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ION-EXCHANGE PROCESSES BETWEEN IMMISCIBLE MOLTEN PHASES

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ABSTRACT

To test the hypothesis that cation distribution in (alkali oxide)-(boron oxide)-(alkali halide) systems occurs by ion-exchange processes, some definitive experiments were devised and carried out. The experiments consisted of equilibrating Na^{22} -labelled sodium borate with KCl at 830°C . Higher concentrations of K^+ than Cl^- in the borate phase and Na^+ than BO_2^- in the salt phase established the operation of cation-exchange processes in the immiscible molten system.

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SUMMARY

If Na^{22} -labelled sodium borate is equilibrated with KCl at 830°C , it is found that the concentration of the foreign cation always exceeded the concentration of the foreign anion in the immiscible phase being considered, i.e., in the oxide phase the concentration of K^+ exceeds that of Cl^- while in the salt phase Na^+ exceeds the concentration of BO_2^- . This observation confirms the existence of ion-exchange processes previously postulated to occur in molten alkali halide-alkali borate systems.

BACKGROUND

Stålhané¹ and Dunicz and Scheidt² have studied the miscibility of molten alkali borates with molten alkali halides (except fluorides) in the region 800-980°C. The ternary systems (alkali oxide)-(alkali halide)-(boron oxide) show miscibility gaps in this temperature range at low alkali-oxide contents. Biscoe and Warren,³ among others, have postulated structures for alkali borate glasses which strongly resemble those of synthetic, organic ion exchangers. Specifically, they are visualized as mobile cations, attracted by coulombic forces to localizations of negative charge, the latter being part of a three dimensional network of covalently bonded atoms.

Adams and Quan⁴ and Krogh-Moe⁵ have further assumed that such structures persist when the glasses are molten. Therefore, current models of liquid borate structure suggest that the immiscible phases of alkali borate are essentially molten ion-exchangers in contact with molten electrolytes. This interpretation is supported by the distribution coefficients of alkali, alkaline-earth, and rare-earth cations reported by Rowell.⁶ Rowell's results show that, in certain regions of alkali oxide content, distribution coefficients resemble those obtained between Dowex-50 and dilute HCl, not only in order of selectivity but also in magnitude.

This report first describes an ion-exchange mechanism for the distribution of cations in these systems. It then presents the rationale for testing the mechanism, and finally, presents data to support the proposed interpretation.

PROPOSED MECHANISM

Figure 1 shows a typical miscibility diagram for the systems in question, plotted in terms of components of the type B_2O_3 , MBO_2 and MX (M=alkali metal, X=Cl, Br or I). The important feature of this diagram

Fig. 1 Compositions Tested for Ion-Exchange Processes (830°C)

for the subject at hand is that the miscibility gap falls into two regions and this is indicated by both the behavior of the tie lines and the shape of the curve.

For brevity, we will call the region of low alkali metaborate content region A. This region extends over borate compositions ranging from pure boric oxide to approximately $M_2O \cdot 5B_2O_3$. In this region there is appreciable alkali halide solubility (i.e., electrolyte penetration) in the oxide (exchanger) phase. The convergence of the tie lines at the alkali halide corner show that the solubility of the oxide (exchanger) in the halide phase (co-phase) is slight. Rowell determined the formula of the soluble species in the sodium chloride system to be B_2O_3 and the solubility to be 0.04 mole %.⁶

Region B extends from the $M_2O \cdot 5B_2O_3$ composition to the plait point. It shows increasing electrolyte penetration but is characterized better by the sharply increasing borate solubility. In the NaCl system Rowell found $NaBO_2$ dissolving at compositions more basic than $M_2O \cdot 5B_2O_3$ and polyborate species, such as MB_3O_5 , at compositions more basic than $M_2O \cdot 3B_2O_3$.⁶

In view of these facts the most reasonable mechanism by which ion-exchange processes can proceed between the oxide and halide phases in region A appears to be that shown in Fig. 2. Here the convention $\emptyset$ is used to indicate an oxygen atom shared between two boron atoms, only one of which is indicated. The figure is otherwise self-explanatory. In region B the figure should be modified to show the presence of $(M^+) - BO_2(B_2O_3)_n^-$ ion pairs and similar structures which arise from the breakdown of the borate structure and dissociate in the halide phase.

RATIONALE

The foregoing considerations indicate certain differences from the familiar aqueous ion exchange system: there is no neutral phase corresponding to water (or organic solvent); there are no conditions of negligible electrolyte penetration and under most conditions penetration is high; at all compositions, there is a sensible exchanger solubility, and at some compositions this solubility is appreciable. In view of these differences, it is worthwhile clarifying what we mean by "ion exchange" in general before proceeding.

Fig. 2 Postulated Behavior of (Boron Oxide)-(Alkali Oxide)-(Alkali Halide) Systems at Low Alkali Oxide Concentrations.

There is no definition which has yet received universal acceptance by workers in the field. However, the following set of definitions appear to represent what workers in the field mean in their correspondence:

Ion-exchange mechanism: A mechanism which produces a heterogeneous, ionic metathesis.

Ion-exchange process: A chemical process which proceeds by an ion-exchange mechanism.

Ion-exchanger process: A chemical process carried out by an ion exchanger(e.g., catalysis, ion exclusion, site sharing, etc., including ion-exchange processes).

This definition of ion-exchange mechanism is operational and applicable to any heterogeneous system.

Returning now to Fig. 2, suppose a solute halide NX is introduced into the salt phase. This can distribute itself between the salt phase and the MX dissolved in the oxide phase according to the equilibrium.

$$K_S = (a_{MX})_O / (a_{NX})_S$$

where a indicates thermodynamic activity and subscripts O and S indicate the oxide and salt phases respectively. If this were the only process occurring, the concentration C_{N^+} of N^+ in the oxide phase would be clearly equal to or less than C_{X^-} the concentration of X^- . However, if ion exchange occurs there is the additional equilibrium

$$K_I = (a_{N^+})_O (a_{M^+})_S / (a_{N^+})_S (a_{M^+})_O.$$

This equilibrium permits additional N^+ to be concentrated in the oxide phase and the possibility that the oxide phase concentration of N^+ will exceed that of X^- . Therefore, a sufficient, but not necessary, condition for proving the occurrence of an ion-exchange process is that

$$(C_{N^+})_O > (C_{X^-})_O$$

The possibility that exchange occur in the salt phase subsequent to dissolution of oxide as MBO_2 leads to the same results. If the halide phase consists of pure NX, similar considerations lead to the alternative condition

$$(C_{M^+})_S > (C_{BO_2(B_2O_3)_n})_S$$

The experiments described here test the presence of these relationships at various points in regions A and B by equilibrating molten phases of composition $Na_2O \cdot x B_2O_3$ with molten KCl at 830°C.

EXPERIMENTAL

Equilibration charges were prepared from reagent grade chemicals. Sodium borate glasses of known composition were labelled with known quantities of sodium-22, the purity of which had been verified by gamma-ray spectrometry. Labelled glasses were dehydrated with a Meker burner. Before equilibration, they were further dried for 15 minutes at 900°C and then equilibrated with potassium chloride at $830 \pm 5^\circ C$. The overall KCl composition was 54 mole % in each case. Equilibrations were carried out in graphite crucibles under a dry argon atmosphere with mechanical stirring. Equilibrations lasted 95 minutes. The crucible was then removed from the furnace and cooled rapidly in a jet of cold air. Crucibles were sawed open and several samples of each phase were removed for analysis. Samples were analyzed in triplicate. Alkali oxide was determined by titration with 0.1 N hydrochloric acid to the methyl-red end point. Boron oxide was determined by conversion to mannitoboric acid and subsequent titration with 0.1 N sodium hydroxide to the phenolphthalein end point. Samples of high salt concentration were analyzed for chloride by the Volhard method. For low salt concentrations, a method using mercuric nitrate and a mixed indicator (bromophenol blue, diphenyl carbazone and xylene cyanole FF in 95 % ethanol) gave more accurate results. Sodium was determined radiometrically and potassium was calculated by difference.

RESULTS AND DISCUSSION

Figure 1 shows the region of the miscibility diagram where each run was carried out.

Figure 3 shows the values of $\bar{C}_{K^+}$ and $\bar{C}_{Cl^-}$ in the oxide phase for each run. The abscissa in this figure is the mole fraction of BO_2^- (regardless of associated cation) that would be present in the oxide phase were no chloride present. This is a convenient measure of position in the miscibility diagram for comparing results between systems containing different alkali halides. The higher value of $\bar{C}_{K^+}$ in every case clearly established the operation of cation-exchange processes.

The results of Fig. 4 confirm the above conclusion. This figure presents the complementary data for $\bar{C}_{Na^+}$ and $\bar{C}_{BO_2^-}$ in the salt phase. Again the concentration of the foreign cation exceeds that of the foreign anion for every case.

Finally, it is of interest to compare these data with Rowell's results for the distribution of tracer Rb^+ and Cs^+ in the system $Na_2O - NaCl - B_2O_3$ at $830^\circ C$. Rowell found that, for Na^+ , Rb^+ and Cs^+ in region A, the larger cation always showed the greater preference for the oxide phase. This situation was exactly reversed in region B: here the larger cation showed the greater preference for the salt phase. Figure 5 shows the distribution data in the present case plotted as

$$K_D = (C_{M^+})_O / (C_{M^+})_S$$

for Na^+ and K^+ . The occurrence of this reversal at the region boundary appears to be coincidental.

The figure shows the same qualitative behavior as that found by Rowell in spite of the increased loading of the exchanger. That is, the larger cation had the greater affinity for the oxide phase in region A, but the lesser affinity in region B. The occurrence of the reversal at the region boundary appears to be coincidental.

Fig. 3 Concentrations of K^+ and Cl^- Ions in the Oxide Phase ($830^\circ C$)

Fig. 4 Concentrations of Na^+ and BO_2^- Ions in the Salt Phase ($830^\circ C$)

Fig. 5 Distribution of K^+ and Na^+ Ions Between Immiscible Phases in the System $(\text{K}, \text{Na}) \text{BO}_2\text{-B}_2\text{O}_3\text{-(K, Na) Cl}$ at 830°C .

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