Vibrational Spectroscopic Studies of Aqueous Alkali Metal Bicarbonate and Carbonate Solutions[1]

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The laser Raman and infrared spectra of Li, Na, K, Rb, Cs bicarbonates and carbonates in H_2O and D_2O have been determined at 25 °C. The relative integrated intensities of the Raman bands have been measured for each salt from 0.01 *M* up to saturation. Changes observed in the carbonate spectrum with concentration have been interpreted in terms of solvation and ion-pairing of the carbonate ion. Based on the vibrational spectrum, there was no evidence for ionic interactions in the bicarbonate solutions. The hydrogen–deuterium exchange on the bicarbonate ion in H_2O–D_2O mixtures has been followed using Raman spectroscopy and the concentration quotients for the pertinent reactions have been calculated.

Les spectres en Raman laser et en infrarouge des bicarbonates de Li, Na, K, Rb, et Cs, ainsi que des carbonates dans l'H_2O et dans le D_2O ont été déterminés à 25 °C. Les intensités relatives intégrées des bandes du spectre Raman ont été mesurées pour chaque sel à partir de 0.01 *M* jusqu'à saturation. Les changements observés dans le spectre du carbonate par rapport à la concentration ont été interprétés en fonction de la solvatation et de la formation en paire d'ions de l'ion carbonate. En se basant sur le spectre vibrationnel, il n'y a aucune raison pour envisager des interactions ioniques dans les solutions de bicarbonate. L'échange hydrogène–deutérium sur l'ion bicarbonate dans des mélanges H_2O–D_2O a été suivi en utilisant la spectroscopie Raman et les quotiens de concentration pour les réactions correspondantes ont été calculés. [Traduit par le journal]

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Introduction

An understanding of the bicarbonate–carbonate equilibrium is important in a study of natural waters, since it is largely responsible for controlling the water's p*H* and thus directly affects many of the chemical equilibria in the water (1). The Raman and infrared spectra of saturated aqueous potassium bicarbonate and carbonate solutions have been used to determine the structure of bicarbonate and carbonate ions in these concentrated solutions (2). It is of interest to extend these studies to lower concentrations approaching natural water levels to see whether the structure of the ions is changed by dilution.

Considerable information about ion–ion and ion–solvent interactions in aqueous nitrate systems has been obtained using vibrational spectroscopy (3–7). The relative importance of the ion-pairing and solvation effects can be assessed by varying the cation and by changing the solvent. In this study the laser Raman and infrared spectra of Li, Na, K, Rb, Cs bicarbonates and carbonates in H_2O and D_2O are reported.

Experimental

Raman and complementary infrared spectra were measured for aqueous solutions of each salt from about 0.01 *M* up to the solubility limit. The solutions were prepared using reagent grade salts and filtered through Solvinert Millipore filters (0.25 μ) prior to recording the spectra. The samples in precision Pyrex cells were placed in a holder thermostated at 25 °C and the Raman spectra measured with a Jarrell-Ash Model 25-300 Raman spectrometer (8). A Spectra Physics Model 125 Helium–Neon laser (632.8 nm, 50 mW) or a Coherent Radiation Model 54A Argon laser (488.0 nm, 200 mW) was used as the excitation source. Infrared spectra were obtained as smears between AgCl plates with a Perkin–Elmer Model 457 Grating Spectrometer. Band contours were resolved with a Dupont Curve Resolver using a Lorentz–Gaussian distribution function. All Raman band intensities were measured relative to the 459 cm^{-1} band of CCl_4. An accuracy of ±2% for band intensities is attainable with this instrumentation for strong well-resolved bands (*e.g.* 1069 cm^{-1} band of carbonate). Decomposition of the bicarbonate solutions results in larger errors for these solutions. In the case of weak or overlapping bands the accuracy of the intensity measurements is about ±10%.

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Results and Discussion

A typical Raman spectrum observed for carbonate solutions is shown in Fig. 1. The relative intensities of the major Raman bands are graphed as a function of concentration in Fig. 2. The plots are linear over the whole concentration range. The bands in the 600 and 1400 cm^{-1} regions have much lower relative intensities than the band in the 1000 cm^{-1} region; so low in fact that feeble water bands in these regions have sufficient intensity to make curve resolving more difficult. Using D_2O as the solvent does alleviate this problem to some extent. The Raman and infrared band positions for potassium carbonate at different concentrations in H_2O and D_2O are shown in Table 1. The carbonate frequencies are virtually independent of alkali metal cation. The Raman band positions are seen to change by a few wave numbers with concentration.

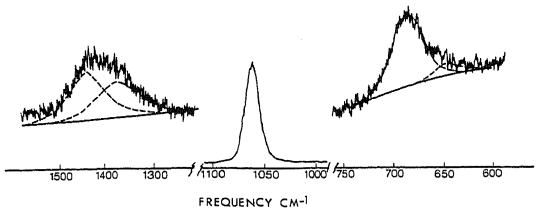

FIG. 1. Resolved Raman spectrum of 8 M Rb_2CO_3 in H_2O. Full scale equals 1×10^4 counts per s for the 100–1100 cm^{-1} region and 2×10^2 c.p.s. for the 600–750 cm^{-1} and the 1300–1500 cm^{-1} region. The weak Raman band at 880 cm^{-1} is observed only at high gain and is not shown in the figure.

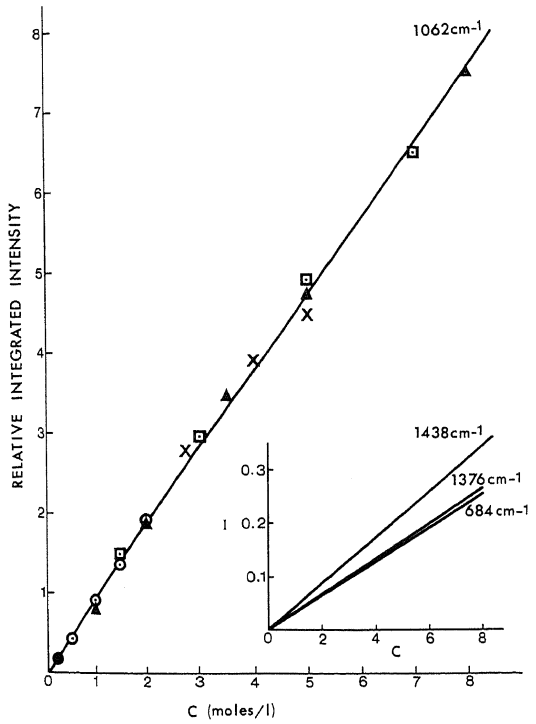

FIG. 2. A plot of relative integrated intensity *vs.* concentration for the major Raman bands of carbonate. ●, Li_2CO_3; ○, Na_2CO_3; △, K_2CO_3; □, Rb_2CO_3; ×, Cs_2CO_3. Only best fit lines shown for weaker bands for clarity.

The symmetry point group for an unperturbed carbonate ion is D_{3h} and the Raman and infrared activity of the expected vibrations are: $\nu_1(A_1')$ R ~1065 cm^{-1}, $\nu_2(A_2'')$ i.r. ~880 cm^{-1}, $\nu_3(E')$ i.r., R ~1400 cm^{-1}, and $\nu_4(E')$ i.r., R ~685 cm^{-1}. The vibrational spectrum of carbonate in aqueous solution is at variance with these selection rules. The infrared forbidden ν_1 band appears in the infrared spectrum of the concentrated solutions at 1052 cm^{-1}. Also the Raman forbidden ν_2 band appears in the Raman spectrum of the concentrated solutions at 880 cm^{-1}. In addition the $\nu_3(E')$ vibration appears to be split into two bands in both the infrared and Raman spectra at all concentrations.

These observations are in many ways similar to those made for alkali metal nitrates by Irish and Davis (3). They interpreted their data in terms of nitrate–water and nitrate–metal interactions. The persistent splitting of the $\nu_3(E')$ band in dilute carbonate solutions where interionic effects should be small, probably indicates that this splitting is due to carbonate–water interaction. This is supported by the fact that the splitting of the $\nu_3(E')$ band is different in the solvent D_2O. Also the band positions in the 1400 cm^{-1} and the 600 cm^{-1} region are different in the two solvents, another indication that the dilute solution spectrum is that of the solvated carbonate ion. The weak bands at 1052 cm^{-1} in the infrared and at 880 cm^{-1} in the Raman could also be features of the solvated carbonate ion spectrum. The weak band at 650 cm^{-1} which is present only in the ultraconcentrated solutions can be assigned to a carbonate ion–water restricted rotation or libration similar to modes found in pure water (9) and those observed for the solvated nitrate ion (3).

Lee and Wilmshurst (10) also observed that the $\nu_3(E')$ band of aqueous K_2CO_3 was split but attributed this to ion-pair formation. Previous studies of aqueous alkali metal nitrates (3, 5, 6)

TABLE 3. Species concentrations and concentration quotients determined by Raman spectroscopy for the system $KHCO_3$–H_2O–D_2O*

Solution	$[HCO_3^-]$	$[DCO_3^-]$	$[H_2O]$	[HOD].	$[D_2O]$	Q_3	Q_4
2.9 *M* $KHCO_3$ in 50 mol% H_2O – 50 mol% D_2O	1.57	1.33	14.66	27.25	13.33	1.73	0.46
2.9 *M* $KHCO_3$ in 25 mol% H_2O – 75 mol% D_2O	0.96	1.94	4.06	21.42	29.72	1.46	0.38
2.9 *M* $KHCO_3$ in 10 mol% H_2O – 90 mol% D_2O	0.37	2.52	0.87	11.82	42.47	1.90	0.50

*Mean concentration quotients $Q_3 = 1.7 \pm 0.2$, $Q_4 = 0.45 \pm 0.05$.

treated as a single band and the missing gap filled with the 1017 cm^{-1} band. In this way it was possible to obtain excellent reproducible fits for the experimental spectrum. The concentration of HCO_3^- was then determined from the 1017 cm^{-1} band intensity and the concentration of DCO_3^- obtained by subtraction. A check on the accuracy of the determination was made using the 1302 cm^{-1} band intensity. The HCO_3^- concentrations from both regions of the spectrum were found to be in good agreement.

The important reactions for the exchange equilibrium are as follows

[2] $H_2O + D_2O \rightleftarrows 2HOD$

$$Q_2 = [HOD]^2/[H_2O][D_2O]$$

[3] $HCO_3^- + D_2O \rightleftarrows DCO_3^- + HOD$

$$Q_3 = [DCO_3^-][HOD]/[HCO_3^-][D_2O]$$

[4] $HCO_3^- + HOD \rightleftarrows DCO_3^- + H_2O$

$$Q_4 = [DCO_3^-][H_2O]/[HCO_3^-][HOD]$$

The value of the concentration quotient Q_2 for reaction 2 at 25 °C is 3.8 (12).

Since $[HCO_3^-]$ and $[DCO_3^-]$ have been obtained experimentally there are five unknowns in the equations: $[H_2O]$, $[D_2O]$, [HOD], Q_3, and Q_4. It is possible to write equations for the known total concentration of hydrogen and deuterium in the solutions.

[5] $[H]_{total} = 2[H_2O] + [HOD] + [HCO_3^-]$

[6] $[D]_{total} = 2[D_2O] + [HOD] + [DCO_3^-]$

From these five equations it is now possible to calculate the concentration quotients Q_3 and Q_4. The species concentrations obtained from Raman intensity data for three 2.9 *M* $KHCO_3$ solutions in H_2O–D_2O mixtures and the calculated concentration quotients are shown in Table 3. The experiment was repeated for 1 *M* $NaHCO_3$ solutions in two H_2O–D_2O mixtures and the quotients, $Q_3 = 1.9 \pm 0.2$, $Q_4 = 0.50 \pm 0.05$, are in close agreement with the $KHCO_3$ results. Therefore, the concentration quotients appear to be independent of cation and molarity.

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