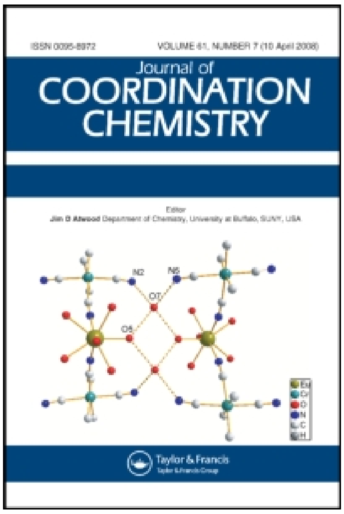

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Stoichiometries and stability constants for the cerium(IV) carbonate complexes in dilute aqueous solution

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Complexation between cerium(IV) and carbonate ions in aqueous solution has been studied by UV/Visible absorption spectroscopy, ^{17}O NMR spectroscopy and potentiometric titration, and it is shown that in dilute solutions at pH 8.8 and 10, both 1 : 1 and 1 : 2 (metal : ligand) complexes are formed. This contrasts with the behaviour of the corresponding Th(IV) complex, where the dominant species is the pentacarbonato complex. From the NMR spectra, it is suggested that these species involve bidentate binding of carbonate ion by the metal, while potentiometric data provided accurate formation constants and indicated the dominant species to be the 1 : 2 complex.

Keywords: Cerium(IV); Carbonate; Complexes; Stability constants

1. Introduction

Complex equilibria involving carbon dioxide and water have been extensively studied [1] and under environmental conditions both carbonate and hydrogen carbonate (bicarbonate) ions are important species. Interaction between heavy metal cations such as actinides and carbonate or hydrogen carbonate ions in aqueous solution is of considerable importance in terms of environmental effects, geochemical transport, and, in general terms, of problems of pollution of surface waters [2]. Much interest has been focussed on the interaction between thorium(IV) and carbonate ions and detailed information obtained on complex structures both in solution and the solid state [3–8]. We have been interested in a comparison of the behaviour of thorium(IV) with the corresponding lanthanide, cerium(IV), and have reported a study of the behaviour of these cations with carbonate ions in dilute solution at pH 8.8 using solvent extraction and neutron activation analysis [9, 10]. However, while the metal ions are closely related, marked differences are observed in complexation behaviour under these conditions. At this pH carbonato complexes are formed and with Th(IV) it was possible to form a pentacarbonato species. In contrast to this and previous reports

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on the solid which precipitates from concentrated Ce(IV) solutions [6, 11–13], in the case of dilute cerium(IV) solutions the dominant species is suggested to be the dicarbonato complex. While solvent extraction coupled with neutron activation analysis has the advantage of high sensitivity, it is less informative with respect to the nature of the species produced than spectroscopic methods and gives less reliable values of stability constants than potentiometric methods. We have therefore extended the study of complexation of Ce(IV) using potentiometry, ^{17}O NMR and electronic spectroscopy, and have confirmed the formation of the $[Ce(CO_3)_2]$ complex. In addition, we demonstrate the formation of $[Ce(CO_3)]^{2+}$and provide reliable values for the stability constants of both species.

2. Experimental

2.1. *Reagents*

All reagents were of the purest grade available and generally used without further purification. Cerium(IV) ammonium nitrate was used in the preparation of all solutions. In all cases addition of ammonium carbonate to Ce(IV) solutions was necessary to avoid reduction to Ce(III) [7]. Doubly distilled water was used in all studies, except for NMR measurements, where the solvent was a mixture of D_2O and deionized water.

2.2. *Instrumentation*

Electronic spectra were recorded in the region 360–600 nm on a Shimadzu UV-260 spectrophotometer at room temperature ($20 \pm 1^\circ C$) in 10 cm quartz cuvettes. Large cells were necessary to give reasonable absorbance in the concentration range studied. In addition, it was not possible to make measurements at shorter wavelengths due to the strong absorbance of nitrate ion [14] under these conditions. Potentiometric measurements were carried out under nitrogen with aqueous solutions in a closed titration cell thermostatted at $25 \pm 0.01^\circ C$. A Metrohm AG 9100 Herisan combined glass electrode was used with a Crison Herisom Dosimat automatic burette. EMF measurements were made with a Crison WTW potentiometer interfaced to a computer. Equilibrium data were treated using the SUPERQUAD [15] program. ^{17}O NMR spectra were obtained on a Varian Unity-500 NMR spectrometer (67.760 MHz), using D_2O ($\delta = 0$ ppm) as external reference. Typically, spectral widths of 100 kHz, acquisition times of 0.02 s, pulse delays of 0 s and 350,000 pulses were used.

2.3. *Solution preparation*

Aqueous solutions for spectroscopic analysis were prepared using cerium(IV) ammonium nitrate and ammonium carbonate at pH 8.8 and 10, ionic strength 2.5 ± 0.2 mM, with pH adjusted by addition of nitric acid. Cerium(IV) concentrations were between 0.5 and 1.8×10^{-4} M, and were determined by redox titration with iron(II) using ferroin as indicator [16, 17]. Complexation was studied in these solutions on addition of carbonate/bicarbonate concentrations in the range 1.7 to 3×10^{-4} M and stoichiometry was determined using Job's method [18, 19], with a fixed total ionic concentration 3.5×10^{-4} M.

For potentiometric titrations, solutions were prepared at a Ce(IV) concentration of 1.0 mM and bicarbonate concentrations between 1 and 2 mM. Ionic strength was adjusted to 1.6×10^{-2} M with ammonium nitrate. These were titrated with standard sodium hydroxide and pH values determined.

For NMR studies, ^{17}O labelled ammonium carbonate solution was prepared by bubbling labelled CO_2 (Aldrich, Madrid, Spain) in deionized water. This was added to cerium(IV) ammonium nitrate with additional ammonium nitrate, the concentration determined by titration, and pH adjusted by addition of ammonia solution.

3. Results and discussion

Electronic spectra of aqueous solutions of cerium(IV) in the presence of carbonate ions at pH 8.8 and 10 were recorded, and Job's method was used to determine the stoichiometry of the complexes formed. The spectra showed red shifts at the absorption edge, and from the application of Job plots to absorbance at the corresponding analytical wavelength (370 nm for pH 8.8 and 380 nm for pH 10) the formation of 1 : 1 and 1 : 2 complexes is indicated (figure 1). These results were confirmed by potentiometric titrations for mol ratios $[Ce(IV)]/[CO_3^{2-}]$ of 0.5 and 1 (figures 2 and 3). From these experiments, formation constants of the two complexes were determined, and these are given in table 1. The high value of the formation constant for the 1 : 2 complex is in agreement with previous solvent extraction/neutron activation analysis measurements [9],

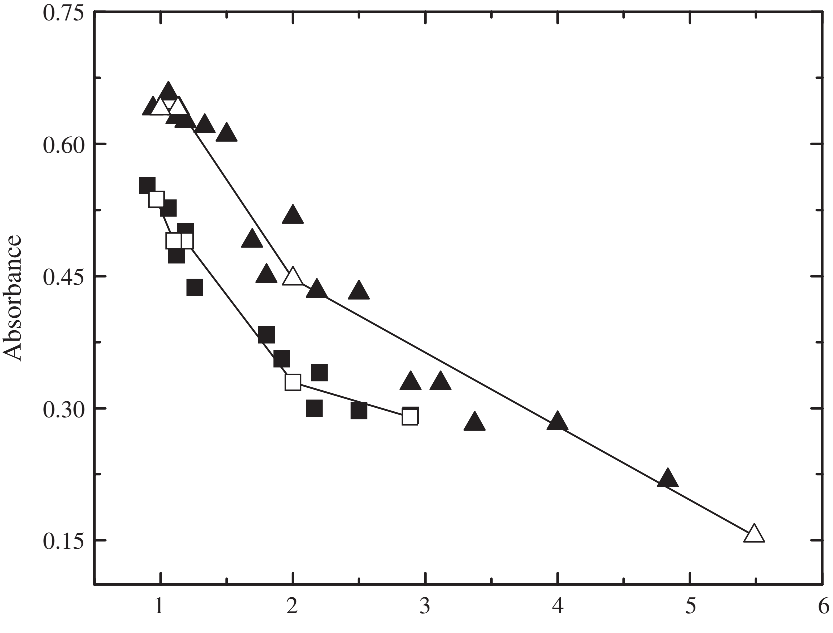

Figure 1. Job plots of absorbance as a function of the number of ligands, *n*, obtained from spectrophotometric data for complexation of cerium(IV) with carbonate ions in aqueous solution at pH 8.8 (triangles) and 10 (squares). The straight lines are the best fits to data (estimated error limits ±10%).

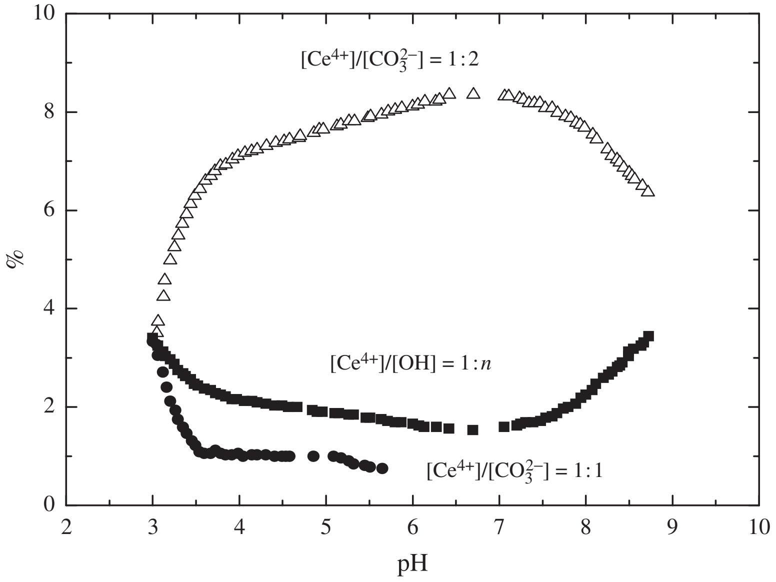

Figure 2. Relative percentages of complex species present in solution from potentiometric titrations for $[\mathrm{Ce(IV)}]/[\mathrm{CO}_3^{2-}]_\mathrm{T} = 0.5$ as a function of pH.

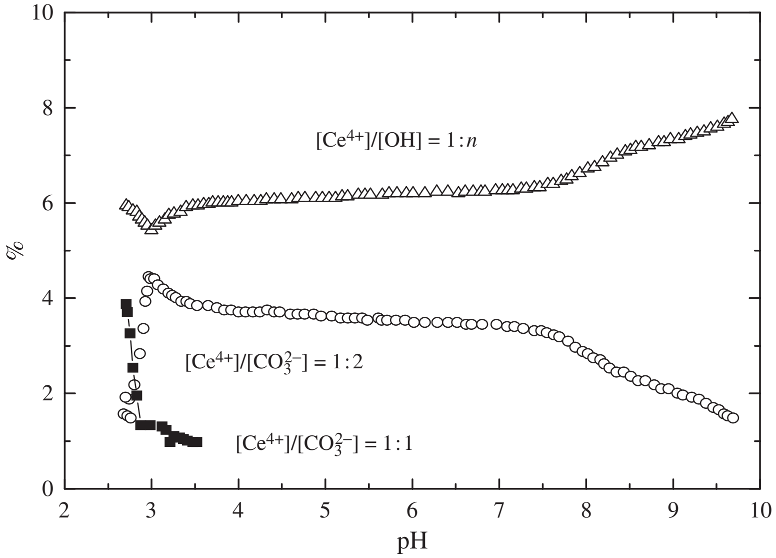

Figure 3. Relative percentages of complex species present in solution from potentiometric titrations for $[\mathrm{Ce(IV)}]/[\mathrm{CO}_3^{2-}]_\mathrm{T} = 1$ as a function of pH.

and confirms that this is the dominant species in solution under these conditions. However, the 1 : 1 complex is also formed in significant amounts.

Further information on complexation equilibria was obtained by ^{17}O NMR spectroscopy. Although it was necessary to use higher concentrations of cerium(IV) than with other techniques, the results do provide information on the structure and dynamics

Table 1. Formation constants (β) for complexes $[CeCO_3]^{2+}$ and $[Ce(CO_3)_2]$ obtained by potentiometric titration at $25.00 \pm 0.01°C$.

Stoichiometric coefficients			
Ligand (carbonate)	Metal (cerium)	H^+	Complex formation constant (β)
1	1	0	$(1.104 \pm 0.020) \times 10^{20}$
2	1	0	$(5.754 \pm 0.230) \times 10^{28}$

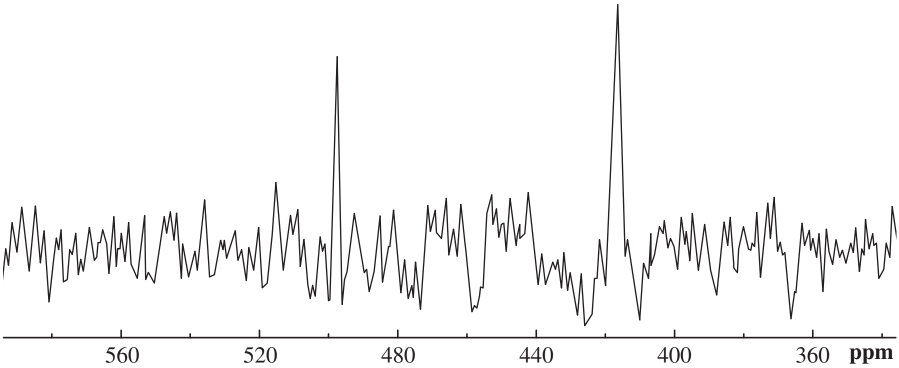

Figure 4. ^{17}O NMR spectrum of a solution of cerium(IV) and carbonate ions in H_2O/D_2O solution.

of the complex species. ^{17}O spectra run in H_2O/D_2O solution at a cerium(IV) concentration of approximately 5.0×10^{-2} M with a metal : carbonate ratio of 1 : 2 showed two sharp signals in the carbonate region at 416 and 497 ppm (figure 4). This is indicative of slow exchange of ligand on the NMR time scale. Taking into account the relative intensities of the two bands, it is possible to assign the signals observed at 416 and 497 ppm to two complexes with metal : ligand ratios of 1 : 2 and 1 : 1, respectively, in agreement with both the potentiometric and spectroscopic data. Previously, homologous complexes of uranium(VI) with carbonate ions have been characterized by ^{17}O NMR spectroscopy, and show a broad signal for complexed carbonate at about 225 ppm [20].

Chemical environment can dramatically influence the resonance frequency of a nucleus. The shielding constant may be written as the sum of diamagnetic and paramagnetic terms, which, respectively, describe the spherical and nonspherical circulation of electron density about the nucleus that is induced by the external magnetic field. For nuclei other than hydrogen, shielding effects are described only in terms of paramagnetic shielding, σ_p. This is strongly dependent on ΔE, the average difference in energy between the ground state and all the excited states of the molecule (including, in particular for these systems, ligand-to-metal charge transfer states) in addition to the charge density. A simplified form of the Ramsey equation is shown in (1),

$$\sigma_p = \frac{-2e^2h^2}{3m^2c^2\langle r^{-3}\rangle} P_u \left(\frac{1}{\Delta E}\right) \tag{1}$$

where r^{-3} is the average inverse volume and P_u is the so-called electron imbalance of a valence p or d orbital of the nucleus under observation.

Although extrapolation of data from the behaviour of other ligands is not without risk, previous studies on peroxocomplexes of chromium, molybdenum, rhenium, titanium, tungsten and vanadium [21] support the above assignment based on the relative intensities of the ^{17}O signals. In fact, ^{17}O NMR spectra show that diperoxocomplexes are more shielded than monoperoxocomplexes, with differences in ΔE being invoked to explain this observation. It is observed that the carbonate ^{17}O signals of carbonate ions complexed to Ce(IV) are shifted to higher frequencies (416 and 497 ppm) than in the homologous complexes of uranium(VI) (225 ppm) [20]. The same trend is observed in the ^{17}O spectra of homologous complexes of tungstate, molybdate and vanadate [21], where the chemical shifts, V(V) > Mo(VI) > W(VI), follow in the inverse order of nuclear charge of the metal. This can be correlated with the effective nuclear charge, with ΔE and with the metal-to-ligand π-bond order.

In conclusion, we have shown by a variety of techniques that in dilute aqueous solutions at pH 8.8 and 10, the dominant complex between cerium(IV) and carbonate ions has a 1 : 2 stoichiometry, with the presence of some 1 : 1 complex. This contrasts with the behaviour of Th(IV), for which the main species present under these conditions is the 1 : 5 complex [9, 16]. This may arise in part from differences in ionic radii of cerium(IV) (94 pm) and Th(IV) (99 pm) [22], or from a greater involvement of the 5f orbitals in bonding in the latter case.

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