MEMBRANE POTENTIALS ACROSS MULLITE IN MIXTURES OF MOLTEN BROMIDES

M.L. Orfield
University of Wisconsin-Stout
Menomonie Wisconsin 54751

ABSTRACT

At high temperatures Mullite functions as an ionic conductor of alkali metal cations. Two mullite membranes, M30 and MV33, were investigated. The membrane potentials of each were measured in mixtures of the alkali metal cations. The selectivity of MV30 for each of the alkali metal cations, Li⁺, Na⁺, and K⁺ and the selectivity of MV33 for Na⁺ were evaluated. The range of composition over which the behavior of each mullite may be predicted is discussed.

INTRODUCTION

Glassy membranes, sensitive to a single ion, form the basis for many separators and ion selective electrodes in use in aqueous systems. The success of such electrodes depends upon an understanding of the relationship between the composition of the solution and the potential generated across the membrane. In aqueous systems this relationship has been thoroughly examined and exploited to prepare glasses selective for a variety of ions.

Since glassy membranes are known to conduct ions well in molten salt solutions, it seems likely that they may obey the same kind of mathematical relationships applicable in aqueous systems. A few investigators have explored this area. Doremus measured the potentials across silica and pyrex glasses in molten nitrates. (1,2) Notz and Keenan also measured potentials across pyrex in molten nitrates. (3,4) Reenan et al., and Stern investigated potentials across silica in molten chlorides to a limited extent. (5-7) However potentials across these glasses could not be measured in higher melting salts because all except silica softened below the melting points of the salts or were quickly degraded in the harsh environment.

As a result most separators, and solid electrolytes used today in molten salt cells are ceramics. Mullite, a cation conductor and zirconia an oxide ion conductor are the most common. Mullite is useful in molten salt systems and other corrosive environments because of its high thermal stability and resistance to corrosion. It is believed to conduct alkali metal cations via a glassy phase at the grain boundaries. Its selectivity might be thought to obey the same mathematical relationships as those employed for glassy membranes in aqueous systems. It is the purpose of this work to investigate the relationship between potential developed across a mullite membrane and the activity of the alkali metal ions on either side of it; to determine if mullite
does obey the same relationships established for glassy membranes in aqueous systems

THEORETICAL BACKGROUND

When two solutions, each containing a unique activity of cation N+, are separated by a membrane which conducts only cation N+ a potential develops across the membrane. The magnitude of the potential is determined by the gradient in the activity of N+ across the membrane. It is described

\[ E_{\text{mem}} = \frac{RT}{nF} \ln \left( \frac{a(N^+)_{\text{I}}}{a(N^+)_{\text{O}}} \right) \]  

where \( R \) is the gas constant, \( T \) is temperature, \( n \) is the absolute value of the charge on the cation, \( F \) is Faraday's constant, and \( a(N^+)_{\text{I}} \) and \( a(N^+)_{\text{O}} \) are the activities of cation N+ on side I and side O of the membrane respectively. A membrane described by this equation is said to be perfectly selective for cation N+. It conducts only that cation.

Most glassy solid electrolytes are not exclusive conductors of one cation. In general they conduct the alkali metal cations, Li+, Na+, and K+ and some other small univalent cations such as Ag+. If a membrane separates two solutions, each of which contains two conducting cations, the potential is described by the equation. (8)

\[ E_{\text{mem}} = \frac{RT}{nF} \ln \left( \frac{a(N^+)_{\text{I}} + K_{NM}^{\text{POT}} a(M^+)_{\text{I}}}{a(N^+)_{\text{O}} + K_{NM}^{\text{POT}} a(M^+)_{\text{O}}} \right) \]  

where the meaning of all terms used in Eq. 1 is the same, \( M^+ \) is the second ion conducted by the electrolyte, and \( K_{NM}^{\text{POT}} \) is the potential selectivity coefficient which describes the relative conductivity of each ion in the electrolyte. \( K_{NM}^{\text{POT}} \) is a measure of the preference of the membrane for \( M^+ \) over \( N^+ \) as a means of moving ionic current. Obviously, if \( K_{NM}^{\text{POT}} = 0 \), the membrane is perfectly selective for \( N^+ \) and will function as an ion selective electrode for that ion. Eq. 2 has been used extensively in characterizing the conductivity of glassy membranes in aqueous solutions, and in formulating those membranes to be highly selective for a single ion. Since mullite is believed to conduct via a glassy phase at the grain boundaries, it seems reasonable to assume that this material may also be characterized by the equation 1 or 2.
EXPERIMENTAL

The experimental apparatus is diagrammed in Fig. 1. A 7.0 cm. diameter mullite tube, 30.48 cm. long, with a stainless steel cap and fittings contained the cell used for membrane potential measurements. A mixture of of alkali metal bromides, M¹Br and M²Br, with an activity of AgBr which was maintained at the same value as the activity of AgBr in the reference melt, was placed in a silver crucible inside the chamber. All salts were Baker Reagent grade. A silver wire, 99.99%, dipped in the melt formed the indicator electrode. The atmosphere in the chamber was dry Argon of 99.99% purity. The membrane was a mullite tube 0.95 cm. in diameter and 45.7 cm. long composed of mullite crystals with 15% by weight additional SiO₂ found as a glassy phase at the grain boundaries. It was purchased as MV30 from McDanel Refractory. The tube contained a reference melt of alkali metal bromides and the same activity of AgBr as found in the indicator melt. The reference electrode was also silver wire dipped into this melt making the cell:

\[
\text{Ag|AgBr(N=Y), M¹Br (N=X), M²Br (N=1-X-Y)|mullite|M¹Br(ref), M²Br(ref), AgBr(ref)|Ag}
\]

where M¹Br and M²Br define one of the combinations, NaBr-KBr, LiBr-KBr, or NaBr-LiBr, and N is the mole fraction of each component in the mixture. The mole fractions of the alkali metal bromide components in the indicator melts were varied from 0.10 to 0.90 for each cation series. The mole fraction of AgBr in the indicator melt was adjusted to maintain equivalent activities of Ag⁺ at the electrodes.

The reference melt composition, ref, was constant for each specific series of M¹Br-M²Br melts. The reference melt compositions were (mol fractions) 0.81 LiBr, 0.11 KBr, 0.08 AgBr for the LiBr-KBr series, 0.085 NaBr, 0.835 KBr, 0.08 AgBr for the NaBr-KBr series, and 0.83 NaBr, 0.08 LiBr, 0.09 AgBr for the NaBr-LiBr series. The reference electrode melt was prepared by premelting the appropriate mixture, grinding it, and storing it in an Ar purged dessicator. A small amount was placed in the membrane tube and then maintained under Argon continuously throughout the time it was used.

The salts were weighed, placed in the silver crucible, and dried in the Lindberg furnace under a flowing Argon atmosphere for 30 minutes at approximately 250°C. The temperature was raised to 755°C and maintained at that temperature ±2°C until the system equilibrated. Equilibration time was usually about 10 minutes. The potential was measured with a Simpson voltmeter and recorded. Individual experiments were repeated with the same mullite membrane and with other tubes. The potentials were reproducible within 5 mv. under all circumstances, and usually within 2 mv.
Some additional experiments were performed using a membrane of stoichiometric mullite. (MV33 from McDanel Refractory). Although this product is sold as non glassy phase mullite, in reality it contains about 2-3% glassy SiO₂ phase at the grain boundaries. (9) A tube, 1.90 cm. OD and 7.62 cm. high, was placed in the molten salt and supported by a gas inlet tube as shown in Fig. 2. The experimental apparatus was similar to that used with the MV30 membranes. The experimental procedure was the same.

CALCULATIONS

Since the membrane potential was to be measured, the Ag|Ag⁺ indicator and reference electrodes were maintained at the same potential throughout the experiments. The activity coefficient for AgBr in each indicator melt was calculated using the equation for a ternary solution, (10)

\[ \text{RT} \ln \gamma_x = k_{12}N_1N_2 + (k_{x1}N_xN_1 + k_{x2}N_xN_2)(N_1 + N_2) \]  

for a ternary solution where \( x \) indicates AgBr and 1 and 2 the alkali metal bromide components of the mixture, \( \gamma_x \) is the activity coefficient of AgBr, and \( k \) is the interaction coefficient of the pair of components indicated by the subscript. Activity coefficients for the alkali metal bromides were calculated with the same equation using appropriate interaction coefficients. (11-15)

The potential selectivity coefficient was calculated from equation 2, using the measured values of the membrane potential and the calculated activities as described above.

RESULTS AND DISCUSSION

A \( K_{Na-K}^{POT} \) has been calculated from each measured potential using equation 2 as written for these experiments

\[ E_{mem} = \frac{RT/nF \ln \left( a(Na^+)\text{i} + K_{Na-K}^{POT} a(K^+)\text{i} \right)}{a(Na^+)\text{ref} + K_{Na-K}^{POT} a(K^+)\text{ref}} \]  

where \( I \) now refers the indicator melt being measured; ref. describes the reference melt and \( E_{mem} \) indicates the measured cell potential. The activities of each salt are calculated from Eq. 3.
The average of the $K_{Na-K}^{POT}$ values so calculated was $0.048 \pm 0.010$, indicating that the mullite behaves reasonably like a glassy membrane which conducts both Na$^+$ and K$^+$ ions.

The experimental membrane potentials $E(\text{meas})$ generated across the mullite membrane (MV-30) are plotted in Fig. 3 as a function of the activity of NaBr in the melt. In addition, the average $K_{Na-K}^{POT}$ has been employed in Eq. 4 to plot a curve of $E(\text{calc})$ vs $a(\text{NaBr})$. Agreement between the experimental data and the theoretical curve substantiates the idea that the potentials generated by a membrane in molten salts may be described by equation 2 similarly to membrane potentials in aqueous systems.

The value of the $K_{Na-K}^{POT}$ for this system suggests that, as an ionic conductor, MV30 is highly selective for Na$^+$ over K$^+$. It suggests further that if the activities of K$^+$ in a melt, and reference melt, are sufficiently low with respect to the activity of Na$^+$, the second terms in the numerator and denominator of Eq. 2 will become insignificant; Eq. 2 will approximate Eq. 1 and the mullite may be characterized as membrane perfectly selective for Na$^+$ with little error. For example, if both salt mixtures were in excess of 0.90 mol fraction Na$^+$ the difference between Eq. 1 and Eq.2 would be only a few tenths of a millivolt. However, at the compositions used in this experiment significant error would result from using Eq. 1. Fig. 4 shows a comparison of potentials calculated using $K_{Na-K}^{POT} = 0.048$ in Eq. 2 and those calculated assuming the electrode is perfectly selective for Na$^+$ using Eq. 1.

A further refinement of Eq. 2 has been suggested by Eisenman et al. They have included a factor, $n$, used to account for nonideality of the activity of sites of conduction in the glass membrane. (16)

$$E_{\text{mem}} = \frac{RT/nF \ln \left( \frac{(a(Na^+))^1/n + (K_{Na-K}^{POT} a(K^+))^{1/n}}{(a(Na^+)^{1/n}) + (K_{Na-K}^{POT} a(K^+)^{1/n})^{1/n}} \right)}{1/n}$$

Equation 5 was used, in conjunction with a least squares iteration program, to calculate simultaneously a $K_{Na-K}^{POT}$ and an $n$ value for the system. The $K_{Na-K}^{POT}$ and the $n$ calculated using this method were 0.066 and 0.77 respectively. The curve calculated from this $K_{Na-K}^{POT}$ and $n$ is plotted in Fig. 5 with the experimental potentials. The agreement between experimental and theoretical
is good. Comparison of these two curves with the two curves in Fig. 4 indicates that very little congruence is gained with the use of the more complicated equation. It suggests that any difference between experimental data and a theoretical curve is not due to non ideality of activity of sites in the glass membrane.

The membrane potentials measured at \( a(\text{NaBr}) > 0.90 \) are not as reproducible as the others. At \( a(\text{NaBr}) < 0.90 \) the error was ±0.002 volts. It was much greater at \( a(\text{NaBr}) > 0.90 \), as can be seen from the two repeated measurements shown on the plot. These potentials result from very large differences in composition between indicating and reference melts, and seem to suggest that the useful range of MV30 as a predictable conducting membrane does not extend to this differential in composition.

The average \( K_{\text{Li-K}}^{\text{POT}} \) for a series of KBr-LiBr melts was calculated in manner similar to that described for the NaBr-KBr system. The average value was \( 0.034 \pm 0.017 \). It varied systematically with the composition of the melt, becoming larger with increasing \( a(\text{LiBr}) \). The variation resulted in a large error for the average value. Again, the \( K_{\text{Li-K}}^{\text{POT}} \) indicates that the electrode is highly selective for \( \text{Li}^+ \) over \( \text{K}^+ \). Apparently the glassy phase of MV30 is of a composition which conducts \( \text{Li}^+ \) ions equally as well as \( \text{Na}^+ \). It could be used as a perfectly selective electrode for \( \text{Li}^+ \) if the activity of the \( \text{K}^+ \) were sufficiently low in both melt and reference melt, and no gradient in \( \text{Na}^+ \) was present.

The potentials generated in the KBr-LiBr system are plotted in Fig. 6 in a manner similar to that described for the NaBr-KBr system. The agreement between the measured potentials and calculated curve is not as satisfactory as in the NaBr-KBr system because of the systematic variance of \( K_{\text{Li-K}}^{\text{POT}} \) with \( a(\text{LiBr}) \).

A \( K_{\text{Li-K}}^{\text{POT}} \) and \( n \) were also calculated using Eq. 5 and found to be 0.0018 and 2.56 respectively. The curve of this equation is plotted in Fig. 7 with the experimental values. The agreement between the experimental and the theoretical is much better with this calculation. Since \( n \) is fairly great and this value of \( K_{\text{Li-K}}^{\text{POT}} \) differs greatly from the average value calculated, one might conclude that the activity of sites for conduction of \( \text{Li}^+ \) is far from ideal where that for \( \text{Na}^+ \) ions is much closer to ideal as evidenced by the NaBr-KBr plots.
A value of $K_{Na-Li}^{POT}$, calculated in a manner similar to that described for the NaBr-KBr melts, was found to be $3.20 \pm 0.50$. The value suggests that mullite conducts both Na$^+$ and Li$^+$ but has a slightly greater selectivity for Li$^+$. Because of the similarity of selectivity between Na$^+$ and Li$^+$ no composition of these salts will result in a negligible potential for either ion and Eq. 1 cannot be used for any composition. Unlike $K_{Li-K}^{POT}$ the $K_{Na-Li}^{POT}$ does not vary systematically with composition.

Experimental data and a theoretical curve using $K_{Na-Li}^{POT} = 3.20$ are plotted in Fig. 8. Agreement between experimental data and theoretical curve is modest. The error in these data appears to be random. When the $K_{Na-Li}^{POT}$ and $n$ are calculated ($2.787$ and $0.685$ respectively) and plotted with the experimental data in Fig. 9 the agreement between the theoretical and the experimental does not improve much over that in Fig. 8.

As previously stated, the conduction of ions by MV30 has been commonly believed to be accomplished via the glassy SiO$_2$ phase at the grain boundaries of the crystalline mullite. With this fact in mind a second series of experiments, similar to those described, was performed using MV33 as the membrane. This material, while marketed as a stoichiometric mullite, ie. no glassy phase, has approximately 2-3% residual glassy SiO$_2$, as opposed to 15% in the MV30. It was assumed that the MV33 would behave like an insulator and no meaningful potentials could be measured. However this was not the case.

Potentials were measured across MV33 and an average $K_{Na-K}^{POT} = 0.153 \pm 0.02$. The measured potentials and a theoretical curve using the average $K_{Na-K}^{POT}$ are plotted in Fig. 10. Not only do these appear consistent with Eq. 2, the agreement is good. While the variation in $K_{Na-K}^{POT}$ is not large, it is systematic with composition of the melt. A $K_{Na-K}^{POT}$ and $n$ were computed to be $0.170$ and $0.787$ respectively. The curve calculated using these values and the experimental data are plotted in Fig. 11. With the small correction for nonideality the agreement between experimental and theoretical is excellent. In fact the MV33 behaves in a more predictable manner than the the MV30.

The $K_{Na-K}^{POT}$ is approximately 3 times that of the MV30 membrane indicating that the glassy phase in the MV33 is less selective for Na$^+$ over K$^+$.
than the MV 30. The difference in selectivity may be due to the differences in composition between the two glassy phases. The bulk composition of impurities in the MV30 differs from that in the stoichiometric mullite. Because of this and processing differences, the final glassy phase composition is likely to differ as well.

The measurements across MV33 are consistent and the percent error small suggesting that the amount of glassy phase necessary to provide good conduction is small. If the grain boundary is very narrow in both mullites and the excess glassy phase is found in the pockets where three or more grains meet then 2 or 3% SiO₂ may be enough to provide a continuous glassy phase for conduction.

Alternatively, one might speculate that an second mode of conduction: directly across the crystalline mullite is active in these membranes. If so each mode of conduction would have a unique \( K_{\text{Na-K}}^{\text{POT}} \) and the measured \( K_{\text{Na-K}}^{\text{POT}} \) would be some combination of the two. If one assumes that the much smaller amount of glassy phase in the MV33 means that the grain boundary conduction is negligible, the excellent convergence with theory is explained.

**SUMMARY**

The behavior of an MV30 membrane may be predicted by equations used for membranes in aqueous solutions. NaBr-KBr mixtures are well described by equation 2, where \( n=1 \). The potential selectivity coefficient suggests that the activity of KBr may be ignored when it is less than 0.10. LiBr-KBr melts may be accurately described by the Eisenman modification of equation 2, where \( n \) does not equal 1. Again the membrane may be treated as perfectly selective for Li⁺ when the activity of K⁺ is less than 0.10 and no other alkali metal cations are present. Melts composed of NaBr-LiBr are not as well described which may be due to the small potentials measured in these melts. The potential selectivity suggests that both ions are conducted well and neither may be ignored in calculating the membrane potential when both are present.

The MV33 membrane is very well characterized by equation 2 and its modification. The potential selectivity coefficient for this membrane in NaBr-KBr melts differs from that for MV30. The variation may be due to differences in composition between the glassy phases in MV33 and MV30.

**ACKNOWLEDGEMENT**

The technical assistance of Robert Ulrich, David Zemke and Andrew Joswiak is gratefully acknowledged.
REFERENCES

1. R. H. Doremus, J. Phys. Chem., 72, 2877 (1968).

2. R. H. Doremus, J. Electrochem. Soc., 115, 924 (1968).

3. K. Notz and A. G. Keenan, J. Phys. Chem., 70, 662 (1966).

4. A. G. Keenan, K. Notz, F. L. Wilcox, J. Phys. Chem., 72, 1085 (1968).

5. T. J. van Reenen, M. van de Niekerk, and W. J. Wet, J. Phys. Chem., 75, 2815 (1971).

6. K. H. Stern, J. Phys. Chem., 72, 1963 (1968).

7. K. H. Stern, J. Phys. Chem., 74, 1323 (1970).

8. G. Eisenman in Glass Electrodes for Hydrogen and Other Cations, G. Eisenman, Ed., Dekker, New York, 1966, Chap. 5.

9. McDanel Refractory, Private Communication.

10. J. Lumsden, Thermodynamics of Molten Salt Mixtures, Academic Press, London, 1966, p. 96.

11. E. Aukrust, B. Bjorge, H. Flood, and T. Forland, Ann. N. Y. Acad. Sci., 79, 830 (1960).

12. E. J. Salstrom and J. H. Hildebrand, J. Am. Chem. Soc., 52, 4650 (1930).

13. E. J. Salstrom, J. Am. Chem. Soc., 53, 1794 (1931).

14. E. J. Salstrom, J. Am. Chem. Soc., 53, 3385 (1931).

15. L. S. Hersh and O. J. Kleppa, J. Chem. Phys., 42, 1309 (1965).

16. G. Eisenman, "The Chemistry of Cation-Sensitive Electrodes" in Advances in Analytical Chemistry and Instrumentation, Vol. 4, C. N. Reilly, Ed., Interscience, New York, 1965.
Fig. 1. Diagram of experimental apparatus for measuring membrane potential across MV30; mullite with 15% glassy phase

Fig. 2. Diagram of experimental apparatus for measuring membrane potential across MV33; mullite with 2-4% glassy phase

Fig. 3. Measured and calculated membrane potentials across MV30 in KBr-NaBr mixtures.

\[
\begin{align*}
E(\text{meas}) & \quad E(\text{calc}) K=.048 \\
0.0 & \quad 0.2 \\
0.1 & \quad 0.4 \\
0.2 & \quad 0.6 \\
0.3 & \quad 0.8 \\
0.4 & \quad 1.0 \\
\end{align*}
\]
Fig. 4. Calculated potentials using Eq. 2, $K=0.048$ and Eq. 1, $K = 0$ for NaBr-KBr melts.

Fig. 5. Cell potentials across MV30 in NaBr-KBr melts. $K = 0.0669$, $n=0.77$.

Fig. 6. Cell potentials across MV30 in LiBr-KBr melts. $K = 0.034$, $n=1$.

Fig. 7. Cell potentials across MV30 in LiBr-KBr melts. $K = 0.0018$, $n=2.56$. 

(please see text for more details)
Fig. 8. Cell potential across MV30 in NaBr-LiBr melts. 
$K = 3.20, \ n = 1$.

Fig. 9. Cell potential across MV30 in NaBr-LiBr melts. 
$K = 2.79, \ n = 0.685$.

Fig. 10. Cell potential across MV33 in NaBr-KBr melts. 
$K = 0.152, \ n = 1$.

Fig. 11. Cell potential across MV33 in NaBr-KBr melts. 
$K = 0.170, \ n = 0.787$. 