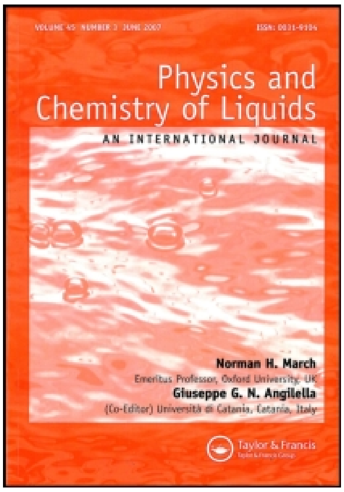


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# Effect of Rare-earth Chlorides on the Structure of Water

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# EFFECT OF RARE-EARTH CHLORIDES ON THE STRUCTURE OF WATER

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The effect of rare-earth chlorides on the structure of water has been investigated at low concentrations by determining the ultrasonic velocity and density at several temperatures around temperatures corresponding to adiabatic compressibility minimum (TACM) and sound velocity maximum (TSVM) of water. Ultrasonic velocity is determined with an accuracy of $\pm 0.003\%$ using single crystal variable path interferometer and densities to an accuracy of $\pm 0.002\%$ using Pycnometer. The results are discussed in the light of structure breaking or structure making of the Rare-Earth chlorides in water.

KEY WORDS: Sound velocity, compressibility, rare-earth chlorides.



## 1 INTRODUCTION

As the utility of lanthanide substitution techniques in bio-chemical systems increases, the need for basic structural information about the lanthanide ions in water and mixed solvent becomes greater. In water, different groups[1] have obtained significantly different results using the same or different techniques.

Studies on enthalphy of mixing indicate partial breakdown of water structure in the presence of rare-earth chlorides. However, several other studies such as density maximum, partial molar volumes, apparent adiabatic compressibility, heat capacity studies are indicative of structure making or structure breaking nature of the rare-earth chlorides.

The close similarity of the properties[2] in aqueous solutions of the chlorides of some of the rare-earth compounds have prompted the present investigations. Lanthanum and neodymium chlorides have been investigated by several workers, but so far no one has attempted to study the interaction of them with water molecules.

It is well known that in pure water the sound velocity has maximum at 74°C and the corresponding compressibility minimum at 64°C. The addition of solute to water either breaks or builds the structure of water, and hence results in a shift of TACM and TSVM of water. A shift in the TSVM towards the lower temperatures can be assumed to be due to the rupture of the open packed structure in water and vice versa.

The present study indicates that neodymium chloride behaves as structure maker even at high temperatures whereas lanthanum chloride behaves as structure breaker. Hence an attempt has been made to study the molecular properties through TSVM and TACM studies.

## EXPERIMENTAL

The ultrasonic velocity was determined using a single crystal interferometer developed in our laboratories, working at 1 MHz. A crystal controlled oscillator with a stability of $\pm 1$ Hz has been developed in our laboratories to excite the quartz transducer. The frequency was measured with a digital frequency meter (Venner Electronics Ltd. England) with an accuracy of 1 ppm. The temperature of the test liquid was maintained constant to better than $\pm 0.002$°C by immersing the interferometer in a water thermostat (VEB Prutgerate-Work; East Germany) whose temperature was maintained steady at any desired value using permanent heaters followed by 'On and Off' low wattage heaters.

The rare-earth chemicals with 99.99% purity were obtained from M/s Rare-Earth India Limited, Udyogmandal, India. The solutions were prepared for different concentrations using triple distilled degassed water. Degassing of water prevents the formation of air bubbles at high temperatures. Formation of air bubbles broadens the dip of the voltage variation across the quartz crystal observed on an oscilloscope and hence limits the accuracy in velocity measurements.

The ultrasonic velocity is measured in the temperature range of about 56°C to 80°C at 2°C intervals. The errors due to thermal fluctuations in the sound velocity measurements are comparatively small because of low temperature coefficients of sound in the temperature range studied. The interferometer technique used to measure the sound velocity is accurate to $\pm 0.003$%. Since the temperature dependence of sound velocity of the solutions is parabolic and resembles that of pure water a transparent template of the curve for water was employed to fix TSVM. Another template was also employed to fix TACM. The accuracies of TACM and TSVM are $\pm 0.4$°C and $\pm 0.2$°C respectively.



## RESULTS AND DISCUSSION

All pure liquids except water[3] and heavy water[4] are found to have a negative temperature coefficient of sound velocity until 74°C. Water is a unique liquid having

**Table 1** Ultrasonic velocities (meter/sec) in dilute aqueous solutions of lanthanum chloride.

| *Concentration gm/lt.* | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|---|
| Temperature °C | 1550+ | 1550+ | 1550+ | 1550+ | 1550+ | 1550+ |
| 68 | 6.24 | 5.98 | 5.96 | 5.64 | 6.18 | 5.86 |
| 70 | 6.45 | 6.70 | 6.24 | 6.56 | 6.65 | 6.16 |
| 72 | 6.60 | 6.86 | 7.07 | 6.34 | 6.83 | 6.34 |
| 74 | 6.52 | 7.18 | 7.14 | 6.56 | 6.68 | 6.44 |
| 76 | 6.36 | 6.68 | 6.78 | 6.08 | 6.10 | 6.10 |
| 78 | 6.20 | 6.26 | 6.38 | 5.80 | 5.92 | 5.85 |
| 80 | 5.60 | 5.78 | 6.08 | 5.58 | 5.66 | 5.54 |

**Table 2** Adiabatic compressibilities (in $\times 10^{12}$ cm$^2$ dyne$^{-1}$) in dilute aqueous solutions of lanthanum chloride.

| *Concentration gm/lt.* | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|---|
| Temperature °C | 42.177 | 42.176 | 42.241 | 42.177 | 42.165 | 42.160 |
| 60 | 42.150 | 42.156 | 42.212 | 42.147 | 42.141 | 42.138 |
| 62 | 42.133 | 42.137 | 42.189 | 42.133 | 42.127 | 42.130 |
| 64 | 42.122 | 42.121 | 42.187 | 42.128 | 42.113 | 42.115 |
| 66 | 42.143 | 42.126 | 42.206 | 42.140 | 42.121 | 42.125 |
| 68 | 42.163 | 42.134 | 42.224 | 42.169 | 42.148 | 42.137 |
| 70 | 42.219 | 42.154 | 42.256 | – | – | – |

**Table 3** Ultrasonic velocities (meter/sec) in dilute aqueous solutions of neodymium chloride.

| *Concentration gm/lt.* | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|---|
| Temperature °C | 1550+ | 1550+ | 1550+ | 1550+ | 1550+ | 1550+ |
| 68 | 5.64 | 5.76 | 5.84 | 5.92 | 6.52 | 6.78 |
| 70 | 6.10 | 6.22 | 6.38 | 6.44 | 7.00 | 7.16 |
| 72 | 6.26 | 6.35 | 6.58 | 6.74 | 7.18 | 7.36 |
| 74 | 6.36 | 6.40 | 6.76 | 6.92 | 7.36 | 7.45 |
| 76 | 6.16 | 6.28 | 6.58 | 6.86 | 7.16 | 7.38 |
| 78 | 5.82 | 5.98 | 6.20 | 6.45 | 6.90 | 7.04 |
| 80 | 5.57 | 5.64 | 5.72 | 6.14 | 6.56 | 6.72 |

**Table 4** Adiabatic compressibilities (in $\times 10^{12}$ cm$^2$ dyne$^{-1}$) in dilute aqueous solutions of neodymium chloride.

| *Concentration gm/lt.* | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|---|
| Temperature °C | | | | | | |
| 60 | 42.087 | 42.114 | 42.129 | 42.168 | 42.198 | 42.272 |
| 62 | 42.050 | 42.086 | 42.104 | 42.142 | 42.162 | 42.238 |
| 64 | 42.021 | 42.068 | 42.092 | 42.129 | 42.144 | 42.225 |
| 66 | 42.027 | 42.069 | 42.094 | 42.128 | 42.144 | 42.215 |
| 68 | 42.039 | 42.081 | 42.105 | 42.146 | 42.147 | 42.215 |
| 70 | 42.058 | 42.100 | 42.120 | 42.164 | 42.168 | 42.241 |
| 72 | 42.087 | 42.139 | 42.139 | 42.186 | 42.199 | 42.270 |

velocity maximum at 74°C and compressibility minimum at 64°C. Water can be regarded as an equilibrium mixture of essentially two species namely close-packed and open-packed structure[5–8]. Increase in temperature produces volume expansion of both the species resulting in a negative temperature coefficient of sound velocity[9,10] with further raise in temperature the concentration of close-packed structure increases leading to a negative temperature coefficient of sound velocity.

The ultrasonic velocities and adiabatic compressibilities of aqueous solution of lanthanum and neodymium chlorides are presented in Tables 1 to 4.

The variation of ultrasonic velocity and adiabatic compressibility with temperature in aqueous solution of lanthanum and neodymimum chlorides are presented in Figures 1 to 4. The shift in TSVM (ΔTSVM) and shift in TACM (ΔTACM) as a

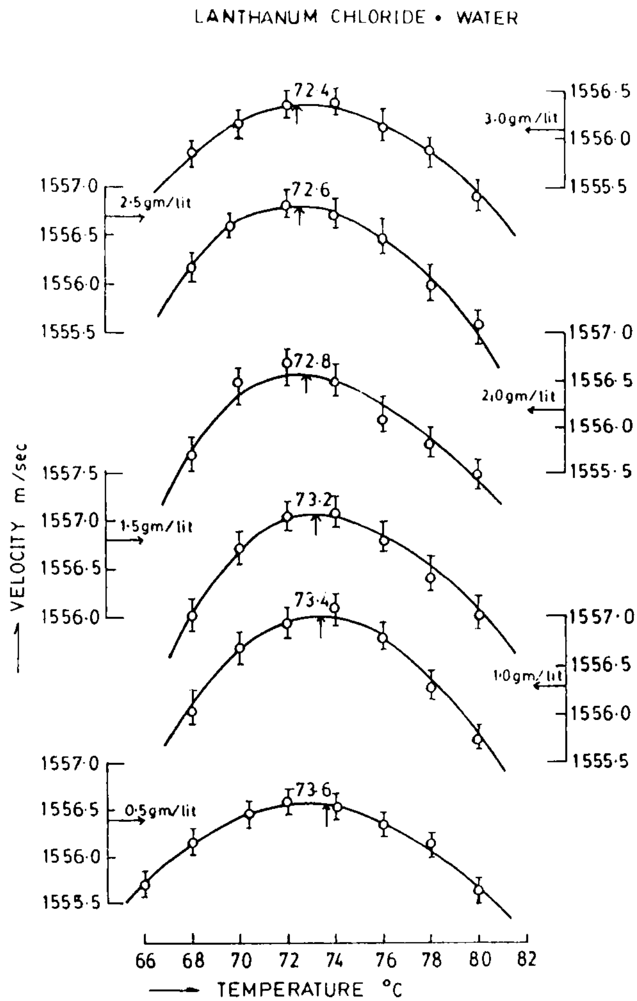


**Figure 1** Variation of ultrasonic velocity with temperature in aqueous solution of lanthanum chloride.

function of concentration of lanthanum and neodymium chlorides are shown in Figures 5 and 6. In the present investigation it was observed that in the case of neodymium chloride the shift in TSVM and TACM is positive where as for solution of lanthanum chloride the shift in TSVM and TACM is negative. The shift in the case of neodymium chloride towards higher temperature can be assumed to be due to the formation of hydrogen bonded molecular (closed packed) structures in water, indicating the structure making property of neodymium chloride. From the ultrasonic absorption studies[11] of aqueous neodymium chloride, the absorption coefficient decreases when the frequency increases, so that it can be assumed that the neodymium chloride acts as a structure promoter. In the present study it was observed that from



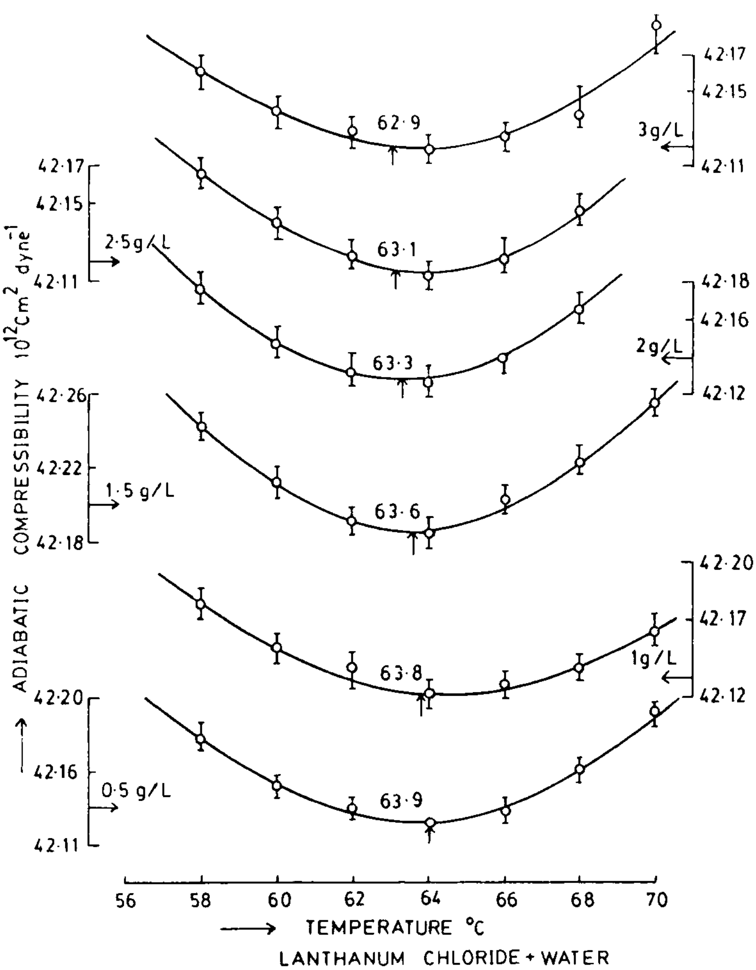


**Figure 2** Variation of adiabatic compressibility with temperature in aqueous solutions of lanthanum chloride.

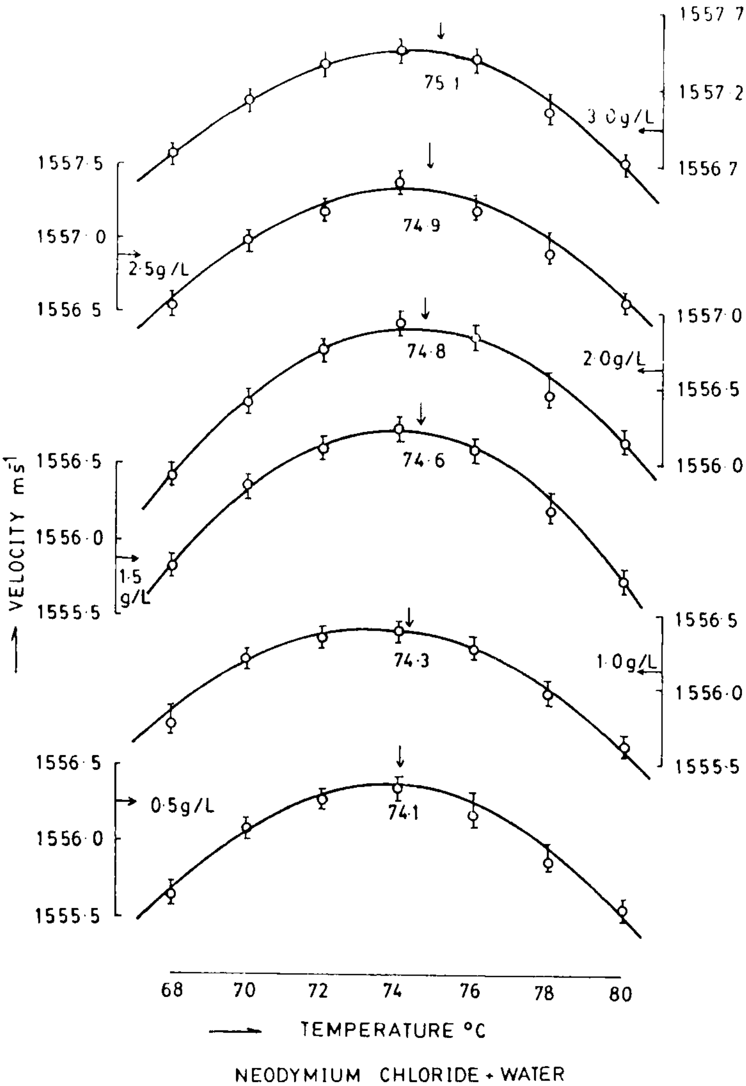


**Figure 3** Variation of ultrasonic velocity with temperature in aqueous solutions of neodymium chloride.

0.5 gm/lit, the shift in TSVM and TACM is towards higher temperatures, which confirms the structure making property of neodymium chloride.

However in the case of lanthanum chloride the ultrasonic absorption[12] increases with the increase in frequency and then decrease. It may be as a result of structure breaking of lanthanum chloride. In the present investigation the TSVM and TACM shifts towards lower temperatures. This trend may be due to the structure breaking property of lanthanum chloride.

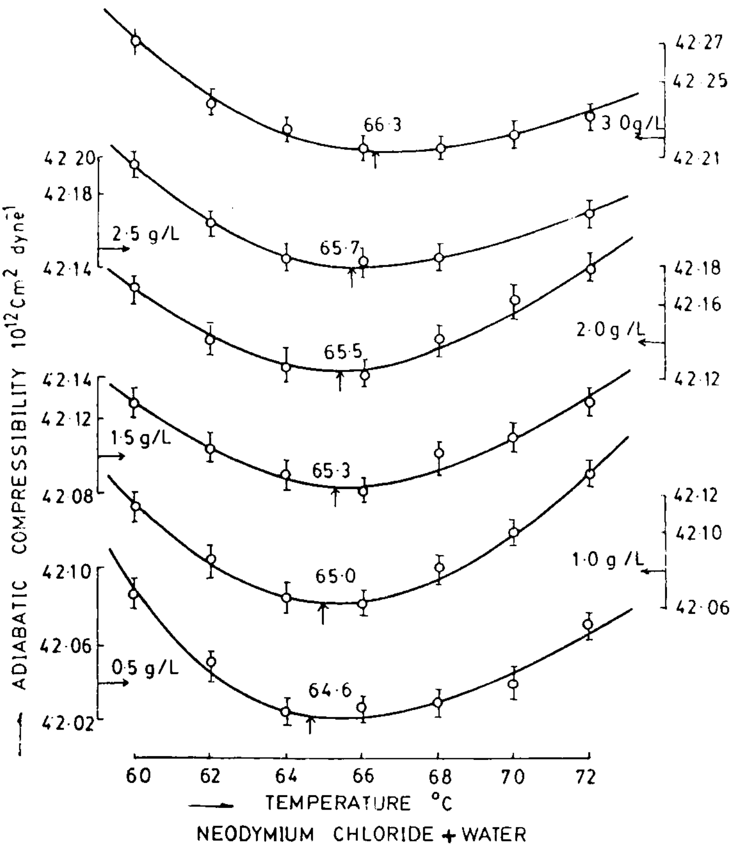


**Figure 4** Variation of adiabatic compressibility with temperature in aqueous solutions of neodymium chloride.

# CONCLUSIONS

The results of present study indicate that the dilute aqueous solution of neodymium chloride is more structured than pure water while aqueous solution of lanthanum chloride is less structured than pure water. Hence it may be concluded that aqueous solution of neodymium chloride shows structure making property and that aqueous solution of lanthanum chloride shows structure-breaking property.

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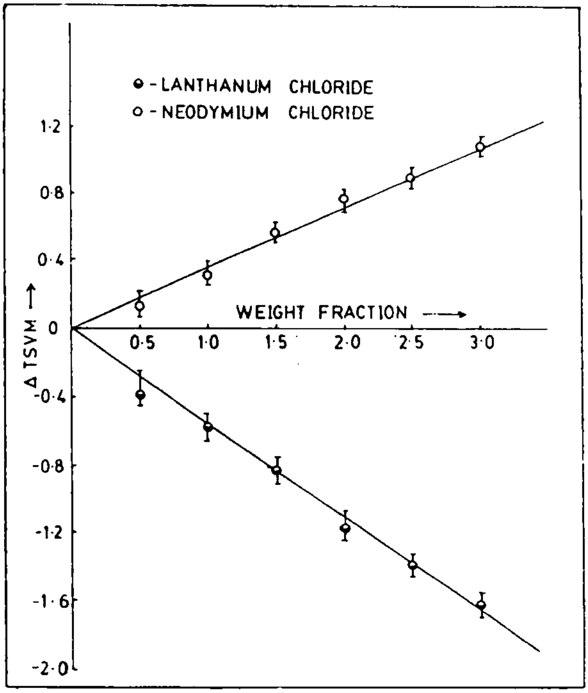


Figure 5 Shift in TSVM as a function of concentration of lanthanum and neodymium chlorides.

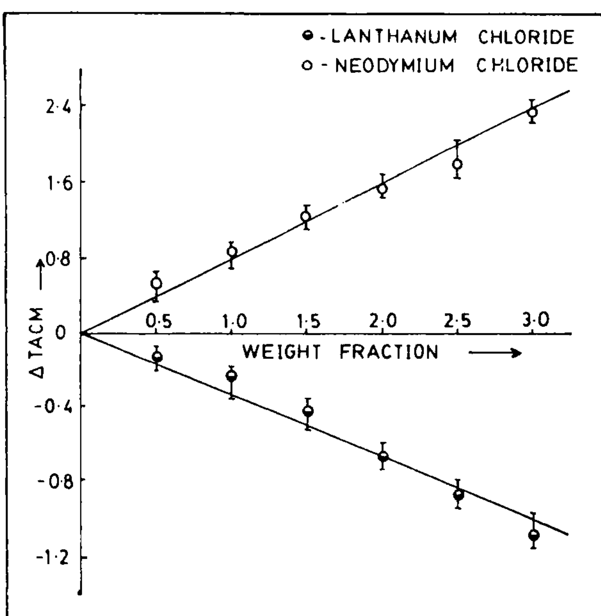


Figure 6 Shift in TACM as function of concentration of lanthanum and neodymium chlorides.

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