it is possible to account for these deviations as caused by the association of the NMA or water.

Apparently, the structure of NMA is less affected, and thus has a greater degree of polymerization in benzene than in dioxane. This is in agreement with the postulate made earlier (*1*) and with the dielectric constant data.

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

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Immiscibility isotherms at 800° and 980° C. were obtained for the boron oxide–sodium metaborate–sodium bromide system. Mixtures of the components were equilibrated in graphite crucibles, which were vacuum-sealed in silica-glass cartridges. The two isotherms differ noticeably in their shapes. In the boron oxide–rich phase, the components appear to form mixed compounds.

IMMISCIBILITY isotherms of molten sodium chloride-sodium polyborate mixtures at 810° and 980° C. have been published (*1*). The study was continued to embrace the corresponding system with sodium bromide at comparable temperatures.

EXPERIMENTAL

The experimental procedures were the same as those employed in studying the immiscibility of sodium chloride-sodium polyborates (*1*). However, in this investigation, the molten sodium bromide phase, denser than the conjugate boron oxide phase, often leaked through the crucible floor owing to the porosity of the graphite. To reduce its porosity, each graphite crucible, prior to use, was lightly dusted on the inside with powdered boron oxide and heated for 1 hour at 980° C. in a capped silica-glass test tube.

The analytical data, expressed in mole per cent B_2O_3, $NaBO_2$, and NaBr, are presented in Table I. The phase diagrams at 800° and 980° C. constructed from these data are depicted in Figure 1. In addition, Figure 2 shows log-log plots of the ratios of $NaBO_2$ to the major components (boron oxide and sodium bromide) in the respective conjugate phases. These plots apply to run numbers 20 to 29 at 800° C. and 7 to 14 at 980° C. The corresponding tie lines in Figure 1 are similarly numbered.

DISCUSSION

Some of the features of the system are outlined below, and, where relevant, are compared with those of sodium chloride-sodium polyborates (*1*):

a. The miscibility gaps for sodium bromide-sodium polyborates are larger than those for sodium chloride-sodium polyborates.

b. The solubility of B_2O_3 in molten sodium bromide (Table I) is much smaller than it is in the molten sodium chloride.

c. Plait-point compositions of the present system are the same at 800° and 980° C. (Table I).

d. At 800° C., a separation is noticeable between the NaBr-$NaBO_2$ composition edge and the binodal curve. For the sodium chloride-sodium polyborate system at 810° C., this separation (disregarding the deformity at the NaCl corner) is barely evident. The difference may be due to a retrograde solubility of B_2O_3, in presence of $NaBO_2$, that is greater in the sodium halide below 810° C. than above it.

e. The quenched boron oxide phases of the mixtures equilibrated both at 800° and 980° C. and having comparable $NaBO_2$-to-B_2O_3 ratios appear alike. But, in contrast to sodium bromide phases, they ostensibly are physically different along the binodal curve. Thus, in the range from the B_2O_3 corner to midway between the 2 to 3 and 1 to 1 $NaBO_2$-to-B_2O_3 ratios, the phases are uniformly glassy and clear. In the subsequent range up to the 2 to 1 $NaBO_2$-to-B_2O_3 ratio, the phases are progressively more opaque and finally are white. From there to the plait point they are increasingly brittle.

f. In Figure 1 (top), a short section on the binary B_2O_3–$NaBO_2$ composition edge, labelled "Solid $Na_2O \cdot 4B_2O_3$ + Liq.", refers to the range within which solid disodium octaborate, m.p. 816° C., separates from the binary melt at 800° C. (Table I). Significantly, only the part of the binodal curve that faces this section is prominently jagged. Although

Table I. Equilibrium Composition of Conjugate B_2O_3 and NaBr Phases (Mole %) for NaBr–B_2O_3–$NaBO_2$ System

	B_2O_3 Phase			NaBr Phase		
Run No.	NaBr	$NaBO_2$	B_2O_3	NaBr	$NaBO_2$	B_2O_3
			800° C.			
B_2O_3–NaBr Mixture[a]	. . .	. . .	100.00	~99.00	. . .	~1.00
1	0.81	2.78	96.41	. . .	. . .	. . .
2	1.47	4.80	93.73	99.65	0.00	0.35
3	3.95	13.45	82.60	99.93	0.00	0.07
4	5.12	17.45	77.43	. . .	. . .	. . .
5	6.19	21.49	72.32	99.93	0.00	0.07
		$NaBO_2 : B_2O_3 = 1 : 3$				
6	6.31	21.32	72.37	. . .	. . .	. . .
7	7.31	26.63	66.06	99.88	0.02	0.10
8	7.73	28.33	63.94	99.66	0.08	0.26
		$NaBO_2 : B_2O_3 = 1 : 2$[b]				
9	8.54	31.14	60.32	99.26	0.28	0.46
10	9.48	31.10	59.42	99.34	0.28	0.38
11	7.61	32.13	60.26	99.48	0.12	0.40
12	9.95	32.02	58.03	99.55	0.16	0.29
13	10.84	31.69	57.47	99.46	0.24	0.30
14	9.60	33.50	56.90	99.11	0.52	0.37
15	11.25	34.59	54.16	. . .	. . .	. . .
		$NaBO_2 : B_2O_3 = 2 : 3$				
16	12.27	36.12	51.61	99.42	0.34	0.24
17	13.24	37.20	49.56	99.28	0.48	0.24
18	14.45	36.96	48.59	99.22	0.66	0.12
		$NaBO_2 : B_2O_3 = 0.78 : 1$[b]				
19	14.01	40.88	45.11	98.54	1.15	0.31
		$NaBO_2 : B_2O_3 = 1 : 1$				
20	14.52	43.20	42.28	96.66	2.47	0.87
21	14.15	43.95	41.90	96.43	2.47	1.10
22	17.55	48.04	34.41	92.52	6.24	1.24
23	19.40	49.70	30.90	88.49	9.78	1.73
24	20.88	50.32	28.80	86.65	11.52	1.83
25	21.68	50.51	27.81	85.56	12.75	1.69
		$NaBO_2 : B_2O_3 = 2 : 1$				
26	26.14	50.59	23.27	81.45	16.46	2.09
27	32.23	48.84	18.93	75.04	21.54	3.42
28	34.30	47.61	18.09	67.13	27.18	5.69
29	39.76	44.97	15.27	61.16	31.52	7.32
Plait point[a]	49.00	39.50	11.50	49.00	39.50	11.50
			980° C.			
B_2O_3–NaBr Mixture[a]	. . .	. . .	100.00	~99.50	. . .	~0.50
1	1.39	4.36	94.25	99.74	0.00	0.26
2	2.82	14.90	82.28	. . .	. . .	. . .
3	4.98	20.03	74.99	99.68	0.08	0.24
4	7.78	26.69	65.53	98.94	0.62	0.44
5	10.44	31.19	58.37	98.62	1.26	0.12
		$NaBO_2 : B_2O_3 = 2 : 3$				
6	11.99	37.04	50.97	97.31	2.53	0.16
7	13.19	43.11	43.70	93.80	5.64	0.56
		$NaBO_2 : B_2O_3 = 1 : 1$				
8	16.45	46.37	37.18	89.66	9.31	1.03
9	19.24	48.38	32.38	85.02	13.12	1.86
10	20.85	48.99	30.16	80.92	16.63	2.45
11	22.62	49.09	28.29	80.05	17.55	2.40
		$NaBO_2 : B_2O_3 = 2 : 1$				
12	28.89	47.93	23.18	76.45	20.40	3.15
13	36.69	46.02	17.29	67.43	26.97	5.60
14	42.19	43.41	14.40	59.64	32.34	8.02
Plait point[a]	49.50	39.00	11.50	49.50	39.00	11.50

[a] Data estimated from conjugation curve. [b] Solid $Na_2O \cdot 4B_2O_3$, m.p. 816° C., separates from the melt of the B_2O_3–$NaBO_2$ binary system, at 800° C., in the range encompassing the 1 : 2 to 0.78 : 1 ratios of $NaBO_2$ to B_2O_3 (*3*).

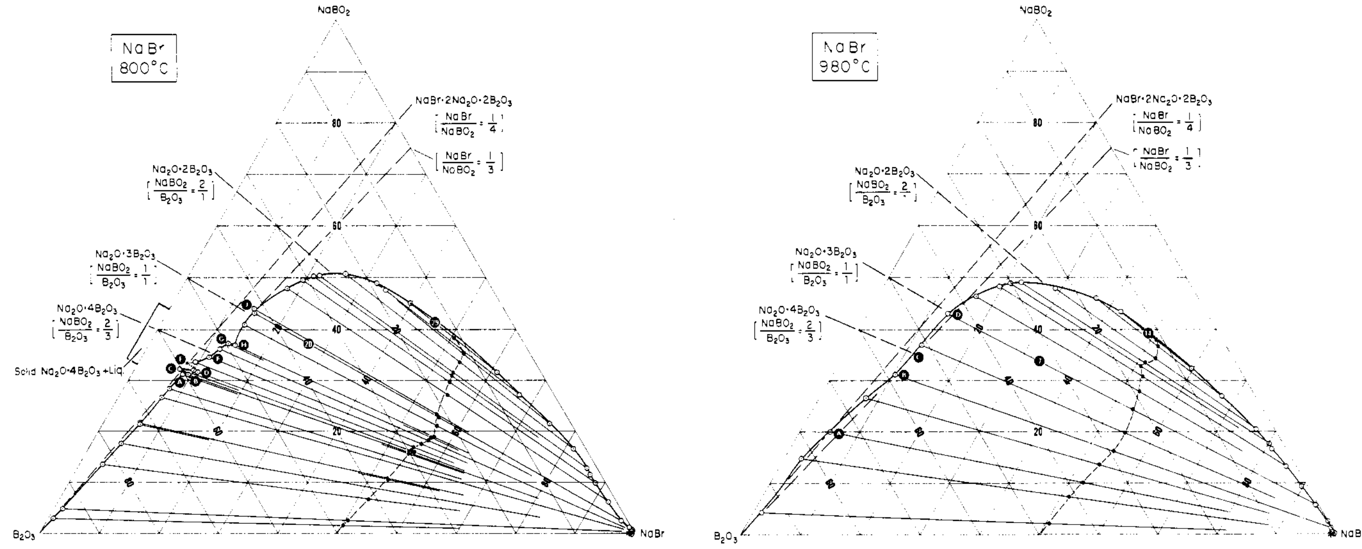

Figure 1. Phase diagram of NaBr–B$_2$O$_3$–NaBO$_2$ system
Components expressed in mole %
Left 800° C. Right 980° C.

it is recognized that the jaggedness may be perplexing, its reality is supported by the orderly sequence of the corresponding tie lines. Besides, the quenched boron oxide phases, where the jagged section of the curve is present, are uniformly glassy and clear (see *e.* above).

Amorphous solids or glasses result most often from cooling of viscous liquids. High viscosity of a liquid signifies greatly restricted motion of the molecules or ions, rendering impossible their orientation favorable for crystal formation during cooling. Furthermore, only with extremely rare exceptions, the viscosity of the liquid increases with cooling. Thus, it is practically inconceivable that during the quenching of the viscous melts under discussion any cross-solution or mixing of the conjugate phases might take place. Anyway, even if the latter could occur, the binodal curve should be jagged near the NaBr corner, because sodium bromide phases at 800° C. are fluid. Since the curve is not jagged at that corner, it is suggested that the observed

Table II. Implied Stoichiometric Combinations of Sodium Bromide with Disodium Octaborate and Disodium Tetraborate in Boron Oxide Phase of NaBr–B$_2$O$_3$–NaBO$_2$ System at 800° and 980° C. and Interpretations

Reference Points, Figure 1	NaBr		Interpretation
	$Na_2O \cdot 4B_2O_3$	$Na_2O \cdot 2B_2O_3$	
		800° C.	
B_2O_3 corner up to *A*	Between 1 : 2 and 2 : 3		Mixtures of $NaBr \cdot 2(Na_2O \cdot 4B_2O_3)$, $2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ and uncombined B_2O_3
B	2 : 3		On the *A* to *B* and *C* to *D* paths $2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ is formed from $NaBr \cdot 2(Na_2O \cdot 4B_2O_3)$ and NaBr; on the *B* to *C* and *D* to *E* paths $NaBr \cdot 2(Na_2O \cdot 4B_2O_3)$ is formed from $2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ and $Na_2O \cdot 4B_2O_3$
C	1 : 2		
D	2 : 3		
E[a]	1 : 2		
F	2 : 3		$2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ alone
G	2 : 3	1 : 1	Mixture of $2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ and $NaBr \cdot Na_2O \cdot 2B_2O_3$
H	2 : 3	3 : 2	Mixture of $2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ and $3NaBr \cdot 2(Na_2O \cdot 2B_2O_3)$
I	2 : 3	2 : 3	Equimolar mixture of $2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ and $2NaBr \cdot 3(Na_2O \cdot 2B_2O_3)$
		980° C.	
B_2O_3 corner up to *A*	1 : 2		Mixture of $NaBr \cdot 2(Na_2O \cdot 4B_2O_3)$ and uncombined B_2O_3
B	2 : 3		Mixture of $2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ and uncombined B_2O_3
C	2 : 3		$2NaBr \cdot 3(Na_2O \cdot 4B_2O_3)$ alone
D	1 : 2	2 : 3	Equimolar mixture of $NaBr \cdot 2(Na_2O \cdot 4B_2O_3)$ and $2NaBr \cdot 3(Na_2O \cdot 2B_2O_3)$

[a] Extrapolated point.

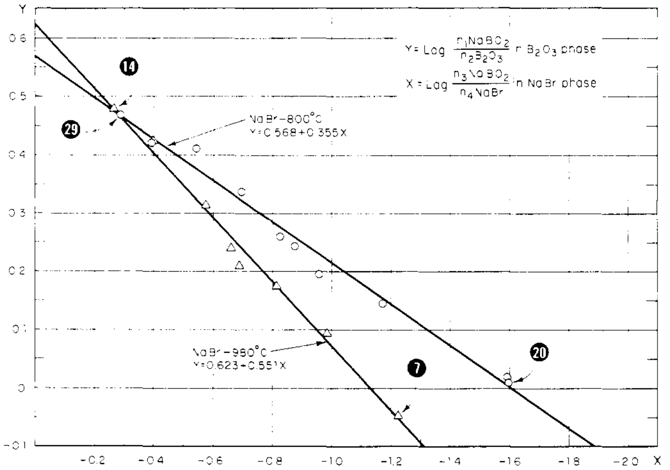

Figure 2. Log-log plots of distribution of $NaBO_2$ between B_2O_3 and NaBr in conjugate phases at 800° and 980° C.

jaggedness stems from formation of diverse additive compounds between disodium octaborate and sodium bromide. A more detailed tentative interpretation of the jaggedness is given in Table II.

g. The log-log regression lines of the molar distribution of $NaBO_2$ between the major components of the conjugate phases (Figure 2) agree with the finding (*1*) that, the ratio of $NaBO_2$-to-B_2O_3 in the boron oxide phase being fixed, proportionately more $NaBO_2$ (as a component) is extracted by the conjugate sodium halide phase with higher temperature.

INTERACTION OF COMPONENTS

Metal halides tend to react additively with polyborates, forming a variety of boratohalides (*2*). Therefore the diagrams (Figure 1) were examined for possible formation of such compounds among disodium octaborate, disodium tetraborate, and sodium bromide in the equilibrated melts. Accordingly, two sets of lines were drawn on the diagrams. These lines project from the B_2O_3 and NaBr corners to the NaBr-$NaBO_2$ and B_2O_3-$NaBO_2$ composition edges, respectively, at the indicated simple stoichiometric ratios of the components. At the point on the isotherm at which such lines mutually intersect, all the components exist in exact stoichiometric combination. For example, the lines representing the ratios 1NaBr:$3NaBO_2$, or 1NaCl : $3NaBO_2$ (*1*), and $2NaBO_2 : 3B_2O_3$ intersect precisely on each of the isotherms. This observation suggests formation of stable complexes: $2NaX \cdot 3(Na_2O \cdot 4B_2O_3)$, where X stands for Cl or Br. This and additional inferences are presented in Table II.

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Editor's Note: In connection with this article, read the critical comment on page 295, submitted as correspondence by M. A. Bredig.

Equilibrium Adsorption of Liquid Phase Normal Paraffins on Type 5A Molecular Sieves

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Normal paraffins were adsorbed from the liquid phase on Type 5A molecular sieves to determine the effect of molecular size, temperature, and concentration on the equilibrium loadings. Single component adsorptive capacities varied irregularly with molecular size and were independent of temperature when loadings were expressed on a volume basis. In liquid phase adsorption from binary systems, the lower molecular weight normal paraffin was adsorbed preferentially. Temperature had a negligible effect on the composition of adsorbate in equilibrium with a given liquid composition. The equilibrium data for each binary system could be correlated by a single value of relative adsorptivity.

MOLECULAR sieves are crystalline adsorbents with pore openings of fixed and uniform dimensions. The surface of adsorption is almost entirely internal and is accessible through channels penetrating the entire volume of the adsorbent (*1*). Molecular sieves are used in the petroleum industry for the efficient separation of normal paraffins from their isomers (*3, 8*). The importance of these separations has increased greatly with the introduction of biodegradable detergents requiring normal paraffins with 10 to 14 carbon atoms.

Equilibrium data for the adsorption of normal paraffins on molecular sieves are incomplete. Most of the available data are for the adsorption of pure normal paraffins from the vapor phase (*2, 5*). The purpose of this study was to provide equilibrium information for liquid phase adsorption of both pure normal paraffins and binary mixtures on Type 5A molecular sieves. The effect of molecular size,

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