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CORRELATING MULTICOMPONENT EQUILIBRIUM DATA FOR THE EXTRACTION
OF LANTHANIDES WITH DI-(2-ETHYLHEXYL) PHOSPHORIC
ACID AS THE SOLVENT*

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ABSTRACT

Single-component equilibrium data, obtained in previous work¹⁻³, were correlated empirically for the systems $MCl_3-HCl-H_2O-1 \text{ M D2EHPA}$ (in Amsco Odorless Mineral Spirits), where M designates Sm, Nd and Ce. The nonlinear models predict the organic concentration as a function of the aqueous lanthanide concentration and acidity over a wide range.

Equilibrium data for the systems $SmCl_3-NdCl_3-HCl-H_2O-1 \text{ M D2EHPA-Amsco}$ and $SmCl_3-NdCl_3-CeCl_3-HCl-H_2O-1 \text{ M D2EHPA-Amsco}$, obtained in previous work²⁻³, were also correlated empirically. The model for the binary system predicts the total organic concentration as a function of mole fraction of Sm in the aqueous phase and acidity, at total aqueous lanthanide concentrations of $\sim 0.64 \text{ M}$ and 0.11 M . The ternary system model predicts the total organic concentration as a function of mole fraction of Ce and acidity, at three different mole fractions of Sm on a cerium-free basis (0.1, 0.5 and 0.9) and at a total aqueous concentration of $\sim 0.64 \text{ M}$. The above models consist of a series of linear terms analogous to Raoult's Law for ideal solutions and a series of nonlinear terms predicting the deviations from ideality (interaction effects).

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INTRODUCTION

Lanthanide extraction by di-(2-ethylhexyl) phosphoric acid (D2EHPA) has been studied by many investigators. However, only in recent years have equilibrium data at macro-concentrations been reported⁴⁻⁸.

The ion exchange mechanism of extraction, proposed by Peppard et al.⁹, at tracer concentrations is:

However, the actual chemistry of the reactions involved at macro-concentrations is extremely complex. Therefore, it is very difficult to optimize a specific process with respect to solvent selectivity and other operating conditions without obtaining an extensive amount of equilibrium data in the laboratory. Thus, it is necessary to correlate multicomponent data empirically. This study involves the system $SmCl_3$ - $NdCl_3$ - $CeCl_3$ - HCl - H_2O -1 M D2EHPA-Amsco.

EXPERIMENTAL

The parameter vectors for the non-linear models used to predict the single component data and the interaction effects for the multi-component systems were estimated by the Hartley Modified Gauss-Newton technique¹⁰. This technique involves the fitting of the experimental data to a mathematical model by minimizing the sum of the squares of the residuals. Since the criterion for the above least-squares technique is that the model be linear in the parameters, it is essential to linearize the model. This is done by expanding the function in terms of a first order Taylor Series around an initial "guess" of the parameter vector. The Newton coefficient or correction parameter vector is then

obtained by solving the matrix equation deduced from the functions which minimize the sum of the squares of the residuals. The computer routine was programmed for the IBM 360 computer.

RESULTS

THE SYSTEMS $\text{MCl}_3\text{-HCl-H}_2\text{O-1 M D2EHPA-AMSCO}$

Single-component equilibrium data for the above systems, where M designates Sm, Nd and Ce, obtained in other studies¹⁻³, were correlated empirically. The range of aqueous lanthanide concentrations studied is 0.1M to 1.5M and the acidity from 0.3M to 0.9M. The mathematical models expressing the lanthanide organic molarity, y_M^* , as a function of the aqueous metal concentration x and acidity H are:

$$y_M^* = a_{1M} x^{a_{2M}} e^{a_{3M} H (a_{4M} + a_{5M} H + a_{6M} H^2)} \quad (2)$$

where $(a_{1\text{Sm}}, \dots, a_{6\text{Sm}}) = (0.08674, 0.2448, -0.4742, 0.9287, 0.3133, -1.4158)$

$(a_{1\text{Nd}}, \dots, a_{6\text{Nd}}) = (0.02048, 0.2577, -0.5758, -0.9282, -2.9195, 0.5755)$

$(a_{1\text{Ce}}, \dots, a_{6\text{Ce}}) = (0.01656, 0.3588, -0.8581, -0.7032, -5.389, 4.927)$

The models for y_{Sm}^* , y_{Nd}^* , and y_{Ce}^* predict the experimental data with an average error (residual divided by experimental) of less than 5%, 6% and 3%, respectively, within the concentration ranges studied.

THE SYSTEMS $\text{SmCl}_3\text{-NdCl}_3\text{-HCl-H}_2\text{O-1 M D2EHPA-AMSCO}$

AND $\text{SmCl}_3\text{-NdCl}_3\text{-CeCl}_3\text{-HCl-H}_2\text{O-1 M D2EHPA-AMSCO}$

The total organic concentrations and compositions for the binary

and ternary systems are plotted against $N_{Sm,A}$ and $N_{Ce,A}$, respectively, as shown in Figures 1 and 2. It should be noted that the data are presented only at one condition of X_T and H^+ for the binary system and one condition of X_T , H^+ and $x_{Sm}/(x_{Sm} + x_{Nd})$ for the ternary system. At different set of conditions the curves are displaced.

From Figures 1 and 2, it is observed that the total lanthanide organic concentration may be predicted with a series of linear terms and a series of terms which is a measure of the deviation from linearity. The straight lines in both figures represent the extraction of each element without interference from other ions during the extraction process (ideal behavior), and are analogous to Raoult's Law for ideal solutions. These lines are obtained by multiplying the concentration of each element in the pure component state by its mole fraction in the aqueous phase ($y_{M,A}^* N_{M,A}$). It is proposed that this term be called the "partial extractability" of each element under a set of conditions, as an analogy to partial pressure. The deviations from ideality Δy_{Sm} , Δy_{Nd} and Δy_{Ce} is a measure of the individual component interaction effects. The models and parameter vectors used to correlate the above terms, including Equation 2, are presented in Table 1. The total lanthanide organic concentrations for the binary and ternary systems may be calculated from Equations 3 and 4, respectively,

$$Y_T = y_{Sm,A}^* N_{Sm,A} + y_{Nd,A}^* N_{Nd,A} + \Delta y_{Sm} + \Delta y_{Nd} \quad (3)$$

$$Y_T = y_{Sm,A}^* N_{Sm,A} + y_{Nd,A}^* N_{Nd,A} + y_{Ce,A}^* N_{Ce,A} + \Delta y_{Sm} + \Delta y_{Nd} + \Delta y_{Ce} \quad (4)$$

Once Y_T is calculated as a function of the aqueous phase variables, the composition of the organic phase is obtained knowing the separation factor of each pair of elements. From the definitions of β and Y_T in the binary system,

$$\beta_{Sm,Nd} = \left(\frac{y_{Sm}}{x_{Sm}}\right) \cdot \left(\frac{x_{Nd}}{y_{Nd}}\right) \quad (5)$$

$$Y_T = y_{Sm} + y_{Nd} \quad (6)$$

one obtains,

$$y_{Sm} = \frac{Y_T}{1 + \frac{1}{\beta_{Sm,Nd}} \left(\frac{x_{Nd}}{x_{Sm}}\right)} \quad (7)$$

From the definitions of $\beta_{Sm,Nd}$, Y_T and y_{Ce}/y_{Sm} for the ternary system,

$$\beta_{Sm,Nd} = \left(\frac{y_{Sm}}{x_{Sm}}\right) \cdot \left(\frac{x_{Nd}}{y_{Nd}}\right), \quad (8)$$

$$Y_T = y_{Sm} + y_{Nd} + y_{Ce}, \quad (9)$$

$$\frac{y_{Ce}}{y_{Sm}} = \frac{x_{Ce}}{x_{Sm}} \frac{1}{\beta_{Sm,Ce}}, \quad (10)$$

one obtains,

$$y_{Sm} = \frac{Y_T}{1 + \frac{1}{\beta_{Sm,Nd}} \left(\frac{x_{Nd}}{x_{Sm}}\right) + \frac{1}{\beta_{Sm,Ce}} \left(\frac{x_{Ce}}{x_{Sm}}\right)} \quad (11)$$

Similarly,

$$y_{Nd} = \frac{Y_T}{1 + \beta_{Sm,Nd} \left(\frac{x_{Sm}}{x_{Nd}}\right) + \frac{1}{\beta_{Nd,Ce}} \left(\frac{x_{Ce}}{x_{Nd}}\right)} \quad (12)$$

Supporting studies²⁻³ show that the β s for the binary and ternary systems remain the same and almost constant for all conditions studied. The arithmetic averages are $\beta_{\text{Sm,Ce}} \sim 19.5$, $\beta_{\text{Sm,Nd}} \sim 9.06$ and $\beta_{\text{Nd,Ce}} \sim 2.16$.

DISCUSSION

The form of the empirical models in Table 1 can be justified in terms of the shape of the curves and their displacement with respect to acidity.

Equation 4 predicts the total organic concentration as a function of N_{Sm} , N_{Nd} , H^+ and mole fraction of Sm in the aqueous phase on a cerium-free basis, $(x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1, 0.5 \text{ and } 0.9)$ at $X_T \sim 0.64M$. If it is desired to predict data at $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ conditions other than the ones studied, one may calculate Y_T for the three conditions given and interpolate to the desired value of $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$.

The total aqueous concentration of $\sim 0.64M$ was chosen for this study because the extraction is near a maximum for any acidity, and thus the interaction effects are larger. However, it is possible to extrapolate linearly to other X_T regions using the given models. This can be done under the assumption that the binary and ternary system curves, as shown in Figure 3, possess a similar shape at different X_T regions. This is because the end-points are obtained directly from the single-component equilibrium data which may be assumed to vary smoothly from one concentration range to the other. The curves in Figure 3 are given for the conditions where $H^+ = 0.6M$, $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$, and at two different X_T ($0.11M$ and $0.64M$). It should be noted that the pure component data allow one to know the end-points on the binary

system. Knowing $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ from the ternary system and the acidity, one may calculate Y_T for the binary system using Equation 3. This point is the left end-point on the ternary system; the right end-point is obtained from the single-component data, y_M^* .

Example 1.

Calculate the organic concentrations in a binary system containing SmCl_3 and NdCl_3 solutes if the equilibrated aqueous conditions are: $\text{H}^+ = 0.6\text{M}$, $X_T = 0.64\text{M}$ and $N_{\text{Sm}} = 0.5$.

a. From Models II and III, $y_{\text{Nd}}^* = 0.0447\text{M}$ and $y_{\text{Sm}}^* = 0.1087\text{M}$, respectively.

b. Using Models IV and V, the interaction effects are

$$\Delta y_{\text{Sm}} = 0.02418\text{M} \text{ and } \Delta y_{\text{Nd}} = 0.01325\text{M}, \text{ respectively.}$$

c. Utilizing Equation 3, $Y_T = 0.08763\text{M}$ compared to the experimental value of 0.0873M .

d. Employing Equation 7 with $\beta_{\text{Sm,Nd}} \sim 8.8$ gives $y_{\text{Sm}} = 0.07869\text{M}$ and $y_{\text{Nd}} = 0.008942\text{M}$. The experimental values are 0.07838M and 0.00892M , respectively.

Example 2.

Calculate the organic concentrations in a ternary system containing SmCl_3 , NdCl_3 and CeCl_3 solutes if the aqueous phase conditions are:

$$\text{H}^+ = 0.4\text{M}, X_T = 0.64\text{M}, N_{\text{Ce}} = 0.1, N_{\text{Nd}} = 0.81 \text{ and } x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1.$$

a. From Models I, II and III, $Y_{\text{Ce}}^* = 0.0246\text{M}$, $y_{\text{Nd}}^* = 0.0446\text{M}$ and $y_{\text{Sm}}^* = 0.1087\text{M}$, respectively.

b. Using Models VIII, IX and X, the interaction effects are: $\Delta y_{\text{Sm}} = 0.01732\text{M}$, $\Delta y_{\text{Nd}} = -0.008179\text{M}$ and $\Delta y_{\text{Ce}} = -0.000629\text{M}$.

- c. Utilizing Equation 4, the total organic molarity $Y_T = 0.05688M$ compared to the experimental value of $0.0574M$.
- d. Employing Equations 9, 11 and 12, the organic compositions are $y_{Sm} = 0.02774M$, $y_{Nd} = 0.02756M$ and $y_{Ce} = 0.001578M$. The experimental values are $0.02795M$, $0.02781M$ and $0.001592M$, respectively.

In order to test the extrapolation technique at total aqueous concentrations other than $0.64M$, the following example is given.

Example 3.

Calculate the organic concentrations in the ternary system given the following aqueous conditions: $H^+ = 0.578M$, $X_T = 0.1004M$, $N_{Ce} = 0.4138M$ and $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.55$.

- a. From Models I, II and III calculate the pure component data at $X_T = 0.10M$ and $0.64M$.

At $X_T = 0.10$, $y_{Ce}^* = 0.0224M$, $y_{Nd}^* = 0.0408M$ and $y_{Sm}^* = 0.0933M$.

At $X_T = 0.64$, $y_{Ce}^* = 0.0265M$, $y_{Nd}^* = 0.0476M$ and $y_{Sm}^* = 0.1119M$.

- b. From Equation 3 and Models IV and V

$$Y_T (Sm, Nd)_{0.64} = 0.09232M$$

- c. Using the end-points of y_M^* calculated in (a), one obtains a linear relationship, for the binary system in Figure 3, between $X_T = 0.64M$ and $0.10M$.

$$\frac{(y_{Sm}^*)_{0.64} - (y_{Nd}^*)_{0.64}}{(y_{Sm}^*)_{0.10} - (y_{Nd}^*)_{0.10}} = \frac{Y_T (Sm, Nd)_{0.64} - (y_{Nd}^*)_{0.64}}{Y_T (Sm, Nd)_{0.10} - (y_{Nd}^*)_{0.10}} \quad (13)$$

From Equation 13, $Y_T (Sm, Nd)_{0.10} = 0.07731M$

- d. From Equation 4 and Models XI, XII and XIII, $Y_T(\text{Sm}, \text{Nd}, \text{Ce})_{0.64} = 0.09309M$.
- e. Using the end-points of $Y_T(\text{Sm}, \text{Nd})$ and y_{Ce}^* , for the ternary system in Figure 3, one obtains a linear relationship between $X_T = 0.64M$ and $0.10M$.

$$\frac{Y_T(\text{Sm}, \text{Nd})_{0.64} - (y_{\text{Ce}}^*)_{0.64}}{Y_T(\text{Sm}, \text{Nd})_{0.10} - (y_{\text{Ce}}^*)_{0.10}} = \frac{Y_T(\text{Sm}, \text{Nd}, \text{Ce})_{0.64} - (y_{\text{Ce}}^*)_{0.64}}{Y_T(\text{Sm}, \text{Nd}, \text{Ce})_{0.10} - (y_{\text{Ce}}^*)_{0.10}} \quad (14)$$

From (14), $Y_T(\text{Sm}, \text{Nd}, \text{Ce})_{0.10} = 0.0779M$ compared to the experimental value of $0.0742M$.

- f. The organic compositions using Equations 9, 11 and 12 are $y_{\text{Sm}} = 0.0687M$, $y_{\text{Nd}} = 0.0086$ and $y_{\text{Ce}} = 0.0006$. The experimental values are 0.06124 , 0.00767 and 0.000532 , respectively. It should be noted that if more accurate results are required for different X_T , more equilibrium data should be taken at each concentration and correlated.

CONCLUSIONS

1. The single-component equilibrium data may be calculated reliably using an empirical model of two independent variables (acidity and aqueous lanthanide molarity). The average error is less than 5%.
2. The total organic concentrations in the binary and ternary systems may be calculated by the sum of a series of linear terms analogous to Raoult's Law for ideal solutions and nonlinear terms which measure the interaction effects (deviations from ideality). The average error for predicting the interaction effects is less than 4%.

SYMBOLS

M	=	Trivalent lanthanide cation
H	=	Equilibrium hydrogen ion concentration in the aqueous phase, mol/l
x_M^*	=	Molarity of lanthanide ion M in the equilibrated aqueous phase for a single-component system
y_M^*	=	Molarity of lanthanide ion M in the equilibrated organic phase for a single-component system
$X_T(M,N)$	=	Total molarity of lanthanides in the equilibrated aqueous phase for a binary system M,N
$Y_T(M,N)$	=	Total molarity of lanthanides in the equilibrated organic phase for a binary system M,N.
$x_M(M,N)$	=	Equilibrium molarity in the aqueous phase of species M for a binary system M,N
$y_M(M,N)$	=	Equilibrium molarity in the organic phase of species M for a binary system M,N
$N_{M,A}(M,N)$	=	Mole fraction of species M in the equilibrated aqueous phase for a binary system M,N = $x_M(M,N)/X_T(M,N)$
$X_T(L,M,N)$	=	Total molarity of lanthanides in the equilibrated aqueous phase for a ternary system L,M,N
$Y_T(L,M,N)$	=	Total molarity of lanthanides in the equilibrated organic phase for a ternary system L,M,N
$x_M(L,M,N)$	=	Equilibrium molarity in the aqueous phase of species M for a ternary system L,M,N
$y_M(L,M,N)$	=	Equilibrium molarity in the organic phase of species M for a ternary system L,M,N

$N_{M,A}(L,M,N)$ = Mole fraction of species M in the equilibrated aqueous phase for a ternary system L,M,N = $x_M(L,M,N)/X_T(L,M,N)$

$\beta_{M,N}$ = Concentration separation factor of species M with respect to N

a = Arbitrary constant

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Table 1. Empirical Model

No.	Model followed by parameter vector	Data predicted	Avg. error less than
I	$y_{Ce}^* = a_1 x^2 e^{a_3 x} H^{a_4 + a_5 H + a_6 H^2}$ $(a_1, \dots, a_6) = (0.01656, 0.3588, -0.8581, -0.7032, -5.3893, 4.927)$	Single-component, $CeCl_3$	3%
II	$y_{Nd}^* = b_1 x^2 e^{b_3 x} H^{b_4 + b_5 H + b_6 H^2}$ $(b_1, \dots, b_6) = (0.02048, 0.2577, -0.5758, -0.9282, -2.9195, 0.5755)$	Single-component, $NdCl_3$	6%
III	$y_{Sm}^* = c_1 x^2 e^{c_3 x} H^{c_4 + c_5 H + c_6 H^2}$ $(c_1, \dots, c_6) = (0.08674, 0.2448, -0.4742, -0.9287, 0.3133, -1.4158)$	Single-component, $SmCl_3$	5%
IV	$\Delta y_{Sm} = a_1 N_{Sm}^{a_2} (1 - N_{Sm})^{a_3} (a_4 - N_{Sm}) e^{a_5 H^+}$ $(a_1, \dots, a_5) = (2.2023, 0.7422, 0.4096, 0.9008, -4.002)$	Interaction effect of Sm in binary system at $X_T(Sm, Nd) \sim 0.64 \underline{M}$	7%

Table 1. (Cont.)

No.	Model followed by parameter vector	Data predicted	Avg. error less than
V	$\Delta y_{Nd} = b_1 N_{Sm}^{b_2} (1-N_{Sm})^{b_3} e^{b_4 H^+}$ $(b_1, \dots, b_4) = (-0.4239, 0.5075, 1.1582, -3.8522)$	Interaction effect of Nd in binary system at $X_T(Sm, Nd) \sim 0.64 \underline{M}$	4%
VI	$\Delta y_{Sm} = c_1 N_{Sm}^{c_2} (1-N_{Sm})^{c_3} e^{c_4 H^+}$ $(c_1, \dots, c_4) = (0.5612, 0.6775, 1.2931, -3.4724)$	Interaction effect of Sm in binary system at $X_T(Sm, Nd) \sim 0.11 \underline{M}$	3%
VII	$\Delta y_{Nd} = d_1 N_{Sm}^{d_2} (1-N_{Sm})^{d_3} e^{d_4 H^+}$ $(d_1, \dots, d_4) = (-0.3099, 0.5959, 1.2315, -3.3533)$	Interaction effect of Nd in binary system at $X_T(Sm, Nd) \sim 0.11 \underline{M}$	3.5%
VIII	$\Delta y_{Sm} = a_1 (N_{Ce} + a_2) (1-N_{Ce})^{a_3} e^{a_4 H^+}$ $(a_1, \dots, a_4) = (0.09574, 1.3466, 0.8669, -3.313)$	Interaction effect of Sm in ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.1$ and $X_T(Sm, Nd, Ce) \sim 0.64 \underline{M}$	2.8%

Table 1. (Cont.)

No.	Model followed by parameter vector	Data predicted	Avg. error less than
IX	$\Delta y_{Nd} = b_1 (1-N_{Ce})^{b_2} (b_3 - N_{Ce}) e^{b_4 H^+}$ $(b_1, \dots, b_4) = (-0.2024, 0.6816, 0.6191, -4.1348)$	Interaction effect of Nd in ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.1$ and $X_T(Sm, Nd, Ce) \sim 0.64 \underline{M}$	2.8%
X	$\Delta y_{Ce} = c_1 N_{Ce}^{c_2} (1-N_{Ce})^{c_3} e^{c_4 H^+}$ $(c_1, \dots, c_4) = (-0.8377, 1.234, 0.9534, -7.086)$	Interaction effect of Ce in ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.1$ and $X_T(Sm, Nd, Ce) \sim 0.64$	3.5%
XI	$\Delta y_{Sm} = d_1 H^+ (N_{Ce} + d_2) (1-N_{Ce})^{d_3 H^+} e^{d_4 H^+}$ $(d_1, \dots, d_4) = (0.7362, 0.4054, 1.2928, -3.2453)$	Interaction effect of Sm in ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.5$ and $X_T(Sm, Nd, Ce) \sim 0.64 \underline{M}$	3.5%
XII	$\Delta y_{Nd} = g_1 (1-N_{Ce})^{g_2} e^{g_3 H^+}$ $(g_1, \dots, g_3) = (-0.1356, 1.5785, -3.8826)$	Interaction effect of Nd in the ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.5$ and $X_T(Sm, Nd, Ce) \sim 0.64 \underline{M}$	3.2%

Table 1. (Cont.)

No.	Model followed by parameter vector	Data predicted	Avg. error less than
XIII	$\Delta y_{\text{Ce}} = h_1 N_{\text{Ce}}^{h_2} (1 - N_{\text{Ce}})^{h_3} e^{h_4 H^+}$ $(h_1, \dots, h_4) = (-0.7586, 1.2834, 0.6870, -5.7577)$	Interaction effect of Ce in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64 \text{ M}$	3.0%
XIV	$\Delta y_{\text{Sm}} = k_1 H^+ (N_{\text{Ce}} + k_2) (1 - N_{\text{Ce}})^{k_3} e^{k_4 H^+}$ $(k_1, \dots, k_4) = (0.9567, 0.006978, 0.9620, -3.0384)$	Interaction effect of Sm in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.9$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64 \text{ M}$	2.2%
XV	$\Delta y_{\text{Nd}} = p_1 (1 - N_{\text{Ce}})^{p_2} e^{p_3 H^+}$ $(p_1, \dots, p_3) = (-0.02864, 1.3877, -3.666)$	Interaction effect of Nd in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.9$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64 \text{ M}$	2.8%
XVI	$\Delta y_{\text{Ce}} = m_1 N_{\text{Ce}}^{m_2} (1 - N_{\text{Ce}})^{m_3} e^{m_4 H^+}$ $(m_1, \dots, m_4) = (-0.6074, 1.2247, 0.4916, -5.3225)$	Interaction effect of Ce in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.9$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64 \text{ M}$	3.0%

FIGURE CAPTIONS

Fig. 1 Organic concentrations for the system $\text{SmCl}_3 - \text{NdCl}_3 - \text{CeCl}_3 - \text{HCl} - \text{H}_2\text{O} - 1 \text{ M D2EHPA} - \text{Amsco}$ at $\text{H}^+ = 0.5\text{M}$ and $X_T \sim 0.64\text{M}$,
 $\circ$ [Molarity of Sm, $y_{\text{Sm}}]_0$, $\square$ [Molarity of Nd, $y_{\text{Nd}}]_0$, Δ [Total Molarity, $Y_T = y_{\text{Sm}} + y_{\text{Nd}}]_0$

Fig. 2 Organic concentrations for the system $\text{SmCl}_3 - \text{NdCl}_3 - \text{CeCl}_3 - \text{HCl} - \text{H}_2\text{O} - 1 \text{ M D2EHPA} - \text{Amsco}$ at $\text{H}^+ = 0.5\text{M}$, $X_T \sim 0.64\text{M}$ and $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) \sim 0.5\text{M}$, $\circ$ [Molarity of Sm, $y_{\text{Sm}}]_0$, $\square$ [Molarity of Nd, $y_{\text{Nd}}]_0$, $\diamond$ [Molarity of Ce, $y_{\text{Ce}}]_0$, Δ [Total molarity, $Y_T = y_{\text{Sm}} + y_{\text{Nd}} + y_{\text{Ce}}]_0$, ---Ideal behavior, no interaction

Fig. 3 Comparison of organic molarities for the systems (SmCl_3 , NdCl_3 , CeCl_3 , $\text{SmCl}_3\text{-NdCl}_3$, $\text{SmCl}_3\text{-NdCl}_3 - \text{CeCl}_3$) - $\text{HCl} - \text{H}_2\text{O} - 1 \text{ M D2EHPA} - \text{Amsco}$ at $\text{H}^+ = 0.6\text{M}$; (a) $\circ$ Sm, Δ Nd, $\square$ Ce;
 (b) $\circ$ $Y_T(\text{Sm}, \text{Nd})$ At $X_T = 0.64\text{M}$, $\Delta Y_T(\text{Sm}, \text{Nd})$ At $X_T = 0.11\text{M}$;
 (c) $\circ$ $Y_T(\text{Sm}, \text{Nd}, \text{Ce})$ At $X_T = 0.64\text{M}$, Δ Predicted $Y_T(\text{Sm}, \text{Nd}, \text{Ce})$.
 At $X_T = 0.11\text{M}$

Fig. 1

Organic concentrations for the system $\text{Sm Cl}_3 - \text{Nd Cl}_3 - \text{Ce Cl}_3 - \text{HC}_1 - \text{H}_2\text{O}$ 1 M D2EHPA - Amsco at $\text{H}^+ = 0.5 \text{ M}$ and $x_{\text{T}} \sim 0.64 \text{ M}$

Fig. 2

Organic concentrations for the system $SmCl_3 - NdCl_3 - CeCl_3 - HC_1 - H_2O - 1\text{ M D2EHPA} - \text{Amsco}$ at $H^+ = 0.5\text{ M}$, $x_T \sim 0.64\text{ M}$ and $x_{Sm}/(x_{Sm} + x_{Nd}) \sim 0.5$

Fig. 3

Comparison of organic molarities for the systems ($SmCl_3$, $NdCl_3$, $CeCl_3$, $SmCl_3 - NdCl_3$, $SmCl_3 - NdCl_3 - CeCl_3$) - $HCl - H_2O - 1 M D2EHPA - Amsco$ at $H^+ = 0.6M$