Application of the Zone Melting Technique to Metal Chelate Systems. XII.[1] Computer-assisted Consideration on the Intermittent Zone Melting

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The solute distribution profile on a columned charge of length L after m-cycles of the intermittent zone melting with j zones of length l, was computed for a range of distribution coefficient, k. The effects of j, l and k upon the separation efficiencies by this method were investigated in terms of the fractional length, α, which was refined to an required purity level, γ, in a limited number of m, and the fractional ratio, σ, of a solute amount which was concentrated into a limited portion of a fractional column length, β. The intermittent method is superior in respect to the separation efficiencies, α as well as σ, over the usual method, if a columned charge was zone-melted with the same number of zones of the same length at the same zone-travelling speed. Results of theoretical calculation were confirmed on systems of azobenzene in naphthalene and those of some metal acetylacetonates in the beryllium chelate of the same ligand compound.

In usual practices of zone melting, more than one molten zone are produced on a columned charge for the sake of time-economy. Two basic modes are useful in the operation with multiple zones.

The first mode, in which all zones traverse through the charge from one end to another, is called a "normal" mode herein, and has been extensively studied in its theory as well as in its practices.[3–5]

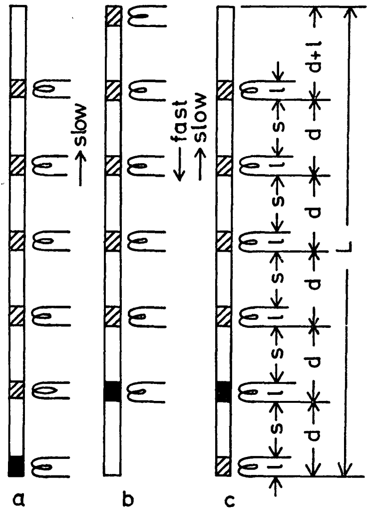


Fig. 1. Reciprocal zone travelling mode in the intermittent zone melting.

The second mode is what is called an "intermittent" method,[6–8] wherein the zones are produced at equal spacings on the charge as shown in Fig. 1(a), and each zone travels in phase to a direction along the charge. After travelling to the distance d between the centers of the nearest neighbor zones, as shown in Fig. 1(b), the heater assembly returns quickly to its initial position as shown in Fig. 1(c). In this cycle, the melt in the first zone is transferred into the second one, meantime the melt initially formed in the second zone transferred into the third one and so forth. In every cycle, the melt in each zone is transferred in a similar manner into its next neighbour in turn.

In the intermittent mode, therefore, the solute distribution is described in terms of the number of reciprocal cycles of the heater assembly, m, and the number of zones produced on a charge, j, in place of the number of zone passes, n, in the normal mode.

In this paper, we consider how the solute distributions vary depending upon m, j and each zone length, l. Also the separation efficiencies are compared between the two modes for systems of a range of distribution coefficient, k.

Results of the theoretical calculation are experimentally confirmed on the system of naphthalene containing azobenzene as a solute and those of bis(acetylacetonato)-beryllium(II), admixed with various metal chelates of the same ligand.

Calculating Procedures of the Solute Distribution. The solute distribution profile on the columned charge of length L after the intermittent zone melting with j zones of l long each, is calculated as follows: The whole columned charge is devided into j divisions of d long except the last one, which is $(d+l)$ long, where d is chosen longer than l. The divisions are assigned with serial numbers, i, in turn from the initial. Since i is defined as

$$i = \{x/d\} + 1$$

and $\quad L = jd + l,$ then $i = 1, 2, 3, \cdots, j,$

where x is the distance from the initial end along the charge, and $\{x/d\}$ the integer part of the numerical value of x/d. Also variable y is defined as

$$0 \leqq y = (x - \{x/d\}d) = x - (i-1)d \leqq d,$$

where $i = 1, 2, 3, \cdots\cdots, (j-1)$, except the last division, wherein

$$0 \leqq y = x - (j-1)d \leqq d + l$$

In the region of $0 \leqq y \leqq d-l$ on a division, a basic equation in the course of zone melting is represented by Eq. 1 on the basis of mass balance,

$$\frac{\mathrm{d}P_{m,i}(y)}{\mathrm{d}y} = \frac{k}{l}[C_{m-1,i}(y+l) - P_{m,i}(y)] \qquad (1)$$

where $P_{m,i}(y)$ represents the solute concentration redistributed into the solid at the position y in the i-th division in the course of m-th cycle, and $C_{m-1,i}(y+l)$ the concentration at $(y+l)$ in the same division after the completion of the $(m-1)$th cycle. The initial conditions for Eq. 1 are

$$P_{m,i}(0) = C_{m-1,i-1}(d)$$

except in the first division, where

$$P_{m,1}(0) = k\int_0^l C_{m-1,1}(y)\mathrm{d}y$$

and $C_{0,i}(y)$ is constant regardless to i and y. In the region of $(d-l) \leqq y \leqq d$ on each division except the j-th one, solute distribution is developed in the basis of distribution profile which has been formed by the preceding zone on the same cycle. A basic equation is, therefore, given by Eq. 2.

$$\frac{\mathrm{d}P_{m,i}(y)}{\mathrm{d}y} = \frac{k}{l}[P_{m,i+1}(y+l-d) - P_{m,i}(y)] \qquad (2)$$

In the corresponding region on the j-th division Eq. 1 is valid, where $C_{m-1,i}(y+l)$ is a constant regardless of y.

When a zone travels to the stroke d, its heating device returns quickly back to the initial position, the molten liquid being left as there it is. Thus after the completion of the m-th cycle, in the region of $0 \leqq y \leqq l$ in each division except the first one, $C_{m,i}(y)$ is constant, being equal to the solute concentration of the melt which was equilibrated with the solid at the crystallizing interface therein, and therefore

$$C_{m,i}(y) = P_{m,i-1}(d)/k \qquad (3)$$

where $0 \leqq y \leqq l$, $i=2, 3, 4, \cdots\cdots, j$.

Similarly in the region of $d \leqq y \leqq (d+l)$ in the j-th division, the solute concentration in the solid is constant after the completion of m-th cycle as indicated by Eq. 4.

$$C_{m,j}(y) = P_{m,j}(d)/k \qquad (4)$$

When the stroke d is more than twice as long as l, the distribution profile of each division after the completion of the m-th cycle is defined by Eqs. 3 and 5,

$$C_{m,i}(y) = P_{m,i}(y) \qquad (5)$$

in the region of $0 \leqq y \leqq l$, and $l \leqq y \leqq d$, respectively, with the exception of the region of $0 \leqq y \leqq l$ on the first division and that of $d \leqq y \leqq d+l$ on the j-th one, where the distribution being defined by Eqs. 4 and 5, respectively. If $d \leqq 2l$, then the distribution profile is defined by Eqs. 3 and 5 in the regions of $0 \leqq y \leqq l$ and $d-l \leqq y \leqq d$, respectively. Those in the regions of length l at the both ends of the charge are represented by Eqs. 3 and 5 in the similar manner to the above case.

Results and Discussion

Solute Distribution Profile. Some examples of the solute distribution profiles after the intermittent zone melting by use of the six-stage of zones ($j=6$) are shown in Figs. 2, and 3, former of which indicates the effect of cycle number, m for the systems of k equal to 0.4, while the latter the effect of distribution coefficient, k, after 12 cycles of m.

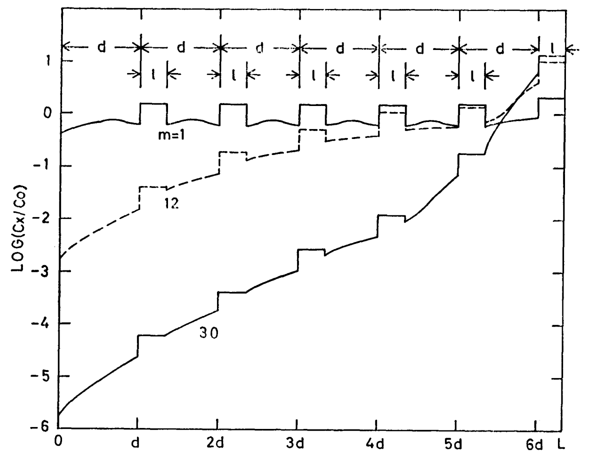


Fig. 2. The solute distributions by the intermittent zone melting after 1, 12, and 30 cyclex of m on the system of $k=0.4$ where $j=6$, $l=0.051L$, and $d=0.16L$. C_x is the solute concentration at x, defined as $C_x = C_{m,i}\{x-(i-1)d\}$ after the m-th cycle.

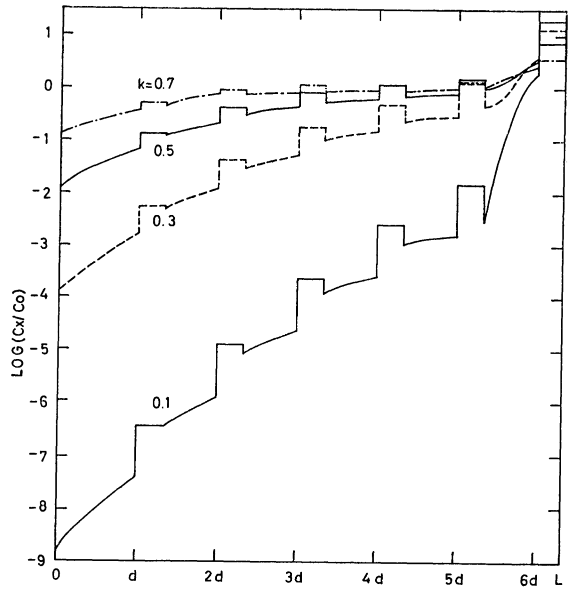


Fig. 3. The solute distributions by the intermittent zone melting after 12 cycles of m on the systems of $k=0.7$, 0.5, 0.3, and 0.1, where $j=6$, $l=0.051\ L$, and $d=0.16L$. C_x means the same as in Fig. 2.

One can readily notice that distribution profiles by the intermittent method are, as a whole, similar to those by the normal method given by Pfann,[3] except protuberant nodes at equal spacings on the curves. The node occurs at the region in which the stroke of a zone overlaps with that of the next neighbor, and the concentration level of a nodal region is equal to that of a molten zone left therein after each cycle. The height or depth of the protuberance decreases with an increase of m, and even in the ultimate stage there remain step-shaped nodes on the distribution curve.

Refining Efficiency. Refining effect can be compared in terms of the length of a refined fraction, of which average concentration decreases to a certain required purity level in a limited period of time. Suppose an α fraction of a columned charge is zone-refined to an average purity, γ, and this value is given as follows:

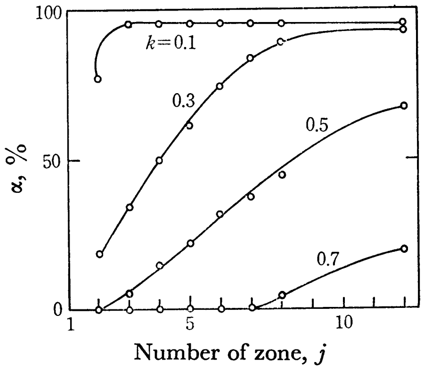


Fig. 4. Relationship between the refining efficiency, α, and the number of zone, j, when $m=2j$, and $l=0.05L$.

$$\gamma = \left[\int_0^{\alpha L} C_m(x)\,\mathrm{d}x\right] \Big/ \alpha L C_0 \quad (k<1) \tag{6}$$

$$\gamma = \left[\int_{(1-\alpha)L}^{L} C_m(x)\,\mathrm{d}x\right] \Big/ \alpha L C_0 \quad (k>1) \tag{7}$$

where $0 \leq \alpha \leq 1$

Figure 4 shows the relationships between the α-value and the zone number, j, when assumed to be $\gamma=0.01$ for a range of k, where m and l are to be $2j$ and $0.05L$, respectively. The higher j-value affords the more efficient refining as expected on the analogy of the effect by the number of zones in the normal mode.

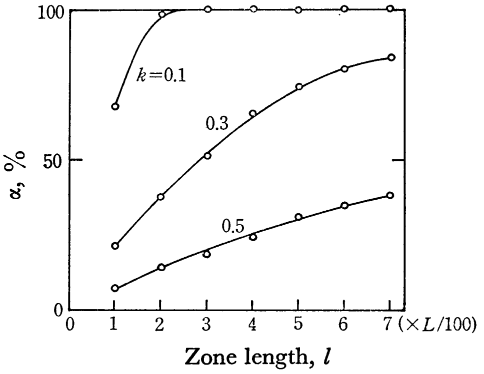


Fig. 5. Relationship between the refining efficiency, α, and zone length, l, when $m=2j$, $j=6$.

On a column of limited length, an increased number of zones leads inevitably to shorter zone-length. However, as shown in Fig. 5, the relationships between α and l indicate that shorter zones do not necessarily give higher refining efficiency in the early stage of the number of m such as in our cases. The column length L is related as $L=l(j+1)+js$, where s means the length of a solid part separating a zone from the next neighbor, and it is practical upon producing more than one zone on a column that the partition solid part is made to be longer than the diameter of the charge for most organic substances. In our case this corresponds to s longer than $0.02L$.

In Fig. 6, α-value after 2j-cycles of m is plotted against l or j. Although the zone length with which the most efficient refining is attained, varied with k, molten zones of 14—19 stage and 0.03—0.05L long seem to be optimal in general for the range of k.

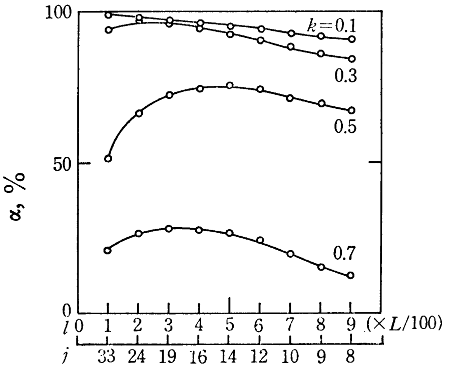


Fig. 6. Dependence of the refining efficiency, α, upon zone length, l, and the number of zone, j, when $m=2j$.

Concentrating Efficiency. In a similar manner to the above, concentrating effect can be compared in terms of the fractional amount, σ, of a solute concentrated into the region of length βL as defined in Eqs. 8 and 9:

$$\sigma = \int_{(1-\beta)L}^{L} C_m(x)\mathrm{d}x/C_0 L \quad (k<1) \tag{8}$$

$$\sigma = \int_0^{\beta L} C_m(x)\mathrm{d}x/C_0 L \quad (k>1) \tag{9}$$

where $0<\beta<1$.

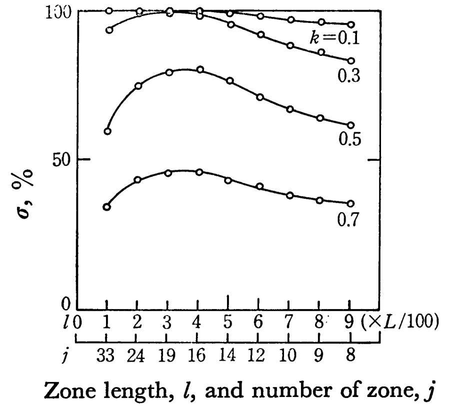


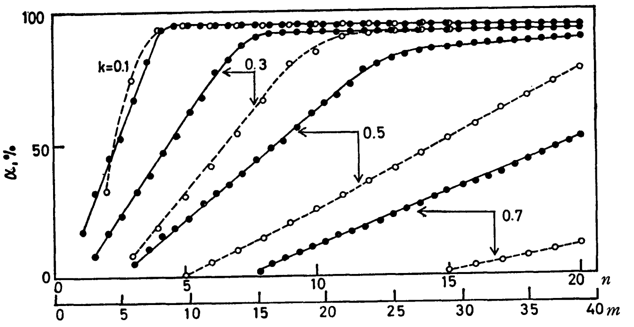
Fig. 7. Dependence of the concentrating efficiency, σ, upon zone length, l, and the number of zone, j, where $m=2j$.

Effects of j and l upon the concentrating efficiency are in a similar manner to those observed in the refining effect, and when s is chosen to be $0.02L$, as shown in Fig. 7, the maximum efficiency is attained with l of 0.03—0.04L long and j of between 16 to 19-stage, in accordance with those conditions under which the optimal refining efficiency is afforded.

Comparison of Separation Efficiency between the Normal and Intermittent Zone Melting. In the normal mode the heater assembly arranged as shown in Fig. 1, required the time of $[d(j-1)+L]/v$ to traverse through the whole columned charge, meanwhile j zones pass through, where v is travelling speed of the assembly. An apparent time, t, required for one zone to pass the charge is given as;

$$\begin{aligned} t &= [(j-1)d+jd+l]/jv \\ &= [(2j-1)d+l]/jv \end{aligned} \tag{10}$$

In the intermittent mode, on the other hand, the



Number of zone passes, n, and strokes, m

Fig. 8. The refining effect, α, by the intermittent- (—●—) and normal (---○---) zone melting, where k less than unity, $j=6$, $l=0.051L$, and $d=0.16L$.

time, t', required for travelling to one stroke is

$$t' = d/v \tag{11}$$

When v is chosen to be constant in the both mode, elimination of v from Eqs. 10 and 11 gives

$$\frac{t}{t'} = \frac{(2j-1)d+l}{jd} \tag{12}$$

Using the relation of t/t' the separation efficiencies by the both methods can be compared on the same scale of operation time. Some comparisons in terms of α are illustrated in Fig. 8, in which α is plotted against n and m, when $\gamma=0.1$ for a range of k less than unity.

Evidently one can notice that the intermittent method affords to attain to the ultimate separation (plateau of the curves) much sooner than the normal method. Situation is the same on the systems of k higher than unity. The reverse situation in a system of lower k-value seems practically of no problem, because such a solute can be readily separated from the matrix in any way. Superiority of the former method is retained upon the comparison in terms of the concentrating efficiency, σ.

Intermittent Zone Melting of Azobenzene in Naphthalene and Metal Acetylacetonates in Beryllium Acetylacetonate. Experimental test of the calculations was performed on the systems of azobenzene in naphthalene and some metal acetylacetonates in bis(acetylacetonato)beryllium(II). The length of a zone, l, and of the partition solid part, s, were chosen to be $0.051L$ and $0.107L$, respectively, for procedural convenience. The k-value of azobenzene in naphthalene was determined according to Sorensen,[10] to give 0.22 ± 0.02 under the same operation conditions. The distribution of the solute on a columned charge forms a quite similar curve to those given in Fig. 3. Concentrating effect in terms of σ-value increases with an increased number of m, as shown in Fig. 9, in good agreement with the theoretical calculation for a system of k of 0.22 ± 0.02, which is indicated by a shaded area enclosed with two solid lines.

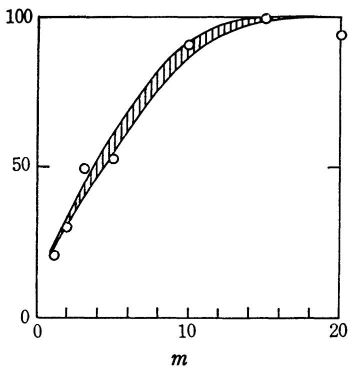


Fig. 9. Concentrated fractions, σ, of azobenzene on a naphthalene column against the number of reciprocal cycles, m. The shaded area indicates the theoretical σ-value for the system of $k=0.22\pm0.02$, when β is chosen to be 0.17.

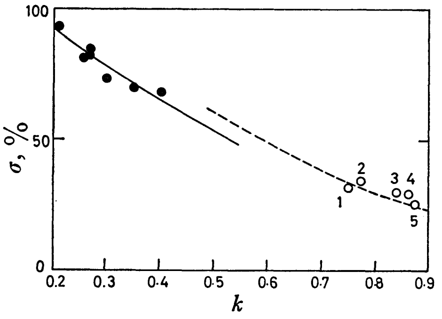


Fig. 10. The σ-value of azobenzene (●) in naphthalene after 10 cycles of m, and those of various metal acetylacetonates (○) in the $Be(AA)_2$ after 12 cycles of m: 1; $Cu(AA)_2$, 2; $Co(AA)_3$, 3; $Al(AA)_3$, 4; $Cr(AA)_3$, and 5; $Fe(AA)_3$, respectively. Dotted- and solid curves indicate the calculated σ-value as the function of k for the corresponding conditions, respectively.

Figure 10 shows σ-values of the solutes of various k-values, where the effective k of azobenzene could be varied between 0.2 to 0.4 by controlling the stirring effect of molten zones on zone melting as well as the Sorensen's measurement of k-value, and k-values of the metal chelates differ depending upon the kind of the central metal ion. Experimental points stand in good agreement with the respective theoretical curves calculated under the corresponding conditions.

Calculating procedures described above were useful for prediction of experimental results of the intermittent method of zone melting.

Experimental

Materials. Bis(acetylacetonato)beryllium(II) and other metal acetylacetonates were prepared by standard procedures.

Apparatus and Procedures. A high speed zone melting apparatus, operation procedures for the intermittent mode and the determination of k according to Sorensen were essentially same as described previously.[9] A columned charge of 253 mm long and 4 mm in diameter was precessed with 6-stage zones of each 13 mm long, separated with solid parts of each 27 mm long. Zone travelling speed was chosen to be 864 mm/h.

Determination of Solute Concentration. Azobenzene in naphtalene was determined in methanol by use of spectrophotometry[9] on a Hitachi 139 instrument. Metal acetylacetonates were determined, after decomposed in a hot mixture (8 ml) of perchloric acid (3 parts), fuming nitric acid (3 parts) and hydrochloric acid (4 parts), in the form of metal ion by atomic absorption spectrophotometry on a Jarrel-Ash AA-1 instrument.

Computation of the Concentration Profiles. Differential equations (Eqs. 1 and 2) were not solved analytically, and computed numerically by the Runge-Kutta-Gill method, with the grid spacing of $L/26000$. The computed concentration profile after each intermittent cycle was counterchecked by whether the Simpson's integration of the solute amount over the entire length of the column gave an amount equal to the initial one, where the integration step being equal to the grid spacing. Integral equations (Eqs. 7—10) were also computed in the similar manner. All computations were performed by use of FACOM 230-60 and 230-75 in the Computation Center of Kyushu University.

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