CORRESPONDENCE

Immiscibility Diagrams of Molten Sodium Bromide–Sodium Polyborates at 800° and 980° C.

SIR: The existence, in sodium polyborate melts, of numerous ternary complexes with NaBr has been suggested [Dunicz and Scheidt (*1*), Table II]. In particular, several closely spaced, sudden digressions (points *B, C, D, E, F, G,* and *H*) on the "binodal" curve (Figure 1, top) have been discussed in terms of these complexes. Their reality is said to be supported by the orderly sequence of the corresponding tie lines. A more direct proof for the reproducibility of these sharp fluctuations in the solubility of NaBr is unfortunately missing. Similar cases are not known among equilibria involving only liquids (*2*). What amounts to discontinuities, large jumps, including abrupt change of sign, in the derivative of the excess free energy of a solute (such as NaBr) as a function of the composition of the solvent ($NaBO_2$–B_2O_3 ratio) are known to occur only as a result of a *phase change*—i.e., in the nature of the (conjugate) phase in equilibrium with the solution. [Examples are the equilibria *b, c, d, e, f,* and *g* of the liquid, aqueous phase of the ternary system H_2O–Na_2O–B_2O_3 with a *pair* each of a sequence of individual *solid* polyborate hydrate phases *M, O, D, P, Q,* and *B* of as many different compositions (*3*).] Obviously no such phase changes are, or could have been, implied by Dunicz and Scheidt for the conjugate bromide-rich *liquid* of the molten bromide-polyborate system; for the binodal curve between *B* and *H*, according to the tie lines given, there is only one phase in equilibrium with the polyborate melt, simply molten NaBr, more than 98% pure. One is led to the conclusion that the observations described are irregularities caused by experimental difficulties which are considered in the following.

Significantly, the severe scattering occurs at 800°, at compositions in the vicinity of disodium octaborate, $Na_2O \cdot 4B_2O_3$, which freezes at 816°—i.e., *above* the test temperature. This strongly suggests a high viscosity of the melts in question, that may have greatly reduced the rate with which complete equilibrium could be reached during the periods of motionless contact between the two liquid layers (*2*). The closeness to the freezing temperatures might have been of still more serious influence during the periods of agitation which took place outside the furnace where the possibility of a temperature drop even involving freezing does not seem to have been excluded. In fact, similar experimental uncertainties are apparent in the entirely improbable results for the chloride phase in the corresponding chloride system at 810°, just above the freezing point of NaCl [(*4*) Figure 3, top, right hand corner]. At the higher temperature of 980°, both the chloride and the bromide diagrams are much more reasonable [(*4*) Figure 3, bottom, and (*1*) Figure 1, bottom]. The absence of "jags" at 810° in the chloride-containing polyborate phase may perhaps be connected with a rapid decrease in viscosity with increasing test temperature (810° *vs.* 800° in the bromide system; note also the much smaller concentration range for solid $Na_2O \cdot 4B_2O_3$ + liquid on the binary edge at 810°, reflecting the safer distance of the test from the freezing temperature).

Another objection of a fundamental nature applies to the interpretation of any liquid-liquid phase equilibria in terms of "rather stable complexes" at "simple stoichiometric ratios of the components." The coincidence of the intersection of two straight lines, drawn for simple stoichiometric ratios, with a point on the binodal curve possesses no significance whatsoever with respect to the possible existence of a "complex." In fact, even if any one of the complexes proposed, five with bromide and two with chloride, were known to exist as a solid *double salt* analogous to boracite, $MgCl_2 \cdot 2Mg_3B_8O_{15}$, there would be no stringent reason to expect its existence as a "complex" in the liquid of corresponding composition, whether saturated with respect to a second liquid or not—i.e., in any form other than with essentially random mixing of halide and polyborate ions.

The real significance of the reported phase diagram data may simply be the following. The electrolytes NaCl or NaBr (contrary to NaF which, because of the smaller size of F, is able to form oxyfluoroborate, with B-F linkages) do not react with B_2O_3 and are hardly at all miscible with, or soluble in, this molecular liquid of low dielectric constant. Added $NaBO_2$, however, does react with B_2O_3 to form polyborates—i.e., salts—of increasing simplicity and, therefore, greater miscibility in the liquid state with the simple halide salt of the same alkali metal.

LITERATURE CITED

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