Distribution of Diethyl Tartrate between Ether and Aqueous Borate Solution and a Contribution to the Studies on the Equilibrium of the Boro-Diol Complex Formation.

By Yojiro TSUZUKI.

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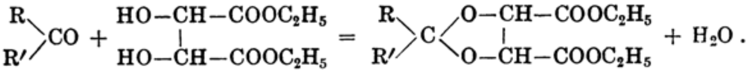
Introduction. In the following condensation reaction, which takes place between a carbonyl compound and diethyl tartrate giving a bridged derivative of tartaric acid, the author⁽¹⁾ has been always successful in removing the unchanged ester (I) (which cannot otherwise be separated with ease) from the reaction product (II) by shaking the ethereal extract of the reaction mixture with saturated aqueous solution of borax.



$$\begin{matrix}R\\R'\end{matrix}\!>\!CO + \begin{matrix}HO-CH-COOC_2H_5\\ |\\ HO-CH-COOC_2H_5\end{matrix} = \begin{matrix}R\\R'\end{matrix}\!>\!C\!<\!\begin{matrix}O-CH-COOC_2H_5\\ |\\ O-CH-COOC_2H_5\end{matrix} + H_2O\,.$$

I II

This success in the separation may probably be attributed to the circumstances that the unchanged ester (I), being a diol, forms some boro-diol complex with borate ion, while the reaction product (II), being insoluble in water, remains in the ethereal phase. It appears therefore that the tartaric ester can easily be transferred to the aqueous layer, although the ester by itself is freely soluble in ether as well as in water.

In the present work the author has made quantitative studies of this phenomenon, intending thus to demonstrate the efficiency of this process of separation.

The results of the measurements actually show that the distribution of diethyl tartrate between ether and water follows simply the distribution law, but in the system of ether and water containing borax the distribution coefficient C_2/C_1 is no more constant, and decreases with the increasing concentration of the ester. It can, however, be obviously shown that the use of borax solution in the extraction process is very advantageous, as was expected.

In order to give an interpretation of these phenomena, the author at first assumed the existence of the equilibrium of complex formation in the aqueous layer, which was later ascertained by the analysis of the experimental results. In consequence of this analytical studies the author

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(1) Y. Tsuzuki, this Bulletin, **10** (1935), 255; **11** (1936), 362; **12** (1937), 487.

has succeeded in demonstrating clearly what is the favourable condition for extracting the ester from the ethereal solution.

Experimental Method. The distribution experiment was carried out in the usual way.(2) The determination of diethyl tartrate is made as follows: For the ethereal phase, ether is carefully evaporated up, and the residue is warmed with a known quantity of N/5 KOH and the excess of the alkali is titrated with N/10 HCl. For the aqueous borate phase, the solution is boiled with potassium hydroxide to saponify diethyl tartrate, and after the resulting alcohol is completely evaporated off, the residue is boiled with a known quantity of N $K_2Cr_2O_7$ to oxidize the liberated tartaric acid, and the excess of bichromate is determined by iodometry.(3)

Results of the Measurements. Distribution experiments were made in the systems of ether–water, ether–1/20 mol borax, and ether–N/4 KBO_2. The influence of temperature was also observed, except in the case of water–borax. The results are given in the accompanying tables and shown graphically in Fig. 1, where c_1 denotes the concentration (g. per 10 c.c. solution) of diethyl tartrate in the ethereal phase, and c_2 concentration (g. per 10 c.c. solution) of diethyl tartrate in the aqueous phase.

The distribution in the system of ether–water follows the Nernst distribution law, as shown in Table 1.

The results of the distribution measurement of diethyl tartrate between ether and aqueous borax solution (Table 2) shows that the ester is distributed in the latter phase much more than in pure water. By these quantitative experiments it can be understood that diethyl tartrate is effectively extracted out of the ethereal solution by shaking with borax solution. Thus it is shown that this extraction method is very useful in the purification process stated above.

It is also worthy of note that the ratio, c_2/c_1 diminishes with increasing concentration (c_1 or c_2).

The data of the distribution experiments between ether and 1/4 mol aqueous potassium borate (KBO_2) solution are given in Table 3, where it is seen that the distribution ratio, c_2/c_1 is yet in a marked degree greater than in the case of water–borax (Table 2), which is obviously shown graphically in Fig. 1.

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(2) Ref. Eucken—Suhrmann, "Physikalisch-chemische Praktikumaufgaben," 158, Leipzig (1928).

(3) Determination of tartaric acid by bichromate method: Heidenhain, *Z. anal. Chem.*, **32** (1893), 357; K. Täufel and C. Wagner, *ibid.*, **67** (1926), 16; Wikul, *ibid.*, **68** (1926), 45.

Table 1. Distribution of diethyl tartrate between ether and water at 20°.

c_1	c_2	$k = c_2/c_1$
0.0172	0.0371	2.16
0.0271	0.0584	2.15
0.0446	0.101	2.26
0.0624	0.133	2.13
0.0910	0.211	2.31
0.114	0.257	2.26
0.228	0.519	2.28
		mean 2.22

Table 2. Distribution of diethyl tartrate between ether and 1/20 mol aqueous solution of borax at 20°.

c_1	c_2	c_2/c_1
0.0109	0.1271	11.7
0.0298	0.2355	7.88
0.0834	0.4159	4.98

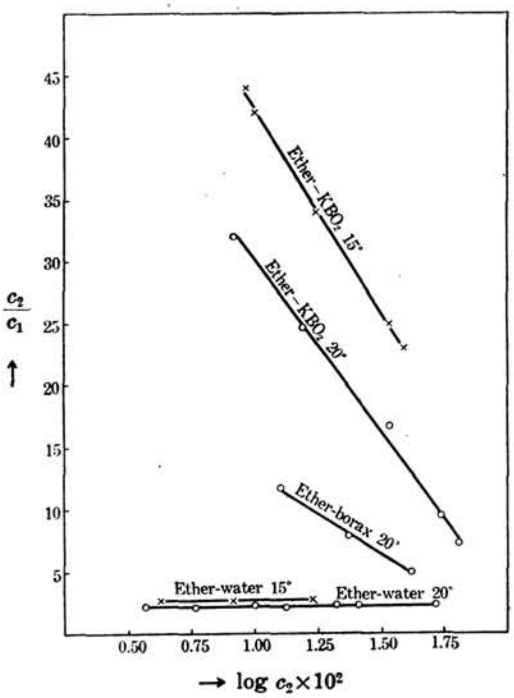


Fig. 1.

Table 3. Distribution of diethyl tartrate between ether and 1/4 mol aqueous potassium borate solution at 20°.

No. of experiment	c_1	c_2	c_2/c_1
I	0.0026	0.083	32.0
II	0.0063	0.155	24.7
III	0.0206	0.343	16.7
IV	0.0577	0.548	9.50
V	0.0876	0.640	7.31

As the ester is very soluble in the borate layer, the quantity of the ester distributed in the ethereal solution is greatly diminished, especially when the concentration of the ester is small. From this experiment we know that in the purification process the extraction of the ester by means of potassium borate is more effective than by the use of borax.

Influence of Temperature. In order to see the temperature influence on the distribution ratio, similar experiments were made at 15° for the systems of ether–water and of ether–1/4 mol aqueous potassium borate. The results are given in Tables 4 and 5.

Table 4. Distribution of diethyl tartrate between ether and water at 15°.

c_1	c_2	$k = c_2/c_1$
0.0164	0.0427	2.60
0.0316	0.0827	2.61
0.0613	0.1700	2.77

Table 5. Distribution of diethyl tartrate between ether and 1/4 mol aqueous KBO_2 solution at 15°.

No. of exp.	c_1	c_2	c_2/c_1
I	0.0021	0.093	44
II	0.0024	0.101	42
III	0.0051	0.177	34
IV	0.0136	0.343	25.1
V	0.0170	0.392	23.0

The distribution ratio $k = c_2/c_1$ in the system of ether–water (Table 4) becomes also nearly constant, but slightly greater than at 20°, while in the system of ether–1/4 mol KBO_2 (Table 5) the ratio c_2/c_1 is remarkably higher as compared with those at 20°. This relation will be clearly seen in Fig. 1.

Equilibrium between Diethyl Tartrate and Borate in the Aqueous Borate Layer.

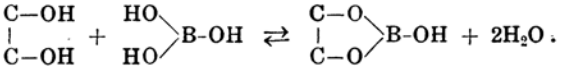
The facts that the distribution coefficient in the system of ether–borate is inconstant as stated above, suggest that in the borate phase the ester exists not merely in free state, but rather combined with borate ion. The author now assumes that this "combined" ester is in equilibrium with the free ester, and the latter is, on the other hand, in constant ratio to the ester in the ethereal phase, in conformity with Nernst distribution law, as shown by the following scheme:

$$\begin{array}{lrl} \text{I. Ethereal layer:} & \mathrm{T} \quad & \text{Conc. of the ester} = c_1 \\ & \downarrow\uparrow \quad & \\ \text{II. Aqueous layer:} & \mathrm{BO_2'} + \mathrm{T} \rightleftarrows \mathrm{TB'} & \text{Total conc. of the ester} = c_2 \end{array}$$

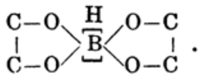
$$\frac{[\mathrm{T}]_{\mathrm{II}}}{[\mathrm{T}]_{\mathrm{I}}} = k \quad \text{(Nernst distribution law),}$$

where T represents diethyl tartrate, TB′ complex ion of boro-tartrate, $[\mathrm{T}]_{\mathrm{I}}$ the concentration of diethyl tartrate in ethereal layer, $[\mathrm{T}]_{\mathrm{II}}$ the concentration of "uncombined" diethyl tartrate in aqueous borate phase, and k the distribution coefficient in ether–water system.

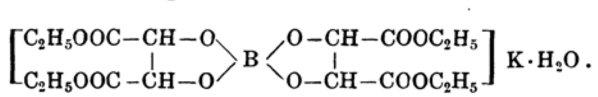
Reaction of Diethyl Tartrate with Borate Ion. Before entering the analysis of the equilibrium, we must investigate the type of the reaction. van't Hoff,(4) considering the facts that mannitol (with 6 hydroxyl groups) required 3 molecules of boric acid, and supposing that the high rotatory power of the complex, assumed the reaction of polyhydroxy-compounds with boric acid shown by the following scheme might be borne out by the cyclisation, since it was generally known that cyclisation in the molecule enhances the rotatory power of the compound.



On the other hand, Hermans(5) considered the complex was formed by the combination of two molecules of diol with one molecule of boric acid, the structure of which was of the cyclic nature containing pentavalent boron atom with the coordination number 4 in the centre of the complex molecule:



And later, in fact, Lowry(6) and Bancroft and Davis(7) isolated a complex compound of this structure, potassium boro-tartrate $KB(C_4H_4O_6)_2$, although it was a potassium salt of a different type of diol (hydroxy-carboxylic). B. Jones(8) described also the isolation of a complex of this sort, potassium ethyl boro-tartrate $C_{16}H_{24}O_{12}BK \cdot H_2O$, which was obtained by the action of boric acid and potassium carbonate on diethyl tartrate. The structure of this complex is considered as follows:



It was, however, demonstrated by H. T. Britton and P. Jackson(9) that in the complex of boro-tartaric acid the ratio, tartaric acid/boric acid is 1 or 2 according to the condition of the formation, by following the change in pH, conductivity, and optical rotation during the progressive

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(4) "Die Lagerung der Atome in Raume," 3rd Ed., 90, Braunschweig (1908).

(5) *Proc. Acad. Sci. Amsterdam,* **26** (1925), 32.

(6) *J. Chem. Soc.,* **1929**, 2853.

(7) *J. Phys. Chem.,* **34** (1930), 2479.

(8) *J. Chem. Soc.,* **1933**, 951.

(9) *J. Chem. Soc.,* **1934**, 1002.

addition of sodium hydroxide to various tartaric-boric acid mixtures. And it was also shown by N. Vermaas⁽¹⁰⁾ that between boric acid and diol (such as mannitol, sorbitol, fructose, etc.) two following equilibria exist:

$$\text{HB (boric acid)} + \text{D (diol)} \rightleftarrows \text{HBD} + 2H_2O\,,$$

$$\text{HBD} + \text{D} \rightleftarrows H^+ + BD_2^- + H_2O\,.$$

It may therefore be assumed that generally in the equilibrium between boric acid and diol both types of complex, i.e. mono-diol type and di-diol type exist, so that in the present case the equilibria between diethyl tartrate and potassium borate (KBO_2) may be considered as follows:

$$BO_2' + \text{T (diethyl tartrate)} \rightleftarrows TB'\begin{pmatrix}\text{complex ion of}\\ \text{mono-diol type}\end{pmatrix} + H_2O \qquad \text{(I)},$$

$$TB' + T \rightleftarrows T_2B'\begin{pmatrix}\text{complex ion of}\\ \text{di-diol type}\end{pmatrix} + H_2O \qquad \text{(II)}.$$

By applying the law of mass action to these equilibria, we have

$$K_1 = \frac{[TB']}{[BO_2'][T]} \qquad (1),$$

$$K_2 = \frac{[T_2B']}{[TB'][T]} \qquad (2),$$

$$K_1K_2 = K_3 = \frac{[T_2B']}{[BO_2'][T]^2} \qquad (3),$$

where the concentration of water is included in the equilibrium constant, as it may be regarded almost constant. The author will now inquire whether in the aqueous borate phase the above equilibria really exist or not. The relation of the concentrations of the substances in the equilibria are expressed as follows:

$$C_1 = \frac{[T]}{k}\,,$$

$$C_2 = 2[T_2B'] + [TB'] + [T] \qquad (4),$$

$$C_3 = [T_2B'] + [TB'] + [BO_2'] \qquad (5),$$

where k is distribution constant, C_1 concentration of diethyl tartrate in the ethereal phase, C_2 total concentration of diethyl tartrate in the aqueous borate phase, and C_3 total concentration of borate ion, all the concentrations being expressed in millimol per litre.

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(10) *Rec. trav. chim.*, **51** (1932), 67, 955; J. Böeseken and N. Vermaas, *ibid.*, **54** (1935), 853.

Of these quantities, what can be analytically determined are C_1, C_2 and C_3. [T] can be estimated from the ratio k, in the case of ether–water system. Concentrations of other substances such as $[T_2B']$, $[TB']$ and $[BO_2']$ can not even indirectly be determined. But in a special case, when the sole product is of the mono-diol type (Reaction I), we are able to estimate $[TB']$ and $[BO_2']$ and thus calculate the equilibrium constant K_1. And in a similar way, if the sole product is of the di-diol type (Reaction II), we can estimate K_3.

Discussion of the Results. The experimental results already given in Table 3 are used for discussions on the equilibria considered above. The concentrations are now rewritten in millimol per litre and shown in Table 6, together with C_3 and [T].

Table 6.

No. of experiment	c_1	C_1	c_2	C_2	C_3	$[T]=C_1\times 2.22$
I	0.0026	1.3	0.0833	40.4	236	2.9
II	0.0063	3.1	0.155	75.4	234	6.9
III	0.0206	10.0	0.343	166.6	229	22.2
IV	0.0577	28.0	0.548	266	225	62.2
V	0.0876	42.5	0.640	310	223	94.4

Case 1. If K_3 is extremely small or $[T_2B']=0$,

then $[TB'] = C_2 - [T]$,

and $[BO_2'] = C_3 - [TB']$.

K_1 can be calculated as shown in Table 7. K_1 is not constant and increases with the increasing concentration of diethyl tartrate.

Table 7.

No. of experiment	[T]	[TB′]	[BO$_2$′]	K_1
I	2.9	37.5	198	0.065
II	6.9	68.5	165	0.062
III	22.2	144	84.6	0.077
IV	62.2	204	21.2	0.155
V	94.4	216	7.0	0.327

Case 2. If K_1 is extremely small or $[TB'] = 0$,

$$\text{then}\qquad [BO_2'] = (2C_3 + [T] - C_2)/2\,,$$
$$\text{and}\qquad [T_2B'] = C_2 + [BO_2'] - C_3 - [T].$$

K_3 can be calculated as shown in Table 8. K_3 is not also constant, and decreases with the increasing concentration of diethyl tartrate, which shows that reaction II is not dominant under this condition.

Table 8.

No. of experiment	[T]	$[BO_2']$	$[T_2B']$	K_3
I	2.9	217	18.4	0.0102
II	6.9	200	34.5	0.0036
III	22.2	157	72.2	0.00093
IV	62.2	123	102	0.000215
V	94.4	115	108	0.000105

We are, therefore, led to the conclusion that both equilibria equally exist in the solution. And if we give some appropriate value to K_3, then we may be able to make the value of K_1 nearly constant. For this purpose the following relations of the concentrations were derived from the formulæ (1), (3), (4) and (5):

$$[BO_2'] = \frac{C_3+[T]-C_2}{1-K_3[T]^2}\,,$$
$$[TB'] = 2C_3+[T]-C_2-2[BO_2']\,.$$

Now if we put $K_3 = 8.5 \times 10^{-5}$ in the above formula, then K_1 becomes fairly constant, as shown in Table 9.

Table 9.

No. of experiment	[T]	$[BO_2']$	$[TB']$	K_1
I	2.9	199	37	0.065
II	6.9	166	67	0.059
III	22.2	88	137	0.070
IV	62.2	37	172	0.074
V	94.4	29	173	0.064
				mean 0.066

K_1 comes out nearly constant in a wide range of the concentration of the ester varying from 2.9 to 94.9, showing that the above considerations are reasonable.

Influence of Temperature on the Equilibrium. In exactly the same way as at 20°, calculations were made for the results of the distribution experiments at 15°. If we assume only one equilibrium, neither K_1 nor K_3 becomes constant also in this case, as shown in Tables 10–12.

Table 10.

No. of experiment	c_1	C_1	c_2	C_2	C_3	$[T] = C_1 \times 2.70$
I	0.0021	1.03	0.093	45	232	2.8
II	0.0024	1.2	0.101	49	234	3.1
III	0.0051	2.5	0.177	86	227	6.8
IV	0.0136	6.6	0.343	166	222	17.8
V	0.0170	8.3	0.392	190	225	22.4

Case 1. If K_3 is extremely small or $[T_2B'] = 0$,

then $[TB'] = C_2 - [T]$,

and $[BO_2'] = C_3 - [TB']$.

The values of K_1 are shown in Table 11.

Table 11.

No. of experiment	[T]	[TB′]	[BO$_2$′]	K_1
I	2.8	42	190	0.080
II	3.1	46	188	0.078
III	6.8	79	148	0.079
IV	17.8	149	73	0.114
V	22.4	168	57	0.134

Case 2. If K_1 is extremely small or $[TB'] = 0$,

then $[BO_2'] = (2C_3 + [T] - C_2)/2$,

and $[T_2B'] = C_2 + [BO_2'] - C_3 - [T]$.

The values of K_3 are given in Table 12.

However, if we assume the equilibria I and II coexist and put $K_3 = 4.5 \times 10^{-4}$, then we see also in this case that K_1 becomes nearly constant, as shown in Table 13.

Table 12.

No. of experiment	[T]	$[BO_2']$	$[T_2B']$	K_3
I	2.8	211	21.2	0.0131
II	3.1	211	22.9	0.0110
III	6.8	187	39.6	0.00463
IV	17.8	148	74.3	0.00158
V	22.4	141	83.8	0.00119

Table 13.

No. of experiment	[T]	$[BO_2']$	$[TB']$	K_1
I	2.8	191	40.6	0.077
II	3.1	189	44.2	0.075
III	6.8	151	72.6	0.071
IV	17.8	85.5	124	0.081
V	22.4	74.0	134	0.081
				mean 0.077

From the above considerations, the value of the equilibrium constant K_1 is estimated as follows: 0.077 at 15°C. and 0.066 at 20°C. By the aid of van't Hoff's reaction isochore

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2} ,$$

the heat of reaction Q is evaluated as 5200 cals.

$$BO_2' + T \rightleftarrows TB' + Q .$$

This is a probable value to be expected of a reaction of this nature. Hermans⁽¹¹⁾ obtained as the heat of reaction values 3738−5450 cals. in the cases of analogous reactions of various cyclic diols with acetone.

Ratio of the Concentration of the Complex Ion of Mono-diol Type to that of Di-diol Type. This ratio can be expressed in the following terms from the relations (2) and (3):

$$\frac{[T_2B']}{[TB']} = K_2[T] = \frac{K_3}{K_1}[T] .$$

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(11) *Z. physik. Chem*, **113** (1924), 337.

The ratio must therefore increase with increasing [T], but may not amount to a high value, because the ratio K_3/K_1 is really found markedly small. Therefore, as an answer to an interesting question whether the main product of the reaction be TB′ or T_2B', the above considerations of these experimental results give a conclusion that under these conditions both reaction products exist, but the main product is that of the mono-diol type (TB′).

Distribution in the Ether—Boric Acid System. The author further measured the distribution of diethyl tartrate between ether and aqueous boric acid solution, the results of which are shown in Table 14.

Somewhat unexpectedly, the distribution ratio is found not only nearly constant, and independent of the concentration, but almost equal to that of ether–water system. We see that the presence of boric acid does not affect the distribution ratio, which shows clearly the inefficiency of the use of boric acid in the purification process already mentioned. This unexpected fact is, however, be explained by the following considerations:

Table 14. Distribution of diethyl tartrate between ether and 1/4 mol boric acid at 15°.

c_1	c_2	c_2/c_1
0.0305	0.0826	2.71
0.0618	0.1595	2.58
0.0921	0.2452	2.66
0.1212	0.3380	2.79

For the sake of generality, we assume at first that free boric acid can combine with the ester in both phases, the distribution coefficient of boric acid in ether–water system being known to be 1:44. Thus the equilibrium of distribution in the ether–boric acid system is represented by the following scheme:

$$\begin{array}{ll} \text{Ethereal phase:} & HBO_2 + T \rightleftarrows TBH \\ & \ \ \downarrow\uparrow \quad \ \ \downarrow\uparrow \\ \text{Boric acid phase:} & HBO_2 + T \rightleftarrows TBH \end{array}$$

By applying the law of mass action to these equilibria, we obtain:

$$K_e = \frac{[TBH]_e}{[HBO_2]_e[T]_e}; \qquad K_b = \frac{[THB]_b}{[HBO_2]_b[T]_b}.$$

If we take into account the following concentration relations:

$$C_1 = [T]_e + [TBH]_e; \qquad C_2 = [T]_b + [TBH]_b,$$

then the distribution ratio may be expressed as follows:

$$\frac{C_2}{C_1}=\frac{[\mathrm{T}]_b(1+K_b[\mathrm{HBO_2}]_b)}{[\mathrm{T}]_e(1+K_e[\mathrm{HBO_2}]_e)}$$

$$=k\times\frac{1+K_b[\mathrm{HBO_2}]_b}{1+K_e[\mathrm{HBO_2}]_e}\ .$$

The actual experimental results show that C_2/C_1 is nearly equal to k, so it must become

$$\frac{1+K_b[\mathrm{HBO_2}]_b}{1+K_e[\mathrm{HBO_2}]_e}=1\ .$$

To satisfy this relation the numerical values of the two terms, $K_b[\mathrm{HBO_2}]_b$ and $K_e[\mathrm{HBO_2}]_e$, must be either equal to each other or be by far smaller than 1. The latter case is considered to be natural. To explain this we take for simplicity only the mono-diol type of the reaction into consideration.

$$\mathrm{HBO_2+T}\rightleftarrows\mathrm{TBH}\quad\text{(undissociated diethyl boro-tartrate)}\qquad(6)$$

$$\mathrm{TBH}\rightleftarrows\mathrm{H^{\cdot}+TB'}\qquad(7)$$

$$\mathrm{HBO_2}\rightleftarrows\mathrm{H^{\cdot}+BO_2'}\qquad(8)$$

$$\mathrm{BO_2'+T}\rightleftarrows\mathrm{TB'}\qquad(9)$$

By applying the law of mass action to these equilibria, we have the following expressions:

$$K_1=\frac{[\mathrm{TBH}]}{[\mathrm{HBO_2}][\mathrm{T}]}\ ;\qquad k_1=\frac{[\mathrm{H^{\cdot}}][\mathrm{TB'}]}{[\mathrm{TBH}]}\ ;$$

$$K_2=\frac{[\mathrm{TB'}]}{[\mathrm{BO_2'}][\mathrm{T}]}\ ;\qquad k_2=\frac{[\mathrm{H^{\cdot}}][\mathrm{BO_2'}]}{[\mathrm{HBO_2}]}\ .$$

It follows:

$$\frac{k_2}{k_1}=\frac{[\mathrm{BO_2'}][\mathrm{TBH}]}{[\mathrm{HBO_2}][\mathrm{TB'}]}\ ;\qquad\frac{K_1}{K_2}=\frac{[\mathrm{BO_2'}][\mathrm{TBH}]}{[\mathrm{HBO_2}][\mathrm{TB'}]}\ ;\qquad\frac{k_2}{k_1}=\frac{K_1}{K_2}\ .$$

As the boro-diol complex is generally a much stronger acid than boric acid, it follows:

$$k_1\gg k_2\ .\quad\therefore\quad K_2\gg K_1\ .\quad(K_2=0.077\text{ at }15^\circ)\ .$$

Now K_1 corresponds to K_b or K_e, so these numerical values must be very small. Consequently its product with the actual concentration of boric acid, $K[HBO_2]$, may be regarded to be small as compared with 1. Thus the fact that the distribution ratio C_2/C_1 is nearly equal to k has been explained.

From the above experiments and the analysis of the results, we see that free boric acid comes into union with diethyl tartrate only in small proportions, and that the extraction of diethyl ester from the ethereal layer by means of boric acid is not favourable, owing to the fact that boric acid itself is soluble in ethereal phase. Thus it is shown both experimentally and theoretically that strongly dissociable borate KBO_2 favours the complex formation than borax, and consequently is suitable for the extraction of diol soluble in ether.

The author wishes to thank Professor M. Katayama for helpful discussions.

Summary

(1) The distribution of diethyl tartrate between ether and water containing boric acid, borax or potassium metaborate (KBO_2), has been measured.

(2) The results of the experiment on the system of ether–water have been found to follow simply the distribution law of Nernst.

(3) The distribution ratio in the system of ether–aqueous borate solution has been found to increase with the increasing electrolytic dissociation of borate, and this relation has been explained theoretically. The order of the magnitude of the distribution ratio to ether is water$<$borax$<$potassium metaborate.

(4) The equilibrium of boro-diol complex in the borate phase has been studied, and it has been shown that in the borate phase two complex compounds, i.e. those of mono-diol and di-diol types, must coexist, and the equilibrium constant (between ions) has been estimated.

(5) By the study of the temperature coefficient, the reaction of complex formation has been found to be exothermic and the heat of reaction has been estimated.

(6) The distribution of diethyl tartrate in the system of ether–water has been found indifferent to the addition of free boric acid, and this fact has been explained to be due to the insignificant dissociation of boric acid.

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