Bull. Chem. Soc. Jpn., **57**, 2021—2022 (1984)

Equilibria in Aqueous Ternary System Containing Na^+, $CH_3CO_2^-$, and HPO_4^{2-} between 38 and 75 °C

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(Received September 1, 1983)

Synopsis. Ternary system CH_3CO_2Na–Na_2HPO_4–H_2O was investigated between 38 and 75 °C. No double salt formation occurs in this temperature range. Saturated CH_3CO_2Na solution has a strong dehydrating influence on $Na_2HPO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 7H_2O$. The lowest formation temperature for anhydrous Na_2HPO_4 is about 57 °C.

Recently, Kimura[1] reported that addition of a small amount of a mixture of disodium hydrogenphosphate and anhydrous sodium acetate to a sodium acetate solution is very effective for the crystal nucleation of sodium acetate trihydrate from the solution. Wada and Matsuo[2] have studied the influence of preheating on the crystallization of sodium acetate trihydrate from its aqueous solution with a small amount of disodium hydrogenphosphate added, proposing an adsorption model to account for the crystal nucleation catalytic effect. To complete the investigation, knowledge is required of the ternary system, sodium acetate–disodium hydrogenphosphate–water. Phase diagrams of the binary systems, sodium acetate–water and disodium hydrogenphosphate–water, based on data from Seidell's compilation,[3] are shown in Fig. 1. In this figure, W_a and W_b are the mass fractions of sodium acetate and disodium hydrogenphosphate, respectively.

This paper reports results from an investigation using disodium hydrogenphosphate together with sodium acetate aqueous solution.

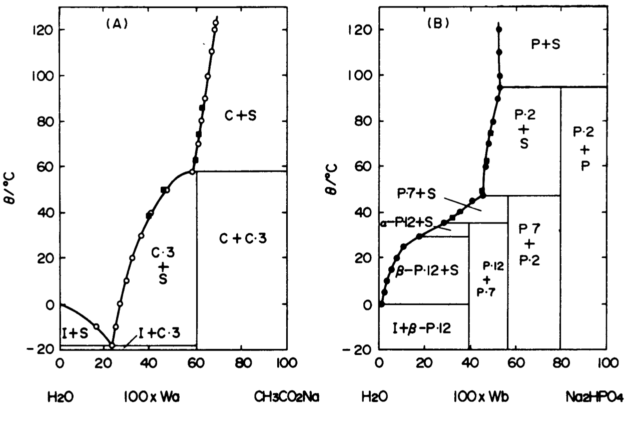

Fig. 1. Phase diagrams of the binary systems, CH_3CO_2Na–H_2O (A) and Na_2HPO_4–H_2O (B). Symbols: I=ICE, C=CH_3CO_2Na, C·3=$CH_3CO_2Na \cdot 3H_2O$, P=Na_2HPO_4, P·2=$Na_2HPO_4 \cdot 2H_2O$, P·7=$Na_2HPO_4 \cdot 7H_2O$, P·12=$Na_2HPO_4 \cdot 12H_2O$, S=Solution.
○: the data obtained by Green,[4] ●: the average of the reported data (the transition temperature between α-P·12 and β-P·12 in the presence of P·7 is not unkown),[3] ■: the data obtained by the present experiment.

Experimental

Sodium acetate trihydrate, anhydrous sodium acetate, and disodium hydrogenphosphate were guaranteed grade reagents. Experiments were conducted as previously described.[5] Phosphate ion was analyzed colorimetrically. The concentration of dissolved total salts was determined by drying the supernatant solution. The sodium acetate concentration was calculated from the difference in concentration between total salts and disodium hydrogenphosphate. The redidual solid existing in equilibrium with the saturated solution was separated out and identified by the X-ray diffraction. The solution in equilibrium with two solid phases was confirmed by analyzing the solution with those solids added.

Results

For the ternary system sodium acetate–disodium hydrogenphosphate–water, four sets of data for isotherms between 38 and 75 °C are shown in Table 1. Solubilities of the binary systems, sodium acetate–water and disodium hydrogenphosphate–water, determined by the present experiment, are plotted in Fig. 1. From Fig. 1, it is clear that the solubilities determined here are in good agreement with the reported data.

There is no formation of double salt in the present system between 38 and 75 °C. It is noteworthy that the saturated sodium acetate solutions contain only a small amount of disodium hydrogenphosphate and that they have a very strong dehydrating influence on the disodium hydrogenphosphate hydrates. The outline of the ternary system below 75 °C is given in Fig. 2, with

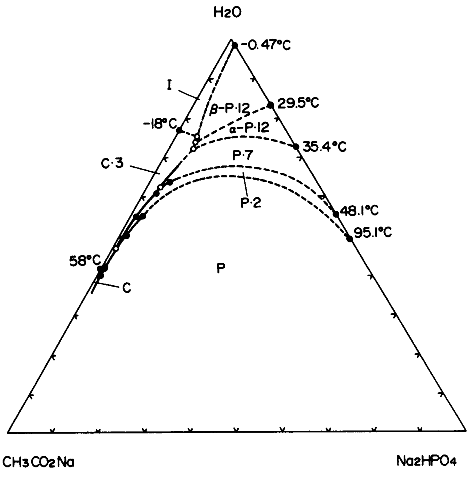

Fig. 2. Synopsis of the composition of the solution at the invariant and univariant equilibria of the ternary system CH_3CO_2Na–Na_2HPO_4–H_2O. The symbols in this figure indicate the same phases as those in Fig. 1. ●: the data obtained by the present experiment, ○: the invariant point.

Table 1. Data for isotherms for ternary system CH_3CO_2Na-Na_2HPO_4-H_2O at 38, 50, 62, and 75 °C

θ / °C	Solution		Solid[c] phase	θ / °C	Solution		Solid[c] phase
	$100 \times W_a$[a]	$100 \times W_b$[b]			$100 \times W_a$[a]	$100 \times W_b$[b]	
38	0	31.9	P·7	62	0	45.4	P·2
	5.3	24.2	P·7		9.2	30.5	P·2
	11.5	16.1	P·7		21.0	14.7	P·2
	18.0	10.3	P·7		34.4	4.4	P·2
	23.6	7.3	P·7		40.4	2.5	P·2
	27.9	6.0	P·7		46.1	1.6	P·2
	32.0	4.4	P·7+P2		48.4	1.3	P·2+P
	34.0	3.6	P·2		52.9	1.0	P
	37.0	2.6	P·2+C3		57.5	0.69	P+C
	38.5	0	C·3		58.2	0	C
50	0	44.4	P·2	75	0	47.4	P·2
	7.6	32.6	P·2		9.1	32.6	P·2
	12.1	22.7	P·2		20.0	17.3	P·2
	20.6	14.2	P·2		32.1	6.5	P·2
	29.6	6.3	P·2		40.0	3.3	P·2
	34.8	3.6	P·2		42.2	2.8	P·2+P
	38.5	2.7	P·2		48.1	1.6	P
	42.3	1.7	P·2		53.0	0.97	P
	43.6	1.4	P·2+C·3		59.2	0.60	P+C
	44.5	0	C·3		59.6	0	C

a) W_a is the mass fraction of CH_3CO_2Na in the system. b) W_b is the mass fraction of Na_2HPO_4 in the system. c) Symbols: C=CH_3CO_2Na, C·3=$CH_3CO_2Na \cdot 3H_2O$, P=Na_2HPO_4, P·2=$Na_2HPO_4 \cdot 2H_2O$, and P·7=$Na_2HPO_4 \cdot 7H_2O$.

some assumptions applied for the lowest temperature. This figure gives a survey of the formation of the solid.

Isothermally invariant points were plotted with temperature on the ordinate and disodium hydrogenphosphate concentration on the abscissa. The lowest formation temperature for anhydrous disodium hydrogenphosphate is determined as about 57 °C from the point of intersection of the curves on which the solution is in equilibrium with two solid phases.

The authors wish to express their thanks to Dr. Ryoichi Kiriyama for his useful discussions and to Drs. Tsuneharu Nitta, Eiichi Hirota, and Masanari Mikoda for their continuous encouragement. They are grateful to Miss Shoko Ueno for the colorimetric analyses and also to Dr. Ryoichi Yamamoto for his discussions throughout this work.

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