Thermochimica Acta, 40 (1980) 261—267
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

HEATS OF IMMERSION OF BORON PHOSPHATES IN PYRIDINE AND MAGNESIA IN BENZOIC ACID SOLUTION

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(Received 31 January 1980)

ABSTRACT

The heats of immersion of the systems B_2O_3—P_2O_5 and Na_2O—B_2O_3—P_2O_5 in pyridine have been measured by the use of a solution microcalorimeter. In the composition range $R < 1$ (R = atomic ratio, B/P) the heat of immersion was relatively small and was almost independent of R. The heat increased markedly with boron content in $R > 1$. The increase of heat qualitatively parallels that of surface acidity. Introduction of the Na_2O component reduced both heat of immersion and acidity. MgO was immersed in a benzene solution of benzoic acid. The heat of immersion increased with an increase of surface basicity.

INTRODUCTION

When a solid is immersed in a liquid, the solid surface comes into contact with the liquid molecules and an exothermic heat effect is observed. The released heat is the enthalpy change, ΔH_i, for the surface change from solid surface or solid—gas interface to solid—liquid interface. Measurement of the heat of immersion provides useful information for investigating the molecular processes taking place at a solid surface. In a previous paper [1] the heats of immersion of alkali borate glasses in several organic bases were reported. The results suggested that the acid—base interaction at the glass—liquid interface made a large contribution to the relatively high values of heats of immersion.

In the present work measurements have been made of the heats of immersion of boron phosphates, including the systems B_2O_3—P_2O_5 and Na_2O—B_2O_3—P_2O_5, in pyridine, and of magnesium oxide in benzoic acid solution. The relations of heats of immersion to acidity and basicity of the solid surfaces are discussed.

EXPERIMENTAL

Boron phosphate was prepared from boric acid and phosphoric acid. The atomic ratios (boron/phosphorus, referred to as R) were 0.50, 0.67, 1.00, 1.50 and 2.00. The requisite amounts of the reagents were dissolved in distilled water. The solution was evaporated to dryness on a water bath. The solid mixture obtained was heated in an alumina crucible at 1000°C for 2 h, and cooled to room temperature in a desiccator. Sodium borophosphate glass was prepared from sodium dihydrogen phosphate and boric acid. The atomic ratios (*R*) were 0.5, 1.0, 1.5 and 2.0. The mixture of the reagents was dehydrated by gentle heating and melted at 800°C for 1 h in an alumina crucible. The melt was quenched on a stainless steel plate. Magnesium oxide was prepared by heating basic magnesium carbonate, $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5\,H_2O$, at 400, 500 and 600°C for 2 h.

Commercial pyridine and *n*-butylamine were purified by distillation immediately after refluxing over calcium hydride for 3 days or more. Benzene was shaken with concentrated sulfuric acid until free from thiophene, then with water and dilute sodium hydroxide and washed with water, dried over calcium chloride, followed by treatment with metallic sodium and distillation.

A twin-microcalorimeter (Tokyo Riko TIC-2S) was used for measurements of heats of immersion. One of the twin-cells is shown in Fig. 1. It consists of a 180 ml Dewar flask placed in one of the holes bored in a large aluminum block which serves as a thermostat. The heater for calibration is made of manganin wire and immersed in a thin glass tube partially filled with silicone oil for better thermal contact. The temperature sensor is composed of a 20 kΩ (at room temperature) thermistor placed in the bottom of a thin glass tube partially filled with silicone oil. The stirrer and ampoule holder are made of fluorocarbon resin. The calorimeter was previously calibrated with the heat of solution of potassium chloride in pure water [2].

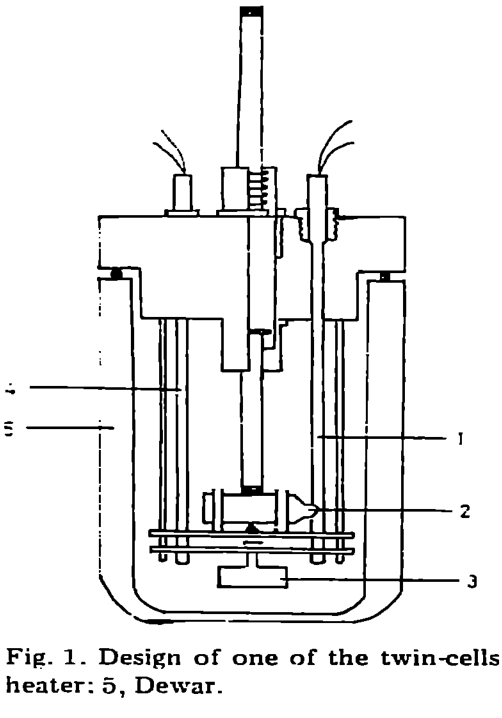

Fig. 1. Design of one of the twin-cells. 1, Thermistor; 2, sample; 3, stirrer; 4, calibration heater; 5, Dewar.

About 0.5 g of powdered sample (—350 mesh) in a 1 ml glass ampoule was degassed at 120°C for several hours, then the ampoule was sealed. The ampoule was held under the liquid in the calorimeter cell and an empty ampoule was in another cell. After thermal equilibrium had been established, the two ampoules were broken simultaneously and the temperature rise caused by evolution of the heat of immersion was recorded as the unbalance potential of the bridge. A known quantity of heat was supplied by the calibration heater before and after breaking of the ampoules. The heat of immersion was determined by comparing the deflection by sample immersion with that by the calibration heat. Deflections were determined on the chart as the differences between the extrapolated lines of the temperature drifts.

Acid and base strengths were measured as follows. Two ml of dry benzene were added to about 0.1 g of powdered sample in a test tube. A few drops of a benzene solution of an indicator were added. The strength was judged by observation of coloration of the sample surface. Acidity was measured by Benesi's method [3]. An ampoule containing the dry sample was broken in 10 ml of dry benzene and a few drops of a benzene solution of an indicator were added. It was titrated with a benzene solution of *n*-butylamine, the concentration of which was about 2×10^{-2} mmole ml^{-1}. Acidity is calculated by

$$A = (cV)/(ws)$$

where A is acidity (mmole m^{-2}), c is the concentration of *n*-butylamine (mmole ml^{-1}), V is the titre (ml), w is the weight of sample (g), and s is the specific surface area of sample ($m^2\ g^{-1}$). Surface basicity was measured in a similar manner to the acidity measurement. The sample dispersed in dry benzene was titrated with a benzene solution of benzoic acid (5×10^{-2} mmole ml^{-1}). Specific surface area was measured by nitrogen adsorption at liquid nitrogen temperature.

RESULTS AND DISCUSSION

The system B_2O_3—P_2O_5

The experimental results of heats of immersion in pyridine are shown in Table 1. In the composition range $R \leqslant 1.0$, ΔH_i is almost independent of the composition and is relatively low. On the contrary, in the range $R > 1.0$, the heat increases markedly with an increase of boron content, as shown in Fig. 2. In the previous work [1] it was found that in a given organic base the heat of immersion decreased with an increase of alkali oxide content. This behavior was interpreted in terms of the structural changes taking place in the glass when the alkali oxide content was changed.

Boric oxide (B_2O_3) glass is considered as being composed of triangular BO_3 groups which shear their oxygen vertices to give a three-dimensional network. Trivalency of the boron results from sp^2 hybridization as in boron trihalides, and one vacant *p*-orbital is left on each boron atom. When alkali oxide is added, some of the BO_3 groups are converted to tetrahedral BO_4

TABLE 1

Heats of immersion and acidity of the system B_2O_3—P_2O_5

R = B/P	Specific surface area (m^2 g^{-1})	$-\Delta H_i$ (J m^{-2})	Acidity (mmole m^{-2})	
			$H_0 \leq +3.3$	$H_0 \leq -3.0$
0.50	2.8	0.527	5.46×10^{-3}	1.25×10^{-3}
0.67	2.0	0.704	6.28×10^{-3}	0.88×10^{-3}
1.00	2.6	0.709	5.79×10^{-3}	0.81×10^{-3}
1.50	1.6	34.0	14.1×10^{-3}	12.6×10^{-3}
2.00	1.5	138	25.7×10^{-3}	11.5×10^{-3}

groups. The oxygen atoms are bonded by tetrahedrally directed bonds resulting from sp^3 hybridization. No vacant orbital is left on each boron atom in BO_4 groups. It is well known that the atomic fraction of three-coordinated boron atoms decreases with an increase of alkali oxide content in the alkali borate glasses [4]. If we assume that the three-coordinated boron atom on the glass surface acts as a Lewis acid site, we may expect high immersional heat to be observed on immersion in a liquid of electron-pair donor.

Since the boron atoms in the materials studied here are considered to be three-coordinated, we can expect high immersional heat for the sample of high boron content. In the present work every sample was always immersed in pyridine, and the relation between ΔH_i and acidity of the sample was investigated. In Fig. 3 the acidity is plotted against R, the lower curve represents the acidity stronger than $H_0 = -3.0$ and the upper curve represents that stronger than $H_0 = +3.3$.

At the composition $R \leq 1.0$, the acidity shows no change, and the amount of strong acid site is very low. On the other hand, in the composition range $R > 1.0$, the acidity increases greatly with boron content. The increase of the

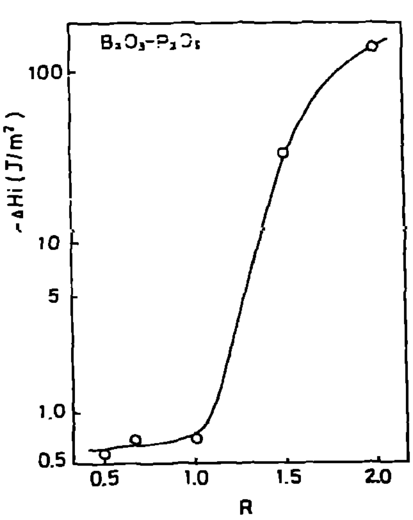

Fig. 2. Plot of $-\Delta H_i$ vs. R.

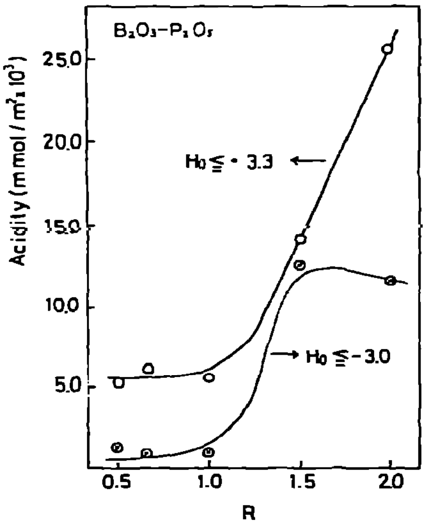

Fig. 3. Plot of acidity vs. R.

stronger acid site is significant. At $R = 1.5$, for instance, the population of the acid sites of $H_0 \leqslant -3.0$ is much greater than that for $R \leqslant 1.0$. For $R > 1.5$ the population of stronger acid sites does not change, while the acid site of $H \leqslant +3.3$ increases steadily with R.

In Fig. 4, ΔH_i is plotted against the acidity of each sample, where the acidity is $H_0 \leqslant +3.3$. As seen from Figs. 2 and 4, the heats of immersion of the samples of $R = 1.5$ and 2.0 are extraordinarily greater than the usual values by several orders of magnitude. On the surface of the borate-rich sample, free boric acid may be formed by hydrolysis of the B—O network by atmospheric moisture. Although the formation of boric acid on the surface has not been confirmed, the extraordinary value of ΔH_i for the sample of high boria content suggests that the main reaction taking place on the surface is between boric acid and pyridine.

The system Na_2O—B_2O_3—P_2O_5

In this system, the molar ratio Na_2O/P_2O_5 was maintained constant (= 1.0). The observed heats of immersion in pyridine are shown in Table 2. In Fig. 5, ΔH_i is plotted against R. The curve has a minimum at $R = 0.67$. It has been reported that in the glasses of the system Na_2O—B_2O_3– P_2O_5 the glass skeleton consisted of B—O—B, P—O—P and B—O—P linkages and was not a mixture of sodium borate and sodium phosphate [5]. The composition of $R = 0.67$ corresponds to $3\,Na_2O \cdot 3\,P_2O_5 \cdot 2\,B_2O_3$. In the glass of this composition, the B—O—P linkage is most prevailing [6]. In the range $R > 0.67$ the B—O—B linkage increases with R, while in the range $R < 0.67$ the P—O—P linkage increases with a decrease of R. As shown in Table 2, the acidity ($H_0 \leqslant +4.8$) was also lowest at $R = 0.67$. The reason why both the heat of immersion and the acidity show minima at this composition is not yet clear.

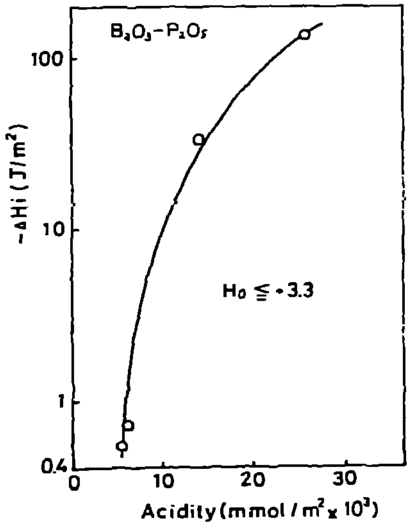

Fig. 4. Plot of $-\Delta H_i$ vs. acidity.

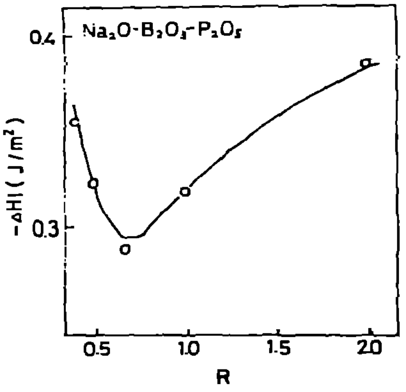

Fig. 5. Plot of $-\Delta H_i$ vs. R.

TABLE 2

Heats of immersion and acidity of the system $Na_2O—B_2O_3—P_2O_5$

R = B/P	Specific surface area ($m^2\ g^{-1}$)	$-\Delta H_i$ ($J\ m^{-2}$)	Acidity ($mmole\ m^{-2}$)
			$H_0 \leqslant +4.8$
0.40	1.0	0.358	3.29×10^{-3}
0.50	1.1	0.324	2.61×10^{-3}
0.67	1.2	0.291	1.48×10^{-3}
1.00	1.3	0.320	1.16×10^{-3}
2.00	1.7	0.387	2.46×10^{-3}

In Fig. 6, ΔH_i is plotted against acidity. The heat of immersion increases with acidity. There are two plots near the acidity = 2.5×10^{-3} mmole m^{-2}, one of which represents the data of $R = 2.0$ and shows a fairly higher heat than the other. Among the samples studied, only in the sample of $R = 2.0$ was the acidic color of butter yellow ($H_0 = +3.3$) developed. A comparison at the same value of R shows the boron phosphate sample to have a much higher heat of immersion and acidity than the sodium borophosphate sample. It is possibly because the introduction of sodium oxide to the system $B_2O_3—P_2O_5$ makes it less hydrophilic and, accordingly, the ease of hydroxylation and formation of boric acid is less on the surface of $Na_2O—B_2O_3—P_2O_5$.

Immersion of magnesia in benzoic acid solution

As described in the previous section, the interaction between a base and an acid site on the surface makes a relatively large contribution to the heat of immersion. A similar examination was carried out for magnesia which is known as one of the solid bases. The results are shown in Table 3. The heats

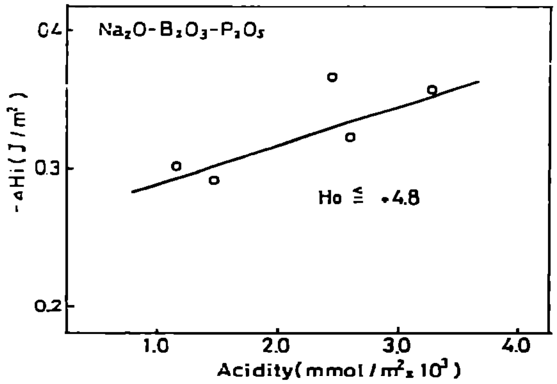

Fig. 6. Plot of $-\Delta H_i$ vs. acidity.

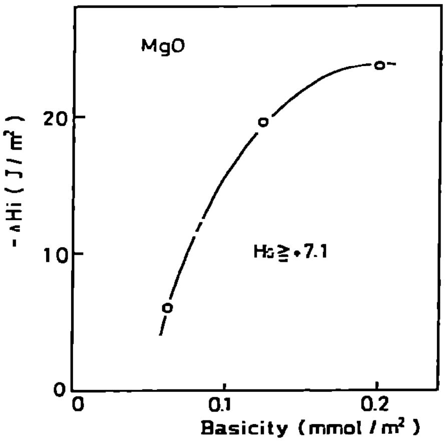

Fig. 7. Plot of $-\Delta H_i$ vs. basicity.

TABLE 3

Heat of immersion and basicity of MgO

T[a] (°C)	Specific surface area (m^2 g^{-1})	$-\Delta H_i$ (J m^{-2})	Basicity (mmole m^{-2})	
			$pK_a \geqslant 7.1$	$pK_a \geqslant 9.3$
400	101	6.06	0.062	2.45×10^{-3}
500	96.5	19.6	0.124	3.98×10^{-3}
600	35.6	23.6	0.175	5.48×10^{-3}

[a] Calcination temperature.

of immersion in benzene, which was used as the solvent, were relatively small for all samples calcined at various temperatures. The surface basicity was measured by using bromothymol blue ($pK_a = 7.1$) and phenolphthalein ($pK_a = 9.3$) as indicators. The amount of stronger basic site was much lower than the weaker one. It has been reported that the maximum value of basicity was obtained for magnesia heated at 500°C [7]. In the present work the basicity ($pK_a \geqslant 7.1$) increased with the calcination temperature.

The heat of immersion is plotted against the basicity in Fig. 7. As in the case of solid acid—liquid base, the heat markedly increased with an increase of basic site.

CONCLUSION

The mixed oxide of the system B_2O_3—P_2O_5 developed a fairly large heat when it was immersed in pyridine. The exothermic heat effect was extraordinarily high in the sample of high boria content. The introduction of the Na_2O component to the system greatly reduced the immersional heat. The heat of immersion increased with an increase of the surface acidity. Magnesia prepared by thermal decomposition of basic magnesium carbonate was immersed in benzoic acid solution. The heat also increased with the surface basicity.

The present work has found that the acid—base interaction taking place on the surface of a solid acid and a solid base made a major contribution to the heat of immersion.

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