and 950 cm⁻¹. At atmospheric pressure, it is possible to produce trioxane from oxalic ion. On that occasion both iron and iron ion play a role as a catalyst. A speculation identifying these two facts may be somewhat indicative of the bonding in the high-pressure product.

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Fourier Transform Carbon-13 Nuclear Magnetic Resonance of Aqueous Nickel(II)–Acetic Acid Solutions. I. Equilibrium Quotients from Relative Abundances of Solution Species[1]

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The complex formation reaction between nickel(II) and acetate ions in aqueous solution has been studied by Fourier transform carbon-13 nuclear magnetic resonance. Equilibrium quotients for the formation of monoacetatonickel(II) complex were calculated from the relative areas of distinct coordinated and bulk acetate signals over the temperature range −5 to +20° and were found to be constant over this range. Equilibrium quotients determined over the ionic strength range 1.2–4.0 *m* were found to be smaller than previously reported values. A minimum in the equilibrium quotient was observed at approximately 2 *m* ionic strength.

Introduction

The weak complex formation reaction between nickel(II) ion and acetate ion in aqueous solution has been investigated by various physical methods.[3–14] It has been generally assumed that only the monoacetatonickel(II) species is formed appreciably, although formation constants for higher acetato species have been reported.[11–14] Wide scatter of the reported formation constants in the ionic strength range 0–1 *M* possibly reflects a high sensitivity of the formation constant to ionic strength or, instead, a high sensitivity to the widely varying reaction conditions required by each method. In addition, no results are available for this reaction at ionic strengths higher than 1 *M*.[15] We report here equilibrium quotients obtained from carbon-13 nuclear magnetic resonance (¹³C NMR) studies of aqueous solutions of nickel(II) and 90 atom % ¹³C-enriched carboxyl-labeled acetic acid, CH₃¹³COOH, for the formation of monoacetatonickel(II) over the ionic strength range 1.2–4.0 *m*.

The combination of selective high ¹³C enrichment and proton-decoupled Fourier transform ¹³C NMR is sufficient to overcome inherent experimental difficulties arising from the low natural abundance and small magnetic moment of carbon-13, as well as paramagnetic line broadening from nickel(II). Simultaneous observation of ¹³C acetate signals in bulk solution and acetate bound to nickel(II) is possible below 20°, the bound acetate signal appearing upfield from that of bulk acetate. Relatively few such systems[16–21] have been studied because the experimental conditions necessary for detection of distinct coordinated and bulk signals are often not attainable.[16,20]

Experimental Section

Materials. Ni(ClO₄)₂·6H₂O and anhydrous NaClO₄ were purchased from the G. F. Smith Chemical Co. and used without further purification. The nickel salt was analyzed by titration with ethylenediaminetetraacetic acid and Murexide indicator, according to Welcher.[22] Acetic acid enriched to 90.0 atom % ¹³C in the carboxyl position was a gift from D. G. Ott and V. Kerr of the Los Alamos Scientific Laboratory. All samples were prepared by weight in 99.5% D₂O and used without further analysis. Samples were adjusted to pH 5.5–6.0 with a 6 *m* solution of NaOD in D₂O. The pH recorded was that observed with an Orion 700 pH meter equipped with a combination electrode. In general, the pD correction (pH = pD − 0.4) and the pK correction for deuterium isotope effects essentially

offset each other.[23,24] Because the differences resulting from these corrections are small for the specific case of acetic acid, no attempt was made to record pD values.

Magnetic Resonance Methods. Proton-decoupled ¹³C NMR Fourier transform spectra were obtained at 25.2 MHz with a Varian Associates XL-100-15-FT spectrometer interfaced to a Data General Supernova computer. The magnetic field was stabilized by locking to the 15.4-MHz deuterium resonance of internal D₂O. Free induction decays of 40-μsec radiofrequency pulses were accumulated as 8192 data points in the time domain and transformed as 4096 data points in the frequency domain. In some cases, when the highest resolution capability was not required, 4096 time domain and 2048 frequency domain data points were used. Samples were contained in 12-mm (o.d.) Pyrex glass tubes spinning at 14–16 revolutions/sec in the probe. Temperature was varied by flowing heated or cooled nitrogen gas through the probe and around the sample tube. The sample temperature was checked before and after individual measurements with a copper–constantan thermocouple inserted into an NMR tube filled with a standard solution. Sample temperatures were found to be constant within ±1.0°.

Relative signal areas were obtained from transformed spectra by various manual integration methods and by analog curve fitting with a Du Pont 301 curve analyzer adjusted to fit lorentzian lines.

Treatment of Data and Results

The spectrum of a representative solution at 0° is shown in Figure 1. The strong alternating magnetic field due to nickel(II) ion's two unpaired electrons broadens the bound acetate resonance, which appears 111.3 ppm upfield in Figure 1. Relative intensities of the separate bound and free acetate signals remain essentially constant in the temperature range −5 to +20°, for a given solution composition. No evidence for other carbon-13 resonances was observed in the spectra, although broad peaks representing less than 10% of total acetate are probably not observable.

Assuming formation of only one complex species, [Ni(OAc)(H₂O)₅⁺], molal concentrations of the various solution components were calculated directly from P_M and P_L, the fractions of bound and free acetate, respectively, according to eq 1, where $(m_{Ni})_0$ and $(m_{HOAc})_0$ are the stoichiometric molal concentrations of Ni(ClO₄)₂ and [1-¹³C]acetic acid; m_{HOAc} and m_{OAc^-} are the molal concentrations of undissociated acetic acid and bulk acetate, respectively; and $m_{Ni^{2+}}$ and m_{NiOAc^+} are the molal concentrations of uncomplexed nickel ion and monoacetatonickel(II) complex, respectively. The

Table I. Equilibrium Quotients for Monoacetatonickel(II)

$(m_{Ni})_0$	$(m_{HOAc})_0$	$m_{NaClO_4}{}^a$	pH	P_M	m_{OAc^-}	I, m	Q_1, m^{-1}
0.192	0.988	0	6.00	0.11_5	0.835	1.24	1.7 ± 0.4
0.258	0.866	0	5.98	0.16_5	0.689	1.25	1.8 ± 0.4
0.466	0.238	0	5.90	0.36	0.143	1.41	1.6 ± 0.1
0.472	0.504	0	5.80	0.31	0.320	1.50	1.6 ± 0.1
0.500	0.584	0	5.70	0.32	0.355	1.58	1.7 ± 0.2
0.427	0.970	0	6.00	0.23	0.705	1.65	1.5 ± 0.3
0.453	0.949	0	5.80	0.24	0.656	1.67	1.5 ± 0.3
0.701	0.552	0	6.01	0.39	0.310	2.09	1.4 ± 0.1
0.823	0.916	0	5.62	0.39	0.451	2.38	1.7 ± 0.4
0.841	0.451	0	5.67	0.43	0.217	2.45	1.4 ± 0.2
0.458	0.969	1.36	5.75	0.28_5	0.569	2.89	2.7 ± 0.4
0.472	0.500	1.59	5.82	0.36	0.270	3.00	2.3 ± 0.3
0.460	0.238	1.89	5.90	0.46	0.107	3.21	2.9 ± 0.3
0.456	0.965	2.71	5.70	0.34	0.455	4.04	5.6 ± 0.6

a Added to vary ionic strength.
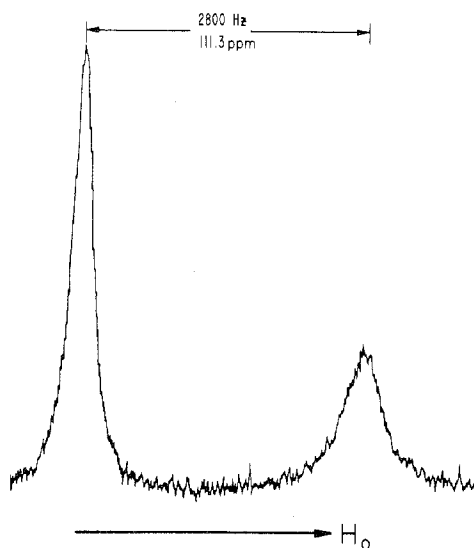
Figure 1. The 25.2-MHz ^{13}C NMR spectrum at 0° of a D_2O solution containing 0.701 m Ni(ClO$_4$)$_2$ and 0.552 m CH$_3$^{13}COOH. The downfield and upfield signals represent bulk acetate and monoacetatonickel(II), respectively.

$$(m_{HOAc})_0 = m_{HOAc} + m_{OAc^-} + m_{NiOAc^+}$$

$$(m_{Ni})_0 = m_{Ni^{2+}} + m_{NiOAc^+}$$

$$m_{NiOAc^+} = P_M(m_{HOAc})_0$$

$$m_{Ni^{2+}} = (m_{Ni})_0 - m_{NiOAc^+}$$

$$m_{OAc^-} = P_L(m_{HOAc})_0 [K_{HOAc}/K_{HOAc} + [H^+])] \tag{1}$$

acetic acid ionization equilibrium constant, K_{HOAc}, was corrected for ionic strength effects according to Ellilä.[25] Deuterium isotope effects were not included for reasons mentioned in the Experimental Section. Total ionic strength of the solutions is defined as

$$I = 0.5 [4m_{Ni^{2+}} + m_{ClO_4^-} + m_{Na^+} + m_{OAc^-} +$$
$$m_{NiOAc^+}] \tag{2}$$

The contributions of hydronium and hydroxide ions to the total ionic strength are negligible in the pH range studied and are not included in eq 2.

Formation of the monoacetato complex, [NiOAc(H$_2$O)$_5$$^+$], according to the equilibrium reaction

$$\underset{I}{Ni(H_2O)_6{}^{2+}} + OAc^- \rightleftharpoons \underset{II}{NiOAc(H_2O)_5{}^+} + H_2O \tag{3}$$

is governed by the expression

$$K_1 = (m_{II}\gamma_+\alpha_{H_2O})/(m_I\gamma_{2+}m_{OAc^-}\gamma_-) \tag{4}$$

in which K_1 is the thermodynamic formation constant for

Table II. Literature Formation Constants for Aqueous Acetatonickel(II) Complexes

Method	$T, °C$	Ionic medium	K_1, M^{-1}	K_2, M^{-1}	Ref
Polarographic	15	0.2 M NaNO$_3$	2.6		6
Polarographic	25	0.2 M NaNO$_3$	2.6		6
Polarographic	35	0.2 M NaNO$_3$	2.4		6
Polarographic	25	1.0 M NaClO$_4$	1.9		8
Polarographic	25	1.0 M NaClO$_4$	2.3	3.3	14
Glass electrode	25	None	27		9
Glass electrode	25	1 M NaClO$_4$	10.0		7
Glass electrode	22	None	13.1	4.9	12
EMF	30	0.01–0.1 M Ba(OAc)$_2$	13.5		3
Quinhydrone electrode	20	1.0 M NaClO$_4$	5.5		11
Ion exchange	20	1.0 M NaClO$_4$	4.7	3.8	11
Spectrophotometric	20	Varied	45	20	13
Spectrophotometric	25	0.1 M NaClO$_4$	5.5		10
Spectrophotometric	22	None	13.2		5
Spectrophotometric	25	None	63		4

[NiOAc(H$_2$O)$_5$$^+$] and a_{H_2O} is water activity; m_I, m_{II}, and m_{OAc^-} are the equilibrium molal concentrations and γ_{2+}, γ_+, and γ_- are the individual ionic activity coefficients for Ni(H$_2$O)$_6$$^{2+}$, NiOAc(H$_2$O)$_5$$^+$, and CH$_3COO^-$, respectively.
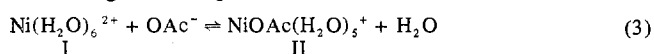
Because individual ionic activity coefficients are thermodynamically indeterminate,[26] expression 4 must be modified in terms of the thermodynamically accessible coefficients

$$\gamma_I = \gamma_{2+}\gamma_-{}^2 \qquad \gamma_{II} = \gamma_+\gamma_- \tag{5}$$

and the experimentally measured equilibrium quotient

$$Q_1 = m_{II}/m_I m_{OAc^-} \tag{6}$$

to yield

$$Q_1 = K_1\gamma_I/\gamma_{II}a_{H_2O} \tag{7}$$

Assuming that K_1 is truly a constant for reaction 3, the quantity $\gamma_I/\gamma_{II}a_{H_2O}$ for a given ionic strength is proportional to Q_1. Calculation of numerical values for the former quantity requires an estimate of Q_1 at $I = 0$, an extrapolation which is hazardous in this instance.

Results of area measurements are given in Table I. The error in P_M is estimated to be less than 10%, based on the reproducibility of the spectra for a given solution composition and temperature. Equilibrium constants obtained by others are listed in Table II. The behavior of Q_1 with respect to ionic strength, I, is shown in Figure 2. A minimum value, $Q_1 \approx$ 1.4 m^{-1}, appears at $I \approx 2.0$ m, followed by rapidly increasing Q_1 values with increasing ionic strength. Addition of sodium
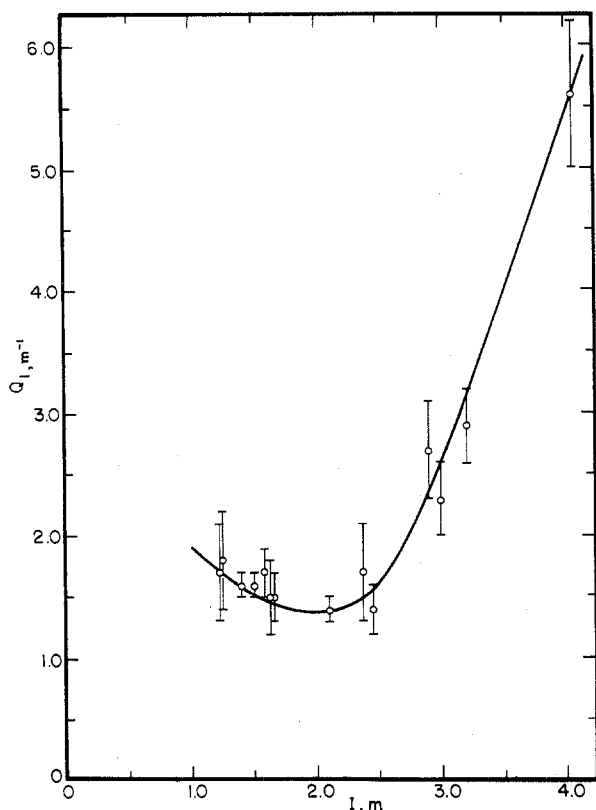
Figure 2. Ionic strength dependence of the equilibrium quotient for monoacetatonickel(II) complex formation.

perchlorate, to vary ionic strength, resulted in an increase in P_M, and therefore Q_1, with increasing ionic strength for a particular stoichiometric nickel(II) to acetic acid ratio at the pH values observed. Results with groups of solutions having similar ionic strengths, but different free acetate concentrations, yield essentially equal equilibrium quotients.

Discussion

Q_1 is an experimentally measured quantity dependent on the assumption that only monoacetatonickel(II) complex is formed, an assumption supported by data in the lower temperature range where distinct coordinated and bulk acetate signals are observed. Tanaka et al.[6,8] found Q_1 to be constant over the temperature range 15–35° in a polarographic study of the same system. Their values $Q_1 = 1.9\ m^{-1}$ at $I = 1.0\ m$[8] and $Q_1 = 2.6\ m^{-1}$ at $I = 0.2\ m$,[6] both at 25°, correspond to a logical extrapolation to lower ionic strength in Figure 2. Thermochemical data available for a series of metal–acetate complexes in aqueous solution indicate that a minimum in the complex formation constant is often found in the range 1–2 M ionic strength.[27-29] The observed increase of Q_1 at higher ionic strengths is best explained in terms of decreasing water activities.

The use of "swamping" ionic media to maintain activity coefficients constant has been extensively employed in formation constant investigations.[15] However, constant ionic strength does not ensure constancy of activity coefficients, because specific ionic effects may dominate the equilibria.[30] Nevertheless, selected groups of solutions at similar ionic strengths, but different acetate and metal ion concentrations, gave essentially equal equilibrium quotients. Extrapolated and interpolated values for the ionic strength range $I = 1–4\ m$ are listed in Table III.

Equilibrium quotients in this study are generally smaller than previously reported values (see Table II). In comparison of equilibrium quotients obtained here and those values, it is worthwhile to examine more closely the nature of P_M and P_L

Table III. Equilibrium Quotients at Various Ionic Strengths

I, m	1.0	2.0	3.0	4.0
Q_1, m^{-1}	1.9	1.4	2.8	5.6

in the NMR experiment. In principle, P_M and P_L are dependent only on the statistical distribution of nuclear spins in different magnetic environments. Assuming that P_M represents only monoacetatonickel(II), then P_L, the unbound fraction, must contain free acetate in bulk solution, undissociated acetic acid, and any other acetate forms not in the primary coordination sphere of nickel(II) ion. These forms include outer-sphere[31] or contact ion complexed acetate. The magnitude of the 13C chemical shift between the bound and unbound fractions is such that acetate represented by P_M can only be attributed to those groups in direct contact with the electronic spin density of the paramagnetic nickel(II) inner sphere. In contrast, formation constants determined by other methods often reflect mass action principles, compromised by experimental conditions and thermodynamic considerations. The effect is that they often cannot distinguish between inner-sphere and outer-sphere complexed ligands for the case of weak complex formation, thus accounting for the larger constants reported.

In general, polarographic results are in best agreement with the 13C NMR values, while those from spectrophotometric methods are least comparable. Although data are reported here only for the first formation constant, investigation of the temperature dependence of the 13C chemical shift indicates the presence of higher species and/or conformational changes above 50°. The chemical shift studies, as well as the temperature dependence of 13C line broadening, will be discussed elsewhere.[32]

Registry No. [Ni(OAc)(H2O)$_5$+], 25403-79-6.

References and Notes

(1) Work performed under the auspices of the U.S. Atomic Energy Commission and with the support of the Robert A. Welch Foundation, Houston, Tex., under Grant No. F-041.
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Hydrogen Bonding. V. Possible Existence of Strongly Hydrogen-Bonded Water–Fluoride and Water–Hydroxide Complex Anions, (F⁻·H2O)2²⁻ and (OH⁻·H2O)2²⁻, in Tetramethylammonium Ion Salt Hydrates[1,2]

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Tetramethylammonium fluoride and hydroxide form stable monohydrates from which water is removed only with difficulty at high temperatures with concurrent decomposition to trimethylamine. The infrared spectra of the monohydrates are completely different from those of the higher clathrate hydrates and show, in addition to cation bands and stretching and bending bands representative of strongly hydrogen-bonded O–H, two intense bands in the region assigned to rocking or torsional modes of tightly coordinated water (tricoordinated oxygen). Cation C–H to anion hydrogen bonding is present but is not strong enough to account for the third coordinate link to water. This fact, coupled with steric limitations on anion size and the appearance of the cation infrared spectra of the hydrates, suggests that discrete, probably dinegative, water–anion species exist in these salts. This is supported by symmetry coordinate analysis of the proposed molecular ions and by topological equivalent-orbital approach comparisons.

Introduction

Tetraalkylammonium ions have a remarkable ability to order water about themselves both in solution[4] and in a wide variety of solid clathrate hydrates.[5-13] Of these latter compound types, Jeffrey[14] has written: "We may expect to find a rational and continuous series of hydrated crystal structures ranging from the pure clathrates of the gas hydrate type through intermediate framework structures, to structures where the water molecules are arranged in hydrogen bonded sheets, ribbons, and chains, and finally structures where the water molecules are isolated from each other as in many of the simpler hydrated salts." This paper reports work on compounds at the low end of Jeffrey's hydration scale for which structures have not been determined, including tetramethylammonium hydroxide trihydrate,[15] the new compounds tetramethylammonium fluoride trihydrate and hydroxide hemihydrate, and most particularly tetramethylammonium hydroxide monohydrate[15] and fluoride monohydrate.[16] These latter two hydrates, which—although known for many years—have not previously been studied by physical–chemical methods, apparently represent the final hydration type listed by Jeffrey, in which water and anion are bound tightly together in discrete molecular ions.

Preparation and Properties of the Hydrates

The higher hydrates of tetramethylammonium fluoride lose water with relative ease to give the white, crystalline monohydrate; however, the salt clings to this last mole of water with great tenacity. We find that drying at 117° and 0.1 Torr over phosphorus pentoxide for 1 week gives no change in the O–H:N–C infrared intensity ratio. The anhydrous salt can be prepared by extended heating in vacuo at 160°,[16] but this process is accompanied by some decomposition to methyl fluoride and trimethylamine. This suggests that the water is unusually tightly bound in the crystal. By comparison, hydroxytropenylium iodide monohydrate, in which the hydrogen bond between cation hydroxyl and water is in the range of 17 kcal/mol and the water is additionally hydrogen bonded to anions,[17] readily loses its water on drying in vacuo at room temperature.

The thermal decomposition of tetramethylammonium hydroxide has been studied in some detail.[18-20] This decomposition, which takes place to some extent even in solution,[18] renders it impossible to prepare completely pure tetramethylammonium hydroxide monohydrate. By means of short-path connection to a liquid nitrogen trap we were able to keep heating to a minimum and prepare monohydrate with satisfactory analyses; however, this material still shows infrared absorptions of trace impurities which are presumed to be polymethylene.[19] Deuterium oxide is removed from tetramethylammonium hydroxide monohydrate-*d*3 more easily than water from the corresponding hydrate, and it is possible to approach the stoichiometry of the monohydrate-*d*3 at room temperature without apparent decomposition.

An interesting side observation was made in early attempts to prepare the monohydrate-*d*3 by treatment of tetramethylammonium chloride with silver oxide in deuterium oxide followed by concentration of the solution and warming of the crystalline mass in vacuo. Even though all reagents and the reaction system were rigorously freed of water and the initial pentahydrate obtained was shown by infrared analysis to contain only deuterium oxide, the material left after drying consisted only of the ordinary monohydrate. Since the only proton source in the system is the cation and the salt was observed to decompose significantly in the drying process, this observation offers strong support for the Musker mechanism of decomposition by ylide formation through proton abstraction.[19,21]

Tetramethylammonium fluoride trihydrate and tetrahydrate and the hydroxide trihydrate were prepared by addition of the required amount of water to the respective monohydrates; the fluoride trihydrate is apparently a new compound. Tetramethylammonium hydroxide hemihydrate was prepared by extended drying of the pentahydrate with mild warming in vacuo. Since this process was accompanied by relatively little overall loss of sample through decomposition, the formation of the ylide does not become prominent until at least this stage of drying has been reached. We are investigating the preparation of the anhydrous hydroxide but are not sanguine.

All of the hydrates are white, crystalline materials which are extremely hygroscopic; tetramethylammonium fluoride monohydrate readily deliquesces in the presence of slightly filmed phosphorus pentoxide, although it is stable in the