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136. Kyoji Hayano and Sataro Imado : Studies on Aluminum Complex Compound of PAS. II.*[2] Hydrates of Alumino-*p*-aminosalicylic Acid and its Calcium Salt.

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It was shown in the preceding paper*[1] that alumino-*p*-aminosalicylic acid*[3] (abbreviated as Al-PAS) and calcium alumino-*p*-aminosalicylate (abbreviated as Al-PAS-Ca) synthesized by the present writers agreed in composition to (I) and (II), corresponding to the chemical formula given by Burrows and others[1] to the aluminum complex compound of salicylic acid.

$$H_2\left[(C_7H_5O_3N)_2Al\begin{matrix}OH\\OH_2\end{matrix}\right]\cdot 3H_2O(\text{or } 6H_2O) \quad \text{(I)} \qquad Ca\left[(C_7H_5O_3N)_2Al\begin{matrix}OH\\OH_2\end{matrix}\right]\cdot 7H_2O \quad \text{(II)}$$

In the present series of experiment, crystal water and dissociation vapor pressure of these hydrates were measured, and stability of the calcium salt at ordinary temperature was examined, which are described in the present paper.

1. Measurement of Crystal Water by Loss in Weight

It is known that hydrates of inorganic complex compounds in general lose its water of crystallization outside the complex group at 105° and, therefore, loss in weight was measured by this method.

Table I. Measurement of Crystal Water by Loss in Weight

Period of drying (hr.)	Loss in weight (%)	
	Al-PAS($3H_2O$)	Al-PAS-Ca
4.5	12.4	22.7
9.0	13.0	23.8
14.0	13.3	23.9
18.5	13.6	24.1
Theoretical	12.9	23.8

The trihydrate of Al-PAS and heptahydrate of Al-PAS-Ca, as shown in Table I, lose approximately theoretical amount of crystal water when dried at 105° for 9 hours to become anhydrous. A slight decrease in weight occurs on drying more than 9 hours but this is thought to be accompanied with partial decomposition. Stability of these hydrates to heating will be described in the following section on the method of measurement using thermobalance. Result of measurement of loss in weight has shown that Al-PAS and Al-PAS-Ca respectively agree with the trihydrate (I) and heptahydrate (II).

2. Measurement of Crystal Water by Thermobalance

Thermobalance has often been used as a tool in examining the amount of crystal water or a state of decomposition of inorganic compounds but it has rarely been used for organic compounds. It was considered that this method might also be used in measuring the amount of crystal water in organic compounds and attempts were made to measure the crystal water in the hydrates of Al-PAS and Al-PAS-Ca. The result

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*2 Part I. This Bulletin, **7**, 756(1959).
*3 See Part I of this series for chemical term of this designation.

1) G. J. Burrows, I. William : J. Chem. Soc., **1928**, 222.

of thermobalance measurement of the trihydrate of Al–PAS is shown in Fig. 1 in which the rate of loss in weight with rise of temperature is represented as the number of moles of water liberated on the ordinate. As will be seen in Fig. 1, crystal water is liberated rapidly up to around 90° and the compound becomes somewhat stable thereafter but the curve does not level off even after it has reached the point of three moles of crystal water, probably due to the lability of Al–PAS to heat. The curve rises gradually, the compound suddenly undergoes decomposition at around 160° to form a sublimate, and the curve rises rapidly.

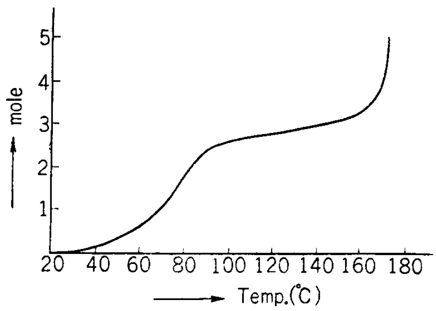

Fig. 1. Thermobalance Graph of Alumino-*p*-aminosalicylic Acid Trihydrate

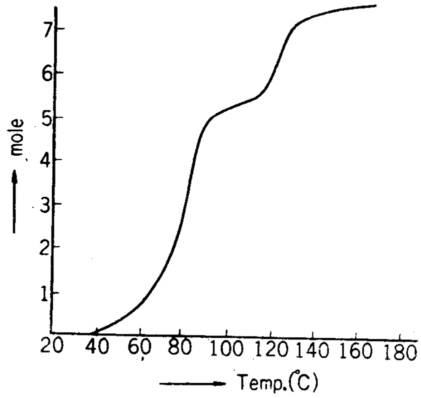

Fig. 2. Thermobalance Graph of Calcium Alumino-*p*-aminosalicylate Heptahydrate

In the case of heptahydrate of Al–PAS–Ca, whose curve is shown in Fig. 2, five moles of crystal water is lost at around 100° and the compound becomes somewhat stable. When the heating is continued further, two moles of crystal water is liberated and the curve becomes level at around 140°, indicating the stability of this substance.

In this case, decomposition is gradual even at 180°, indicating that Al–PAS–Ca is comparatively stable even after loss of crystal water outside the complex group. The curve in Fig. 2 suggests the presence of a pentahydrate, besides the heptahydrate, but, as will be described later, the pentahydrate is unstable in the air and is assumed to transit to the heptahydrate.

3. Measurement of Dissociation Vapor Pressure of the Hydrate of Calcium Alumino-*p*-aminosalicylate

Substances possessing water of crystallization indicate a definite dissociation vapor pressure at a definite temperature. In order to know the stability of Al–PAS–Ca crystal at room temperature and in the air, its dissociation vapor pressure was measured. Two methods, dynamic and static, are known for the measurement of vapor pressure. The dynamic method is somewhat more complicated than the static method in experimental procedures and the error tends to be greater. In the present series of experiments, both methods were carried out, the dynamic at first, followed by the static. For the dynamic method, a flow process was used and the experiment was carried out with an apparatus shown in Fig. 3.

About 20 g. of Al–PAS–Ca crystals was placed in the sample tube F, water was dropped into B from A at the rate of 2 L./6 hr. by adjusting the flow rate with the screw cock to drive out the air in B. At the same time, the screw cock on L was opened to flow water from J. A preliminary experiment was carried out first with crystals of $Na_2SO_4 \cdot 10H_2O$ in order to test the validity of this apparatus and dissociation vapor pressure, π, was calculated from the following formula :

$$\pi = \frac{62370 \times TgP}{(P'-p) \times MV + 62370 \times Tg}$$

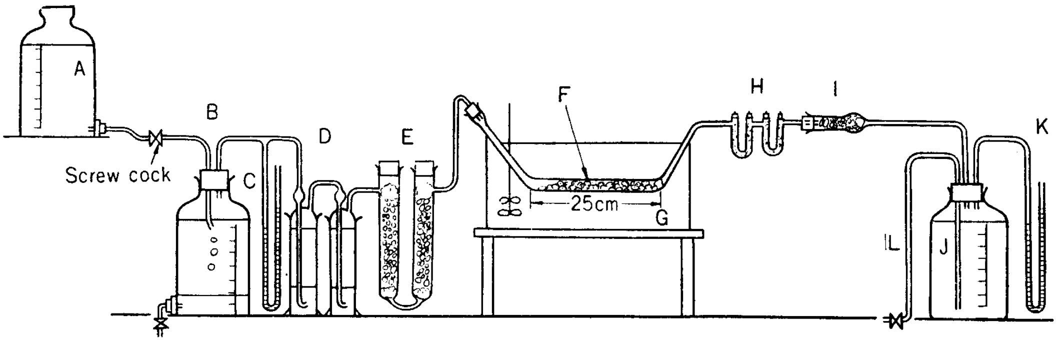

Fig. 3. Apparatus for Measurement of Dissociation Vapor Pressure

A : 5-L. Glass bottle
B : 5-L. Glass bottle
C : Manometer
D : Gas washer (conc. H_2SO_4)
E : Drying tube ($CaCl_2$, P_2O_5)
F : Sample tube (diam., 2 cm.) (length, 25 cm.)
G : Thermostatic bath
H : Absorption tube ($CaCl_2$)
I : $CaCl_2$ tube
J : 5-L. Glass bottle
K : Manometer
L : Water outlet tube

where T is the temperature (°K) of the air trap, P the external atmospheric pressure (mm. Hg), P' the pressure of air sent in (mm. Hg), p the saturated vapor pressure (mm. Hg) at temperature T, V the volume (cc.) of air passed, and M is the molecular weight of the vapor (water in this case).

Dissociation vapor pressure of the hydrate of Al–PAS–Ca measured at 20~30° is given in Table II.

TABLE II. Dissociation Vapor Pressure of the Hydrate of Calcium Alumino-*p*-aminosalicylate (Dynamic Method)

Expt. No.	Thermostat (°C)	B (mm. Hg)	J (mm. Hg)	Air trap (°C)	Ext. press. (mm. Hg)	Air vol. (cc.)	Water (g.)	Vapor pressure (mm. Hg)
0*	20	5	− 6	16	754	2,075	0.0257	12.35
1	20	6	− 5	15	763.5	2,100	0.0145	6.68
2	22	11	−15	18	761.5	2,100	0.0198	9.12
3	22	8	− 4	18	759.16	2,125	0.0228	10.92
4	25	12	− 2	20	757.93	2,075	0.0291	14.36
5	28	11	− 7	16	761.5	1,550	0.0170	11.12
6	28	8	− 6	17	758.57	2,025	0.0227	11.31
7	28	10	− 4	17.5	762.4	2,050	0.0255	12.60
8	30	9	− 5	18	763.5	2,125	0.0255	12.24
9	30	10	− 3	18	760.2	2,100	0.0271	12.84

* Values obtained with $Na_2SO_4 \cdot 10H_2O$

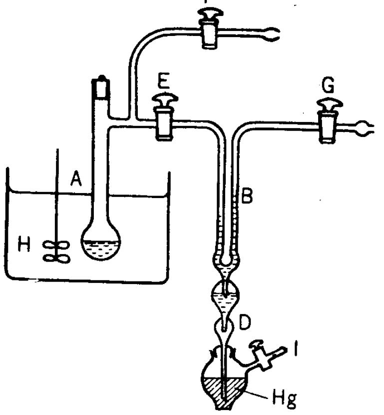

Fig. 4. Apparatus for Static Measurement of Crystal Water in Calcium Alumino-*p*-aminosalicylate Heptahydrate

A : Sample bottle (40 cc.)
B : Manometer
C : Mercury trap
D, E, F, G, I : Cocks
H : Thermostatic bath

Dissociation vapor pressure was then measured by the static method using an apparatus shown in Fig. 4. About 5 g. of the hydrate of Al–PAS–Ca was placed in A, cocks D and E were closed, cock G was opened, and this end was connected to a high-vacuum pump to bring the apparatus to a reduced pressure. The cock D was then cautiously opened to let mercury rise to the lower end of manometer B. The cocks D and F were then closed, the cock E opened, and the apparatus was evacuated with a high vacuum pump (to 0.001 mm. Hg), while chilling the sample bottle A in dry–ice bath. The cock E was then closed and bottle A taken out of the dry–ice bath to allow slight evaporation of water in the sample at room temperature. This procedure was repeated several times to bring the apparatus evacuation to 0.001 mm. Hg, the cock G closed, the cock D was cautiously opened to bring mercury up the manometer B, and the bottle A was again immersed in the thermostat to maintain it at a constant temperature. After 24 hours, difference in mercury column was read on the cathetometer. Experimental result is given in Table III.

TABLE III. Dissociation Vapor Pressure of the Hydrate of Calcium Alumino-*p*-aminosalicydate (Static Method)

t°	0	25	35
π (mm. Hg)	1.75	11.43	22.64

The values obtained by the foregoing dynamic and static methods agreed approximately. Fig. 5 is the graph obtained by plotting $\log \pi$ on the ordinate and $1/T$ on the abscissa, and the heat of dissociation Q at around room temperature and empirical formula were calculated from the graph.

$$\log \pi/760 = A - \frac{Q}{RT} \qquad Q = 12.345 \text{ K cal./mole} \qquad A = 7.237$$

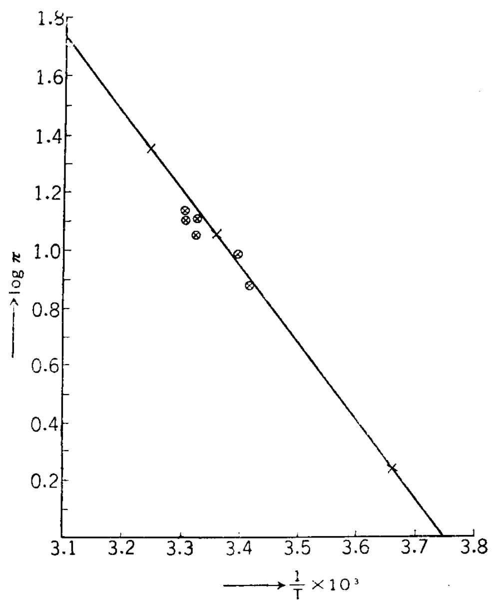

Fig. 5.

Dissociation vapor pressure of the heptahydrate of Al–PAS–Ca at various temperatures was calculated from this empirical formula and the values so obtained were compared with the saturated vapor pressure at respective temperatures and with mean humidity of the atmosphere (calculated with saturated vapor pressure as 66%). These data are given in Table IV.

Vapor pressure of the saturated water solution of Al–PAS–Ca was also measured and the values obtained were 16.5 mm. (20°), 22.9 mm. (25°), and 30.7 mm. (30°). Therefore, the heptahydrate is stable at room temperature.

TABLE IV.

t (°C)	0	5	10	15	18	20	22	25	28	30	35
Satd. vapor pressure (mm. Hg)	4.58	6.54	9.21	12.79	15.48	17.54	19.83	23.7	28.35	31.82	42.18
Mean humidity	3.02	4.32	6.08	8.44	10.22	11.58	13.09	15.68	18.71	21.00	27.84
Al-PAS-Ca (mm. Hg)	1.74	2.51	3.72	5.25	6.76	7.95	9.12	11.22	18.31	15.85	22.39

Experimental

(I) a) Measurement of Loss in Weight of Alumino-*p*-aminosalicylic Acid—
Sample of Al-PAS($3H_2O$) taken: 0.6936 g.
Anal. found: PAS, 74.1; Al, 6.69%. PAS:Al=2:1.02
Experimental result is shown in Table I.
Analysis of the dried residue:

	PAS (%)	Al (%)	Molar ratio (PAS:Al)
Found	84.2	7.78	2:1.05
Calcd.	83.6	7.38	2:1

b) Measurement of Loss in Weight of Calcium Alumino-*p*-aminosalicylate—
Sample of Al-PAS-Ca taken: 0.4654 g.
Analysis of the sample:

	PAS (%)	Al (%)	Ca (%)	Molar ratio (PAS:Al:Ca)
Found	57.8	5.09	7.55	2:0.99:1.0
Calcd.	57.7	5.06	7.55	2: 1 :1

Experimental result is given in Table I.
Analysis of the dried residue:

	PAS (%)	Al (%)	Ca (%)	Molar ratio (PAS:Al:Ca)
Found	75.9	6.75	9.77	2:1.01:0.98
Calcd.	75.6	6.69	9.90	2: 1 :1

(II) a) Thermal Decomposition of Trihydrate of Al-PAS with Thermobalance—

Analysis of sample: PAS, 75.0; Al, 6.76%. PAS:Al=2:1.02
Calcd.: PAS, 72.8; Al, 6.42%. PAS:Al=2:1

The sample had been dried at 50°. As indicated by its analytical values, it had lost 2.86% of water as a trihydrate and had 2.2% more of PAS. Experimental result is shown in Fig. 1.

b) Thermal Decomposition of Al-PAS-Ca by Thermobalance—

Analysis of sample: PAS, 58.7; Al, 5.47; Ca, 7.82%.
Calcd.: PAS, 57.7; Al, 5.06; Ca, 7.55%.

Experimental result is shown in Fig. 2. The thermobalance used was a quartz spring balance.

(III) Heat of Dissociation (Q) of Al-PAS-Ca (Heptahydrate)—

$$\log \pi/760 = A - \frac{Q}{RT}$$

From Table III:

t (°C)	T	π	$\log \pi$	log 760=2.8808		$\log \pi/760$
0	273 (T_3)	1.75	0.243	〃	〃	$\bar{3}.3622$ (P_3)
25	298 (T_2)	11.43	1.0580	〃	〃	$\bar{2}.1772$ (P_2)
35	308 (T_1)	22.64	1.3549	〃	〃	$\bar{2}.4712$ (P_1)

Value of Q:

$$P_1 - P_2 = A - A + \frac{Q}{1.988 \times 2.302}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad 0.2969 = \frac{Q}{4.576} \times 0.109 \times 10^3$$

$$Q = 12.46 \times 10^3 \text{ cal./mole}$$

Similarly:

$$P_1 - P_3 = \frac{Q}{4.576}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \qquad 1.119 = \frac{Q}{4.576} \times 0.416 \times 10^{-3}$$

$$Q = 12.23 \times 10^3 \text{ cal./mole}$$

Therefore:

$$Q = \frac{12.46 + 12.23}{2} \times 10^3 = 12.345 \times 10^3 \text{ cal./mole}$$

Value of A: By interpolation of $Q = 12.345$ Kcal./mole into

$$\log \pi/760 = A - \frac{Q}{RT}$$

P_1	T	T_2	T_3	Mean value
A	7.234	7.231	7.245	7.237

Summary

Crystal water and dissociation vapor pressure of the hydrates of alumino-*p*-aminosalicylic acid and calcium alumino-*p*-aminosalicylate were measured. Measurement of loss in weight showed that there are three moles of crystal water in Al-PAS and seven moles in Al-PAS-Ca. Thermobalance method showed that a pentahydrate of Al-PAS-Ca would be present besides the heptahydrate. Al-PAS is labile above 140° and undergoes decomposition but Al-PAS-Ca was found to be comparatively stable even at 180°.

Dissociation vapor pressure of the heptahydrate of Al-PAS-Ca was measured and heat of dissociation at around room temperature was calculated. Stability of these complex compounds in the air was also examined.

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137. **Kyoji Hayano and Sataro Imado**: Studies on Aluminum Complex Compound of PAS. III.*2 On the Structure of Alumino-*p*-amimosalicylic Acid and its Calcium Salt.

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Syntheses and determination of crystal water in alumino-*p*-aminosalicylic acid*3 (hereinafter abbreviated as Al-PAS) and its calcium salt (hereinafter abbreviated as Al-PAS-Ca) were described in the preceding two papers. Structural studies were then carried out on Al-PAS-Ca which are described herein.

Single crystal of Al-PAS-Ca of the size necessary for structural studies was successfully prepared and with this crystal, morphological and optical studies were carried out. Examination was then made for the presence of a center of symmetry in the molecule which would be necessary in finding the structure of Al-PAS-Ca. As one of the methods for examining the center of symmetry, infrared absorption spectrum and Raman effect of Al-PAS-Ca were meaured. Since all the Raman lines were found to be infrared active, it was concluded that there is no center of symmetry in the Al-PAS-Ca molecule.

1. Preparation of Single Crystal Sample

Al-PAS-Ca dissolves in water at room temperature at the rate of only 0.7~0.8 g. per 100 g. and heating of this mixture results in partial decomposition. Therefore, recrystallization from water is not desirable while the salt is extremely sparingly soluble in various organic solvents, and it is very difficult to obtain a well-developed, translucent single crystal suitable for crystallomorphological studies by the usual method. Various measures were tried and the following method gave the best result.

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*2 Part II : This Bulletin, 7, 761(1959).
*3 See Part I of this series (p. 756) for chemical term of this designation.