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LOCAL ORDER AND DYNAMICS IN LIQUID ELECTROLYTES: SMALL ANGLE NEUTRON SCATTERING

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The existence of dynamically correlated regions of intermediate range of ordering was verified for ZnCl₂ solutions in D₂O by means of small angle neutron scattering. The data also show the presence of two characteristic lengths in the solutions for solute concentration below about 3 Molar. At higher concentration, the secondary "bump" due to the interference of these two distances disappears, indicating perhaps a percolation threshold. Such result is confirmed by the detection of a characteristic length in the small angle spectra of pure D₂O.

Aqueous solutions of strong II-I electrolytes have been investigated for some time because of the unusual and strong structure making effects they show (1). At sufficiently high concentrations, the local structure in the liquid is imposed by the solute and turns out to be very similar to the corresponding crystalline structure (EXAFS measurements). Raman and inelastic neutron scattering spectroscopy (see also papers B1-6 and D1-4 at this conference) show the existence of solute-connected collective vibrational excitations which indicate that the range of ordering may extend well beyond the mean interionic separation. These effects may be particularly evident in ZnCl₂ solutions, and the contrast between ordered regions and the remaining fluid sufficiently high to make the intermediate range dynamical correlations detectable by small angle neutron scattering.

For monodisperse, spherical, non interacting "regions" the Guinier approximation to the structure factor yields:

\[ S_{\text{Coh}}(Q)|_{Q \to 0} \sim \exp \left( - \frac{R_G^2 Q^2}{5} \right) \]

i.e. for \( Q \to 0 \), the scattered intensity should rise exponentially. Independently of the details of the Guinier approximation, such a rise will be indicative, in a homogeneous system, of density or concentration fluctuations spacial correlations, with characteristic range \( R_G \).

Although we performed measurements on ZnCl₂, CuBr₂, NiCl₂ solutions, here we shall discuss mainly the data we obtained for ZnCl₂ in D₂O and pure D₂O.
Experimental

We have used the D17 and D11 small angle cold neutrons spectrometers at I.L.L. Grenoble. The working wavelength was 10 Å and the Q ranges spanned were 0.019 < Q < 0.25 Å⁻¹ (with D17) and 0.002 < Q < 0.25 Å⁻¹ (with D11). Solutions were held in a 2x2x0.1 cm fused quartz cell at room temperature, and were prepared by standard methods. The data were corrected for empty cell, detector efficiency, sample absorption.

In fig. 1 we show the $S_{\text{coh}}(Q)$ behavior at intermediate values of the "small angle" region (data obtained with D17), for ZnCl₂, NiCl₂, CuBr₂ solutions at 0.1 of the saturation concentration. Note the rise for Q → 0 and the bump at ca. Q = 0.1 Å⁻¹. The rise for larger Q's is due to the tail of the metal-metal correlation peak and the stronger but more distant water peak in the structure factor. The study of $S_{\text{coh}}(Q)$ vs concentration shows that the bump disappears for concentration higher than about 3 Molar for ZnCl₂ in D₂O (Fig. 2).

Fig. 1 - Small angle data in CuBr₂, NiCl₂, ZnCl₂ solutions in D₂O. The molar concentration is 0.1 of the saturation value.

Fig. 2 - Small angle scattering data for ZnCl₂ solutions at various concentrations. The case of pure D₂O is also shown.
These results indicate that:

- In the solutions there are dynamically correlated regions with fairly well defined range \( d_0 \).
- The secondary maximum suggests that such regions are themselves spatially correlated with a characteristic distance \( d \).
- Using a dumbbell model (Guinier) to perform a preliminary analysis of the spatial correlations yielding the observed \( S_{\text{Coh}}(Q) \) shape, we obtain \( d_0/d \sim 0.7 \) with \( d \approx 50 \) Å for \( c = 1 \)M.
- The regions loose their identity and merge into an "infinite cluster" at \( c \sim 3 \)M. This effect may indicate the existence of a percolation limit in this system.

The small angle spectra obtained for \( D_2O \) confirm the validity of the application of percolation theory concepts to these systems. Since the data shown in Fig. 1 for \( D_2O \) were not sufficiently accurate, we repeated the measurements using the high resolution D11 spectrometer. Actually the measurements were repeated for the solutions also, and the data are still under analysis and will be reported elsewhere. The data for \( D_2O \) show a clear rise of \( S_{\text{Coh}}(Q) \) all the way to 0.01 Å\(^{-1}\).

In Fig. 3 we show a Guinier plot of the data. From the slope of the straight line fit of \( S_{\text{Coh}}(Q) \) for \( Q \gg 0.01 \) Å\(^{-1}\) we obtain \( R_G \approx 35 \) Å

\[ (2) \]

This result confirms and extends to low \( Q \)'s the results obtained by Bosio et al. (2) by means of Small Angle X-Ray Scattering (their lower \( Q \) limit was \( \sim 0.015 \) Å\(^{-1}\)), which they interpreted in terms of the recently proposed site percolation model for water (3), in which tetrabonded sites tend to clusterize (forming low density patches).

The sharp rise in \( S_{\text{Coh}}(Q) \) at the smallest \( Q \)'s (which would yield an apparent coherence length of about 600 Å) is not understood at present: it may be due to interfacial effects between water and the cell walls.

References