Behavior of lanthanides in countercurrent chromatography using dihexyl-N,N-diethylcarbamoyl methylene phosphonate as stationary phase

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Abstract

Counter-current chromatography is a real liquid–liquid chromatography. The retention volume of the solute can be calculated from the batch distribution ratio in organic separations. In the separations of metal ion, there are several complex and dissociation reactions involved in the two phases, and the retention volume cannot be always predicted from the batch distribution ratio. A mass transfer model is proposed in this paper and an expression of V_R is derived. The retention volume of metal ion is determined not only by the batch distribution ratio but also by the mechanism of the extraction reaction. When 25% dihexyl-N,N-diethylcarbamoyl methylenephosphonate in cyclohexane is used as stationary phase and 2.91 mol/l HNO_3 as mobile phase, the dynamic distribution ratios obtained from the chromatogram are not equal to but proportional to the batch distribution coefficients. These results are in agreement with the theoretical expression. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Counter-current chromatography; Stationary phases, LC; Dihexyldiethylcarbamoyl methylenephosphonate stationary phases; Distribution constants; Lanthanides; Metal cations; Rare earth ions

1. Introduction

Counter-current chromatography (CCC) is one of the forms of liquid–liquid partition chromatography in which centrifugal or gravitational force is employed to maintain one liquid as stationary phase in coil or train chambers, while the second immiscible phase (mobile phase) is passed through the stationary phase. CCC is so far mainly used for the separation

and determination of organic and biological substances. The investigations in the last 15 years have shown that CCC can also be applied to the separation and preconcentration of inorganic solutes. The separation of alkali metals [1], rare earth elements [2–4] and other inorganic ions [5] by CCC were reported.

The theory of CCC as a chromatographic technique has been established on the basis of classical expression used in extraction chromatography. The retention volume (V_R) can be predicted precisely by use of Eq. (1), provided the volume of mobile phase

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(V_m) and stationary phase (V_s) and the batch distribution ratio (D^{bat}) are known. That is, the dynamic distribution ratio (D^{dyn}) calculated from the chromatogram is equal to D^{bat} and CCC can be used to measure the distribution ratios of organic substances [6].

$$V_R = V_m + D^{bat}V_s \qquad (1)$$

In the separation of metal ions, the retention volumes of Dy, Ho, Y, Er are coincide with the calculation when di(2-ethylhexyl)phosphoric acid mono-2-ethylhexyl ester is used as the stationary phase [7]. However, several reports [8–11] have pointed out that retention volumes of inorganic solutes are different with the prediction by Eq. (1).

In the present paper, dihexyl-*N,N*-diethylcarbamoyl methylenephosphate (DHDECMP) is used as the separation reagents to reveal the dependence of retention behavior on the extraction mechanism.

2. Experimental

2.1. Reagents

Nitrate solutions of 14 single lanthanide element standards were obtained from the National Center of Standard Substances of China. DHDECMP was synthesized at the Institute of Uranium Ore Exploration (Beijing, China). Water (18.5 MΩ cm) was prepared by Ultra-Pure Water System (Millipore, USA). Other reagents were analytically pure.

2.2. Inductively coupled plasma (ICP)-MS determination

External standard calibration method in ICP-MS (Element, Finnigan, Germany) was used to determine the concentration of metal ions. The calibration curves were established as follows: a series of solutions, of which the concentrations of the metal ions of interest are is 0.01, 1.00, 10.00, 20.00, 50.00, 100.00 and 200.00 ng/ml, and the concentration of the internal standard (I.S.) is the same 20.00 ng/ml, were prepared. The counts of interested metal ions and In were determined by ICP-MS. The normality concentration, which is the product of the ratio of counts of metal ions to that of In multiplying 20.00 ng/ml was used as ordinate, and the concentration of metal ions was used as abscissa. The linear correlation coefficients of calibration curves are better than 0.9999. The operation parameters of the ICP-MS are listed in Table 1.

The same quantity of I.S. was added to the equilibrium aqueous phase of batch extraction as well as the eluted fractions. The solution was then diluted with 1% nitric acid until concentration of I.S. was 20 ng/ml. The intensity of metal ions of interest and I.S. was determined by ICP-MS, and the concentration of metal ions was calculated using the aforementioned calibration curves.

2.3. Measurement of batch distribution ratio

Mixed and single metal ion solutions are dried and dissolved in a solution of nitric acid. Equal volumes of this solution and 25% DHDECMP in cyclohexane

Table 1
Operating parameters of ICP-MS

Parameter	Value	Unit	Parameter	Value	Unit
Resolution	Low		X-Deflection	−3.78	V
Focus offset	18.65	%	Y-Deflection	−6.91	V
UaUb	−1.267	%	Shape	129.51	V
Cool gas	13.20	1/min	Rotation quadruple 1	−2.96	V
Aux gas	1.08	1/min	Rotation quadruple 2	0.77	V
Sample gas	0.58	1/min	Focus quadruple 1	−3.59	V
Additional	0.00	1/min	Focus quadruple 2	2.75	V
Plasma power	1300	Watt	MATSUDA-Plate	96.03	V
Extraction	−1964.8	V	SEM-Deflection	−355.80	V
Focus	−966.1	V	SEM	2700.0	V

in a polyethylene bottle were shaken to reach equilibrium. The phases were separated. The concentrations of metal ion in aqueous phase were measured by ICP-MS. The batch distribution ratios (D^{bat}) were calculated using Eq. (2):

$$D^{bat} = \frac{C_0\, C}{C} \tag{2}$$

where C_0 is the initial concentration of metal ion and C is the equilibrium concentration of metal ion in the aqueous phase.

2.4. CCC procedure

Chromatographic investigations were performed in a GS-20A HSCCC instrument (a multilayer coil partition centrifuge, constructed at the Beijing Institute of New Technology Application, Beijing, China). The apparatus is driven by a rotational frame through a set of nylon gears around the stationary pipe mounted on the central axis of a centrifuge. Polytetrafluoroethylene tubing of 1.0-mm inner diameter was wound around the holder hub making multiple coil layers. The total capacity was 30.48 ml, the distance of revolutionary axis to the center of rotation is 50.00 mm, with the β values ranging from 0.4 at the internal terminal to 0.74 at the external terminal. An adjustable counter weight was mounted on the opposite side of the column holder, symmetrically, in order to balance the centrifuge system. The revolution speed of this machine was regulated with a speed controller in the range between 0 and 2000 rpm.

The two phases were simultaneously saturated and placed in a thermostat overnight. The coiled column was first filled with mobile phase (aqueous phase) by a pump. Then the apparatus was rotated at a fixed speed of 1200 rpm and organic phase (10 ml), which was the stationary phase, was pumped into the column. Subsequently, mobile phase was pumped into the column at a flow-rate of 1.0 ml/min. After 5 ml mobile phase had been pumped into the column, the sample of mixed ions (~0.1 ml), which was dissolved in the mobile phase, was introduced into the column through a sample loop. The effluent was collected in plastic test tubes with a fraction collector. The concentrations of metal ions in each fraction were measured by ICP-MS. After the elution was

ended, the contents in the column were pushed out with mobile phase, and the volume of stationary phase was measured.

The chromatogram was depicted using the concentration of metal ions as ordinate and the elution volume as abscissa. The elution volume of each fraction is the sum of the total elution volume up to the last fraction and the half-collected volume of itself. Cs is used as an unretained solute to designate the solvent front in the chromatogram.

The other chromatographic data dynamic distribution ratio (D^{dyn}), separation factor ($\alpha_{D^{dyn}}$), resolution (R_s), and number of theoretical plates (n) are calculated in the Eqs. (3–6):

$$D^{dyn} = \frac{V_R - V_0}{V_s} \tag{3}$$

$$\alpha_{D^{dyn}} = \frac{D_2^{dyn}}{D_1^{dyn}} \tag{4}$$

$$R_s = \frac{2(V_{R,2} - V_{R,1})}{V_{w1} + V_{w2}} \tag{5}$$

$$N = 16 \cdot \left(\frac{V_R}{V_w}\right)^2 \tag{6}$$

where V_0 is the retention volume of Cs, V_s is the volume of stationary phase, V_w is the peak-width, and subscripts 1 and 2 denote two adjacent peaks.

3. Results and discussions

3.1. CCC separation

D^{dyn} may be alien from D^{bat} for a given separate system in the inorganic separation; however, D^{bat} is still useful to optimize the separation condition. It can always be used to predict the elution order of the metal ions. A lower D^{bat} will lead to a smaller V_R, a larger D^{bat} will induce a greater V_R and it needs a longer time for separation. For the organic separation D^{bat}, a range from 0.1 to 10 is recommended in order to perform a good separation. In the present work, batch distribution ratios of 14 lanthanoids with DHDECMP in cyclohexane were examined. The D^{bat} of lanthanoids increases with the rising concentration of nitric acid and DHDECMP. The sepa-

Table 2
Results of chromatographic separation

Metal ion	D^{bat} (SD)	D^{dyn}	α^{bat}	α^{dyn}	R_s	N
La	7.19(0.27)	10.39	1.11	1.04	0.102	130
Ce	6.47(0.24)	9.947	1.002	1.10	0.202	131
Pr	6.46(0.24)	9.074	1.17	1.17	0.306	155
Nd	5.50(0.21)	7.756	1.35	1.30	0.469	163
Sm	4.06(0.15)	5.965	1.23	1.23	0.346	185
Eu	3.31(0.12)	4.848	1.48	1.44	0.533	192
Gd	2.24(0.08)	3.372	1.13	1.21	0.250	206
Tb	1.98(0.15)	2.788	1.42	1.30	0.302	214
Dy	1.39(0.10)	2.152	1.33	1.41	0.324	231
Ho	1.05(0.08)	1.529	1.51	1.49	0.283	241
Er	0.69(0.05)	1.024	1.72	1.90	0.300	257
Tm	0.40(0.05)	0.538	1.79	1.74	0.162	285
Yb	0.23(0.04)	0.309	1.56	2.50	0.138	300
Lu	0.14(0.04)	0.124				309

ration factors are slightly different with the variation of the concentration of nitric acid and DHDECMP. DHDECMP (25%) in cyclohexane was selected as stationary phase and 2.91 mol/l HNO_3 as mobile phase. The D^{bat} of 14 lanthanides in these two phases is in the range from 0.14 to 7.2 (Table 2). The standard deviations (SDs) of D^{bat} are also listed in Table 2.

The chromatogram of 14 lanthanoids is illustrated

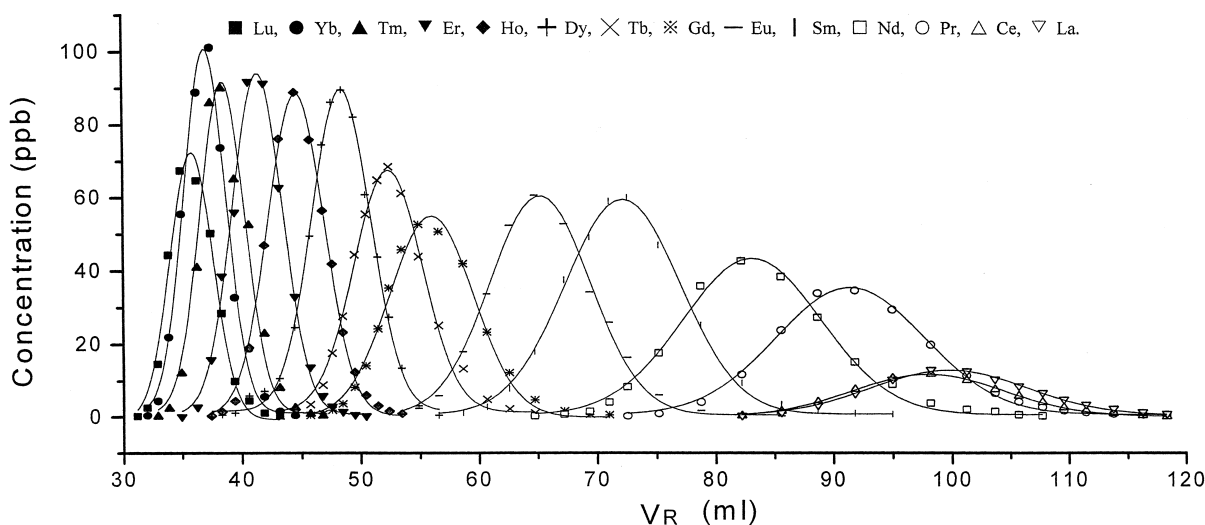in Fig. 1. The values of α^{bat} and α^{dyn} are low and insufficient for the mutual separation of lanthanides by CCC since the mutual separation for lanthanides requires the value of α greater than 2 [12]. Fig. 1 and Table 2 show that light and heavy lanthanides can be partially separated and could be grouped provided a higher retention ratio is obtained using present separation system. But mutual separation of the adjacent lanthanides will be very difficult.

3.2. D^{dyn} to D^{bat}

Several authors [8–11] have observed this phenomenon using the other two-phases in the inorganic separation. Abe et al. [8] reported that D^{dyn} values calculated from chromatograms were lower than those of the batch experiments when tributyl phosphate (TBP) was used to separate lanthanides using centrifugal partition chromatography (CPC). The deviation was the result of the concentration effects and the 'bleeding' problem. In their experiments, the concentrations of solutes used for batch experiments were much lower than that used for CPC experiments, and the D^{bat} is decreased with the increase of the concentration. The leak rate of the stationary phase was 3 ml/h.

In the present paper high sensitivity ICP-MS was

Fig. 1. The chromatogram of metal ions in counter-current chromatography. Mobile phase, 2.91 mol/l HNO_3; stationary phase, 25% DHDECMP in cyclohexane; flow-rate, 1 ml/min; revolution rate, 1200 rpm, temperature, 22°C; retention ratio, 20.41%: $\beta = 0.4$–0.72, $V_c = 30.48$.

used to determine the solutes. The solute used in extraction and CCC experiments was of trace level (~10 μg), and the difference of D^{bat} using mixed ion and single solute was within the experimental error. The V_s used in the present work was much lower than the maximum retention volume that could be provided by the rotation rate and flow-rate of the apparatus and no detectable stationary phase leakage was observed during the CCC process. Table 2 shows that D^{dyn} is not the same as but greater than D^{bat}. That is, $V_R \neq V_m + D^{bat}V_s$. This deviation of D^{dyn} and D^{bat}, therefore, should not be attributed to the concentration effect and the leakage of stationary phase.

Nakamura et al. [7] found that the V_R was coincide with Eq. (1) when 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester was used as stationary phase to separate lanthanides in CCC, but the V_R was

greater than the prediction when Versatic10 was used as stationary phase. They proposed that the latter phenomenon might be due to an increase in the distribution ratio, perhaps caused by a local rise in temperature in column cartridge near a heater.

The D^{bat} of 14 lanthanides under different temperature were measured and are depicted in Fig. 2. The figure shows that D^{bat} of lanthanide decreases with rising temperature. Therefore, the result ($D^{dyn} > D^{bat}$) cannot be attributed to the increase in heat of the multilayer coil column during the separation process, and the fundamentals of the separation of solutes in CCC columns need to be studied, especially with respect to metal ions.

3.3. Influence of extraction mechanism on D^{dyn}
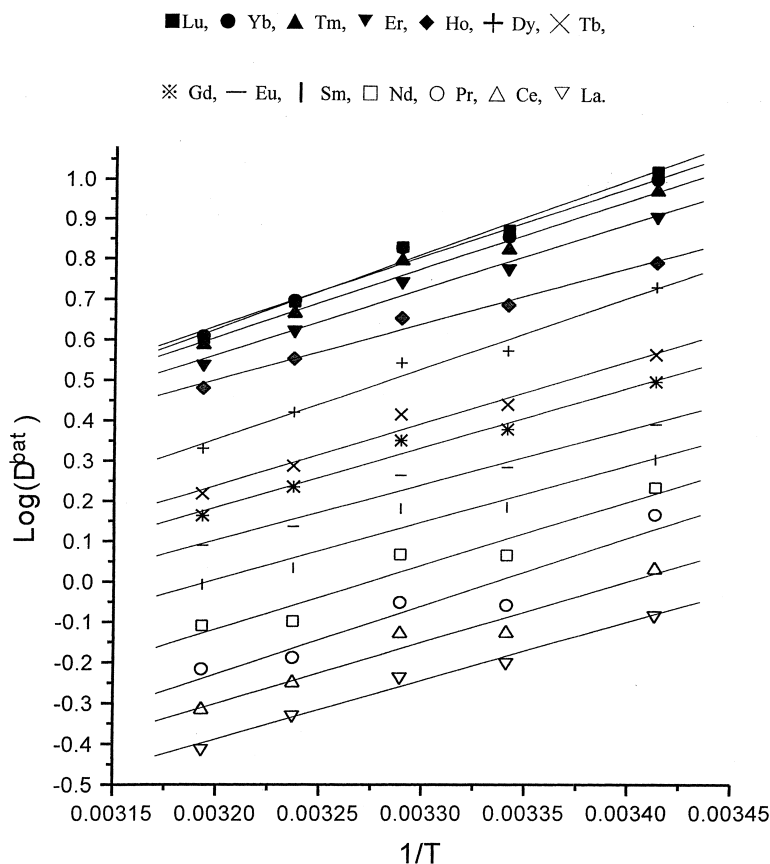
Organic substances generally exist in the same

Fig. 2. The dependence of D^{bat} on T. Organic phase, 25% DHDECMP in cyclohexane; aqueous phase, 3.35 mol/1 HNO$_3$.

chemical form in the two phases of CCC. In the separation of metal ions, the chemical forms are different in the two phases. The distribution species in the organic phase is in the form of a neutral extraction complex, while in the aqueous phase the solute may exist in forms of ions. It needs several chemical reactions to form the neutral extraction complex.

The overall extraction reaction [13] of DHDECMP extracting lanthanides is:

$$M^{3+} + 3DHDECMP_{(o)} + 3NO_3^-$$

$$= \underset{k_r}{\overset{k_f}{=\!=\!=}} M(DHDECMP)_3(NO_3^-)_{3,(o)} \tag{7}$$
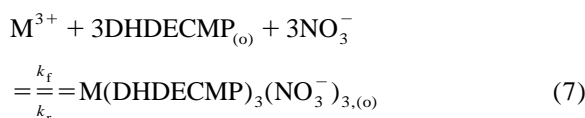
The mass transfer model of metal ions in CCC column is illustrated in Fig. 3. The metal ion (M^{3+}) complexes with the extractant, DHDECMP, dissolved in aqueous phase, and combine with NO_3^- to form a neutral extraction complex, $M(DHDECMP)_3(NO_3)_3$. The extraction complex distribute between two phases according to the distribution rule. The metal ion leaves the column, eventually, via a series of complex, distribution, dissociation processes between the two phases.

Assuming that the cross-sectional area of the column is q, the flow-rate of the mobile phase is u, the concentration of metal ion in mobile phase is c, and the concentration of the extraction complex in stationary phase is a. The retention ratio of stationary phase is S_f. ($S_f = V_s/V_c$, where V_c is the total volume of the column). The organic phase was designated as stationary phase and the aqueous phase as mobile phase.

In the dx unit of the column in Fig. 3, the quantity of M^{3+} entering into the dx unit is dm_1, and the quantity leaving the dx unit is dm_2, in the time of dt. Then:

$$dm_1 = cu(1 - S_f)q\, dt \tag{8}$$

$$dm_2 = u(1 - S_f)q\left[c + \left(\frac{\partial c}{\partial x}\right)_t dx \right] dt \tag{9}$$

The quantity of M^{3+} varied in dx units of mobile phase is dm_3, and the variation in stationary phase is dm_4, then:

$$dm_3 = (1 - S_f)q\left(\frac{\partial c}{\partial t}\right) dt\, dx \tag{10}$$

$$dm_4 = S_f q\left(\frac{\partial a}{\partial t}\right) dt\, dx \tag{11}$$
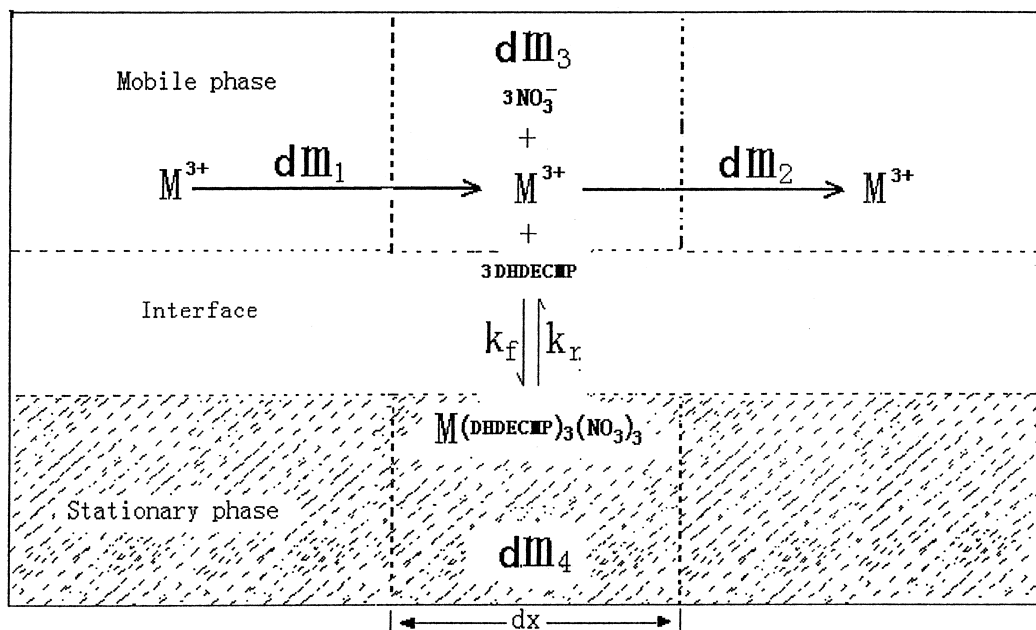

Fig. 3. The mass transfer model of counter-current chromatography for the separation of metal ion.

According to the equilibrium of materials,

$$\mathrm{d}m_1 - \mathrm{d}m_2 = \mathrm{d}m_3 + \mathrm{d}m_4 \tag{12}$$

Substituting Eqs. (8–10), and (11) into Eq. (12), we obtain:

$$(1 - S_f)u\left(\frac{\partial c}{\partial x}\right) + (1 - S_f)\left(\frac{\partial c}{\partial t}\right) + S_f\left(\frac{\partial a}{\partial t}\right) = 0 \tag{13}$$

According to the extraction reaction (7), the variation of the concentration in organic phase could be expressed in Eq. (14), generally:

$$\frac{\partial a}{\partial t} = k_f c[\mathrm{DHDECMP}]^d[\mathrm{NO_3^-}]^e$$
$$- k_r a[\mathrm{DHDECMP}]^g[\mathrm{NO_3^-}]^h$$
$$= k_f' c - k_r' a \tag{14}$$

with

$$k_f' = k_f[\mathrm{DHDECMP}]^d[\mathrm{NO_3^-}]^e \tag{15}$$

$$k_r' = k_r[\mathrm{DHDECMP}]^g[\mathrm{NO_3^-}]^h \tag{16}$$

where the exponential orders d, e and g, h are determined by the mechanism of extraction reaction (7). k_f and k_r are forward rate constant and back rate constant, respectively. Assuming that the sample is injected instantaneously into the head of the column, the sample injection function is:

$$c(0,t) = f(t) = m\delta(t) \tag{17}$$

The retention time of the metal ion, according to this mass transfer model, could be expressed in Eq. (18) by using the same derivation of the rate theory in chromatography [14]:

$$t_R = \frac{L}{u} \cdot \left[1 + \frac{k_f' S_f}{k_r'(1 - S_f)}\right] \tag{18}$$

According to the definition of S_f and the relationship between t_R and V_R, Eq. (18) can be written as:

$$V_R = V_m + \frac{k_f'}{k_r'} \cdot V_s \tag{19}$$

Eq. (19) shows that V_R is determined by the mechanism of extraction reaction. Defining k_f'/k_r' as D^{dyn}, Eq. (19) can be rewritten as Eq. (20):

$$V_R = V_m + D^{\mathrm{dyn}} V_s \tag{20}$$

According to Eqs. (15) and (16):

$$D^{\mathrm{dyn}} = \frac{k_f}{k_r}[\mathrm{DHDECMP}]^i[\mathrm{NO_3^-}]^j \tag{21}$$

where i and j are related to the mechanism of the extraction reaction. According to the extraction reaction (7), the D^{bat} could be expressed in Eq. (22):

$$D^{\mathrm{bat}} = \frac{k_f}{k_r} \cdot [\mathrm{DHDECMP}]^3[\mathrm{NO_3^-}]^3 \tag{22}$$

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

$$D^{\mathrm{dyn}} = D^{\mathrm{bat}}[\mathrm{DHDECMP}]^{i-3}[\mathrm{NO_3^-}]^{j-3} \tag{23}$$

It can be concluded from Eq. (23) that D^{dyn} is not always equal to D^{bat} for the chemism of Eq. (7) may not give out $i = j = 3$. Eq. (23) shows that, however, D^{dyn} is linear with D^{bat} for a given two phases. Fig. 4 illustrated the plot of D^{dyn} against D^{bat}, where line 1 is a regression of D^{dyn} and D^{bat} in Table 2. Its
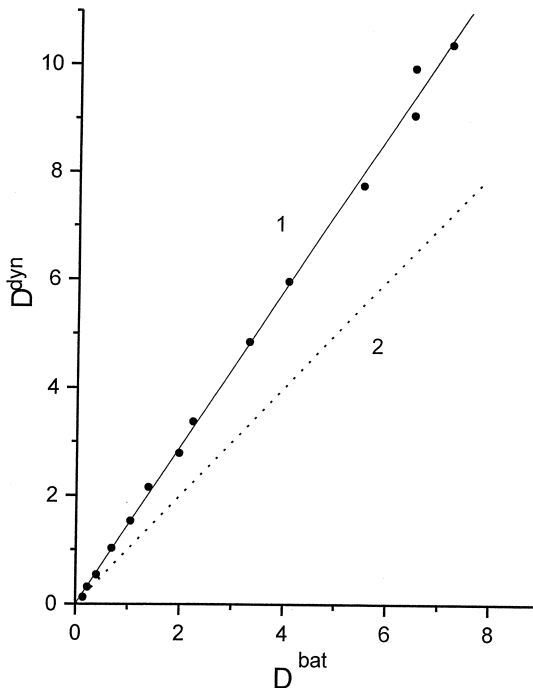

Fig. 4. Dependence of D^{dyn} on D^{bat}. (Line 1) D^{dyn} to D^{bat}, $r = 0.9986$, SD $= 0.22$; (Line 2) $D^{\mathrm{dyn}} = D^{\mathrm{bat}}$.

linear correlation coefficient is 0.9986. Dotted line 2 represents the case when $D^{\mathrm{dyn}} = D^{\mathrm{bat}}$, that is, in the case of organic separation. The deviation of lines 1 and 2 proves Eq. (23) tenable. Therefore, the mechanism of the extraction reaction has an important influence on the retention behavior of the metal ions during the separation process of CCC. The situation, $D^{\mathrm{dyn}} = D^{\mathrm{bat}}$, could occur when the chemical reactions involved in the separation process of CCC are very fast. In that case, the expression of D^{dyn} derived from any assumed chemism will be the same as D^{bat}.

4. Conclusion

DHDECMP (25%) in cyclohexane–2.91 mol/l HNO_3 was used as the two phases in CCC for its moderate distribution ratio of 14 lanthanides. The dynamic distribution ratios obtained from the chromatogram are different with the batch distribution ratios. Theoretical investigation shows that this deviation is caused by the existence of the chemical reactions in the chromatographic process. For a given two phases, the D^{dyn} is linear with D^{bat}. This experimental result coincides with the theoretical expression.

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