

**152. The Systems Sodium Chloride–Butyric Acid–Water, Sodium Chloride–isoButyric Acid–Water, and Potassium isoButyrate–iso-Butyric Acid–Water at 25°.**

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For comparison with previous work on the system sodium butyrate–butyric acid–water (Bury and Owens, *Trans. Faraday Soc.*, 1935, **31**, 480), the systems named in the title have been examined. Sodium butyrate and potassium *isobutyrate* are abnormal in their influence on the critical solution point and the mutual solubility of acid and water. Analogous phenomena are quoted, and the cause briefly discussed.

AN investigation of the system sodium hydroxide–butyric acid–water at 25° (Bury and Owens, *loc. cit.*) has shown that no separation into two layers occurs even when the solution is saturated with sodium butyrate, *i.e.*, addition of 1.95 mols. of sodium butyrate per 1000 g. of a mixture of butyric acid and water of the critical composition does not raise the critical solution temperature from – 3° to 25°. In view of what is known of the influence of salts on a critical solution point, this seemed remarkable, and we have therefore examined the system sodium chloride–butyric acid–water. Sodium chloride behaves in the normal manner: only 0.22 mol. per 1000 g. of a critical solution mixture is necessary to raise the critical solution point to 25°. For the sake of comparison we have examined the influence of sodium chloride and potassium *isobutyrate* on mixtures of *isobutyric acid* and water.

EXPERIMENTAL.

Suitable mixtures were shaken in hard-glass vessels until analysis showed that equilibrium was established. Butyric or *isobutyric acid* was determined by titration, and potassium *isobutyrate* by conversion into potassium chloride. All results given in the tables are the mean of two concordant determinations.

System: Butyric Acid–Sodium Chloride–Water.

(1) Solutions in equilibrium with solid sodium chloride.

Solution.		Moist solid.		Solution.		Moist solid.		Solution.		Moist solid.	
$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %
0	26.45	—	—	1.47	25.68	0.21	87.16	94.06	0.06	—	—
0.22	26.30	0.25	91.50	89.25	0.12	0.29	94.94	97.44	0.03	0.21	97.09
0.68	26.05	0.50	89.24	90.37	0.11	0.25	96.55	99.98	0.02	—	—
1.30	25.76	—	—	93.27	0.07	0.19	97.49				

(2) Two-layer mixtures.

Upper layer.		Lower layer.		Upper layer.		Lower layer.		Upper layer.		Lower layer.	
$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %	$C_4H_8O_2$ , %	NaCl, %
88.12	0.31	1.77	25.48*	67.79	0.90	8.08	8.89	41.50	1.49	27.10	2.26
85.65	0.50	3.00	21.15	64.08	0.95	11.50	5.92	40.19	1.56	28.47	2.20
79.52	0.58	4.32	17.48	60.42	0.97	12.62	4.44	38.73	1.58	28.90	2.20
76.38	0.65	5.65	14.05	50.78	1.35	18.64	3.20	38.20	1.58	29.11	2.19
73.30	0.73	6.01	12.36	44.78	1.42	22.76	2.50	36.50	1.69	31.75	2.07
70.20	0.85	7.75	10.15	42.31	1.45	26.24	2.30	34.86	1.90	32.70	2.00

## System: isoButyric Acid-Sodium Chloride-Water.

## (1) Solutions in equilibrium with solid sodium chloride.

Solution.		Moist solid.		Solution.		Moist solid.	
<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %	<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %	<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %	<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %
0	26.45	—	—	95.53	0.06	6.35	91.61
0.24	26.31	0.06	94.32	96.24	0.04	7.21	92.40
0.73	26.11	0.09	90.90	98.24	0.03	6.91	93.47
1.17	25.88	0.51	86.85	99.99	0.01	—	—

## (2) Two-layer mixtures.

Upper layer.		Lower layer.		Upper layer.		Lower layer.	
<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %	<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %	<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %	<i>iso</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	NaCl, %
94.78	0.14	1.40	25.77*	82.93	0.12	8.32	6.82
		1.80	23.75	78.40	0.11	10.80	3.95
94.13	0.14	2.43	20.88	74.11	0.10	12.85	2.33
		2.55	20.40	69.34	0.10	15.80	1.25
		2.95	18.50	58.74	0.06	19.05	0.60
90.10	0.14	3.67	15.54	57.26	0.00	24.10	0.00
		4.40	13.50				
86.86	0.14	5.59	10.63				
		7.10	9.15				

## System: isoButyric Acid-Potassium isoButyrate-Water.

Upper layer.		Lower layer.		Upper layer.		Lower layer.	
<i>i</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	<i>i</i> -C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> K, %	<i>i</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	<i>i</i> -C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> K, %	<i>i</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	<i>i</i> -C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> K, %	<i>i</i> -C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> , %	<i>i</i> -C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> K, %
57.26	0	24.10	0	51.20	0.20	30.17	0.32
57.08	0.02	24.23	0.09	49.81	0.23	30.99	0.33
56.90	0.05	25.09	0.18	49.00	0.24	31.21	0.34
55.54	0.08	26.43	0.23	47.91	0.26	31.80	0.34
54.76	0.10	27.14	0.25	46.89	0.28	32.56	0.34
53.81	0.13	27.72	0.27	45.72	0.29	34.02	0.35
53.17	0.16	28.00	0.28	44.54	0.30	35.21	0.36
52.50	0.18	29.03	0.29	43.48	0.32	37.62	0.36
51.72	0.19	29.69	0.30	42.00	0.34	39.57	0.37
51.11	0.20	30.08	0.32				

\* Triple point: Water-rich solution-acid-rich solution-sodium chloride.

## DISCUSSION.

The chief difference between the systems butyric acid-water and *isobutyric* acid-water is that in the first the critical solution point lies below the experimental temperature, and in the second case above it. In both cases the action of sodium chloride is normal: addition renders acid and water less soluble in each other and raises the critical point. Potassium *isobutyrate* is, on the other hand, abnormal; its addition causes acid and water to be more miscible in each other. Similarly, benzoic acid is "salted-in" by sodium benzoate, whereas normal salts such as sodium chloride exercise the normal salting-out effect (Larsson, *Z. physikal. Chem.*, 1927, 127, 233; Kolthoff and Bosch, *J. Physical Chem.*, 1932, 36, 1685), and analogous phenomena are shown by the mandelates (Ross and Morrison, J., 1933, 1016; 1936, 867; Ross, Morrison, and Johnstone, J., 1937, 608; 1938, 264). To explain these results, the formation of a complex ion between a molecule of a carboxylic acid and its negative ion  $[R\cdot CO_2H, R\cdot COO]^-$  has been suggested, and is supported by the frequency with which solid compounds of the type  $R\cdot CO_2H, R\cdot CO_2M$ , *e.g.*, the acid soaps, separate out. It must, however, be remembered that no proof of the existence of such complex ions in solution has yet been obtained. The increase of solubility of *isobutyric* acid in water on the addition of potassium *isobutyrate* is much greater than would be expected on this hypothesis; for every molecule of potassium *isobutyrate* added about eight molecules of *isobutyric* acid enter the water layer (in the limiting case for small additions of potassium *isobutyrate*). Lastly, the salting-in effect, though abnormal, is not rare, and frequently occurs where complex formation is improbable (Thorin, *Z. physikal. Chem.*, 1915, 89, 688; Euler and Svanberg, *Z. Elektrochem.*, 1917, 23, 192; Schryver, *Proc. Roy. Soc.*, 1910, B, 83, 96;

Kruyt and Robinson, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1244; see also Lester Smith, *J. Physical Chem.*, 1932, **36**, 1401, 1672, 2455; Hartley, J., 1938, 1968; Lawrence, *Trans. Faraday Soc.*, 1937, 325). In the present state of our knowledge, it would appear more probable that the solvent properties of the water are sufficiently modified by the large organic anions to hide the normal salting-out effect (Kruyt and Robinson, *loc. cit.*).

Our thanks are due to the Chemical Society for a grant for the purchase of materials.

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[Received, February 9th, 1939.]

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