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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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W. M. Steyn[a]; W. J. De Wet[a]
[a] CHEMISTRY DIVISION, NATIONAL NUCLEAR RESEARCH CENTRE, PRETORIA, SOUTH AFRICA

To cite this Article Steyn, W. M. and De Wet, W. J.(1972) 'A Study of the Separation Possibilities of Cations Using Glass Membranes', Separation Science and Technology, 7: 5, 457 — 464

To link to this Article: DOI: 10.1080/00372367208056046

URL: http://dx.doi.org/10.1080/00372367208056046

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SEPARATION SCIENCE, 7(5), pp. 457–464, 1972

A Study of the Separation Possibilities of Cations Using Glass Membranes

W. M. STEYN and W. J. DE WET

CHEMISTRY DIVISION
NATIONAL NUCLEAR RESEARCH CENTRE
PRETORIA, SOUTH AFRICA

Abstract

The separation possibilities of Pyrex glass membranes at high temperatures have been investigated for the separation of sodium and potassium. A separation factor of 11 was obtained for this separation. The limitations of glass membranes for separation purposes are discussed, particularly for the separation of the alkali metal ions.

The use of ion-exchange membranes has found wide application over the past decade in several analytical and separation methods. For analytical applications, ion-selective membranes feature most prominent. Their use in ion-selective electrodes for specific element determinations in aqueous solutions include ion-exchange membranes of glass, solid inorganic precipitates, and organic liquid ion exchangers in a variety of physical membrane forms (*1*). The type of ion-selective electrode generally applicable to molten salt media is the glass electrode, which is essentially only responsive to monovalent cations, particularly the light alkali cations (*2*).

In separation applications, organic polymer membranes are predominantly used for miscellaneous small and preparative scale production purposes (*3*). At elevated temperatures certain inorganic membranes, such as ceramics, have found restricted separation applications

(*4*). Several types of membranes have received considerable attention as selective conductive barriers in low and high temperature fuel cells (*5*). The material transport and electrical phenomena of ion exchange and other types of membranes are furthermore of immense basic interest in biological and physical research (*6*).

Although ion permeabilities of glass membranes at high temperatures are at present being studied by a number of research groups (*7–12*), very limited work has been reported in the literature in which the separation possibilities of glass membranes in particular have been evaluated and applied (*13*). These possibilities are admittedly very limited, but nevertheless justify attention because of the total impermeability of glass membranes to a majority of ions, which implies very high selectivities for permeable ions. From published permeability values of the alkali ions in Pyrex, it was decided to study separation of sodium from potassium at 550°C, using Pyrex membranes. This system affords the best choice to demonstrate the separation possibilities of glass membranes.

EXPERIMENTAL PROCEDURE AND RESULTS

The apparatus (Fig. 1) consisted of a large outer Pyrex glass container into which a certain amount of a specific NaCl–KCl mixture, admixed with an amount of $ZnCl_2$ as solvent, was placed. In this case only the sodium and potassium cations are mobile in the glass, and for the experiments a sodium atom fraction of 0.122 was selected for the mixtures used relative to total mobile ion content. This composition of the NaCl–KCl mixture was chosen for compatibility with the apparatus, where size of the glass membrane and electrolysis-time were the main considerations. The separating properties of the glass membranes were also taken into account. The container was heated to 550°C in an oven to obtain a clear melt. The amount of $ZnCl_2$ was varied, dependent on the amount of NaCl–KCl mixture, to maintain a melt height of 6.5 cm in the container.

A Pyrex glass tube, closed at the bottom, containing an amount of $ZnCl_2$ was placed into the outer container. In order to minimize the surface of the glass membrane, the portion of this tube in contact with the melt was of much smaller diameter than the rest of the tube. Electrolysis was performed through this glass membrane, a tungsten cathode being inserted in the inner compartment and a graphite anode in the outer container.

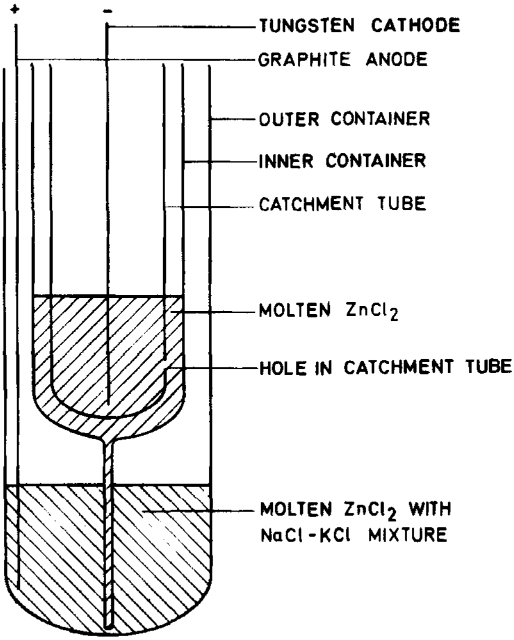

FIG. 1. Fused-salt electrolytic cell.

Voltages of the order of 30 V were applied; far in excess of membrane potentials. The membrane current densities used were approximately 10 mA/cm^2. In order to prevent any molten zinc, formed at the cathode during electrolysis, from collecting in the narrow glass tube, the tungsten rod was placed within a catchment tube. This catchment tube was electrically connected to the inner compartment by means of a hole situated approximately 2 cm from the closed end. Samples of the melts in the inner and outer containers were taken at regular intervals during the electrolysis and analyzed for Na and K on a flame photometer. A number of runs were carried out in this fashion by making use of varying amounts of NaCl–KCl mixture in the outer container.

The results are graphically depicted in Figs. 2 and 3. The left-hand side of Fig. 2 (solid lines) indicates the change in composition of the melt in the outer container vs. coulombs for varying amounts of the NaCl–KCl mixture: (a) represents a mixture containing 0.9 g NaCl, (b) 1.2 g NaCl, (c) 1.8 g NaCl, and (d) 2.4 g NaCl. The right-hand side of Fig. 2

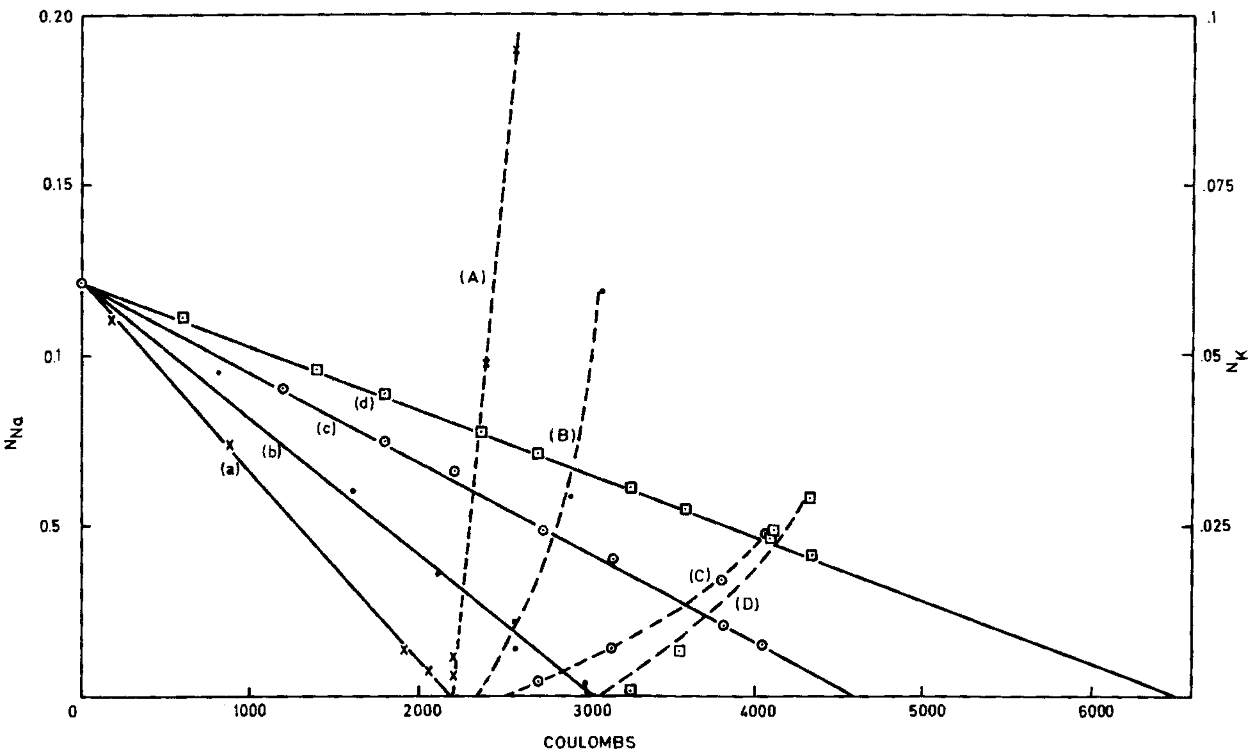

Fig. 2. Composition of the outer (solid lines) and inner (dashed lines) containers vs. coulombs for varying amounts of the NaCl–KCl mixture.

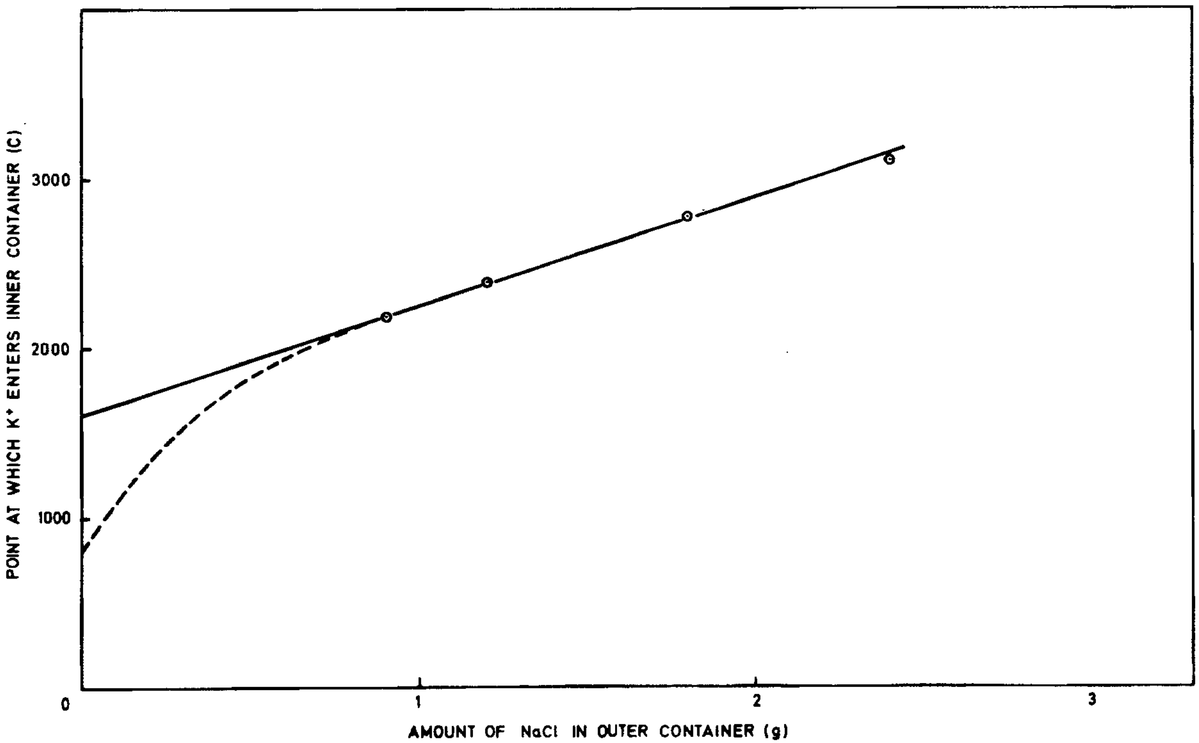

FIG. 3. Point at which potassium starts entering the cathode compartment (in coulombs) vs. the amount of mixture placed in the anode compartment.

(dashed lines) shows the corresponding change in composition in the inner container: (A) corresponding to (a), etc. Figure 3 represents the point at which potassium starts entering the cathode compartment vs. the amount of mixture placed in the anode compartment. It therefore indicates the amount of sodium separable from the mixture in each instance.

DISCUSSION

When electrolysis voltages which are large in comparison with membrane potentials over membranes are applied, the flux ratio of two mobile cations in a binary case through a cationic membrane is determined by the composition of the anodic solution, the thermodynamic ion-exchange constant (for ion-exchange interactions of the ions with the membrane), and finally the mobility ratio of the two ions in the membrane. The product of the last two factors is the permeability ratio or separation factor. Under steady-state conditions, viz., when the composition of the anodic solution remains constant and ion-exchange equilibrium has been established throughout the membrane, the permeability ratio of two ions can be very easily obtained experimentally for virtually any type of membrane for any set of experimental conditions. In the case where the composition of the anodic solution changes as in the present experiments, however, the situation becomes less amenable to description, especially for glass membranes. In the latter case it was found experimentally that the mobility ratio for two ions is a function of the ionic composition of the glass (i.e., relative numbers of ion-exchange sites occupied by each cation). Furthermore, glasses such as Pyrex consist of more than one phase and thus also have different types of ion-exchange sites (*14*). This further complicates the situation since mixed thermodynamic ion-exchange constants have to be considered and the picture of ion migration in such glasses is also still not clear.

For the system Na–K–Pyrex discussed in this paper, it is known that the sodium has a high affinity relative to potassium for the silicate phase in contrast to that for the dispersed borate phase, the latter having about 95% of the total ion-exchange sites and showing virtually no preference for sodium above potassium. Less is known about the mobility ratio of sodium to potassium in Pyrex, especially at sodium contents of less than 10% of the total exchangeable cations. It is known, however, that sodium on an average is about 13 times more mobile in Pyrex than potassium (*15*). For the purpose of this study it was felt that, taking all the above points into consideration, a critical study should involve mixtures of sodium and potassium having low sodium content, and varying amounts should be used to the point where all the sodium is depleted in the outer container when potassium just appears in the inner container. This has been achieved, as can be seen in Fig. 2. From the results in this figure, average separation factors have been calculated over the range $N_{\mathrm{Na}} = 0.122$ to 0 taking an average anodic composition of $N_{\mathrm{Na}} = 0.061$. The values obtained for the selectivity constants of sodium to potassium are 11.66, 11.16, 11.10 and 10.81, respectively, with increasing mixture weight. These values are in good agreement with the value of approximately 13 which would be expected on the basis of published work (*15*). The decreasing values of the selectivity constants with increasing mixture weight can be explained by the high affinity of the silicate phase of Pyrex for sodium which becomes particularly pronounced in the region of low sodium content. Support for this in similar situations can be found in the literature (*7*).

Although a straight-line relationship has been obtained in Fig. 3 for the range covered by the experiments, it should be expected that the slope will flatten out toward larger amounts of the mixture and that eventually the graph should run parallel to the abscissa. The intercept by the solid line on the ordinate is not indicative of the absolute amount of sodium initially present in the glass membrane, and for small amounts of salt mixture it can be expected that a curve such as is indicated by the dashed line in Fig. 3 should be obtained.

The results in Fig. 3 indicate that by using Pyrex, fairly large amounts of sodium can be separated completely from potassium using the technique described. Because the heavier alkali metal cations are even less mobile than potassium in Pyrex, sodium can be separated from these elements even more successfully. Unfortunately, as the selectivity coefficient for sodium relative to lithium is about unity, these two elements cannot be separated satisfactorily by this method. The only other ions that readily penetrate glass at high temperatures are those of silver, copper, and gold. Copper and gold ions, however, result in structural damage of glass and further, because of reduction problems experienced with solutions of these elements, especially gold, at high temperatures, their glass migration characteristics do not appear to be exploitable. This limits the usefulness of glass membranes for separation purposes to the separation of sodium (and lithium) from other ions for which there are specific applications.

Acknowledgment

The authors are indebted to the South African Atomic Energy Board for permission to publish this paper.

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Received by editor February 2, 1972