Thermodynamics of Liquid—Liquid Extraction of Metal β-Diketonates. II. Comparison of Enthalpies of Distribution from Calorimetric and Equilibrium Measurements on Beryllium Acetylacetonate

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The enthalpy of distribution of beryllium acetyl-acetonate between 0.1 M aqueous $NaClO_4$-solution and heptane has been determined from calorimetric measurements and from the temperature dependence of the distribution constant giving 26.0 ± 1.0 kJ/mol and 25.6 ± 0.1 kJ/mol, respectively, at 25 °C. Contributions from partial processes to the overall process are discussed.

Enthalpies of reaction can be determined directly by calorimetry or indirectly from measurements of the temperature dependence of the equilibrium constant, using the van't Hoff equation. However, there are many examples when data obtained from the temperature dependence method do not agree with calorimetric data.[1] This can be attributed to difficulties in identifying what reactions are actually occurring, *i.e.* what partial processes of the overall reaction contribute to the measured enthalpy value. In this investigation the enthalpy of distribution of beryllium acetylacetonate between 0.1 M aqueous $NaClO_4$-solution and heptane has been determined, both from enthalpies of solution of the solid compound in each of the two solvents and from the temperature dependence of the distribution constant. Such a comparison is of interest since for many metal extraction systems direct measurements by calorimetry cannot be made, due to low solubility of the extracted species, especially in the aqueous phase. Slow kinetics and increased contributions from hydrolysis and other side reactions may also complicate the measurements, if the metal concentration is too high.

EXPERIMENTAL

Chemicals. Acetylacetone (HA) was purified and 0.1 M $NaClO_4$ solution prepared as previously described.[2] Heptane (*p.a.* Merck, Darmstadt) was used without further purification. Beryllium acetylacetonate (BeA_2) was prepared by standard methods[3] and recrystallized from hexane.

Calorimetric measurements. The calorimetric measurements were performed with an LKB 8721-1 Reaction-Solution Calorimeter.[4] The measurements were made at 25.0 °C using a 25 ml glass reaction vessel.

A mutually saturated two-phase system (I) was first prepared by mixing heptane with an initial HA-concentration of 0.1 M with a 0.1 M aqueous $NaClO_4$-solution of equal volume. The pH of the aqueous phase was adjusted to 6.5—7.0. Another mutually saturated two-phase system (II) was obtained by dissolving BeA_2 in some organic phase of (I) to a concentration of 0.04—0.05 M (the maximum solubility of BeA_2 was determined to be 0.0590 M in heptane at 25 °C), and then mixing this solution with an equal volume of aqueous phase of (I). Under these conditions the dominating Be-species is the non-charged BeA_2. Less than 0.1 percent of the total Be-concentration would be hydrolyzed species such as $BeAOH$, $Be(OH)_2$, *etc.*, as calculated from complex formation and hydrolysis constants.[5]

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Table 1. Enthalpies of solution for BeA_2.

Heptane Dissolved BeA_2 g	$(\Delta H^\circ_{sol})_{org}$ kJ/mol	0.1 M $NaClO_4$ Dissolved BeA_2 g	$(\Delta H^\circ_{sol})_w$ kJ/mol
0.02305	26.4	0.01044	−0.8
0.02379	25.7	0.01559	−0.4
0.01860	25.1		
0.04103	24.4		
Mean	25.4 ± 0.4		−0.6 ± 0.4

For the determination of enthalpies of solution of BeA_2, a sample of 25 ml of one of the liquid phases of (I) was placed in the calorimetric vessel and an ampoule containing solid crystalline BeA_2 (10−40 mg) was broken in it. Enthalpy effects from ampoule breaking and evaporation of the solvents were determined from separate experiments.

Experiments on mixing the aqueous and heptane phases with simultaneous transfer of BeA_2 did not give satisfactory results due to difficulties in obtaining adequate mixing of the two phases in the calorimeter vessel.

Distribution measurements. The distribution experiments were carried out using the AKUFVE-technique [6,7] and with [7]Be as a radiotracer. The initial concentration of HA in the organic phase was 0.1 M, just as in the calorimetric experiments. The total metal concentration was between 10^{-4} and 10^{-5} M, which was obtained by adding BeA_2 to the organic phase. The pH of the aqueous phase was adjusted to 6.5−7.0, where the dominating Be-species is the non-charged BeA_2. The distribution of BeA_2 between the two phases was determined at 19 temperatures between 8 and 43 °C.

RESULTS AND DISCUSSION

Calorimetric measurements. The heats of ampoule breaking and vaporization of the solvent were 0.10 ± 0.01 J for heptane and 0.05 ± 0.01 J for 0.1 M $NaClO_4$-solution. The enthalpies of solution, ΔH°_{sol} for BeA_2 corresponding to the reaction

$$BeA_2(s) \rightarrow BeA_2(sol) \qquad (1)$$

are given in Table 1.

The uncertainties, expressed as standard deviations of the mean are as expected. They correspond to an uncertainty of about ±0.05 J in the experiments in heptane and *ca.* ±0.02 J in water.[4] The

larger uncertainty in heptane is caused by the higher volatility of this solvent.

Distribution measurements. The two-phase distribution of Be in the pH-range 6.5−7.0 can be described by the reaction

$$BeA_2(w) \rightarrow BeA_2(org) \qquad (2)$$

where (org) denotes the organic phase and (w) the aqueous phase. The temperature dependence of the distribution constant of BeA_2, K_D according to eqn. 2, is shown in Fig. 1. The points in the figure represent experimental points from two independent runs.

The best least squares fit of the experimental data to a polynomial log $K_D = A + B/T + C/T^2$ gives the parameters A, B and C and their standard errors.[8] The enthalpy and entropy of distribution were calculated according to
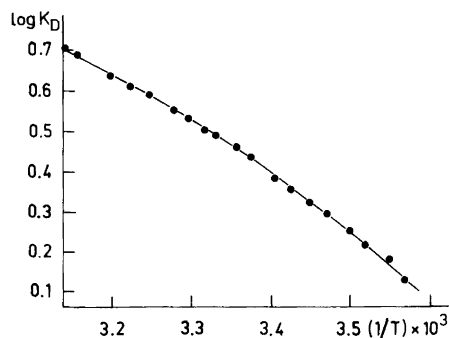

Fig. 1. The temperature dependence of the distribution constant for BeA_2 (*T* in K). Experimental points and calculated curve.

$$\Delta G_D^\circ = -RT \ln K_D \qquad (3)$$

$$\Delta H_D^\circ = -R \, \partial(\ln K_D)/\partial(1/T) \qquad (4)$$

$$\Delta S_D^\circ = (\Delta H_D^\circ - \Delta G_D^\circ)/T \qquad (5)$$

The error limits for the estimated ΔH° and $T\Delta S^\circ$ were calculated from the error square sum and the inverse matrix element obtained in the least squares fit. The equilibrium temperatures are assumed to be error-free and the log K_D-values have equal unit weight. The low σ-value for the enthalpy value obtained from the temperature measurements illustrates the good precision obtainable with the AKUFVE. The accuracy, however, depends on several factors such as errors in the determination of the ratio between the counting efficiencies *etc.*[7] and the variation in the composition of the organic and aqueous phase with temperature caused by, for this system, minor changes in the distribution of acetylacetone ($\sim 0.0 > \log K_{D_{HA}} > \sim -0.1$) and mutual miscibility of the phases.

Since K_D is determined in molar concentrations, corrections including the coefficient of thermal expansion α of the solvents have to be made.[9] These corrections are $RT^2(\alpha_{org} - \alpha_w) = 0.7$ kJ/mol for ΔH_D° and $RT^2(\alpha_{org} - \alpha_w) + RT\ln(v_{org}/v_{ag}) = 5.9$ kJ/mol for $T\Delta S_D^\circ$, where v is the molar volume. At 25 °C the values $\Delta H_D^\circ = 25.6 \pm 0.1$ kJ/mol and $T\Delta S_D^\circ = 33.5 \pm 0.1$ kJ/mol were obtained (mol fraction scale).

Thermochemical cycle. The dissolution and distribution of the uncharged BeA$_2$-complex can be represented by a thermochemical diagram according to Fig. 2. The enthalpy of distribution for BeA$_2$ according to (2) can be obtained from the enthalpies of dissolution according to eqn. (6).

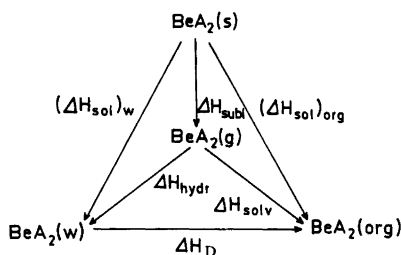$$\Delta H_D^\circ = (\Delta H_{sol}^\circ)_{org} - (\Delta H_{sol}^\circ)_w \qquad (6)$$

*Fig. 2.* Thermochemical diagram of the dissolution/-distribution of BeA$_2$ in a two-phase system.

From the calorimetric measurements ΔH_D° is calculated to 26.0 ± 1.0 kJ/mol, which is in good agreement with the value of 25.6 ± 0.1 kJ/mol obtained from the temperature dependency of the distribution constant.

The main reactions of Fig. 2 can be divided into partial processes:

(1) Lattice destruction, ΔH_{subl} $\qquad (7)$

$$BeA_2(s) \rightarrow BeA_2(g)$$
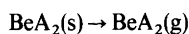
(2) Solvation of the gaseous species in the organic phase, ΔH_{solv}

$$BeA_2(g) \xrightarrow{\text{org}} BeA_2(org)$$
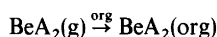
(3) Hydration of the gaseous species in the aqueous phase, ΔH_{hydr}

$$BeA_2(g) \xrightarrow{w} BeA_2(w) \qquad (9)$$

The dissolution processes will correspond to[10] $\Delta H_{subl} + \Delta H_{solv} = 25.4 \pm 0.4$ kJ/mol and $\Delta H_{subl} + \Delta H_{hydr} = -0.6 \pm 0.4$ kJ/mol for the organic and aqueous phases, respectively.

The enthalpy of sublimation for BeA$_2$ at a mean temperature of 180 °C is 90 kJ/mol as obtained from vapour pressure measurements and estimated values for enthalpy of fusion.[11,12] The heat of vaporization for BeA$_2$ was recalculated from the experimental data in Ref. 11, since the values for ΔH_{subl} stated in that paper disagree with the experimental values given. Using the estimated value of 40 J/mol K for the difference in heat capacity between gaseous and solid forms of metal chelates, ΔH_{subl} at 25 °C will be about 84 kJ/mol for BeA$_2$. Thus, the estimated enthalpy values according to Fig. 2 are $\Delta H_{solv} = -59$ kJ/mol and $\Delta H_{hydr} = -85$ kJ/mol.

Formally, ΔH_{solv} and ΔH_{hydr} can be divided into $\Delta H_{hole} + \Delta H_{int}$, corresponding to hole formation and to solute-solvent interactions. This approach was used by Uhlig, Eley and Pierotti[13-15] in their theories for the solubility of gases in liquids. Application of their different methods to calculate ΔH_{hole} on our system results in different values for ΔH_{hole} and consequently for ΔH_{int}. The results obtained using the theory of Uhlig, which includes the macroscopic surface tension of the solvents, indicate a stronger exothermic interaction in the aqueous phase than in the organic phase. The

theories of Eley and Pierotti give different values of ΔH_{int}, but the solute-solvent interactions in aqueous and organic media, respectively, would be of the same order of magnitude. Thus independent calculations of ΔH_{int} are needed before one can say if any of the ΔH_{hole} values are plausible. Theoretically, this is possible by the theory of scaled particle used by Pierotti; however, all parameters needed are not yet known for BeA_2.

However, an indication that there is no tendency for hydrogen bonding with BeA_2 was given by Davies and Fackler.[16] They made an infrared spectral examination of hydrogen bonding to various neutral bis-, tris- and tetrakis β-diketonates. Their data indicate weak or no hydrogen bonding with tetrahedral bis complexes such as BeA_2, whereas for the tris and for tetrakis complexes a pronounceed interaction with the solvents was shown.

According to the models of Frank and Evans[17] and of Neméthy and Scheraga,[18] the introduction of a non-polar solute into aqueous media would result in an increased degree of hydrogen bonding in the solvation layer around the solute. To meet with the theory of Pierotti,[15] the degree of hydrogen bonding outside the solvation layer must be decreased, since the difference in ΔH_{int} between aqueous and organic media is to small to account for any significant change in the total extent of hydrogen bonding in water. The large positive entropy value of distribution ($T\Delta S° = 33.5$ kJ/mol at 25 °C), would then reflect the destruction of the ordered water layer around the ligand, which would largely be an entropic effect.

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