Quasi-Elastic Scattering of Slow Neutrons by Water and an Aqueous Solution of Sodium Chloride*

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Using chopper time-of-flight techniques and a beryllium-filtered incident spectrum, we have examined the quasi-elastic scattering of neutrons by water and by a $4N$ solution of NaCl at a scattering angle of 90°. After substracting an inelastic component attributed to scattering by a gas of mass-18 particles, we completed our analysis in terms of the continuous-diffusion model of neutron scattering by fitting a Lorenztian-broadened incident spectrum to our corrected data. In this way we determined the self-diffusion coefficient D of water in each sample. The two values obtained are 2.2×10^{-5} cm²/sec and 1.7×10^{-5} cm²/sec for pure water and for the salt solution, respectively. These values are in good agreement with NMR and radiotracer measurements. When considered in the light of current theories of water structure and hydration, they have led us to the conclusion that the quasi-elastic peak in the neutron spectrum of water arises primarily from the diffusive motion of individual water molecules.

I. INTRODUCTION

ONE of the first liquids to be investigated by means of slow-neutron inelastic-scattering techniques was ordinary water.[1] Although many subsequent studies have been reported,[2] a generally accepted explanation for the observed neutron spectra in terms of an assumed structure for water is still lacking. Comparing the published data, one finds that in some cases, experimental results are in disagreement, while in others the interpretations of similar data differ markedly. One important question that recurs regularly in these studies is the extent to which the diffusive motion of the scattering centers influences the long-time behavior of the neutron-scattering process as revealed by the width of the quasi-elastic peak. The purpose of this paper is to show that one can obtain some information which bears upon the issue by comparing the quasi-elastic scattering of neutrons by pure water and by an aqueous salt solution. We propose to show that this comparison, when viewed within the framework of existing self-diffusion data for H_2O molecules in pure water and in aqueous solutions, leads to the conclusion that diffusion does play an important role in the quasi-elastic scattering region.

About twenty years ago, Samoilov[3] began to investigate the effect of ionic solutes upon the translational motion of water molecules in the vicinity of the ions. The theory of hydration which he subsequently proposed is based upon a consideration of the activation energy for exchange of neighboring water molecules in the presence or absence of ions. Suppose that a given water molecule spends, on the average, a time τ in the

immediate vicinity of another water molecule and the corresponding time τ_i in the vicinity of an ion. Then, Samoilov pointed out, the two times τ and τ_i are related through the expression,

$$\tau_i/\tau = \exp(\Delta E/RT), \qquad (1)$$

where R is the universal gas constant and ΔE is the difference between the activation energy for the exchange of two water molecules in pure water and the exchange of two water molecules in an aqueous solution where one of the molecules is initially bound to an ion. Samoilov was able to deduce values of ΔE for individual ions by combining experimental self-diffusion data with the measured temperature dependence of ion mobilities in solutions. He found that ΔE could assume positive or negative values. In other words, water molecules near those ions for which $\Delta E < 0$ will be more mobile, while those near ions for which $\Delta E > 0$ will be less mobile than in pure water. These phenomena have been designated negative and positive hydration, respectively. One would expect, then, that an experimentally observable manifestation of this phenomena would be a measured coefficient of self-diffusion of water in aqueous solutions that is greater or less than the coefficient of self-diffusion in pure water. Indeed, Wang[4] had already reported such results at the time that Samoilov proposed his theory. Using H_2O^{18} as a radiotracer, Wang had discovered that the coefficient of self-diffusion of water in solutions of KCl and KI is actually greater than that in pure water. At the same time he found that the self-diffusion coefficient of water in NaCl solution is less than that in pure water. Other investigators[5-7] have subsequently confirmed Wang's results and have extended them to include other salts. At least two different techniques,

[1] B. N. Brockhouse, Nuovo Cimento Suppl. **9**, 45 (1958).
[2] K. E. Larsson, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), Chap. 8.
[3] O. Ya Samoilov, *Struktura Vodnykh Rastvorov Elektrolitov I Gidratatsiya Ionov* (USSR Academy of Science, Moscow, 1957) [English transl.: *Structure of Aqueous Electrolyte Solutions and the Hydration of Ions* (Consultant's Bureau Enterprises, Inc., New York, 1965), Chap. 3].

[4] J. H. Wang, J. Phys. Chem. **58**, 686 (1954).
[5] J. Tamas, S. Lengyel, and J. Giber, Acta Chim. Acad. Sci. Hung. **38**, 225 (1963).
[6] K. A. Valiev and M. I. Emel'yanov, Zh. Strukt. Khim. **5**, 670 (1964) [English transl.: J. Struct. Chem. **5**, 625 (1964)].
[7] D. W. McCall and D. C. Douglass, J. Phys. Chem. **69**, 2001 (1965).

radiotracer diffusion and NMR spin-echo have been employed and have yielded similar results.

II. EXPERIMENTS

The experiments we wish to report were performed on the slow-chopper time-of-flight equipment at the Brookhaven Graphite Reactor. Two samples were employed: triply-distilled water, and a $4N$ aqueous solution of NaCl. The sample holder was constructed entirely of aluminum and the sample thickness was fixed at 10 mils through the use of shim-stock spacers. Larsson et al.[8] have shown that for this thickness multiple scattering is not significant. During the experiments liquid was continuously circulated through the holder by means of a pump; inside the pump, the liquid came into contact only with tygon tubing. Thus, the holder remained full and the sample remained free from contamination throughout the counting period. Data were collected at a scattering angle of 90°, the maximum value accessible to the chopper counter arm. The data were taken first with a channel width of 32 μsec to provide the full time-of-flight spectra. Next, the channel width was decreased to 16 μsec, and the scattering experiments were repeated. The latter data yielded neutron energy distributions in the quasi-elastic scattering region with an energy resolution of 2.5%. The resolution was determined by fitting time-of-flight spectra for vanadium with a Gaussian-broadened, beryllium-filtered incident-neutron spectrum. In Fig. 1 are shown the spectra for water and the $4N$ aqueous NaCl solution taken with a channel width of 32 μsec. The important point to notice is that no new structure is introduced by the addition of NaCl in this concentration to pure water. This observation is consistent with the current model of water structure and with the state of ions in aqueous solutions as described by Samoilov[9] and by Bergqvist and Forslind,[10] for example. They regard the solute as being integrated into the existing water structure by ordinary chemical bonding. Thus, the solute ions are not surrounded by a hydration sheath of water molecules that is separated from the main water lattice and moving independently in the solvent. These conclusions are based upon coordination numbers for ions deduced from measurements of heats of solution, as well as upon x-ray and neutron-scattering data and proton-magnetic-resonance studies of the water-lattice structure in aqueous alkali halide solutions. Of course, at some high concentration the struc-
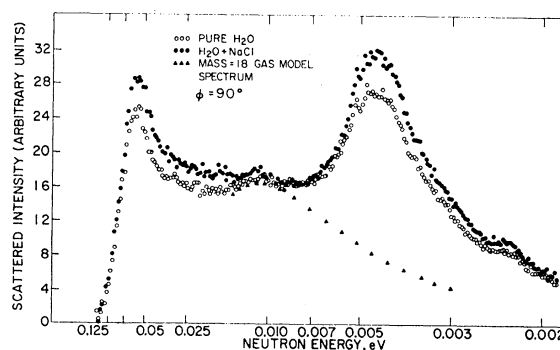

FIG. 1. Neutron time-of-flight spectra observed at 90° for pure water and for a $4N$ aqueous solution of NaCl. The sample thickness in each case was 0.010 in. and the channel width was 32 μsec. The triangles represent the scattering by a gas of mass-18 scattering centers.

ture of a salt solution must begin to approach that of the hydrated salt. For NaCl, this limiting concentration is evidently much greater than that used here. The neutron time-of-flight spectra of Fig. 1 imply that the structure of the salt solution is determined by the water structure so that the conclusions of dilute-solution theory are applicable.

III. ANALYSIS OF RESULTS

Brockhouse[1] has pointed out that the shape of the broad inelastic spectrum in the vicinity of the elastic peak resembles that from a monatomic gas of mass 18. Therefore, he fitted the mass-18 gas-scattering cross section to his experimental spectrum and, by subtraction, obtained the elastic contribution. Sköld et al.[11] have employed the same method more recently. We have performed our analysis in the same manner. The curve represented by triangles in Fig. 1 corresponds to our fit of the mass-18 gas-scattering cross section to the inelastic spectrum in the appropriate energy range. The resulting gas-scattering curve then was scaled to the 16-μsec data for pure water and for the salt solution. It should be pointed out that before the fitting procedure was carried out the experimental data were corrected for background, chopper transmission, detector efficiency, absorption along the flight path, and for Bragg scattering by aluminum in the flight path and by the iron walls of the BF_3 detectors. Finally, each mass-18 scattering distribution was subtracted from its corresponding experimental time-of-flight spectrum. The results of the subtraction process are shown in Fig. 2. In the same figure is shown the spectrum of vanadium in this region.

The current theoretical and experimental aspects of thermal-neutron scattering by liquids have been reviewed recently by Sjölander[12] and Larsson,[2] respec-

[8] K. E. Larsson, S. Holmryd, and K. Otnes, in Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, October 1960 (International Atomic Energy Agency, Vienna, 1961), p. 329.

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[11] K. Sköld, E. Pilcher, and K. E. Larsson, Atomic Energy Report No. AE-133, Stockholm, Sweden, 1964 (unpublished).

[12] A. Sjölander, in Thermal Neutron Scattering, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), Chap. 7.
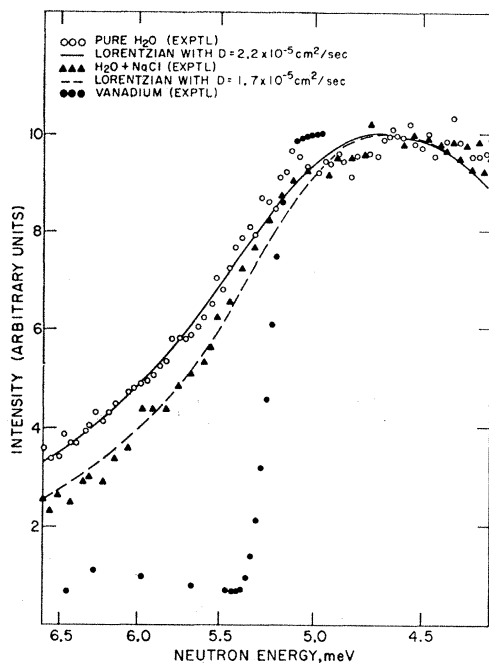
FIG. 2. Open circles represent the quasi-elastic peak at 90° for pure water after subtraction of the inelastic contribution according to the gas model for mass-18 scattering centers. The solid line represents the Lorentzian-broadened incident spectrum for a D value of 2.2×10^{-5} cm²/sec. The neutron spectrum of vanadium in this region is represented by closed circles. Solid triangles represent the quasi-elastic peak at 90° for a $4N$ aqueous solution of NaCl after subtraction as above. The corresponding D value is 1.7×10^{-5} cm²/sec. The incident-beam neutron energy begins at 5.2 meV.

tively. In the absence of a fundamental theory of liquids, numerous simplified models have been proposed. The simplest of these, applicable to incoherent scatterers such as hydrogen, is that first proposed independently by Brockhouse[1] and Vineyard[13] and later rederived by others.[12] Vineyard suggested that the self-correlation function $G_s(\mathbf{r},t)$ be assumed to satisfy the macroscopic diffusion equation with the initial condition that $G_s(\mathbf{r},0)$ equal $\delta(\mathbf{r})$. This assumption leads directly to a Gaussian solution for $G_s(\mathbf{r},t)$, and a Lorentzian scattering law for fixed momentum transfer whose full width at half-maximum is given by the expression

$$\Delta E = 2\hbar D\kappa^2. \qquad (2)$$

In this equation $\hbar$ has its usual meaning, D is the macroscopic self-diffusion coefficient, and κ is the wave-vector transfer in a scattering event.

Thus, if the broadening of the quasi-elastic peak is related to the macroscopic self-diffusion coefficient, the data shown in Fig. 2 should fit a Lorentzian-broadened Be-filtered spectrum. The Lorentzian should have a half-width of $2\hbar D\kappa^2$, and the value of D should agree with that obtained from the self-diffusion experiments mentioned earlier. The solid curves in Fig. 2 represent

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[13] G. H. Vineyard, Phys. Rev. 110, 999 (1958).

such Lorentzian-broadened spectra obtained by integration over the incident energy spectrum, the energy dependence of κ being included in the integration. The value of D that fits the pure-water data was found to be 2.2×10^{-5} cm²/sec, while that which best fits the NaCl data is 1.7×10^{-5} cm²/sec. Wang's[4] values for the quantities deduced from radiotracer studies are 2.57×10^{-5} and 1.85×10^{-5} cm²/sec, respectively. The corresponding nuclear-magnetic-resonance results recently reported by McCall and Douglass[7] are 2.45×10^{-5} and 1.7×10^{-5} cm²/sec, respectively. Reviewing the existing data for pure water, the latter authors suggest that an acceptable average value for the self-diffusion coefficient of pure water would be $2.3 \pm 0.23 \times 10^{-5}$ cm²/sec. It would be surprising if the agreement between our results and those quoted by McCall and Douglass were any better in view of the many corrections that were employed in reducing the time-of-flight data to final form. The good agreement between the two sets of measurements suggests to us that the quasi-elastic peak in the water spectra arises primarily from the diffusive motion of individual water molecules.

IV. DISCUSSION

Current attempts to understand the behavior of water have led to a structural model consisting of a tetrahedrally bonded ice-like framework and nonassociated individual water molecules.[3,10] With such a complicated structure to consider it is reasonable to inquire into the meaning of self-diffusion measurements. In this regard, Wang[14] has shown that the quantity $D\eta/T$, where η is the viscosity and T the absolute temperature, remains constant between 5°C and 25°C to within ±0.5%. From the Einstein-Stokes theory for diffusion in liquids Wang then infers that the effective volume of the diffusing species must remain essentially constant over this temperature interval. It is noteworthy that in an earlier study using deuterium as a tracer rather than O^{18}, Wang[15] concluded that the effective volume of the diffusing entity was constant between 0°C and 55°C. Thus, Wang's results lead to the conclusion that around room temperature only one type of molecule is diffusing. From the magnitude of the self-diffusion coefficients it seems most probable that the diffusing entity is a single water molecule. The recent spin-echo results substantiate this viewpoint. McCall and Douglass[7] have measured the self-diffusion coefficient of water in many aqueous solutions as a function of concentration. Their results are in excellent agreement with those of Wang, and they have concluded that the proton resonance technique measures the same quantity as the radiotracer technique, namely, the true macroscopic self-diffusion coefficient of water.

The most recent attempt by Pelah and Imry[16] to

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[15] J. H. Wang, J. Am. Chem. Soc. 73, 510 (1951).
[16] I. Pelah and Y. Imry, Phys. Letters 21, 248 (1966).

explain the quasi-elastic scattering of neutrons by water in terms of energy transfers between scattered neutrons and the translational motion of large aggregates of water molecules seems to us unsatisfactory in view of our results. The narrowing of the quasi-elastic peak produced by the addition of NaCl to water would require an appreciable increase in the size of the aggregate in the Pelah and Imry model. However, even if one adopts the older picture of hydrated ions, one finds that the estimated number of water molecules associated with one ion is only of the order of ten[17] rather than several hundred as required by Pelah and Imry. Moreover, neutron time-of-flight experiments[18] have firmly established the similarity between water and ice spectra. These results lend credence to the defect model of water

structure in which lattice defects (interstitials and vacancies) are created when hydrogen bonds are broken. The nonassociated interstitial molecules enter the cavities in the open tetrahedral structure of the water lattice and are free to diffuse. The vacancies likewise are free to diffuse in the lattice. Large aggregates with a distribution in size are not required in this model. That neutrons can "see" the translational motion of individual molecules is substantiated by the fact that the 60-cm^{-1} band in the frequency distribution of water does not shift when protons are replaced by deuterons.[17] Thus, the 60-cm^{-1} band is due to the translational motion of individual molecules in which the oxygen atom and the proton undergo displacement together.

ACKNOWLEDGMENT

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Single-Particle States of an Electron-Ion Gas in the Random-Phase Approximation*

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The formulation of quantum statistical mechanics by means of Green's functions or propagators is used to discuss some new results for the electron-ion gas in the random-phase approximation. The theory is formulated in terms of the density variation, the difference between the mean density and the equilibrium value, which is nonvanishing because of the existence of an external field. This method is closely associated with the more familiar formulation in terms of current-current correlation functions. The contribution from the single-particle states occurs in two forms—the particle-hole continuum and the "exchange effect" between noninteracting particles. The density variations and "relaxation times" of these contributions are derived and discussed in detail. It is shown that the "exchange effect" is not an exchange effect at all since the results for this contribution are derivable on the basis of classical theory. This situation is also discussed in detail. The hierarchy of relaxation times for the various contributions to the density variation is considered. It is shown that the hierarchy has structure for collective states different from that for single-particle states.

I. INTRODUCTION

O NE of the most powerful tools in the development of quantum statistical mechanics in recent years has been the method of Green's functions or propagators.[1–4] This method has been used to study various physical systems which, at first sight, do not seem to have many properties in common.

A system which has been studied a great deal is the interacting electron-ion gas, both in the limit of low temperature and high density[1–10,14] and in the limit of high temperature and low density.[11–14] The first limit

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