catalyzed by $[RuPt_2(CO)_5(Ph_2P\text{-Ⓟ})_3]$ and $[Fe_2Pt(CO)_8(Ph_2P\text{-Ⓟ})_2]$ is surprising; it suggests that the mechanisms were similar and that the clusters provided the active sites for hydrogenation. Different activities for the two catalysts would have been expected if the sites had been provided by aggregated metal.

The synthesis method was unsuccessful with some clusters. For example, contacting of $[H_2FeRu_3(CO)_{13}]^{10}$ with phosphine-functionalized silica at room temperature in hexane resulted in the formation of primarily $[Ru(CO)_4(Ph_2P\text{-SIL})]$ (SIL = silica) rather than a substituted metal cluster; attempts to prepare the silica-supported analogue of $[Fe_2Pt(CO)_8(PPh_3)_2]$ resulted in the decomposition of the cluster to give aggregated metal.

The silica-supported clusters $[H_2Os_3(CO)_9(Ph_2P\text{-SIL})]^2$ and $[HAuOs_3(CO)_{10}(Ph_2P\text{-SIL})]^{11}$ exhibited no measurable activity for propylene hydrogenation at 100 °C. These same two catalysts, however, were active for 1-butene isomerization at 110 °C, with $[H_2Os_3(CO)_9(Ph_2P\text{-SIL})]$ being ~10 times more active than $[HAuOs_3(CO)_{10}(Ph_2P\text{-SIL})]$.

Acknowledgment. This cooperative research was supported by NATO; the work in Delaware was supported by the National Science Foundation and the work in Munich by the Deutsche Forschungsgemeinschaft.

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Received April 30, 1979

Structural Order in Liquid $CaCl_2·6H_2O$

Sir:

Recently, increasing attention has been devoted to the microscopic structure and to possible structural changes that may take place with an increase of concentration in aqueous solutions of strong II-I electrolytes.[1,2] Indications obtained with different experimental techniques do not not always appear to be consistent, though great care should be used when comparing structural information from measurements of different observables.

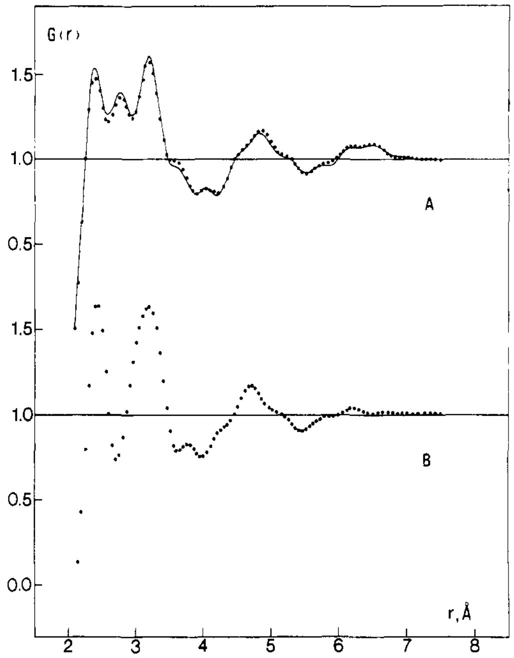

Figure 1. (A) Experimental (circles) and model (solid line) correlation functions for liquid $CaCl_2·6H_2O$. (B) Experimental correlation function for the solution $CaCl_2·12H_2O$.

Some open questions follow. Do qualitative changes in local order around ions occur and, if so, at what concentrations? Does the evolution of structural phenomena move toward an order more marked than the one involving only first hydration shells? Do very concentrated solutions show a tendency toward an order similar to the one existing in the corresponding hydrated crystal?

As diffraction patterns perhaps contain the most direct information about average molecular configurations in a liquid, meaningful contributions in clarifying these questions may come from X-ray diffraction studies on different electrolyte solutions, in a range of concentration including, when possible, the one with the same H_2O/salt ratio as the corresponding hydrated crystal.

Working within these general lines, we collected X-ray diffraction data from liquid $CaCl_2·6H_2O$. As this hydrated salt melts near room temperature, it is possible to compare structural information obtained in this case with the results obtained under similar conditions in previous investigations on $CaCl_2$ aqueous solutions[3] with higher H_2O/salt ratios. From the diffracted intensities, measured in the range $0.3 < s < 15.5$ $Å^{-1}$ ($s = 4\pi \sin \theta/\lambda$, θ being half the scattering angle and λ the wavelength of the Mo $K\alpha$ radiation), we obtained the structure function, from which, via Fourier transform, the average correlation function $G(r)$ which describes the positional correlation between different atoms or ions in the system was calculated.

In the distance range containing information on nearest-neighbor interactions, the $G(r)$ curve for liquid $CaCl_2·6H_2O$ (Figure 1A, circles) shows three resolved peaks centered at ~2.40, 2.75, and 3.20 Å, respectively; this curve is significantly different from the analogous one obtained[3] for the solution $CaCl_2·12H_2O$ (Figure 1B) which exhibits a first peak at ~2.40 Å ascribed to sharp Ca^{2+}–H_2O interactions, a second peak at ~3.20 Å due to weaker Cl^-–H_2O interactions, and a deep minimum in the region 2.7 Å. It is therefore impossible to interpret the "structure" of the liquid $CaCl_2·6H_2O$ as done in the case of less concentrated solutions, where X-ray diffraction data from solutions 1 to 4 M were explained[3] in terms of

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nearest-neighbor models, that is, considering the hydrated ions as independent units with octahedral mean coordination geometries. On the contrary, it is interesting to notice that, in the hexagonal crystals of hexahydrate calcium chloride, as well as in other isomorphous hydrates,[4] each cation is surrounded by three H_2O molecules in the positions $(u, 0, 0)$, $(0, u, 0)$, and $(\bar{u}, \bar{u}, 0)$ at the nearest distance (~2.4 Å) and by the other six H_2O molecules at a greater distance (~2.7 Å) in the positions $(v, 0, \tfrac{1}{2})$, $(0, v, \tfrac{1}{2})$, $(\bar{v}, \bar{v}, \tfrac{1}{2})$, $(v, 0, \overline{\tfrac{1}{2}})$, $(0, v, \overline{\tfrac{1}{2}})$, and $(\bar{v}, \bar{v}, \overline{\tfrac{1}{2}})$. These last six water molecules contribute to forming Ca–H_2O–Ca chains along the c axis with Ca–Ca distance of ~4 Å. Chloride ions are interposed between parallel chains and each of them has six water molecules at distances near 3.2 Å and three others at ~3.6 Å. So the main three peaks observed in the correlation function of liquid $CaCl_2 \cdot 6H_2O$ may be explained in terms of an arrangement of nearest neighbor similar to that of the hydrated crystal.

We then constructed a structure model for the liquid using the crystal lattice of $CaCl_2 \cdot 6H_2O$ to describe the distance spectrum around each atom up to a distance which measures the extent of order; in this way the model fulfills the necessary requirements that structurally equivalent atoms have the same distance spectra and that spectra of different atoms are geometrically compatible.

In order to choose the order range around each atom, we considered that deviations from a uniform distribution of distances are evident in the correlation function only up to ~6.5 Å, whereas the shortest Ca–Ca distance in the layers normal to the axis of the Ca–H_2O–Ca chains in the hydrated crystal is ~8 Å. Therefore, only the discrete distances Ca–Ca, Ca–H_2O and H_2O–H_2O shorter than 7 Å among atoms in the same chain were included in the model, thus excluding a positional correlation between atoms of different chains. Two discrete distances Cl–H_2O were also included, while a uniform distribution of distances was assumed for the other interactions.

This model was systematically refined by least squares, fitting a synthetic structure function to values derived from the measurements. Five distances were treated as independent parameters: the shorter Ca–Ca distance (r_{CC}), the two nearest-neighbor Ca–H_2O distances ($r_{C(1)}$, $r_{C(2)}$), and the two Cl–H_2O distances ($r_{A(1)}$, $r_{A(2)}$). The other discrete distances were related to them by the geometry of the model. Mean square deviations of the discrete distances as well as mean distances and mean square deviations characterizing the uniform distributions boundaries were adjusted to obtain the best fit.

The results of the calculation are shown in Figure 1, where observed (circles) and model (solid line) correlation functions are compared: the good agreement proves the compatibility of the model used with the experimental data. The values obtained in the refined model for the independent discrete distances are the following: $r_{CC} = 3.98$; $r_{C(1)} = 2.35$; $r_{C(2)} = 2.69$; $r_{A(1)} = 3.21$; and $r_{A(2)} = 3.62$ Å. Since distances greater than nearest-neighbor ion–water interactions were essential to yield a good fit, the liquid $CaCl_2 \cdot 6H_2O$, unlike less concentrated $CaCl_2$ aqueous solutions, appears to be characterized by a middle range order involving cation–cation correlations and retaining "memory" of the hydrated crystal lattice structure.

It is worth pointing out that this "memory" of lattice structure must be understood, in the sense of the statistical order characteristic of the liquid state, as coming from time average of different instantaneous situations and/or space average of different local structures. In this view discussions as to whether order phenomena observed correspond to "quasi-lattice" structure come down to a secondary question of terminology.

More details about this study will be reported soon.[5]

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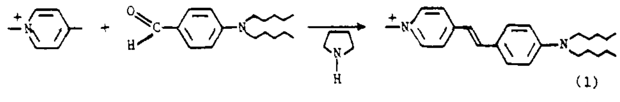
Received February 24, 1979

An Unexpected Blue Shift Caused by Differential Solvation of a Chromophore Oriented in a Lipid Bilayer

Sir:

As the first experimental realization of a qualitative theoretical scheme[1] for the design of electrochromic[2] molecular probes of membrane potential, we have prepared 4-(p-dipentylaminostyryl)-1-methylpyridinium iodide (di-5-ASP)[3] (eq 1). The calculations indicate that most of the positive charge in the ground state is concentrated in the pyridinium ring and that it shifts to the aniline ring upon excitation.[1] This charge migration is a component of our interpretation of an unusual blue shift in the visible absorption spectrum when di-5-ASP binds to lipid bilayer membranes.



(1)

The "unexpected" nature of this blue shift is apparent from inspection of the data in Table I. Spectra of di-5-ASP obtained in less polar solvents than H_2O are red shifted and sharpened; since the ground state can be solvated more effectively than the vertically excited state of a polar chromophore, this behavior is quite common. Another common experimental observation is that a lipid bilayer or a micelle shifts the spectrum of a bound chromophore in the same direction as a nonpolar solvent. This is indeed true for di-5-ASP bound to sodium dodecylsulfate micelles, but lecithin vesicles induce a significant blue shift (an accompanying increase in extinction suggests that the probes are more uniformly solvated than in water).

A possible explanation for this behavior might involve aggregation[4] due to the high effective concentration of the probes in the membrane.[5] On the other hand, an aggregate is expected to have lowered extinction and quenched fluorescence; vesicle bound di-5-ASP has a higher extinction (Table I) and a fluorescence which is approximately a factor of 100 stronger than aqueous di-5-ASP. If the proportion of lipid to probe is varied, it is only at ratios lower than 100:1 that the fluorescence intensity and extinction begin to drop and the absorption maximum begins a further blue shift (to 450 nm at 1:1 egg lecithin-di-5-ASP); above ratios of 100:1 the spectral parameters are essentially constant. The fact that we observe typical evidence for aggregation only under forcing conditions assures us that di-5-ASP obeys the usual criteria for this behavior and that we must find an alternate explanation for the (concentration independent) blue shift.

Our explanation is based on the most reasonable orientation of the bound probe in the lipid bilayer, as depicted in Figure

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