

# **$^{133}\text{Cs}$ NMR Spectroscopic Investigation of the Interaction of $^{133}\text{Cs}^+$ with Monovalent Cations in Aqueous Solution**

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$^{133}\text{Cs}$  NMR spectroscopy was used to study the interaction of  $^{133}\text{Cs}^+$  with monovalent cations in aqueous solution. The interaction between  $^{133}\text{Cs}^+$  and the cations causes a repulsive polarization in the electron environment of  $^{133}\text{Cs}^+$ , which is detected by a change in its resonance frequency. The resulting  $^{133}\text{Cs}$  chemical shift seemed to be dependent on the activities and the single-ion enthalpies and entropies of hydration of the cations. The hydration cospheres of an ion are the barriers through which  $^{133}\text{Cs}^+$  must pass in order to come into contact with the cation. These hydration cosphere barriers can be related to the single-ion enthalpy and entropy of hydration of the cation. The experiments revealed that  $^{133}\text{Cs}^+$  is not nearly as sensitive a probe as  $^{129}\text{Xe}$ , presumably due to its more tightly bound hydration cospheres. However,  $^{133}\text{Cs}$  NMR was moderately successful in predicting trends in the chemical shift behavior induced by the cations studied.

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**KEY WORDS:**  $^{133}\text{Cs}$  NMR; monovalent cations; polarization; chemical shift; activity; single-ion enthalpy of hydration; single-ion entropy of hydration; hydration cospheres; structure making; structure breaking.

## **1. INTRODUCTION**

The structure of liquid water is predominately due to its extensive network of hydrogen bonding.<sup>(1)</sup> This hydrogen bonding structure within water can be enhanced or disrupted by the addition of ionic compounds. When ions are present in water, structures known as hydration cospheres are formed.<sup>(2)</sup> A hydration cosphere is the region around an ion having the thickness of one water molecule in which the properties of the surrounding water are affected by the presence of the ion.<sup>(2)</sup>

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Some nomenclature used to describe the states of cosphere water are the following: (1) hydration of the first kind, *i.e.*, states in which the water is oriented by ionic fields or other directional ion-solvent forces and (2) hydration of the second kind, *i.e.*, states in which the water is perturbed by the proximity of an ion but the effect cannot be ascribed to directional ion-solvent forces.<sup>(2)</sup> The water outside the cospheres is assumed to be in the same state as in the bulk liquid, except for certain electric field effects.<sup>(2)</sup> States I<sub>c</sub> and I<sub>a</sub> are characteristic of the inner cospheres of small cations and anions, respectively, where hydration of the first kind is occurring.<sup>(2)</sup> State II<sub>sb</sub> is characteristic of the outer cospheres of small ions, where hydration of the second kind is taking place.<sup>(2)</sup> The water molecules in cosphere states I<sub>c</sub> and I<sub>a</sub> are always assumed to be in an organized state (where  $S_{X,I}$ , *i.e.*, the entropy of water in type I cosphere states, is taken to be  $-50 \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$  for all monatomic ions).<sup>(2)</sup> However, the situation is not as definitive for cosphere II<sub>sb</sub> water. Those ions whose cosphere II<sub>sb</sub> water is in a disorganized or structure-broken state, in fact, more disorganized than in the bulk liquid (as indicated by a positive  $S_{X,II}$ , *i.e.*, the entropy of water in type II cosphere states), are known as structure-breaking ions.<sup>(2)</sup> This structure-breaking layer can even extend to the surface of the ion.<sup>(2)</sup> In addition, this disorganized state is further evidenced by the fact that the water molecules in the cospheres of structure-breaking ions have lower rotational activation energies than water molecules in the bulk liquid.<sup>(2)</sup> Examples of cations considered to be structure-breaking are  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{NH}_4^+$ .<sup>(2)</sup> The structure-breaking phenomenon is also evidenced, to an extent, in ions classically considered not to be structure-breaking.<sup>(2)</sup> Ions with a negative  $S_{X,II}$  term, where the cosphere II<sub>sb</sub> water molecules are more restricted/ordered than in the bulk liquid, are said to be structure-making or structure-forming ions.<sup>(2)</sup> The water molecules in the cospheres of structure-making ions have higher rotational activation energies than water molecules in the bulk liquid.<sup>(2)</sup> Two cations considered to be structure-making are  $\text{Li}^+$  and  $\text{Na}^+$ .<sup>(2)</sup>

In a previous study,  $^{129}\text{Xe}$  NMR spectroscopy was used to study the  $^{129}\text{Xe}$  chemical shift of Xe gas dissolved in aqueous solutions of various salts.<sup>(3)</sup> The  $^{129}\text{Xe}$  chemical shift was found to be dependent on the activities, charges, and the single-ion enthalpies ( $\Delta H_{\text{hyd, ion}}^{\circ}$ ) and entropies ( $\Delta S_{\text{hyd, ion}}^{\circ}$ ) of hydration of the ions.<sup>(3)</sup> It was determined that the interaction between  $^{129}\text{Xe}$  and the ions caused a polarization in the electron environment of  $^{129}\text{Xe}$ , which was detected by a change in its resonance frequency.<sup>(3)</sup> The hydration cospheres of an ion are the barriers surrounding the ion through which  $^{129}\text{Xe}$  must pass in order to come into contact with the ion. These hydration cosphere barriers can be related to the  $\Delta H_{\text{hyd, ion}}^{\circ}$  and  $\Delta S_{\text{hyd, ion}}^{\circ}$  of the ion. As a result, a relationship was observed between the  $^{129}\text{Xe}$  chemical shift and the  $\Delta H_{\text{hyd, ion}}^{\circ}$  and  $\Delta S_{\text{hyd, ion}}^{\circ}$ .<sup>(3)</sup>

Because of this previous study, it was of interest to investigate whether an ionic species, such as  $^{133}\text{Cs}^+$ , would also be a useful probe of ion interactions

in aqueous solution. Although not a neutral species like  $^{129}\text{Xe}$ , and thus not possessing nearly as deformable and polarizable an electron cloud as  $^{129}\text{Xe}$ ,  $^{133}\text{Cs}^+$  is the most logical choice for an ionic probe species. This results from its NMR "user-friendly" status (*i.e.*, monovalence, large chemical shift range, etc.)<sup>(4)</sup> and small  $\Delta H_{\text{hyd, ion}}^{\circ}$  and large positive  $\Delta S_{\text{hyd, ion}}^{\circ}$ ,<sup>(2)</sup> the latter two factors having a direct bearing on the ease of polarization of the  $^{133}\text{Cs}^+$  electron cloud. The chemical shift of a NMR active ion like  $^{133}\text{Cs}^+$  in a mixed aqueous electrolyte solution arises from the averaging of the interactions of  $^{133}\text{Cs}^+$  with water molecules, other ions, aggregates of ions, and uncharged ionic molecular species.<sup>(2,4)</sup> Although one would expect the  $^{133}\text{Cs}^+$ -anion interaction to be predominant in such a solution,  $^{133}\text{Cs}^+$ -cation interactions are also known to influence the  $^{133}\text{Cs}$  chemical shift.<sup>(4,5-12)</sup>

## 2. EXPERIMENTAL

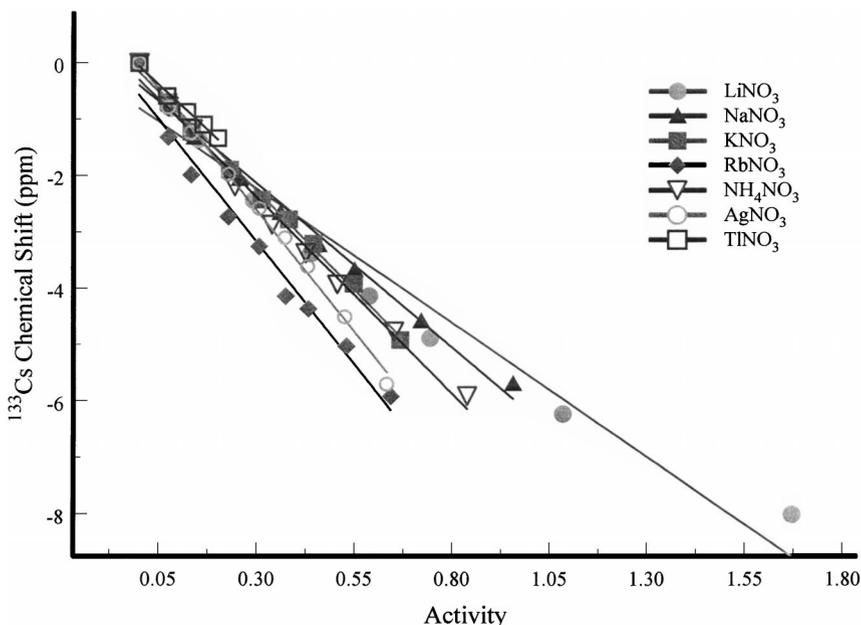
The salts  $\text{LiNO}_3$  (Mallinckrodt),  $\text{NaNO}_3$  (J. T. Baker),  $\text{KNO}_3$ ,  $\text{RbNO}_3$ ,  $\text{CsNO}_3$ ,  $\text{AgNO}_3$ ,  $\text{TlNO}_3$ , and  $\text{NH}_4\text{NO}_3$  (Aldrich) utilized in the experiments were reagent grade and used without further purification. These particular salts were chosen due to the diamagnetic and nonhydrolyzing nature of the cation. In addition, the nitrate salts were chosen, in each case, for their solubility and constant counteranion. Thus,  $^{133}\text{Cs}$  chemical shift differences between the samples should be due solely to the cation. A 10 mM aqueous solution of  $\text{CsNO}_3$  was prepared to serve as a reference standard, solvent, and diluent. Saturated solutions of each salt were prepared by dissolving the appropriate amount of the salt in question in 10 mM  $\text{CsNO}_3$ .<sup>(13)</sup> The desired molal concentrations of the salt solutions were made, in each case, by diluting the saturated solution of the salt using 10 mM  $\text{CsNO}_3$ . This procedure produced a constant  $\text{Cs}^+$  concentration in each sample. The activities of the salts were determined using activity coefficients at 25°C.<sup>(14)</sup> Norell 1005-P 10 mm o.d., 7-in. NMR tubes were used. These tubes contained 5 ml of sample.

$^{133}\text{Cs}$  has a spin quantum number  $I = 7/2$ , a quadrupole moment  $Q = -3 \times 10^{-31} \text{ m}^2$ , and a magnetogyric ratio  $\gamma = 3.5339 \times 10^7 \text{ rad}\cdot\text{s}^{-1}\cdot\text{T}^{-1}$ .<sup>(4)</sup> In addition,  $^{133}\text{Cs}$  is approximately 275 times more sensitive to the NMR experiment than  $^{13}\text{C}$ , and its isotopic abundance is 100%.<sup>(4)</sup> All  $^{133}\text{Cs}$  NMR spectra were obtained at an ambient probe temperature of 20°C using a Chemagnetics A-200 Superconducting Broad Band Multinuclear NMR Spectrometer, where the  $^{133}\text{Cs}$  NMR resonance frequency is 26.332273 MHz. Each sample was allowed 10 min of thermal equilibration within the probe before acquisitions began. The  $^{133}\text{Cs}$  chemical shifts were referenced to the  $^{133}\text{Cs}$  resonance signal of  $^{133}\text{Cs}^+$  in 10 mM  $\text{CsNO}_3$ . All shifts were upfield with respect to the reference signal set to 0.000 ppm, a phenomenon noted elsewhere.<sup>(4)</sup>

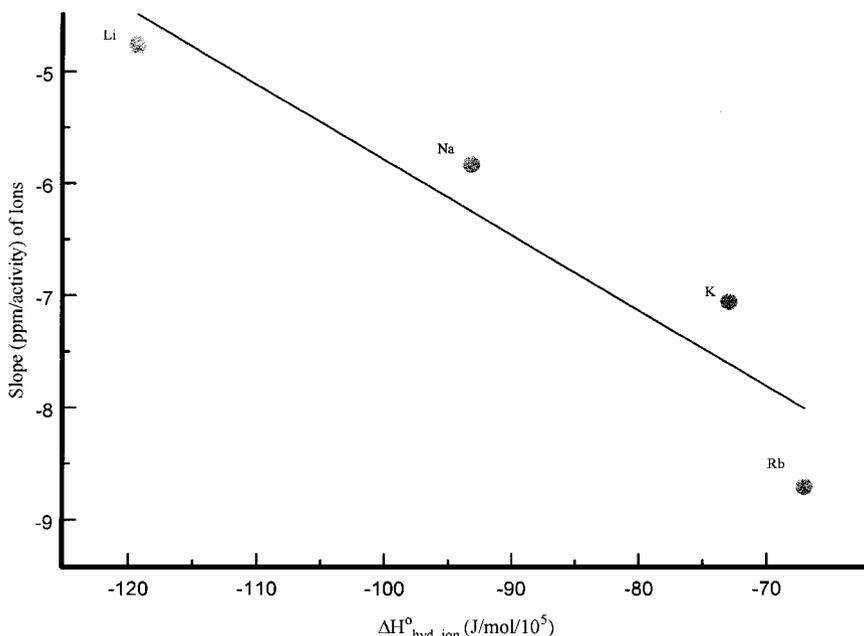
### 3. RESULTS AND DISCUSSION

The  $^{133}\text{Cs}$  chemical shift of  $^{133}\text{Cs}^+$  in the presence of a series of monovalent nitrate salts was studied to find out what factors could account for the influence of cations on the  $^{133}\text{Cs}$  chemical shift. No single factor, as expected, was found to be solely responsible for the  $^{133}\text{Cs}$  chemical shift, but several factors were found that perhaps could explain the observed chemical shift.

The effect of the activity of the cations on the  $^{133}\text{Cs}$  chemical shift can be seen in Fig. 1. The slopes of the lines in Fig. 1, representing the monovalent cations, are not equal. These results show that within a family of ions, the larger the ionic radius of the ion or the more structure-breaking the ion is ( $\text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ ),<sup>(2)</sup> the larger is the  $^{133}\text{Cs}$  chemical shift. Therefore, charge alone cannot account for the  $^{133}\text{Cs}$  chemical shift produced by each ion. Since one assumes that the induced chemical shift is the result of  $^{133}\text{Cs}^+$  coming into contact with or close proximity to the ions, the penetration of the ion hydration cospheres by  $^{133}\text{Cs}^+$  should be an important factor in determining the resulting  $^{133}\text{Cs}$  chemical shift. The effectiveness with which  $^{133}\text{Cs}^+$  can penetrate these ionic hydration cospheres should be determined largely by how tightly the hydration cospheres are bound by



**Fig. 1.** Plots of the activities of the seven nitrate salts in aqueous solution vs. the  $^{133}\text{Cs}$  chemical shift (ppm) in these solutions at  $20^\circ\text{C}$ . All  $^{133}\text{Cs}$  chemical shifts were calculated by setting the  $^{133}\text{Cs}$  chemical shift in the reference solution ( $10\text{ mM CsNO}_3/\text{DI H}_2\text{O}$ ) to  $0.000\text{ ppm}$ .



**Fig. 2.** Plots of the  $\Delta H_{\text{hyd, ion}}^{\circ}$  (g  $\rightarrow$  w) of the alkali metal nitrates vs. the slopes (ppm/activity) of the lines representing those ions from Fig. 1.

the ion and/or how ordered the water molecules are in these hydration cospheres. In Fig. 2, the plots of the slopes (ppm/activity) of the lines of the cations (except  $\text{NH}_4^+$ ,  $\text{Ag}^+$ , and  $\text{Tl}^+$ ) from Fig. 1 as a function of their  $\Delta H_{\text{hyd, ion}}^{\circ}$  (g  $\rightarrow$  w) are shown.<sup>(2)</sup> In addition, Fig. 3 contains the plots of the slopes (ppm/activity) of the lines of the cations (except  $\text{NH}_4^+$ ,  $\text{Ag}^+$ , and  $\text{Tl}^+$ ) from Fig. 1 as a function of their  $\Delta S_{\text{hyd, ion}}^{\circ}$ .<sup>(2)</sup> The  $\Delta H_{\text{hyd, ion}}^{\circ}$ , the energy needed to remove the hydration cosphere water molecules away from 1 mol of a particular ion in aqueous solution, and the  $\Delta S_{\text{hyd, ion}}^{\circ}$ , representing the order of the water molecules in the hydration cospheres of an ion, might be two additional factors that could help to explain the variation in the  $^{133}\text{Cs}$  chemical shift among the ions. As the  $\Delta H_{\text{hyd, ion}}^{\circ}$  of the cations decreases and the  $\Delta S_{\text{hyd, ion}}^{\circ}$  of the ions becomes more positive, the slopes (ppm/activity) of the ions increase. If the ion has tightly bound, well-ordered hydration cospheres (*i.e.*, large  $\Delta H_{\text{hyd, ion}}^{\circ}$  and negative to small positive  $\Delta S_{\text{hyd, ion}}^{\circ}$ ),  $^{133}\text{Cs}^+$  cannot very easily penetrate this cosphere barrier. Consequently, a relatively small ion-induced chemical shift will occur. An ion with more loosely bound, less-ordered hydration cospheres (*i.e.*, small  $\Delta H_{\text{hyd, ion}}^{\circ}$  and large positive  $\Delta S_{\text{hyd, ion}}^{\circ}$ ) will have a greater effect on the  $^{133}\text{Cs}$  chemical shift since its hydration cospheres can be penetrated more easily by  $^{133}\text{Cs}^+$ .

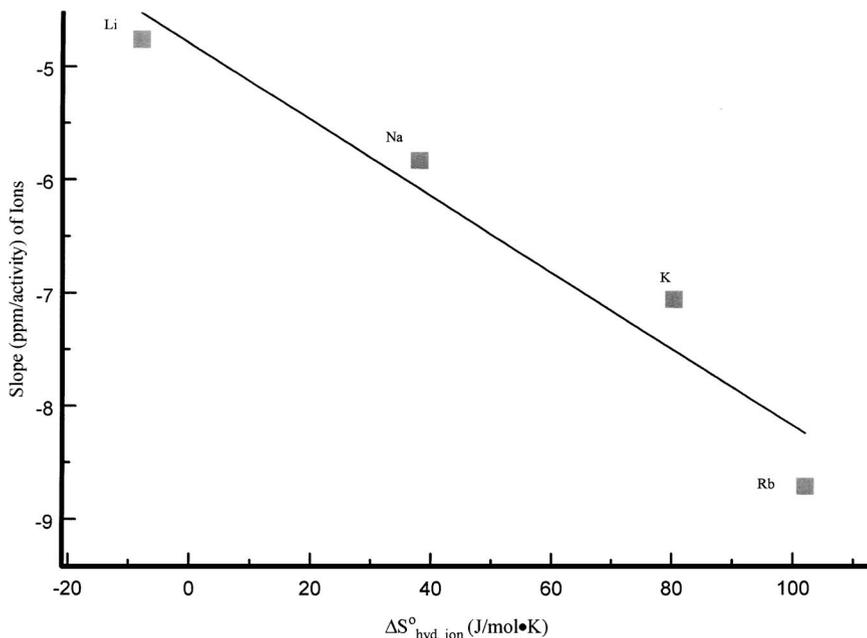


Fig. 3. Plots of the  $\Delta S^{\circ}_{\text{hyd, ion}}$  of the alkali metal nitrates vs. the slopes (ppm/activity) of the lines representing those ions from Fig. 1.

The activity,  $\Delta H^{\circ}_{\text{hyd, ion}}$ , and  $\Delta S^{\circ}_{\text{hyd, ion}}$  appear to be factors that can account for the influence of a particular cation on the  $^{133}\text{Cs}$  chemical shift. To quantify the relationship between the  $^{133}\text{Cs}$  chemical shift and these factors, equations were derived relating these parameters to the slopes of the monovalent cations. The equations of the lines displayed in Figs. 2 and 3 can be used to predict, to a certain degree, the chemical shift of  $^{133}\text{Cs}^+$  present in an aqueous solution containing these particular monovalent cations. The equations are

$$\delta \text{ (ppm)} = \alpha (-1.582 \times 10^{-5} \Delta H - 13.32) \quad (1)$$

$$\delta \text{ (ppm)} = \alpha (-0.03384 \Delta S - 4.793) \quad (2)$$

where  $\alpha$  is the activity,  $\Delta H$  is the  $\Delta H^{\circ}_{\text{hyd, ion}}$ , and  $\Delta S$  is the  $\Delta S^{\circ}_{\text{hyd, ion}}$ . The error in the predicted  $^{133}\text{Cs}$  chemical shifts was  $\pm 0.773$  ppm using the  $\Delta H^{\circ}_{\text{hyd, ion}}$  and  $\pm 0.740$  ppm using the  $\Delta S^{\circ}_{\text{hyd, ion}}$ . The experimental and predicted  $^{133}\text{Cs}$  chemical shifts for the monovalent cations using these two factors are listed in Table I. In both cases, the equations give a decent prediction of the  $^{133}\text{Cs}$  chemical shift of  $^{133}\text{Cs}^+$  in these solutions. From these results, it seems that the equations can predict, to a certain degree, the  $^{133}\text{Cs}$  chemical shift of  $^{133}\text{Cs}^+$  in the salt solutions studied. There is a surprisingly negligible difference between  $\Delta H^{\circ}_{\text{hyd, ion}}$  and  $\Delta S^{\circ}_{\text{hyd, ion}}$  in terms of

**Table I.** Monovalent Ion-Induced Chemical Shifts of <sup>133</sup>Cs<sup>+</sup> in Aqueous Solution and Predicted <sup>133</sup>Cs Chemical Shifts Using Eqs. (1) and (2)<sup>a</sup>

Ion	Activity <sup>b</sup>	10 <sup>-5</sup>		Actual	Predicted <sup>d</sup>	Predicted <sup>e</sup>
		$\Delta H_{\text{hyd, ion}}^{\circ}$ (g → w)	$\Delta S_{\text{hyd, ion}}^{\circ}$	<sup>133</sup> Cs chemical shift	<sup>133</sup> Cs chemical shift	<sup>133</sup> Cs chemical shift
Li <sup>+</sup>	0.0788	-5.586	-7.9	-0.806	-0.353	-0.357
	0.1504			-1.356	-0.674	-0.681
	0.2912			-2.439	-1.305	-1.318
	0.4362			-3.381	-1.955	-1.974
	0.5864			-4.138	-2.629	-2.654
	0.7430			-4.888	-3.331	-3.363
	1.0836			-6.231	-4.858	-4.904
Na <sup>+</sup>	1.6700	-4.439	38	-8.012	-7.487	-7.558
	0.0762			-0.742	-0.480	-0.463
	0.1406			-1.321	-0.885	-0.855
	0.2552			-2.056	-1.607	-1.551
	0.3594			-2.664	-2.263	-2.185
	0.4560			-3.228	-2.872	-2.772
	0.5480			-3.673	-3.451	-3.331
K <sup>+</sup>	0.7196	-3.60	80.3	-4.586	-4.532	-4.374
	0.9560			-5.699	-6.020	-5.811
	0.0739			-0.690	-0.563	-0.555
	0.1326			-1.224	-1.011	-0.996
	0.2304			-1.892	-1.757	-1.730
	0.3114			-2.426	-2.374	-2.339
	0.3808			-2.775	-2.904	-2.860
Rb <sup>+</sup>	0.4430	-3.39	102	-3.205	-3.378	-3.327
	0.5460			-3.918	-4.163	-4.101
	0.6660			-4.920	-5.078	-5.002
	0.0734			-1.317	-0.584	-0.605
	0.1316			-1.985	-1.047	-1.085
	0.2260			-2.727	-1.798	-1.863
	0.3048			-3.247	-2.425	-2.513
	0.3720			-4.137	-2.960	-3.067
	0.4300			-4.360	-3.422	-3.545
	0.5278			-5.028	-4.200	-4.352
	0.6420			-5.918	-5.108	-5.293

<sup>a</sup>Units  $\Delta H^{\circ}$ , J·mol<sup>-1</sup>;  $\Delta S^{\circ}$ , J·mol<sup>-1</sup>·K<sup>-1</sup>; chemical shifts, ppm.

<sup>b</sup>Data from Ref. 14.

<sup>c</sup>Data from Ref. 2.

<sup>d</sup>Using Eq. (1).

<sup>e</sup>Using Eq. (2).

**Table II.** Calculation of  $\Delta H_{\text{hyd, ion}}^{\circ}$  and  $\Delta S_{\text{hyd, ion}}^{\circ}$  for Three Selected Monovalent Cations Using  $^{133}\text{Cs}$  Chemical Shift Data and Eqs. (1) and (2)<sup>a</sup>

Ion	Predicted		Actual $\Delta S_{\text{hyd, ion}}^{\circ}$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	Predicted $\Delta S_{\text{hyd, ion}}^{\circ}$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
	Actual $\Delta H_{\text{hyd, ion}}^{\circ}$ (g → w)	$\Delta H_{\text{hyd, ion}}^{\circ}$ (g → w) (J·mol <sup>-1</sup> 10 <sup>5</sup> )		
NH <sub>4</sub> <sup>+</sup>	-3.01 <sup>b</sup>	-4.01	90.8	64.6
Ag <sup>+</sup>	-5.134	-2.95	51.9	114.0
Tl <sup>+</sup>	-3.64	-4.29	105	51.6

<sup>a</sup>For units see Table I.

<sup>b</sup>From Ref. 15.

their predictive power. This was not the case with  $^{129}\text{Xe}$ , where clearly the  $\Delta S_{\text{hyd, ion}}^{\circ}$  was the more important factor in predicting the  $^{129}\text{Xe}$  chemical shift of Xe in salt solutions.<sup>(3)</sup> In addition, the above equations were tested to see how well they would predict the  $\Delta H_{\text{hyd, ion}}^{\circ}$  and  $\Delta S_{\text{hyd, ion}}^{\circ}$  for three additional monovalent cations studied, namely, NH<sub>4</sub><sup>+</sup>, Ag<sup>+</sup>, and Tl<sup>+</sup>. The results and comparison with literature values are shown in Table II. The percentage error in the predicted values of  $\Delta H_{\text{hyd, ion}}^{\circ}$  and  $\Delta S_{\text{hyd, ion}}^{\circ}$  for NH<sub>4</sub><sup>+</sup> were high, but acceptable (≈30%). The percentage error in the predicted  $\Delta H_{\text{hyd, ion}}^{\circ}$  for Tl<sup>+</sup> was quite acceptable (18%), whereas the percentage error for the  $\Delta S_{\text{hyd, ion}}^{\circ}$  of Tl<sup>+</sup> (51%) and the percentage error for both the  $\Delta H_{\text{hyd, ion}}^{\circ}$  and  $\Delta S_{\text{hyd, ion}}^{\circ}$  values of Ag<sup>+</sup> (43% and 120%, respectively) are too high. The reasons for the lack of predictive success in these particular cases are not fully understood. Perhaps one of the other solution interactions (ionic aggregates and/or uncharged ionic molecular species)<sup>(2)</sup> assumes greater importance for some ions, more so than others. Nevertheless, although  $^{133}\text{Cs}^+$  is obviously not as sensitive a probe as  $^{129}\text{Xe}$ ,<sup>(3)</sup> it proved its utility in being able to predict, to a certain degree, the trends in the  $^{133}\text{Cs}$  chemical shift behavior induced by the monovalent cations studied.

## ACKNOWLEDGMENTS

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## REFERENCES

1. F. Franks, ed., *Water: A Comprehensive Treatise*, Vol. 1 *The Physics and Physical Chemistry of Water* (Plenum Press, New York, 1972).
2. F. Franks, ed., *Water: A Comprehensive Treatise*, Vol. 3 *Aqueous Solutions of Simple Electrolytes* (Plenum Press, New York, 1973).
3. S. McKim and J. F. Hinton, *J. Magn. Reson.* **A104**, 268 (1993).
4. J. Mason, ed., *Multinuclear NMR* (Plenum Press, New York, 1987).

5. F. Hirata, H. L. Friedman, M. Holz, and H. G. Hertz, *J. Chem. Phys.* **73**, 6031 (1980).
6. P. Reimarsson, *J. Magn. Reson.* **38**, 245 (1980).
7. R. K. Harris and B. E. Mann, eds., *NMR and the Periodic Table* (Academic, New York, 1978).
8. C. Hall, R. E. Richards, and R. R. Sharp, *Proc. Roy. Soc. Lond. A* **337**, 297 (1974).
9. C. Deverell, *Progr. NMR Spectros.* **4**, 235 (1969).
10. O. Lutz, *Z. Naturforsch. A* **23**, 1202 (1968).
11. O. Lutz, *Z. Naturforsch. A* **22**, 286 (1967).
12. A. Carrington, F. Dravnicks, and M. C. R. Symons, *Mol. Phys.* **4**, 174 (1960).
13. M. Windholz, ed., *The Merck Index*, 10th edn. (Merck & Co., Rahway, New Jersey, 1983).
14. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths, London, 1955).
15. P. Atkins, *Physical Chemistry*, 6th edn. (Freeman, New York, 1998).