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ENTHALPY DETERMINATION FOR AN EXTRACTION REACTION BY DIRECT STATIC MEASUREMENT WITH A CALVENT CALORIMETER *

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ABSTRACT

The enthalpy determination of an extraction reaction by a direct static measurement with a Calvent calorimeter is developed. The $-\Delta H^\circ$ value measured in this work is larger than that obtained using the temperature coefficient measurement.

INTRODUCTION

Two ways of obtaining the enthalpy of an extraction reaction are reported in the literature: temperature coefficient measurement [1] and calorimetric titration [2,3]. In this work, the enthalpy determination of an extraction reaction by a direct static measurement with a Calvent calorimeter is developed. It is found that the extraction reaction is completed via diffusion between the two phases, and the thermochemical parameters of this process are recorded using a Calvent calorimeter [4].

EXPERIMENTAL

Preparation of the stock solutions

The stock solutions for the aqueous phase contained 0.03 M $Nd(NO_3)_3$ or $Nd(ClO_4)_3$ and 6 M $NaNO_3$, $NaClO_4$ or NaNCS, respectively. The stock solution for the organic phase contained 0.6 M methyl phosphine acid di(methylheptyl)ester (abbreviated as P350) in hexane as diluent. The concentrations were the same as for the reference cell, except in the case of the neodymium salts.

Calorimetric measurement

2.000 ± 0.005 ml of the aqueous phase was pipetted into a tiny glass tube set in the reaction cell, and an equal volume of the organic phase was

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TABLE 1

Enthalpy values for extraction reactions of three P350–neodymium salt systems at 25 °C

System	Nd concentration in the aqueous phase		Heat of reaction (J)	$-\Delta H°$ (kJ mol^{-1})
	Initial	Final		
P350–$Nd(NO_3)_3$	0.0302	0.0023	1.26	22.5
	0.0302	0.0023	1.27	22.7
P350–$Nd(NCS)_3$	0.0306	0.0000	1.84	30.1
	0.0306	0.0000	1.81	29.6
P350–$Nd(ClO_4)_3$	0.0308	0.0042	1.98	74.5
	0.0308	0.0042	1.97	74.5

pipetted into the reaction cell outside the glass tube. The reference cell was set up in the same manner as the reaction cell. Both cells were placed in the body of the calorimeter. After thermal equilibrium of the system had been established, the two phases were caused to come into contact with each other by turning the body of the calorimeter through 90°. The extraction reaction went to completion within 24 h. The thermochemical effects were recorded using an integrator and a typewriter.

RESULTS

On comparing the values of $-\Delta H°$ available, namely 22.6 kJ mol^{-1} for the P350–$Nd(NO_3)_3$ system and those of 21.63, 14.34 and 7.07 kJ mol^{-1} for the systems P350–$La(NO_3)_3$, P350–$Tb(NO_3)_3$ and P350–$Yb(NO_3)_3$, respectively [5], we find that the $-\Delta H°$ value measured in this work is larger than that obtained using the temperature coefficient measurement.

This conclusion was checked further by the following experiment. The experimental conditions were taken from the literature [1]. In this case, 2.0 M TBP was used as the organic phase (with *n*-dodecane as diluent) to extract 0.5 M $Pr(NO_3)_3$ from a 1 M HNO_3 medium. Comparing the $-\Delta H°$ value of 27.26 kJ mol^{-1} measured in this work with that of 20.60 kJ mol^{-1} from the temperature coefficient measurement reported in ref. 1, it can be seen that the former is greater than the latter by about 30%.

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