Thermodynamic Studies on the Solvent Extraction of Europium Nitrate into Versatic Acid 911-Benzene Solution*

By Tatsuhiko Shigematsu**, Teruo Tanabe***, Sanji Nishimura**** and Yoshio Kondo***

The extraction equilibrium of Eu(NO₃)₃ from aqueous solution into Versatic acid 911-benzene solution was studied. The vapor pressure of benzene in this binary organic solution was measured by the transpiration method at 15, 25 and 35°C. And the activity coefficient of Versatic acid 911 in this solution was calculated by the Gibbs-Duhem equation.

On the other hand, the distribution equilibrium of Eu³⁺ ion between aqueous and organic solutions was measured at the above-mentioned temperatures by using a mixture of Eu¹⁵² and Eu¹⁵⁴ as the radioactive tracer. The composition of extracted species and the equilibrium constant of extraction were determined by taking the calculated values of activity of Versatic acid 911 into consideration. Furthermore, enthalpy and entropy changes of the extraction were calculated in the following way:

Extracted species: EuR₃⁺⁴RH

\[\Delta H^\circ = 15.4 \text{ (kcal/mol)} \quad \Delta S^\circ = 37.8 \text{ (e.u.)}\]

(Received May 1, 1973)

I. Introduction

Liquid-liquid solvent extraction technique has been extensively applied to the extraction of less common metals(1). Along with the recent technical development in petroleum industry, on the other hand, various kinds of extractants of lower prices are being explored, and this technique becomes widely employed also in the hydrometallurgy of common metals(2)(3).

It is of basic importance in the studies of solvent extraction to determine the composition of extracted species and the extraction equilibrium. This is indispensable not only for clarifying the extraction mechanism but also for designing the industrial processes. The systems of solvent extraction are usually complicated, and it is rather difficult to establish an exact thermodynamic description. For this reason, many attempts have been made to describe the equilibrium relationship of the extraction as precisely as possible(4)–(6).

The equilibrium of extraction of europium into carboxylic acid is studied in this work. From the experimental results of previous workers on the extraction chromatograph(7)(8) and on the solvent extraction(9)–(11) of rare earth elements, it was disclosed that there exists a certain regularity among the elements: this is expressed by the separation factor of adjacent rare earth elements in the solvent extraction. Provided that the compositions of extracted species of rare earth elements are the same, this separation factor represents the ratio of equilibrium constants of the extraction of both elements. And this regularity is dependent on the enthalpy and entropy changes in the extraction.

Long chain carboxylic acid is one of the attractive industrial extractants(12). In the previous paper by the present authors(13), the extraction of europium into the solution of Versatic acid 911 and benzene was studied. And the composition of extracted species and the apparent equilibrium constant of extraction were determined by the procedure proposed by Fletcher(14). It is assumed in this procedure that the activity coefficients of the species in both aqueous and organic phases are constant.

It is known(15), however, that monoacidic carboxylic acid is in the associated form in nonpolar organic diluent. And in the binary solution of Versatic acid 911 and benzene, the former component is presumed to be in the dimeric form. It can easily be shown that the

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* This paper was presented at the 1972 Autumn Meeting of the Japan Institute of Metals.

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(3) E. Wigstol and K. Froyland: ibid., p. 62.


(6) H. A. C. McKay: ibid., 48 (1952), 1103.


(8) I. Fidelis and S. Siekierski: ibid., 17 (1963), 542.


activities of both components in this binary solution exhibit a positive departure from Raoult’s law (16). Because of this departure, measuring the activity coefficient of Versatic acid 911 in the equilibrated organic solution becomes necessary. The mutual solubilities of Versatic acid 911 and water are negligible and it can be presumed that the activity coefficient of Versatic acid 911 does not significantly change when the organic solution contacts with the aqueous solution of sufficiently low Eu³⁺ ion concentration.

In order to establish the thermodynamic relationship in the solvent extraction in the present system, it is further necessary to determine the activity coefficients of Eu³⁺ ion in the equilibrated aqueous solution and of the extracted species in the organic solution. In order to cope with this problem, the experimental conditions were so chosen in this work as to maintain the activity coefficient of Eu³⁺ ion at a constant value in the aqueous solution. And the initial Eu³⁺ ion concentration was chosen to be extremely low.

II. Experimental Procedure

1. Materials

Versatic acid 911 used in this work was supplied from the Shell Chemical Company, and it was used without further purification. A prescribed amount of this acid was mixed with benzene and the organic binary solution was prepared. The mixture of Eu¹⁵² and Eu¹⁵⁴ nitrates was used as a radioactive tracer. The mixture of these radioactive chlorides was purchased from the Amersham Radiochemical Center in England and it was converted into the nitrate by repeating evaporation and dissolution in nitric acid three times in a quartz beaker. A prescribed amount of Eu₂O₃ of above 99.99% purity supplied by the Shin-Etsu Chemical Engineering Company was dissolved in nitric acid and the solution was evaporated to dryness in order to remove free nitric acid. Aqueous solution was obtained by mixing the prescribed amounts of these solutions and water. A small amount of sodium nitrate was further added as the buffer solution. The concentration of Eu³⁺ ion in the aqueous solution was maintained at 9.89 × 10⁻⁶ mol/L.

Sodium hydroxide, sodium nitrate and benzene used in this work were of analytical reagent grade. Deionized water was used throughout the work.

2. Measurement of vapor pressure

Many experimental methods were proposed for measuring the fugacity of components in binary solution (17)–(19) and the transpiration technique (19) was employed in this work. This was because of the large difference in the vapor pressure of Versatic acid 911 and benzene.

The experimental apparatus is illustrated in Fig. 1. The saturator of about 45 mL capacity is shown in Fig. 2. Helium gas was used as the carrier gas because of its lower boiling point than that of nitrogen. The measurement was conducted at 15, 25 and 35 ± 0.05°C, respectively.

The transpiration was conducted by passing helium gas through the saturator at a constant flow rate between 0.7 and 1.5 L/hr. Helium gas was dried by passing it through a series of driers of CaCl₂, silica gel, P₂O₅ and activated alumina. Two glass bulbs were installed in front of the saturator which served for heating the gas stream up to the measuring temperature before it entered into the saturator. The sample solution was stirred by a magnetic stirrer during the transpiration. Other glass bulbs installed at the rear of the saturator prevented the entrainment of mist into the gas stream. The condenser was immersed in liquid nitrogen. After the transpiration was finished, the condenser was evacuated down to about 30 mmHg by

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using an aspirator, and it was heated up to room temperature, dried and weighed. The refractive index of the remaining solution in the saturator was measured after transpiration in order to determine the concentration. Figure 3 illustrates the relationship between the refractive index and the concentration of Versatic acid 911 in the binary solution at 25 ± 0.5°C.

3. Measurement of density

By using a pycnometer of 3 mL capacity, the density of binary solution of Versatic acid 911 and benzene was measured at 15, 25 and 35 ± 0.05°C. It was assumed in this measurement that the inner volume of the pycnometer remains unvaried in this temperature range, and the volume measured at 25°C was taken as the standard.

4. Measurement of distribution equilibria

An amount of 10 mL of the aqueous solution and the same amount of organic solution, both mentioned in 2.1, were poured together into a glass bottle with a stopper. Furthermore, aqueous NaOH solution was added in order to adjust pH of the aqueous solution. The concentration of NaOH and NaNO₃ in the aqueous solution was so chosen that the ionic strength is maintained at about 5 × 10⁻⁴. The glass bottle was then installed on a shaking device. The shaking time was chosen at 30 minutes which was confirmed in the preliminary test to be sufficient for attaining the equilibrium. The temperature was maintained at 15, 25 and 35 ± 0.5°C during the equilibration.

Then the aqueous and organic phases were separated by centrifuging at 2500 rpm for 30 min. An amount of 3 mL of solution was gently pipetted out from each of the aqueous and organic solutions, and the gamma activities of both solutions were separately measured for 3 min with a well-type scintillation counter. The background gamma activity was counted for 15 min before and after the measurement, and it was subtracted from the gamma activity of the solution. The pH value of the equilibrated aqueous solution was also measured.

III. Experimental Results

1. Partial molar volume of benzene and Versatic acid 911

The molar volume of binary solution of Versatic acid 911 and benzene was calculated from the measured density. The molar volume was found to be proportional to the mole fraction of Versatic acid 911, indicating that the partial molar volume of both components was constant. They were calculated by the least squares method. The results of calculation are shown in Table 1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Benzene (cm³/mol)</th>
<th>Versatic acid 911 (cm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>88.5</td>
<td>189.3</td>
</tr>
<tr>
<td>25.0</td>
<td>89.5</td>
<td>190.0</td>
</tr>
<tr>
<td>35.0</td>
<td>90.7</td>
<td>191.3</td>
</tr>
</tbody>
</table>

2. Vapor pressure and the activity coefficient of benzene

The gas phase is regarded as being ideal when the pressure is below about 1 atm, and the transpiration was carried out under this condition. The vapor transpired from the saturator was found to be entirely composed of benzene because of the extremely lower vapor pressure of Versatic acid 911 which is shown in Table 2(20).

Presuming that the carrier gas of V litre is passed through the saturator and the amount of W g of benzene is condensed, the vapor pressure of benzene, \( P_1 \), is calculated by the following equation:

\[
P_1 = \frac{22.4 \times (W/M_1)}{V + 22.4 \times (W/M_1)} \times 760 \text{ (mmHg)}
\]

where \( M \) denotes the molecular weight. The subscripts 1 designates benzene. (In the following, benzene and Versatic acid 911 are denoted by the subscripts 1 and 2, respectively.)

The results are demonstrated in Fig. 4. In this measurement, the concentration of benzene in the sample solution is assumed to be unchanged during the transpiration and is equal to the average of concentrations from the gamma activity of the solution.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Vapor pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.02</td>
</tr>
<tr>
<td>100</td>
<td>3.0</td>
</tr>
</tbody>
</table>

centrations before and after the transpiration; the concentration change is very minor, which is, for example, only 1.5% when the solution of 40% benzene is used.

From the vapor pressure of benzene, $P_1^*$, the mole fraction of Versatic acid, $x_2$, and the vapor pressure of benzene in the binary solution, $P_1$, the activity coefficient of benzene in the solution is calculated by

$$\gamma_1 = \frac{P_1}{P_1^*(1-x_2)}. \quad (2)$$

And the plots of log $\gamma_1$ against $x_2$ are shown in Figs. 5 to 7.

3. Activity coefficient of Versatic acid 911

In case that the vapor pressure of one component in a binary solution is extremely low, the activity coefficient of this component cannot directly be measured. And the activity coefficient is calculated from the activity coefficient of another component of higher vapor pressure.

The following two assumptions were made.

(1) The stable and predominant forms of Versatic acid 911 in this binary solution are monomer and dimer. No other associated forms are presumed.

(2) These two associated forms are in equilibrium with each other in the solution.

Concerning this associated solution, the following two kinds of mole fractions are defined:

$$x_A = \frac{n_A}{n_A + n_{B_1} + n_{B_2}}, \quad x_{B_1} = \frac{n_{B_1}}{n_A + n_{B_1} + n_{B_2}}, \quad (3)$$

$$x_1 = \frac{n_A}{n_A + n_{B_1} + 2n_{B_2}}, \quad x_2 = \frac{n_{B_1} + 2n_{B_2}}{n_A + n_{B_1} + 2n_{B_2}}. \quad (4)$$

Here the subscripts $B_1$ and $B_2$ denote the monomeric and dimeric Versatic acid 911, respectively. The symbols $n$ and $x$ are the number of moles and the mole fraction, respectively.

The free energy of solution, $G$, is

$$G = n_A \mu_A + n_{B_1} \mu_{B_1} + n_{B_2} \mu_{B_2}. \quad (5)$$

Under the condition of constant temperature and pressure,

$$dG = \mu_A dn_A + \mu_{B_1} dn_{B_1} + \mu_{B_2} dn_{B_2} \quad (6)$$

where $\mu$ is the chemical potential of the components.

On the other hand, the differential form of eq. (5) is

$$dG = \mu_A dn_A + \mu_{B_1} dn_{B_1} + \mu_{B_2} dn_{B_2} + n_A d\mu_A + n_{B_1} d\mu_{B_1} + n_{B_2} d\mu_{B_2}. \quad (7)$$

By comparing eq. (7) with eq. (6), we obtain

$$n_A d\mu_A + n_{B_1} d\mu_{B_1} + n_{B_2} d\mu_{B_2} = 0. \quad (8)$$

From the above-mentioned assumption of the equilibrium between $B_1$ and $B_2$, we have
Substituting eq. (9) in eqs. (8) and (5),

\[ n_A d\mu_A + (n_{B_1} + 2n_{B_2}) d\mu_{B_2} = 0 \]  

and

\[ G = n_A\mu_A + (n_{B_1} + 2n_{B_2})\mu_{B_2} \]  

respectively.

The free energy of the solution can also be written as

\[ G = n_A\mu_A + (n_{B_1} + 2n_{B_2})\mu_{B_2} \]  

where \( \mu_A \) and \( \mu_{B_2} \) are

\[ \mu_A = \mu_A^* + RT \ln \gamma_A x_A \]  

and

\[ \mu_{B_2} = \mu_{B_2}^* + RT \ln \gamma_{B_2} x_{B_2} \]  

respectively. From eqs. (11) and (12), we obtain

\[ \mu_{B_1} = \mu_{B_1}^* \]  

On the other hand, the chemical potentials \( \mu_A \) and \( \mu_{B_1} \) in eq. (11) are defined by the following eqs. (16) and (17) in which the activity coefficients \( f_A \) and \( f_{B_1} \) are used. Both activity coefficients are based on the mole fraction unit of eq. (3)

\[ \mu_A = \mu_A^* + RT \ln f_A x_A \]  

and

\[ \mu_{B_1} = \mu_{B_1}^* + RT \ln f_{B_1} x_{B_1} \]  

From eqs. (13) to (17), we have

\[ \mu_A^* + RT \ln \gamma_A x_A = \mu_A^* + RT \ln f_A x_A \]  

and

\[ \mu_{B_1}^* + RT \ln \gamma_{B_1} x_{B_1} = \mu_{B_1}^* + RT \ln f_{B_1} x_{B_1} \]  

The asymmetric reference system is employed. Because Versatic acid 911 exists only in the form of monomer at infinite dilution, we have

\[ x_A = x_1, x_{B_1} = x_2 \]  

when \( x_2 \) approaches to 0. And the activity coefficients of both components converge into unity, and thus

\[ \gamma_1 \rightarrow 1, \gamma_2 \rightarrow 1 \]  

when \( x_2 \rightarrow 0 \)  

and

\[ f_A \rightarrow 1, f_{B_1} \rightarrow 1 \]  

when \( x_{B_1} \rightarrow 0 \).

From eqs. (18) to (22), we have

\[ \mu_A^* = \mu_A^* \]  

and

\[ \mu_{B_1}^* = \mu_{B_1}^* \]  

at infinite dilution.

Substitution of eqs. (23) and (24) in eqs. (18) and (19) yields

\[ \ln \gamma_1 x_1 = \ln f_A x_A \]  

and

\[ \ln \gamma_2 x_2 = \ln f_{B_1} x_{B_1} \]  

respectively.

From eqs. (25) and (26), it is seen that \( \gamma_1 x_1 \) and \( \gamma_2 x_2 \) are the activities of the component \( A \) and \( B_1 \), re-

spectively. It can also be said that the activity of Versatic acid 911 which is determined from the experiment is equal to the activity of the acid in monomeric form.

From eqs. (10), (16), (17), (25) and (26), we have

\[ x_1 \cdot d \ln \gamma_1 + x_2 \cdot d \ln \gamma_2 = 0 \]  

as the expression of Gibbs-Duhem equation in this binary solution.

Based on this eq. (27), the activity coefficient of Versatic acid 911 is calculated from the partial pressure of benzene obtained in 3.2.

Logarithmic activity coefficient of a component in binary solution can be approximated to a power series of the mole fraction(21). And the following power series was employed as an expression of the activity coefficient of benzene.

\[ \log \gamma_1 = a_1 x_1^2 + a_2 x_2^3 + a_3 x_3^4 \]  

Each coefficient, \( a_i \), in this equation was determined by using the least squares method. They are summarized in Table 3. Equation (28) is inserted into eq. (27) and the integration yields

\[ \log \gamma_2 = -2a_1 x_2 + (a_1 - \frac{3}{2}a_2) x_2^2 + (a_2 - \frac{3}{2}a_3) x_2^3 + a_3 x_2^4 \]  

The activity coefficient of Versatic acid 911 was calculated by this equation and it is summarized in Fig. 8.

In the studies of solvent extraction, the concentration of extractant is usually expressed in molarity unit (mol/L). The activity coefficient in the unit of mole fraction, \( \gamma_2 \), is transformed into the coefficient in molarity unit, \( \gamma_2 \), by the following equation(17):

\[ \gamma_2 = \left( \frac{\rho_1}{\rho_2} \right) \frac{1000 \gamma_2}{1000 + (\rho_1 - \rho_2) c_2} \]  

where \( \rho_1 \) is the molar volume of component 1, and

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>15</th>
<th>25</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1 )</td>
<td>3.10</td>
<td>2.88</td>
<td>3.66</td>
</tr>
<tr>
<td>( a_2 )</td>
<td>-12.19</td>
<td>-10.81</td>
<td>-14.82</td>
</tr>
<tr>
<td>( a_3 )</td>
<td>13.85</td>
<td>11.87</td>
<td>17.27</td>
</tr>
</tbody>
</table>

Table 3 Coefficients of eq. (28).

![Fig. 8 Activity coefficient of Versatic acid 911.](21) O. Redlich and A. T. Kister: Ind. Eng. Chem., 21 (1948), 345.
The partial molar volume of the components 1 and 2 in the binary solution, respectively. The symbol $c_2$ is the concentration of component 2 in molarity unit. And the activity coefficient of Versatic acid 911 in molarity unit was calculated and demonstrated in Fig. 9.

4. Extraction equilibrium of europium

The extraction of trivalent europium ion into Versatic acid 911 which is symbolized as RH is expressed as

$$
\text{Eu}^{3+} + m\text{RH}_{(org)} = \text{EuR}_3 \cdot (m-3)\text{RH}_{(org)} + 3\text{H}^+_{(aq)}, \tag{31}
$$

where the subscripts (org) and (aq) denote the organic and aqueous phases, respectively. It was assumed in this equation that Eu$^{3+}$ ion is stable in the aqueous solution and that only one extracted species is formed in the organic solution.

And the equilibrium constant is

$$
K = \frac{a_{\text{complex}} \cdot a_{\text{RH}}^{2\times}}{a_{\text{Eu}^{3+}} \cdot a_{\text{RH}}^{2\times}} \tag{32}
$$

where $a_{\text{complex}}$ denotes the activity of the extracted species, Eu$R_3 \cdot (m-3)$RH.

By using the distribution coefficient, $D$, defined as

$$
D = \frac{[\text{EuR}_3 \cdot (m-3)\text{RH}]_{(org)}}{[\text{Eu}^{3+}]_{(aq)}.} \tag{33}
$$

The equilibrium constant is rewritten as

$$
K = D \cdot \frac{a_{\text{complex}} \cdot a_{\text{RH}}^{2\times}}{a_{\text{Eu}^{3+}} \cdot a_{\text{RH}}^{2\times}} \tag{34}
$$

where $a_{\text{complex}}$ denotes the activity coefficient of the extracted species.

Because the initial concentration of Eu$^{3+}$ ion in the aqueous solution was chosen at about $1 \times 10^{-5}$ mol/L and the ionic strength of the aqueous solution was maintained at about $5 \times 10^{-4}$ in this work, the activity coefficient of Eu$^{3+}$ ion in equilibrated aqueous solution is calculated at 0.776, 0.786 and 0.796 at 15, 25 and 35°C, respectively, from the Debye-Hückel's limiting law^{(22)}. The activity coefficient of the extracted species in the organic solution, on the other hand, is regarded as unity^{(23)(24)}. And the logarithmic expression of eq. (34) is

$$
\log D - 3\; \log \text{pH} = m \log a_{\text{RH}} + \log K + \log \gamma_{\text{Eu}^{3+}}
$$

where $A$ is $-0.110$, $-0.104$ and $-0.099$ at 15, 25 and 35°C, respectively. It is obvious that the composition of extracted species and the equilibrium constant $K$ can be determined from the plot of ($\log D - 3\; \log \text{pH}$) against $\log a_{\text{RH}}$. The plot of ($\log D - 3\; \log \text{pH}$) against $\log a_{\text{RH}}$ is illustrated in Figs. 10 to 12. It is seen in these

Fig. 9 Activity coefficient of Versatic acid 911 in molarity units.

Fig. 10 Dependence of ($\log D - 3\; \log \text{pH}$) on activity of Versatic acid 911 at 15°C.

Fig. 11 Dependence of ($\log D - 3\; \log \text{pH}$) on activity of Versatic acid 911 at 25°C.

Fig. 12 Dependence of ($\log D - 3\; \log \text{pH}$) on activity of Versatic acid 911 at 35°C.

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References:


figures that there exists a linear relationship in the lower concentration region of Versatic acid 911 and that a steeper slope is observed in the higher concentration region. A curve break is observed at about 0.1 mole fraction of the acid, which may suggest some possible change in the composition of extracted species. And it is intended in this work to determine the extraction equilibrium in this lower concentration region.

It is presumed in this concentration region that the composition of extracted species remains unvaried at the temperatures of 15 to 35°C; by applying F-test on the regression coefficients, any significant difference was not found among the slopes at each experimental temperature. And the slope of these lines was calculated at 6.6 by the least squares methods. This m value in eq. (35) is very close to 7 which was already proposed in the previous paper. And the logarithmic equilibrium constant, \( \log K \), is estimated from the following equation:

\[
\log K = \frac{(\log D - 3 \; \text{pH}) - 7 \log a_{RH}}{A} \quad (36)
\]

where \( (\log D - 3 \; \text{pH}) \) and \( \log a_{RH} \) are the mean of \( (\log D - 3 \; \text{pH}) \) and \( \log a_{RH} \), respectively. The results are summarized in Table 4.

The following thermodynamic quantities of extraction were also calculated from the value of \( \log K \) by using the following eqs. (37), (38) and (39):

\[
\Delta G^\circ = -RT \ln K \quad (37)
\]

\[
\Delta H^\circ = \left[ \frac{\partial (\Delta G^\circ / T)}{\partial (1/T)} \right]_p \quad (38)
\]

\[
\Delta S^\circ = -\frac{\Delta G^\circ - \Delta H^\circ}{T} = -\left[ \frac{\partial \Delta G^\circ}{\partial T} \right]_p \quad (39)
\]

The values of \( \Delta G^\circ / T \) obtained from eq. (37) are plotted against \( 1/T \) in Fig. 13, and we obtain

\[\Delta H^\circ = 15.4 \text{ kcal/mol}\]

\[\Delta S^\circ = 37.8 \text{ e.u.}\]

### IV. Discussion

The vapor pressure of benzene measured in this work is in good accordance with the previous work. And the activity coefficients of benzene and of Versatic acid 911 in binary solution indicate positive departure from the Raoult's law.

In spite of this minor experimental error in the vapor pressure measurement, the plots in Figs. 10 to 12 are somewhat scattered. This is thought to be mainly caused by the error in the pH measurement. The amount of Eu\(^{3+}\) ion extracted into the organic solution was so small because of very low concentration of this ion in the initial aqueous solution, and accordingly, the change of pH value was rather slight.

Many works have been made on the solvent extraction of rare earth elements. Some of them suggested that rare earth elements are sexidentate, and Peppard et al. proposed that the extraction of a rare earth element into organo-phosphoric acid is expressed by the following eq. (42) which is very similar to the extraction with chelating reagents. According to them, this is caused by the dimeric form of this acid in organic solution.

\[
M^{3+} + 3(R_2H_3) = M(R_2H)_3 + 3H^+ \quad (42)
\]

In the solvent extraction with carboxylic acid, a presumption that the carboxylic acid of the dimeric form reacts with the rare earth element may lead to a similar mechanism of extraction, from which the coordination number, \( m \), in eq. (31) is to be an even number such as 6.

On the other hand, Tanaka et al. proposed that carboxylic acid is slightly dissolved in the aqueous solution and it forms a complex of the form of \( MR_3 \). This complex is distributed both in aqueous and organic phases and the molecules of carboxylic acid are further solvated in the organic phase to form a complex with hydrogen bonding. The higher pH values in the initial aqueous solution in this work may be favorable to the formation of this complex. And it is possible that other four molecules of carboxylic acid are coordinated in the organic phase.

The coordination of seven molecules of Versatic acid 911 to Eu\(^{3+}\) ion in the extracted species may also

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**Table 4 Extracted species and equilibrium constant.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \log K )</th>
<th>Extracted species</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>-3.44</td>
<td>EuR(_2)-4RH</td>
</tr>
<tr>
<td>25.0</td>
<td>-3.16</td>
<td></td>
</tr>
<tr>
<td>35.0</td>
<td>-2.68</td>
<td></td>
</tr>
</tbody>
</table>

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lead to a presumption that one water molecule is further coordinated, though the measurement of water content in the organic phase was not carried out in this work. And it may be presumed that the total coordination number is 8. Based on this \( m \) value, the thermodynamic quantities of extraction were calculated.

The activity coefficient of \( \text{Eu}^{3+} \) ion in the equilibrated aqueous solution was calculated in this work from the ionic strength of the solution by using the Debye-Hückel's limiting law. The concentrations of \( \text{NaNO}_3 \) and NaOH added to the aqueous solution were 1 to 3\( \times 10^{-4} \) and 2 to 9\( \times 10^{-4} \) mol/L, respectively. And the concentration of \( \text{Eu}^{3+} \) ion in the equilibrated aqueous solution was below 8\( \times 10^{-6} \) mol/L. Furthermore, the pH value was in the range of 4 to 5. From the concentration of ions present in the equilibrated aqueous solution, the ionic strength was calculated between 2.2 and 8.2\( \times 10^{-4} \). The above-mentioned activity coefficient of \( \text{Eu}^{3+} \) ion of 0.786 at 25°C was estimated from the ionic strength of 5.2\( \times 10^{-4} \). So that it is possible that \( \gamma_{\text{Eu}^{3+}} \) varies within the range of 0.74 to 0.86. However, this variation of \( \gamma_{\text{Eu}^{3+}} \) slightly affects the standard free energy, \( \Delta G^0 : \) its variation is only \( \pm 0.04 \) kcal/mol.

Among the values of enthalpy and entropy changes, the large positive value of entropy is similar to those in the extraction of rare earth element by the acidic solvents, such as 2-ethylhexyl phenyl phosphonic acid\(^{(33)}\), acetylacetone\(^{(33)}\), etc. This is, on the other hand, quite different from the extraction by organophosphorus solvents in which small negative entropy changes were reported\(^{(34)}\).

V. Summary

The equilibrium in the extraction of europium ion into a binary solution of Versatic acid 911 and benzene was studied. The vapor pressure of benzene was measured by the transpiration method at 15, 25 and 35°C. And the activity coefficients of benzene and of Versatic acid 911 were determined. The concentration of \( \text{Eu}^{3+} \) ion in the aqueous solution was maintained extremely low, and the composition of the extracted species and the enthalpy and entropy changes in the process of extraction were determined in the region below 0.1 mole fraction of Versatic acid 911. They are as follows:

- Extracted species: \( \text{EuR}_3 \cdot 4\text{RH} \)
  - \( \Delta H^0 = 15.4 \) (kcal/mol)
  - \( \Delta S^0 = 37.8 \) (e.u.).

Acknowledgments

The authors are very grateful to Dr. Z. Asaki for his kind help in the preparation of computing programs used in this work. The calculations were carried out by using the digital computer KDC-II at Kyoto University.

The authors are also very thankful to the Shell Chemical Company and the Shin-Etsu Chemical Engineering Company for their kindness in offering the reagents.

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