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Gel Chromatography of β-Diketones and Their Metal Complexes. IV. The Partition Concept in Gel Chromatography

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A new theoretical treatment of the solute distribution in gel chromatography is proposed. Practical gel chromatography can be regarded as one based on a combined function of the molecular sieve effect and the partition effect. Introducing the concept of a regular solution to the column system of gel chromatography, the contribution of the partition effect can be estimated from the data on the physical properties of the solute, the solvent, and the gel matrix. The argument being proposed is supported by the experimental data on the gel chromatography of metal (II, III) chelates with acetylacetone and normal alkanes previously obtained in the systems of a poly(vinyl acetate) gel and various eluting solvents.

In the previous work of this series, the solvent dependence of the gel-chromatographic behavior of some metal (II, III) chelates with acetylacetone (2,4-pentanedione: Hacac) on a cross-linked poly(vinyl acetate) gel (Merckogel OR-2000) was examined.$^{1)}$ The experimental results showed that the distribution coefficients of a chelate were strongly dependent on the eluting solvent used. The effective molar volume, V_{eff}, for every chelate obtained by the use of the calibration charts prepared on the basis of the elution data for normal alkanes also depended on the solvents; the volmes were different from the expectation derived from the literature values of the molar volume, V_{m}, for the chelate. On the basis of these facts, it seems reasonable to assume that the solute distribution in a given column system is governed not only by the molecular sieve effect related to the molecular dimensions of the solute, but also by some secondary effects related to interactions among the solute, the solvent, and the gel.

In order to explain the separation mechanism in gel chromatography, various theories, such as steric exclusion,$^{2)}$ restricted diffusion,$^{3)}$ and thermodynamic equilibrium,$^{4)}$ have been proposed. In these theories, the dominant factor governing the solute distribution in a given column system is considered to be the radius of the solute molecule, and the contributions of the secondary effects are not taken into account. Some anomalies were occasionally observed, however, such as the reversal of the predicted elution order of the solutes and the unexpectedly large values of the elution volume.$^{5,6)}$ These facts could not be explained simply in term of the molecular sieve effect. The importance of the secondary effect was stressed in such a case, therefore. It has thus far been generally agreed that the secondary effect is due to the solute-gel matrix adsorption,$^{7,8)}$ but this adsorption has not been argued quantitatively in terms of the physical properties inherent in the solute, solvent, and gel materials.

In the course of our previous study, we felt it necessary to understand fully the essence of the secondary effect and the solvent effect in gel chromatography. The present paper thus deals with this problem theoretically. The theoretical investigation of the solute distribution in a column system is developed by assuming that gel chromatography is essentially based on the combined function of the molecular sieve effect and the partition effect. This investigation has been undertaken to explain the gel-chromatographic behavior of metal chelates with Hacac previously observed.

Theoretical

Overall Distribution Coefficient. When a substance is chromatographed in a column system consisting of a liquid phase with the volume of V_0 (void volume) and a gel phase with the volume of V_{x}, the elution volume, V_{e}, of the substance is expressed by the following general equation:

$$V_{\mathrm{e}} = V_0 + K_{\mathrm{av}}V_{\mathrm{x}}, \tag{1}$$

where K_{av} is the distribution coefficient characterizing the solute distribution in the column system. When the solute distribution is governed not only by the molecular sieve effect, but also by some other effects, K_{av} is essentially a combined function of all the effects.

When the concept of the theoretical plate is applied to the gel-chromatographic-column system, the solute distribution in a theoretical plate is as will be discussed below.

The column system in the theoretical plate consists essentially of a solvent phase (hereafter abbreviated as the O phase) with the volume of v_0 and a gel phase (hereafter abbreviated as the X phase) with the volume of v_{x}. The former and the latter phases correspond to the moving and the stationary phases in this chromatographic system respectively. A solute material, S, introduced in this system equilibrates between these two phases. Only a certain fraction, K_{size}, of the latter phase is, however, available for S, because of the molecular sieve effect. This leads to the following relation:

$$v_{\mathrm{p}} = K_{\mathrm{size}}v_{\mathrm{x}}, \tag{2}$$

where v_{p} is the volume of the available part (hereafter designated as the P phase) for S. According to the theories proposed by Ogston$^{9)}$ and Laurent and Killander$^{10)}$, K_{size} is expressed by the equation:

$$K_{\mathrm{size}} = \exp\left[-\pi L(r_{\mathrm{r}}+r_{\mathrm{s}})^2\right], \tag{3}$$

where r_{s} is the radius of the solute molecule, r_{r} is the radius of the polymer chain of the gel matrix, and L is the concentration of the polymer chains in the gel phase. Both L and r_{r} are constant in a combination of the gel matrix and a solvent. The v_{p} value in a given column system, therefore, varies according only to the size of the solute molecule.

Considering that S is distributed strictly between the O phase and the P phase, and also that these two phases are not always equilivalent with respect to the interaction with S, it is reasonable to assume that, in general, the concentration of S in P phase, C_p, is different from that in the O phase, C_o. When the P phase can be assumed to be such a medium as a mixture of a solvent and a polymer of gel matrix, into which S can be incorporated, the O and P phases can be regarded as constituting a system of partition chromatography. Thus, the K_{part} given by Eq. 4 corresponds with the partition coefficient of S in this system:

$$K_{\text{part}} = C_p/C_o \tag{4}$$

The effective plate volume, v_e, in this partition chromatographic system is expressed by this equation:

$$\begin{aligned} v_e &= v_o + K_{\text{part}}v_p \\ &= v_o + K_{\text{part}}K_{\text{size}}v_x \end{aligned} \tag{5}$$

When the number of the theoretical plates in the total column system, N, is sufficiently larger than unity, Eq. 6 can be derived:

$$V_e = Nv_e = V_o + K_{\text{part}}K_{\text{size}}V_x \tag{6}$$

From Eqs. 1 and 6, one arrives at:

$$K_{\text{av}} = K_{\text{part}}K_{\text{size}} \tag{7}$$

According to Eq. 6, gel chromatography can be regarded as a special case of partition chromatography, in which the volume of the stationary phase varies with the molecular size of the solute substance introduced. It is reasonable to term K_{av} the overall distribution coefficient.

Partition Concept and the Physical Properties of the Solute, the Solvent, and the Gel. When the partition constant of the solute, S, $K^{x}_{\text{part},s}$, is given by Eq. 8, the overall distribution coefficient, K_{av}, can be expressed by Eq. 9, provided both C_o and C_p are small:

$$K^{x}_{\text{part},s} = X_{s,p}/X_{s,o} \tag{8}$$

where $X_{s,p}$ and $X_{s,o}$ are the mole fractions of S in the P phase and the O phase respectively.

$$K_{\text{av}} = K^{x}_{\text{part},s}(\bar{V}_{m,o}/\bar{V}_{m,p})K_{\text{size}} \tag{9}$$

where $\bar{V}_{m,o}$ and $\bar{V}_{m,p}$ are the average molar volume of the O phase and the P phase respectively.

According to the regular solution theory,[11] the activity of Component 2, a_2, in a binary mixture of Components 1 and 2 is expressed as a function of the mole fraction, X; the molar volume, V_m; the volume fraction, ϕ, and the solubility parameter, δ, by means of the following equation:

$$\ln a_2 = \ln X_2 + V_{m,2}\phi_1^2(\delta_1-\delta_2)^2/RT \tag{10}$$

where R and T are the gas constant and the temperature respectively, and where the subscripts 1 and 2 distinguish the components of the mixture. When the number of moles of a component is denoted by the symbol n, X_2 and ϕ_1 are, respectively, given by these two equations: $X_2=n_2/(n_1+n_2)$ and $\phi_1=n_1V_{m,1}(n_1V_{m,1}+n_2V_{m,2})$. The solubility parameter is defined as the square root of the cohesive energy density, *e.g.*, of the energy of vaporization, ΔE^{v}, per unit of volume ($\delta=(\Delta E^{\text{v}}/V_m)^{1/2}$). The regular solution theory can be successfully applied to discussing the solute distribution in solvent extraction.[12-14]

It is expected that the concept of a regular solution can be applied to discussing the solute distribution between the O phase and the P phase when the following two assumptions are accepted: i) the P phase can be regarded as a homogeneous mixture of a solvent and a gel matrix polymer, and ii) specific interactions among the solute, the solvent, and the polymer, such as hydrogen bonding, are absent in the system. In our earlier work, the solvent dependence of gel swelling could be successfully explained quantitatively by introducing the concept of regular solution into the solvent-gel matrix binary system.[15]

The activities of the solute, S, in the O phase, $a_{s,o}$, and in the P phase, $a_{s,p}$, are expressed by Eqs. 11 and 12:

$$\ln a_{s,o} = \ln X_{s,o} + V_{m,s}\phi_o^2(\delta_o-\delta_s)^2/RT \tag{11}$$

$$\ln a_{s,p} = \ln X_{s,p} + V_{m,s}\phi_p^2(\delta_p-\delta_s)^2/RT \tag{12}$$

The subscripts s, o, and p distinguish the components in these systems. When the partition equilibrium of S is achieved between these two phases ($a_{s,o}=a_{s,p}$), the following relation is derived:

$$\ln K^{x}_{\text{part},s} = V_{m,s}[(\delta_o-\delta_s)^2-(\delta_p-\delta_s)^2]/RT, \tag{13}$$

provided that the concentration of S is so small that both ϕ_o and ϕ_p can be equated with unity. The solubility parameter, δ_p, is approximately expressed by Eq. 14:

$$\delta_p = \phi_g\delta_g + (1-\phi_g)\delta_o, \tag{14}$$

where ϕ_g is the volume fraction of the gel-matrix polymer in the P phase, δ_g is the solubility parameter of the polymer, and δ_o is, of course, the solubility parameter of the solvent. Then, Eq. 13 is modified to:

$$\ln K^{x}_{\text{part},s} = V_{m,s}[2(\delta_s-\delta_o)(\delta_g-\delta_o)\phi_g-(\delta_g-\delta_o)^2\phi_g^2]/RT \tag{15}$$

This equation reveals the quantitative relationship between the partition effect in gel chromatography and the physical properties of the solute, the eluting solvent, and the packing material (gel). It is quite an important and interesting suggestion that ($\ln K^{x}_{\text{part},s}$) is equal to zero under such a condition as $\delta_o=\delta_g$.

It is well known that the molar volume can be used as an effective size parameter for low-molecular-weight compounds in gel chromatography.[16-18] We assume here, for the sake of simplification, that various compounds with a equal molar volume have K_{size} values identical to each other in a given column system. When two different substances, S and S′, are chromatographed in a column system, the K_{av} values of these substances are expected by the $K_{\text{av},s}=K^{x}_{\text{part},s}K_{\text{size},s}$ and $K_{\text{av},s'}=K^{x}_{\text{part},s'}K_{\text{size},s'}$ equations. When the V_m values of S and S′ are equal to each other, $K_{\text{size},s}=K_{\text{size},s'}$. Then the following equation can be written:

$$R_{s/s'} = K_{\text{av},s}/K_{\text{av},s'} = K_{\text{part},s}/K_{\text{part},s'} \tag{16}$$

According to Eq. 15, the above equation is modified to give:

$$\ln R_{s/s'} = 2V_{m,s}(\delta_s-\delta_{s'})(\delta_g-\delta_o)\phi_g/RT \tag{17}$$

This equation predicts that the $R_{s/s'}$ value is always constant at unity under the condition $\delta_o=\delta_g$. In usual column systems, $K_{\mathrm{av,s}}$ are not always equal to $K_{\mathrm{av,s'}}$, even if $V_{\mathrm{m,s}}=V_{\mathrm{m,s'}}$. It is stressed that the choice of eluting solvent is quite important in gel chromatography. Ideal gel-chromatographic separation based only on the molecular sieve effect is carried out by the use of an eluting solvent in which the solubility parameter of the solvent is equal to that of the gel matrix; then one can estimate the size of a solute molecule by the use of a calibration chart prepared on the basis of the elution data for other compounds.

Discussion

In order to examine the validity of the above arguments, the theory is then applied to the experimental data already obtained. The elution data for normal alkanes,[19] bis(acetylacetonato) beryllium(II) and tris(acetylacetonato)chromium(III) (hereafter abbreviated as Be(acac)$_2$ and Cr(acac)$_3$ respectively),[1,20] in column systems consisting of Merckogel OR-2000 and various organic solvents are taken. The data on gel swelling[15] are also available.

Equation 15 shows that the solvent dependence of the partition effect can be discussed quantitatively in terms of the solubility parameters of the solvents. However, it is not easy to evaluate K^{*}_{part} experimentally. Only K_{av} values can be obtained by means of usual chromatographic techniques. When the K_{av} values of two different compounds with equal V_{m} values are available, the validity of Eq. 15 must be examined indirectly by discussing Eq. 17.

We suppose here two hypothetical normal alkanes: one (hereafter designated by r(Be)) whose V_{m} value is equal to that of Be(acac)$_2$, and the other (hereafter designated by r(Cr)) whose V_{m} value is equal to that of Cr(acac)$_3$. An equation analogous to Eq. 17 can be written for the solute pair of Be(acac)$_2$ and r(Be):

$$\begin{aligned}\ln R_{\mathrm{Be/r(Be)}} &= \ln\left(K_{\mathrm{av,Be}}/K_{\mathrm{av,r(Be)}}\right)\\ &= 2V_{\mathrm{m,Be}}(\delta_{\mathrm{Be}}-\delta_{\mathrm{r(Be)}})(\delta_{\mathrm{g}}-\delta_{\mathrm{o}})\phi_{\mathrm{g}}/RT, \qquad (18)\end{aligned}$$

where the subscript Be denotes Be(acac)$_2$. Introducing the degree of swelling for gel, Q, defined as $Q=1/\phi_{\mathrm{g}}$, into the above equation, one can write Eq. 19:

$$Q\ln R_{\mathrm{Be/r(Be)}} = [-2V_{\mathrm{m,Be}}(\delta_{\mathrm{Be}}-\delta_{\mathrm{r(Be)}})/RT](\delta_{\mathrm{o}}-\delta_{\mathrm{g}}) \qquad (19)$$

It is expected that $(Q\ln R_{\mathrm{Be/r(Be)}})$ shows a linear relationship to δ_{o} with a slope of $[-2V_{\mathrm{m,Be}}(\delta_{\mathrm{Be}}-\delta_{\mathrm{r(Be)}})/RT]$. The $V_{\mathrm{m,Be}}$ value was estimated to be 184 cm^3 mol^{-1}.[1] The $K_{\mathrm{av,r(Be)}}$ values in the column systems of Merckogel OR-2000 and various eluting solvents can be estimated by introducing the $V_{\mathrm{m,Be}}$ value into the K_{av} *versus* V_{m} relationship for normal alkanes observed in the column systems (see Fig. 2 in Ref. 1). The δ_{Be} value has not been reported. Considering that the solubility parameters of metal chelates with the same ligand are approximately independent of the metals,[14] we estimate δ_{Be} to be at 9.7 cal$^{1/2}$ cm$^{-3/2}$. This value is equal to the reportd value of δ_{Cr}.[21] The $\delta_{\mathrm{r(Be)}}$ value is estimated to be 7.7 cal$^{1/2}$ cm$^{-3/2}$ from the δ *versus* V_{m} relationship for normal alkanes shown in Fig. 1. According to these values, it can be predicted that the slope of the $(Q\ln R_{\mathrm{Be/r(Be)}})$ *versus* δ_{o} plot is about -1.2 at 25 °C. The relation of $(Q\ln R_{\mathrm{Be/r(Be)}})$ plotted against δ_{o}, prepared based on the data summarized in Table 1, is shown in Fig. 2. All the plots, except for chloroform (1), fall approximately on a line. According to the regression analysis, the slope of this line is $(-0.92\pm$

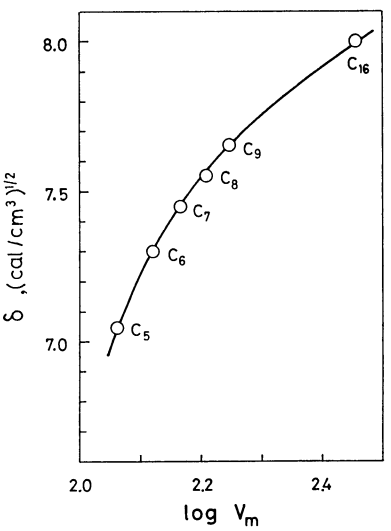

Fig. 1. Relationship between solubility parameter and molar volume for normal alkanes.
C$_5$, C$_6$, C$_7$, C$_8$, C$_9$, and C$_{16}$ denote pentane, hexane, heptane, octane, nonane, and hexadecane, respectively 1 cal=4.1840 J.

Table 1. Values of δ_{o}, Q, K_{av}, and R in the systems of Merckogel OR-2000 and an organic solvent at 25 °C

Solvent			Q[15]	$K_{\mathrm{av,Be}}$[1]	$K_{\mathrm{av,r(Be)}}$	$K_{\mathrm{Be/r(Be)}}$	$K_{\mathrm{av,Cr}}$[1]	$K_{\mathrm{av,r(Cr)}}$	$R_{\mathrm{Cr/r(Cr)}}$
No.	Name	δ_{o}[a]							
1	Chloroform	9.3[24]	4.10	0.271	0.385	0.704	0.218	0.268	0.813
2	Benzene	9.15[24]	3.12	0.816	0.373	1.45	0.342	0.255	1.34
3	Toluene	8.9[24]	2.26	0.653	0.319	2.05	0.400	0.207	1.93
4	1,4-Dioxane	10.0[24]	3.32	0.570	0.513	1.11	0.436	0.383	1.14
5	Tetrahydrofuran	9.32[b]	3.18	0.620	0.398	1.56	0.517	0.281	1.84
6	Ethyl acetate	9.05[25]	2.99	0.702	0.468	1.50	0.609	0.360	1.69
7	Acetone	9.89[26]	3.15	0.660	0.532	1.24	0.622	0.439	1.42
8	Ethyl methyl ketone	9.3[26]	2.98	0.653	0.462	1.41	0.628	0.351	1.79
9	Butyl acetate	8.55[25]	2.43	0.828	0.399	2.08	0.790	0.284	2.78

a) In cal$^{1/2}$ cm$^{-3/2}$. b) Calculated from the value of the heat of vaporization (7.65 kcal/mol).[27]

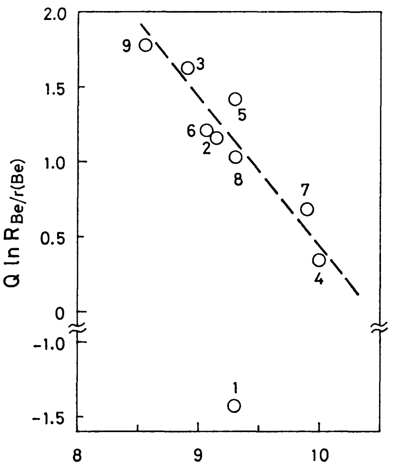

Fig. 2. The Q ln $R_{\mathrm{Be/r(Be)}}$ *versus* δ_0 relationship in the systems of Merckogel OR-2000 and various eluting solvents at 25 °C. Figures 1—9 denote solvents as in Table 1. Dashed line shows the regression line.

0.12) at a level of significance of 5%. This value is close to the expected one ($=-1.2$). The δ_0-axis intercept of the line, which corresponds with the δ_g value of Merckogel OR-2000, is observed to be (10.4±0.2). This value is near to the δ_g value estimated from the gel-swelling data ($\delta_g=9.7$).[15]

It is shown in Fig. 2 that the relationship expressed by Eq. 17 can be approximately accepted in practice, even in various types of solvents, including both polar and nonpolar ones. Some deviation of the plots from the linearity can still be found. It has not been clarified whether the deviation results from the uncertainty of the original data or from the disregard for the specific interactions among solute, solvent, and gel. Considering that many metal chelates with Hacac form the solvated species in chloroform.[22,23] the remarkable deviation of the plot for chloroform found in Fig. 2 may be referred to the solvation. The concept of the regular solution can be accepted on the assumption that the specific interaction between the solute and the solvent is absent.[11]

One can modify Eq. 17 to give the relation between $\mathrm{Cr(acac)_3}$ (designated by the subscript Cr) and r(Cr). Thus,

$$\ln R_{\mathrm{Cr/r(Cr)}} = \ln (K_{\mathrm{av,Cr}}/K_{\mathrm{av,r(Cr)}}) = 2V_{\mathrm{m,Cr}}(\delta_{\mathrm{Cr}}-\delta_{\mathrm{r(Cr)}})(\delta_{\mathrm{g}}-\delta_0)\phi_{\mathrm{g}}/RT \qquad (20)$$

From Eqs. 18 and 20, the following equation is derived:

$$\ln R_{\mathrm{Cr/r(Cr)}}/\ln R_{\mathrm{Be/r(Be)}} = (V_{\mathrm{m,Cr}}/V_{\mathrm{m,Be}})(\delta_{\mathrm{Cr}}-\delta_{\mathrm{r(Cr)}})/(\delta_{\mathrm{Be}}-\delta_{\mathrm{r(Be)}}) \qquad (21)$$

It can be expected that (ln $R_{\mathrm{Cr/r(Cr)}}$) is in direct proportion to (ln $R_{\mathrm{Be/r(Be)}}$). The proportional coefficient should be independent of the solvent used, and we should be able to predict it from the physical properties of the solutes. Taking the value of $V_{\mathrm{m,Cr}}$ as 267 $\mathrm{cm^3\ mol^{-1}}$,[21] $\delta_{\mathrm{r(Cr)}}$ is estimated to be 7.9 $\mathrm{cal^{1/2}\ cm^{-3/2}}$ from Fig. 1. The δ_{Cr} value has been reported to be *ca.* 9.7 $\mathrm{cal^{1/2}\ cm^{-3/2}}$.[21] Then, the proportional coefficient can be predicted to be 1.3.

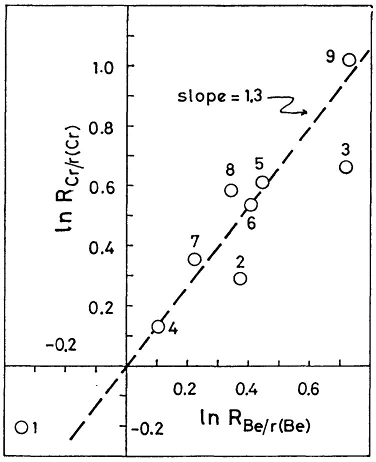

Fig. 3. Correlation between ln $R_{\mathrm{Cr/r(Cr)}}$ and ln $R_{\mathrm{Be/r(Be)}}$. Figures. 1—9 denote solvents as in Table 1.

The values of $K_{\mathrm{av,r(Cr)}}$ and $R_{\mathrm{Cr/r(Cr)}}$ are estimated in a manner analogous to that used in the case of the $\mathrm{Be(acac)_2}$-r(Be) pair and are exhibited in Table 1. When these values are taken, the relationship of (ln $R_{\mathrm{Cr/r(Cr)}}$) plotted against (ln $R_{\mathrm{Be/r(Be)}}$) is as shown in Fig. 3. The dashed line in the figure shows the slope 1.3. It is quite interesting that the plots for many solvents lie close to the prediction. However, benzene (2) and toluene (3) give plots somewhat deviating from the expected line. We have, to data, no clear-cut evidence to explain this deviation.

The facts shown graphically in Figs. 2 and 3 lend some support to the theoretical treatment of the solute distribution in gel chromatography proposed in this paper. The solvent dependence of the gel-chromatographic behavior of metal chelates with Hacac previously observed can be appreciablly explained in terms of the partition effect. The contribution of the partition effect to the overall solute distribution in gel chromatography may be predicted quantitatively in terms of the molar volumes and the solubility parameters of the solute and the solvent. Equation 15 predicts that the partition effect in gel chromatography is not remarkable, provided that the δ value of the eluting solvent is close to that of the gel matrix.

In view of the above arguments, the most reasonable conclusion to be drawn from the available data is that 1,4-dioxane is the nearest to the ideal eluting solvent for the column system including Merckogel OR-2000 as a column packing material, while butyl acetate is farthest from the ideal.

The introduction of the partition concept may give a powerful approach to elucidate the so-called secondary effect in gel chromatography.

References

1) Part 3 in this series: N. Suzuki and K. Saitoh, *Bull. Chem. Soc. Jpn.*, **50**, 2907 (1977).
2) J. Porath, *Pure Appl. Chem.*, **6**, 233 (1963).
3) G. K. Ackers, *Biochemistry*, **3**, 723 (1964).
4) E. F. Casassa, *Separ. Sci.*, **6**, 305 (1971).
5) M. Milk, J. Rochlitz, and H. Bende, *J. Chromatogr.*, **24**, 414 (1966).
6) J. G. Bergmann, L. J. Duffy, and R. B. Stevenson,

Anal. Chem., **43**, 131 (1971).

7) C. A. Streuli, *J. Chromatogr.*, **56**, 219 (1971).

8) S. Mori and T. Takeuchi, *J. Chromatogr.*, **50**, 419 (1970).

9) A. G. Ogston, *Trans. Faraday Soc.*, **54**, 1754 (1958).

10) T. C. Laurent and J. Killander, *J. Chromatogr.*, **14**, 317 (1964).

11) J. H. Hildebrand and R. S. Scott, "The Solubility of Nonelectrolytes," Dover, New York (1964).

12) T. Wakahayashi, S. Oki, T. Omori, and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2255 (1964).

13) N. Suzuki and K. Akiba, *J. Inorg. Nucl. Chem.*, **33**, 1897 (1971).

14) M. Tanaka, "Proceedings of International Solvent Extraction Conference, ISEC '77," Soc, Chem. Ind., London (1971), p. 18.

15) K. Saitoh, T. Ozawa, and N. Suzuki, *J. Chromatogr.*, **124**, 231 (1976).

16) W. B. Smith and A. Kollmansberger, *J. Phys. Chem.*, **69**, 4157 (1965).

17) G. D. Edward and Q. Y. Ng, *J. Polym. Sci.*, **C21**, 105 (1968).

18) A. Lambert, *Anal. Chim. Acta*, **51**, 63 (1971).

19) K. Saitoh and N. Suzuki, *J. Chromatogr.*, **111**, 29 (1975).

20) K. Saitoh and N. Suzuki, *J. Chromatogr.*, **109**, 333 (1975).

21) H. M. N. H. Irving, "Ion Exchange and Solvent Extraction," Vol. 6, ed by J. A. Marinsky and Y. Marcus, Dekker, New York (1970), p. 139.

22) J. F. Steinbach and J. H. Burns, *J. Am. Chem. Soc.*, **80**, 1839 (1958).

23) F. R. Clark, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964).

24) Ref. 11, p. 435.

25) D. Mangaraj, S. Petra› and S. B. Rath. *Macromol. Chem.*, **67**, 84 (1963).

26) M. Magat, *J. Chim. Phys.*, **46**, 344 (1949).

27) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York (1970), p. 220.