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Esterification of Boric Acid with 1,2-Propanediol, 3-Amino-1,2-propanediol, and (±)-3-Dimethylamino-1,2-propanediol as Studied by ^{11}B NMR Spectroscopy

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Ester formations of borate ion with 1,2-propanediol, 3-amino-1,2-propanediol, and (±)-3-dimethylamino-1,2-propanediol and stabilities of the formed esters were studied by ^{11}B NMR spectroscopy. For each of the boric acid–diol systems, esters with the 1 : 1 mole ratio of borate ion and diol and with the 1 : 2 mole ratio were formed. In each of the amino–diol-containing systems the 1 : 1 ester was in fact composed of two esters; one from a borate ion and a diol molecule and the other from a borate ion and a protonated diol. Similarly, the 1 : 2 ester consisted of two esters; one from a borate ion and two diol molecules and the other from a borate ion and two protonated diols. The stability constants of the esters formed were calculated based on the peak areas of the signals of the boron species on the ^{11}B NMR spectra. The stability of an ester was strongly correlated with the electronegativity of the anchor moiety of the diol; a higher electronegativity in general yielded a more stable ester.

It is well known that boric acid reacts with polyols to form esters with large stability constant values in aqueous solutions as exemplified by the use of mannitol when the boron concentration in an aqueous solution is determined by the conventional acid-base titration. It seems Boeseken[1) who first studied systematically the chemistry of esters of boric acid and borates, using conductometry and polarimetry. Other techniques that have since been applied include electrophoresis, refractometry, cryoscopic and calorimetric measurements and spectroscopic techniques.[2–7) Boron-11 NMR spectroscopy is certainly one of the most powerful means to study boric acid and borate esters, since it provides direct information on concentrations of boron species involved in the system in concern. Kennedy and How[8,9) first used ^{11}B NMR to identify borate-hydroxy compound esters in aqueous solutions. Since mid 80's, van Bekkum and his coworkers[10–16) have extensively studied stabilities, structures and cation-sequestering abilities of borate esters of polyols and polyhydroxy acids by means not only of ^{11}B NMR spectroscopy but also of ^{1}H and ^{13}C NMR techniques.

By making use of the specific affinity of polyols to boric acid and borate ion, boron-specific adsorbents, which have as functional group polyol-containing groups, have been developed and practically used.[17,18) We are interested in boron isotope separation by ion exchange chromatography using these boron specific adsorbents as column packing material.[19) To elucidate experimentally obtained boron isotope effects, it is necessary to identify boron species and to determine their contents both in the adsorbent phase and in the external solution phase. ^{11}B NMR could be used for such an identification. As a part of study on the ^{11}B NMR spectroscopic determination of boron species in aqueous systems, we measured ^{11}B NMR spectra of aqueous solutions containing boric acid and various polyols, some having amino groups. In this paper, we report on the esterification of boric acid with three diols studied by the ^{11}B NMR technique: 1,2-propanediol, $CH_2(OH)CH(OH)CH_3$ (**1**); 3-amino-1,2-propanediol, $CH_2(OH)CH(OH)CH_2NH_2$ (**2**); and (±)-3-dimethylamino-1,2-propanediol, $CH_2(OH)CH(OH)CH_2N(CH_3)_2$ (**3**). The three diols differ structurally from each other only in anchor moieties, and hence they are expected to provide information about the influence of the difference in anchor moiety on the stability of esters formed. Furthermore, the amino-diols, **2** and **3**, could serve as simple model compounds of boron-specific adsorbents.

The equilibria considered between boric acid (B^0) molecule, monomeric borate ion (B^-), **1** and possible esters of B^- with **1** in the boric acid–**1** system are as follows:[8,10)

$$B^0 + OH^- = B^- \qquad K_B = [B^-]/[B^0][OH^-] \tag{1}$$

$$B^- + L = B^-L + 2H_2O \qquad K_{BL} = [B^-L]/[B^-][L] \tag{2}$$

$$B^-L + L = B^-L_2 + 2H_2O \qquad K_{BL2} = [B^-L_2]/[B^-L][L] \tag{3}$$

(L=**1**)

where [A] represents the concentration of Species A and K's are equilibrium (stability or formation) constants. The value of K_B is known.[20)

The equilibria in the boric acid–amino diol systems are more complicated than those of the above system, because of the association of the amino groups in the former systems. Thus, in addition to the equilibria (1)~(3), the following equilibria should be taken into consideration:[16)

$$L + H^+ = LH^+ \qquad K_L = [LH^+]/[L][H^+] \tag{4}$$

$$B^- + LH^+ = B^-LH^+ + 2H_2O$$

$$K_{BLH} = [B^-LH^+]/[B^-][LH^+] \quad (2')$$

$$B^-LH^+ + LH^+ = B^-LH^+_2 + 2H_2O$$

$$K_{BLH2} = [B^-LH^+_2]/[B^-LH^+][LH^+] \quad (3')$$

(L=**2** or **3**)

where $LH^+ = CH_2(OH)CH(OH)CH_2NH_3^+$ or $CH_2(OH)CH(OH)CH_2NH^+(CH_3)_2$. The K_L value of **2** is reported[21] but that of **3** is not.

Experimental

Chemicals. Triply distilled water was used throughout the experiments. All the chemicals used except for diethyl ether–boron trifluoride (1/1) were of analytical grade. Boric acid was used after being dried in a silica gel desiccator. **1** was purchased from Wako Chemical Co. and **2** and **3** from Aldrich Chemical Co., and they were used without further purification.

Preparation of Samples for ^{11}B NMR Measurements. For each boric acid–diol pair, 500 cm^3 of a stock solution was first prepared, which contained 0.1 M (1 M=1 mol dm^{-3}) boric acid and 0.5 M diol. A 20 cm^3 aliquot of the solution was then pH-adjusted with sodium hydroxide solution or hydrochloric acid. The pH-adjusted aliquot (the NMR sample) was finally subject to the ^{11}B NMR measurements. The pH adjustment resulted in that the boric acid and diol concentrations differed slightly from NMR sample to NMR sample. The ionic strength was kept constant at 3.0 mol dm^{-3} by adding sodium chloride to each NMR sample.

^{11}B NMR Measurements. The NMR probe unit used was schematically depicted in Fig. 1. The unit consisted of a 10 mm o.d. quartz probe, a 5 mm o.d. quartz probe and a 3 mm o.d. capillary quartz tube. The quartz tube containing diethyl ether–boron trifluoride (1/1), $(C_2H_5)_2OBF_3$, used as an external reference (chemical shift, δ=0.0 ppm), was sealed at its both ends and put into the 5 mm o.d. probe. The 5 mm o.d. probe in which D_2O used as a lock was put was capped, inserted into the 10 mm o.d. probe and fixed to it with Teflon fixing kits. 2—3 cm^3 of an NMR sample was placed into the 10 mm o.d. probe.

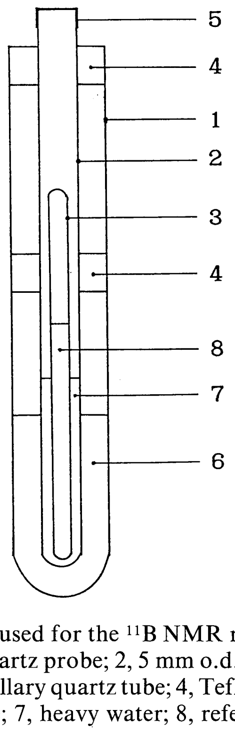

Fig. 1. Cell unit used for the ^{11}B NMR measurements. 1, 10 mm o.d. quartz probe; 2, 5 mm o.d. quartz probe; 3, 3 mm o.d. capillary quartz tube; 4, Teflon fixing unit; 5, cap; 6, sample; 7, heavy water; 8, reference.

The FT-NMR spectrometer used was a JEOL JNM-GX270, operated at 86.55 MHz and at about 25 °C. The number of pulses accumulated was 64 and the repetition time was 1.0 second. When the signal peak of the reference was expected to overlap seriously with peaks of boron species in the sample, measurements were often carried out without the reference at the cost of accuracy and stability of the peak positions of the boron species in the sample to some extent.

When peaks of multiple ^{11}B NMR signals were overlapped with each other, peak resolution was performed to determine the areas and full widths at half maximum (FWHMs) of constituent peaks. The computer program used for this task was a modified version of the one written by Kato et al.,[22] in which Lorentz-type peak shapes were assumed.

Results and Discussion

Peak Assignments. The ^{11}B NMR spectra obtained are drawn for selected pH values in Figs. 2—4; the results of the boric acid–**1** system in Fig. 2, those of the boric acid–**2** system in Fig. 3 and those of the boric acid–**3** system in Fig. 4. In each figure, the reference signal of diethyl ether–boron trifluoride (1/1) at δ=0.0 is omitted

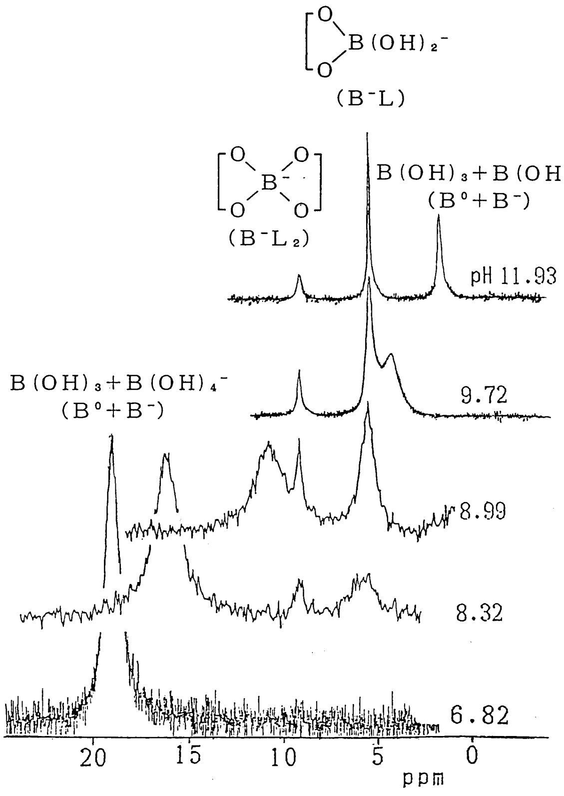

Fig. 2. ^{11}B NMR spectra obtained for boric acid-1,2-propanediol solutions at various pH values.

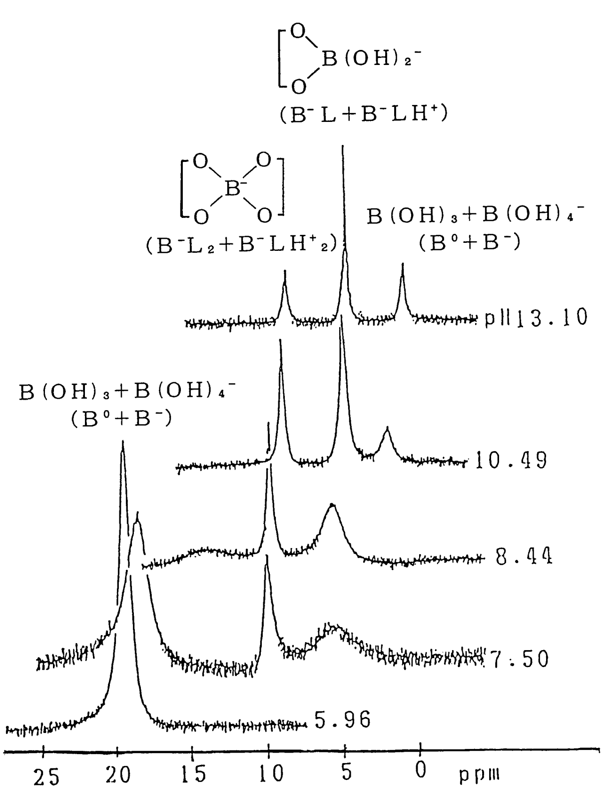

Fig. 3. ^{11}B NMR spectra obtained for boric acid–3-amino-1,2-propanediol solutions at various pH values.

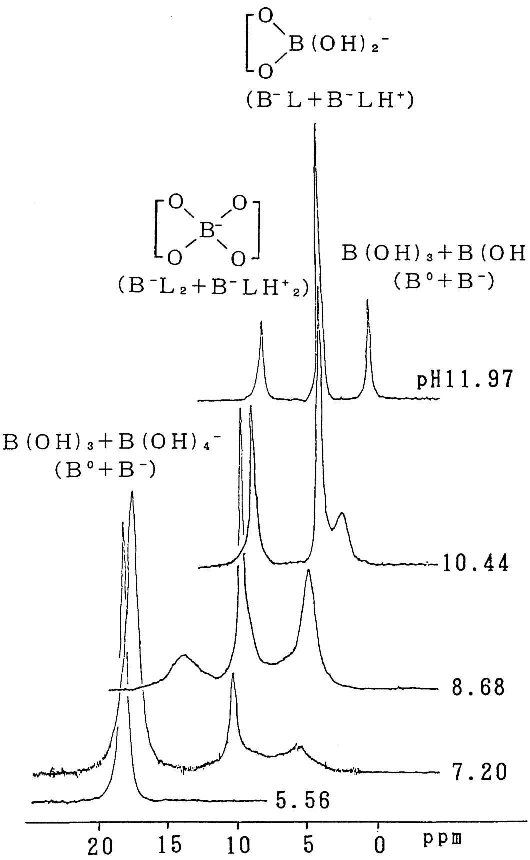

Fig. 4. ^{11}B NMR spectra obtained for boric acid–(±)-3-dimethylamino-1,2-propanediol solutions at various pH values.

for simplicity and clarity. In each of the three systems, at most three signals were observed; two being pH-independent or very slightly pH-dependent, and the remaining one being pH-dependent with its chemical shift showing an upfield shift upon increasing the pH. It is known that the boron exchange between B^0 and B^- in aqueous solution is fast on the ^{11}B NMR time scale[8] and the equilibrium between B^0 and B^- yields a single signal whose chemical shift is the average of those of B^0 and B^- weighted by their respective concentrations (The B^0 and B^- signals are observed at δ=19.4 and 1.6, respectively.). Thus, the strongly pH-dependent signals in Figs. 2—4 were attributable to the sum of B^0 and B^- (B^0+B^-).

Based on the pH-dependences of the peak areas and making reference to the literatures,[10,16] the signals at δ=5.5 and 9.3 in the boric acid–**1** system were assigned to the ester with the 1 : 1 mole ratio of borate ion and the diol (1 : 1 ester B^-L) and to the 1 : 2 ester (B^-L_2), respectively. These signals disappeared when the pH was below 8.2, showing that in that pH region no appreciable ester formation occurred. In a similar way, the signals at about δ=5.8 and 9.9 in the boric acid–**2** system can be assigned to the 1 : 1 and 1 : 2 esters, respectively, and the signals at about δ=5.6 and 9.6 in the boric acid–**3** system to the 1 : 1 and 1 : 2 esters, respectively. The signals of the esters were observed below pH=7.0 neither for the boric acid–**2** system nor for the boric acid–**3** system.

Tables 1—3 summarize the chemical shifts, peak areas and FWHMs obtained for the three systems. The signals at about δ=5.8 and 9.9 in the boric acid–**2** system (Table 2) showed very slight upshield shifts with increasing pH, although some fluctuation in peak positions was observed, which was mostly due to the omission of the reference in some ^{11}B NMR measurements and to difficulty in controlling the temperature stability during the measurements. As was pointed out by van Haveren et al.[16] these upshield shifts were considered to be caused by the fact that the signals do not come from a single boron species but in fact come from two species, i.e., the signal at about δ=5.8 consisted of the signals of B^-L and B^-LH^+ (1 : 1 ester of borate ion and protonated **2**) and the one at about δ=9.9 was composed of the signals of B^-L_2 and $B^-LH^+_2$ (1 : 2 ester of borate ion and protonated **3**). The electronic environment around a ^{11}B nucleus was not influenced much by the protonation of the amino group, and hence the ^{11}B signals of B^-L and B^-LH^+ show similar δ values and so do the signals of B^-L_2 and $B^-LH^+_2$. Likewise, the fact that signals at δ=5.5—6.1 and at δ=9.4—9.9 in the boric acid–**3** system (Table 3) also showed the very slight upshield shifts upon increase in pH value can be attributable to the existences of two kinds of 1 : 1 esters (B^-L and B^-LH^+) and two kinds of 1 : 2 esters ($B^-L_2$and $B^-LH^+_2$), respectively.

Table 1. ^{11}B NMR Spectroscopic Data for Boric Acid–1,2-Propanediol Solutions

pH	B concn	Diol concn	Chemical shift/ppm[a]			Peak area/%[a]			FWHM/Hz[a]		
	mol dm^{-3}	mol dm^{-3}	B^0+B^-	B^-L	B^-L_2	B^0+B^-	B^-L	B^-L_2	B^0+B^-	B^-L	B^-L_2
12.93	0.0965	0.487	1.65	5.48	9.21				34	34	13
12.81	0.0965	0.487	1.90	5.65	9.39	33.16	58.93	7.91	32	17	24
11.95	0.0980	0.494	1.69	5.49	9.22				28	11	19
11.93	0.0980	0.494	1.87	5.61	9.34	31.19	59.70	9.11	25	12	21
10.95	0.0919	0.464	2.04	5.49	9.22				29	15	19
10.65	0.0919	0.464	2.39	5.58	9.34	30.91	57.11	11.98	34	21	25
10.02	0.0951	0.480	3.66	5.42	9.23	33.42	51.17	15.41	70	29	25
9.72	0.0946	0.477	4.39	5.54	9.32	33.63	50.38	15.99	91	43	24
9.61	0.0946	0.477	—	5.42	9.22				—	39	44
8.99	0.0929	0.468	10.84	5.56	9.22	39.54	47.37	13.09	160	47	75
8.66	0.0960	0.484	13.73	5.49	9.15	48.39	42.01	9.60	163	91	33
8.32	0.0957	0.483	16.27	5.49	9.22	59.30	32.84	7.86	150	158	55
8.14			17.10			100	0	0	106		
8.03			17.44			100	0	0	410		
7.82			18.01			100	0	0	416		
7.40			18.73			100	0	0	85		
6.82			19.11			100	0	0	77		
4.72			19.36			100	0	0	78		

a) The meanings of the symbols are given in the text. —: The peaks could not be resolved from other peaks.

Calculations of Stability Constants. For the boric acid–**1** system, the following two material balances hold:

$$C_B = [B^0] + [B^-] + [B^-L] + [B^-L_2] \tag{5}$$

$$C_L = [L] + [B^-L] + 2[B^-L_2] \tag{6}$$

where C_B and C_L are the total concentrations of boron and **1**, respectively. Since the values of the quantities in Eqs. 5 and 6 were all determinable a priori or from peak areas of the boron species on the ^{11}B NMR spectra and the K_B value, the formation constants, K_{BL} and K_{BL2}, were obtained at every pH at which all the three peaks attributable B^0+B^-, B^-L and B^-L_2 are observed at appropriate levels. The values of K_{BL} and K_{BL2} thus calculated were listed in Table 4 and compared with the values found in the literature. Our values were close to the values obtained with the pH-change technique[4,23] rather than to those obtained with the ^{11}B NMR method by other researchers.[10,16]

For the boric acid–**2** system, Eqs. 5′ and 6′ hold instead of Eqs. 5 and 6:

$$C_B = [B^0] + [B^-] + [B^-L] + [B^-LH^+] + [B^-L_2] + [B^-LH^+_2] \tag{5$'$}$$

$$C_L = [L] + [LH^+] + [B^-L] + [B^-LH^+] + 2[B^-L_2] + 2[B^-LH^+_2] \tag{6$'$}$$

In this case, K_{BL} and K_{BLH} are indeterminable at a given pH value because $[B^-L]$ and $[B^-LH^+]$ are not individually determined but only the sum of $[B^-L]$ and $[B^-LH^+]$ was measured on ^{11}B NMR spectra. The similar situation holds for K_{BL2} and K_{BLH2}; these two formation constants can not be determined at a given pH value.

To determine the values of K_{BL}, K_{BLH}, K_{BL2} and K_{BLH2} individually in the boric acid–**2** system, we adopted the least-squares-fit (LSF) technique. K_{BL} and K_{BLH} were determind from the condition that

$$\sum(C_{BL}/[B^-] - K_{BL}[L] - K_{BLH}[LH^+])^2 \tag{7}$$

took on the minimum value. In Eq. 7, C_{BL} is the sum of $[B^-L]$ and $[B^-LH^+]$, and the summation was taken over all the data points in which the B^-L+B^-LH^+ signal had a sufficiently large peak area and was resolved from the B^0+B^- signal and the B^- concentration was not very low. Using the values of K_{BL} and K_{BLH} thus obtained, the values of K_{BL2} and K_{BLH2} were determined from the condition that

$$\sum(C_{BL2} - K_{BL2}[B^-L][L] - K_{BLH2}[B^-LH^+][LH^+])^2 \tag{8}$$

took on the minimum. In Eq. 8, C_{BL2} is the sum of $[B^-L_2]$ and $[B^-LH^+_2]$. The LSFed values of K_{BL}, K_{BLH}, K_{BL2}, and K_{BLH2} thus obtained were listed in Table 4, together with the results obtained by van Haveren et al.[16] The second entry for This work of **2** in Table 4 was obtained by the other LSF calculation in which K_L was also taken for an unknown instead of using a literature value of $10^{9.41}$ dm^3 mol^{-1}.[21] By this method, K_L was calculated to be $10^{8.750}$ dm^3 mol^{-1}. Table 4 shows that even if we use $10^{8.570}$ as the value of K_L instead of $10^{9.41}$, the stability constant values of the esters between B^- and **2** are not influenced much, suggesting that the method is applicable to systems in which association constant values of polyols are not given.

The ester formation constants in boric acid–**3** system were determined in a similar manner to that of the boric

Table 2. ^{11}B NMR Spectroscopic Data for Boric Acid-3-Amino-1,2-Propanediol Solutions

pH	B concn	Diol concn	Chemical shift/ppm$^{a)}$			Peak area/%$^{a)}$			FWHM/Hz$^{a)}$		
	mol dm^{-3}	mol dm^{-3}	B^0+B^-	$B^-L+B^-LH^+$	$B^-L_2+B^-LH^+_2$	B^0+B^-	$B^-L+B^-LH^+$	$B^-L_2+B^-LH^+_2$	B^0+B^-	$B^-L+B^-LH^+$	$B^-L_2+B^-LH^+_2$
13.10	0.0929	0.451	2.01	5.86	9.80	20.16	61.56	18.28	36	14	34
12.99	0.0929	0.451	1.93	5.80	9.75				28	10	60
12.21	0.0943	0.458	1.73	5.61	9.55	19.93	60.74	19.33	21	16	35
11.56	0.0965	0.468	1.97	5.76	9.72				20	10	29
11.46	0.0965	0.468	2.07	5.75	9.71	16.77	55.43	27.80	37	23	38
11.00	0.100	0.486	2.01	5.62	9.59	16.77	54.41	28.82	39	26	34
10.49	0.0949	0.461	2.79	5.70	9.73				74	47	31
10.03			7.13	5.62	9.79				—	—	33
9.47			—	5.76	9.87				—	58	33
9.04			—	5.92	9.94				—	—	41
8.74	0.0913	0.443				19.82	52.07	28.11	309	132	41
8.44	0.0930	0.452	14.15	5.90	10.00	22.06	47.97	29.97	358	144	42
8.01	0.0925	0.449	17.00	5.92	10.04	37.08	40.57	22.35	234	207	47
7.50	0.0942	0.457	18.42	5.97	10.03	56.44	25.81	17.75	156	303	58
7.22	0.0923	0.448	18.84	6.07	10.03	66.66	18.76	14.58	130	268	73
7.02	0.0872	0.423	19.01			75.99	13.66	10.35	107	267	75
6.64			19.25			100	0	0	98		
5.96			19.42			100	0	0	81		

a) The meanings of the symbols are given in the text. —: The peaks could not be resolved from other peaks.

Table 3. ^{11}B NMR Spectroscopic Data for Boric Acid-(±)3-Dimethylamino-1,2-Propanediol Solutions

pH	B concn	Diol concn	Chemical shift/ppm$^{a)}$			Peak area/%$^{a)}$			FWHM/Hz$^{a)}$		
	mol dm^{-3}	mol dm^{-3}	B^0+B^-	$B^-L+B^-LH^+$	$B^-L_2+B^-LH^+_2$	B^0+B^-	$B^-L+B^-LH^+$	$B^-L_2+B^-LH^+_2$	B^0+B^-	$B^-L+B^-LH^+$	$B^-L_2+B^-LH^+_2$
12.53	0.100	0.493	1.95	5.70	9.60	21.82	62.43	15.75	39	22	50
12.30			1.80	5.53	9.41				32	23	50
11.97	0.0946	0.467	1.95	5.72	9.58	21.92	61.01	17.07	37	29	55
11.57	0.0948	0.468	1.95	5.55	9.39	19.99	58.54	21.47	63	50	65
10.94	0.0944	0.466	2.41	5.70	9.63	20.49	56.86	22.65	66	42	49
10.44	0.0973	0.480	3.31	5.52	9.55	17.66	50.30	32.04	172	60	61
9.96			—	5.59	9.68				—	59	55
9.65			—	5.75	9.61				—	83	45
9.14			—	5.82	9.77				—	128	46
8.68	0.0916	0.452	15.64	5.78	9.82	23.60	45.54	30.86	286	163	46
8.19	0.0920	0.454	17.30	6.00	9.85	36.67	38.63	24.70	217	190	49
8.15			17.61	5.98	9.95				236	219	50
7.57	0.0936	0.462	18.30	5.73	9.83	56.04	24.87	19.09	147	281	49
7.20	0.0929	0.458	18.85	6.12	9.87	72.57	15.06	12.37	127	294	68
6.32			19.11	—	—	100	0	0	80		

a) The meanings of the symbols are given in the text. —: The peaks could not be resolved from other peaks.

Table 4. Stability Constants of Esters Formed between Borate Ion and Diols

Diol	Method	Stability constant/$dm^3\ mol^{-1}$ [a)]				Comment[a)]	Ref.
		K_{BL}	K_{BLH}	K_{BL_2}	K_{BLH_2}		
1,2-Propanediol	pH-change	4.05		0.951			4)
	pH-change	3.10		0.52			23)
	^{11}B NMR	1.8		1.5		at pH=12	8)
	^{11}B NMR	3		0.2		at pH=7	16)
	^{11}B NMR	2.2		0.29		at pH=11	16)
	^{11}B NMR	4.4		0.57			This work
3-Amino-1,2-propanediol	^{11}B NMR	8		0.8		at pH=6.5	16)
	^{11}B NMR	7.0		0.8		at pH=10.5	16)
	^{11}B NMR	8.4	21	1.0	1.9	$K_L=10^{9.41}$	This work
	^{11}B NMR	8.6	22	1.2	1.9	$K_L=10^{8.750}$	This work
(±)-3-Dimethylamino-1,2-propanediol	^{11}B NMR	7.5	18	1.0	1.9	$K_L=10^{8.302}$	This work

a) Definitions of the stability constants and the association constants are given in the text. The association constants are given in units of $dm^3\ mol^{-1}$.

acid–2 system. Since the K_L value of **3** has not been reported, K_L was also taken as an unknown in the LSF calculations. The K_L value thus obtained was $10^{8.302}$ $dm^3\ mol^{-1}$ and the calculated stability constant values are listed in Table 4.

In the stability constant calculations of the 1 : 2 esters in the boric acid–amino diol systems above, we assumed the existence of the doubly protonated species $B^-LH^+_2$ as was done by van Haveren et al.[16)] Instead, it may be possible to assume the existence of the singly protonated species B^-LLH^+ and to calculate stability constants related to it. In this case, the following two reactions are conceivable;

$$B^-L + LH^+ = B^-LLH^+ + 2H_2O,$$

$$K_{BLLH} = [B^-LLH^+]/[B^-L][LH^+] \qquad (9)$$

and

$$B^-LH^+ + L = B^-LLH^+ + 2H_2O,$$

$$K_{BLHL} = [B^-LLH^+]/[B^-LH^+][L] \qquad (10)$$

We attempted to obtain the values of K_{BLLH} and K_{BLHL}, but the LSF calculations did not work well. This is probably the consequence of the fact that the species B^-L and LH^+ do not exist in adequately high concentrations at the same time and a chance of forming the species B^-LLH^+ is very scarce; in the pH region where B^-H exists in relatively high concentration, LH^+ virtually does not exist and vice versa. In the pH=9—10 region where the possibility of the formation of the B^-LLH^+ species is expected to be the highest, the peaks of the ^{11}B NMR signals of the 1 : 1 species totally overlapped with those of B^0+B^-, and consequently the data in this pH region were, unfortunately, not used in the LSF calculations. Similar situations hold for the B^-LH^+ and L pair (Eq. 10).

For **1** and **2** diols, van Haveren et al.[16)] also reported the values of formation constants of the esters between boric acid molecule and **1** or **2**,

$$B^0 + L = B^0L + 2H_2O, \qquad K_{B0L} = [B^0L]/[B^0][L] \qquad (11)$$

We did not elaborate the determination of this kind of B^0-related formation constants; their values are indeed very small and neglection of them will not influence much the values of the other formation constants.

Stability of the Esters Formed. The stability constant values of the 1 : 1 esters obtained were in the sequence of **1**<**3**<**2** and that of the 1 : 2 esters were in the sequence of **1**<**3**≒**2**. And for each of **2** and **3**, $K_{BL}<K_{BLH}$ and $K_{BL2}<K_{BLH2}$. It is obvious from these sequences that the introduction of amino groups substantially enhanced the stabilities of the esters formed. This is also suggested by the fact that the borate ion–**1** esters appear in the pH>8.3 region while borate ion–**2** and borate ion–**3** esters appear in the pH>7 region.

Since the diols studied in this paper are all 1,2-diols and the coordination struture is very similar among them, the difference in the stability of the esters formed is considered to be related to a large extent to the difference in the electron densities on the oxygen atoms in the OH groups among the diols. The oxygen in a OH group with a low electron density would release the hydrogen ion in the group to a larger extent and hence would attract the negatively charged B^- species to give esters with larger stability contants than an oxygen atom with a high electron density. The difference in electron density on oxygen atoms of OH groups among the diols would primarily be determined by the difference in electron withdrawing inductive effect exerted by the anchor moieties, and the magnitude of the effect is governed to a large extent by their electronegativity. To summarize, it is expected that a moiety with a larger electronegativity results in a larger stability of the ester formed.

In Table 5, we compiled the stability constant values obtained in the present study and group electronegativities (χ)[24)] and inductive substitution parameters (ι)[25)] of

Table 5. Group Electronegativities and Stability Constants[a)]

Group	χ	ι	K_{BL} or K_{BLH}/dm^3 mol^{-1}	K_{BL_2} or K_{BLH_2}/dm^3 mol^{-1}
$-H$	2.18	2.00	4.4	0.57
$-NH_2$	2.99	2.47	8.4	1.0
$-N(CH_3)_2$	3.01	2.48	7.5	1.0
$-NH(CH_3)_2^+$	3.67	2.91	18	1.9
$-NH_3^+$	3.71	2.93	21	1.9

a) The values of χ and ι are cited from Refs. 24 and 25, respectively. Definitions of the stability constants are given in the text.

the moieties involved. An inductive substitution parameter is a measure of electronegativity introduced by Inamoto and Masuda.[25)] As is seen in the table, an excellent correlation is observed between the order of the magnitude of the stability constant and that of χ (or ι) value for the 1 : 1 esters except for that between the $-NH_2$ and $-N(CH_3)_2$ groups. As for the 1 : 2 esters, the sequence of the stability constant data are consistent with that of the χ (or ι) values.

The above sequence of stability constants is also explainable qualitative based on a consideration on entropy changes. Compared to an anchor moiety with a small electronegativity, a moiety with a large electronegativity causes delocalization of the negative charge on a borate ion to a large extent, which leads to the reduction of degree of hydration and hence to entropy increase, yielding a large stability constant.

Other factors such as existence of electric charges and the differences in flexibility of C–C–C chain and in steric hindrance effect among the three diols are also expected to affect the difference in stability of the esters formed among them to a lesser extent.

Conclusion

The borate ion and the 1,2-diols (**1**,**2**,**3**) form esters with 1 : 1 and 1 : 2 mole ratios of borate ion and diol in aqueous solution. The stabilities of the esters formed are very strongly influenced by the group electronegativity values of the anchor moieties attached to the end methyl carbons. In general, the higher the electronegativity value is, the more it enhances the stability of the ester formed. The least-squares-fit technique can be used to calculate stability constants of borate ion–amino-diol esters even when the association constant value of the amino-diol is not known.

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