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ノート・Note

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Heats of Immersion of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ Glasses in *n*-Butylamine-Cyclohexane Solution

By

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$\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ ガラスの *n*-ブチルアミン-シクロヘキサン溶液への浸漬熱

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It is well known that some physical properties of alkali borate glasses, such as thermal expansion and viscosity, show a peculiar dependence on the content of alkali oxide. This anomaly, which is known as "boric oxide anomaly", has been explained by many authors in terms of the change of the co-ordination number of boron atom to oxygen atoms. B_2O_3 glass is considered to be mainly composed of triangular BO_3 groups which share their oxygen vertices to give a disordered three-dimensional network. When alkali oxide is added to B_2O_3 glass, some of the three-co-ordinated borons (3B), or BO_3 groups, are converted to four-co-ordinated borons (4B), or tetrahedral BO_4 groups.

In a BO_3 unit, where the trivalency of boron results from the sp^2 hybridization, one vacant p-

orbital is left on boron atom. Thus the boron atoms in BO_3 groups on the glass surface are expected to act as acid sites to electron-pair donors. In BO_4 units the oxygen atoms are bonded by tetrahedrally directed bonds which result from the sp^3 hybridization. Thus no vacant p-orbital is left on each boron atom in BO_4 groups. The purpose of the present work is to study the contribution of acid-base interaction to the heat of immersion of borate glasses in organic base.

$\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses were prepared from Na_2CO_3 and H_3BO_3 . The organic base used was *n*-butylamine, which was of reagent grade and was purified by distillation before use. The specific surface area of glass sample was determined by BET method. Heat of immersion, H_i , was measured with a twin-

Table 1. Compositions and specific surface areas of glass samples and heats of immersion, H_i .

Sample	Composition (mol% of Na ₂ O)	Specific surface area (m ² /g)	H_i (J/m ²)
B ₂ O ₃	0.0	0.37	936
Na ₂ O·10 B ₂ O ₃	9.1	0.84	404
Na ₂ O·6 B ₂ O ₃	14.5	0.12	396
Na ₂ O·4 B ₂ O ₃	20.0	0.52	393
Na ₂ O·2 B ₂ O ₃	33.3	0.77	136

Fig. 1. Heats of immersion as a function of Na₂O content.

microcalorimeter which was used in the previous work¹⁾. The details of the apparatus and the procedure are described in the previous paper¹⁾. The powdered sample in a glass ampoule was degassed at 120°C for 5 hours. The sample was immersed in 50 ml of the solution of *n*-butylamine in cyclohexane (1 : 9 by weight). Cyclohexane was selected as the solvent because of its non-polar character. Indeed, the H_i of the present glasses in cyclohexane ranged from 0.3 to 0.8 J/m².

In table 1 the compositions and the specific surface areas of the samples studied are shown together with the observed values of H_i . Fig. 1 shows the plot of H_i against the molar percentage of Na₂O. It is apparent from the figure that H_i decreases with increasing Na₂O content. The result suggests that H_i directly depends on the numbers of 3B on the surface of the glass. When Na₂O is added to B₂O₃ glass, some of 3B are converted to 4B. In the glass of the composition $xR_2O \cdot (1-x)B_2O_3$, where R₂O is an alkali oxide and x the molar fraction, the atomic fraction of 4B increases with x as $x/(1-x)$ up to $x \div 0.33$. Therefore, the fraction of 3B is given by

$$1 - \frac{x}{1-x} = \frac{1-2x}{1-x} \dots\dots\dots (1)$$

The atomic percentage of boron atoms in the glass of the composition $xNa_2O \cdot (1-x)B_2O_3$ is given by

Fig. 2. Heats of immersion as a function of atom % of three-co-ordinated boron.

$$\frac{2(1-x)}{[3x+5(1-x)]} \times 100 = \frac{2(1-x)}{5-2x} \times 100 \dots\dots (2)$$

Thus the atomic percentage of 3B, N_3 , is given by the equation (3), which is obtained by (1) × (2).

$$N_3 = (1) \times (2) = \frac{2(1-2x)}{5-2x} \times 100 \dots\dots\dots (3)$$

Fig. 2 shows the plots of H_i against N_3 . H_i increases with an increase of N_3 . Since the density of 3B on the glass surface may increase with increasing of N_3 in bulk, the result indicates that the predominant factor which contributes to the heat of immersion in the present case is the acid-base interaction between the three-co-ordinated boron atoms on the glass surface and *n*-butylamine molecules.

It has been well known that hydroxyl groups are formed on silica surfaces. Extensive studies have been made on the silanol groups, Si-OH, because of the use of silica gel or silica alumina as a catalyst. There are some evidences that the silanol groups interact with basic molecules such as benzene and amines^{3),4)}. The surfaces of borate glasses probably have the same type of hydroxyl groups, B-OH, as those in silica or silicate glasses. The density of the B-OH groups on the surface is considered to be similar to that of the silanol on silica surfaces, which has been calculated as several groups per 100 Å²²⁾. The heat of immersion of silica gel in the solution of *n*-butylamine in benzene has been measured³⁾, the observed value was about 200 erg/cm² (=0.2 J/m²). The values of H_i observed in the present measurements are too high to attribute to the energy of interaction between the hy-

droxyl groups and the amine molecules. Taking the facts mentioned above into consideration, we can conclude at present that the remarkably large heats of immersion of borate glasses in the solution of *n*-butylamine in cyclohexane result from the acid-base interaction between the three-co-ordinated borons on the glass surfaces and the amine molecules.

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