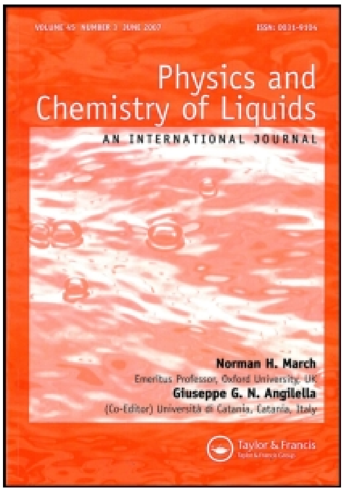

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Acoustic Velocity and High Frequency Relaxation Effects of Ionic $CdCl_2$ Solutions.†

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The hypersonic velocity and absorption have been measured in aqueous $CdCl_2$ solutions in the temperature range between 9.30 and 70.0°C by Brillouin light scattering techniques, as a function of the concentration.

The experimental results indicate the existence of a structural relaxation in the Ghz region, which is discussed in terms of the collective structural properties involved to explain various physical quantities in the same system.

A detailed analysis is also carried out for the ultrasonic velocity data, whose values increase by adding electrolyte to the solvent, revealing as a function of the temperature a peculiar behaviour which is discussed in terms of the current acoustic theories.

1 GENERAL REMARKS

The problem of understanding the nature of the ion-ion and ion-solvent interactions in aqueous electrolytic solutions has been widely investigated in the past[1] by the scientific community. In particular, at large enough concentration values, beyond the range of validity of the Debye–Hückel theory, actually no theoretical treatment exists to understand the physical-chemical properties of this class of ionic liquids. A tentative way of tackling

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the problem is to investigate both the statical and dynamical properties as a function of temperature and concentration. The latter, however, no longer behaves like a parameter: solutions at different concentrations are in fact to be considered as different physical systems.

Following Samoilov,[2] at very low concentrations, the structural properties are due to the intra and intermolecular forces of pure water, while at large enough concentrations of salt the structure is similar to that of the corresponding hydrated crystal.

During the past years, a new effort concerning the study of the structural properties of divalent metal halide solutions ($NiCl_2$, $CuCl_2$, $CuBr_2$, $ZnCl_2$, $ZnBr_2$, $CdCl_2$ and so on) has been made especially on the basis of a lot of neutron scattering results by Enderby and co-workers (see Refs. 3 and 4 for a comprehensive review of the static properties of these systems).

Owing to their structural peculiarities, these systems have been extensively studied by our group too, by using a wide spectrum of experimental techniques. Thermodynamic,[5,6] transport[7] and ultrasonic[8] measurements, Raman scattering,[9–11] EXAFS,[12–15] SANS,[16] quasi-elastic and inelastic neutron scattering[17,18] have furnished direct information on the microscopic structure and on the dynamical properties of these strong electrolytes. On these basis it is possible, in fact, to get an overall picture in which hydrated ions and ionic pairs of Metal–Halogen coexist and, by increasing the concentration, some kind of interaction between the two species takes place. This evidence allows the existence of an extended structure characterized by a finite spatial and temporal expansion. The response of the above-mentioned systems to the various experimental probes could be explained only if cooperative effects have to be taken into account. Strong many-body interactions take place and these ionic systems are well described as an ensemble of elementary excitation,[19] rather than an ensemble of diffusive particles.

Very recently, a possible explanation of the various behaviours of metal-halogen solutions has been given,[20] by taking into account specific effects on the coordination chemistry. The authors, on the basis of the different electronic configurations of divalent cations, are able to predict the existence of the purely hydrated complexes, as in the case of alkaline-earth metal halogens, or ionic pairs, as in the case of concentrated zinc-halide solutions. On the other hand, this different behaviour has been shown by a lot of our experimental results.

As far as the acoustic behaviour is concerned, in a previous paper[8] the ultrasonic absorption of $CdCl_2$ aqueous solutions in the $5 \div 260$ Mhz range as a function of temperature and concentration, has been investigated in some detail. A relaxation phenomenon was observed for the first time, whose parameters are both temperature and concentration dependent. These acoustic anomalies were interpreted as having a chemical origin, involving a rearrangement of both ions and solvent in two structures, with an exchange process fixed by a "quasi-unimolecular" kinetic reaction. The two states between which the system relaxes was identified as a state dominated by the salt structure and a second one in which the solvent forces play the main role. In this case, rather than discuss the results in terms of specific bimolecular or multi-step reactions involving complex ions of $(MeXn)^{2-n}$ type, in which a definite stechiometric description of the process involved cannot be made, the experimental data were handles with a more simple formalism. The relaxation parameters were evaluated with an interpretation of the involved thermodynamics. In particular it was shown that at low concentrations the relaxation process can be related to the building up of the complex ions that behave like "order embryos". In addition some kind of change in the acoustic parameters at intermediate concentrations ($\sim 2M$) take place, confirming the Raman scattering results on the same system.[10] The relaxed values of the absorption were larger than the "classical" one clearly indicating the presence of a high frequency dissipative process. Furthermore the bulk to shear viscosity ratio was evaluated together with a correlation with the entropy change[21] involved in the relaxation process. In other words the bulk flow processes are not simply linked to jumps of molecules towards a new structural arrangement, but are to be considered from a cooperative point of view: the system, locally ordered in some kind of structure, undergoes a "melting" transition before reaching a new structural arrangement.

The aim of the present work, especially on the basis of the conclusions inferred from the previous paper, is to carefully investigate the high frequency behaviour of this system as a function of T and C by means of a Brillouin scattering technique.

We will show that a second relaxation phenomenon is present in the hypersonic velocity and absorption. This high frequency anomaly, which is connected to the frequency dependence of the bulk viscosity η_v, is interpreted in terms of a fast structural process involving the mean life-time of the bonds that cause the middle range connectivity in the system.

Finally a comparison between hypersonic and ultrasonic velocity is made with a consequent interpretation in the frame of the current theories.[22]

2 EXPERIMENTAL PROCEDURES

A Preparation of the samples

All the solutions were prepared starting from high chemical-purity grade $CdCl_2$ and double-distilled deionized water, following a well established procedure elsewhere described.[7,10] The saturated solutions were filtered with a 0.01 μm Amicon filtering system in order to obtain dust and particle free samples. From this solution we prepared our sample by means of successive dilutions. We measured, on the other hand, the density as a function of temperature and concentration. This evenience gives us knowledge of the concentration expressed in molality and in molar fraction.

The saturated value of concentration was 5.05 Molar, corresponding to 10.07×10^{-2} molar fraction, at 9.30°C, in close agreement with the data in literature.[23]

B Techniques

The ultrasonic velocity measurements were performed by means of an acoustic interferometer in connection with a standard Matec pulse-echo apparatus. Details on all the experimental set-up were described in Ref. 8. We have spanned the entire range of concentrations ($0.25 \div 5.05$ M) between $9.30 \div 70$°C, with a constancy of temperature better than 10^{-2}°C. The experimental data are taken at a fixed frequency value of 5 Mhz. In this case, to increase the accuracy of the measurements, the r.f. signals have been directly superimposed. We estimate a global accuracy of 0.2% in the velocity value.

For the polarized light scattering measurements we used a Tropel mod. 350 plane Fabry-Perot piezoelectrically scanned interferometer with a typical 90° scattering geometry, described elsewhere.[24] In particular we used a specially built optical thermostat with a temperature control better than 10^{-2}°C for the range similar to that investigated in the ultrasonic measurements and for 0, 0.5, 2.0, 5.05 M solutions. The purified, colourless solutions of good optical quality were put for the experimental analysis in a quartz optical cuvette and extreme care was taken to avoid any chemical and physical contamination.

The transferred wavevector values $\kappa = 4\pi/\lambda_0 . n(T, c) \cdot \sin \theta/2$ range from 4.57×10^4 cm^{-1} (for the solution at 5.05 M and 9.30°C) to 4.22×10^4 cm^{-1} (for the solution at 0.5 M and 9.30°C). A free spectral range of 18.4 Ghz was chosen in order to furnish a sufficient separation and better resolution between the thermal phonon doublet and the diffusive Rayleigh line.

The resulting overall working finesse for all the investigated solutions was 45. We used the 5145 Å line of a unimode Ar$^+$ laser (Spectra Physics mod. 170) with a mean power of 900 mW. The output of the optical collecting system was detected by a thermoelectrically cooled RCA C-31034 photomultiplier with a dark photon count $\lesssim 10$ ph./sec. The spectrometer operations, as well as the collection and normalization of the experimental data, were on line controlled by a Digital MINC 11/23 mini-computer.

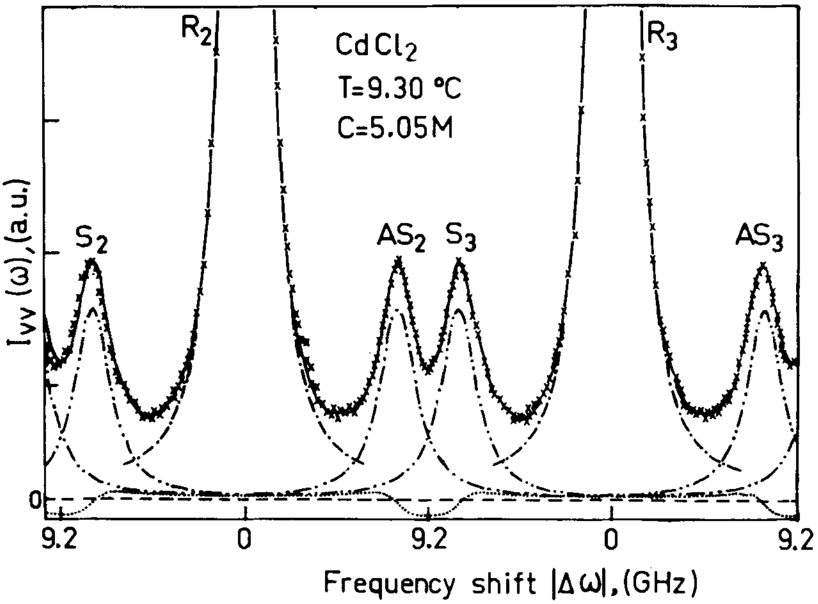

FIGURE 1 Brillouin spectrum of 5.05 M $CdCl_2$ solution at 9.30°C. S and AS refer to the Stokes and Anti-Stoked components respectively; R refers to the central component. × : Exp. points; ——— : Theoretical fitting with Eq. 1; — — — — : Rayleigh line; —·—·— : Symm. Brillouin components; ············ : Asymm. Brillouin components.

Furthermore, in order to reject any unwanted contribution to the spectra, appearing as a flat background (Raman, fluorescence and so on), an optical filter was inserted on the collecting optics. Finally, to increase the photon statistics, many spectra were taken at each temperature and concentration and then computer added. Therefore we obtained a good data reproducibility with an error in the hypersound velocity value of the order of 2%.

In Figure 1 a typical polarized (VV) spectrum that refers to 5.05 M and 9.30°C, with a theoretical fit (see Section 3 for details) is shown as an example.

C Auxiliary measurements

The refractive index $n(C, T)$ in the $CdCl_2$ aqueous solutions, necessary to calculate the hypersonic velocity from Brillouin data, was measured by means of an Abbé refractometer. The measurements were performed at 5145 Å as a function of concentration and temperature. The estimated accuracy was about 0.1%, the error source being caused by the temperature and concentration indetermination.

The density $\rho(C, T)$ was determined by a standard picnometer.

Finally, the viscosity measurements were performed by a calibrated Ubbelhode viscometer furnishing the kinematic viscosity ν. The experimental data turn out to be reproducible with an indetermination lower than one part per thousand. The shear viscosity $\eta(C, T)$ data, that enters in the "classical" absorption $(\alpha/f^2)_{\text{class}}$ was deduced from the density and kinematic viscosity values through the relation $\eta = \rho \cdot \nu$.

3 REDUCTION OF THE DATA AND RESULTS

In a light scattering experiment, the intensity and hence the double differential scattering cross-section is related to the structure factor $S(\kappa, \omega)$. The latter is defined as the Fourier transform of the pressure and temperature-induced density fluctuation correlation function.[25] It is well known that, by using the usual hydrodynamics equations, $S(\kappa, \omega)$ and, as a consequence, the polarized spectrum can be written as:

$$\begin{aligned} I_{VV}(\kappa, \omega) = {} & \frac{A_R \cdot \Gamma_R(\kappa)}{\omega^2 + \Gamma_R^2(\kappa)} + \frac{A_B \cdot \Gamma_B(\kappa)}{\{\omega - [\omega_0^2(\kappa) - \Gamma_B^2(\kappa)]^{1/2}\}^2 + \Gamma_B^2(\kappa)} \\ & + \frac{A_B \cdot \Gamma_B(\kappa)}{\{\omega + [\omega_0^2(\kappa) - \Gamma_B^2(\kappa)^{1/2}\}^2 + \Gamma_B^2(\kappa)} + \frac{\Gamma_B(\kappa)}{[\omega_0^2(\kappa) - \Gamma_B^2(\kappa)]^{1/2}} \\ & \times \left\{ \frac{\omega - [\omega_0^2(\kappa) - \Gamma_B^2(\kappa)]^{1/2}}{\Gamma_B^2(\kappa) + \{\omega + [\omega_0^2(\kappa) - \Gamma_B^2(\kappa)]^{1/2}\}^2} \right. \\ & \left. - \frac{\omega - [\omega_0^2(\kappa) - \Gamma_B^2(\kappa)]^{1/2}}{\Gamma_B^2(\kappa) + \{\omega - [\omega_0^2(\kappa) - \Gamma_B^2(\kappa)^{1/2}\}^2} \right\} \end{aligned} \tag{1}$$

where the first term represents the Rayleigh line, the second the symmetric Brillouin doublet and the last two terms the asymmetric ones.

We have fitted the experimental spectra by the equation (1), with the width appropriately deconvoluted with the instrumental resolution function. We extract as a consequence the true frequency shift ω_0 and Γ_B, from which the hypersonic velocity $V_0 = \omega_0/\kappa$ and the absorption $\alpha/f^2 = 2\pi \cdot \Gamma_B/V_0 \cdot \omega_0^2$ are calculated. As far as a comparison with the corresponding low frequency quantities is concerned,[27] our ultrasonic and hypersonic data have been appropriately reduced[24,28] to obtain the two probe independent acoustic quantities.

In Figure 2 and 3 the velocity V_0 and the absorption α/f^2 are plotted as a function of the temperature for 0.5, 2 and 5.05 M. A visual inspection of Figure 2 shows that a dispersive behaviour exists for the velocity V_0, varying from $\sim 2\%$ for diluted solutions to $\sim 5\%$ for the hydrated melt. This dis-

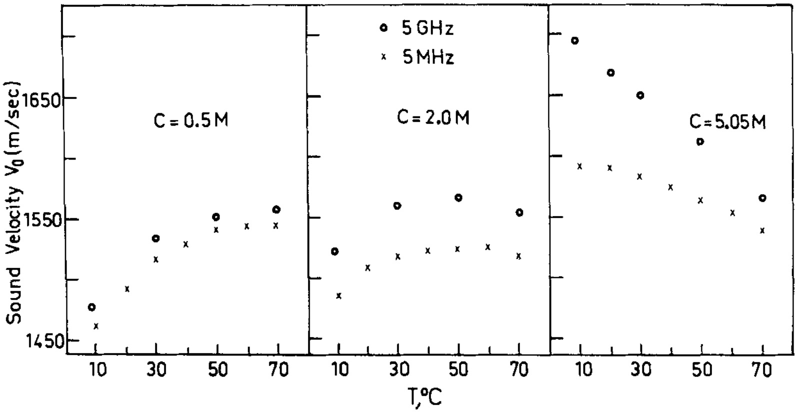

FIGURE 2 Sound velocity V_0 vs. T, at three concentrations. ○: Hypersonic data. ×: Ultrasonic data.

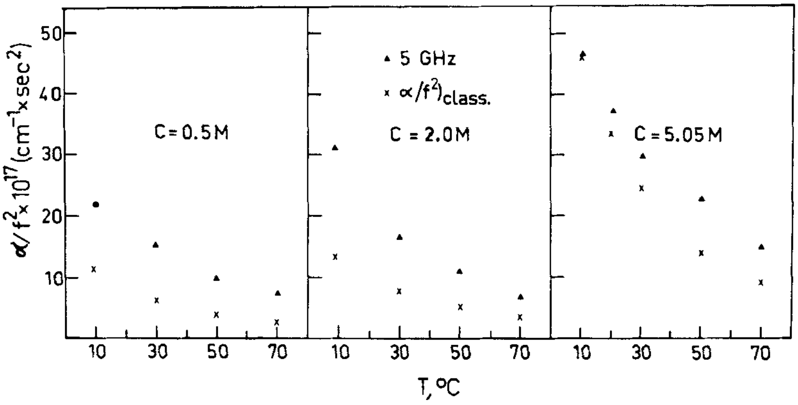

FIGURE 3 Sound absorption vs. T, at three concentrations. △: Hypersonic data. ×: $(\alpha/f^2)_{\text{classical}}$.

persion takes into account both the low frequency chemical relaxation[8] and the actually observed high frequency structural relaxation. Figure 3 clearly confirms this acoustic anomaly with a temperature and concentration dependent relaxation (see the next sections for details).

As far as the temperature and concentration dependence of the ultrasonic velocity is concerned, Figure 4 shows the obtained results.

A typical behaviour[22] is quite evident: the data, starting from pure solvent show a parabolic behaviour as a function of temperature, with a maximum that shifts towards low temperature for increasing values of the concentration. A similar behaviour, with a minimum at lower temperatures, is also observed

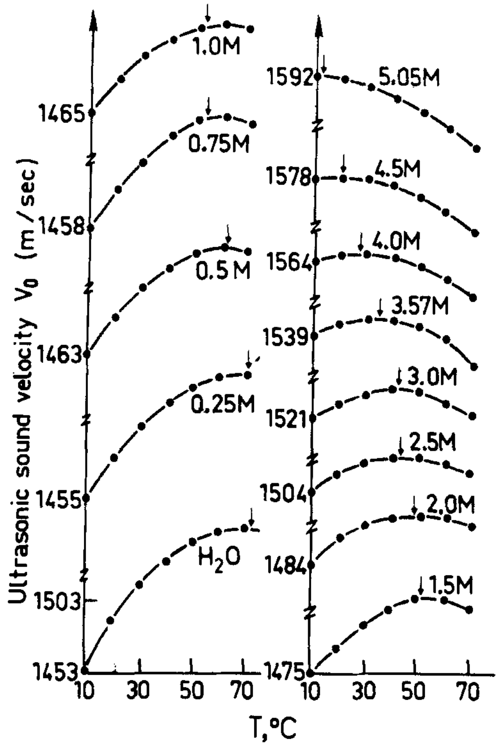

FIGURE 4 Temperature evolution of the ultrasonic velocity, at different concentrations. ● Exp. Data. ——— Parabolic fit. The arrows mark the maxima in the velocity.

for the adiabatic compressibility β_S, which is connected to the sound velocity through the relation $V_0 = (\rho \cdot \beta_S)^{-1/2}$. This phenomenon already observed for many electrolytic solutions could be due to the destructuring effects of salts on the hydrogen bonded structure of pure water.

We will now discuss the various experimental results above sketched in the framework of current theories.

4 DISCUSSION

A Ultrasonic velocity

In order to understand the peculiar behaviour of the low frequency velocity as a function of temperature and concentration, as shown in Figure 4, we first need to analyze the characteristic evolution of the same quantity in pure water. Apparently, in fact, by adding $CdCl_2$ in H_2O the resulting effect is to shift the temperature of the velocity maximum towards lower values. Since water is an associated liquid in which the H-bond plays a noticeable role, the temperature effects on the velocity, and hence on the adiabatic compressibility β_S, could be explained on the basis of some modification of the structural properties[22,29–31] as the temperature increases. Following the old Bernal and Fowler model, many authors explain the temperature of the velocity maximum in water at ~74°C and the consequent minimum in the adiabatic compressibility at ~64°C, on the basis of a two states model or more complex theories. In synthesis, these theories have a common point in the circumstance that a noticeable memory of the ice structure is present in the liquid phase. This "open" structure[32] is similar to that of ice-*I* with vacancies or cavities in which interstitial molecules are found. The latter are in interaction with the tetrahedral environment and a resulting rate exchange process takes place in which the bonds are constantly broken and reformed, with a mean life time of few psec.[33] On these basis, by increasing the temperature, the relaxational compressibility decreases due to the decrease of the percentage of the open structure. On the other hand, the compressibility usually increases as a function of temperature, due to the increase of the mean distance between the molecules for a given structure. The former effects exceeds the latter one up to a temperature value of ~64°C if the adiabatic compressibility is evaluated. As a consequence, the velocity shows this effect at ~74°C, this variation being induced by the simultaneous density and compressibility temperature behaviour. In general, the addition of salts to water results in a lowering of the Tm value.[29–31] In our case the Cadmium–Chloride in solution tends to destroy the open structure of the water, making a new more closed structure, in which the hydrated ions and the cation-ligand complex are more or less interacting. This evidence justifies, at least qualitatively, the observed shift of Tm to lower temperature as a function of concentration.

Furthermore, from the fitting of the experimental velocity data with an empirical parabolic law (see Figure 4), we have extracted the behaviour of Tm as a function of concentration. Figure 5 shows the obtained results. The evolution of the peak temperature clearly shows some changes in the behaviour of our system. The data, in fact, fall roughly on two straight lines, with an intermediate transition region in the 2 ÷ 3 M of concentration range. In such a range of concentration, the properties of the system change as stressed in Section 1. The system evolves from a structure characteristic of water (in which the dissolved salt acts as a perturbing element) to a more packed ordered structure solute imposed. From this point of view, in the 3 ÷ 5.05 M region, it is not the water that loses its original structure, but rather the strong interactions between ions and H_2O molecules that produce a new interconnecting structure. Furthermore, it is to be noted that the

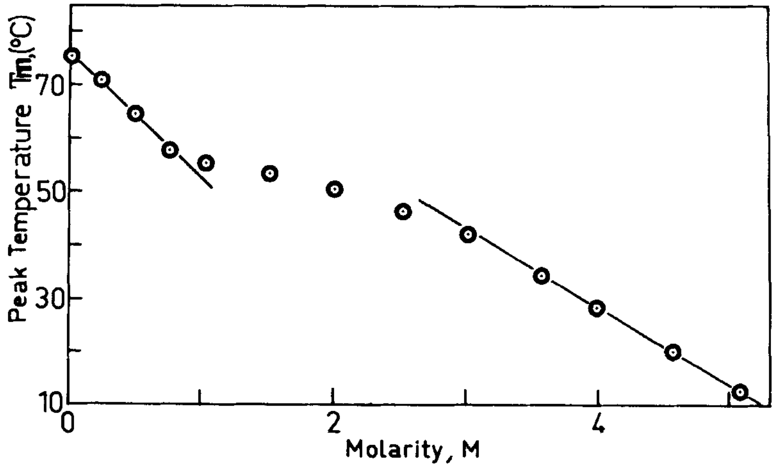

FIGURE 5 ⊙ Peak temperature T_m vs Molarity M. The straight lines indicate the two structured regions.

value of Tm turns out to be just coincident with the limiting value of ~10°C for $C = 5.05$ M. This evidence implies that the saturated (at 9.30°C) solution has a well-defined structure and the effect of the temperature on the system merely produces a variation of the intermolecular distances, not allowing any structural evolution for the system. The observed evolution of Tm is, on the other hand, in close agreement with the behaviour, on the same system, of the low frequency "chemical" relaxation parameters.[8]

Finally, a structural parameter that can be extracted from the low frequency ultrasonic velocity, is the hydration number[22,34] n_s. This value could be obtained by assuming that at very low concentrations (i.e. in the limit of zero concentration value extrapolation), the hydrated ions behave like incompressible cavities, giving rise to the "incompressible part" of the system. This primary hydration number n_s is obtained from the relation:

$$n_s = \frac{\Phi_S + \Phi_V}{V_0} = \frac{[10^3 \cdot (\beta_{S0} - \beta_S)/(M \cdot \beta_{S0})] + \Phi_V}{V_0} \tag{2}$$

where Φ_S and Φ_V are the apparent molar compressibility and the apparent molar volume, respectively, and V_0 is the solvent molar volume. The obtained n_s value is shown in Figure 6 for $T = 10$°C. Surprisingly, the limiting value of n_s turns out to be ~6, which is close to the value of the sixfold coordination in the cadmium-water octahedral arrangement. Furthermore, for the saturated solution the obtained n_s value is 2.3, again this value roughly corresponds to the total water molecules (2.5) contents of the hydrated crystals.[25] As already shown,[8] such a manner of deducing the hydration

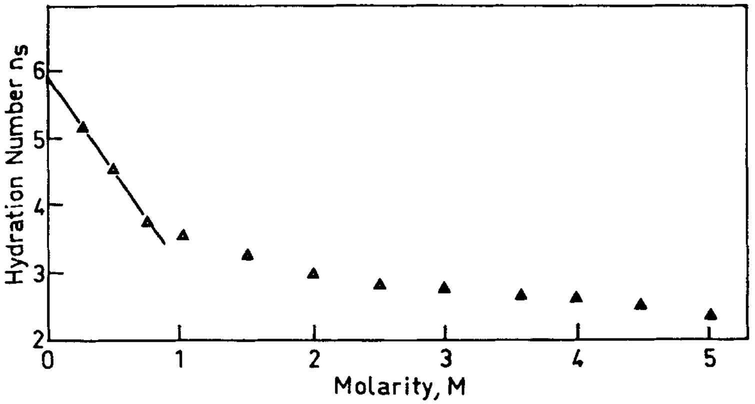

FIGURE 6 Ultrasound deduced Hydration number as a function of concentration, at $T = 9.30°C$. △: Exp. Results. ———: Extrapolation line to zero concentration value.

number appears to be questionable. Actually, the compressibility could be related to the structural arrangement of the whole system, rather than to specific entities.

B High frequency relaxation

It is well known that the ultrasonic and hypersonic acoustic probes furnish relevant information on the dynamic behaviour of the liquid systems.

In particular, Brillouin scattering allows a direct evaluation of the frequency dependence of the transport coefficients $\eta_V(\omega)$ and $\eta_S(\omega)$. As a consequence, it is possible to observe in electrolytes[35–37] some type of relaxation processes (structural, viscous and so on) which could be connected to the collective dynamic evolution in the $10^{-9} \div 10^{-12}$ sec of time scale. Usually, on the other hand, the vibrational contribution[10] lies at higher frequencies and is decoupled (at low κ value) with the translational and diffusional motions.

Viscothermal (gas-like) and viscoelastic (solid-like) theories are able to describe acoustic properties of these systems. It is possible in fact for a system exhibiting various relaxation processes, to derive for the complex longitudinal modulus[38] M_c, an expression like:

$$\begin{aligned} M_c = M' + iM'' &= K_0 + K_r^{\text{ch}} \cdot \frac{\omega^2 \cdot (\tau^{\text{ch}})^2}{1 + \omega^2 \cdot (\tau^{\text{ch}})^2} + i\omega \cdot \eta^{\text{ch}}(\omega) \\ &+ K_r^{\text{str}} \cdot \frac{\omega^2 \cdot (\tau_L^{\text{str}})^2}{1 + \omega^2 \cdot (\tau_L^{\text{str}})^2} + i\omega \cdot \eta_V(\omega) + \frac{4}{3} \cdot G_\infty \cdot \frac{\omega^2 \cdot (\tau_s^{\text{visc}})^2}{1 + \omega^2 \cdot (\tau_s^{\text{visc}})^2} \\ &+ i \cdot \frac{4}{3} \omega . \eta_S(\omega). \end{aligned} \qquad (3)$$

In (3) $\eta^{ch}(\omega)$, $\eta_V(\omega)$ and $\eta_S(\omega)$ are the frequency-dependent volume chemical viscosity, the structural high frequency volume viscosity and the shear viscosity respectively: τ^{ch}, τ_L^{str} and τ_S^{visc} are the relaxation time for the chemical, structural and viscous relaxation process: the various K are the compressional modula for the same processes and the other symbols have the usual meaning. In the Cadmium-Chloride aqueous solutions, as above stressed, a chemical relaxation has been discovered and analyzed[8] in the 30 + 180 Mhz of the frequency values, with a single relaxation time process. The relaxed value of the acoustic absorption turns out to be higher respect to the $(\alpha/f^2)_{class}$, indicating a higher frequency structural ω-dependent process. In Figure 4 the value of the "classical" absorption is shown as a function of the temperature for three values of concentration. By a comparison between the $(\alpha/f^2)_{class}$ and the absorption at 5 Ghz, the second process could be taken into account. In our case, we have analyzed the obtained results with a single relaxation process (Eq. 3). At this point some criticism could be raised on the assumption that structural processes in electrolytic solutions, with complex dynamics, follow an exponential decay law with a single relaxation time. A distribution function of relaxation time was in some circumstances assumed.[36] As a consequence, the complex longitudinal modulus M_c becomes:

$$M_c = M_{\omega=0} - (M_{\omega=\infty} - M_{\omega=0})\cdot \int_0^{\infty} f(\tau_L^{str})\cdot\frac{i\cdot\omega\cdot\tau_L^{str}}{1 - i\omega\tau_L^{str}}\cdot d\tau_L^{str} \tag{4}$$

It is to be noted, however, that when the various processes (chemical, structural, viscous) are very well decoupled (as in our case), the assumption of a single relaxation time process is quite reasonable. On the other hand, if the width of the distribution $f(\tau_L^{str})$ of relaxation times is narrow, then the centre of the distribution could be identified with the single relaxation time. In this case, the temperature evolution of this latter parameter could be directly connected to the microscopic nature of the process.[35] On this basis, for the structural relaxation process alone, we can write:

$$\left(\frac{\alpha}{f^2}\right) = \frac{2\pi^2}{\rho\cdot V_0^3}\cdot\left[K_r^{str}\cdot\frac{\tau_L^{str}}{1+\omega^2\cdot(\tau_L^{str})^2} + \frac{4}{3}\eta_s\right] \tag{5}$$

$$V_0^2 = \frac{1}{\rho}\left[K_0 + K_r^{str}\cdot\frac{\omega^2\cdot(\tau_L^{str})^2}{1+\omega^2\cdot(\tau_L^{str})^2}\right] \tag{6}$$

from which τ_L^{str} and K_r^{str} can be deduced.

It is to be noted that Eqs 5 and 6 hold when the viscous process relaxes at higher frequencies. In our case, since the chemical and the structural relaxation process are well separated in the frequency scale, the relaxed velocity of the chemical relaxation process becomes the zero frequency velocity for the structural process.[38]

Furthermore, because we have performed Brillouin scattering measurements at a fixed wavevector κ, we have information on the structural processes only in a limited $\omega \cdot \tau_L^{str}$ range. In any case, our derived values range from $12.6.10^{-11}$ sec to $6.0.10^{-11}$ sec. (for 5.05 M) and from $3.2.10^{-11}$ sec. to $2.6.10^{-11}$ sec. (for 0.5 M) within the range of temperature investigated.

As already pointed out[8] this structural process for the hydrated melt could arise from a "melting" and "building up" of a locally ordered structure. The obtained values of τ_L^{str} give an indication on the temporal evolution of this structural rearrangement. This latter may be regulated by a rate process that evolves in a complicated and still not fully understood manner. For example, if fast multistep reactions with a large number of descrete states are present, τ_L^{str} in this case is identified as the "mean" longitudinal relaxation time.

As far as the concentration dependence of τ_L^{str} is concerned, this value increases with the concentration, indicating that the relaxation process becomes faster at lower concentrations.

For 0.5 M the relaxation process could have a different physical nature, because the solute imposed structure is still not present. In our opinion, this process could arise from a restructuring of the water molecules or anionic replacement in the cationic coordination sphere.

Furthermore an Arrhenius simple law fitting of the τ_L^{str}vs. Tgives an activation energy value of ~0.8 Kcal/mole (at 0.5 M) and ~2.8 Kcal/mole (at 5.05 M). This evidence could be explained supposing that the faster process is less hindered respect to the slower one. This is true if one supposes that in the hydrated melt any exchange process, which is the cause of the presence of $\eta_V(\omega)$, is hindered by the long life middle range ordered patches.

As far as the relaxation strength is concerned, Figure 7 shows the temperature evolution of Kr/T for three values of concentration in an Arrhenius plot. A concentration dependent behaviour still exists. At low concentration values (0.5, 2.0 M) the data fall on a straight line, that gives an energy value of 3.1 Kcal/mole and 3.5 Kcal/mole respectively. For 5.05 M the data do not follow the same law. This can be explained by considering a single structural process with a single step mechanism, at low concentration, and a more complex process at higher values of the concentration. For this latter in fact the system has a well-defined structural identity, in which the ions and water molecules are linked together. The breaking of the bond in some point of the structure could cause temporal induced effects on the full structural environment.

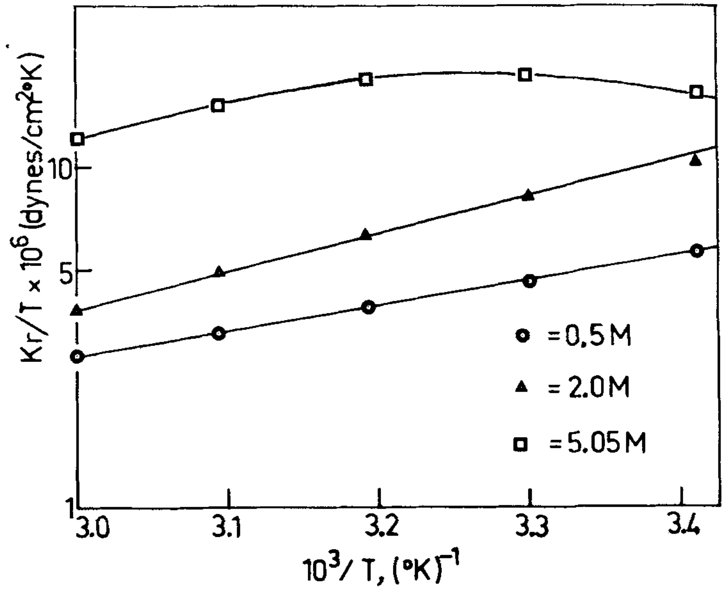

FIGURE 7 Arrhenius plot of the relaxational bulk modulus *Kr*/*T* at different concentrations.

5 CONCLUSIONS

The analysis of the ultrasonic velocity and of the hypersonic velocity and absorption in $CdCl_2$ aqueous solutions allows us to draw the following conclusions:

i) the temperature of the maximum of the ultrasonic velocity shifts towards low values as the concentration increases. The experimental results are directly connected with the structural variation induced by the solute.

ii) the high frequency longitudinal velocity and absorption show the existence of a second structural relaxation phenomenon that is temperature and concentration dependent. The analysis of the observed structural relaxation is better carried out if a cooperative point of view is assumed. The relaxation time τ_L^{str} and relaxation strength K_r^{str} are hence obtained and discussed. Although a rigorous evaluation of the observed process at present is not possible due to both the limited range of temperature and frequency investigated, the evaluation of the relaxation parameters is interpreted in the frame of the existing structural models for electrolytes. On this basis the system locally reproduces the hydrated crystal structure, with a breaking and making of the bonds resulting in the presence of a frequency dependent structural viscosity $\eta_v^{str}(\omega)$.

High frequency acoustic measurements as a function of the exchanged wavevector K, as well as a detailed experimental study of the structurally induced Raileigh wing, are at present in progress in our laboratory, for a better understanding of the dynamic evolution of this peculiar system.

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