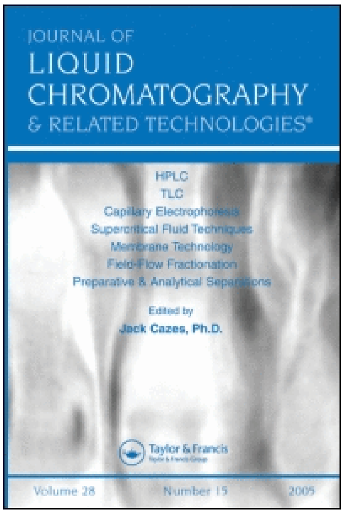

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FUNDAMENTAL INVESTIGATIONS AND TRENDS IN CCC

THEORY OF COUNTERCURRENT CHROMATOGRAPHY FOR THE SEPARATION OF INORGANIC SOLUTES

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ABSTRACT

When countercurrent chromatography (CCC) is used for the separation of inorganic solutes, the retention volume may be different with the predicted one, and the separation efficiency is lower than that for organic separation. These discrepancies are illustrated by expressions of the retention volume and the height of theoretical plate from a mass transfer model, which is established in the present research.

The theoretical results show that the existence of chemical reactions plays a great role in the retention and the separation efficiency of CCC; a fast extraction reaction is preferable in the separation of inorganic solutes, and promoting the reaction rate can also improve the separation efficiency. CCC might be explored as a technique to measure kinetic data of extraction reactions.

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INTRODUCTION

Countercurrent chromatography (CCC) is a form of liquid-liquid extraction chromatography in which centrifugal or gravitational force is employed to maintain a bed of one liquid phase in a coil or train of chambers in the absence of a porous supporting matrix, and the second immiscible phase is passed through the system in contact with the stationary phase.[1] CCC is developed from the distribution extraction chromatography.[2,3] It has been developed into a novel high efficiency chromatographic method since Ito discovered specific phase movement in coils.[4,5] So far, CCC is mainly used for the separation and determination of organic and bioorganic substances.[6,7] Investigations of the last decade have shown that CCC can also be used for inorganic separations.[8,9]

The retention behavior of a solute can be depicted by the retention volume. V_R, and V_R was determined by the volumes of mobile phases, V_m, volumes of stationary phases, V_s, and the batch equilibrium distribution ratio, D^{bat}, in the chromatographic separation of organic substance.

$$V_R = V_m + D^{bat} V_S \tag{1}$$

Therefore, V_R can be predicted from the D^{bat} value provided V_m and V_S are known. Nakamura et al. reported that the retention volumes of the lanthanide elements Dy, Ho, Y, Er were proportional to their distribution ratios according to equation (1) when the solution of di- (2-ethylhexyl) phosphoric acid mono-2-ethylhexyl ester in toluene was used as the stationary phase.[10] Nevertheless, several research works discovered that the distribution ratios obtained from the CCC profile, D^{dyn}, is different from D^{bat}, that is, V_R can not be calculated directly from equation (1).[11-14] Some authors explained this discrepancy by the concentration effect[11] and the heat of the column[10] during the separation process. Fedotov[15] and others[12,13] attributed this difference to the complex reactions existing in the two phases.

Surakibanharn et al. reported that the separation efficiency of a palladium complex is much lower than that of 3-picoline in the comparative conditions.[13] Also, the number of theoretical plates obtained from the separation of lanthanides is considerably smaller than that obtained from organic molecules.[12] Fedotov et al. also reported that the efficiency is low when CCC was used to separate metal ions using neutral or acidic organic phosphoric extractant as stationary phases.[16] They asserted that the chemical reaction existing in the two phases during the CCC process contributed to this lower efficiency.

Muralidharan et al. correlated the Channel Equivalent of Theoretical Plate caused by slow back extraction, $CETP_{ck}$, to the half-time of the back extraction reaction, $t_{1/2}$ and found that $CETP_{ck}$ is proportional to $t_{1/2}$.[17] Fedotov et al.[14, 16] established an empirical equation (2) to correlate the solvent extraction and chromatographic data.

$$\frac{\dfrac{D_{(1)}^{bat}V_{s(1)}}{W_{1/2(1)}}}{\dfrac{D_{(2)}^{bat}V_{(2)}}{W_{1/2(2)}}} \approx \frac{k_{(1)}}{k_{(2)}} \tag{2}$$

where $W_{1/2}$ denotes the half-width of a chromatographic peak, indices (1) and (2) relate to two different extraction systems, and k is mass transfer coefficient obtained from stirred diffusion cell. However, there are no reports about theoretical or chemical kinetic investigation of CCC for the separation of inorganic elements.[8] The present work aims to elucidate the effects of reactions in the two phases on the retention and the separation efficiency of inorganic solutes.

MASS TRANSFER MODEL

Unlike organic substance, which normally exist as the same chemical form in the two phases, an inorganic solute usually exists as different forms during the CCC separations. The species distributed in the organic phase is normally in the form of a neutral extraction complex, while it exists as ion in the aqueous phase. It needs several steps of chemical reactions to form the extraction complex from ions, and vise versa. Therefore, the retention behavior may be determined not only by the distribution equilibrium but also by the mechanism of the chemical reactions.

As an example, a neutral extractant was used as the separation reagent in the present work. The mobile phase was the aqueous phase and the stationary phase was the organic phase. The overall reaction in the CCC separation process is assumed as follows:

$$M_{(a)}^{n+} + n\,L_{(a)}^{-} + b\,E_{(o)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ML_nE_{b\,(o)} \tag{3}$$

where k_f and k_r are the forward and back extraction reaction rate constant, respectively, subscript (a) and (o) denote aqueous and organic phase. The extractant (E) diffuses from the organic phase via interface, reacts with the metal ion (M^{n+}) and the inorganic anion (L^-) in aqueous phase, and forms the extraction complex (ML_nE_b). ML_nE_b will be distributed in two phases according to distribution law. The process described above is reversible. When the aqueous solution passes through the column, the metal ions in the solution will undergo a series of such processes.

Assuming that the cross-sectional area of the CCC column is q, the linear flow rate of the mobile phase is u. Considering the dx unit of the column in

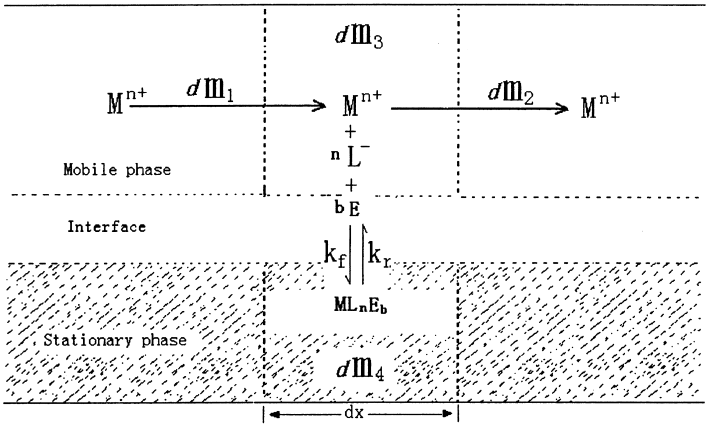

Figure 1. The mass transfer model of inorganic ions during CCC process.

Figure 1, the concentration of metal ion in mobile phase is *c*, and the concentration of extraction complex in stationary phase is *a,* the retention rate of stationary phase is S_f (S_f equals to V_S/V_c, where V_c is the total volume of the column). In the time of *dt*, the quantity of M^{n+} entering into *dx* unit is dm_1, and the quantity leaving the *dx* unit is dm_2, with the flow of mobile phase. The variation of M^{n+} in *dx* unit of mobile phase is dm_3, and the variation in stationary phase is dm_4.

Then

$$dm_1 = cu(1-S_f)qdt \tag{4}$$

$$dm_2 = u(1-S_f)q\left[c+\left(\frac{\partial c}{\partial x}\right)_t dx\right]dt \tag{5}$$

$$dm_3 = (1-S_f)q\left(\frac{\partial c}{\partial t}\right)dtdx \tag{6}$$

$$dm_4 = S_f q\left(\frac{\partial a}{\partial t}\right)dtdx \tag{7}$$

According to the equilibrium of materials,

$$dm_1 - dm_2 = dm_3 + dm_4 \tag{8}$$

Substituting equations (4), (5), (6), and (7) into equation (8), one can obtain

$$(1-S_f)u\left(\frac{\partial c}{\partial x}\right)+(1-S_f)\left(\frac{\partial c}{\partial t}\right)+S_f\left(\frac{\partial a}{\partial t}\right)=0 \tag{9}$$

Assuming that the reaction of the metal ion is of one order, from the extraction reaction (3), the variation of the concentration in organic phase could be expressed in Eq. (10)

$$\frac{\partial a}{\partial t}=k_f c\left[L^-\right]^i_{(a)}\left[E\right]^j_{(o)}-k_r a \tag{10}$$

Define k'_f as

$$k'_f = k_f[L^-]^i_{(a)}[E]^j_{(o)} \tag{11}$$

then

$$\frac{\partial a}{\partial t}=k'_f c-k_r a \tag{12}$$

where the exponential orders *i* and *j* are related to the chemical mechanism of the reaction (3). Assuming that the amount of the solute injected instantaneously is very little in the column, the concentration of the extractant and L^- remain constant during the CCC process. The expressions of the retention time, t_R and the height of theoretical plate caused by the kinetic effect, H_1 are derived by using the similar mathematical treatment in the rate theory of chromatography.[18-20]

$$t_R=\frac{L}{u}\left[1+\frac{k'_f}{k_r}k_v\right] \tag{13}$$

$$H_l=\frac{2uk_V D^{dyn}}{k_r\left[D^{dyn}k_v+1\right]^2} \tag{14}$$

where

$$k_V=\frac{S_f}{1-S_f} \tag{15}$$

THE RELATIONSHIP BETWEEN D^{DYN} AND D^{BAT}

According to the definition of S_f and the relationship between t_R and V_R, Eq. (13) can be written as

$$V_R = V_m + \frac{k'_f}{k_r} V_s \tag{16}$$

D^{dyn} can be expressed in Eq. (17), according to its definition.

$$D^{dyn} = \frac{k'_f}{k_r} \tag{17}$$

Substituting Eq. (11) into Eq. (17), then

$$D^{dyn} = \frac{k_f}{k_r}\left[L^-\right]^i_{(a)}\left[E\right]^j_{(o)} \tag{18}$$

D^{bat} can be written as Eq. (19) according to the extraction reaction (3),

$$D^{bat} = \frac{k_f}{k_r}\left[L^-\right]^n_{(a)}\left[E\right]^b_{(o)} \tag{19}$$

Thus the relationship between D^{dyn} and D^{bat} is

$$D^{dyn} = D^{bat}\left[L^-\right]^{i-n}_{(a)}\left[E\right]^{j-b}_{(o)} \tag{20}$$

It is known that the reaction orders i and j are not equal to the stoichiometric coefficients n and b, therefore, D^{dyn} is not equal to D^{bat} in most cases. But D^{dyn} is proportional to D^{bat} for a specified two phases and other experimental parameters; this conclusion had been verified by our previous work.[21] The case, D^{dyn} equal to D^{bat}, can occur when all the steps related in reaction (3) are very fast,[22] and the expression of D^{dyn} derived from any assumed mechanism of reaction (3), using a stationary state method,[23] is the same as D^{bat}.

TOTAL HEIGHT OF THEORETICAL PLATE

Both the number of theoretical plates and the height of theoretical plates can be used to characterise the separation efficiency of a given chromatographic separation system. The latter is used in the present research. Among the factors affecting the separation efficiency of CCC, the vortex diffusion could be neglected because there is no solid support in CCC, and the extra column diffusion is also negligible. We will mainly deal with (1) kinetic effect due to the existence of chemical reactions, (2) the molecule vertical diffusion, and (3) mass transfer diffusion in the two phases.

Kinetic Effect

Muralidharan et al. found that the $\mathrm{CETP}_{\mathrm{ck}}$ was proportional to half-time ($t_{1/2}$) of the back-extraction reaction, when 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone was used to separate Eu^{3+} in Centrifugal Partition Chromatography (CPC).[17] One can derive, from Eq. (14), that H_1 is proportional to $t_{1/2}$ because the back-extraction rate constant, k_{r}, is inversely proportional to $t_{1/2}$, namely, Muralidharan's experiment supports the theoretical expression of Eq.14; this is because CETP in CPC should be equivalent to the height of theoretical plate of the present work, accordingly, $\mathrm{CETP}_{\mathrm{ck}} \propto \mathrm{H}_1 \propto t_{1/2}$.

It can be concluded from the expression of H_1, that the separation efficiency of inorganic separation of CCC is affected by the mechanism of the extraction reaction. H_1 will decrease with the increases of k_f and k_r. The fast extraction system, consequently, will have a high efficiency. Furthermore, all the factors, which increase the reaction rate, such as high temperature, high concentration of inorganic anion, as well as high concentration of extractant, will improve the separation efficiency of CCC.

Molecular Diffusion

The concentration gradient in the column of CCC will lead to molecular diffusion, which is proportional to the retention time. The distribution curve of solute in the aqueous and the organic phases caused by the molecule diffusion, is a Gauss shape. The square deviations of the curves are

$$\sigma^2(\mathrm{m}) = \mathrm{C}_{\mathrm{m},1}\mathrm{D}_{\mathrm{m}}\mathrm{t}_{\mathrm{m}} \tag{21}$$

$$\sigma^2(\mathrm{S}) = \mathrm{C}_{\mathrm{s},1}\mathrm{D}_{\mathrm{s}}\mathrm{t}_{\mathrm{s}} \tag{22}$$

where $\sigma^2(m)$ and $\sigma^2(s)$ are squared deviations in the mobile and stationary phase, respectively. D_m is the diffusion coefficient of the metal ion in mobile phase. D_S is the diffusion coefficient of extraction complex in stationary phase. t_m is the retention time of metal ion in the aqueous phase. t_{s} is the retention time of extraction complex in stationary phase. $C_{\mathrm{m},1}$ and $C_{\mathrm{s},1}$ are characteristic coefficients of metal ion and its extraction complex related to the molecular diffusion in aqueous and organic phase, respectively.

The height of theoretical plates caused by the molecular diffusion is H_2.

$$H_2 = \frac{\sigma^2(m) + \sigma^2(s)}{L} \tag{23}$$

Taking into account, that

$$t_m = \frac{V_m}{F} \tag{24}$$

$$L = \frac{4V_c}{\pi d^2} \tag{25}$$

where F is the volumetric flow rate. According to equation (13):

$$t_s = \frac{k'_f S_f}{k_r(1 - S_f)} t_m \tag{26}$$

H_2 could be expressed as Eq. (27) according to equations (21-26).

$$\begin{aligned} H_2 &= \frac{\pi d^2}{4F}(C_{m,1}D_m(1 - S_f) + C_{s,1}D_s S_f D^{dyn}) \\ &= \frac{C_{m,1}D_m + C_{s,1}D_s k_v D^{dyn}}{u} \end{aligned} \tag{27}$$

where $u = \frac{4F}{\pi d^2(1 - S_f)}$.

Eq. (27) shows that molecular diffusion is mainly determined by the diameter of the column, flow rate, the diffusion coefficients and the D^{dyn} for a given separation system.

Mass Transfer Diffusion

Ma derived an expression of height of theoretical plate attributed to the mass transfer diffusions in the two phases.[24] Considering that the chemical forms of distribution species in two phases are different in inorganic separation, the expression should be rearranged in the form of equation (28)

$$H_3 = \frac{4}{\pi d^2}\left(\frac{C_{m,2}d_m^2}{D_m}+\frac{C_{s,2}d_s^2k_r}{D_sk_vk'f}\right)\frac{F}{1-S_f} = u\left(\frac{C_{m,2}d_m^2}{D_m}+\frac{C_{s,2}d_s^2}{D_sk_v}\frac{1}{D^{dyn}}\right) \tag{28}$$

where $C_{m,2}$ and $C_{s,2}$ are characteristic constants related to the apparatus parameters, as well as the chemical form of species distributed in the two phases. d_m and d_s are lengths of the fragment of two phases or the thickness of the dispersed droplets of the two phases.

The height of the theoretical plate caused by mass transfer diffusion is determined by parameters of instrument, D^{dyn} and the properties of the two phases used. The total height of the theoretical plate is H.

$$\begin{aligned} H &= H_1 + H_2 + H_3 \\ &= \frac{2uk_VD^{dyn}}{k_r\left[D^{dyn}k_v+1\right]^2}+\frac{C_{m,1}D_m+C_{s,1}D_sk_vD^{dyn}}{u}+u\left(\frac{C_{m,2}{d_m}^2}{D_m}+\frac{C_{s,2}{d_s}^2}{D_sk_v}\cdot\frac{1}{D^{dyn}}\right) \end{aligned} \tag{29}$$

H could be expressed in a simplified form,

$$H = H_0 + C_1D^{dyn} + C_2\frac{1}{D^{dyn}}+\frac{2uk_VD^{dyn}}{k_r\left[D^{dyn}k_v+1\right]^2} \tag{30}$$

where

$$H_0 = \frac{C_{m,1}D_m}{u}+\frac{uC_{m,2}d_m^2}{D_m} \tag{31}$$

$$C_1 = \frac{C_{s,1}D_sk_v}{u} \tag{32}$$

$$C_2 = \frac{uC_{s,2}d_s^2}{D_sk_v} \tag{33}$$

For a given separation system and CCC operating parameters, H_0, C_1, and C_2 are constants, and they could be determined by CCC chromatograms of three organic solutes. When an inorganic solute was separated using the same separation system and the back-extraction rate, k_r could be calculated using Eq.(30).

CONCLUSION

CCC is a high performance method for organic separation; the retention volumes of organic species could be predicted on the basis of the batch distribution ratio. However, when the CCC is used for the separation of inorganic solutes, the retention volume is not equal to the predicted value by using the batch distribution ratio, and the efficiency is low. This phenomenon was attributed to the mass transfer process of inorganic solute between two immiscible phases, which needs the metal ions to exist as neutral extraction complexes, which is formed by the reactions with extractant and/or inorganic anion. This mass transfer process involved several steps of chemical reaction; the kinetic and the mechanism of the reaction influence the retention behavior as well as the separation efficiency. In most cases, the retention volume cannot be predicted from the batch distribution ratio unless a fast extraction system is used. The efficiency of inorganic separation is not only determined by the molecular diffusion and physical mass transfer diffusion, but also by the extraction and back-extraction rate.

A fast extraction system is much desired for inorganic separation, and all measures should be taken to accelerate the reactions in order to accomplish the separation process quickly and effectively. The mechanism information of the extraction reaction could be reflected in the separation efficiency of CCC, and CCC might be explored as an instrumental method for the determination of kinetic parameters of extraction reactions.

SYMBOLS AND ACRONYMS

a	the concentration of metal ion in stationary phase of the dx unit of the column
$_{(a)}$	subscript (a) denote aqueous phase
b	stoichiometric coefficient of E
CCC	Countercurrent Chromatography
CETP_{ck}	Channel Equivalent of Theoretical Plate caused by slow back extraction
CPC	Centrifugal Partition Chromatography
$C_{m,1}$	characteristic coefficient of metal ion related to the molecular diffusion in mobile phase
$C_{m,2}$	characteristic constant related to the apparatus parameters as well as the chemical form of distribution species in mobile phase
$C_{s,1}$	characteristic coefficient of extraction complex of metal ion related to the molecular diffusion in the stationary phase

$C_{s,2}$	characteristic constant related to the apparatus parameters as well as the chemical form of distribution species in stationary phase
c	the concentration of metal ion in mobile phase of the *dx* unit of the column
D^{bat}	batch equilibrium distribution ratio
D^{dyn}	distribution ratio obtained from the CCC profile
D_m	the diffusion coefficient of the metal ion in mobile phase
D_s	the diffusion coefficient of extraction complex in stationary phase
d_m	length of the fragment or the thickness of the dispersed droplet of the mobile phase
dm_1	the quantity of metal ion entering into *dx* unit
dm_2	the quantity of metal ion leaving the *dx* unit
dm_3	the amount of variation in *dx* unit of mobile phase
dm_4	the amount of variation in *dx* unit of stationary phase
d_s	length of the fragment or the thickness of the dispersed droplet of the stationary phase
E	extractant
F	volumetric flow rate
H	total height of theoretical plate
H_1	the height of theoretical plate caused by slow kinetic effect
H_2	the height of theoretical plate caused by molecular diffusion
H_3	the height of theoretical plate caused by physical mass transfer diffusion
i	the reaction order of L^- in the extraction reaction
j	the reaction order of E in the extraction reaction
k	mass transfer coefficient obtained from stirred diffusion cell
k_f	forward extraction reaction rate constant
	abbreviate form of $k_f[L^-]^i_{(a)}[E]^j_{(o)}$
k_r	back-extraction reaction rate constant
k_v	phase ratio of stationary phase to mobile phase, $k_v = S_f/(1-S_f)$
L^-	inorganic anion
M^{n+}	metal ion
n	stoichiometric coefficient of L^-
$_{(o)}$	subscript (o) denote organic phase
q	cross-sectional area of the CCC column
S_f	retention rate of stationary phase, $S_f = V_S/Vc$
$t_{1/2}$	half-time of the back extraction reaction
t_m	retention time of metal ion in mobile phase
t_R	retention time in the CCC column
t_s	retention time of extraction complex in stationary phase

u	linear flow rate of the mobile phase
V_c	total volume of the column
V_m	volume of mobile phase
V_R	retention volume of solute
V_s,	volume of stationary phase
$W_{1/2}$	half-width of a chromatographic peak
$\sigma^2 (m)$	square deviations in the mobile phase
$\sigma^2 (s)$	square deviations in the stationary phase.

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