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Borate Glass Ion Exchangers for Fused Salts[1]

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A number of materials have been previously investigated regarding their suitability for ion-exchange or chromatographic separations of cation solutes in fused salts.[2-17] These materials include natural mineral zeolites,[2,3] synthetic zeolites,[4,5] porcelain,[6] silica gel,[7] powdered Pyrex glass,[8,9] γ-alumina,[9-12] zirconium silicate,[13] zirconium phosphate,[13,14] glass-fiber paper,[15,16] and glass-fiber paper impregnated with zirconium phosphate, zirconium oxide, and γ-alumina.[17] Exchange of alkali ions has also been observed between molten alkali salts and certain minerals.[18,19] The alkali ions in most glasses are exchangeable, and an extensive investigation has been made of the exchange of ions between melts and silicate glass.[20] Practical use has been made of fused-salt ion exchange for the strengthening of glasses, but the slow rate of ion diffusion in most glasses makes them inefficient ion exchangers for chemical separation purposes.

While all of the above materials perform in certain applications as ion exchangers or chromatographic adsorbents, none has been shown to be as generally effective as organic resin exchangers with aqueous solutions. They also lack the wide latitude of formulation possible with resins, which allows exchangers to be tailor-made to fit specific purposes. Unfortunately, resins are unstable at most fused-salt temperatures.

Molten alkali borate glasses are immiscible with many molten salts and have been found to show remarkable selectivity between trace amounts of various solutes in molten sodium chloride.[21] The mechanism for solute distribution appeared to be largely that of cation exchange on functional groups within the polymeric borate network. The ion-exchange mechanism was, in fact, shown by a separate experiment[22] to be operative. Since really effective solid ion-exchange materials, capable of much variety in formulation, would be of fundamental and practical interest in the field of molten-salt chemistry, some solid borate glasses were prepared and tested with sodium nitrate to see whether the same selectivity between solutes prevailed. To test further their usefulness as ion-exchange materials, a cursory examination was made of the completeness of exchange equilibrium, the rate at which it was approached, and the feasibility of column operation.

Experimental Section

Preparation of Borate Glasses.—The glasses were made by melting together in a platinum crucible weighed mixtures of reagent grade boron oxide and sodium borate, $Na_2B_4O_7$. In one instance sodium chloride was added to the limit of its solubility. The molten glasses were heated at about 900° until they were clear and bubbling had ceased; then they were poured, cooled, crushed, and sieved to various particle size fractions.

Batch Equilibrations.—For each equilibration run, 0.25–0.5 g of the appropriate glass was placed in a 18 × 150 mm Pyrex test tube, followed by 10 g of reagent grade sodium nitrate. To the top of the salt was added a small volume of a radioactive tracer solution in dilute nitric acid. The tracer solution contained either Na^{22}, Cs^{137}, Sr^{85}, Ba^{133}, or $Eu^{152-154}$. The tracer solution contained enough of the corresponding inactive metal nitrates to make the melt 1–10 ppm in Cs, Sr, or Ba and 250 ppm in Eu. The higher concentration of Eu was necessary to prevent undue adsorption difficulties, especially during filtration. The tracer solution was dried on the salt; then the charge was heated to the equilibration temperature in a crucible furnace controlled to about $\pm 5°$. The glass and molten salt were allowed to equilibrate for a specified time, during which they were stirred frequently with a Pyrex glass rod.

After each equilibration, the glass was allowed to settle to the bottom of the tube; then the tube was removed from the furnace, cooled, and broken to remove the charge. The bottom portion containing the glass was quickly washed with water to dissolve the salt and then filtered, washed with alcohol, air-dried on a suction filter, and oven-dried at 110° for about 30 min. The top portion of salt was filtered to remove any glass particles by placing it in the top of a coarse sintered-glass filter tube in the furnace and allowing the salt to filter into a clean tube as it melted. Portions of the cooled, filtered salt and the washed glass were then weighed and radioassayed in a well-type γ-ray scintillation counter. From the specific activities of the two phases the distribution coefficient, K_d, was calculated

$$K_d = \frac{\text{specific activity of glass phase}}{\text{specific activity of salt phase}}$$

The sintered-glass filter adsorbed no Cs, Sr, or Ba from the melt, but did adsorb about 40% of the Eu. Accordingly, a correction was made for Eu in the filtrate by measuring the holdup from a standard melt containing the same Eu concentration as the melt from which exchange occurred, about 3 ppm.

The foregoing procedure measured the K_d for uptake by the glass, since the radioactive tracer started in the salt phase. To measure the K_d for desorption, the glass containing solute was placed in a tube with fresh sodium nitrate and the procedure was repeated from there on.

Column Operation.—To a Pyrex glass column 145 mm long and 3 mm in diameter was added about 13 cm of 60–80 mesh sodium borate glass of approximate composition $Na_2O \cdot 3B_2O_3$. To the top of this column was added about 1 cm of the same glass which had been in contact for 10 min with molten $LiNO_3$–KNO_3 eutectic

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containing dissolved $Co(NO_3)_2$ and which was colored blue by the cobalt. Eluants used were $LiNO_3$–KNO_3 eutectic and $LiNO_3$–KNO_3 eutectic containing about 20 wt % of an equimolar mixture of LiCl and KCl.

Results

Sodium borate glass of composition $Na_2O \cdot 3B_2O_3$ showed good selectivity between solutes, but a rather slow exchange rate. Good selectivity would be expected of borate glasses in this composition region, since molten sodium borate shows the best selectivity at about this same $Na_2O:B_2O_3$ ratio.[21] Exchange rate measurements with Na^{22}-labeled phases showed that higher temperature and smaller particle size allowed equilibrium to be approached more quickly. However, the exchange rate was not really satisfactory until a borate glass was prepared which had been presaturated with salt while molten. The composition of this glass in mole % was 21.8 Na_2O, 60.2 B_2O_3, and 18.0 NaCl. Na^{22} reached nearly its equilibrium value between molten $NaNO_3$ and this glass of 60–100 mesh size in 45 min at 500°. Table I shows K_d values of the solutes between this glass and molten $NaNO_3$ at 550°. Shown for comparison are equilibrium K_d values of the same solutes between molten borate glass of the same $Na_2O:B_2O_3$ ratio and molten NaCl at 830°.[21]

TABLE I

COMPARISON OF K_d[a] VALUES FOR SALT-SATURATED BORATE GLASS OF $Na_2O:B_2O_3$ RATIO 0.326: SOLID GLASS IN $NaNO_3$ *vs.* LIQUID GLASS IN NaCl

	80–115 mesh glass in $NaNO_3$ at 550°				Liquid borate in NaCl at 830°
Solute	K_d (adsorption)	Equil. time, hr	K_d (desorption)	Equil. time, hr	K_d (equilibrium)[21]
Cs^+	0.0015	0.5	...	...	0.26
Na^+	0.84[b]	...	0.84[b]	...	0.55
Ba^{2+}	1.6	0.5	17	1	2.2
Sr^{2+}	191[c]	2	204	0.5	5.7
Eu^{3+}	3900	1	4000	1	2600

[a] K_d = (moles of solute per gram of glass)/(moles of solute per gram of salt). [b] Calculated from analysis of macro constituents. [c] 450°.

The nitrate eutectic apparently eluted no cobalt from the column but the melt containing chloride promptly removed the blue cobalt, leaving only a small black oxide residue.

Discussion

From even these preliminary results it appears that borate glasses are more generally effective than any other exchanger yet tested in molten salts. They show higher selectivity for solute ions in molten nitrate than do any of the other exchangers for which selectivity has been measured and even show a wider spread of K_d values than do molten borates with molten NaCl.[21]

The manner in which borate glasses show selectivity toward cations is probably the result of the special nature of the functional groups in the borate network. Data obtained so far indicate that the order of selectivity of high-alkali borates, both molten and solid, for uncomplexed cations in fused-salt solvents is that of increasing field strength of the cation. This order and the magnitude of the K_d values suggest a distribution mechanism based on the attraction of unsolvated cations to sites of highly localized negative charge within the borate network. A different selectivity sequence is found with zeolites,[2] where selectivity is based more upon a cation's size than its charge. From the structure of zeolites[23] it may be concluded that the functional groups for ion exchange are $Al(O/2)_4^-$ tetrahedra, where O/2 denotes a shared, bridging oxygen atom. The negative charges on these tetrahedra are not highly localized, and high field-strength cations do not seem to prefer greatly this environment to that of a nitrate melt. In borate glasses, the functional groups probably consist mostly of $B(O/2)_4^-$ and a few $B(O/2)_2O^-$ groups. The negative charge on these groups is more localized than that of the $Al(O/2)_4^-$ group: in the case of $B(O/2)_2O^-$ because the charge is centered on the nonbridging oxygen and in the case of $B(O/2)_4^-$ because this group is smaller than $Al(O/2)_4^-$ and probably not as symmetrical. Actually, the main reason for the high selectivity of borates for highly charged cations may be the pairing of negative charges in polyborate groups. Evidence of such pairing comes from the observation in molten silver borate that the silver ions seem to occur in pairs.[24] Molten and solid borates tend to retain elements of polyborate structural groups which are present and identifiable in crystalline borates.[25] Groups which contain paired negative charges and which may prevail in the borate glasses used here are $B_8O_{13}^{2-}$ and $B_4O_7^{2-}$, evidence for which comes from the treatment of phase diagram data in the Na_2O–B_2O_3 system.[25]

Ion-exchange separations on borate glasses should be possible from a variety of fused-salt solvents. Distribution behavior of individual solutes will differ greatly according to the solvent system and glass formulation.

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Phosphoryl Fluorosulfate

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The new compound phosphoryl fluorosulfate, $PO(OSO_2F)_3$, has been prepared by the reaction of peroxydisulfuryl difluoride with phosphoryl bromide. It

$$POBr_3 + 6S_2O_6F_2 = PO(OSO_2F)_3 + 3Br(OSO_2F)_3$$

appears that phosphoryl fluorosulfate is the first example of a compound in which a fluorosulfate group is