QNS MEASUREMENTS ON WATER IN BIOLOGICAL AND MODEL SYSTEMS*

E. C. Trantham and H. E. Rorschach
Rice University, Houston, TX 77001

J. C. Clegg
University of Miami, Coral Gables, FL 33124

C. F. Hazlewood
Baylor College of Medicine, Houston, TX 77030

† R. M. Nicklow
ORNL, Oak Ridge, TN 37830

ABSTRACT

Results are presented on the quasi-elastic spectra of 0.95 THz neutrons scattered from pure water, a 20% agarose gel and cysts of the brine shrimp (*Artemia*) of hydration 1.2 gms H₂O per gm of dry solids. The lines are interpreted with a two-component model in which the hydration water scatters elastically and the "free" water is described by a jump-diffusion correlation function. The results for the line widths $\Gamma(Q^2)$ are in good agreement with previous measurements for the water sample but show deviations from pure water at large Q for agarose and the *Artemia* cysts that suggest an increased value of the residence time in the jump-diffusion model.

INTRODUCTION

The diffusive motion of protons in water solutions has often been studied by NMR spin-echo techniques. Present pulse technology requires a measuring time of a few milliseconds, which for water gives a diffusion distance $\sqrt{2Dt} \approx 1$ micron. This introduces difficulties in the interpretation of the results for a heterogeneous system such as the biological cell where the scale size is also of the order of a micron. The measured diffusion coefficient is then an average over the cellular environment.

The method of quasi-elastic neutron scattering (QNS) offers the possibility both to reduce the "measuring distance" to a few angstroms and to obtain details about the diffusion dynamics not available from NMR data. The results of measuring QNS spectra are usually interpreted within the framework of the Van Hove theory,¹ which relates the scattering law $S(Q, \omega)$ to the space-time (self) correlation function $G_S(\vec{r}, t)$ of the scattering nuclei. $G_S(\vec{r}, t)$ can be calculated for various models chosen to represent the motion of the diffusing particles, and the parameters of the models can be determined by a fit to the experimental spectra.

*Supported in part by ONR Contracts N00014-79-C-0492 and N00014-760 C-0100, and by ORAU Participation Agreement S-2016.

†Operated by Union Carbide Corporation under contract W-7405-eng-26 with the U.S. Department of Energy.

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering the article.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
MGW

DISCLAIMER

This paper was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, or method disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily imply endorsement, recommendation, or approval by the United States Government or any agency thereof. The views and opinions of authors included herein do not necessarily state or reflect those of the United States Government or any agency thereof.

We have measured the QNS spectra of a 20% gel of the polysaccharide agarose and the cyst of the brine shrimp (Artemia) and compared them with the spectrum of pure water.

EXPERIMENTAL

Agarose gel is a polymer $(C_{12}H_{17}O_9)_n$ of known structure.² It contains 4 OH groups and 13 covalently bonded protons in each repeat unit. It was selected for a pilot study to determine if the spectrometer resolution was sufficient to separate the quasi-elastic line due to the water protons from the elastic line of the polymer protons. The brine shrimp cysts have a diameter of ~ 0.2 mm and consist of an inner mass of about 4000 cells surrounded by a complex non-cellular shell. Their biochemical and physical properties have been studied,³ and the diffusion coefficient of water for various degrees of hydration has been measured by NMR methods.⁴ The degree of hydration can be varied over a wide range (0.02-1.5 gm H_2O /gm dry cyst) while still retaining viability for the extended periods needed for the neutron spectrometer scans. The neutron spectra were determined on the triplex spectrometer HB-2 at ORNL. The samples were contained in aluminum sample holders sealed with an indium gasket. The sample thickness was 1 mm for the water and agarose gel and 2 mm for the brine shrimp cysts. Spectrometer scans of neutron energy loss were made at five Q values between 0.7 and $1.9 \text{ \AA}^{-1}$. The lines were analyzed by a least-squares fit with a 5-parameter function which included a linear background and the convolution of the spectrometer resolution function with an elastic line and a Lorentzian quasi-elastic line. The width Γ of the Lorentzian line and the intensities of the two components were determined at each value of Q from the fitting parameters. The contribution from the agarose protons was determined by scattering from a D_2O gel. For the brine shrimp, the contribution from the protons of the "dry" cyst was determined from an extrapolation of line intensity vs. hydration to zero water content.

*not on
10-11
See figure 1*

RESULTS

Figure 1 shows the line width Γ as a function of Q^2 for pure water (solid curve) and for the 20% agarose and the 1.2 g H_2O /g dry solids cysts. The data points are not shown for water. Their error bars are similar to those for the agarose and brine shrimp results.

DISCUSSION AND CONCLUSIONS

The line width $\Gamma(Q^2)$ for water and the agarose gel could be fitted by a jump diffusion model⁵ with Γ given by

$$\Gamma = \frac{Q^2 D}{1 + Q^2 D \tau_0}$$

For water, a fit of $\Gamma(Q^2)$ gives $D = 2.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $\tau_0 \approx 10^{-12} \text{ sec}$. For agarose, the initial slope of $\Gamma(Q^2)$ is nearly the same as for pure water, although data at smaller Q are needed to be certain

of this. There are deviations from the water curve at large Q , indicating an increased value of τ_0 .

The brine shrimp data show substantial deviations from pure water. The line width is relatively independent of Q and is much narrower than that of pure water. This behavior is consistent with the NMR data on translational diffusion⁴ which shows that the diffusion coefficient is greatly reduced from the pure-water value. The constancy of the line width with Q is also consistent with a rotational diffusion model,⁶ but we have not yet developed a model which is consistent with all the features of the spectra.

REFERENCES

1. L. Van Hove, Phys. Rev. 95, 259 (1954).
2. C. R. Noller, "Chemistry of Organic Compounds" (Philadelphia, 1965) p. 432.
3. J. S. Clegg in "Cell-Associated Water," ed. by W. Drost-Hansen and J. S. Clegg, Academic Press (N.Y. 1979) pp. 165-259.
4. P. K. Seitz, D. C. Chang, C. F. Hazlewood, H. E. Rorschach and J. S. Clegg, "The Self-Diffusion of Water in Artemia Cysts," Arch. Biochem. and Biophys., in press.
5. T. Springer, "Quasi-Elastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids" (Springer-Verlag, NY 1972) pp. 41-44.
6. Ibid., pp. 64-69.