Spectroscopic Studies of Ionic Solvation. 
XX. Cesium-133 NMR Study of Cesium Salts in Different Solvents

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Cesium-133 chemical shifts were measured in a number of solvents as a function of salt concentration and of the counterion. Infinite-dilution chemical shifts (vs. aqueous Cs⁺ ion at infinite dilution) ranged from +59.8 ppm for nitromethane solutions to -29.4 ppm for pyridine. In general, the magnitude of the downfield chemical shift reflected the donor ability of the solvents. Ion-pair formation constants were calculated from the concentration dependences of 133Cs chemical shifts in several nonaqueous solvents.

KEY WORDS: Cesium-133 NMR chemical shifts; nonaqueous solvents; solvation; ion pairs; ion-pair formation constants.

1. INTRODUCTION

During the past few years we and others have reported studies in which nuclear magnetic resonance of alkali metal nuclei was used as a probe of ionic equilibria and ionic solvation in aqueous and in nonaqueous solutions of alkali salts.1-7 In particular, our previous efforts were directed toward sodium-23 and lithium-7 magnetic resonances.6,7 Recently we extended these studies to solutions of cesium salts in various solvents using cesium-133 resonance as a probe. A preliminary report of this work has been published previously.8

Although the 133Cs nucleus has a spin of 7/2, the electrical quadrupole moment is small (~ 3 x 10⁻⁳ barns), and consequently the resonance has a very narrow natural linewidth of < 1 Hz. The sensitivity is relatively high and

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resonances of 0.001 M cesium salt solutions can readily be detected under our experimental conditions.

In this paper we report the influence of solvent properties, salt concentrations, and counterions on cesium-133 chemical shifts.

2. EXPERIMENTAL

The description and operation of the NMR spectrometer has been reported previously. All solvents used in this investigation were purified and dried by conventional methods. The water content was measured by Karl Fischer titration and was found to be less than 100 ppm.

Cesium chloride, bromide, iodide, and perchlorate (Alfa) were of highest purity available (≥ 99.9%) and were used without further purifications except for drying at 180°C for 48 h. Cesium thiocyanate (Rocky Mountain Res., Inc.) was dried under vacuum over phosphorus pentoxide for 48 h before use. Cesium tetraphenylborate was prepared by the metathetical reaction between cesium chloride and sodium tetraphenylborate in a tetrahydrofuran–water mixture. Sodium contamination of the final product was measured by atomic emission and was found to be less than 0.01%. Cesium triiodide solutions were prepared by mixing equimolar amounts of cesium iodide and iodine in an appropriate solvent. Cesium picrate was synthesized by an acid–base neutralization reaction between picric acid and cesium hydroxide. The insoluble cesium picrate was filtered, recrystallized from ethanol, and vacuum dried at 70°C for 5 h. The yellow crystals began to decompose at ~300°C; the literature value is 308°C.

All data reported here have been corrected for bulk magnetic susceptibility of the solvents and are referenced to the chemical shift of cesium ion at infinite dilution in water. The uncertainty in the measurement is ≤ 0.15 ppm. The chemical shift at infinite dilution was obtained by extrapolation of plots of the chemical shift vs. concentration. The data were fitted to a regular polynomial equation, and the limiting shifts were determined on a CDC 6500 computer system by using the weighted nonlinear least-squares program KINFIT described previously. Each set of data was fitted individually and the values reported here have been averaged over the different salts in each solvent.

The shielding constant for a nucleus is a sum of several terms

$$\delta = \delta_d + \delta_p + \delta_o$$

where $\delta_d$ is the diamagnetic shielding factor arising from the induced motion of a spherically symmetric electron cloud at a nucleus, $\delta_o$ represents shielding of the resonant nucleus by other atoms, and $\delta_p$ is caused by mixing of the ground state with excited electronic states in the presence of the magnetic field, resulting in induced paramagnetic currents. In the case of cesium-133