291. *Estimation of Deuterium Oxide–Water Mixtures. Part II. The Solubility Curves with* n-*Butyric Acid and with* iso*Butyric Acid.*

By William H. Patterson.

The solubility curves which these acids give, severally, with various mixtures of light and heavy water have been traced. The result gives an easy and speedy method of analysing small samples of heavy water.

In a recent note (J., 1937, 1745) the author recorded determinations of the mutual solubility of various deuterium oxide–water mixtures with phenol, and suggested this as a means of estimating the D_2O content of small samples (a few cg.) of the isotopic mixtures. The method has now been extended to the use of either *n*- or *iso*-butyric acid instead of phenol. These reagents have two advantages: (1) The effect is greater, for replacement of water by 99·6% deuterium oxide raises the *C.S.T.* with phenol by 12·2°, that with *n*-butyric acid by 23·6°, and that with *iso*butyric acid by 19·5°. (2) In these systems the range of opalescence, wider in regions beyond those near critical concentration, is much reduced. On the other hand, it is apparently impossible to obtain pure, or standard, samples of either of the above acids.

EXPERIMENTAL.

The sample of *n*-butyric acid used for the following determinations, *i.e.*, Kahlbaum's synthetic, gave reliable results reproducible after several months; although it had a lower f. p. than that of Kahlbaum's purest (— 7·1°; cf. — 6·8°), it gave a flatter curve and lower *C.S.T.* In addition, samples obtained from it by fractional freezing showed much smaller variation and alteration of the *C.S.T.* than did samples similarly obtained from the higher-f. p. acid.

The sample of *iso*butyric acid, f. p. *ca.* — 44°, had a *C.S.T.* of 21·90° in water; the miscibility curve with water was similar to, but higher than, that obtained by Smirnoff (*Z. physikal. Chem.*, 1907, **58**, 667), and also to one previously obtained with a different sample, but was lower than many recorded. The rise of *C.S.T.* with *n*-butyric acid when heavy replaces ordinary water is given by Timmermans and Poppe (*Compt. rend.*, **1935**, **201**, 608) as 23·45° with acid giving a *C.S.T.* with water of — 3·8°; whereas it was 23·60° with the present sample, which has a *C.S.T.* of — 1·60°. No data have hitherto been published for *iso*butyric acid.

The following figures represent results with different samples of heavy water, used as a check on the guaranteed D_2O content. The determinations were made soon after mixing with the acid, otherwise results tended to be low; *e.g.*, 1° lowering was found after a month in sealed glass, and the rate of lowering was not affected by temperature up to 100°. It was also found necessary to reject any samples when water of high deuterium oxide content had been confined in tubes with rubber stoppers for more than an hour, for these, too, yielded low results.

n-*Butyric acid.*

D_2O 99·95% ($N = 0·999$).

Acid, %	51·1	38·03	23·44
M.M.T.	17·20°	21·28°	21·80°

D_2O 99·6% ($N = 0·996$).

Acid, %	47·4	43·4	42·2	41·6	37·0	33·2	30·2	27·8
M.M.T.	18·6°	20·16°	20·30°	20·45°	21·10°	21·40°	21·80°	21·94°
Acid, %	27·24	25·70	25·68	24·5	23·9	22·3	18·9	17·0
M.M.T.	22·00°	21·97°	21·92°	22·0°	21·8°	21·6°	19·8°	16·5°

Max., 22·00°; *n*-butyric acid, 25·5%.

D_2O 79·44% ($N = 0·777$).

Acid, %	55·6	47·3	40·6	38·0	33·8	30·4	29·2
M.M.T.	9·8°	14·6°	16·1°	16·5°	17·0°	17·25°	17·30°
Acid, %	26·1	24·9	23·2	21·6	19·1	17·3	
M.M.T.	17·40°	17·30°	17·0°	16·7°	15·0°	12·3°	

Max., 17·40°; *n*-butyric acid, 27%.

D_2O 66·76% ($N = 0·644$).

Acid, %	53·6	48·6	40·9	29·0	23·9	18·7
M.M.T.	8·2°	10·9°	12·75°	13·78°	13·2°	10·9°

Max., 13·78°; *n*-butyric acid, 28%.

D_2O 52·65% ($N = 0·500$).

Acid, %	51·8	43·7	35·9	29·2	25·5
M.M.T.	6·3°	8·6°	8·3°	9·65°	9·5°

Max., 9·65°; *n*-butyric acid, 29%.

D_2O 20·07% ($N = 0·184$).

Acid, %	33·3	30·2	27·6
M.M.T.	3·2°	3·25°	3·16°

Max., 3·25°; *n*-butyric acid, 31%.

D_2O 19·53% ($N = 0·179$).

Acid, %	49·1	45·8	41·0	36·7	36·6	28·7	26·1	22·0
M.M.T.	1·1°	1·75°	2·3°	2·6°	2·6°	2·8°	2·45°	1·1°

Max., 2·9°; *n*-butyric acid, 31%.

H_2O ($N = 0$).

Acid, %	67·6	55·7	54·6	52·0	46·1	43·4	40·5	37·5
M.M.T.	*ca.* —14·7°	—5·2°	—5·0°	—3·9°	—2·4°	—1·92°	—1·90°	—1·70°
Acid, %	36·9	35·9	31·4	29·5	28·9	27·6	26·1	24·4
M.M.T.	—1·67°	—1·60°	—1·60°	—1·65°	—1·7°	—1·80°	—2·05°	—2·18°
Acid, %	23·5	23·4	20·0					
M.M.T.	—2·2°	—3·2°	*ca.* —6·7° (metastable)					

Max., —1·60°; *n*-butyric acid, 33%.

iso*Butyric Acid.*

D_2O 99·6% (N = 0·996).

Acid, %	52·1	46·6	38·9	34·1	29·9	28·1	26·9	26·2	22·3	15·8	15·3
M.M.T.	36·40°	38·64°	40·21°	40·81°	41·23°	41·40°	41·23°	41·05°	40·20°	29·0°	28·8°

Max., 41·40°; *iso*butyric acid, 28%.

D_2O 52·65% (N = 0·500).
Acid, % 47·5; *M.M.T.* 28·41°.

D_2O 19·53% (N = 0·179).

Acid, %	32·4	27·4	19·5
M.M.T.	25·60°	25·25°	18·2°

H_2O (N = 0).

Acid, %	58·1	49·7	49·0	42·1	38·6	35·97	35·95
M.M.T.	17·00°	20·01°	20·15°	21·20°	21·54°	21·79°	21·76°
Acid, %	33·24	31·35	28·25	26·3	24·8	20·5	
M.M.T.	21·89°	21·90°	21·50°	20·90°	20·25°	15·2°	

Max., 21·90°; *iso*butyric acid, 32%.

On plotting the curves for these figures, the method of analysis of the D_2O content of an unknown sample of heavy water is simple. An inclined straight line joins all the maxima of the curves. A similar straight line is also drawn on a sheet of celluloid and one of the curves traced on it also. The acid is then added to the heavy water sample so that its content is 22—50% : with a fine dropper, it is surprising how nearly the critical concentration can be achieved. With practice also the position on the curve can be judged by the opalescence phenomena; but apart from this the curve on the celluloid is placed on the *M.M.T.* found, with the straight lines coincident, and then the corresponding *C.S.T.* can at once be read.

The same curve may be used for all positions between the maximum and higher acid content; but on the water side the curve becomes steeper with higher D_2O content, and for accuracy the shape of the nearest curve should be used.

Having obtained the *C.S.T.* for the unknown sample, a graph gives the corresponding percentage, or molar fraction (N), of D_2O. This is not quite a straight line as it is inflected at 52·65%, *i.e.*, when it corresponds to HDO : a straight line would give a 3% error at this point.

The only advantage of *iso*butyric acid over *n*-butyric lies in its being available at temperatures above that of the room when mixtures of low D_2O content are being tested.

The method of analysis has already proved very useful in experiments on adsorption and interchange.

QUEEN MARY COLLEGE, UNIVERSITY OF LONDON.

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