Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Pruett, D. J. and McTaggart, D. R.(1982) 'The Solvent Extraction Behavior of Rhenium. Part II. The Hydrochloric Acid-Tributyl Phosphate System', Separation Science and Technology, 17: 8, 1091 — 1100

To link to this Article: DOI: 10.1080/01496398208060273

URL: http://dx.doi.org/10.1080/01496398208060273

SEPARATION SCIENCE AND TECHNOLOGY, 17(8), pp. 1091–1100, 1982

The Solvent Extraction Behavior of Rhenium. Part II. The Hydrochloric Acid–Tributyl Phosphate System

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Abstract

The solvent extraction of heptavalent rhenium from aqueous hydrochloric acid by tributyl phosphate (TBP) in *n*-dodecane (NDD) has been studied over a wide range of TBP and HCl concentrations at 25, 40, and 60°C. The extraction was found to proceed according to the reaction $3TBP + H^+ + ReO_4^- \rightleftharpoons [HReO_4 \cdot 3TBP]$. A discussion of the possible nature of the organic phase complex is presented, along with values of ΔG, ΔH, ΔS, and the equilibrium constant for the extraction reaction. The behavior of the $KReO_4$–H_2O–HCl–TBP system is compared and contrasted with that of the $KReO_4$–H_2O–HNO_3–TBP system and with the analogous $KTcO_4$ systems.

INTRODUCTION

The first paper in this series (*1*) analyzed the behavior of perrhenate in HNO_3–TBP solvent extraction systems. It was found that rhenium can be used as an excellent nonradioactive model compound for technetium, a troublesome fission product in the nuclear fuel cycle. However, in HNO_3–TBP solvent extraction systems, nitric acid itself competes very strongly for the extractant molecules, reducing the distribution of the metal anions into the organic phase and complicating the interpretation of the distribution curves. In order to avoid these complications and to obtain higher distribution coefficients for potential analytical applications, a study of HCl–TBP solvent extraction systems were undertaken.

EXPERIMENTAL

Rhenium and tributyl phosphate stock solutions were prepared as described previously (*1, 2*). Note that all tributyl phosphate-*n*-dodecane

(TBP–NDD) solutions were saturated with water when they were prepared and analyzed. Analyses were carried out as described in Part I.

RESULTS AND DISCUSSIONS

Dependence of the Distribution Coefficient on Acidity and TBP Concentration

Figures 1–3 summarize the solvent extraction behavior of $KReO_4$ in HCl–TBP systems as log-log plots of D_{Re} ($D_{Re} = [Re]_{organic}/[Re]_{aqueous}$) versus HCl

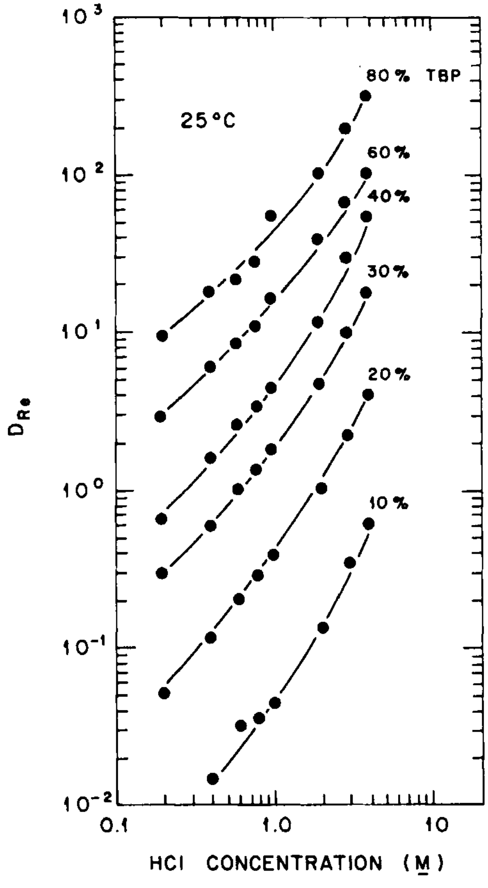

FIG. 1. D_{Re} as a function of HCl concentration at 25°C.

concentration at 25, 40, and 60°C. Since the perrhenate species are not competing with the mineral acid for extractant molecules, the distribution coefficient rises smoothly with increasing acid concentration. [In the HNO_3–TBP system, D_{Re} passes through a maximum near 0.8 *M* HNO_3 and decreases rapidly at higher acid concentrations (*1*).] Introducing KCl (up to 3 *M*) into these solutions demonstrated that the increase in D_{Re} was due to increasing hydrogen ion activity and not to changes in the ionic strength or chloride ion concentration. Addition of the neutral salt had essentially no effect on D_{Re}.

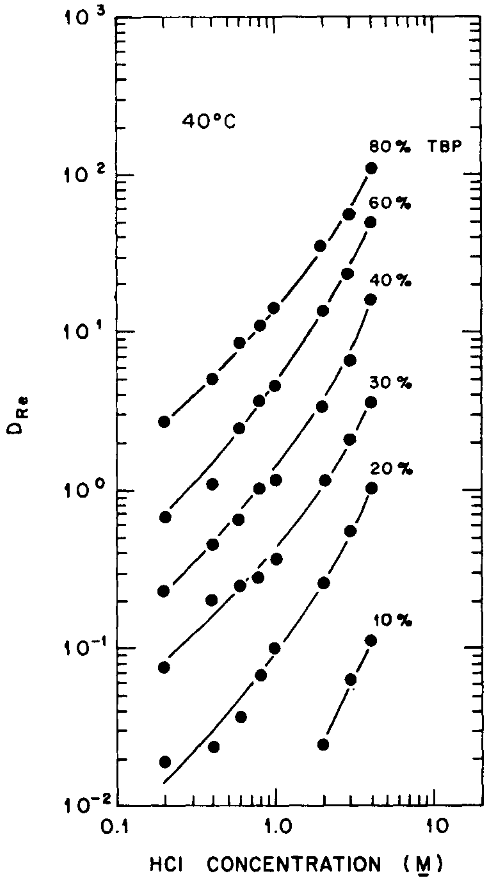

FIG. 2. D_{Re} as a function of HCl concentration at 40°C.

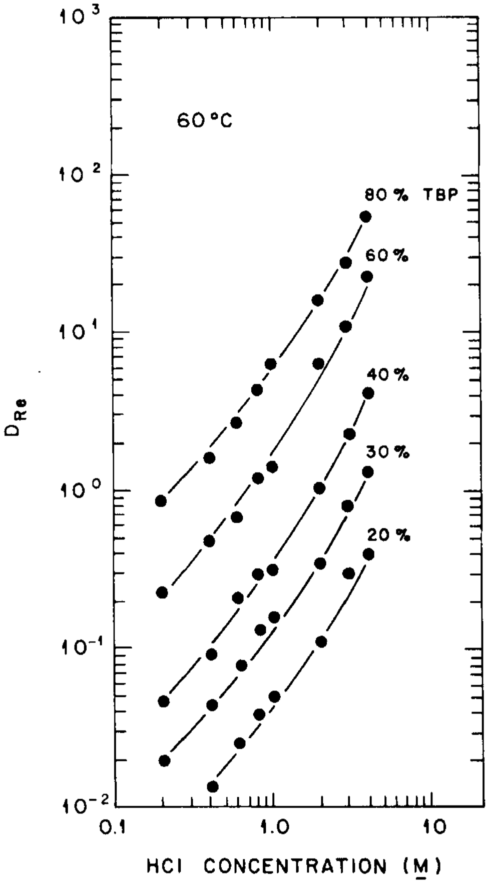

FIG. 3. D_{Re} as a function of HCl concentration at 60°C.

When log D_{Re} is plotted as a function of the logarithm of the mean molar activity of HCl, the data shown in Figs. 1–3 are linear over the entire range studied as shown in Fig. 4. Furthermore, the slopes of the lines obtained are all very close to 1.0, indicating that one proton is involved in the extraction reaction. This is in agreement with previous results for the extraction of perrhenate and pertechnetate (*1*, *3*–*5*). While the validity of this method has been subject to some debate (*6*, *7*), the slopes of such plots are often used to obtain the stoichiometry of extraction reactions (e.g., Refs. *3* and *4*). The constancy of the results obtained over the extended range of conditions used

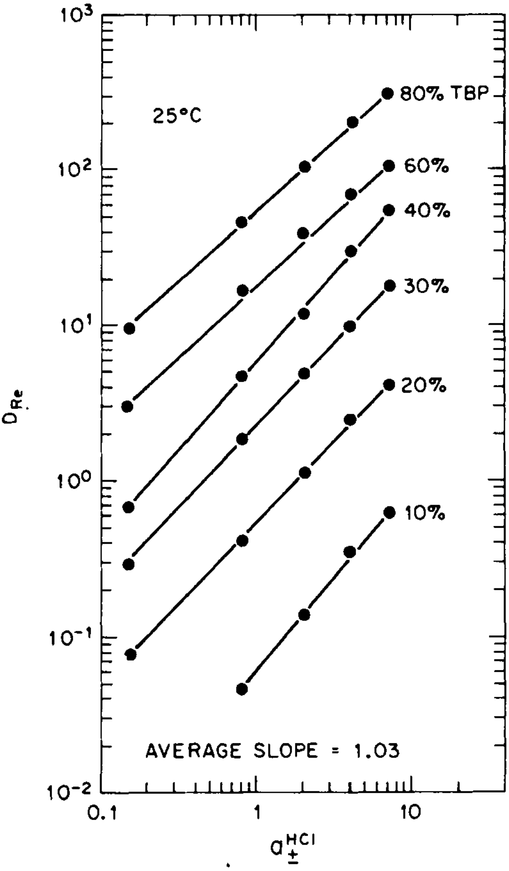

FIG. 4. D_{Re} as a function of mean molar HCl activity at 25°C.

in these experiments lends credence to the conclusions drawn for this system.

Log-log plots of D_{Re} as a function of TBP concentration (Fig. 5) are also linear and have slopes of 3.2 ± 0.1 at all three temperatures. In HNO_3–TBP systems, the slopes of these curves increase with temperature and with TBP concentrations, suggesting the formation of a tetrasolvated perrhenate species in the organic phase (*1*). No systematic trends were observed in the HCl–TBP systems, although in some cases the slopes were slightly greater than 3.

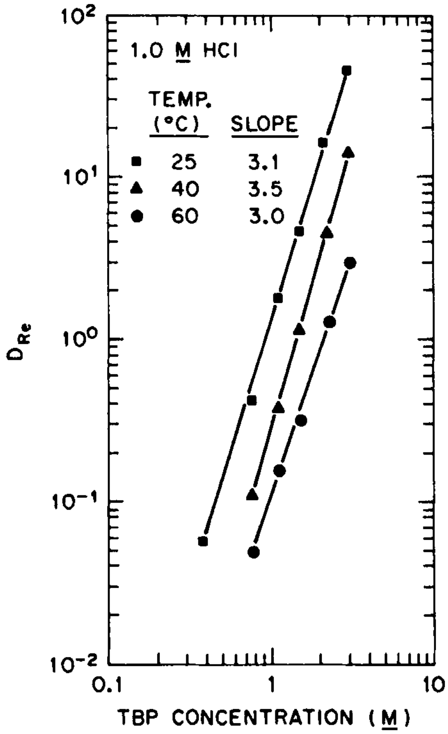

FIG. 5. D_{Re} as a function of TBP concentration.

Reaction Stoichiometry

The dominant equilibrium reaction for the extraction of both perrhenate and pertechnetate from acid solution from TBP may be written

$$H^+ + MO_4^- + 3TBP \rightleftharpoons [HMO_4 \cdot 3TBP]_{\text{organic}} \qquad (1)$$

While perhaps some evidence for higher and lower solvates exists, the trisolvate is most strongly indicated over a very wide range of conditions. Further, the large, negative entropy for this reaction indicates that several water molecules may be involved in the organic phase complex (*8*). These water molecules may be introduced by the participation of the TBP monohydrate complex in the extraction reaction (*5*, *8*).

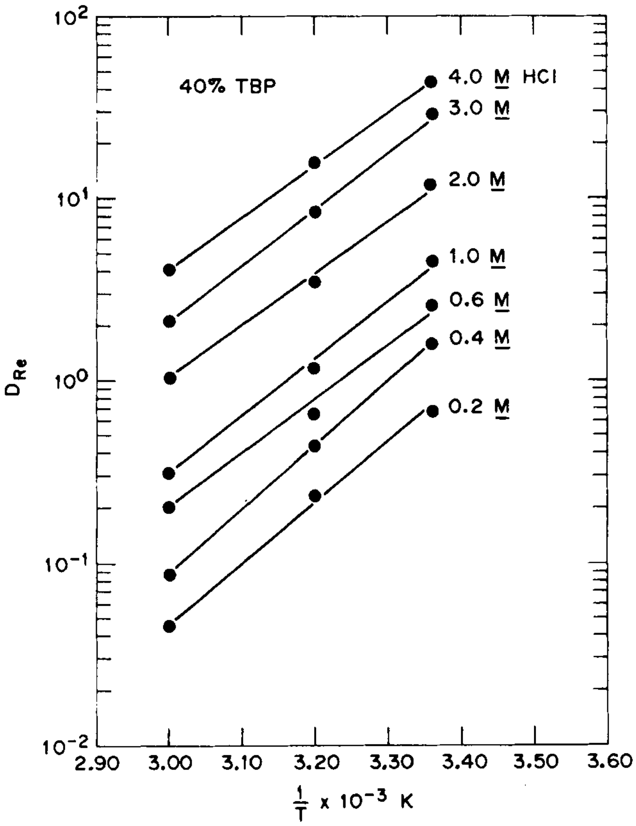

FIG. 6. D_{Re} as a function of inverse absolute temperature.

Thermodynamic Constants

Despite a lack of the appropriate activity coefficients, studies of the temperature dependence of the distribution coefficient allow calculation of the enthalpy and entropy changes associated with the extraction reaction that are generally in good agreement with values obtained by calorimetric methods when a wide enough temperature range is examined (*8*). Plots of ln D_{Re} versus the reciprocal of the absolute temperature are expected to be linear with slopes of $-\Delta H/R$, as shown previously (*1*). When the data in Figs. 1–3 are analyzed in this way (Fig. 6), a value of −59 ± 5 kJ/mol is obtained for ΔH. This may be compared with a value of −71 ± 1 kJ/mol obtained for the HNO_3–TBP–ReO_4^- system, and a value of −62 ± 4 kJ/mol obtained for the HCl–TBP–TcO_4^- system.

A concentration equilibrium constant expression for Eq. (1) may be written

$$K_c = \frac{[HReO_4 \cdot 3TBP]}{[ReO_4^-][TBP]^3[H^+]} \tag{2}$$

It was found empirically that using the mean molar activity of the HCl ($a_{\pm} = \gamma_{\pm} M_{\pm}$) in place of the $[H^+]$ and using stoichiometric (molar) concentrations for each of the other terms gave the most consistent values for K_c at each temperature. These values were 1.65 ± 0.32, 0.48 ± 0.13, and 0.14 ± 0.03 at 25, 40, and 60°C, respectively.

Using these values for K_c to calculate values for ΔG at each temperature, a value of −200 J/mol K is obtained for ΔS from the slope of a plot of ΔG versus temperature. This value is essentially the same as that obtained in the HNO_3–TBP system. This large negative value for ΔS reflects the ordering that occurs as the five molecules and ions on the left side of Eq. (*1*) condense into a single complex; the reordering of the aqueous phase that occurs when the large, structure-breaking perrhenate ions are removed (*9*); and indicates that several water molecules may be involved in the organic phase complex (*8*).

An equation to correlate all of these data may be readily derived. Substituting D_{Re} for $[HReO_4 \cdot 3TBP]/[ReO_4^-]$ in Eq. (2) and taking logarithms, it is easily shown that

$$\ln D_{Re} = \ln K_c + \ln [H^+] + 3 \ln [TBP] \tag{3}$$

But since $\Delta G = -RT \ln K = \Delta H - T\Delta S$, then $\ln K = (\Delta S/R) - (\Delta H/RT)$ and, substituting the calculated values of ΔS and ΔG,

$$\ln D_{Re} = -24.8 + 7460/T + \ln [H^+] + 3 \ln [TBP] \tag{4}$$

As in Eq. (2), the mean molar activity of the HCl, rather than the stoichiometric concentration, yields calculated values of D_{Re} that are in better agreement with the experimental results. Nonetheless, values for D_{Re} calculated using Eq. (4) are, on the average, only 21% lower than the experimental values shown in Figs. 1–3.

An improved correlation was obtained by assuming the functional form of Eq. (4) and using the Multiple Linear Regression Program on the Regression Analysis Application Pac of an HP-85 desk-top computer to determine the values of the constants that best fit the experimental data. Some typical values of D_{Re} calculated from the resulting Eq. (5) are compared with the experimental values in Fig. 7:

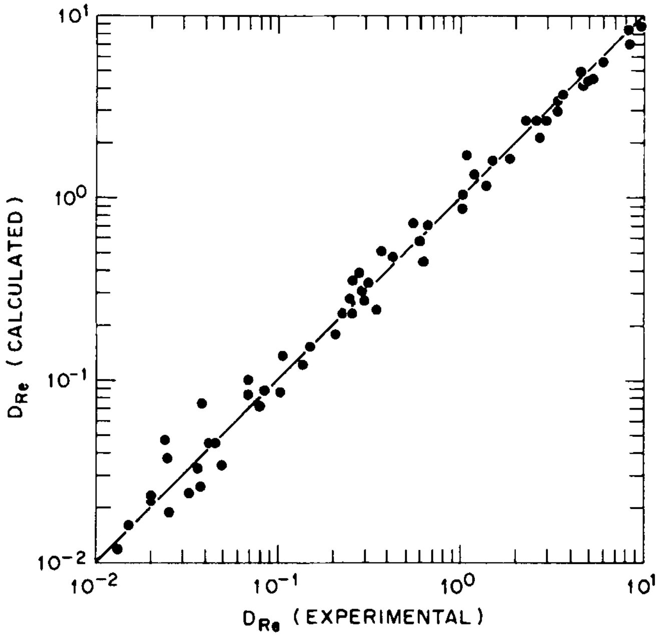

FIG. 7. Comparison of calculated and experimental values of D_{Re}.

$$\ln D_{Re} = -22.1 + 6684/T + 1.04 \ln a_{\pm}^{HCl} + 3.28 \ln [TBP] \quad (5)$$

The need for correlative models of solvent extraction data has been well documented in the literature (*10*).

Acknowledgments

Analyses were carried out by the Analytical Chemistry Division, Oak Ridge National Laboratory. Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corp.

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Received by editor October 12, 1981