Proton Magnetic Resonance Spectra of Calcium Nitrate Tetrahydrate Melts

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Abstract: To assess the validity of the analogy between molten salts and highly concentrated aqueous solutions of multivalent cations, pmr spectra of melts of calcium nitrate tetrahydrate with anhydrous potassium nitrate (0–50 mole %), tetramethylammonium nitrate (0–50 mole %), and magnesium nitrate (0–20 mole %) have been measured in the temperature interval 33–96°. The observed shifts of the water proton magnetic resonance signal indicate that in melts with nitrates of univalent cations the Ca^{+2} ion is selectively hydrated and that the degree of selective hydration increases with decreasing temperature. In melts with magnesium nitrate the Mg^{+2} ion is selectively hydrated at the expense of the Ca^{+2}. The temperature dependence of the melt chemical shifts indicates an increasing deviation of the water molecule orientation in the primary hydration sphere of an ion from one of minimum potential energy with increasing temperature.

In the past few years there has been a resurgence of interest on the part of some molten-salt chemists in concentrated electrolyte solutions in which the water content is insufficient to satisfy more than the first coordination sphere of the ions. Angell[1] has termed such systems "hydrate melts." Particularly interesting have been studies[1–7] of hydrate melts containing multivalent cations such as Mg^{+2} or Ca^{+2} which bind water strongly. On the basis of a comparison of transport properties of hydrate melts of this sort with transport properties of analogous anhydrous systems, Angell[1–3] has suggested that these melts might be profitably considered as fused salts of large hydrated multivalent cations such as $Ca(H_2O)_4^{+2}$ or $Mg(H_2O)_6^{+2}$ and that in cases in which the water content of these melts is sufficient to satisfy only the coordination spheres of the Ca^{+2} or Mg^{+2} ions, cations with a lower affinity for water are unhydrated. Braunstein and co-workers[4] have found that molar volumes in the $Ca(NO_3)_2 \cdot 4H_2O$–KNO_3 system are additive, which is consistent with Angell's suggestion that the cations in this system should behave as a mixture of hydrated $Ca(H_2O)_4^{+2}$ ions and unhydrated K^+ ions. Even more direct evidence for the existence of selectively hydrated cations as independent entities in hydrate melts stems from the spectroscopic study of Angell and Gruen[5] of dilute solutions of $NiCl_2$ in aqueous $MgCl_2$ solutions. Here it was found that at concentrations at which the H_2O/Mg^{+2} ratio was 6 or less the larger, more polarizable Ni^{+2} ions were unhydrated and all of the water was presumably bound to the Mg^{+2} ions.

Several pmr studies[8–13] have shown that the addition of electrolytes to water induces a displacement in the water proton magnetic resonance signal and that the magnitude and direction of this displacement depend upon the concentration and nature of the electrolyte ions. Hindman[8] suggests that the observed displacement of the water signal in these solutions is the net result of upfield shifts caused by disruption of bulk water hydrogen bonds on forming the primary and secondary ionic hydration spheres and downfield shifts due to polarization and proton deshielding of water in the primary ionic hydration spheres and to nonelectrostatic interactions between water molecules and polarizable, noninert gas configuration cations. In hydrate melts the bulk water structure is lacking, and, if there are no highly polarizable, noninert gas configuration cations present in the melt, changes in the position of the water proton magnetic resonance signal with changes in the melt cationic composition can be ascribed principally to changes in the extent of proton deshielding due to cationic polarization of the water molecules. The efficacy of a cation in inducing polarization and proton deshielding in a water molecule bound in its primary hydration layer in turn increases with increasing charge to the radius-squared ratio (z/r^2) of the cation, if the bound water molecules exhibit a constant orientation with respect to the cation.[8] Consequently the transfer of water molecules from one cation to another of smaller z/r^2 in a hydrate melt is expected to cause an upfield shift in the water proton resonance, and *vice versa.* The position of the water resonance signal in a hydrate melt containing appreciable concentrations of more than one cationic species should thus provide an effective monitor of the average cationic environment of the water molecule if the cations are sufficiently different in their z/r^2 ratios. The proton magnetic resonance studies of calcium nitrate tetrahydrate–anhydrous metal nitrate melts described below were carried out to assess in a quantitative fashion the degree of selective cation hydration and the validity of the fused salt analogy for systems of this type.

Experimental Section

In preparing the hydrate melts Mallinckrodt AR quality $Ca(NO_3)_2 \cdot 4H_2O$ and Baker and Adamson AR quality $Mg(NO_3)_2 \cdot$

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$6H_2O$ were used without further purification. Baker and Adamson AR quality KNO_3 and $(CH_3)_4NNO_3$ prepared by ion exchange from Eastman $(CH_3)_4NBr$ were oven dried at 110° before use. Melts of $Ca(NO_3)_2 \cdot 4H_2O$ with KNO_3 or $(CH_3)_4NNO_3$ were made up by weight and fused at 100° in sealed ampoules. Melts of $Ca(NO_3)_2 \cdot 4H_2O$ with anhydrous $Mg(NO_3)_2$ were prepared indirectly by fusing a mixture of weighed amounts of $Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ and boiling off a mass of water equivalent to that added with the magnesium salt. Other melts were prepared by weight directly in the nmr sample tubes. In all solutions in which it was not a major component tetramethylammonium nitrate was included as an internal standard at a concentration of 0.005 cation mole fraction.

The proton magnetic resonance spectra of the hydrate melts contained in sealed nmr tubes were measured with a Varian A-60 nmr spectrometer equipped with a Varian V-6057 variable-temperature system. The spectrum of each sample was recorded at least three times at each temperature. Probe temperatures were measured periodically during each series of runs in terms of the splitting of the two-peak spectrum of a Varian standard ethylene glycol sample and were constant to within ± °1.

Results

The proton magnetic resonance spectra of all hydrate melts consisted of two unsplit peaks. In each case the peak due to the tetramethylammonium ion appeared upfield from the water peak. The distances, δ, in cycles per second between the water peak and $(CH_3)_4N^+$ peak for the hydrate melts at various temperatures are listed in Table I. The reproducibility of the spectra and the uncertainties in sample temperature indicate an accuracy of ± 1 cps for these chemical shifts.

Table I. Chemical Shifts, δ (cps), of Hydrated Water with Respect to Tetramethylammonium Ion at 60 Mc[a]

System	Mole fraction of $Ca(NO_3)_2 \cdot 4H_2O$	δ at 33°	δ at 68°	δ at 96°
$Ca(NO_3)_2 \cdot 4H_2O$–KNO_3	1.00	92	83	77
	0.80	93	82	76
	0.60	93	81	75
	0.50	92	80	73
$Ca(NO_3)_2 \cdot 4H_2O$–$(CH_3)_4NNO_3$	1.00	92	83	77
	0.80	93	82	76
	0.60	93	81	74
	0.50	91	80	71
$Ca(NO_3)_2 \cdot 4H_2O$–$Mg(NO_3)_2$	1.00	92	83	77
	0.90	98	89	83
	0.80	105	96	89
13.9 *m* KNO_3 $(KNO_3 \cdot 4.0H_2O)$	0	. . .	. . .	38
9.3 *m* $(CH_3)_4NNO_3$ $((CH_3)_4NNO_3 \cdot 6.0H_2O)$	0	. . .	. . .	44
$Mg(NO_3)_2 \cdot 6H_2O$	0	. . .	. . .	115

[a] The H_2O signal appears downfield from the $(CH_3)_4N^+$ signal.

Discussion

Hertz and Spalthoff[10] have shown that tetraalkylammonium ion is suitable as an internal reference for chemical shifts in electrolyte solutions and that the position of the methyl proton resonance peak in these ions is unshifted by concentration or temperature changes. For the small concentration (0.005 cation mole fraction) of $(CH_3)_4N^+$ ion used as an internal standard in melts in which it was not a major component it is evident from the data in Table I that the effect of the $(CH_3)_4N^+$ ion itself on the position of the water resonance signal should be at least an order of magnitude smaller than the experimental uncertainty in δ. Further, since the nitrate anion is common to all the melts investigated here, the observed changes in the chemical shifts can be attributed primarily to changes in the position of the water proton resonance due to changes in temperature or melt cationic composition.

The data in Table I for the chemical shifts at 96° in pure $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, 13.9 *m* KNO_3, and 9.3 *m* $(CH_3)_4NNO_3$ show roughly the expected trend of a shift of the proton resonance of water in the primary hydration sphere of a cation to higher fields as the z/r^2 radius of the cation decreases. That K^+ and $(CH_3)_4N^+$ are out of order in the expected correlation of decreasing δ with decreasing z/r^2 is probably in part due to the concentration difference of the two solutions, since even at concentrations above 10 *m*, where practically all of the water should be present in the primary hydration layer, the position of the water proton resonance continues to change with concentration in uni-univalent electrolyte solutions.[8-11] This is in turn undoubtedly a reflection of the fact that large univalent cations are apparently unable to bind primary hydration water firmly in a position of minimum potential energy and maximum proton deshielding and consequently that the z/r^2 *vs.* δ correlation breaks down for these cations.[8] What is important for our purposes here, however, is the demonstrated fact that the proton resonance of water in the primary hydration sphere of the K^+ or the $(CH_3)_4N^+$ ion occurs well upfield from that of water bound to Ca^{+2}.

Increasing temperature causes a linear upfield shift of the water proton resonance in pure $Ca(NO_3)_2 \cdot 4H_2O$ of magnitude $4.0 \pm 0.5 \times 10^{-3}$ ppm/deg. This may be compared with the temperature coefficients of δ reported for pure water[10,13,14] ($9.5\text{-}10.2 \times 10^{-3}$ ppm/deg) and those reported for more dilute electrolyte solutions[10,11,13] which are intermediate between $d \ln \delta/dT$ for pure water and for $Ca(NO_3)_2 \cdot 4H_2O$. The upfield shift of the proton resonance with increasing temperature in pure water has generally been attributed to a decrease in hydrogen bonding.[15] The decrease in $d \ln \delta/dT$ with increasing concentration in aqueous electrolyte solutions has in turn been attributed to a decrease in the fraction of bulk water which should accompany ion hydration, on the presumption that the temperature dependence of δ arises solely from the bulk water in these solutions.[13] If this presumption were correct, $d \ln \delta/dT$ for $Ca(NO_3)_2 \cdot 4H_2O$ in which there is no bulk water should be zero, while in fact it is approximately 40% that of pure water. Hence it would appear that water molecules in the primary hydration layer of a cation do contribute to the temperature dependence of the water proton chemical shift. The most reasonable explanation for this is that the water molecule–ion orientation of minimum potential energy in a hydrated ion is also the orientation which effects maximum proton deshielding.[8] (This is probably the orientation in which the axis of the oxygen–cation bond bisects the H–O–H angle in the water molecule.) As the temperature is increased the increased thermal energy of the water molecules permits increasing deviation of the average H_2O–ion orientation from that of

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minimum potential energy and hence the observed upfield shift of the water resonance. Unfortunately the high melting point of $Mg(NO_3)_2 \cdot 6H_2O$ and the decreased solubilities of KNO_3 and $(CH_3)_4NNO_3$ at lower temperatures precluded an investigation of $d\delta/dT$ in the temperature region covered here for the other systems in Table I in which only one cation is present as a major component of the melt.

The data in Table I for melts of $Ca(NO_3)_2 \cdot 4H_2O$ with KNO_3 and $(CH_3)_4NNO_3$ show that at 33° as the mole fraction of the univalent cations is increased from 0 to 50 mole% the position of the water proton resonance is unshifted within experimental error from that in pure $Ca(NO_3)_2 \cdot 4H_2O$. The inescapable conclusion here is that at low temperatures nearly all of the water is bound to the Ca^{+2} ion and that the univalent ions are virtually unhydrated. At high temperatures, however, a slight upfield shift in the water resonance is detectable with increasing univalent ion concentration at constant temperature. The magnitude of the shift from the pure $Ca(NO_3)_2 \cdot 4H_2O$ resonance induced by a given concentration of univalent ion increases with increasing temperature and is in the direction expected to accompany the transfer of a water molecule from the hydration sphere of a Ca^{+2} ion to that of a univalent ion.

$$Ca(H_2O)_4{}^{+2} + M^+ = Ca(H_2O)_3{}^{+2} + M(H_2O)^+$$

This process is undoubtedly endothermic, and hence the observed temperature dependence of the shapes of the δ *vs.* concentration isotherms for calcium nitrate tetrahydrate–univalent nitrate melts is in accord with the expectation that increased temperature should shift the above equilibrium to the right. The addition of comparatively small concentrations of anhydrous $Mg(NO_3)_2$ to $Ca(NO_3)_2$ produces, as expected, relatively large downfield shifts in the water proton resonance, since the much smaller z/r^2 ratio of Mg^{+2} favors both its selective hydration and proton deshielding when Mg^{+2} is permitted to compete with Ca^{+2} for available water.

Hydration numbers for the cations in these mixed melts may be calculated if the reasonable assumption is made that due to rapid exchange of water molecules the observed position of the water resonance, δ_{obsd}, is a weighted average of the position of the water resonance for water in the primary hydration spheres of each of the competing cations.

$$\delta_{obsd} = X_{Ca}\delta_{Ca} + (1 - X_{Ca})\delta_M$$

X_{Ca} is the average fraction of the water molecules in the melt in the Ca^{+2} hydration sphere, and δ_{Ca} and δ_M are the positions of the water resonance for water in the hydration spheres of the Ca^{+2} ion and the second melt cation, respectively. Hydration numbers calculated in this fashion for the melts at 96° most concentrated in the second cation are given in Table II. The values of δ_M used in these calculations were the values of δ reported in Table I for 13.9 *m* KNO_3, 9.3 *m* $(CH_3)_4NNO_3$, and $Mg(NO_3)_2 \cdot 6H_2O$. The validity of the use of these values of δ_M for KNO_3 and $(CH_3)_4NNO_3$ is open to some question, particularly in the latter case, since, as previously mentioned, in uni-univalent electrolyte solutions the position of the water resonance is still changing with concentration above 10 *m*. It would appear that the appropriate values of δ_M would be the ones for melts containing approximately 1 mole of water per mole of salt. Nonetheless, since the concentration dependence of δ for uni-univalent electrolyte solutions decreases markedly both with increasing concentration above 10 $m^{8,11}$ and with increasing temperature,[13] the errors in the calculated hydration numbers of K^+ and $(CH_3)_4N^+$ introduced by using these values of δ_M should at worst be no greater than the errors quoted in Table II which arise from the experimental uncertainties in the measured values of δ. Because the water resonance in both KNO_3 and $(CH_3)_4NNO_3$ solutions is shifted upfield with increasing concentration,[8,10] the effect of errors in δ_M would be to make the hydration numbers for K^+ and $(CH_3)_4N^+$ listed in Table II too large.

Table II. Cation Hydration Numbers in Hydrate Melts at 96°

Melt	Cation	Hydration number
$0.50Ca(NO_3)_2 \cdot 4H_2O$–	Ca^{+2}	3.6 ± 0.2
$0.50KNO_3$	K^+	0.4 ± 0.2
$0.50Ca(NO_3)_2 \cdot 4H_2O$–	Ca^{+2}	3.3 ± 0.3
$0.50(CH_3)_4NNO_3$	$(CH_3)_4N^+$	0.7 ± 0.3
$0.80Ca(NO_3)_2 \cdot 4H_2O$–	Ca^{+2}	2.7 ± 0.3
$0.20Mg(NO_3)_2$	Mg^{+2}	5.1 ± 1.1

The data in Tables I and II indicate that in melts of $Ca(NO_3)_2 \cdot 4H_2O$ with nitrates of large univalent cations the selective hydration of the Ca^{+2} is moderately complete at temperatures above about 50° and that at temperatures below this probably fewer than one out of five univalent cations possesses a water in its primary hydration sphere at any given instant. In the $Ca(NO_3)_2 \cdot 4H_2O$–$Mg(NO_3)_2$ melts the situation is reversed, and the results suggest that in melts dilute in the latter component, where extensive dehydration of the Ca^{+2} would not be necessary, the Mg^{+2} probably satisfies its full first coordination sphere requirement of six water molecules.

It would seem from the results of the present study that the fused salt analogy for hydrate melts of high-field cations is in the main a good one. Application of fused salt theories to these systems should continue to yield reasonable results, particularly if the differences between fused salts and hydrate melts arising from the changes with temperature in average ion–water molecule orientation and in the degree of selective ion hydration in mixtures are taken properly into account in assessing experimental results in which these phenomena should be of importance. More significant, however, is the impact that studies on hydrate melts can be expected to have on theories of electrolyte solutions of moderate concentration, since the hydrate melt affords an opportunity to study ion–solvent interactions in the absence of contributions to measurements from the so-called excess or bulk solvent and to evaluate quantitatively the competition between different ions for water molecules.

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