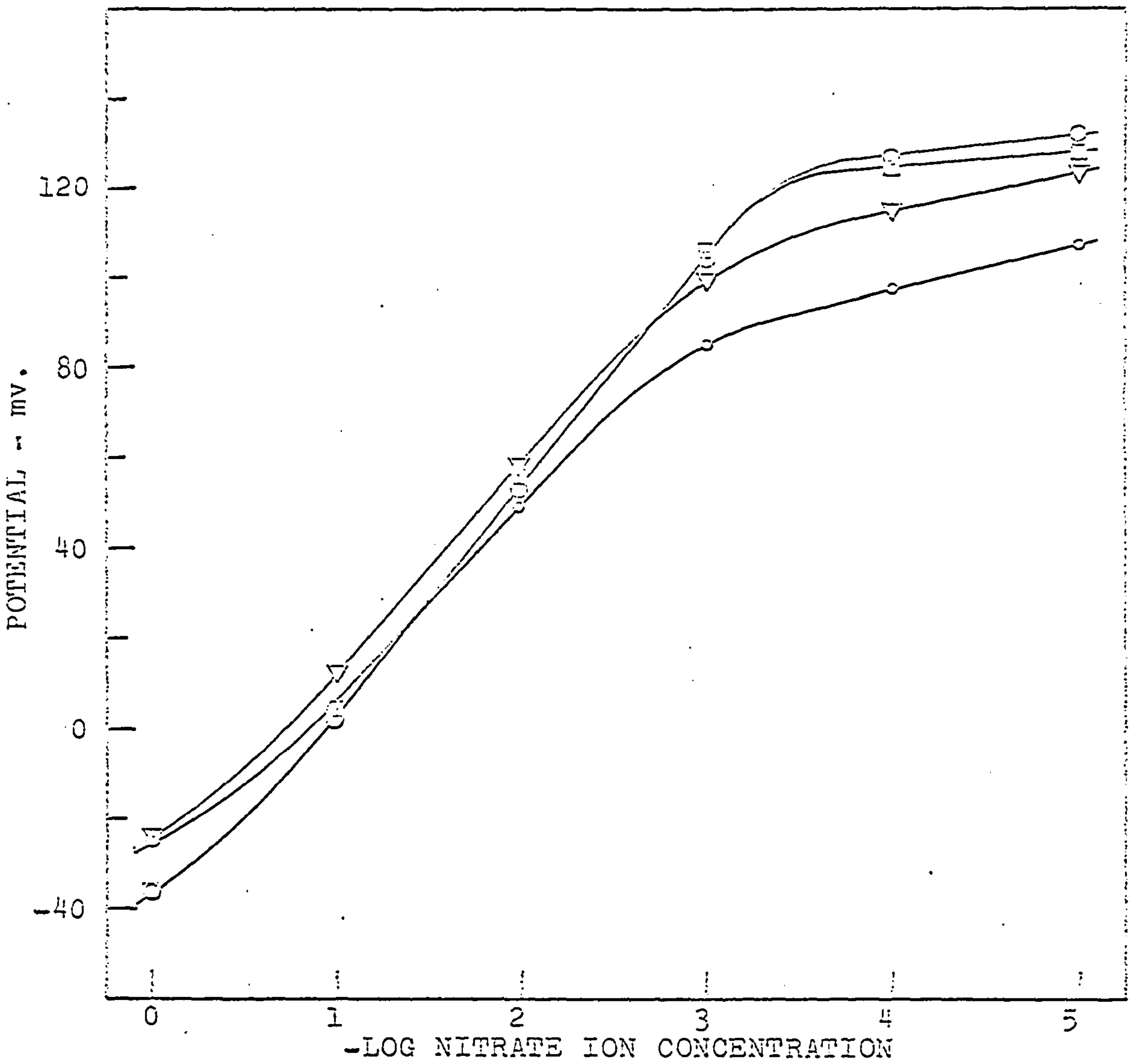


Figure 16. The effect of incorporating various nitrates into a phenol-formaldehyde-ammonium hydroxide membrane

∘ copper(II) nitrate

▽ nitric acid

○ magnesium nitrate

□ zinc nitrate

and lithium nitrate membranes was also found to be poor. With the exception of cobalt, the charge-to-size ratios of these cations are considerably different from that of the nickel ion. The response of the membrane containing cobalt nitrate, after soaking for several days with 0.10 M potassium nitrate solution and water on opposite sides of the membrane, became approximately equivalent to the response of the membrane prepared with nickel nitrate. However, after several days the membrane no longer responded well to nitrate. None of the other membranes of this group exhibited even a temporary response of satisfactory nature.

The response of membranes prepared with magnesium nitrate and zinc nitrate was equivalent to that of the nickel nitrate membrane; the charge-to-size ratios of the zinc ion and of the magnesium ion are about the same as that of the nickel ion. Thus, the response appears to depend on the charge-to-size ratio of the cation added.

The response of the membranes prepared from magnesium nitrate and zinc nitrate was not reproducible after several days of immersion of the membrane in the 0.10 M potassium nitrate reference solution and water. The response of the nickel nitrate membrane was stable and reproducible even after several months of soaking. Because of these findings, nickel nitrate was used in all subsequent preparations.

Membranes were prepared incorporating nickel chloride and nickel perchlorate into phenol-formaldehyde membranes.

The response curves of these membranes are shown in Figure 17. The response of the nickel chloride membrane was not as good as the response of the nickel perchlorate membrane; the response of the nickel perchlorate membrane being equivalent to that of the nickel nitrate membrane. A white precipitate was formed with the addition of nickel chloride hexahydrate to a solution of bakelite A in ethanol. A white, curdy layer remained in the petri dish after evaporation of the solvent at 65°C., the white layer became a clear, green film of irregular thickness and the clear film was polymerized into a membrane. This precipitation during the formative stages of the membrane apparently affected the development of exchange sites within the membrane which are necessary for the attainment of a good response. There was no precipitate formation during the preparation of the nickel perchlorate membrane.

Membranes containing sodium iodide and sodium thiocyanate were also prepared. The response of these membranes to nitrate was poor, as shown in Figure 18, and the response of the membranes to anions other than nitrate was not good.

Optimum Conditions for the Preparation of a Phenol-Formaldehyde Polymer Membrane Responsive to Nitrate

It was found that the best resin preparation was obtained from an ammoniacal condensation of a mixture of equal weights of phenol and 37 per cent formaldehyde solution

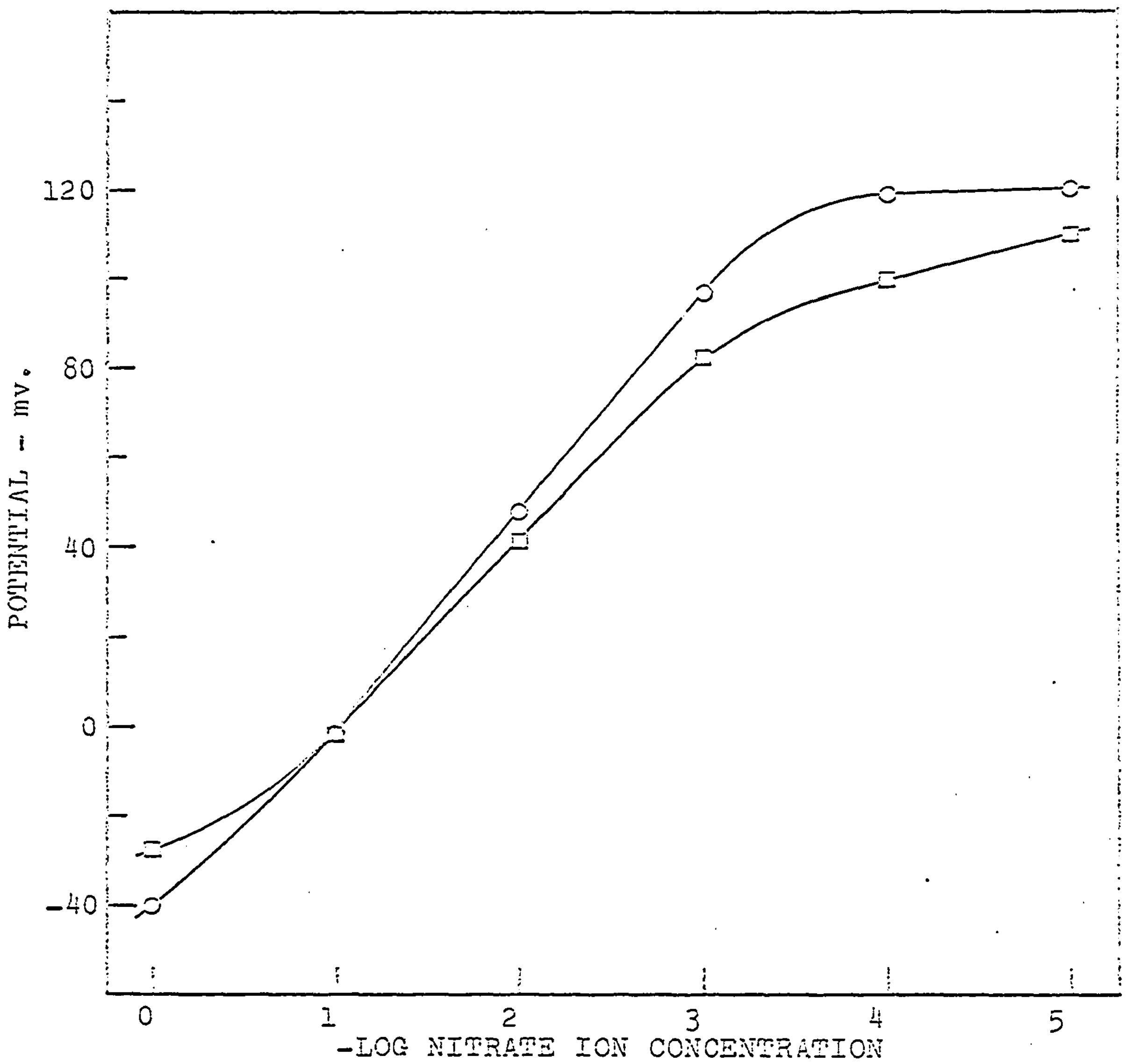


Figure 17. The effect of varying the nickel salt on the response of a phenol-formaldehyde-nickel membrane to nitrate

○ nickel perchlorate

☐ nickel chloride

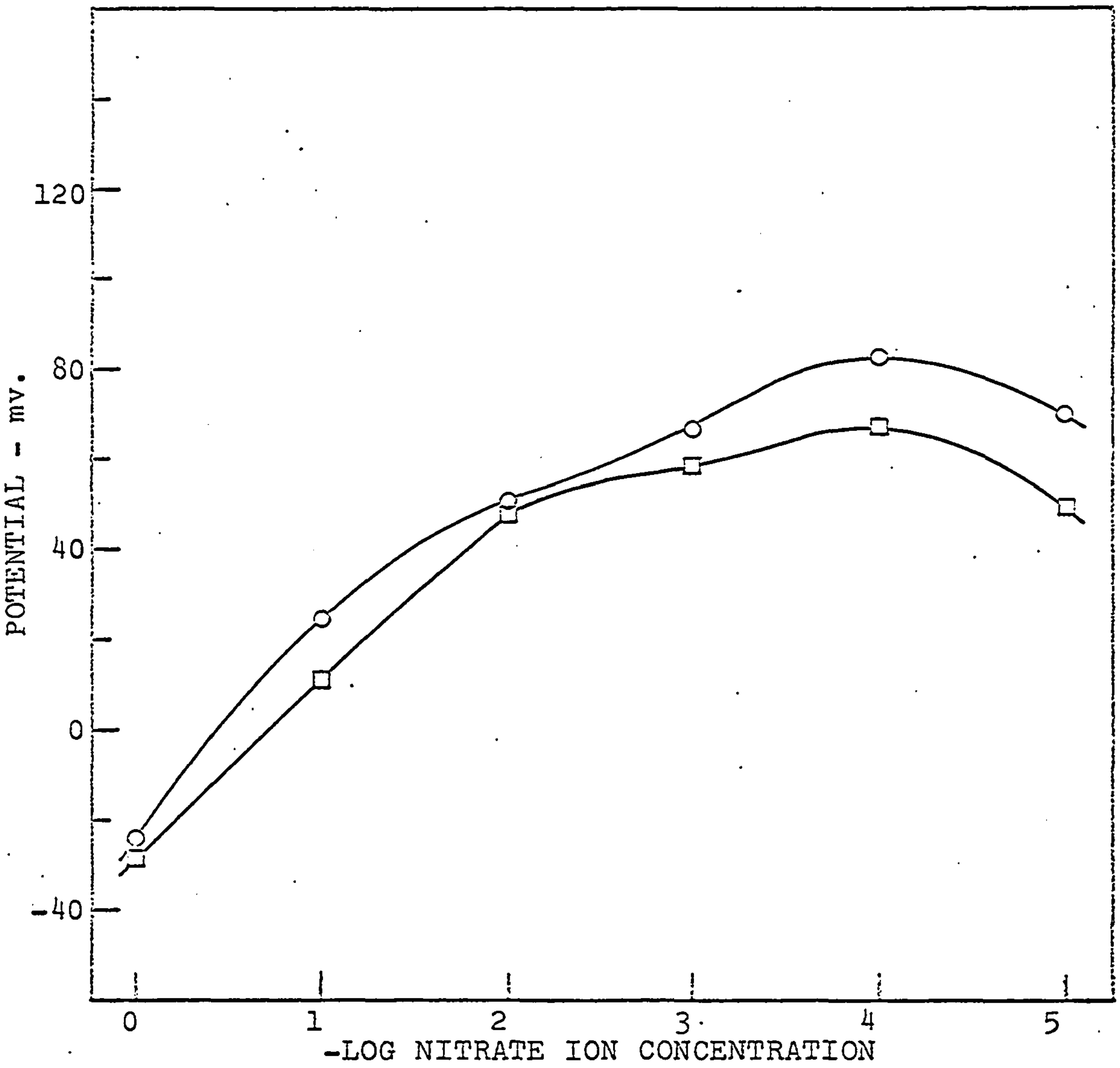


Figure 18. The effect of incorporating sodium thiocyanate and sodium iodide into a phenol-formaldehyde resin on the response of the membrane to nitrate

○ sodium thiocyanate

☐ sodium iodide

in a covered container at 65°C. for 8 hours, with stirring every 30 minutes. The container was then uncovered and maintained at 65°C. for approximately 5 hours, with stirring every 30 minutes, until the mixture became clear. Additional formaldehyde solution in an amount of 20 per cent of the initial amount was then added to the mixture and the container again covered and maintained at 65°C., with stirring every 10 minutes, for 30 minutes. The cover was then removed and the mixture was maintained at 65°C., with stirring every 30 minutes, until a clear yellow-orange resin was formed. This resin was dissolved in ethanol with an ethanol-soluble salt and 1.0 ml. of 37 per cent formaldehyde solution per 1.8 g. resin. The solvent was then evaporated off at 65°C. and the temperature maintained at 65°C. for at least 10 hours and then increased at a rate of 10 degrees per hour until a temperature of 130°C. was attained. The temperature was maintained at 130°C. for at least 12 hours and then slowly cooled to room temperature. The membrane was soaked in water at 65°C. for 20 hours and mounted for testing. The addition of nickel nitrate hexahydrate to the resin resulted in membranes having the highest degree of stability as compared to membranes containing other ethanol-soluble salts.

The resulting nickel nitrate membrane was mechanically strong, exhibited stable potential response to nitrate and, with the exception of the hydrogen ion, did not respond to any changes in cation content or activity.

Summary of Developmental Work

A membrane has been prepared from a modified phenol-formaldehyde resin which responds to changes in the concentration of nitrate. The modification consists of incorporating nickel nitrate into the resin. A thorough study of the preparation conditions and materials was undertaken to determine the necessary conditions for the attainment of a reproducible preparation procedure.

Resins were prepared using various phenols and membranes were prepared from each resin. The best response was obtained with membranes prepared from phenol alone.

The optimum conditions for the polymerization of bakelite A were: a phenol-formaldehyde ratio of one to one with more formaldehyde added after the aqueous phase that forms during the polymerization is evaporated, a polymerization temperature of 65°C., a total polymerization time of about 15 hours, and the use of ammonia to effect polymerization. There is a minimum amount of ammonia necessary to effect polymerization to a bakelite A that can be used to prepare responsive membranes and the membrane response is not improved with the use of ammonia in excess of the minimum. A good response is obtained from resins prepared using ammonia or a primary amine but not a secondary or a tertiary amine as condensing agent.

The response of membranes, polymerized to bakelite C at temperatures ranging from 110° to 130°C., is good and membranes polymerized at 130°C. are mechanically stronger than membranes polymerized at 110°C.

Membranes containing various ethanol-soluble salts were prepared and optimum response was obtained by incorporating nickel nitrate into the membrane.

Thus, the optimum conditions for the preparation of a phenol-formaldehyde polymer membrane that responds to nitrate have been determined.

PROPERTIES OF PHENOL-FORMALDEHYDE-NICKEL NITRATE POLYMER MEMBRANES

As described in the previous part of this thesis, a membrane which is responsive to nitrate was prepared by polymerizing phenol and formaldehyde with ammonia and incorporating nickel nitrate during the final polymerization step. The properties of this phenol-formaldehyde-ammonia-nickel nitrate membrane were then investigated in detail with particular reference to composition, exchange properties, resistance, crystallinity, response to cations, response to anions other than nitrate, and application to chemical analysis.

The Effect of pH on the Response of the Membrane

The effect of pH on the potential developed across the phenol-formaldehyde-nickel nitrate membrane was studied by titrating citric acid with 0.1 M sodium hydroxide and measuring both the pH and the potential of the membrane at each step in the titration. The titration curve obtained with the pH meter (glass electrode) is shown in Figure 19; variation in the potential of the membrane is shown in Figure 20. The pH was measured using a Beckman number 40495 high alkalinity glass electrode and a Corning model 10 pH meter.

The membrane obviously responds to the hydrogen ion as well as to nitrate. In fact, the curves shown in Figures 19

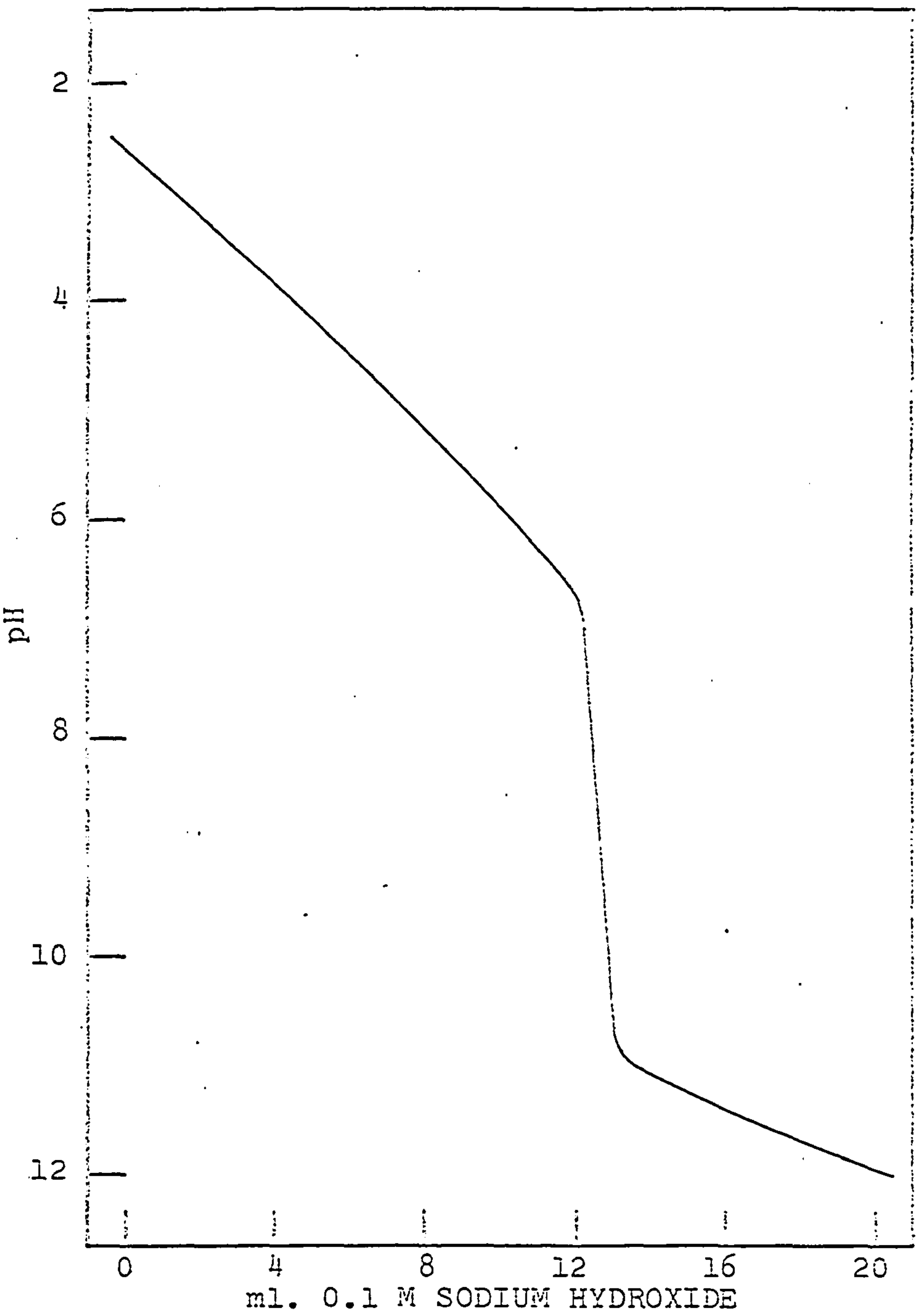


Figure 19. Titration of citric acid with sodium hydroxide. pH measured using a pH meter and glass electrode

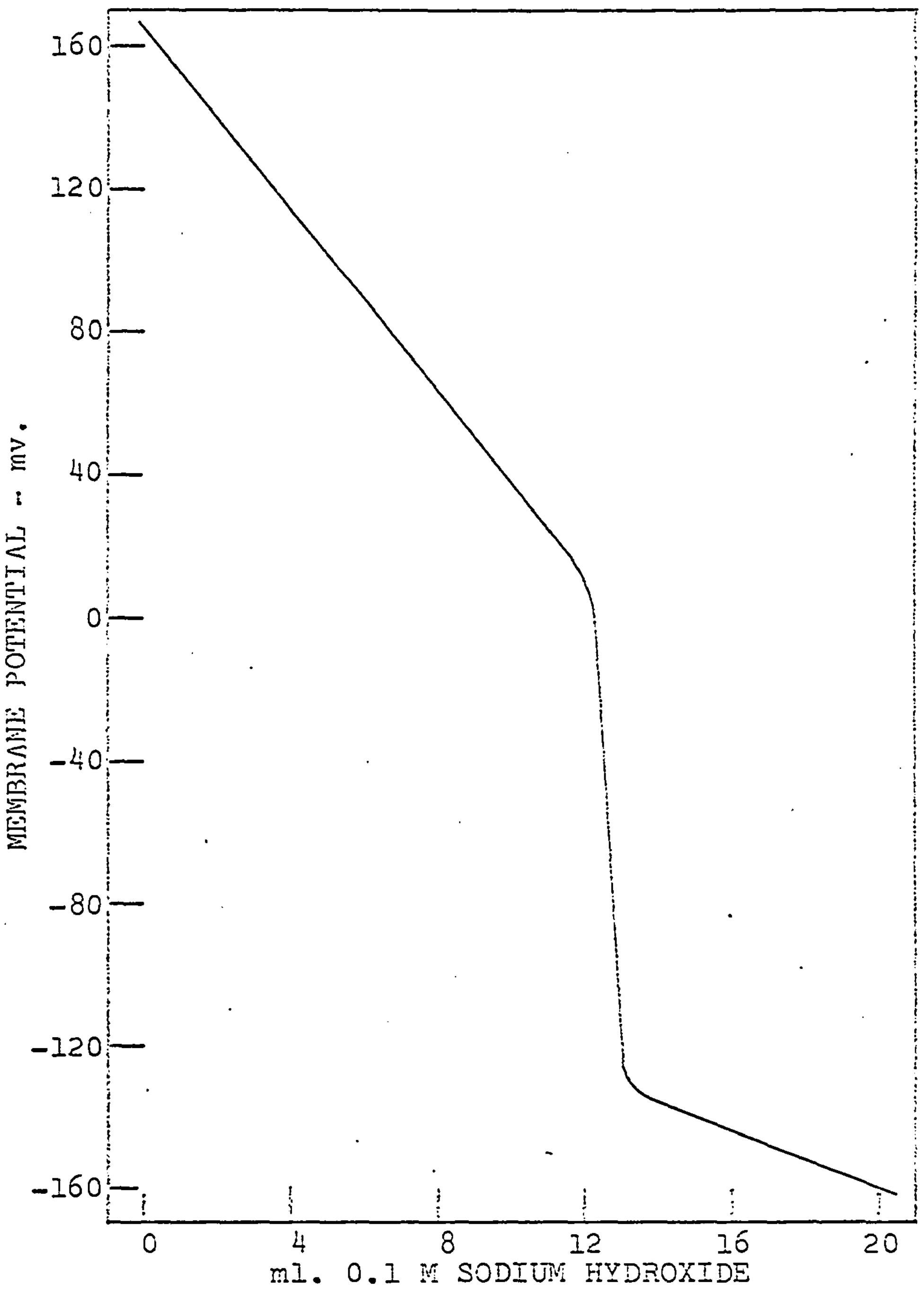


Figure 20. Titration of citric acid with sodium hydroxide. Membrane potential measured using a vibrating reed electrometer and phenol-formaldehyde-nickel nitrate membrane

and 20 superimpose in the end-point region and do not differ greatly in the buffer regions before and after the end-point. A plot of potential of the membrane as a function of pH is shown in Figure 21. Solid potassium hydroxide was added to the solution to obtain pH values greater than 12.5. The sudden increase in potential at pH values greater than 12 is probably caused by the formation of phenol salts within the membrane[1].

The effect of pH on the potential response to nitrate was studied by preparing solutions of varying potassium nitrate concentrations from buffer solutions of pH values of 2.1, 3.0, 4.0, and 5.1. The buffer solutions were prepared from citric acid and disodium hydrogen phosphate. The potential response to changes in nitrate concentration with respect to changes in pH is shown in Figure 22. The response of the membrane to nitrate is greater at lower pH values. Because of this, the majority of the remaining response studies were made using solutions buffered at pH 2.1 with citric acid.

Potential Response to Anions

To study the membrane potential response to changes in anion content and concentration, 1 M solutions of sodium thiocyanate, sodium nitrate, sodium bromide, potassium chloride, sodium perchlorate, sodium dihydrogen phosphate and potassium ferricyanide and a 0.1 M solution of potassium

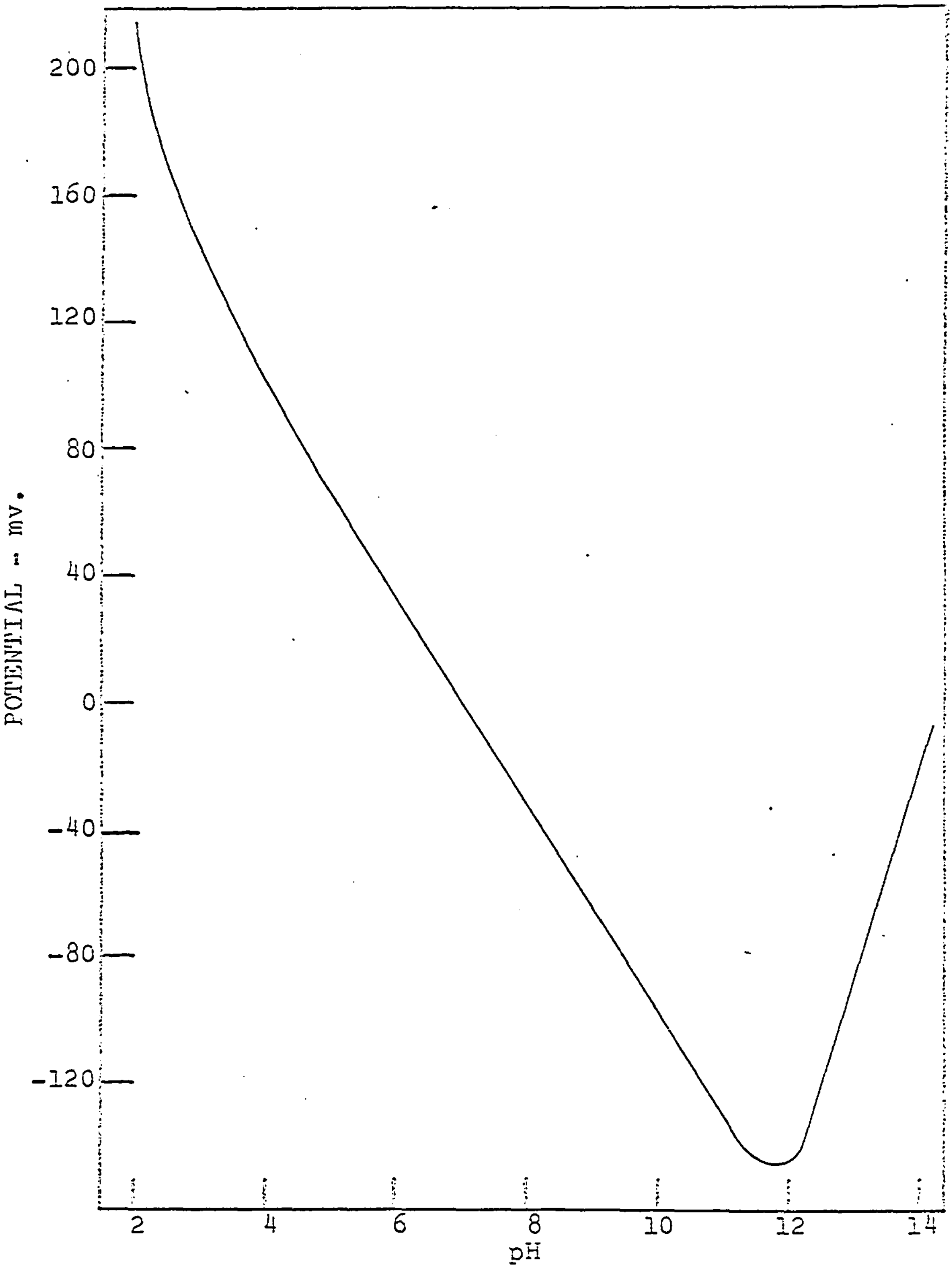


Figure 21. The potential of the phenol-formaldehyde-nickel nitrate membrane as a function of pH

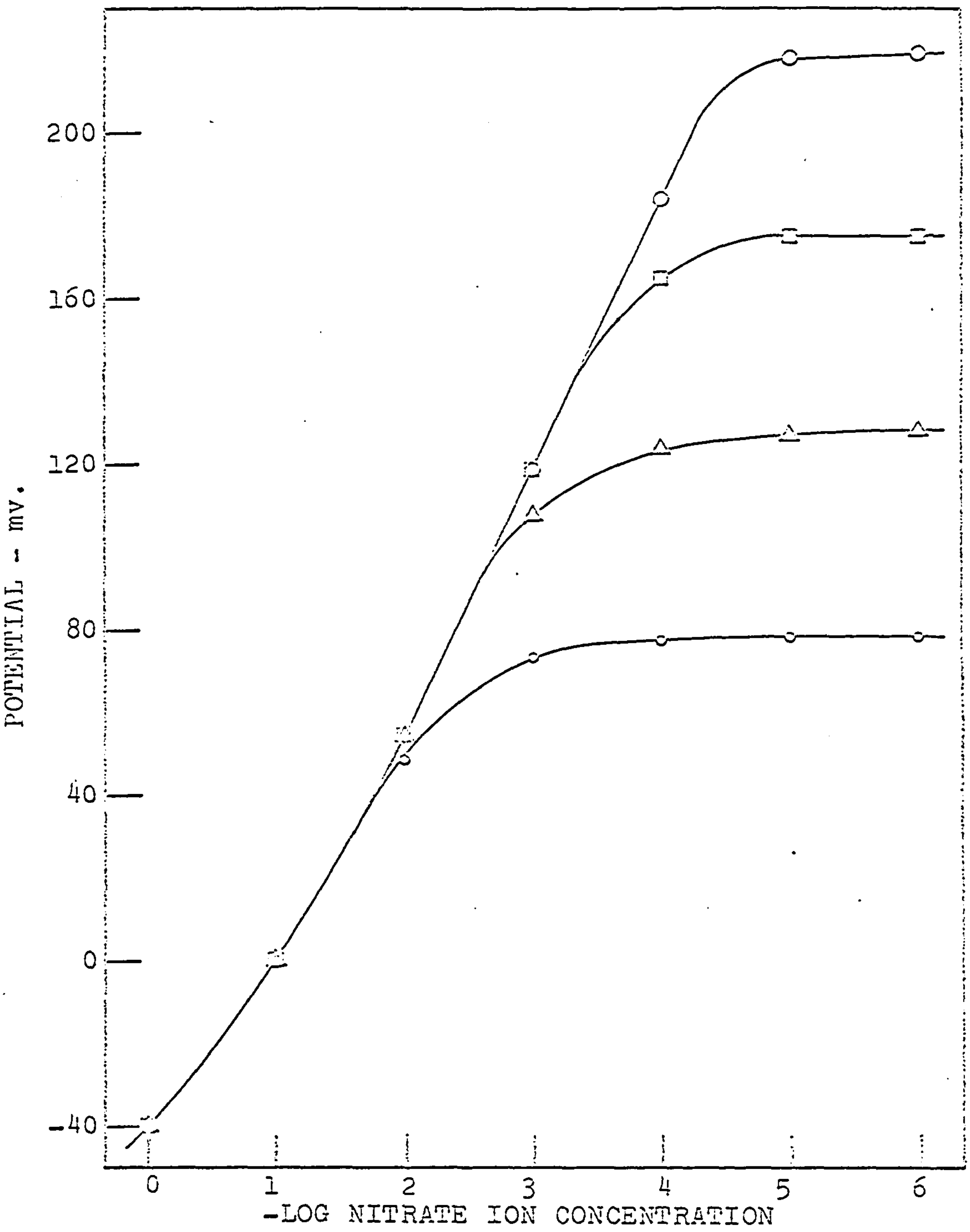


Figure 22. The effect of pH on the response of the phenol-formaldehyde-nickel nitrate membrane to nitrate

○ pH 2.1 △ pH 4.0

□ pH 3.0 ∘ pH 5.1

sulfate were prepared and serially diluted to 10^{-5} M. The response of the membrane to each member of each series was then determined, Figure 23.

The membrane responded to the monovalent anions but not to bivalent and trivalent anions. The activity coefficients listed in Table 1 indicate that the difference in potential response to the various monovalent anions cannot be explained by the difference in activities. For example, the activities of sodium perchlorate and sodium nitrate are essentially the same for concentrations 1.0 M and less. However, the membrane response to 1, 10^{-1}, 10^{-2}, and 10^{-3} M sodium nitrate differs from the response to 1, 10^{-1}, 10^{-2}, and 10^{-3} M sodium perchlorate by 62, 65, 60, and 51 mv. respectively. The slope of the linear portions of the perchlorate and nitrate response curves is 60 and 52 mv., respectively, per ten-fold change in concentration. If the response to the various anions was

Table 1. Activity coefficients of strong electrolytes[6]

Electrolyte	1.0 M	0.1 M	0.01 M	0.001 M
KCl	0.606	0.769	0.901	0.965
NaBr	0.686	0.800	0.914	0.966
$NaClO_4$	0.58	0.77	0.90	0.97
$NaNO_3$	0.55	0.77	0.90	0.966

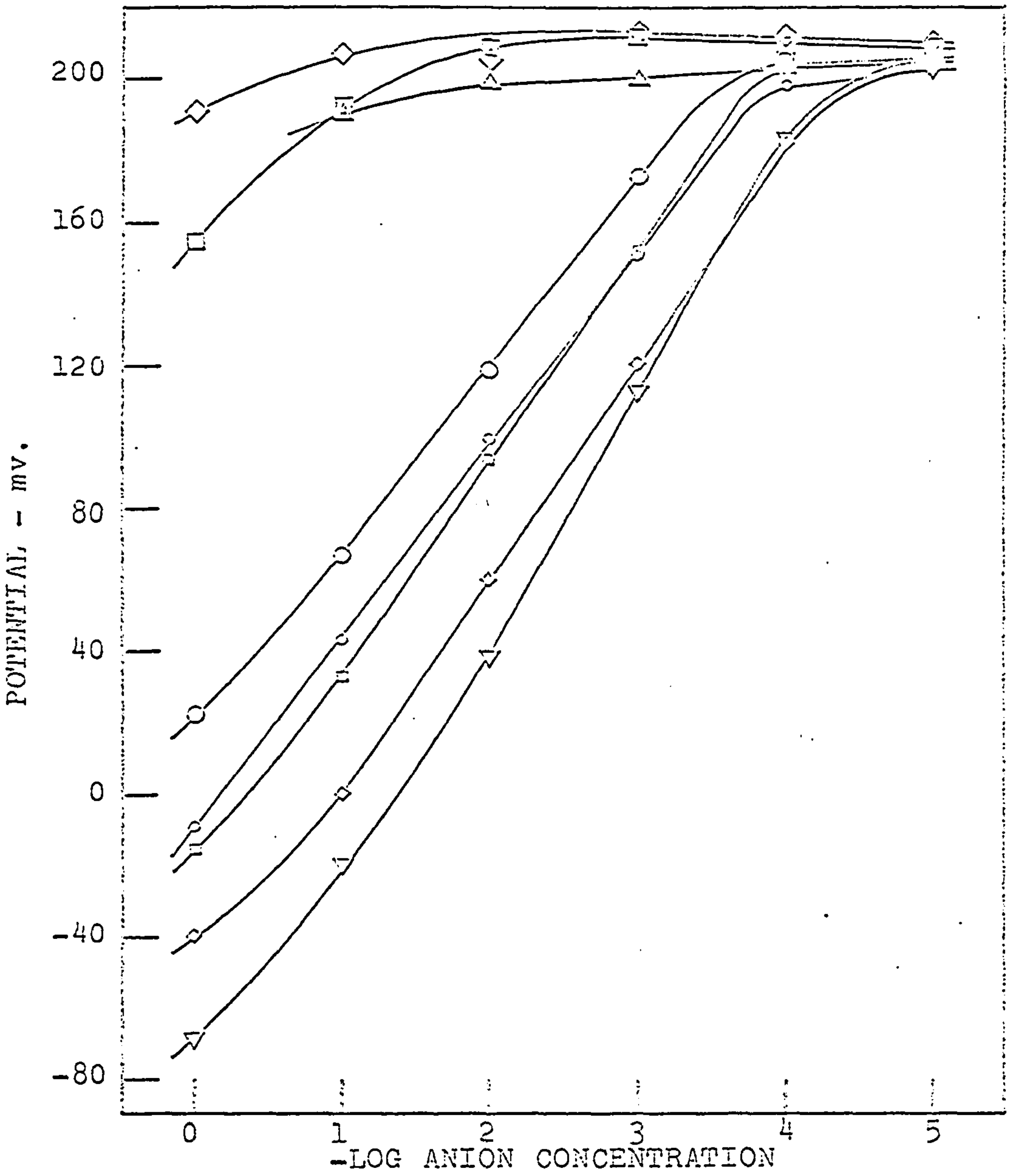


Figure 23. The response of the phenol-formaldehyde-nickel nitrate membrane to various anions

o potassium chloride	▫ sodium bromide
△ potassium sulfate	▽ sodium thiocyanate
○ sodium perchlorate	◇ potassium ferricyanide
□ sodium dihydrogen phosphate	⋄ sodium nitrate

dependent only on the activity of the anion, the response to a solution 1.0 M in sodium perchlorate would be identical to the response to a solution 1.0 M in sodium nitrate and the slopes of the perchlorate and nitrate response curves would also be equal. Thus, the difference in response is not due to a difference in activity. This difference in response is probably caused by a difference in the size of the anions, Table 2, which determines the interaction of the ion with the charged sites on the membrane.

Table 2. Anion radii[4]

Anion	Radius (Å)
Br^-	1.95
Cl^-	1.81
ClO_4^-	2.5*
NO_3^-	1.5*

*Estimated from covalent radii.

The potential response to changes in nitrate concentration in the presence of varying amounts of other anions was also studied. The curves for the potential response to changes in nitrate concentration in the presence of thiocyanate, bromide, chloride, perchlorate, sulfate, phosphate and ferricyanide are shown in Figures 24 through 30, respec-

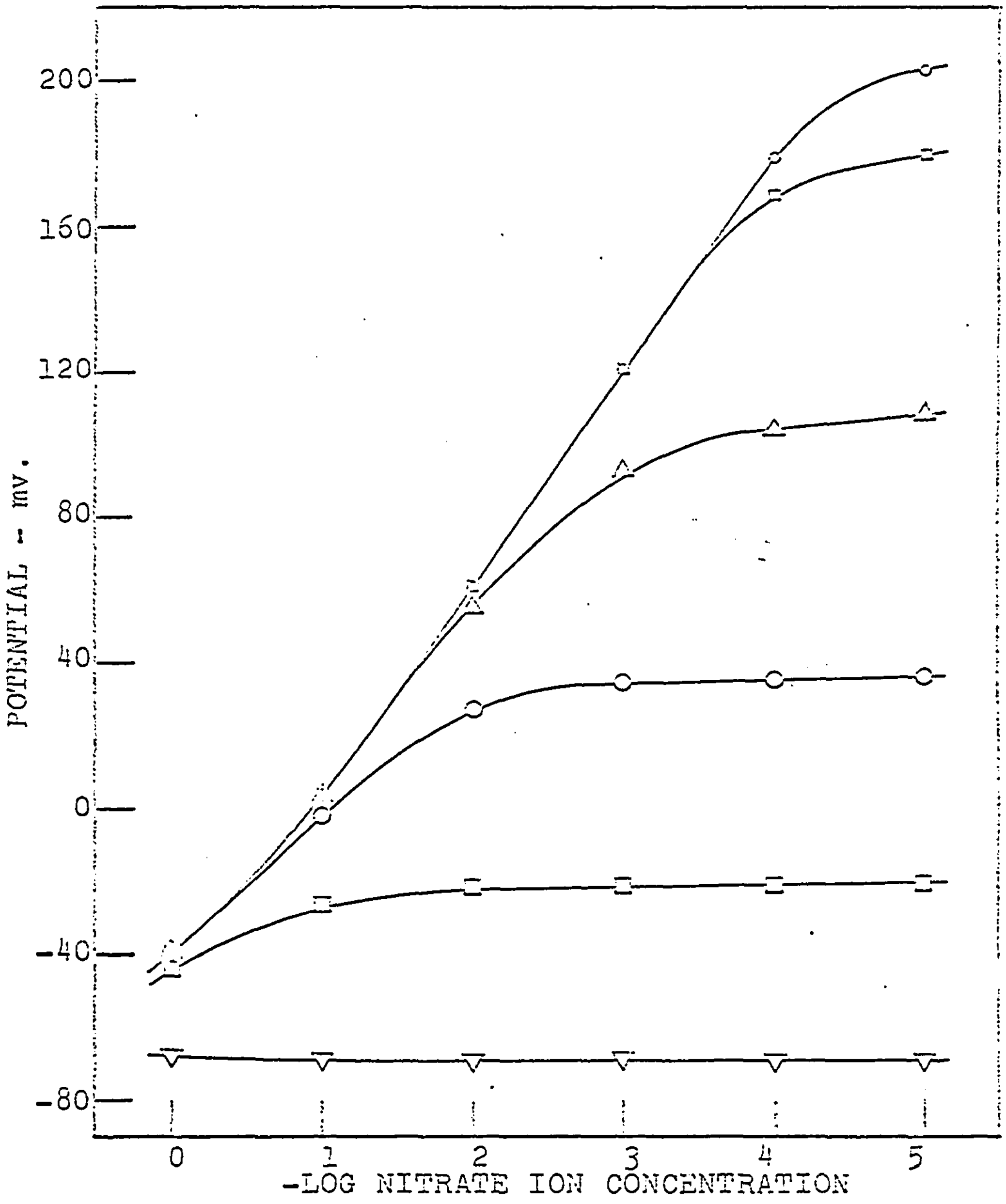


Figure 24. The potential response of a phenol-formaldehyde-nickel nitrate resin to nitrate in the presence of thiocyanate

○	10^{-5} M sodium thiocyanate	◯	10^{-2} M sodium thiocyanate
▫	10^{-4} M sodium thiocyanate	□	10^{-1} M sodium thiocyanate
△	10^{-3} M sodium thiocyanate	▽	10^{0} M sodium thiocyanate

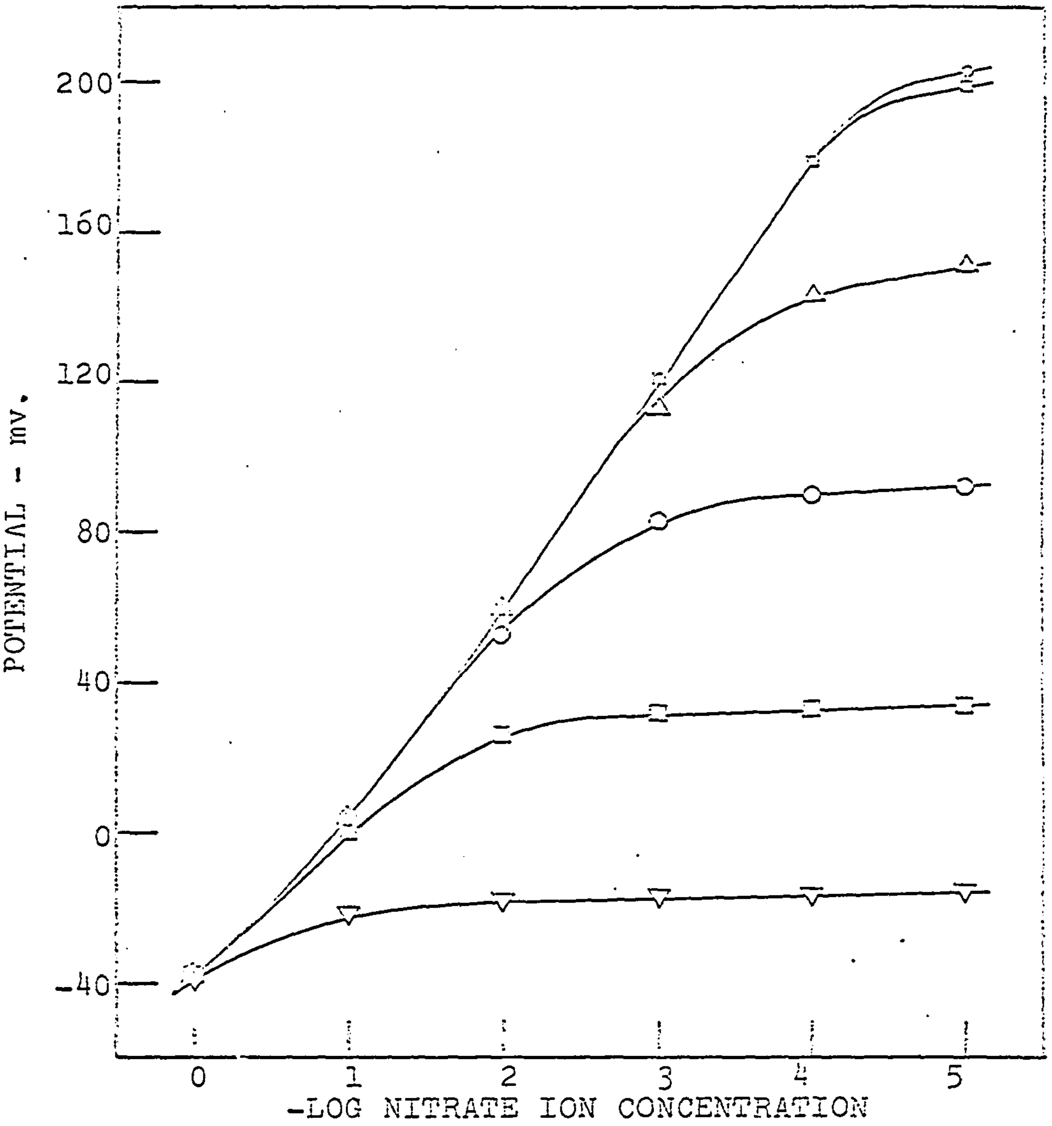


Figure 25. The potential response of a phenol-formaldehyde-nickel nitrate resin to nitrate in the presence of bromide

∘ 10^{-5} M potassium bromide

▫ 10^{-4} M potassium bromide

△ 10^{-3} M potassium bromide

○ 10^{-2} M potassium bromide

□ 10^{-1} M potassium bromide

▽ 10^{0} M potassium bromide

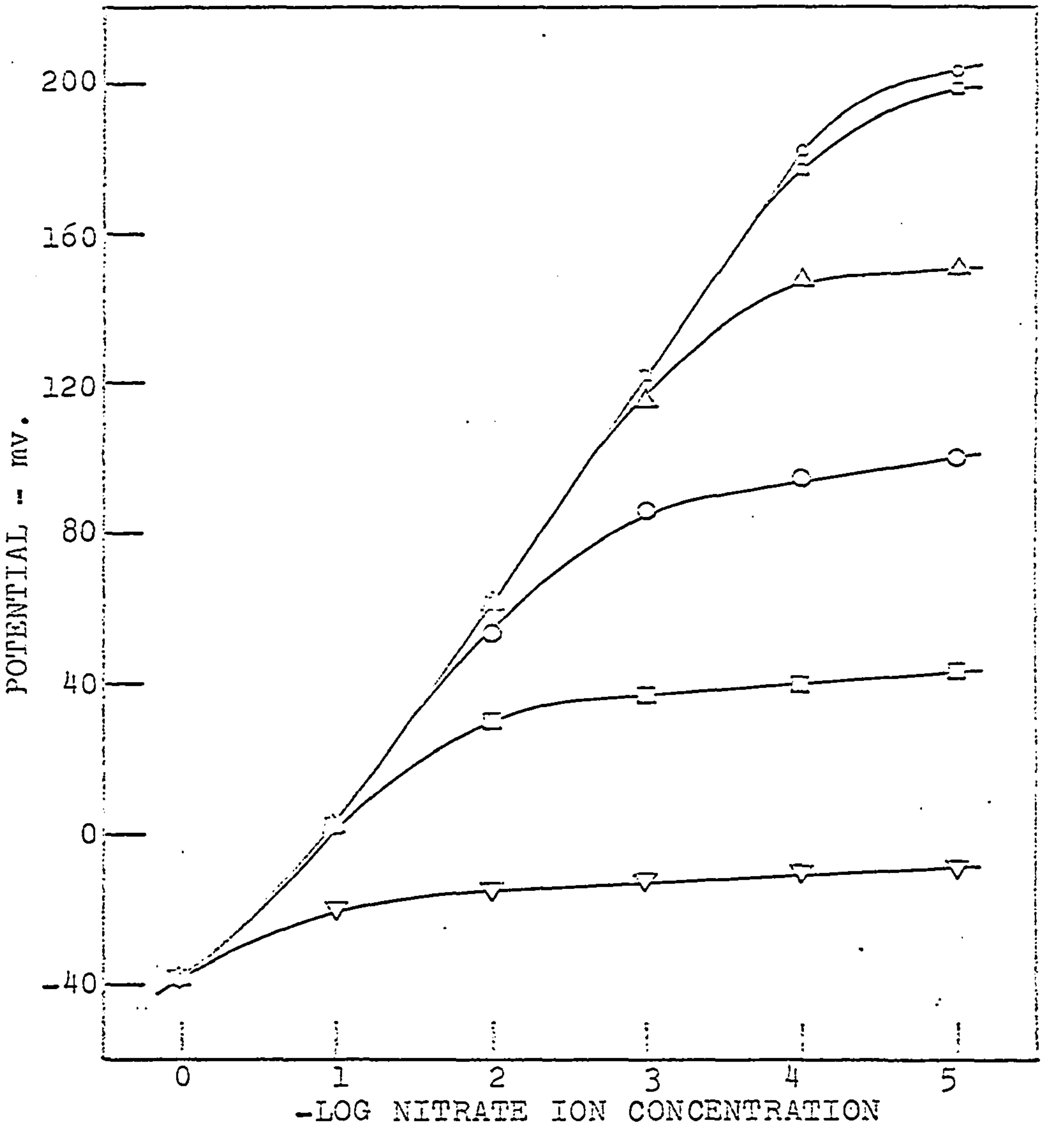


Figure 26. The potential response of a phenol-formaldehyde-nickel nitrate resin to nitrate in the presence of chloride

∘	10^{-5} M potassium chloride	○	10^{-2} M potassium chloride
▫	10^{-4} M potassium chloride	□	10^{-1} M potassium chloride
△	10^{-3} M potassium chloride	▽	10^{0} M potassium chloride

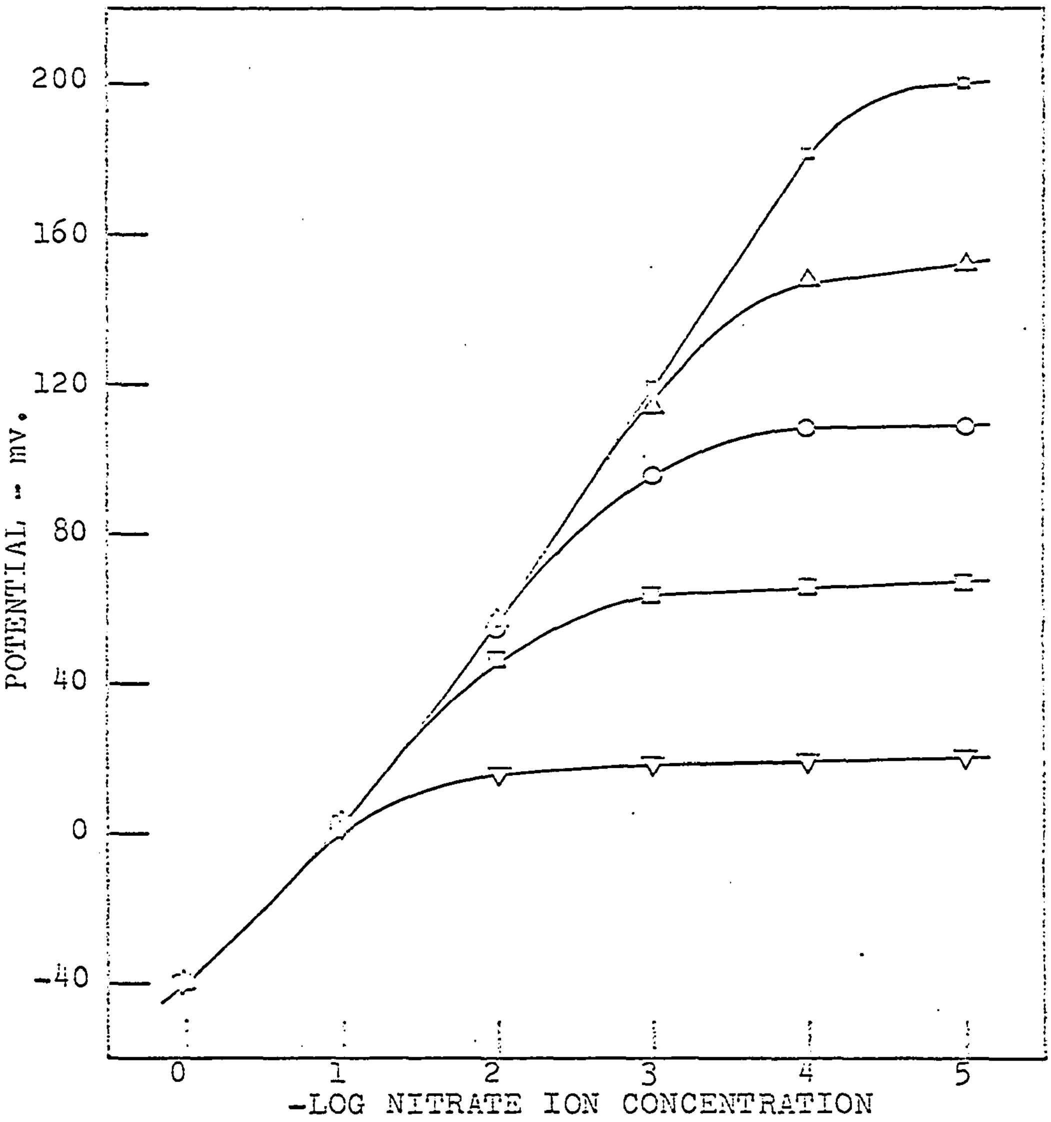


Figure 27. The potential response of a phenol-formaldehyde-nickel nitrate resin to nitrate in the presence of perchlorate

∘ 10^{-5} M sodium perchlorate	○ 10^{-2} M sodium perchlorate
▫ 10^{-4} M sodium perchlorate	□ 10^{-1} M sodium perchlorate
△ 10^{-3} M sodium perchlorate	▽ 10^{0} M sodium perchlorate

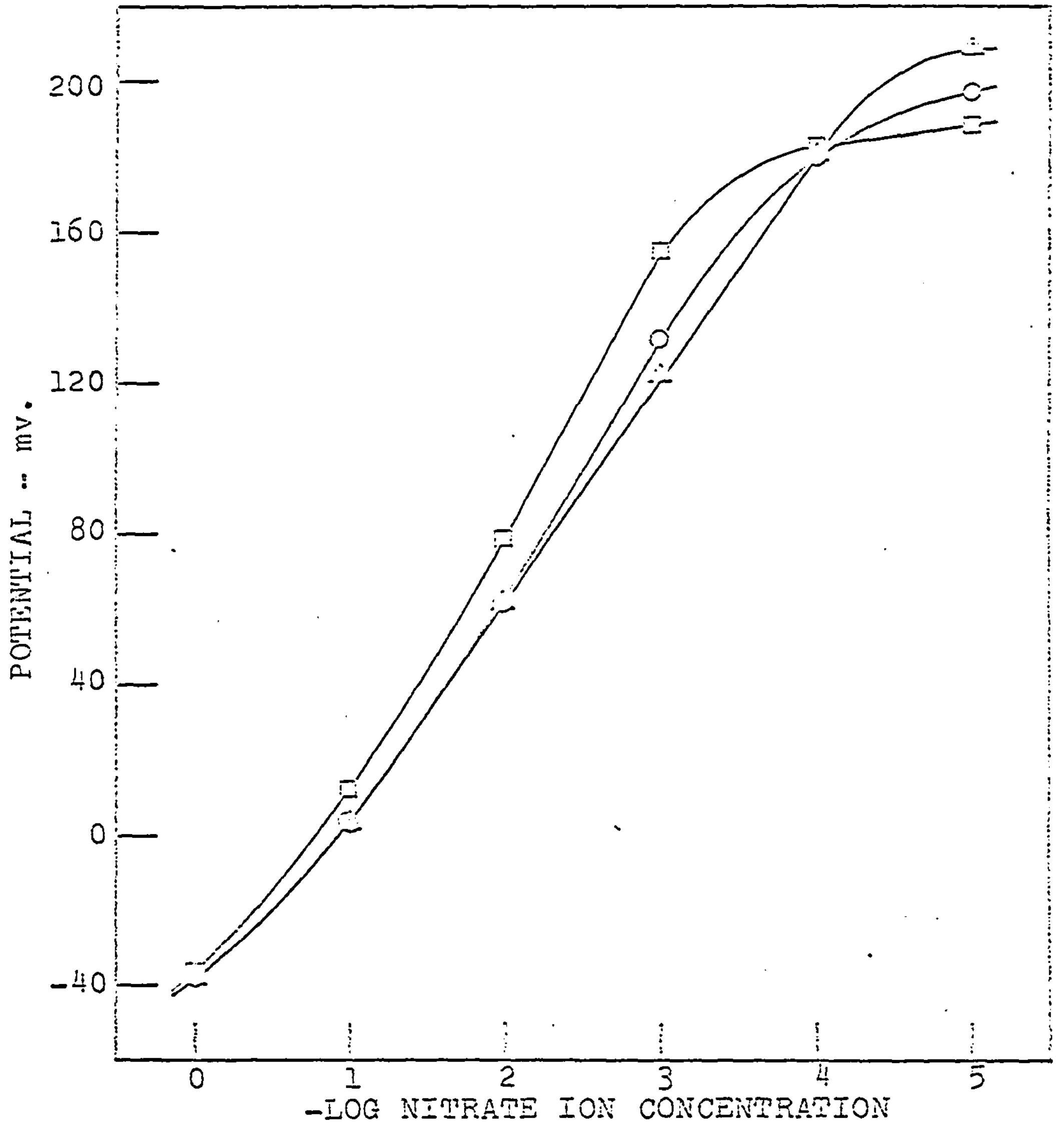


Figure 28. The potential response of a phenol-formaldehyde-nickel nitrate resin to nitrate in the presence of sulfate

∘ 10^{-5} M potassium sulfate

▫ 10^{-4} M potassium sulfate

△ 10^{-3} M potassium sulfate

○ 10^{-2} M potassium sulfate

□ 10^{-1} M potassium sulfate

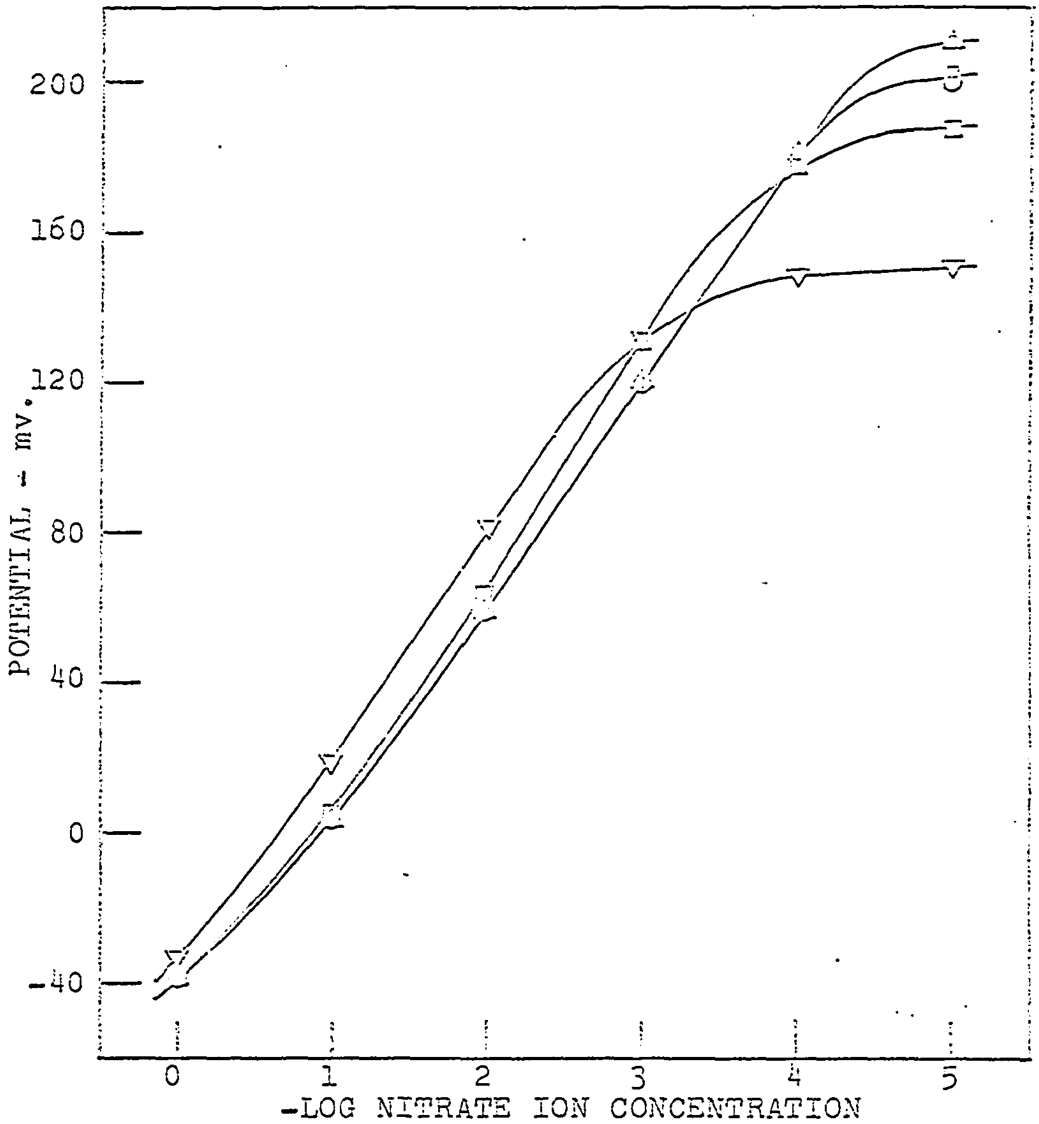


Figure 29. The potential response of a phenol-formaldehyde-nickel nitrate resin to nitrate in the presence of phosphate

∘ 10^{-5} M sodium dihydrogen phosphate

○ 10^{-2} M sodium dihydrogen phosphate

▫ 10^{-4} M sodium dihydrogen phosphate

□ 10^{-1} M sodium dihydrogen phosphate

△ 10^{-3} M sodium dihydrogen phosphate

▽ 10^{0} M sodium dihydrogen phosphate

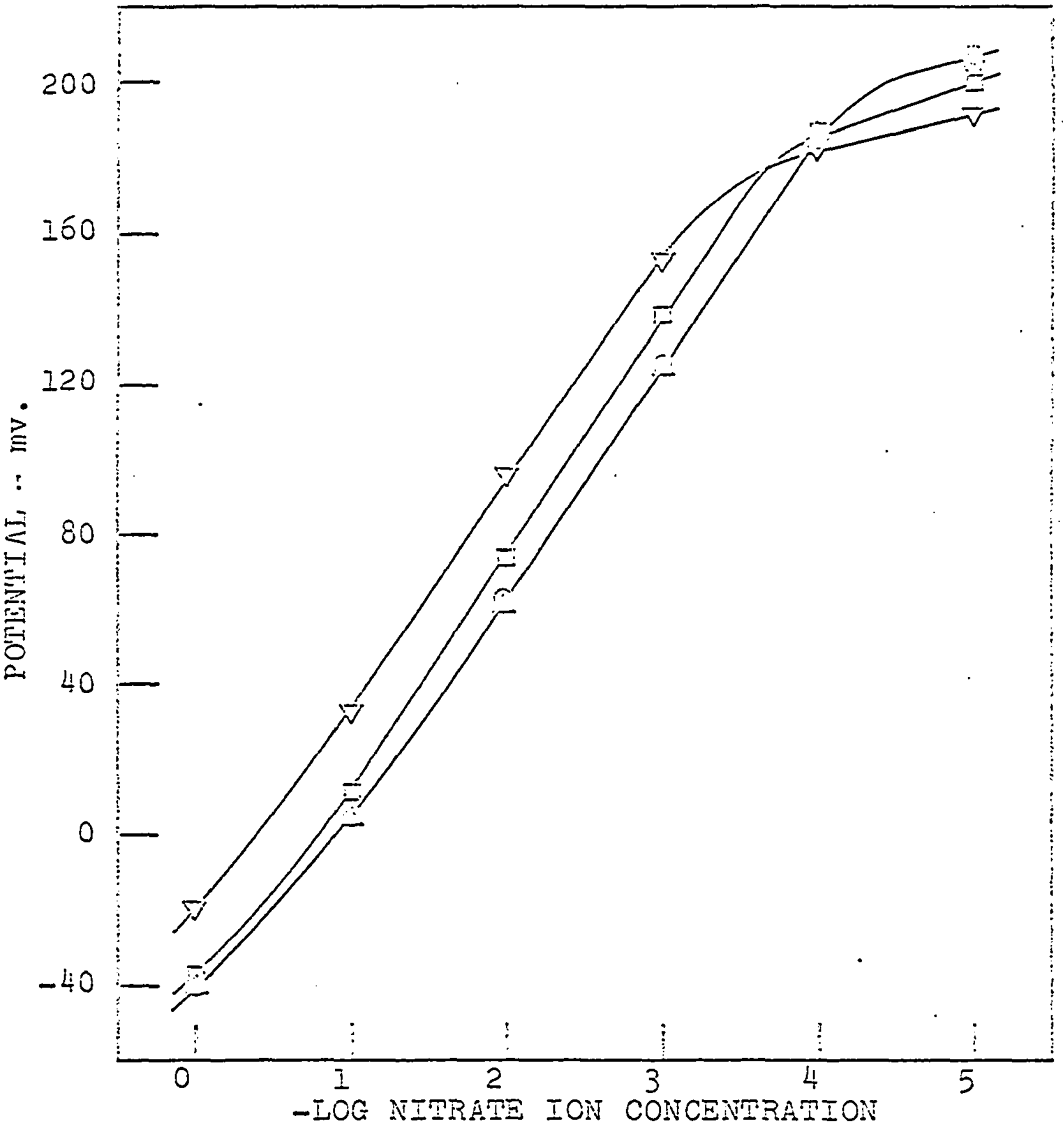


Figure 30. The potential response of a phenol-formaldehyde-nickel nitrate resin to nitrate in the presence of ferricyanide

∘ 10^{-5} M potassium ferricyanide	○ 10^{-2} M potassium ferricyanide
▫ 10^{-4} M potassium ferricyanide	□ 10^{-1} M potassium ferricyanide
△ 10^{-3} M potassium ferricyanide	▽ 10^{0} M potassium ferricyanide

tively. The solutions were prepared by serial dilution of 1 M sodium nitrate solutions with solutions of the desired anion content buffered at pH 2.1. It can be seen that the presence of other univalent anions interferes with the response to nitrate and that the presence of divalent or trivalent anions has no effect on the response to nitrate except in concentrations of 10^{-2} or greater.

Stability of the Potential Response

Because the phenol-formaldehyde-nickel nitrate membrane responds to chloride and the commercial saturated calomel reference electrodes used were so constructed that a slow drain of saturated potassium chloride solution from the electrode occurred, reference electrodes containing sulfate were used. The electrodes were prepared by pouring enough mercury into a glass tube to cover the end of a platinum wire fused through the bottom of the tube, spreading a paste consisting of mercury, mercury(I) sulfate, and a saturated solution of potassium sulfate, on top of the mercury in the tube, and then filling the remainder of the tube with a solution of saturated potassium sulfate. A lead from the electrometer was connected to the platinum wire at the bottom of the tube and a saturated potassium sulfate-agar bridge was used to provide electrical contact between the saturated potassium sulfate solution of the reference electrode and the solution in contact with the membrane. The two reference electrodes used differed less than 1 mv. in potential.

To determine the stability of the potential response of the membrane, a test solution was placed in one arm of the membrane cell and a 0.1 M potassium nitrate reference solution was placed in the other arm, a reference electrode was then dipped into each solution and the resulting membrane potential was determined as a function of time.

As shown in Figure 31, the potential response was stable for at least 10 hours and the potential for the cell 10^{-1} M potassium nitrate//10^{-6} M potassium nitrate remained constant even after a period of 24 hours. It was also found that stirring of the test solution had no effect on the potential response of the system.

The stability of the potential response with the same reference solution used over a long time period was also determined. A 0.1 M potassium nitrate reference solution was used. The response to a series of standard potassium nitrate solutions was determined, the sample arm of the membrane cell was then filled with deionized distilled water, and the reference solution was left in the reference arm. Both arms of the cell were stoppered and the cell was allowed to stand for 4 months. The response to the same series of standard potassium nitrate solutions was then determined without changing or mixing the reference solution. The potentials measured were identical with those measured earlier.

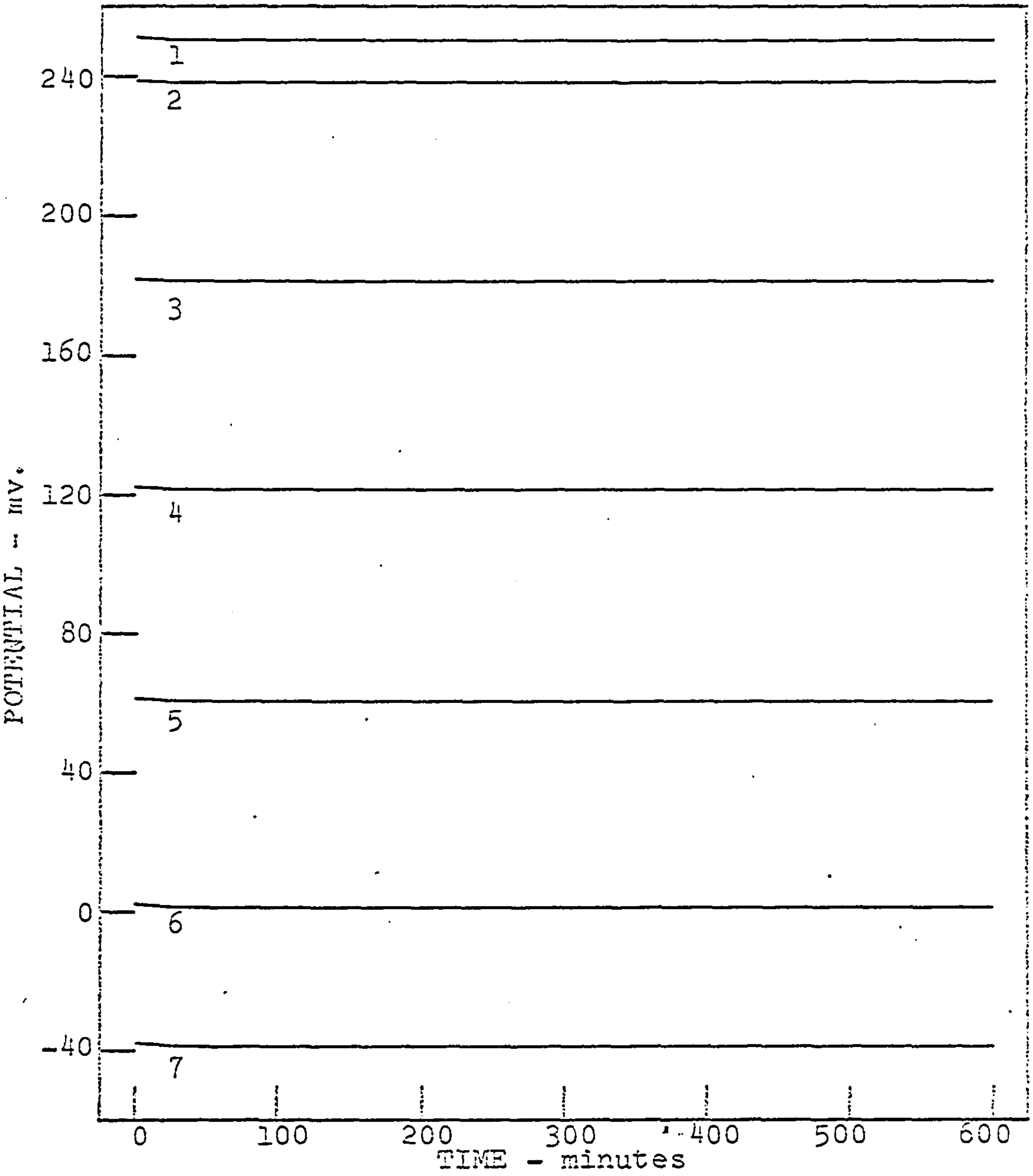


Figure 31. Stability of the potential response of a phenol-formaldehyde-nickel nitrate membrane to nitrate

1. 10^{-6} M potassium nitrate
2. 10^{-5} M potassium nitrate
3. 10^{-4} M potassium nitrate
4. 10^{-3} M potassium nitrate
5. 10^{-2} M potassium nitrate
6. 10^{-1} M potassium nitrate
7. 10^{0} M potassium nitrate

Elemental Analysis

Two membranes were prepared from the same bakelite A preparation, one with and one without the addition of nickel nitrate, the bakelite A preparation used having been made from a mixture of phenol, formaldehyde, and ammonia. By weight the nickel nitrate hexahydrate was 20 per cent of the mixture. No ethylene glycol was added. Portions of the membranes were dried in an oven at 110°C. for 24 hours and then sent to Huffman Laboratories, Inc. for elemental analysis. The results of the analyses are tabulated in Tables 3 and 4.

Table 3. Elemental analysis of the phenol-formaldehyde-ammonia resin

Element	Per cent	Atom ratio	Atom ratio x 7.46
C	75.58	6.30	47.0
H	5.93	5.88	43.8
N	1.87	0.134	1.00
O*	16.62	1.04	7.76

*By difference.

The analyses indicate that about one amine group is present for every seven phenol groups within the membrane, that one nickel atom is present for every two and four-tenths

Table 4. Elemental analysis of the phenol-formaldehyde-ammonia-nickel nitrate resin

Element	Per cent	Atom ratio	Atom ratio x 20.6	(Atom ratio x 20.6) $-Ni(NO_3)_3$	((Atom ratio x 20.6) $-Ni(NO_3)_3$) ÷ 2.42
C	66.90	5.57	115	115	47.5
H	5.14	5.11	105	105	43.4
N	3.69	0.263	5.42	2.42	1.00
O*	21.43	1.34	27.6	18.6	7.69
Ni	2.84	0.0484	1.00	0.00	

*By difference.

amine groups and that three nitrate groups are present for every nickel atom.

In conjunction with the study of the effect of the initial nickel nitrate content on the potential response of phenol-formaldehyde-nickel nitrate membranes described previously, the amount of nickel nitrate soaked from the membranes during the soaking step was determined and from the initial amount of nickel nitrate taken, the amount of nickel and nitrate remaining in the membrane was estimated. Membranes ranging in concentration from 10 to 25 per cent by weight nickel nitrate hexahydrate were prepared in the usual manner and the solutions in which the membranes were conditioned, or soaked, were recovered, diluted to 100 ml.

in a volumetric flask, and analyzed for nickel.

The nickel content of these soaking solutions was determined by adding an excess of ethylenediaminetetraacetic acid (EDTA) to a 20-ml. aliquot of each solution, buffered at pH 7 with ammonium acetate, and back titrating the excess EDTA with a standard copper(II) solution to a calcein end-point. The result of this study is shown in Table 5 and in Figure 32. The amount of nickel retained in the membranes proved fairly constant for initial amounts of 10, 13, and 16 per cent nickel nitrate hexahydrate. The amount retained decreased sharply as the initial amount of nickel nitrate hexahydrate increased from 16 to 25 per cent.

Table 5. The amount of nickel remaining in phenol-formaldehyde-nickel nitrate membranes

Per cent $Ni(NO_3)_2 \cdot 6H_2O$ taken	Mmoles nickel added	Mmoles nickel soaked out	Mmoles nickel remaining per 1.8 g. resin
10	0.786	0.009	0.775
13	1.057	0.276	0.781
16	1.347	0.564	0.783
19	1.660	1.016	0.644
22	1.997	1.412	0.585
25	2.358	1.796	0.562

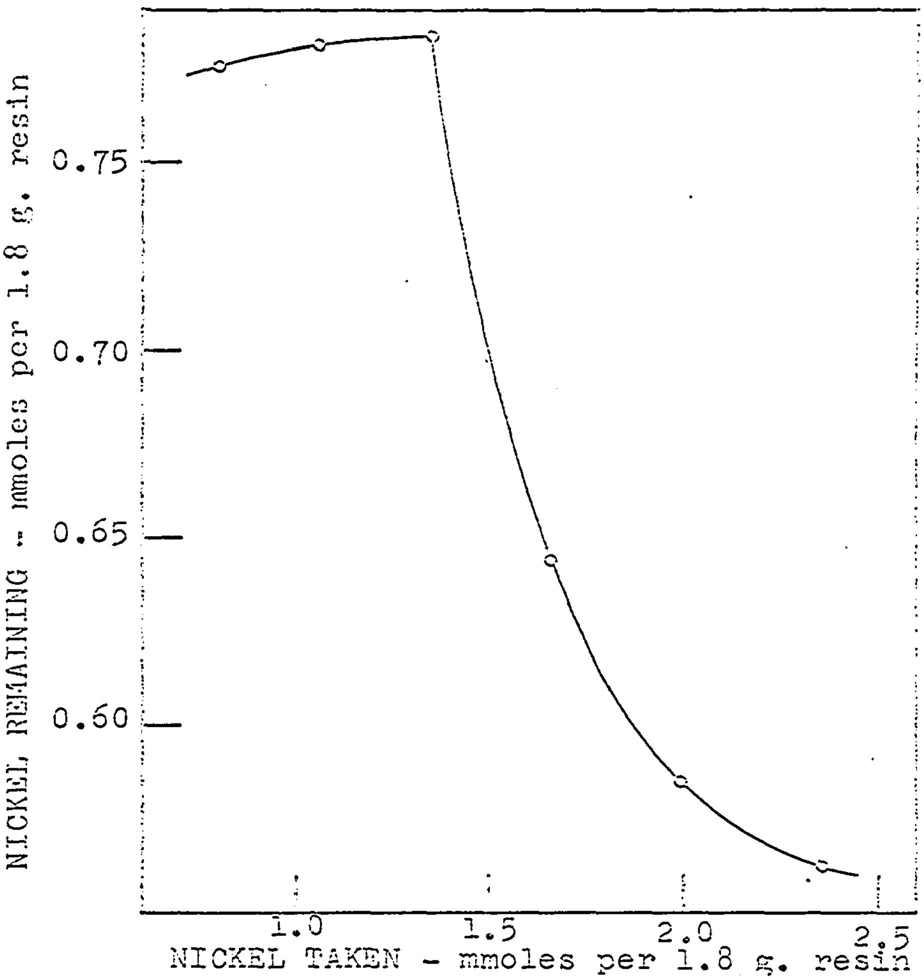


Figure 32. The amount of nickel remaining in the phenol-formaldehyde-nickel nitrate membrane as a function of the initial amount of nickel nitrate added to the polymerization mixture

The amount of nitrate soaked out of the membranes was determined using a phenol-formaldehyde-nickel nitrate membrane. The membrane potential was calibrated using sodium nitrate solutions, buffered at pH 2.1 with citric acid and prepared by serial dilution of 1 M sodium nitrate in powers of ten to 10^{-5} M. The soaking solutions were buffered at pH 2.1 with citric acid, the membrane potential of each of the solutions was determined, and the nitrate concentration calculated using the calibration curve. The result of this study is shown in Table 6 and Figure 33. The amount of nitrate remaining in the membranes prepared with initial amounts of 10, 19, 22, and 25 per cent nickel nitrate

Table 6. The amount of nitrate remaining in phenol-formaldehyde-nickel nitrate membranes

Per cent $Ni(NO_3)_2 \cdot 6H_2O$ taken	Mmoles nitrate added	Mmoles nitrate soaked out	Mmoles nitrate remaining per 1.8 g. resin	Ratio of nitrate to nickel remaining
10	1.57	0.0692	1.50	1.94
13	2.11	0.158	1.96	2.51
16	2.70	1.00	1.70	2.18
19	3.32	2.04	1.28	1.99
22	4.00	2.82	1.18	2.02
25	4.72	3.55	1.17	2.08

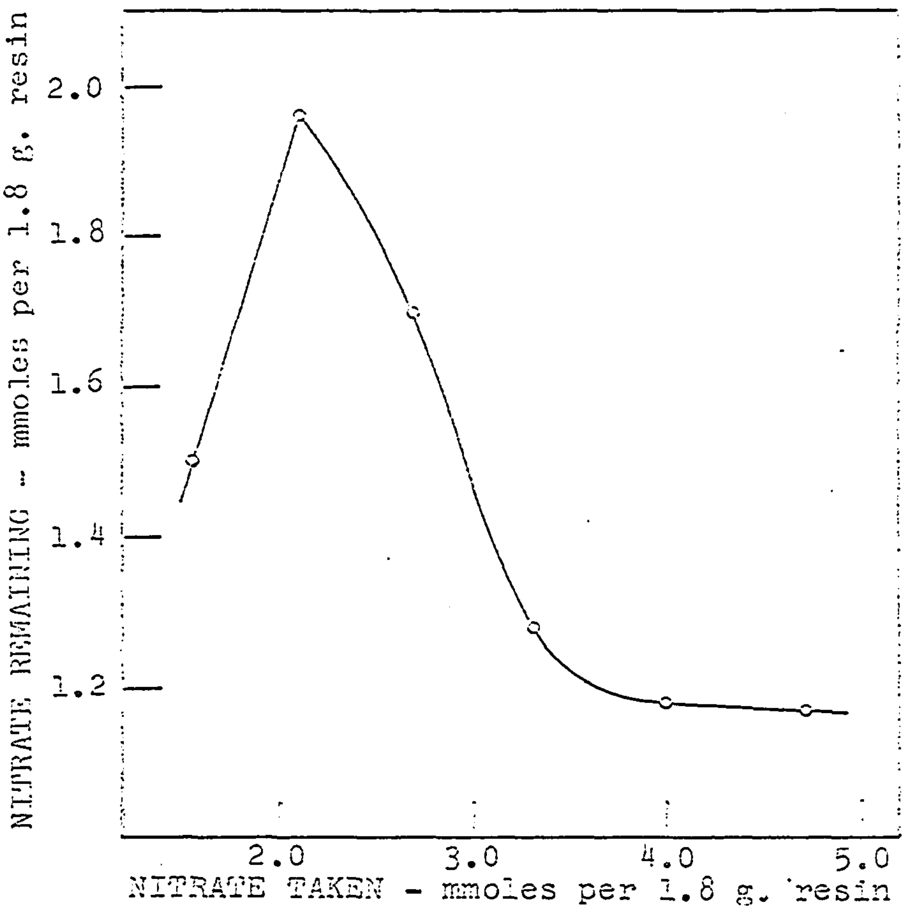


Figure 33. The amount of nitrate remaining in the phenol-formaldehyde-nickel nitrate membrane as a function of the initial amount of nitrate taken

hexahydrate was in good agreement with the amount of nickel remaining in the membranes in that there are about two nitrate radicals for every atom of nickel remaining. The amount of nitrate remaining in the membranes prepared with initial amounts of 13 and 16 per cent nickel nitrate hexahydrate was found to be greater than two nitrate radicals per atom of nickel.

Exchange Properties

In the current theory used to explain the potential developed across an ion-responsive membrane, it is assumed that ion exchange between membrane and solution occurs at each membrane-solution interface. An attempt was made to show directly that such exchange takes place between the phenol-formaldehyde-nickel nitrate resin and nitrate-bearing solutions.

A weighed amount, 35 g., of the resin was ground to 60 mesh or smaller in a Wylie mill. The ground resin was then washed with deionized distilled water, soaked in water for 1 week, thoroughly washed with water and then poured into a glass tube. The resulting resin bed was a column 9 mm. in diameter and 30 cm. long. The resin column was washed with 500 ml. of water and 50.00 ml. of 10^{-2} M nickel nitrate was then passed through the column. The eluate was collected in a 100-ml. volumetric flask, the column was washed with water and the wash solution was also collected in the volumetric flask until a volume of 100 ml. was obtained.

In addition, a batch exchange process was attempted. The resin was thoroughly washed, filtered and placed in a 125-ml. conical flask with 75 ml. of 10^{-2} M nickel nitrate. The mixture was stirred for 48 hours and then filtered.

The nickel in the 10^{-2} M nickel nitrate solution, the solution passed through the resin column, and the filtrate from the batch exchange process was determined by titration with EDTA and the nitrate content of each of the solutions was determined using a calibrated nitrate-responsive membrane. There was no change in either the nickel or the nitrate content of the solution passed through the resin column or the solution equilibrated with the resin for 48 hours.

It appears that the phenol-formaldehyde-nickel nitrate resin does not behave as an ion exchange resin with either nickel or nitrate.

Infrared Spectrum

The infrared spectra of both the phenol-formaldehyde resin and the phenol-formaldehyde-nickel nitrate resin were obtained using a Beckman IR 8 infrared spectrophotometer. Absorption bands were present in the spectrum of the nickel-free resin, as expected, for aromatic rings, methylene groups, and phenolic groups. In addition, weak absorption bands were present at 2330 and 2060 cm.$^{-1}$ and a strong band at 1645 cm.$^{-1}$ indicating the presence of a saturated amine.

The absorption bands at 2330, 2060, and 1645 cm.$^{-1}$ present in the nickel-free resin were barely detectable in the nickel-bearing resin and there was increased absorption in the range of 1350 to 1410 cm.$^{-1}$ which is the nitrate absorption wavelength.

Thus, the infrared spectra indicate that saturated amine groups are present in the nickel-free resin and that they are altered in some manner by the addition of the nickel nitrate. The infrared spectrum of the nickel-bearing resin indicates also the presence of nitrates.

Resistance

The electrical resistance of the phenol-formaldehyde membrane and the phenol-formaldehyde-nickel nitrate membrane were determined. Each membrane was mounted as shown in Figure 1 and a 0.10 M sodium sulfate solution was poured into each arm of the cell. A saturated calomel reference electrode was dipped into each solution and the membrane potential determined. The potential was less than 1 mv. for all membranes tested, an amount too small to interfere with the resistance measurement. The saturated calomel reference electrodes were then replaced with platinum electrodes and the resistance of the membrane was determined using a Keithley Model 601 electrometer.

The resistance of a phenol-formaldehyde membrane and a phenol-formaldehyde-nickel nitrate membrane which had been dried at 110°C. for 48 hours were 5.7×10^{13} and 1.7×10^{13} ohms/cm.^{2}, respectively, and the resistance of a phenol-formaldehyde membrane and a phenol-formaldehyde-nickel nitrate membrane which had been soaked in water at a temperature of 65°C. for 12 hours were 3.3×10^{10} and 3.3×10^4 ohms/cm.^{2}, respectively.

As expected, the resistance of the membranes decreased after the membranes had been soaked in water. There was a thousand-fold decrease in the resistance of the phenol-formaldehyde membrane and a billion-fold decrease in the resistance of the phenol-formaldehyde-nickel nitrate membrane after the soaking operation. Thus, the incorporation of nickel nitrate into the phenol-formaldehyde polymer caused a million-fold decrease in the resistance of the soaked membrane.

Crystallinity

X-ray powder diffraction patterns of the phenol-formaldehyde and phenol-formaldehyde-nickel nitrate resins were obtained. No bands were detected in the pattern of the phenol-formaldehyde resin. One band only was present in the pattern of the phenol-formaldehyde-nickel nitrate resin; this corresponded to a distance of 1.887 Å. Evidently the phenol-formaldehyde-nickel nitrate resin is crystalline in character.

Examination in the polarizing microscope showed that the nickel-free membranes were non-birefringent, Figure 34, except for strain birefringence occurring along the edges, along cracks in the membranes, and within membranes which had been rigorously flexed. The nickel nitrate membranes were birefringent.

A series of membranes prepared using from 10 to 25 per cent nickel nitrate in one per cent increments was prepared and the potential response and birefringent properties of each were determined. The response of the 10 through 13 per cent membranes was poor. The response improved with increasing amounts of nickel nitrate. The membranes were birefringent with imperfect rows of non-birefringent dots or crosses apparent when each of the four membranes were viewed through the polarizing microscope. An example is shown in Figure 35. The non-birefringent dots decreased in number in the resins prepared with increasing amounts of nickel nitrate and could not be detected as an ordered pattern in the 14 per cent membrane. It appears that the non-birefringent crosses and dots are caused by imperfections in the membrane structure and that the structural defects cause a decrease in the response of the membranes.

The response of the 14 to 23 per cent membranes was good and the membranes were all uniformly birefringent when viewed through a polarizing microscope, Figure 36. It appears that the structural defects are at a minimum in this

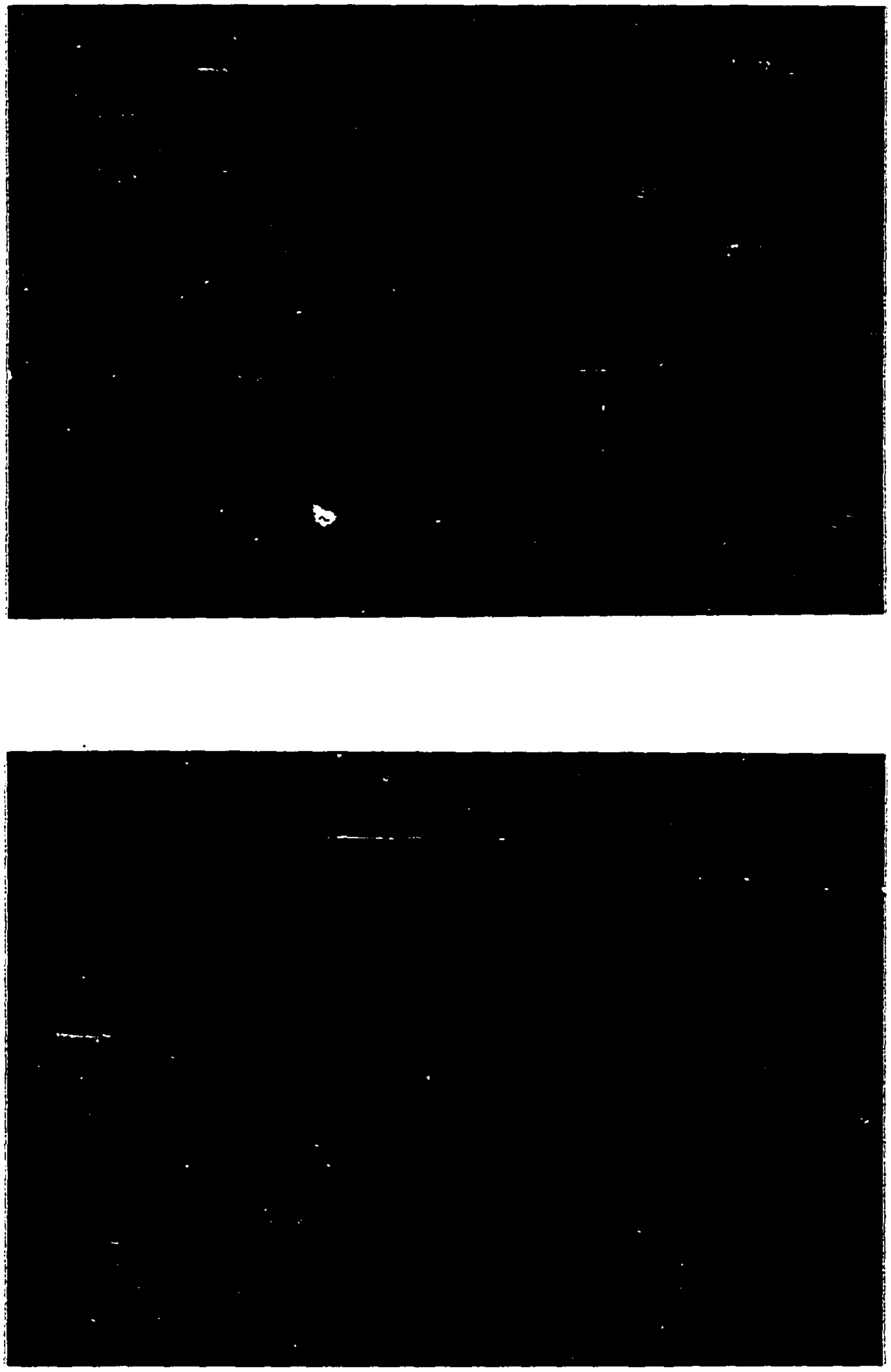
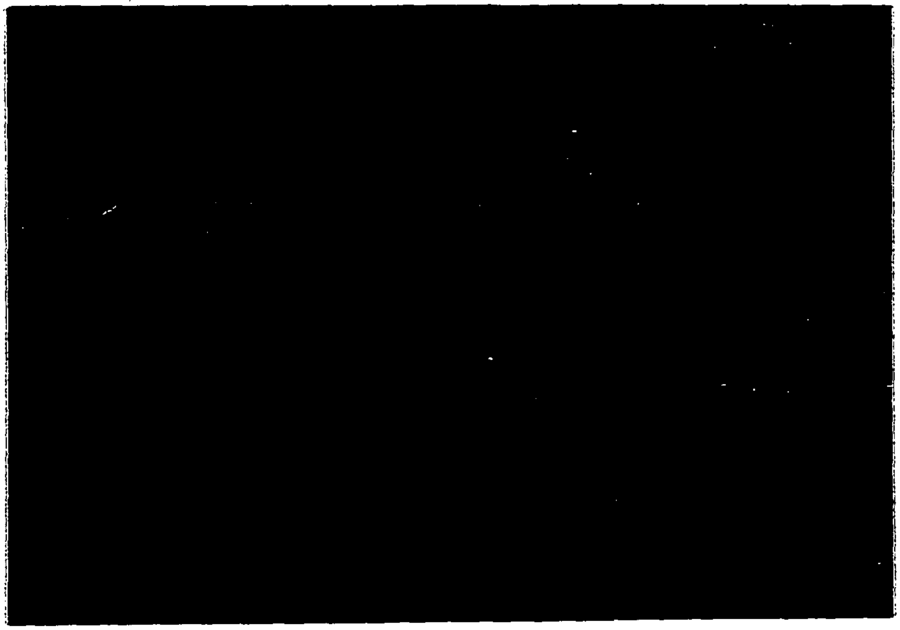


Figure 34. Photographs of a phenol-formaldehyde membrane as viewed through a polarizing microscope with the stage rotated 90° between photographs

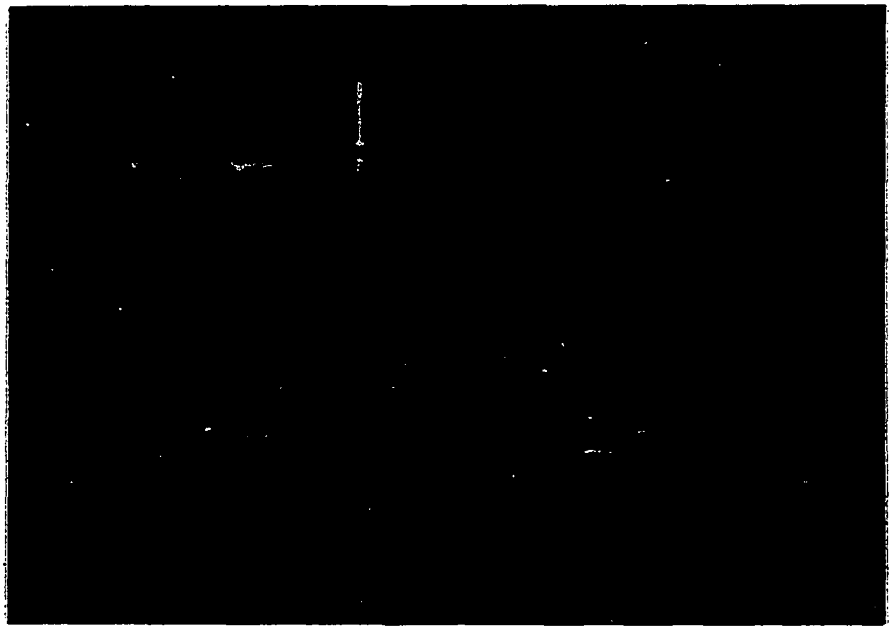
Birefringent



Extinct

Figure 35. Photographs of a phenol-formaldehyde membrane containing 10 per cent nickel nitrate as viewed through a polarizing microscope

Birefringent



Extinct

Figure 36. Photographs of a phenol-formaldehyde membrane containing 18 per cent nickel nitrate as viewed through a polarizing microscope

range and this is related to the response properties.

The response of the 24 and 25 per cent membranes was fairly good; the membranes were birefringent. No non-birefringent dots could be seen, however, the field was mottled in appearance, Figure 37.

In summary, then, the phenol-formaldehyde membrane is amorphous, the phenol-formaldehyde-nickel nitrate membrane is crystalline when prepared with 14 to 23 per cent nickel nitrate. The potential response of the membrane appears to be related to the formation of a uniform, crystalline structure.

Birefringent

Extinct

Figure 37. Photographs of a phenol-formaldehyde membrane containing 25 per cent nickel nitrate as viewed through a polarizing microscope

APPLICATIONS

Two applications of the phenol-formaldehyde-nickel nitrate membrane were made: to the direct potentiometric determination of nitrate and to the end-point detection in titrimetric methods using silver sulfate as a standard solution.

Potentiometric Determinations

In direct potentiometric determinations, the membrane potential response to changes in activity of the ion to be determined is calibrated by determining the potential response to several solutions of known activities. A calibration curve is then prepared by plotting potential response versus activity. The potential response to the ion being determined is then measured and from the calibration curve, the activity obtained. The first application of this was to the practical problem which arose in the course of this very work, the problem of determining the nitrate which was removed from the resin during the operation of conditioning the resin by soaking it in water; this is reported on page 73. The amounts of nitrate and nickel removed were equivalent and thus evidence was obtained that the procedure was functioning well as an analytical method.

Titrimetric Determinations

Use was made of the phenol-formaldehyde-nickel nitrate membrane to locate the end-point in the titrations of bromide, chloride, and thiocyanate with silver sulfate. A sharp and reproducible change in potential was obtained in each titration. The titration curve obtained in one titration of potassium chloride with silver sulfate is shown in Figure 38. The change in potential at the end-point is about 120 mv., a very satisfactory value which provides great precision. During the titration, a film of silver chloride formed on the surface of the membrane and the membrane responded to the silver ion beyond the end-point in the same manner that a silver chloride-impregnated membrane responds to the anion or cation in common with the precipitate anion or cation[9]; the potential was greater than expected or experienced when no film of silver salt is formed.

A potentiometric titration of nitrate with nitron, a precipitating agent for nitrate, was attempted, but the nitron nitrate proved too soluble and a sharp change in potential at the end-point was not obtained.

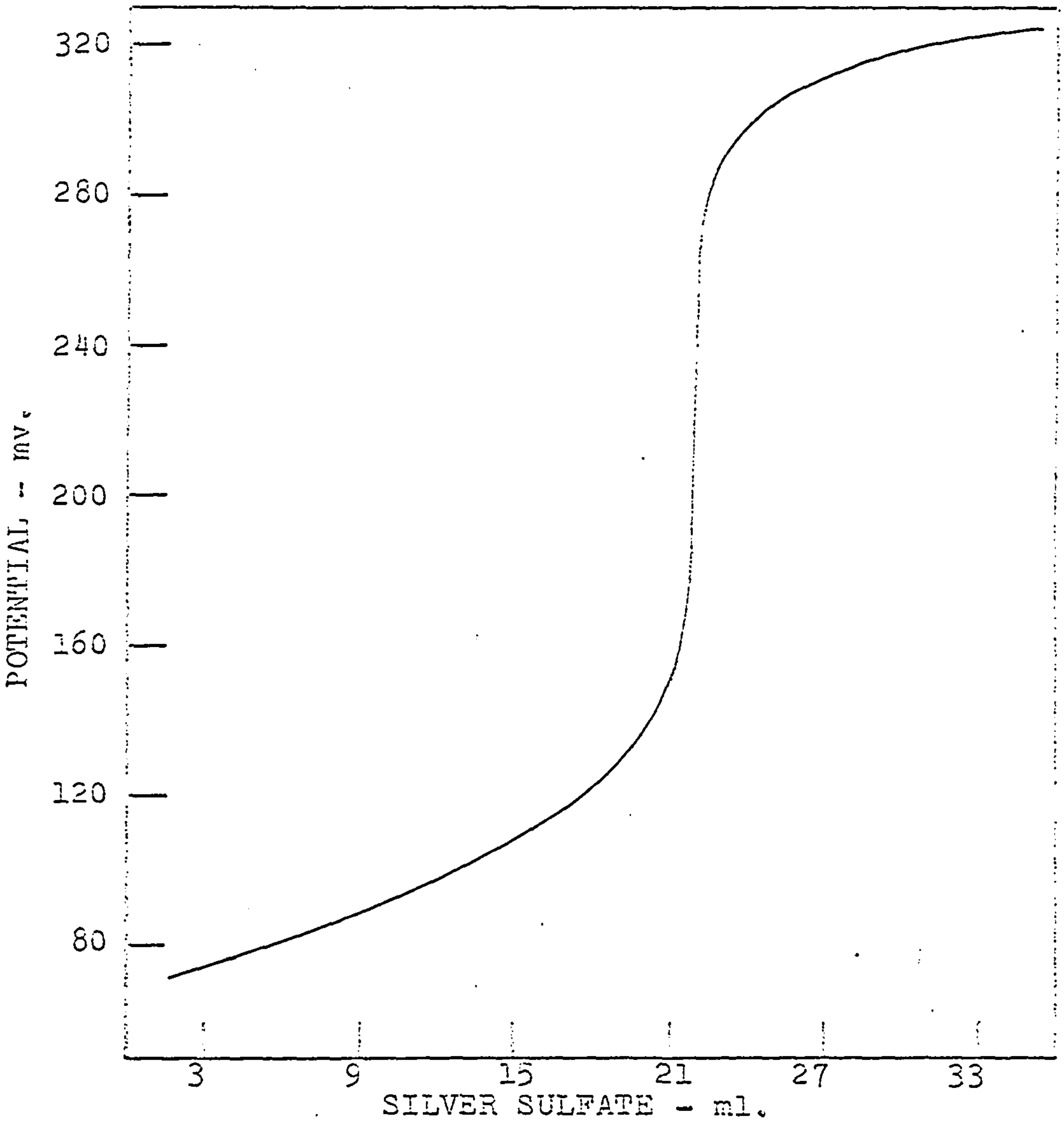
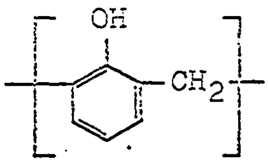


Figure 38. The potentiometric titration of chloride with silver using the phenol-formaldehyde-nickel nitrate membrane as an indicator electrode

RESULTS AND DISCUSSION

It is apparent from the foregoing work that a phenol-formaldehyde resin can be used as a membrane electrode but that ammonium hydroxide rather than sodium or potassium hydroxide must be used as the polymerizing catalyst and that the resin must be further modified by the incorporation of a metal salt, nickel nitrate having been found best. Membranes made from phenol-formaldehyde resins prepared using sodium hydroxide or potassium hydroxide as the polymerization catalyst respond to a variety of cations and lack specificity. Membranes made from the phenol-formaldehyde-ammonium hydroxide resin do not respond to either cations or anions, the electrical resistance being exceptionally high. The phenol-formaldehyde-ammonium hydroxide-nickel nitrate membrane responds only to anions, and indeed only to univalent anions. Positively charged sites must exist in the resin, at least in the surface layers where anion exchange between resin and solution can take place. Electrical conduction, even though of only the most minute sort, must also be provided. Incorporation of the nickel salt somehow brings about both functions.

At its simplest, the unit of the phenol-formaldehyde resin is the hydroxyphenylmethylene unit



C_7H_6O. The results of the analytical work on the nickel-free resin (Table 3) indicate a composition not too far from this, $C_{6.3}H_{5.9}O_{1.0}N_{0.13}$, with one nitrogen atom introduced for about every 6.8 hydroxyphenylmethylene groups. This ratio is not significantly altered by the incorporation of the nickel nitrate as indicated by the results of analysis and calculations (Table 4) on the basis that three nitrate anions enter for every atom of nickel. Close to one atom of nickel is incorporated for each three atoms of amino nitrogen and for each twenty-three phenolic groups. During the conditioning (soaking) operation about two-thirds of the nickel is leached from the membrane. This gives a good idea of the composition of the membrane although the approximate nature of the calculations should be emphasized, for the simple polymerizing unit used, C_7H_6O, is only an approximation owing to cross linkage (two methylene groups per phenolic group), and water, which is undoubtedly present in the polymer, has not been considered.

Inasmuch as the use of secondary and tertiary amines did not result in satisfactory polymerization, it is likely that the amine is involved in the linkage, probably as the methyleneimino group, $-CH_2-N<$, the usual product of the Mannich condensation of ammonia, formaldehyde and a phenol. This is supported by the presence of absorption bands in the infrared spectrum in the position customary for secondary amines and tertiary amines. These amino groups would provide a site for the attachment of the hydrogen ion and thus account for the response of the membrane to hydrogen ion. The amino groups also provide a site for attachment of the nickel ion; differences in the infrared absorption spectra of the nickel-free and nickel-bearing resins indicate that such union has occurred. The nickel atom may be bound to more than one amino nitrogen atom forming chelate rings or cages within the polymer. Irrespective of the number of attachments of the nickel atom, the nickel atom will bear a bi-positive charge and have associated with it two nitrate anions. These nitrate anions can, of course, occupy positions in the coordination sphere about the nickel atom. Inasmuch as the resin has become a conductor it is more likely that these anions are free to move. That is, the electrical conduction through the membrane is conceived to be essentially electrolytic in nature with the nitrate anions carrying the major share of the current, the positively charged amine nickel sites being stationary and simply providing a pathway for the anions.

The situation in the boundary layer is more complicated. The extraction of nickel nitrate, the so-called conditioning or soaking operation, is essential to obtain a membrane which is responsive, but the extraction of nickel nitrate stops after a time. There would appear to be no way to determine if nickel has been removed completely from the boundary layers leaving a high concentration of nickel in the interior or if the remaining nickel is distributed throughout the membrane uniformly. In any case, the membrane responds to hydrogen ions but to no other cations and to univalent anions but barely to bivalent anions. There must, therefore, be present in the boundary layer, amino groups to accept the hydrogen ion and positively charged groups so arranged spatially and so charged as to permit exchange of univalent anions with the solution but not of bivalent anions.

That the nickel-free phenol-formaldehyde-ammonium hydroxide resin is amorphous and the nickel-bearing resin crystalline as judged by X-ray powder photographs and by examination in the polarizing microscope must be of significance although no physical relation between crystallinity and potential response is immediately obvious. However, it can hardly be accidental that only over the range of 14 to 22 per cent of nickel nitrate hexahydrate in the polymerizing mixture is a uniformly crystalline resin obtained and only over this range a responsive membrane prepared.

The preparation of the phenol-formaldehyde-ammonium hydroxide-nickel nitrate resin is, of course, highly empirical. No apology for this need be offered for each step in the procedure finally evolved was the result of observation and tests. Thus, the two-step polymerization, the correct base to use as polymerization catalyst, the best salt to incorporate into the resin, the amounts of phenol, formaldehyde and nickel nitrate, the time, temperature and manner of effecting the polymerization, the method of casting the membrane, and the method of conditioning (soaking) it, were all carefully worked out. Naturally, in a technique as involved as this, not all the variations have been tested nor have explanations been advanced to account for all the effects of certain of the variables. The conditions have, however, been well enough defined to make the preparation of a satisfactory membrane reproducible.

As shown in various Figures in the foregoing pages, the response of the phenol-formaldehyde-nickel nitrate membrane over the range of nitrate concentration 10^{-2} to 10^{-4} is linear when the potential measured is plotted against the negative logarithm of the concentration. The response falls off abruptly at concentrations below 10^{-4}. The potential developed is also less than expected in the range 1 to 10^{-2} (response curve concave up). Activity, that is, apparent effective concentration, rather than concentration is measured by a membrane electrode. The curve shown in Figure 39 was obtained by using the activity coefficients listed in Table 1 for various concentrations of sodium nitrate to calculate the activity of the nitrate and by plotting the negative logarithm of the nitrate activity versus the potential measured. The curve is linear for nitrate activities ranging from 10^{-1} to 10^{-5} and is slightly concaved upward above 10^{-1} and the slope of the linear portion of the curve is 60 mv. per ten-fold change in activity of the nitrate.

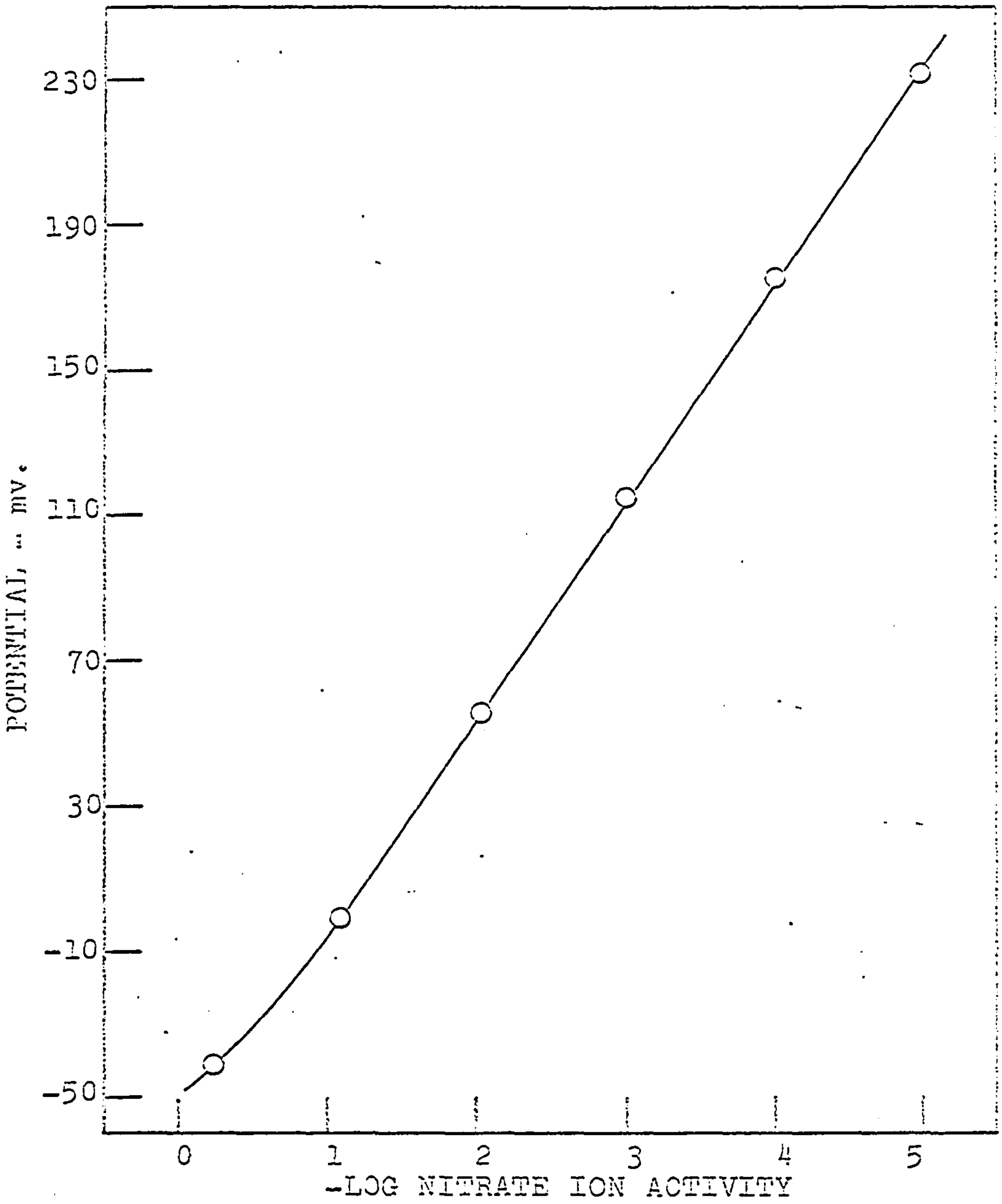


Figure 39. The potential response of the phenol-formaldehyde-nickel nitrate membrane as a function of activity of nitrate

The data used to obtain the curve shown in Figure 39 and a comparison of the response as a function of concentration of nitrate with the response as a function of activity of nitrate are given in Table 7.

Table 7. A comparison of the phenol-formaldehyde-nickel nitrate membrane response to concentration of nitrate with the response to activity of nitrate

Potential response, mv.	Concentration of nitrate, *M*	Change in potential per 10-fold change in concentration, mv.	Activity of nitrate	Change in potential per 10-fold change in activity, mv.
-41.1	1		5.5×10^{-1}	
-0.1	10^{-1}	41.0	7.7×10^{-2}	43.0
55.5	10^{-2}	55.6	9.0×10^{-3}	60.0
115	10^{-3}	59.5	9.7×10^{-4}	60.0
175	10^{-4}	60.0	1.0×10^{-4}#	60.0
234	10^{-5}	59.0	1.0×10^{-5}#	59.0

#Activity coefficient assumed to be unity.

Thus, the membrane responds to activity and because the membrane responds to the activity of a given ion and not to the total concentration of the ion, the membrane can be used in the study of complex formation and to determine the activity of an ion when it is necessary to know the amount of an ion in an active form rather than the total content of the ion. This may be the best method of obtaining activity values.

The membrane response is rapid, stable, reproducible, and theoretical for nitrate in concentrations ranging from 1 M to 10^{-5} M. Consequently, the membranes can be calibrated for the direct potentiometric determination of nitrate. The membrane also responds to other univalent anions which, therefore, cannot be present during nitrate determinations. The membrane can, however, be calibrated with and used for the determination of other univalent anions.

SUMMARY

A membrane has been prepared from a suitably modified phenol-formaldehyde polymer which responds to differences in the concentration of univalent anions in two solutions placed respectively in contact with the opposite sides of the membrane. The electrical potential developed across this membrane is detected by two, identical, saturated calomel electrodes placed in the solutions, the potential being measured with a high-impedance, vibrating reed electrometer. The membrane should prove useful for measuring low concentrations, or more correctly activities, of univalent anions, particularly nitrate.

It has been found that phenol-formaldehyde resin membranes, prepared using potassium or sodium hydroxide as the polymerizing catalyst, are not specific in potential response. When prepared with ammonium hydroxide as catalyst, the membranes are inert, although nitrogen is incorporated into the resin. By incorporating nickel nitrate into the phenol-formaldehyde-ammonium hydroxide resin, a membrane is obtained which gives a potential response proportional to differences in concentration of nitrate.

In the preparation of the membrane, a preliminary polymerization of phenol, formaldehyde and ammonia is first effected, yielding a product known as bakelite A. Bakelite A, nickel nitrate, and formaldehyde are then dissolved in

ethanol and poured into a petri dish. The ethanol and any excess water present are evaporated away leaving a film which is then polymerized to bakelite C. The resulting film is soaked in water, stripped from the dish, mounted between pieces of flanged glass tubing in such a way that different solutions can be placed on opposite sides of the membrane, and the potential developed across the membrane measured.

Membranes prepared in this way have been shown to develop a potential response to nitrate and other univalent anions over the concentration range 1 M to 10^{-5} M. They do not respond to multivalent anions in concentrations less than 0.10 M. The membranes respond to hydrogen ion (pH) but to no other cations. The potentials developed by differences in the concentrations of anions are stable, reproducible, and of the values predicted by theory.

The response of membranes prepared from resins prepared from phenolic compounds other than phenol or mixtures of other phenolic compounds with phenol was found to be inferior to the response of membranes prepared from phenol alone.

Optimum phenol-formaldehyde ratio, catalyst, polymerization temperature, and polymerization time for the preparation of bakelite A have been determined.

The effect of the amount of ammonia used as condensing agent, during the polymerization to bakelite A, on the response of membranes prepared from the bakelite A has been studied. It was found that a minimum amount of ammonia was required during the polymerization to bakelite A for the attainment of good membranes, and that the use of an amount of ammonia in excess of the minimum did not increase the response.

It has been found that a good response is obtained with membranes prepared from a bakelite A condensed with ammonia or methylamine but not with dimethylamine or trimethylamine.

Membranes prepared using various other metal nitrates in place of nickel nitrate either did not respond or responded over a much more limited range. Membranes prepared using nickel chloride were unsatisfactory but those using nickel perchlorate were as satisfactory as those using nickel nitrate. The amount of nickel nitrate incorporated into the resin may vary from 16 to 22 per cent by weight of the polymerizing mixture, the range of difference in concentration of nitrate to which the membranes responded falling off markedly above and below these amounts.

Membranes prepared with amounts of nickel between 14 and 23 per cent of the polymerizing mixture are crystalline in character as revealed by examination with the polarizing microscope, a membrane prepared without nickel being amorphous and completely opaque between crossed Nicols.

The membrane responded to univalent anions and not to multivalent anions in concentrations less than 0.10 M or, with the exception of the hydrogen ion, to cations.

The response of the membrane to univalent anions was found to be stable and reproducible over a four-month period.

It has been found that the membrane responds to pH changes and that greater sensitivity to univalent anions is obtained at lower pH values.

Some nickel is lost from the membrane during the soaking operation, a good, "working" membrane being about 2.80 per cent nickel (dry weight basis), and the amount of nitrate remaining in the membrane ranges from 2 to 3 nitrate radicals per nickel atom. There is one nickel atom for every 2.5 amine groups in the resin.

Infrared studies indicated that amine groups are present in the membrane and are altered by the incorporation of nickel nitrate into the membrane.

The incorporation of nickel nitrate into the phenol-formaldehyde membrane was found to cause a million-fold (3.3×10^{10} to 3.3×10^{4} ohms/cm.^{2}) decrease in the resistance of the membrane.

It was also found that no detectable ion exchange process occurred when a membrane was ground to 60 mesh and placed in a solution 10^{-2} M in nickel nitrate.

The membrane developed has been used to determine the end-point in the potentiometric titration of chloride, bromide, and thiocyanate with silver sulfate.

The mechanism by which these membranes function as indicator electrodes for univalent anions is a dual one:

electrical conduction within the membrane and ion exchange between membrane and solution at the two surfaces. The internal conduction is probably electrolytic in character, charged sites being provided by the amine and nickel-amine groups present. The exchange occurring at the surfaces is considered to be simply that common to anion exchange resins in general.

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