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A Calorimetric Study of Aquo Complex Formation of Cobalt(II) and Nickel(II) Perchlorates in 1-Butanol

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The reaction of liquid water with anhydrous solutions of $\text{Co}(\text{ClO}_4)_2$ and $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol has been studied calorimetrically at 25°. Equilibrium constants, enthalpies, and entropies for the reaction $\text{M}(\text{ClO}_4)_2 + n\text{H}_2\text{O} = \text{M}(\text{H}_2\text{O})_n(\text{ClO}_4)_2$ have been found for $n \leq 5$ by application of Bjerrum's method of *corresponding solutions* to the thermal data. Enthalpy and entropy changes for the substitution of the first two water molecules are clearly differentiated from values for subsequent substitutions in relative magnitude and/or sign. The results are consistent with a model in which water substitutes for butanol in the *trans* form of an outer-sphere complex with perchlorate ligands in the outer sphere and butanol in the inner. Both $\text{Co}(\text{ClO}_4)_2$ and $\text{Ni}(\text{ClO}_4)_2$ appear to be electrolytically undissociated in 1-butanol, and an extension of the theory of corresponding solutions to mixed ligand complexes is presented.

Introduction

Recent studies of the solvation of copper(II) ions in nitromethane,¹ in acetone,^{2,3} and in ethanol^{3,4} have shown that water, even at small concentrations in these organic solutions, is preferentially coordinated by the metal. The same conclusion has been drawn for ethanol and acetone solutions of cobalt(II) and nickel(II) ions, though the formation constants are such that some replacement of water by organic solvent can be expected.⁵

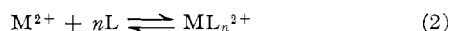
The organic phases in the liquid-liquid extraction of salts always contain residual water, and our studies of the 1-butanol phases from the extraction of cobalt(II) and nickel(II) perchlorates have shown that the visible absorption spectra for both salts are almost indistinguishable from those of the aqueous phases. This investigation was therefore undertaken to characterize thermodynamically aquo complex formation of cobalt(II) and nickel(II) perchlorates in 1-butanol.

Experimental Section

(A) **Method.**—A complete thermodynamic description of complex formation in solution is possible in principle from a thermometric or enthalpy titration. For solutions of metal ion M^{2+} the data are of the theoretical form⁶

$$\Delta\bar{H} = \frac{\sum_1^N h_n \beta_n [\text{L}]^n}{\sum_0^N \beta_n [\text{L}]^n} \quad (1)$$

where $\Delta\bar{H}$ is the heat of reaction for 1 mole of metal with ligand L; h_n is the enthalpy change accompanying the reaction



and β_n is the corresponding equilibrium or formation constant.

Series of solutions, each of constant salt concentration, were titrated with water in the calorimeter at 25°. Corresponding solution concentrations were found after correction for the heat of mixing of water with the solvent by the method of Bjerrum.⁷

Correction for the heat of mixing of water with butanol was

- (1) R. C. Larson and R. T. Iwamoto, *Inorg. Chem.*, **1**, 316 (1962).
- (2) I. V. Nelson and R. T. Iwamoto, *ibid.*, **3**, 661 (1964).
- (3) N. J. Friedman and R. A. Plane, *ibid.*, **2**, 11 (1963).
- (4) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 175 (1954).
- (5) R. F. Pasternak and R. A. Plane, *Inorg. Chem.*, **4**, 1171 (1965).
- (6) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 322.
- (7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

made by determination of the heat of reaction of water with butanol as a function of concentration. Since it was found that the integral heat of mixing is a nearly linear function of the concentration up to 1 *m* water concentration, the average value of 0.43 kcal (mole of H_2O)⁻¹ (kg of butanol)⁻¹ was used for the partial molal enthalpy of solution of water in all subsequent calculations. Results of replicate runs are shown in Figures 1 and 2.

Values of the average number of bound ligands \bar{n} and free ligand (water) concentration were calculated from the slopes and intercepts of the curves of Figure 3, determined by least squares. The points on each curve correspond to the same value of $\Delta\bar{H}$, and curves were spaced at 100-cal intervals. These quantities were used to construct the "formation curves" of Figure 4.

To find the formation constants from the (\bar{n} , pH_2O) data, pseudo-constants were calculated as suggested by Poe,⁸ and these were refined by iterative procedures to give the final constants of Table I. The calculated formation curves based upon the values of the constants in Table I are the solid lines of Figure 4, and the experimental values are the closed ($\text{Co}(\text{ClO}_4)_2$) and open circles ($\text{Ni}(\text{ClO}_4)_2$). In the calculations the maximum coordination number $N = 6$ was used, as discussed later.

Enthalpies and entropies of formation were obtained from the data of Figures 1 and 2 and that in Table I through eq 1. When the stepwise formation of complexes is statistical, *i.e.*, $h_n = nh_1$, then

$$\Delta\bar{H} = h_1 \bar{n} \quad (3)$$

Our data conformed reasonably closely to eq 3 at small values of \bar{n} so that an estimate of h_1 could be made. Other values of h_n were then determined by successive approximations. Values are found in Table I, and the quality of the fit of the ($\Delta\bar{H}$, $C_{\text{H}_2\text{O}}$) curve calculated from the constants of Table I to the experimental data is shown in Figures 1 and 2.

Entropy values were calculated from the formation values and are also presented in Table I.

(B) **Calorimeter.**—The microcalorimeter consisted of an approximately 35-ml silvered dewar flask mounted in an isothermal air bath. Ports were provided through the 50/40 top for a 25-ohm heater of 0.0034-in. diameter platinum wire, a stirrer, a Victory Engineering Co. 32A30 2000-ohm thermistor, and a Teflon hypodermic needle. The 12-in. needle was 18 gauge with a 22-gauge tip. It was coiled and submerged so that it served as a constant-temperature reservoir for titrant to be delivered. The volume of the submerged coil was several times that of the titrant increments so that, in the time interval between additions, complete thermal equilibrium was established with the solution being titrated.

Titrant (water) was injected into the calorimeter from an RG

(8) A. J. Poe, *J. Phys. Chem.*, **67**, 1070 (1963).

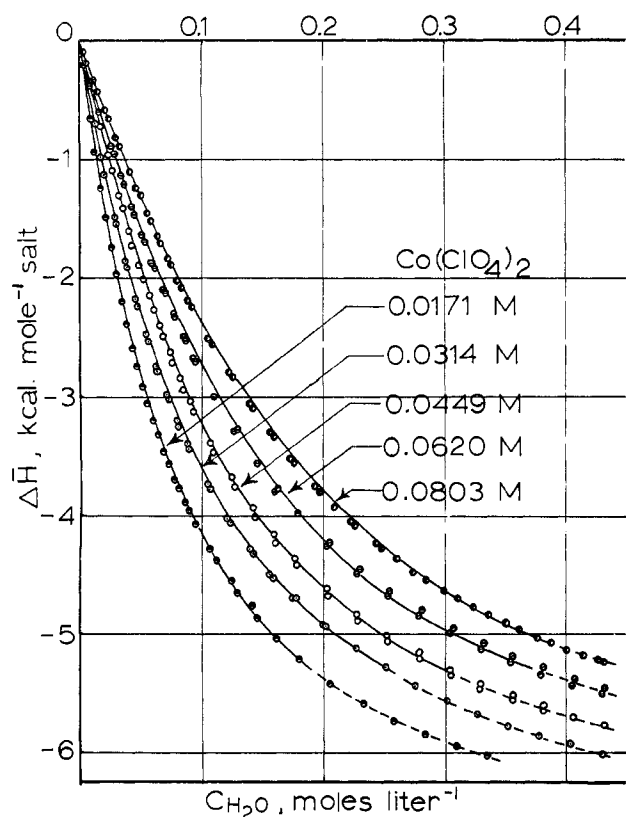


Figure 1.—Integral heat of reaction of water with $\text{Co}(\text{ClO}_4)_2$ solutions in butanol. Lines are calculated from values of β_n and h_n . Values have been corrected for the heat of mixing of liquid water with butanol at a concentration of 1 mole kg^{-1} .

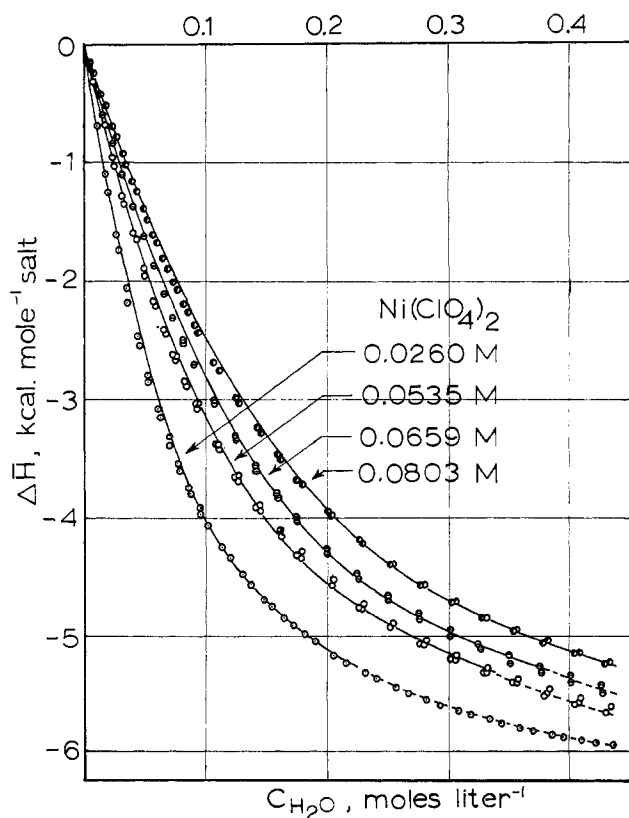


Figure 2.—Integral heat of reaction of water with $\text{Ni}(\text{ClO}_4)_2$ solutions in butanol. Lines are calculated from values of β_n and h_n . Values have been corrected for the heat of mixing of liquid water with butanol at a concentration of 1 mole kg^{-1} .

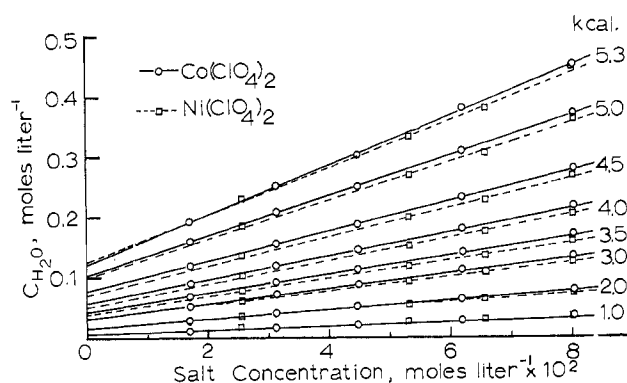


Figure 3.—Corresponding solutions. Lines are calculated by least squares.

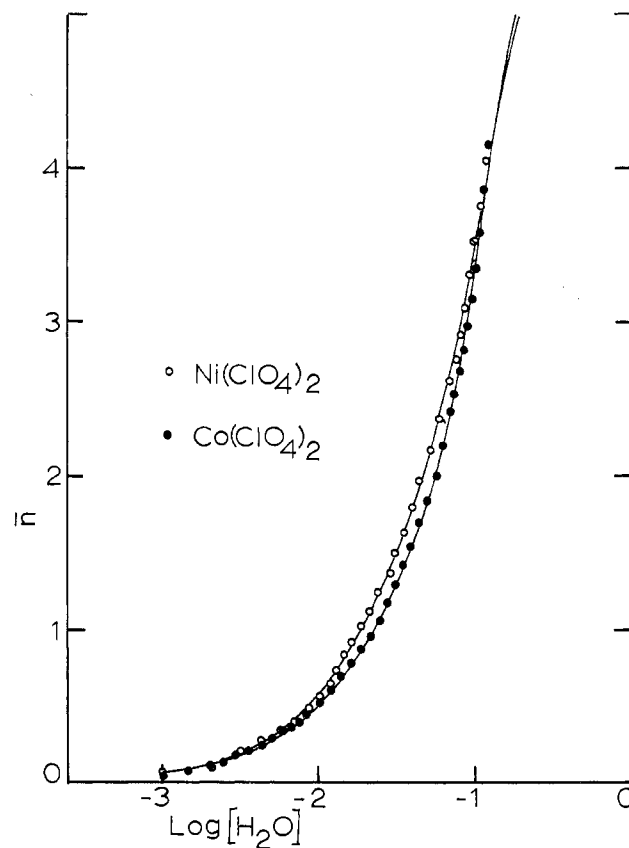


Figure 4.—Formation functions. Lines are calculated from the values of β_n .

precision micrometer syringe (0.0001-ml divisions, 0.02% accuracy). Increments were of the order of 10 μl . Reaction was rapid and appeared to be limited only by the rate of mixing.

The thermistor was made one arm of a Wheatstone bridge, the unbalanced output from which was recorded by a Sargent SR 1-mV recorder. With butanol solutions in the calorimeter, the "working" sensitivity was found to be 0.0025 cal or about 0.0001°. Individual heat measurements were of the order of 0.5 cal or less per increment, both positive and negative.

The calorimeter was provided with electrical calibration. Potentials across the heater and a calibrated General Radio Type 500-B 10-ohm resistance in series with the heater were measured with a potentiometer. Time was measured with an X-ray timer (0.001 sec) and time switch connected to the heater and matching dummy heater through a relay system. Heat capacity measurements were made at intervals during the titrations since the composition of the solutions, and hence the heat capacity, changed slightly during the course of an experiment.

TABLE I
OVER-ALL FORMATION CONSTANTS, ENTHALPIES, AND ENTROPIES
FOR AQUO COMPLEXES IN 1-BUTANOL AT 25°^a

<i>n</i>	Log β _{<i>n</i>}	Δ <i>H</i> _{<i>n</i>} (= <i>h</i> _{<i>n</i>}), kcal mole ⁻¹	Δ <i>S</i> , cal deg ⁻¹ mole ⁻¹
Co(ClO ₄) ₂			
1	1.76 ± 0.04	-2.85 ± 0.13	-1.5 ± 0.5
2	3.08 ± 0.04	-4.70 ± 0.21	-1.7 ± 0.7
3	4.10 ± 0.04	-5.35 ± 0.24	0.8 ± 0.8
4	4.64 ± 0.06	-5.60 ± 0.36	2.4 ± 1.2
5	(5.6 ± 0.1)	(-5.8 ± 0.5)	(6 ± 2)
Ni(ClO ₄) ₂			
1	1.80 ± 0.05	-3.05 ± 0.14	-2.0 ± 0.5
2	3.23 ± 0.05	-4.80 ± 0.22	-1.3 ± 0.8
3	4.36 ± 0.05	-5.25 ± 0.24	2.3 ± 0.8
4	5.20 ± 0.08	-5.45 ± 0.36	5.5 ± 1.3
5	(5.8 ± 0.1)	(-5.7 ± 0.5)	(8 ± 2)

^a An over-all enthalpy change for the completed reaction of 6.6 kcal mole⁻¹ for both salts is indicated from the experimental data. Values of \bar{n} or $\Delta\bar{H}$ calculated from the constants in the table have an average deviation of 2% from values determined from least-square slopes and experimental heat of reaction data. Corresponding uncertainties in the values of β_{*n*} and *h*_{*n*} are based upon a mean 2% curve fit and the principle of error propagation, assuming constant values for the probable average fractional error in β_{*n*} and *h*_{*n*}: A. G. Worthing and J. Gefner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p 255. For *n* > 3 the uncertainties arbitrarily have been increased successively by 50%.

Over-all performance of the calorimeter was checked by measurement of the heat of neutralization of 0.1445 *m* HCl titrated with 3.474 *m* NaOH. Conditions were maintained so as to correspond both in the quantity of heat developed in the calorimeter and in the volume increments of titrant to those of the other experiments, *i.e.*, of the order of 1 cal and 15 μl, respectively. The average of a series of such measurements at 27° gave -13.3 ± 0.1 kcal for Δ*H*_{*f*} for water at 25° after correction for the heat of dilution⁹ and temperature.¹⁰ The agreement with the value reported by Vanderzee and Swanson (-13.34 kcal) is within the 1% over-all accuracy sought for incremental heat measurements with the calorimeter.

(C) **Solutions.**—Great care was exercised in the preparation and manipulation of all solutions in order to keep the initial water concentration at very low levels. Stock solutions of the metal perchlorates were prepared from reagent grade butanol and the hexahydrates. The bulk water was first removed by azeotropic distillation, leaving a residual water content of about 0.02%. The final traces were removed by refluxing at 15 torr over a bed of Linde Type 3A Molecular Sieve in a modified Soxhlet apparatus for 6 hr.¹¹ Water content, by Karl Fischer analysis, was 0.0001% after this treatment.

All transfers of solutions were done by syringe, and the calorimeter was flushed with dried nitrogen before the solutions were admitted. Allowing for some moisture introduced from the baked glassware, an upper limit of 0.001% water can be placed upon the initial water concentration in the calorimeter.

(D) **Conductivity.**—The electrical conductivity of certain of the solutions was measured as a function of water concentration over the range of concentrations studied calorimetrically. A precision Leeds and Northrup Jones-type conductivity bridge, 1000-cps oscillator, and dilution cell were used. Water was added by a micrometer syringe to the cell immersed in an oil bath at 25.000 ± 0.005°.

(9) C. E. Vanderzee and J. A. Swanson, *J. Phys. Chem.*, **67**, 2608 (1963).

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 754.

(11) P. W. Arthur, W. M. Haynes, and L. P. Varga, *Anal. Chem.*, **38**, 1930 (1966).

Results

Nature of Butanol Solutions.—In a solvent of relatively small dielectric constant such as butanol (*D* ≈ 17), 2:1 transition metal perchlorates could be expected to be only partially ionized at concentrations of 10⁻³ *M* or more; this is confirmed qualitatively by the equivalent conductance curves for Ni(ClO₄)₂ shown in Figure 5. Not only are the shapes of the curves typical of those for weak electrolytes, but in the range of water concentrations (<0.5% by weight) and salt concentrations (8 × 10⁻² *M* > *C* > 1 × 10⁻² *M*) corresponding to the calorimetric measurements the conductance is quite small and changes little (<1 ohm⁻¹) with either water or salt concentration. By estimating the limiting conductances from Walden's viscosity-conductance product rule it can be shown that even in mixtures high in water content (*ca.* 20% by weight) the first-order ion association may be as much as 50% at concentrations of the order of 10⁻⁴ *M*.¹²

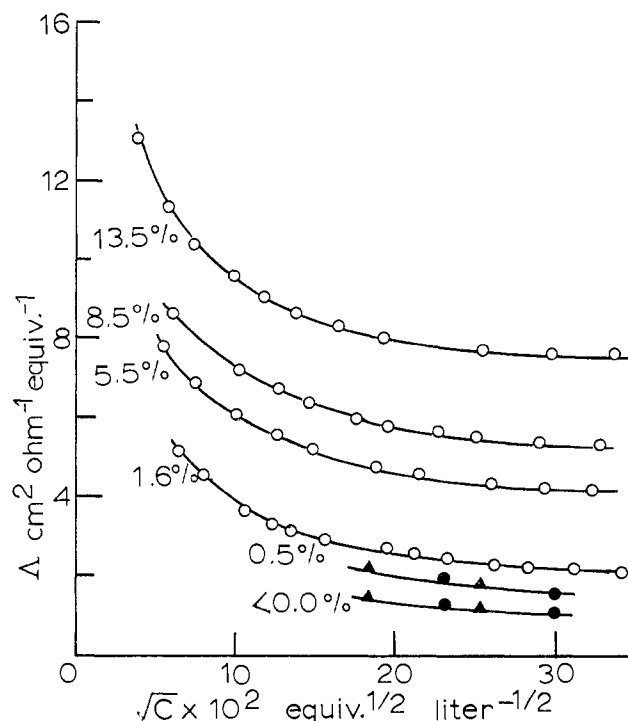


Figure 5.—Equivalent conductance at 25° as a function of water content of solutions. Solid circles and triangles refer to Ni(ClO₄)₂ and Co(ClO₄)₂ solutions, respectively, of this study; open circles refer to Ni(ClO₄)₂ solutions of larger water content than those of the calorimetric measurements.

The assumption of a simple substitution reaction of butanol-solvated Co²⁺ or Ni²⁺ ions with water (eq 2) does not seem to be justified, therefore, for the solutions studied except as applied to inner-sphere substitution for butanol in coordination complexes with perchlorate ions. The small values of the conductance suggest that both metal salts should be regarded as essentially electrolytically undissociated, and the thermal data have been treated on this basis.

Corresponding Solutions Treatment of Mixed Com-

(12) P. L. Cheung, Ph.D. Thesis, Oklahoma State University, Stillwater, Okla., 1967.

plexes.—The implications of the above assumption are made clearer by extension of the theory of corresponding solutions to include the mixed ligand complexes ML_nX_p where L is water and X is the perchlorate anion. Solvent butanol is not explicitly included in the formulation for convenience, though it is assumed to occupy coordination positions. For such complexes one has from equilibrium considerations

$$(ML_nX_p) = \beta_n \beta_{np}^* (M)(L)^n (X)^p \quad (4)$$

where

$$\beta_n = \prod_0^n k_n, \beta_{np}^* = \prod_0^p k_{np}^* \\ k_n = \frac{(ML_n)}{(ML_{n-1})(L)}, k_{np}^* = \frac{(ML_nX_p)}{(ML_nX_{p-1})(X)} \quad (5)$$

The ligand number for L (water) is formulated as usual from the stoichiometric concentrations of metal and ligand by

$$\bar{n} = \frac{C_L - (L)}{C_M} = \frac{\sum_0^n \sum_0^p n \beta_n \beta_{np}^* (L)^n (X)^p}{\sum_0^n \sum_0^p \beta_n \beta_{np}^* (L)^n (X)^p} \quad (6)$$

$$\bar{n} = \sum_0^n \sum_0^p n w_{np} \quad (7)$$

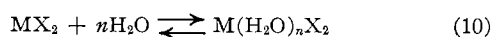
where the fraction w_{np} of M in the form of the complex ML_nX_p is

$$w_{np} = \frac{\beta_n \beta_{np}^* (L)^n (X)^p}{\sum_0^n \sum_0^p \beta_n \beta_{np}^* (L)^n (X)^p} \quad (8)$$

The heat of mixing per mole of metal is, corresponding to eq 1

$$\Delta \bar{H} = h_{np} w_{np} \quad (9)$$

Thus two solutions for which $\Delta \bar{H} = \Delta \bar{H}'$ are corresponding, and for these $w_{np} = w'_{np}$. The excellent agreement of the experimental results of Figure 3 with the linear relation predicted by eq 6 between C_L and C_M , when these are chosen on the basis of eq 9, substantiates the applicability of the corresponding solutions treatment to the thermal data. However, if \bar{n} is to be a function of (L), the concentration of water, only, it can be seen from eq 6 that the concentration of perchlorate must remain constant throughout; this is possible only in the limiting cases of complete dissociation or complete association. In the latter case eq 2 becomes



The thermodynamic quantities of Table I apply to eq 10. No attempt was made to maintain a constant ionic strength medium in order to minimize changes in activity coefficients for two reasons: first, a large concentration of background salt would be expected to produce thermal effects masking the primary reaction of interest through competitive reaction with water; second, activity coefficients justifiably may be taken as approximately unity for uncharged com-

plexes under the conditions of the small (and approximately constant) degree of ionization obtained in the experiments.

Thermodynamic Properties.—The formation constants of Table I are based upon the normal coordination number N of 6 for both cobalt and nickel ions in their complexes. Support for this coordination number comes also from the octahedral ligand field spectra of the solutions. As water is added to the anhydrous solutions, the peaks shift somewhat toward higher frequencies, but there is no change in the band system indicative of a change in coordination number; when the solutions become saturated with water, the spectra are almost identical with those of aqueous solutions of the salts.

In principle, the $(\bar{n}, -\log(L))$ curve should become asymptotic to the $\bar{n} = N$ line. However, corresponding solutions for the determination of the limiting value N of \bar{n} could not be selected reliably from the curves of Figures 1 and 2 at water concentrations above about 0.5 M , particularly for the more concentrated salt solutions. This is largely due to the small increase in the heat of reaction with further increase in water concentration. For example, at $\bar{n} = 2$ over 60% of the total heat of the reaction has been evolved, and beyond $\bar{n} = 2$ the quantity of heat produced decreases rapidly.

Although the data could not be fitted satisfactorily with $N < 6$, it was necessary to extrapolate the pseudo-constant curve to estimate values for K_n with $n > 4$. Table I lists the first five over-all formation constants based upon $N = 6$, together with the corresponding enthalpy and entropy values. Those corresponding to β_5 are enclosed in parentheses to indicate a lower degree of confidence.

A maximum coordination of $N > 6$ is not ruled out by the experimental data. By choosing corresponding solutions from among only the less concentrated salt solutions of relatively high water content, one can construct plots similar to those of Figure 3 whose slopes (\bar{n} values) suggest that the experimental points of Figure 4 may not necessarily approach $N = 6$ as a limit. However, this conclusion is based upon linear plots involving fewer salt concentrations and being at ligand concentrations where there is more error inherent in the determination of the composition of solutions which are corresponding.

It is easily seen from eq 2 of ref 8 and the data of Figure 3 that arbitrary choice of any value of $N > 6$ can make only insignificant changes in the values of the first few formation constants. Hence the values listed in Table I may be considered valid for $N \geq 6$.

The magnitudes of the formation constants are comparable to those reported for Cu^{2+} in nitromethane¹ and are quite close to those in acetone² where some degree of ion pairing is indicated in mixtures with 0.1 M $LiClO_4$. Affinity of nickel for water relative to butanol appears to be slightly greater than that of cobalt. Similar preference has been observed by Pasternack and Plane⁵ in ethanol-water mixtures of the

perchlorates, though the opposite has been reported for solutions of nitrates in ethanol.⁴

The enthalpies of formation of aquo complexes for cobalt and nickel perchlorates from their butanol solutions are small and almost the same for the two salts. Significantly, there is observed a marked disparity in the values of the first two stepwise energies of binding and the values of the others. In aqueous solutions where complete dissociation may be assumed the enthalpies of formation of complexes with neutral ligands in most cases have been found to be consistent with eq 3 which is based upon the empirical relation

$$h_n = nh_1 \quad (11)$$

implying that the binding energy is the same for each successive ligand added and does not depend upon the number and position of prior substituted ligands. The much larger values of the first (~ 3 kcal mole⁻¹) and second (~ 2 kcal mole⁻¹) stepwise enthalpy changes compared with the third (~ 0.6 kcal mole⁻¹) or fourth (~ 0.3 kcal mole⁻¹) support the contention that the metal species has a lower symmetry than the free solvated ion.

Over-all entropy of formation values are small, as would be expected for uncharged ligands, and when reduced to the mole fraction (unitary) basis by

$$\Delta S'_n = \Delta S_n + nR \ln (10^3/W) = \Delta S_n + 5.17n \quad (12)$$

where W is the formula weight of butanol and ΔS_n is the entropy change on the molality scale, they are all positive. Table I shows that the entropy change in eq 10 does not become favorable until after the first two coordination positions have been occupied, but then the (positive) entropy change is about equally

as important as the enthalpy change for further substitution of water for butanol.

Unfortunately, the experiments cannot resolve the question of inner-sphere *vs.* outer-sphere coordination of perchlorate. The relatively larger enthalpy changes for the first two substitution reactions by water are explicable on either basis. A rather large number of solid perchlorato complexes of copper and nickel have been found to contain monodentate and even bidentate perchlorate ligand. These include nickel perchlorate dihydrate¹³ and numerous complexes having nitrogen donors where structural requirements of the ligand may be critical.¹⁴ Perchloratobis(2,2'-bipyridyl)copper (II) ion may be formed in nitrobenzene solution also.¹⁵

There is no evidence that perchlorato complexes are formed in alcohol solutions, and we favor ion association for the butanol system. A model shows that substitution of water for butanol in the *trans* position permits a closer approach of the perchlorate anions to the metal with the result that the water dipoles aligned along the axis are in positions of lower potential energy than are molecules in equatorial positions. This could lead to stronger binding of the water ligand in such positions and a greater loss in entropy relative to the bulkier butanol molecule.

Acknowledgment.—The support of the U. S. Atomic Energy Commission under Contract AT(11-1)-1175 is gratefully acknowledged. The authors also wish to thank Dr. David G. Rands for permission to include some of his conductance data for Ni(ClO₄)₂ solutions in butanol–water solvent.

(13) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(14) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965).

(15) N. T. Barker, C. M. Harris, and E. D. McKenzie, *Proc. Chem. Soc.*, 335 (1961).

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On the Ternary System Samarium–Nitrogen–Oxygen and the Question of Lower Oxides of Samarium¹

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The ternary compounds SmN_{1-x}O_x ($0 < x \leq 0.5$) have been prepared; preparations where $x = 0.5$ have the same properties as substances previously thought to be SmO. The lattice parameter of SmN_{1-x}O_x, which has the NaCl structure, decreases continuously with increase in x . This suggests that as the nitrogen of SmN is replaced by oxygen, the 3+ valency of the samarium ion is retained although, formally, the oxygen–nitrogen exchange must result in the reduction of an equivalent amount of Sm³⁺ to Sm²⁺. SmN_{1-x}O_x undergoes hydrolysis on exposure to the atmosphere, and, on dissolving it in acid, hydrogen is evolved. The compound previously thought to be Sm₂O was found to be, in reality, SmH₂.

Introduction

This paper presents results of a study of phases previously thought to constitute part of the SmO_x–O₂ system in the range where x is between 0 and 1.5.

(1) This research was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-1109. It was taken from a dissertation by T. L. F. submitted for the Ph.D. degree in 1966 and was presented at the Fifth Rare Earth Research Conference, Ames, Iowa, 1965.

No lower oxide of samarium could be prepared during the course of this investigation although substances fitting the description of those reported to be SmO and Sm₂O^{2,3} have been prepared and found to be

(2) H. A. Eick, Ph.D. Thesis, Department of Chemistry, State University of Iowa, 1956.

(3) H. A. Eick, N. C. Baenziger, and L. Eyring, *J. Am. Chem. Soc.*, **78**, 5147 (1956).