

## Thermodynamic Properties of Rare Earth Complexes

### V. Free Energy, Enthalpy, and Entropy Changes for the Formation of Rare Earth Acetate Complexes in 5 volume per cent Water/Methanol

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The changes in free energy, enthalpy, and entropy for the formation of La, Pr, Nd, Sm, Gd, Dy, Er, and Yb (3+) acetate complexes have been determined in a 5 volume per cent water/methanol solvent. All data refer to a 0.500 M Na<sup>+</sup>(ClO<sub>4</sub><sup>-</sup>) medium and a temperature of 25.00°C. The stability constants, and thus the free energy changes, were measured potentiometrically and the enthalpy changes were measured with a calorimeter. The entropy changes were calculated from the relationship:

$$\Delta G_n^\circ = \Delta H_n^\circ - T\Delta S_n^\circ$$

The general patterns in the variations of the changes in free energy, enthalpy, and entropy for complex formation reactions throughout the lanthanoid series were similar to those found previously in water.

It was suggested<sup>1</sup> that the experimentally observed variations of the free energy, enthalpy, and entropy changes upon forming complexes of the trivalent lanthanoides may be caused by differences in the hydrations of the central metal ions. To elucidate this point further, we decided to study the formation of acetate complexes of these ions in a mixed solvent. To ensure the solubility of the participants, we used a "waterlike" solvent, *S*, containing 5 volume per cent water/methanol. In a previous investigation<sup>2</sup> we studied the complex formation between the acetate ion and the proton in *S* at 25.00°C in a 0.500 M Na<sup>+</sup>(ClO<sub>4</sub><sup>-</sup>) medium. The stability constants of these complexes were determined by a potentiometric technique, *viz.* the determination of hydrogen ion concentrations by means of a glass electrode. In this investigation, the same method was employed to measure the stability constants of the acetate complexes of eight different lanthanoides in the solvent *S* at 25.00°C.

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The free energy changes of formation of the rare earth acetate complexes were thus found and were then combined with the corresponding enthalpy changes to yield the changes in entropy pertinent to each step of the complex formation. The enthalpy values were measured by a calorimetric titration procedure.<sup>3</sup> The modifications necessary for using  $S$  are described under experimental.

#### CALCULATION OF STABILITY CONSTANTS FROM POTENTIOMETRIC DATA

Using the stability constants of the proton-acetate complexes, the relationship:

$$C_H = C_{HA} + C_{HClO_4} = [H^+] + [HA] + [HA_2^-] + 2[H_2A_2]$$

is expressed in terms of  $\beta_{ij}$ ,  $[H^+]$ , and  $[A^-]$  to give:

$$C_H = [H^+] \{1 + [A^-] [\beta_{11} + [A^-]\beta_{12} + 2[H^+][A^-]\beta_{22}]\} \quad (1)$$

$[H^+]$  is calculated from the measured  $E_0$  and  $E$  values:

$$-\log[H^+] = (E_0 - E)/59.16 \quad (2)$$

and eqn. (1) is solved for  $[A^-]$  by a computer. The average number of acetate ions per central metal ion,  $\bar{n}$ , is computed from

$$\bar{n} = \frac{C_A - [H^+][A^-][\beta_{11} + 2[A^-]\beta_{12} + 2[H^+][A^-]\beta_{22}]}{C_M} \quad (3)$$

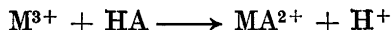
using the  $[A^-]$  and  $[H^+]$  values from eqns. (1) and (2).

The stability constants for the various complexes are then calculated from the  $\bar{n}$  vs.  $\log[A^-]$  data for each set of titrations by the "Letagrop Vrid" method.<sup>4</sup>

#### CALCULATION OF ENTHALPY CHANGES FROM CALORIMETRIC DATA

A method for calculating the stepwise enthalpies of complex formation from calorimetric data has been outlined in a previous communication.<sup>3</sup> For the present investigation, this method has to be modified for the following reasons:

In the calorimetric titrations a solution,  $S$ , containing metal ion of total concentration  $C_M$  and acetic acid of total concentration  $C_{HA}$  is titrated with a solution  $T$  (*vide infra* p. 350). A certain amount of complex formation has already occurred in the initial solution by the reaction:



This effectively means that the total concentration of acetic acid is not constant throughout the titration and so a correction, for the heat of protonation of acetic acid, must be applied to the measured reaction heats.

For each point in the titration,  $C_A$ ,  $C_H$ ,  $C_M$ , and  $Q$ , (the enthalpy change for each point corrected for heats of dilution), are known together with the stability constants for the metal acetate, and the proton-acetate complexes.

From these known parameters values for  $\bar{n}$  and  $[A^-]$  are computed for each experimental point using a high speed digital computer in the following manner:

*Input:*  $C_A, C_M, C_H, \beta_{ij}, \beta_n$ .

*Computing.* A value of  $[A^-]$  is calculated from eqn. (4) by Newtons iterative procedure using a value of  $\bar{n} = C_A/C_M$  as a first approximation.

$$\bar{n} = \frac{\sum_{n=1}^4 n \beta_n [A^-]^n}{\sum_{n=0}^4 \beta_n [A^-]^n} \quad (4)$$

This value for  $[A^-]$  is then placed into eqn. (1) and a  $[H^+]$  value is found. The  $[A^-]$  and  $[H^+]$  values are then used in eqn. (3) to yield a better value of  $\bar{n}$ . This  $\bar{n}$  is sent back to the beginning and the process is repeated until all the equations are satisfied to better than 0.1 %.

*Output:*  $\bar{n}, [A^-], [H^+], \alpha_j, \quad j = 1 - n$

where  $\alpha_j$  is the fraction of the total metal present as  $MA_i^{3-i}$ . The change in acetic acid concentration upon each addition of titrant is then calculated. This value, in conjunction with the heat of protonation of the acetate ion is sufficient information for calculating the heat changes arising from rare earth acetate formation for each point.

The heats of formation of each metal complex are computed from the equation:

$$Q_{\text{corr.}} = C_{M,f} \cdot V_f \left[ \sum_{n=1}^4 (\alpha_{n,f} - \alpha_{n,i}) \Delta H_n^\circ \right]$$

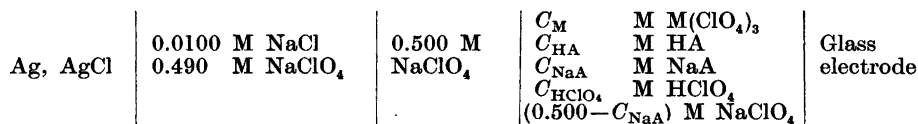
where  $Q_{\text{corr.}}$  is corrected heat of reaction, in calories, from the initial state,  $i$ , to the final state,  $f$ .  $C_{M,f}$  is the total metal concentration in the final state.  $V_f$  is the final total volume in litres that is present in the calorimeter vessel.

$\alpha_{n,i}$  and  $\alpha_{n,f}$  are the fractions of metal complexes in the initial and final states. The "best" constants are then obtained by a least squares program<sup>5</sup> which minimises the error square sum  $U = \sum_k (Q_k^{\text{corr.}} - Q_k^{\text{corr. calc.}})^2$ ,  $k$  being the number of the experimental point.

## EXPERIMENTAL

*Chemicals used.* Stock solutions of the rare earth perchlorates were prepared and analysed as before.<sup>3</sup> Other chemicals were as described in a previous investigation.<sup>2</sup>

*Potentiometric procedure.* The emf,  $E$ , of galvanic cells of the following composition was measured:



The solution in the half-cell to the right was prepared by adding known volumes of a solution T<sub>1</sub> to 30.00 ml. of a solution S. The additions were made from a thermostated

piston burette as described previously.<sup>2</sup> The solutions S and T<sub>1</sub> had the following compositions:

$$S \begin{cases} C_M \text{ M } M(\text{ClO}_4)_3 \\ C_{\text{HA}} \text{ M } \text{HA} \\ C_{\text{HClO}_4} \text{ M } \text{HClO}_4 \\ 0.500 \text{ M } \text{NaClO}_4 \end{cases} \quad T_1 \begin{cases} C_M \text{ M } M(\text{ClO}_4)_3 \\ C_{\text{HA}} \text{ M } \text{HA} \\ C_{\text{NaA}} \text{ M } \text{NaA} \\ C_{\text{HClO}_4} \text{ M } \text{HClO}_4 \\ (0.500 - C_{\text{NaA}}) \text{ M } \text{NaClO}_4 \end{cases}$$

The titration procedure and the method of measurement have been described before. All measurements were made at 25.00°C. and 0.500 M Na<sup>+</sup>(ClO<sub>4</sub><sup>-</sup>).

*Calorimetry procedure.* 99.60 ml of the S solution was titrated with a solution, T<sub>2</sub>, of composition:

$$T_2 \begin{cases} C_{\text{HA}} \text{ M } \text{HA} \\ C_{\text{NaA}} \text{ M } \text{NaA} \\ (0.500 - C_{\text{NaA}}) \text{ M } \text{NaClO}_4 \end{cases}$$

using the titration procedure described previously. Since the rare earth acetate complex formation reactions are endothermic, the starting temperature for the titrations was arranged to be just above 25.00°C so that this temperature was traversed when the reaction occurred. The heat equivalent of the calorimeter was determined by electrical calibrations. The heat of dilution of the ligand was determined by titrating T<sub>2</sub> into a solution of 0.500 M NaClO<sub>4</sub> containing acetic acid of total concentration C<sub>HA</sub>. The heats of dilution of metal perchlorates were determined by titrating C<sub>M</sub> molar metal perchlorate solution in S with 0.500 M sodium perchlorate. The heat of protonation of the acetate ion was determined by titrating perchloric acid in solvent S with T<sub>2</sub>.

*Modifications to the calorimeter.* To prevent evaporation of solvent, the chimney containing the pipette (F in Ref. 7, p. 2191) was fitted with a plastic extruded p.t.f.e. gasket. No over-pressure had to be applied to the pipette in order to empty it completely. The tip of the pipette was smeared with a small amount of Apiezon grease to prevent leakage.

## RESULTS

*Potentiometric measurements.* The titration data are given in Table 1. The reproducibility of these data was checked by repeating each series. Titrations were performed for different values of C<sub>M</sub> and C<sub>HA</sub> in order to determine if polynuclear or acid complexes (of the type M<sub>x</sub>H<sub>y</sub>A<sub>z</sub>; x > 1, y > 0) were formed. These titrations were applied only to neodymium and ytterbium. The experimental results are given in graphs of  $\bar{n}$  vs. log[A<sup>-</sup>] in Fig. 1. It is obvious

*Table 1.* The experimental results and formation curves for rare earth acetate complexes in 5 vol. % water/methanol at 25.00°C. The results are given as ml T, -log[H<sup>+</sup>],  $\bar{n}$  and -log[A<sup>-</sup>]. Approximately one third of the the experimental results is given.

### Lanthanum

S: C<sub>M</sub> = 19.05 mM, C<sub>HA</sub> = 19.92 mM, C<sub>HClO<sub>4</sub></sub> = 0.08 mM; T = S + C<sub>NaA</sub> = 100.0 mM: 0, 2.803, 0.078, 5.907; 2.00, 3.578, 0.337, 5.101; 5.00, 4.194, 0.747, 4.482; 9.00, 4.762, 1.201, 3.913; 11.00, 4.966, 1.394, 3.708; 15.00, 5.301, 1.723, 3.373; 19.00, 5.575, 1.988, 3.099; 23.00, 5.809, 2.199, 2.864; 30.00, 6.129, 2.464, 2.545; 34.00, 6.269, 2.568, 2.404; 40.00, 6.425, 2.686, 2.249; 50.00, 6.601, 2.812, 2.073.

### Praeseodymium

S: C<sub>M</sub> = 20.00 mM, C<sub>HA</sub> = 19.18 mM, C<sub>HClO<sub>4</sub></sub> = 0.44 mM; T = S + C<sub>NaA</sub> = 100.0 mM: 0, 2.605, 0.102, 6.136; 1.00, 2.936, 0.197, 5.772; 4.00, 3.627, 0.577, 5.060; 8.00, 4.275,

1.031, 4.409; 12.00, 4.739, 1.401, 3.943; 16.00, 5.089, 1.704, 3.593; 20.00, 5.392, 1.951, 3.290; 24.00, 5.656, 2.151, 3.026; 28.00, 5.874, 2.310, 2.808; 34.00, 6.117, 2.492, 2.565; 40.00, 6.295, 2.621, 2.388; 50.00 6.494, 2.764, 2.188.

#### Neodymium

S:  $C_M = 16.93$  mM,  $C_{HA} = 18.52$  mM,  $C_{HClO_4} = 1.32$  mM. T = S +  $C_{NaA} = 100.0$  mM; sign = O; 1.00, 2.845, 0.197, 5.867; 3.00, 3.382, 0.483, 5.306; 7.00, 4.156, 1.042, 4.524; 10.00, 4.603, 1.395, 4.077; 14.00, 5.068, 1.787, 3.612; 20.00, 5.649, 2.227, 3.030; 24.00, 5.938, 2.435, 2.741; 30.00, 6.234, 2.654, 2.445; 35.00, 6.401, 2.771, 2.278; 40.00, 6.519, 2.870, 2.159.

S:  $C_M = 8.46$  mM,  $C_{HA} = 18.49$  mM,  $C_{HClO_4} = 0.66$  mM. T = S +  $C_{NaA} = 100.0$  mM; sign = □; 1.00, 3.227, 0.372, 5.481; 3.00, 4.148, 0.999, 4.547; 7.00, 5.553, 2.067, 3.141; 10.00, 6.151, 2.521, 2.543; 14.00, 6.525, 2.845, 2.169; 20.00, 6.793, 3.096, 1.900; 24.00, 6.898, 3.198, 1.796; 30.00, 7.003, 3.315, 1.691; 35.00, 7.069, 3.358, 1.625; 40.00, 7.118, 3.398, 1.576.

S:  $C_M = 16.93$  mM,  $C_{HA} = 48.67$  mM,  $C_{HClO_4} = 1.32$  mM. T = S +  $C_{NaA} = 100.0$  mM; sign = Δ; 1.00, 2.583, 0.266, 5.721; 3.00, 3.012, 0.516, 5.278; 7.00, 3.763, 1.047, 4.520; 10.00, 4.205, 1.396, 4.076; 15.00, 4.777, 1.871, 3.505; 20.00, 5.255, 2.222, 3.026; 24.00, 5.544, 2.426, 2.737; 30.00, 5.833, 2.639, 2.448; 33.00, 5.939, 2.714, 2.342; 40.00, 6.119, 2.841, 2.162.

S:  $C_M = 16.93$  mM,  $C_{HA} = 98.68$  mM,  $C_{HClO_4} = 1.32$  mM. T = S +  $C_{NaA} = 100.0$  mM; sign = ∇; 1.00, 2.422, 0.335, 5.584; 3.00, 2.784, 0.555, 5.213; 7.00, 3.494, 1.056, 4.498; 10.00 3.928 1.399, 4.062; 15.00, 4.499, 1.869, 3.491; 20.00, 4.978, 2.214, 3.012; 24.00, 5.262, 2.410, 2.728; 30.00, 5.541, 2.615, 2.449; 35.00, 5.698, 2.729, 2.292; 40.00, 5.815, 2.808, 2.176.

#### Samarium

S:  $C_M = 20.00$  mM,  $C_{HA} = 19.03$  mM,  $C_{HClO_4} = 0.97$  mM; T = S +  $C_{NaA} = 100.0$  mM. 0, 2.542, 0.094, 6.198; 1.00, 2.867, 0.180, 5.838; 4.00, 3.533, 0.553, 5.148; 8.00, 4.091, 1.006, 4.585; 12.00, 4.508, 1.373, 4.167; 16.00, 4.868, 1.683, 3.806; 20.00, 5.194, 1.930; 3.479; 24.00, 5.487, 2.139, 3.187; 28.00, 5.732, 2.305, 2.942; 34.00, 6.007, 2.494, 2.666; 40.00, 6.200, 2.632, 2.474; 50.00, 6.415, 2.788, 2.259.

#### Gadolinium

S:  $C_M = 20.00$  mM,  $C_{HA} = 19.40$  mM,  $C_{HClO_4} = 0.60$  mM. T = S +  $C_{NaA} = 100.0$  mM. 0, 2.644, 0.084, 6.083; 2.00, 3.303, 0.308, 5.382; 5.00, 3.844, 0.692, 4.834; 9.00, 4.319, 1.125, 4.357; 11.00, 4.518, 1.310, 4.157; 15.00, 4.870, 1.630, 3.805; 19.00, 5.188, 1.893 3.487; 23.00, 5.475, 2.108, 3.199; 30.00, 5.864, 2.390, 2.811; 35.00, 6.061, 2.536, 2.613; 40.00, 6.212, 2.648, 2.462; 50.00, 6.428, 2.799, 2.246.

#### Dysprosium

S:  $C_M = 20.00$  mM,  $C_{HA} = 19.99$  mM,  $C_{HClO_4} = 0.97$  mM. T = S +  $C_{NaA} = 100.0$  mM. 0, 2.566, 0.087, 6.148; 0.50, 2.750, 0.122, 5.942; 1.00, 2.933, 0.171, 5.746; 3.00, 3.431, 0.424, 5.230; 7.00, 4.028, 0.901, 4.628; 10.00, 4.356, 1.201, 4.299; 12.00, 4.552, 1.377, 4.102; 16.00, 4.877, 1.682, 3.777; 20.00, 5.171, 1.935, 3.483; 27.00, 5.586, 2.275, 3.067; 30.00, 5.734, 2.388, 2.920; 40.00, 6.078, 2.669, 2.575.

#### Erbium

S:  $C_M = 20.00$  mM,  $C_{HA} = 19.95$  mM,  $C_{HClO_4} = 1.02$  mM. T = S +  $C_{NaA} = 100.0$  mM. 0, 2.539, 0.094, 6.179; 0.50, 2.698, 0.132, 5.999; 2.00, 3.120, 0.299, 5.549; 4.00, 3.523, 0.552, 5.137; 6.00, 3.835, 0.789, 4.821; 8.00, 4.111, 1.004, 4.544; 12.00, 4.557, 1.375, 4.097; 16.00, 4.919, 1.679, 3.735; 20.00, 5.223, 1.930, 3.431; 23.00, 5.419, 2.089, 3.235; 30.00, 5.801, 2.376, 2.853; 40.00, 6.159, 2.638, 2.494.

## Ytterbium

S:  $C_M = 20.00$  mM,  $C_{HA} = 18.50$  mM,  $C_{HClO_4} = 1.50$  mM; T = S +  $C_{NaA} = 100.0$  mM; sign =  $\circ$ ; 0, 2.365, 0.141, 6.414; 3.00, 3.002, 0.429, 5.694; 7.00, 3.551, 0.885, 5.129; 10.00, 3.879, 1.181, 4.798; 15.00, 4.307, 1.592, 4.368; 20.00, 4.642, 1.921, 4.033; 25.00, 4.914, 2.189, 3.760; 30.00, 5.152, 2.409, 3.522; 35.00, 5.349, 2.593, 3.324; 40.00, 5.466, 2.749, 3.208.

S:  $C_M = 19.42$  mM,  $C_{HA} = 48.50$  mM,  $C_{HClO_4} = 1.46$ ; T = S +  $C_{NaA} = 100.0$  mM; sign =  $\triangle$ ; 0, 2.211, 0.241, 6.126; 3.00, 2.694, 0.497, 5.604; 7.00, 3.215, 0.929, 5.071; 10.00, 3.544, 1.226, 4.739; 15.00, 3.991, 1.643, 4.291; 20.00, 4.339, 1.980, 3.942; 25.00, 4.653, 2.253, 3.628; 30.00, 4.927, 2.474, 3.354; 33.00, 5.071, 2.587, 3.210; 40.00, 5.335, 2.802, 2.946.

S:  $C_M = 20.00$  mM,  $C_{HA} = 98.50$  mM,  $C_{HClO_4} = 1.50$  mM; T = S +  $C_{NaA} = 100.0$  mM; sign =  $\nabla$ ; 0, 2.069, 0.351, 5.955; 3.00, 2.439, 0.561, 5.563; 7.00, 2.890, 0.935, 5.101; 10.00, 3.196, 1.206, 4.793; 15.00, 3.622, 1.601, 4.365; 20.00, 3.959, 1.925, 4.028; 24.00, 4.200, 2.140, 3.786; 30.00, 4.519, 2.405, 3.467; 35.00, 4.751, 2.582, 3.235; 40.00, 4.936, 2.728, 3.051.

S:  $C_M = 10.00$  mM,  $C_{HA} = 19.25$  mM,  $C_{HClO_4} = 0.75$  mM; T = S +  $C_{NaA} = 100.0$  mM; sign =  $\square$ ; 0, 2.069, 0.351, 5.955; 1.00, 2.194, 0.406, 5.820; 3.00, 2.439, 0.561, 5.563; 7.00, 2.890, 0.935, 5.101; 10.00, 3.196, 1.206, 4.793; 15.00, 3.622, 1.601, 4.365; 20.00, 3.959, 1.925, 4.028; 23.00, 4.143, 2.089, 3.844; 30.00, 4.521, 2.405, 3.465; 40.00, 4.936, 2.728, 3.051.

from the figure that  $\bar{n}$  varies slightly with  $C_M$  and  $C_{HA}$  for a given value of  $[A^-]$ . The variation is small, usually within 0.02 units in  $\bar{n}$  for values of  $\bar{n}$

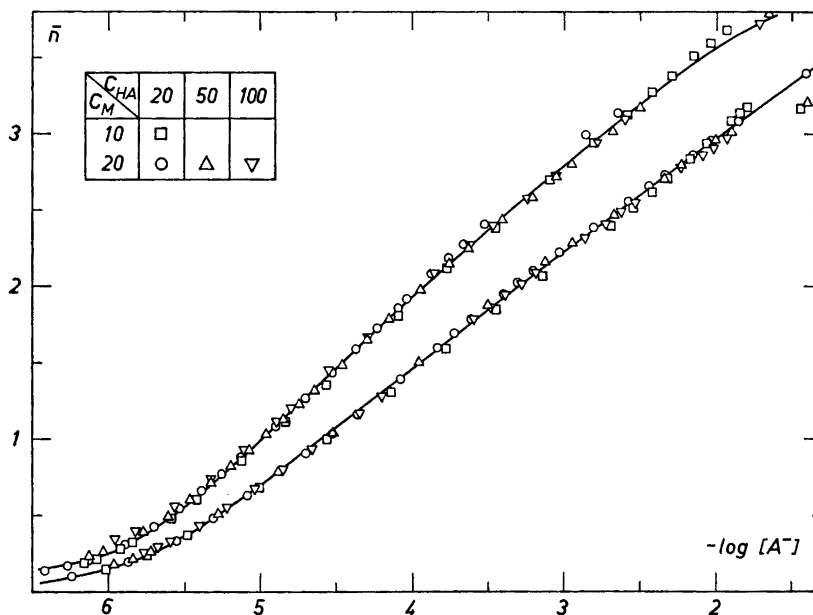


Fig. 1. Experimental values of  $\bar{n}$  vs.  $-\log[A^-]$  for the neodymium and ytterbium acetate systems. The full-drawn curves have been calculated using the constants given in Table 2. The curve to the left is for the ytterbium acetate system.

$< 3$ . The spread is larger at higher  $\bar{n}$ -values. The reason for the spread in  $\bar{n}$  may be the presence of small amounts of complexes  $M_xH_yA_z$ ;  $x > 1$ ,  $y > 0$  and/or the presence of a systematic error in the potentiometric measurements.

The experimental findings for neodymium and ytterbium indicate that the complexes formed are predominantly of the type  $MA_n$ . It was then assumed that the other elements formed only mononuclear complexes.

All measurements were extended to above  $\bar{n} = 3$ , the highest free ligand concentration was approx. 40 mM. The highest complex formed in the  $[A^-]$  range investigated was the fourth. No levelling off of the various  $\bar{n}$  vs.  $[A^-]$  curves was observed. Thus it cannot be ascertained from these measurements whether the maximum coordination number is four or higher than four. The experimental  $\bar{n}$ -data for ytterbium can be well described up to  $\bar{n} = 3.8$  by using only four stability constants, indicating a maximum coordination number of four, or an inflexion at four for this system.

Table 2. Stability constants of rare earth acetate complexes in 5% water/methanol at 25.00°C. The standard deviations in the various constants and the standard deviations in  $\bar{n}$  are also given.

Metal ion	$\beta_1 \times 10^{-5}$ (M <sup>-1</sup> )	$\beta_2 \times 10^{-8}$ (M <sup>-2</sup> )	$\beta_3 \times 10^{-11}$ (M <sup>-3</sup> )	$\beta_4 \times 10^{-12}$ (M <sup>-4</sup> )	$\sigma_{\bar{n}}$
La	0.56 ± 0.01	2.09 ± 0.04	0.80 ± 0.02	0.58 ± 0.07	0.011
Pr	1.30 ± 0.02	8.6 ± 0.1	3.49 ± 0.07	3.1 ± 0.5	0.011
Nd	1.71 ± 0.04	15.3 ± 0.3	6.5 ± 0.2	13.1 ± 0.6	0.024
Sm	1.37 ± 0.02	15.7 ± 0.2	7.8 ± 0.2	10.0 ± 1	0.009
Gd	0.95 ± 0.01	9.47 ± 0.08	4.60 ± 0.05	6.8 ± 0.4	0.006
Dy	1.06 ± 0.02	10.3 ± 0.2	6.2 ± 0.1	15.0 ± 1	0.016
Er	1.41 ± 0.03	13.0 ± 0.3	7.5 ± 0.2	11.5 ± 1	0.017
Yb	3.38 ± 0.07	100 ± 2	233 ± 6	3250 ± 100	0.027

The stability constants were calculated from values of  $\bar{n}$  and  $\log[A^-]$  by the "Letagrop Vrid" method using a SAAB D21 computer. The four stability constants and their corresponding standard deviations are listed in Table 2.

*Calorimetric measurements.* The heat equivalent of the calorimetric system, determined by electrical calibrations, was found to obey:

$$\varepsilon_V = 1.628 + 0.0129v \text{ cal. } \Omega^{-1}$$

for all solutions.  $V$  is the total volume of the solution in the calorimeter (99.60 +  $v$  ml) and  $v$  is the volume, in ml, of titrant added.

Heats of dilution were determined for the rare earth perchlorate solutions and were found to be negligible within the experimental error. The heats of dilution of the various T solutions were small and constant for the  $C_A$  range investigated. The results are given in Table 3.

The titration data for the determination of the heat of formation of acetic acid were as follows: after correcting for heats of dilution of the perchloric acid and of  $T_2$ , the heat evolved for each addition was

$$\Delta H_{HA}^\circ = -2.12 \pm 0.04 \text{ kcal.mole}^{-1}$$

Table 3. The heats of dilution of solutions used in the calorimetric procedure. The  $C_{HA}$  values are mutual to T and S solutions. The  $Na^+$  content was maintained at 0.500 g ions  $l^{-1}$  by using appropriate quantities of  $NaClO_4$  in S or T.

Dilutions of	S $C_{HA}$ (mM)		T	ml initial	ml T added	Heat in calories
	$C_M$ (mM)		$C_{NaA}$ (mM)			
Metal solution, <i>e.g.</i> $Nd^{3+}$	10.0	20.0	—	99.62	2.856	<0.005
	20.0	100.0	—	119.6	2.856	<0.005
$T_2$ solutions	—	20.0	300.0	102.5	2.856	0.030
	—	20.0	300.0	113.9	2.856	0.033
	—	100.0	300.0	106.3	1.904	0.049
	—	100.0	300.0	121.5	1.904	0.054

The error quoted is sufficient to encompass the heat of formation of any further acetate complexes.

The experimental results of the calorimetric investigation of the rare earth acetate complexes are given in Table 4. The possible occurrence of polynuclear or acid complexes was further checked calorimetrically by titrating the

Table 4.  $\bar{n}$ ,  $\sum Q$  and  $\sum Q_{corr}$  (cal.) for calorimetric titrations of rare earth perchlorates with buffered sodium acetate in 5 vol. % water/methanol at 25.00°C.

#### Lanthanum

S:  $C_{HA} = 19.92$  mM,  $C_{HClO_4} = 0.08$  mM,  $C_M = 20.00$  mM; T:  $C_{NaA} = 300.0$  mM,  $C_{HA} = 20.00$  mM; ml T,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{corr}$ : 0.952, 0.169, 0.470, 0.713; 2.856, 0.434, 2.025, 2.355; 5.712, 0.855, 4.506, 4.864; 7.616, 1.139, 6.149, 6.511; 10.47, 1.556, 8.275, 8.639; 12.38, 1.830, 9.438, 9.804; 15.23, 2.208, 10.981, 11.349; 18.09, 2.529, 11.849, 12.215; 20.94, 2.682, 12.310, 12.676; 23.80, 2.918, 12.560, 12.926. 1.904, 0.296, 1.212, 1.517; 4.760, 0.715, 3.749, 4.100; 6.664, 0.997, 5.369, 5.729; 9.520, 1.417, 7.544, 7.910; 11.42, 1.694, 8.887, 9.251; 14.28, 2.087, 10.544, 10.912; 17.14, 2.433, 11.665, 12.031; 19.99, 2.695, 12.240, 12.606; 22.85, 2.838, 12.562, 12.928; 25.70, 3.065, 12.763, 13.129.

#### Praeseodymium

S:  $C_{HA} = 19.56$  mM,  $C_{HClO_4} = 0.44$  mM,  $C_M = 20.00$  mM; T:  $C_{NaA} = 300$  mM,  $C_{HA} = 20.00$  mM; ml T,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{corr}$ : 0.952, 0.181, 0.346, 0.604; 2.856, 0.427, 1.603, 2.033; 5.712, 0.840, 3.763, 4.256; 10.47, 1.546, 7.327, 7.839; 12.38, 1.824, 8.627, 9.139; 15.23, 2.214, 10.437, 10.951; 18.09, 2.540, 11.518, 12.032; 20.94, 2.699, 12.377, 12.891. 1.904, 0.295, 0.913, 1.283; 4.760, 0.701, 2.974, 3.455; 6.664, 0.981, 4.529, 5.031; 9.520, 1.404, 6.620, 7.130; 11.42, 1.685, 8.037, 8.549; 14.28, 2.086, 10.004, 10.521; 17.14, 2.436, 11.216, 11.730; 19.99, 2.706, 12.180, 12.694; 22.85, 2.858, 12.766, 13.280; 25.70, 3.083, 13.089, 13.603.

#### Neodymium

S:  $C_{HA} = 19.99$  mM,  $C_{HClO_4} = 0.01$  mM,  $C_M = 20.00$  mM; T:  $C_{NaA} = 300.0$  mM,  $C_{HA} = 20.00$  mM; ml T,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{corr}$ : 0.952, 0.215, 0.159, 0.388; 1.904, 0.328, 0.555, 0.906; 2.856, 0.457, 1.162, 1.581; 4.760, 0.727, 2.202, 2.685; 6.664, 1.006, 3.432, 3.946; 7.616,



1.149, 4.035, 4.551; 9.520, 1.429, 5.286, 5.811; 10.47, 1.570, 5.840, 6.365; 12.38, 1.848, 7.064, 7.591; 13.33, 1.983, 7.651, 8.178; 15.23, 2.236, 8.731, 9.260; 18.09, 2.568, 9.793, 10.322; 20.94, 2.741, 10.428, 10.957; 21.90, 2.817, 10.515, 11.044; 23.80, 2.971, 10.977, 11.506.

S:  $C_{\text{HA}} = 99.98$  mM,  $C_{\text{HClO}_4} = 0.02$  mM,  $C_{\text{M}} = 20.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 100.0$  mM; ml  $T$ ,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 0.952, 0.341, -0.324, 0.142; 2.856, 0.534, -0.082, 1.012; 5.712, 0.893, 1.437, 2.622; 8.568, 1.299, 3.189, 4.472; 11.42, 1.714, 5.014, 6.322; 14.28, 2.112, 6.604, 7.912; 17.14, 2.465, 7.894, 9.202.

S:  $C_{\text{HA}} = 19.99$  mM,  $C_{\text{HClO}_4} = 0.01$  mM,  $C_{\text{M}} = 10.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 20.00$  mM; ml  $T$ ,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 0.952, 0.361, 0.165, 0.377; 1.433, 0.477, 0.439, 0.701; 1.904, 0.603, 0.712, 1.010; 2.856, 0.873, 1.223, 1.562; 3.808, 1.151, 1.841, 2.194; 5.712, 1.699, 3.057, 3.421; 6.664, 1.961, 3.612, 3.976; 8.568, 2.404, 4.536, 4.902.

#### Samarium

S:  $C_{\text{HA}} = 19.03$  mM,  $C_{\text{HClO}_4} = 0.97$  mM,  $C_{\text{M}} = 20.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 20.00$  mM; ml  $T$ ,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 0.952, 0.165, 0.211, 0.518; 8.808, 0.543, 1.892, 2.430; 6.664, 0.961, 3.714, 4.296; 9.520, 1.385, 5.388, 5.983; 12.38, 1.843, 6.926, 7.527; 15.23, 2.203, 8.404, 9.007; 18.09, 2.545, 9.543, 10.142; 20.94, 2.728, 10.233, 10.834; 23.80, 2.960, 10.602, 11.203; 26.65, 3.228, 10.864, 11.465. 1.904, 0.272, 0.754, 1.188; 4.760, 0.673, 2.539, 3.098; 6.664, 0.953, 3.737, 4.319; 9.520, 1.377, 5.399, 5.994; 11.42, 1.661, 6.413, 7.010; 14.28, 2.069, 7.946, 8.549; 17.14, 2.523, 9.204, 9.805; 19.99, 2.717, 10.017, 10.618; 22.85, 2.875, 10.563, 11.164; 25.70, 3.100, 10.872, 11.473.

#### Gadolinium

S:  $C_{\text{HA}} = 19.40$  mM,  $C_{\text{HClO}_4} = 0.60$  mM,  $C_{\text{M}} = 20.00$  mM;  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 20.00$  mM; ml  $T$ ,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 0.952, 0.165, 0.440, 0.707; 2.856, 0.417, 1.859, 2.274; 5.712, 0.833, 4.176, 4.638; 7.616, 1.118, 5.604, 6.076; 10.47, 1.540, 7.387, 7.868; 12.38, 1.820, 8.433, 8.918; 15.23, 2.214, 9.810, 10.295; 18.09, 2.554, 10.774, 11.257; 20.94, 2.731, 11.361, 11.846; 23.80, 2.968, 11.736, 12.221. 1.904, 0.283, 1.022, 1.386; 4.760, 0.693, 3.412, 3.865; 6.664, 0.975, 4.882, 5.350; 9.520, 1.399, 6.725, 7.201; 11.42, 1.681, 7.846, 8.327; 14.28, 2.087, 9.413, 9.898; 17.14, 2.410, 10.526, 11.009; 19.99, 2.731, 11.227, 11.710; 22.85, 2.889, 11.453, 11.938; 25.70, 3.120, 11.862, 12.347.

#### Dysprosium

S:  $C_{\text{HA}} = 19.99$  mM,  $C_{\text{HClO}_4} = 0.01$  mM,  $C_{\text{M}} = 20.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 20.00$  mM; ml  $T$ ,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 0.952, 0.187, 0.634, 0.793; 2.856, 0.443, 2.557, 2.914; 5.712, 0.859, 5.647, 6.028; 7.616, 1.144, 7.444, 7.838; 10.47, 1.566, 9.739, 10.137; 12.38, 1.847, 11.028, 11.428; 15.23, 2.243, 12.623, 13.027; 18.09, 2.593, 13.512, 13.914; 20.94, 2.761, 14.032, 14.434; 23.80, 2.998, 14.326, 14.728. 1.904, 0.308, 1.601, 1.891; 4.760, 0.719, 4.666, 5.039; 6.664, 1.001, 6.529, 6.916; 9.520, 1.425, 9.067, 9.463; 11.42, 1.707, 10.449, 10.849; 14.28, 2.115, 12.193, 12.595; 17.14, 2.485, 13.452, 13.854; 19.99, 2.773, 13.979, 14.381; 22.85, 2.917, 14.177, 14.579; 25.70, 3.142, 14.281, 14.683.

#### Erbium

S:  $C_{\text{HA}} = 19.95$  mM,  $C_{\text{HClO}_4} = 0.05$  mM,  $C_{\text{M}} = 20.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 20.00$  mM; ml  $T$ ,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 0.952, 0.199, 0.849, 1.067; 2.856, 0.447, 2.850, 3.229; 5.712, 0.860, 6.106, 6.546; 7.616, 1.144, 8.005, 8.460; 10.47, 1.566, 10.597, 11.059; 12.38, 1.847, 12.178, 12.644; 15.23, 2.241, 14.369, 14.837; 18.09, 2.585, 15.361, 15.827; 20.94, 2.748, 15.664, 16.132; 23.80, 2.968, 15.772, 16.240. 1.904, 0.316, 1.814, 2.136; 4.760, 0.721, 4.953, 5.383; 6.664, 1.002, 6.910, 7.359; 9.520, 1.425, 9.881, 10.340; 11.42, 1.707, 11.438, 11.902; 14.28, 2.114, 13.554, 14.020; 17.14, 2.481, 14.931, 15.397; 19.99, 2.760, 15.479, 15.945; 22.85, 2.891, 16.065, 16.531.

#### Ytterbium

S:  $C_{\text{HA}} = 18.50$  mM,  $C_{\text{HClO}_4} = 1.50$  mM,  $C_{\text{M}} = 20.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 20.00$  mM; ml  $T$ ,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 0.952, 0.256, 0.406, 0.527; 3.808, 0.537, 3.108, 3.864;

6.664, 0.941, 6.382, 7.239; 9.520, 1.361, 9.574, 10.467; 12.38, 1.824, 12.955, 13.859; 15.23, 2.207, 15.837, 16.747; 18.09, 2.616, 18.740, 19.648; 20.94, 2.980, 20.841, 21.749; 23.80, 3.241, 21.871, 22.979; 26.65, 3.550, 22.295, 23.203.

S:  $C_{\text{HA}} = 19.25$  mM,  $C_{\text{HClO}_4} = 0.75$  mM,  $C_{\text{M}} = 10.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 20.00$  mM; ml T,  $\bar{n}_{\text{corr}}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 1.428, 0.449, 0.965, 1.321; 2.856, 0.819, 2.573, 3.058; 3.808, 1.091, 3.612, 4.131; 5.712, 1.643, 5.635, 6.179; 6.664, 1.924, 6.710, 7.260; 8.568, 2.464, 8.693, 9.248; 11.42, 3.052, 10.443, 10.998; 14.28, 3.422, 10.932, 11.487; 17.14, 3.783, 11.101, 11.656.

S:  $C_{\text{HA}} = 99.25$  mM,  $C_{\text{HClO}_4} = 0.75$  mM,  $C_{\text{M}} = 10.00$  mM; T:  $C_{\text{NaA}} = 300.0$  mM,  $C_{\text{HA}} = 100.0$  mM, ml T,  $\bar{n}$ ,  $\sum Q$ ,  $\sum Q_{\text{corr}}$ : 1.428, 0.632, 0.530, 0.947; 2.856, 0.923, 1.529, 2.264; 3.808, 1.153, 2.384, 3.233; 5.712, 1.656, 4.129, 5.082; 6.664, 1.942, 5.322, 6.317; 8.568, 2.460, 7.173, 8.147.

neodymium and ytterbium systems at different values of  $C_{\text{M}}$  and  $C_{\text{HA}}$ . It was confirmed that only mononuclear complexes  $\text{MA}_n$  were formed. This is illustrated in Fig. 2, where  $\sum Q_{\text{corr}}$ , the heat of reaction, corrected for the heat of protonation of acetic acid, is plotted vs.  $\bar{n}$ . Curves for the different titration series are parallel. This is caused by the  $\bar{n}$  values of the S solutions not being zero because of the acetic acid-metal interactions. When this is taken into account, all the curves coincide with the dashed curve. The stepwise enthalpies, calculated by applying the least square method to the  $Q_{k, \text{corr}}$  and  $\alpha_{k, j}$  data are given in Table 6. The standard deviations in the enthalpy changes are also given. We then compared the sums of the measured and corrected heat changes with values,  $\sum Q_{\text{calc}}$  calculated using the stability constants and enthalpies given in Tables 2 and 6. The agreement was always found to be within the accuracy expected from the calorimetric procedure. These comparisons are exemplified using neodymium in Table 5. Using values of the free energy

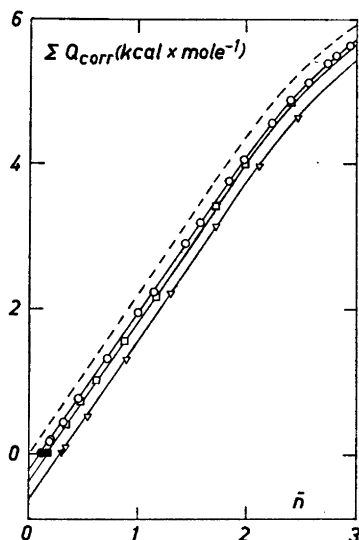


Fig. 2. Experimental values of the heat change  $\sum Q_{\text{corr}}$  (kcal.mole<sup>-1</sup>) vs.  $\bar{n}$  for the neodymium acetate system. The full-drawn curves are calculated using the stability constants of Table 2 and the enthalpy values of Table 6. The black points indicate the  $\bar{n}$  of the various S solutions. The symbols are the same as in Fig. 1.

Table 5. The enthalpy changes when neodymium perchlorate was titrated with an acetate buffer and the computed corrections for each experimental point.

S: $C_M = 20.00$ mM, $C_{HA} = 20.00$ mM, $C_{HClO_4} = 0.01$ mM. T: $C_{HA} = 20.00$ mM, $C_{NaA} = 300.0$ mM.							
ml T	$C_A$ (mM)	$C_M$ (mM)	$\bar{n}$	$[A^-]$ (M)	$\Sigma Q$ (cal.)	$\Sigma Q_{corr}$ (cal.)	$\Sigma Q_{calc}$ (cal.)
0.952	22.85	19.81	0.215	$1.40 \times 10^{-6}$	0.159	0.388	0.397
2.856	28.37	19.44	0.457	$4.02 \times 10^{-6}$	1.162	1.581	1.513
4.760	33.68	19.09	0.727	$9.98 \times 10^{-6}$	2.202	2.685	2.670
6.664	38.81	18.75	1.001	$2.48 \times 10^{-5}$	3.432	3.946	3.920
7.616	41.33	18.58	1.149	$3.92 \times 10^{-5}$	4.035	4.551	4.542
9.520	46.16	18.26	1.429	$9.16 \times 10^{-5}$	5.286	5.811	5.815
10.47	48.52	18.09	1.570	$1.37 \times 10^{-4}$	5.840	6.365	6.381
13.33	55.43	17.64	1.983	$4.60 \times 10^{-4}$	7.651	8.178	8.137
18.09	66.11	16.93	2.568	$2.63 \times 10^{-3}$	9.793	10.322	10.316
21.90	74.06	16.40	2.817	$5.82 \times 10^{-3}$	10.515	11.044	11.132

Table 6. The stepwise values of  $\Delta H_n^\circ$ ,  $\Delta G_n^\circ$  and  $\Delta S_n^\circ$  for the formation of rare earth acetate complexes in 5 vol% water/methanol at 25.00°C. The values of  $\Delta H_n^\circ$  are given with their standard deviations.

Metal ion	$\Delta H_1^\circ \pm \sigma \Delta H_1^\circ$ (kcal-mole <sup>-1</sup> )	$-\Delta G_1^\circ$ (kcal-mole <sup>-1</sup> )	$\Delta S_1^\circ$ (e.u.)	$\Delta H_2^\circ \pm \sigma \Delta H_2^\circ$ (kcal-mole <sup>-1</sup> )	$-\Delta G_2^\circ$ (kcal-mole <sup>-1</sup> )	$\Delta S_2^\circ$ (e.u.)
La	$3.28 \pm 0.04$	6.457	32.7	$2.60 \pm 0.04$	4.872	25.0
Pr	$2.89 \pm 0.05$	6.977	33.1	$2.64 \pm 0.07$	5.213	26.3
Nd	$2.20 \pm 0.06$	7.136	31.3	$2.21 \pm 0.08$	5.407	25.6
Sm	$2.77 \pm 0.05$	7.009	32.8	$1.54 \pm 0.05$	5.538	23.7
Gd	$3.38 \pm 0.04$	6.790	34.1	$1.71 \pm 0.04$	5.457	24.0
Dy	$4.09 \pm 0.07$	6.857	36.7	$2.72 \pm 0.07$	5.440	27.4
Er	$4.58 \pm 0.07$	7.026	38.9	$2.92 \pm 0.08$	5.409	27.9
Yb	$4.84 \pm 0.05$	7.545	41.5	$3.50 \pm 0.09$	6.101	32.2
Metal ion	$\Delta H_3^\circ \pm \sigma \Delta H_3^\circ$ (kcal-mole <sup>-1</sup> )	$-\Delta G_3^\circ$ (kcal-mole <sup>-1</sup> )	$\Delta S_3^\circ$ (e.u.)	$\Delta H_4^\circ \pm \sigma \Delta H_4^\circ$ (kcal-mole <sup>-1</sup> )	$-\Delta G_4^\circ$ (kcal-mole <sup>-1</sup> )	$\Delta S_4^\circ$ (e.u.)
La	$1.08 \pm 0.04$	3.532	15.5	$0.41 \pm 0.1$	1.16	5.2
Pr	$1.56 \pm 0.11$	3.559	17.2	$0.66 \pm 0.6$	1.25	6.5
Nd	$1.94 \pm 0.13$	3.548	18.4	$-1.71 \pm 0.5$	1.78	0.3
Sm	$1.93 \pm 0.06$	3.675	18.8	$-0.44 \pm 0.2$	1.51	3.6
Gd	$1.59 \pm 0.06$	3.666	17.7	$-0.34 \pm 0.3$	1.59	4.1
Dy	$1.00 \pm 0.06$	3.789	16.0	$0.26 \pm 0.1$	1.90	7.3
Er	$1.88 \pm 0.13$	3.766	19.0	$-3.5 \pm 1$	1.62	- 6.2
Yb	$4.17 \pm 0.15$	4.595	29.4	$-0.11 \pm 0.1$	2.93	9.4

change, and the corresponding enthalpy changes, the entropy changes were calculated and listed in Table 6.

#### DISCUSSION

A number of comparisons may be made between the thermodynamic quantities for the formation of rare earth acetate complexes in water and in water/methanol.

*a.* The stability constants are considerably larger for the mixed solvent than for those in water. This was also found for the proton acetate complexes. However, whereas the stability constants of the proton acetate complexes increase a hundredfold upon changing to water/methanol, the stability constants of the rare earth complexes have increased by a factor of about one thousand.

*b.* The patterns exhibited by the stepwise enthalpy and entropy changes throughout the rare earth series are similar in *S* and in water.

It has been suggested<sup>1</sup> that the variations in  $\Delta G_n^\circ$ ,  $\Delta H_n^\circ$  and  $\Delta S_n^\circ$  within the lanthanoide series may be caused by changes in the solvations of the central ions. The results of this investigation imply that the solvation sheaths are similar in the two solvents. This may be a consequence of preferential solvation by water in the mixed solvent or of methanol having similar solvating properties to water. Investigations by Bjerrum and Jørgensen,<sup>8</sup> Sayre *et al.*<sup>9</sup> and by Jayne and King<sup>10</sup> indicate that a preferential solvation by water occurs in mixed water/methanol solvents. The "waterlike" behaviour that we found presumably arises from the water content of solvent *S* being too large for methanol solvates to form. Thus, to obtain more conclusive information concerning the possible influence of solvation on the measured thermodynamic quantities, it appears necessary to decrease the water content of our solvent *S* or to work in a less "waterlike" solvent.

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