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The Separation of Aluminum from Iron by the Zone-melting of Their Complexes

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The separation of Al from Fe was attempted as a first step in the chromatographic application of the zone-melting method to metal complexes. *N,N'*-ethylenedianthranilic acid and benzoic acid complexes, and various organic solid solvents were prepared. The experiment was carried out with a zone speed of 6 cm/hr and a molten-zone length of 0.6—1.0 cm at 75°C. When stearic acid was used as the solvent, the recovery percentage of Al was about 75% with the benzoic acid complex and about 99% with the *N'N'*-ethylenedianthranilic acid complex. Furthermore, the effective distribution coefficient and phase diagram supported due idea of the behavior of the complexes.

It has widely been known that pure germanium may be prepared by a zone-melting method.[1] Nowadays, it is used in various fields.[2,3] There are two methods of zone-melting for the separation and condensation of metals. One is used for the metallic state, and the other is used for the metal chelate state. Though the latter is easier than the former, because metal chelates have relatively low melting points and various organic characteristics, good results seem not yet to have been obtained.[4]

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[1] W. G. Pfann, *Trans. AIME*, **194**, 747 (1952).

[2] W. G. Pfann, "*Zone Melting*," John Wiley & Sons, Inc., New York, (1958), 128.

[3] H. Schildknecht, "*Zoneschmelzen*," Verlag Chemie, Weinheim, (1964).

[4] K. Ueno, *et al. Talanta* **14**, 1403, 1411, (1967); K. Ueno, H. Kaneko, and Y. Watanabe, *Micro. Chem. J.*, **10**, 244 (1966); K. Ueno, H. Kaneko, and N. Fujimoto, *Talanta*, **11**, 1371 (1964).

In this study, in order to separate one metal from other, the chromatographic development[5] by the zone-melting method was carried out with the metal chelates of benzoic acid[6] and *N,N'*-ethylenedianthranilic acid (NEA)[7] as solutes, and with stearic acid, benzoic acid, and naphthalene as their solvents. When stearic acid was used as the solvent, good results in the separation of aluminum from iron were obtained. Furthermore, the effective distribution coefficient[8] and the phase diagram were examined, so that the operation of this method could be discussed.

Experimental

Zone-melting Procedure. A vertical type zone-melting apparatus was used, by which a sample in a glass tube was zone-melted. The apparatus had several ring heaters, and it was cooled with water or air. The apparatus was of our own making. Long glass tubes 5 mm in inner diameter were used as the sample columns. As Fig. 1 shows, about 0.1 mg of the complex with about 250 times as much solid solvent was melted into the bottom of the glass tube and then cooled to solidify it, then the pure solvent was placed on it. Finally, the column length was 20 cm. When a 30-cm column was used, it took very long to zone-melt, and the results were similar to those obtained with the 20-cm column. Therefore, the 20-cm column was mainly used in this experiment. Besides it, the 10-cm column was also used for the sake of comparison. The experiment was carried out at a rate of zone travel of 6 cm/hr. The width of the molten zone was 1 cm in the apparatus with air cooling and 0.6 cm in the one with water cooling. The temperature of the molten zone was about 75°C. At temperatures higher than 75°C, the molten zone became wider and it became unstable at the solid-liquid intersurface.

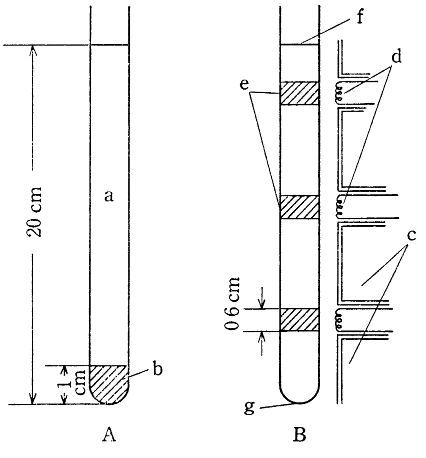

Fig. 1. Diagrammatic representation of sample column(A) and that in zone apparatus with water-cooling(B).
(a) Solid solvent, (b) Complex as solute, (c) Cooler, (d) Heater, (e) Molten zone, (f) Upper end, (g) Bottom

Preparation of Metal Complexes. A metal ion solution was adjusted to pH 4—5 with ammonium acetate; then a 50 : 50 water-alcohol solution which contained a little more excess ligand than the calculated quantity of a solution of NEA[9] or benzoic acid was added to the solution. A precipitate was formed immediately; it was then collected in a suction filter. It was washed with water and sucked to dryness. These precipitates were determined photometrically. In both the benzoic acid complexes and the NEA complexes, we found a 1 : 3 rate of metal to ligand.[6,7] These metal complexes and such organic compounds as stearic acid, benzoic acid, naphthalene, and acetoanilide were solutes and solid solvents respectively.

Analysis of Zone-melted Samples. Zone-melted samples were cut, weighed, and dissolved in chloroform; after these complexes had then been decomposed with 6 N HCl, aluminum and iron ions were removed into the HCl phase. The HCl phase separated from chloroform phase was added to a 1% oxine acetic acid solution, and the solution was adjusted to pH 4.8—5.2 with 2 N ammonia water and ammonium acetate. The oxinates were extracted with 10 m*l* of chloroform. The aluminum and iron were then determined photometrically.[10]

Results and Discussion

At first, the NEA complex in stearic acid solvent was zone-melted with an air-cooling apparatus. The molten zone traveled upwards. The Al and Fe complexes contained 0.3 and 0.6 mg of metal respectively. The zone passes were done 12 and 15 times. One of these chromatograms is shown in Fig. 2. The metal concentration (%), the quantity of metal (mg) per

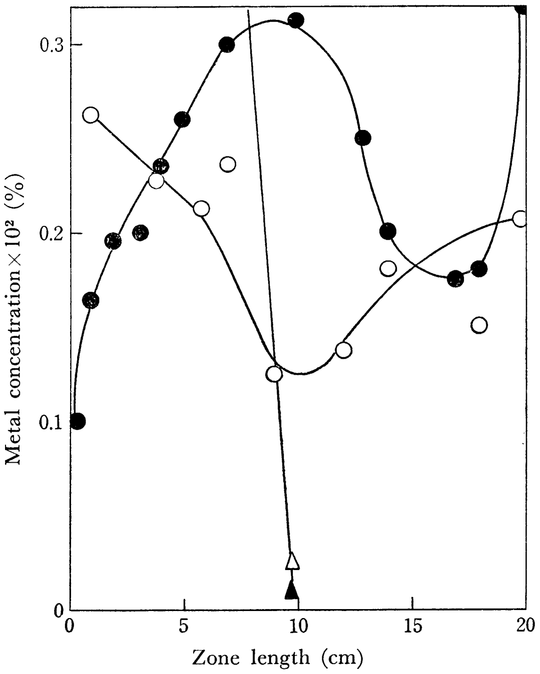

Fig. 2. Distribution of NEA-complexes with 12 and 15 zone passes.
Al: 12 ○, 15 ●, Fe: 12 △, 15 ▲

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[5] W. G. Pfann, *Anal. Chem.*, **36**, 2231 (1964).

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[7] B. Amberger and V. Goldberger, *Ann.*, **305**, 362.

[8] R. H. Mcfee, *J. Chem. Phys.*, **15**, 856 (1947).

[9] M. Mashima, Bunseki Kagaku, **9**, 199 (1960).

[10] K. Motojima and H. Hashitani, This Bulletin, **29**, 458 (1956).

gram of the solvent is plotted as the ordinate, and the length from the bottom to the center of a piece of the sample is plotted as the abscissa. Though the Al-complex moved toward the upper end with an increase in the number of zone passes, the Fe-complex moved only to the center of the column even after zone passes. Therefore, it may be possible to separate Al from Fe. If the column was cut at the point where Fe was absent, 40 and 51% of the total Al could be separated with 12 and 15 zone passes respectively. This was defined as the "recovery percentage." As a large quantity of the Al-complex was still present at the bottom in the above case, the experiments were carried out with a smaller amount of complexes later.

Figure 3 shows a chromatogram when 0.02 mg of Al and 0.03 mg of Fe were used. Most of the Al-complex moved to the upper end, while the Fe-complex could not be found more than 9 cm from the bottom; thus, the Al-complex was separated efficiently.

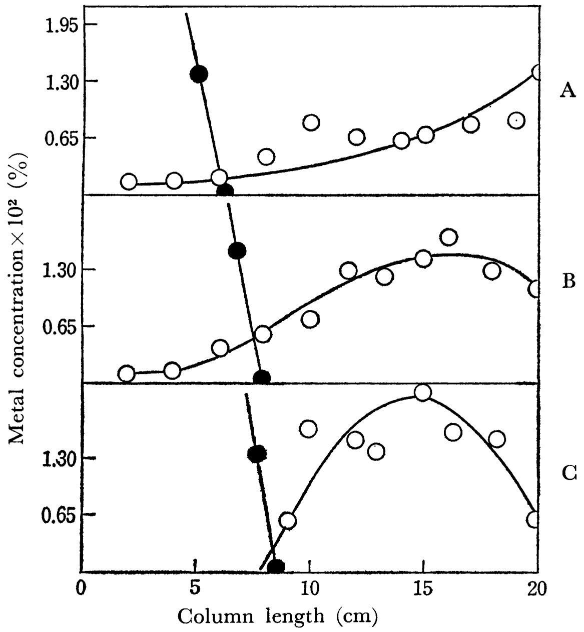

Fig. 3. Distribution of NEA-complex in stearic acid after zone melting process, using 2.0×10^{-2} mg of Al(○) and 3.0×10^{-2} mg of Fe(●).
A: 12 zone passes, B: 16 zone passes,
C: 18 zone passes

Table 1. Recovery percentage of Al as NEA complex

Exp. No.	Column length (cm)	Rate of zone travel (cm/hr)	No. of zone passes	Weight of Al (cm)	Weight of Fe (mg)	Recovery percent (%)
1	10	6	10	1.05	0.47	17
2	10	6	12	1.15	0.54	17
3	10	6	10	1.07	1.09	16
4	10	6	12	1.11	1.09	20
5	20	6	10	1.16	0.62	17
6	20	6	12	1.16	0.62	25
7	20	6	5	3.36	7.15	55
8	20	3	5	2.36	5.21	56
9	20	6	12	0.013	0.025	88
10	20	6	16	0.022	0.041	89
11	20	6	18	0.021	0.038	99

The recovery percentages of Al were 88, 89, and 99% with 12, 16, and 18 zone passes respectively; Al was thus almost completely separated from Fe with 18 zone passes. In Figs. 3B and C, the decrease in the Al concentration at the top of the chromatogram may be attributed to the following cause. Stearic acid evaporated from the top of the charge and condensed on the inner wall of the glass tube, and then this stearic acid was present in the top section of the sample during the analysis.

Table 1 shows the recovery percentage for the quantity of the complexes used, the column length, and the rate of zone travel. A comparison of No.1 with No. 3 reveals that the recovery percentage was not affected by the quantity of the Fe-complex; the recovery percentages were 17 and 16% for about 0.5—1 mg of Fe. Furthermore, a comparison of No. 2 with No. 6 reveals that the recovery percentage increased with the column length; the recovery percentages were 17 and 25% for the column lengths of 10 and 20 cm respectively.

No. 7 and No. 8 show the variation with the rate of zone travel. The recovery percentages were 55 and 57% in 6 and 3 cm/hr respectively.

Figure 4 shows a chromatogram of the Al and Fe complexes of benzoic acid in a stearic acid solvent obtained by the use of the apparatus with water-cooling. Here, the solubility of the benzoic acid complexes in stearic acid was about 2.5%, the same

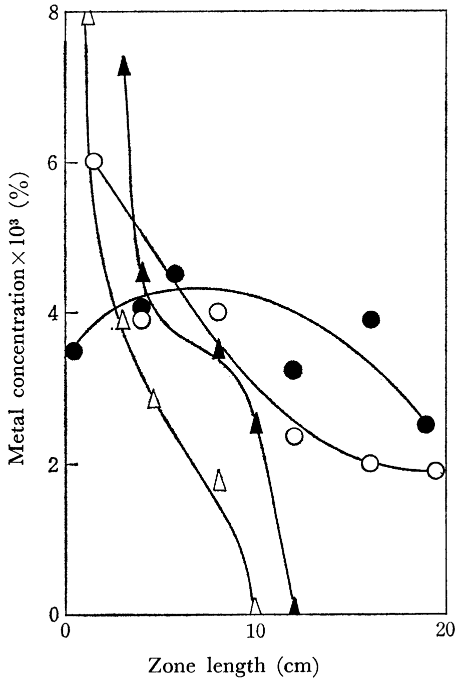

Fig. 4. Distribution of benzoic acid-complex. with 4 and 8 zone passes.

Al {○ 4 zone passes, ● 8 zone passes
Fe {△ 4 zone passes, ▲ 8 zone passes

Table 2. Recovery percentage of Al as benzoic acid complex

Exp. No.	Column length (cm)	Rate of zone travel (cm/hr)	No. of zone passes	Weight of Al $\times 10^2$ mg	Weight of Fe $\times 10^2$mg	Recovery percent (%)
1	20	6	8	7.49	7.22	49
2	20	6	12	9.90	7.16	46
3	20	6	10	8.86	4.75	49
4	20	6	14	7.54	3.82	58
5	20	6	5	2.88	1.77	44
6	20	6	9	3.26	2.03	63
7	10	6	9	2.55	1.47	58
8	10	6	12	2.50	1.86	75

as that of the NEA complex in stearic acid. In this case also, the results obtained were similar to those obtained with the NEA complex. The recovery percentages were 25 and 49% in 4 and 8 zone passes respectively; the percentage thus increased with the number of zone passes.

Table 2 shows the recovery percentage for the Al-complex of benzoic acid, obtained in the same manner as in Table 1. The separation of Al from Fe seems to be efficient in No. 4, 6, 7, and 8.

The normal freezing equation has also been derived theoretically and experimentally by Mcfee *et al.*[2,8] Thus;

$$\log [C_s(x)/C_0] = \log K + (K-1)\log[1-(x/L)]$$

where C_0 is an initial concentration. Both the slope and the intercept at $x=0$ provided a measure of the effective distribution coefficient, K. Figure 5 shows the relationship between $\log C_s(x)$ and $\log[1\text{-}(x/L)]$ with the complexes in stearic acid. The initial concentrations were all 0.2%. The effective distribution coefficient was obtained from the slope of the linear line; in normal freezing, the column of the complex and stearic acid mixture was melted, then it was frozen from the bottom by means of a cooler, and the frozen sample was analyzed by the above-mentioned method. The concentration of the complex, $C_s(x)$, at any distance, x, from the bottom along a frozen column with a total length of L was obtained from the normal freezing. The effective distribution coefficients of NEA and benzoic acid complexes of Fe were 1.08 and 1.01, while those of the Al-complex were 0.61 and 0.89 respectively. These results suggest that only the Al-complexes travel to the upper end, while Fe-complexes do not; the results presuppose the possibility of the separation of Al from Fe.

Table 3 shows the effective distribution coefficients of these complexes in other solvents. From the table, it seems that benzoic acid could also be used as a solvent in this method, but it was not used because the column of the benzoic acid solvent was easily broken when several zones were passed.

Figure 6 shows the phase diagrams of these complexes in stearic acid; the concentration of the complex in stearic acid was less than 3%. A Coblle automatic thermoanalyzer was used in this experiment. These results suggest that the tendency of the NEA-complex

Table 3. Effective distribution coefficient

	NEA-complex		Benzoic acid-complex	
	Al	Fe	Al	Fe
Solvent				
Benzoic acid	0.9	1.27	1.3	0.99
Naphthalene	1.27	1.27	1.28	0.98
Cetyl alcohol	0.8	1.50		
Acetoanilide	1.7	1.10		

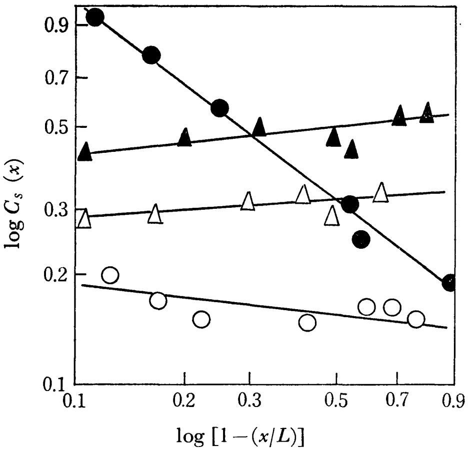

Fig. 5. Distribution coefficient of NEA and benzoic acid complex in stearic acid solvent.
NEA-Al-complex ●, NEA-Fe-complex ▲,
Benzoic acid-Al-complex ○, Benzoic acid-Fe-complex △

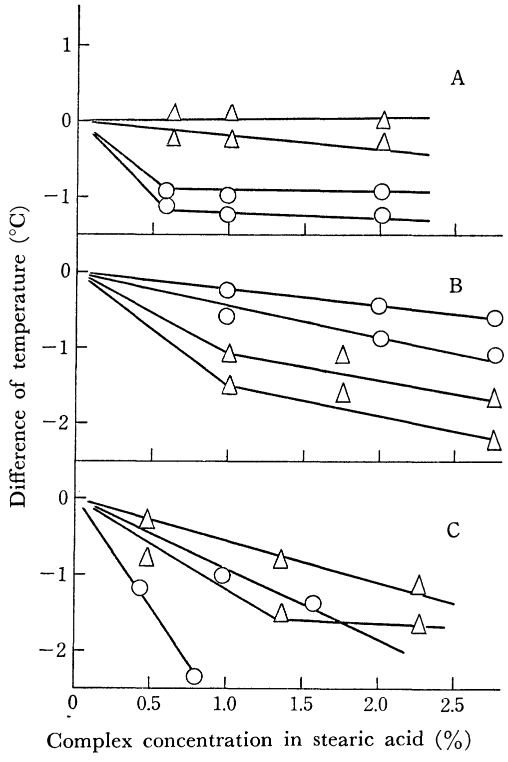

Fig. 6. Phase diagram of Al(○) and Fe(△) complex.
A: Stearic acid-complex, B: NEA-complex,
C: Benzoic acid-complex

was different from that of the benzoic acid complex, and each complex may not change its ligand in this zone-melting method. Here, the difference in temperature is based on the melting point of stearic acid. In each figure 6A, B, and C, the upper curve and lower curve were liquidus and solidus lines respectively. In Fig. 6A, the liquidus curve of Al-complex is not horizontal; it may decrease slightly with the concentration. A more detailed analysis of these phase diagrams will be reported latter.