Table 1. Self-diffusion coefficient of water, $D \times 10^5$ cm²/sec. T, temperature.

T (°C)	Faujasites			Bulk water	
	Na X	Ca X	Ca Y	This work	Simpson and Carr (*10*)
0				1.04	
10		0.74	0.81	1.44	1.36
20	1.00				1.85
25				2.23	
30	1.34	1.65	1.88		2.46
40	2.11	2.41	2.78	3.40	3.14
60	4.10	4.61	5.47	5.47	4.82
69	5.30				
70					5.78

equilibrated with the atmosphere. Four windows about 8 Å in diameter lead from each cavity to four similar adjacent cavities. Charge-compensating cations (for example, sodium) occupy various positions in the structure.

Because of the presence of these large accessible cavities, faujasite has recently received a great deal of attention as an adsorbent and catalyst. It was decided to use this material in order to reexamine the possible effect of the solid on liquid structure and to measure self-diffusion of water in faujasite by means of pulsed gradient spin-echo nuclear magnetic resonance (NMR), as described by Stejskal and Tanner (*4*). This method, which evolved from the original one of Carr and Purcell (*5*), has many advantages of speed and simplicity that make it much more desirable than the conventional techniques previously used in such work.

The apparatus we used has been described in detail (*6*). The basic spin-echo spectrometer was the model ELH-15 constructed by Magnion Inc., Burlington, Massachusetts. Magnetic field gradients G were applied by winding a pair of magnetically opposed coaxial coils on tapered forms with their axis parallel to the laboratory field. The coils were designed so as to produce as large a region of homogeneous gradient as possible. They were calibrated with pure water by assuming a value for D equal to 2.51×10^{-5} cm² sec^{-1} (*7*) and by determining G with the use of the expressions given by Abragam (*8*) which also relate D to the spin-echo amplitude data. The gradient switch was activated by the pulse output of two Tektronix type 163 pulse generators, which were referenced to the transmitter pulse sequence. Two near-faujasite samples were obtained from the Linde Company. They were in the sodium form and designated as Na X and Na Y, the main difference between the two being in the Si:Al ratio (approximating 1 for X and 2 for Y). The Ca X and Ca Y samples were prepared from those by ion exchange.

The self-diffusion coefficients of pure water and of water in the various zeolites are given in Table 1. Eight different gradients were used at each temperature, and the indicated value for D is an average of the eight values obtained. The data of Table 1 yield straight lines in plots of ln D versus $1/T$. Activation energies E_D corresponding to $D = D^* \exp(-E_D/RT)$ are 6.9, 6.8, 5.6, and 5.0 kcal/mole for water in Na X, Ca X, Ca Y, and bulk water, respectively. These minor differences in temperature coefficient are further compensated by corresponding minor variations in preexponential factors D^*, so that values of D for water in faujasite are only slightly lower (by less than a factor of 2 at low temperature) than the value of D in pure water.

This then is the main result of our investigation: as revealed by very similar values of D, the motion of water molecules in faujasite resembles very much that of pure water. It appears that the cavities and windows in the structure are large enough so that the influence of the crystal lattice becomes minor. It is important to note that the spin-echo NMR technique concerns itself with motion of protons over large distances that cover many cages and windows. Indeed the duration of a gradient pulse is of the order of 10^{-3} second, and during this time a water molecule will have diffused over a distance of the order of 10^{-4} cm.

Barrer *et al.* (*9*) have remarked that molecular sieves provide a macromolecular framework not unrelated to that found in many biological systems. If this is so, the results of this work may be of interest not only to those concerned with molecular sieves as adsorbents and catalysts. Finally, for studies of diffusion in these and other porous materials, the NMR method used here seems to have very wide applicability.

CARLO PARRAVANO
J. D. BALDESCHWIELER
MICHEL BOUDART
John Stauffer Laboratories for Chemistry and Chemical Engineering, Stanford University, Stanford, California 94305

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12 January 1967

Crystallization of Human Lysozyme

Abstract. *Lysozyme, isolated from the urine of patients with monocytic leukemia, has been crystallized as the chloride at* p*H 4.5 and at* p*H 10.5. The crystal forms of the human enzyme show certain similarities as well as distinct dissimilarities compared with the crystal forms of lysozyme chloride from hen's egg white.*

There are large quantities of lysozyme in the serum and urine (up to 4 g per day) of patients with monocytic and monomyelocytic leukemia (*1*). The enzyme has been isolated from the urine of several patients; physicochemical and immunochemical analyses indicate that it is a low-molecular-weight (≅ 14,000) basic protein with an isoelectric point at about *p*H 10.5. The lysozyme present in these serums and urines is apparently identical to that of normal human tears, saliva, leukocytes, and serum; but it is structurally different from the lysozyme of hen's egg white (*1*). Whereas the human and egg-white lysozymes are of similar molecular size and basicity, they differ significantly in amino acid composition, tryptic peptide ("fingerprint") patterns, antigenic structure, and enzymatic activities. When assayed with heat-killed *Micrococcus lysodeikticus* organisms, the activity of the human enzyme has been found to be 3 to 12 times greater than that of twice-crystallized egg-white enzyme.

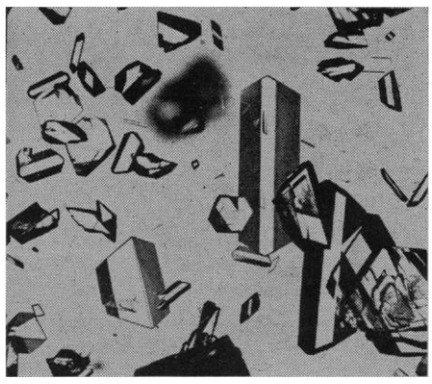

Fig. 1. Human lysozyme chloride; *p*H 10.5; 6 days at 25°C.

I now report the crystallization of human lysozyme chloride. The procedure was essentially identical to that described by Alderton, Ward, and Fevold (*2*, *3*) for the crystallization of hen's egg-white lysozyme chloride. The enzyme was isolated from the urine of patients with monocytic leukemia by its adsorption to bentonite and elution with 5 percent aqueous pyridine adjusted to *p*H 5.0 with sulfuric acid. After exhaustive dialysis against distilled water, the solution of amorphous enzyme was lyophilized. It was then dissolved to a concentration of 50 mg/ml in 5 percent sodium chloride solution adjusted either to the isoelectric region (*p*H 10.5) with sodium hydroxide or to *p*H 4.5 with hydrochloric acid. When cooled to 9°C, copious crystallization in the form of needles occurred within a few hours at both *p*H 10.5 and *p*H 4.5. The needle-like crystals at *p*H 4.5 were randomly dispersed, whereas those at *p*H 10.5 were grouped in bundles resembling wheat sheaves (see cover). After several days at 9°C, the needles of lysozyme chloride at *p*H 10.5 developed into hexagonal prisms up to 2 mm in length. When crystallization from these solutions proceeded more slowly at room temperature (23° to 25°C), polygonal plates and polyhedrons formed with a preponderance of hexagonal prisms, particularly at *p*H 10.5 (Fig. 1). These hydrated crystals were birefringent; but, after drying, this property was lost, concomitant with the appearance of transverse fractures.

The sheaves of needle-like crystals of human lysozyme chloride formed in the cold at *p*H 10.5 resemble those of hen's egg-white lysozyme chloride developed under similar conditions (*3*). The polyhedral and hexagonal prismatic forms of the crystallized human enzyme, however, are distinct from the first-order tetragonal bipyramidal and second-order short prismatic forms of egg lysozyme chloride (*3*, *4*) and are consistent with the previously noted structural and chemical differences between these two enzymes. Detailed optical and x-ray crystallography studies of the human enzyme, similar to those carried out on egg-white lysozyme (*4*, *5*) should provide useful information on the comparative structures of two different enzymes with very similar substrate specificities.

ELLIOTT F. OSSERMAN
Department of Medicine, Columbia University College of Physicians and Surgeons, and *Francis Delafield Hospital, New York*

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6. Supported by PHS grant CA-02332.

4 January 1967

Activity Coefficients of Aqueous Potassium Chloride Measured with a Potassium-Sensitive Glass Electrode

Abstract. *Values of $\gamma_{\pm KCl}$ over temperature and molality ranges of 10° to 50°C and 0.01 to 1.0 molal were determined with an electromotive-force cell: potassium-sensitive glass electrode, KCl (molality), Ag–AgCl. A more satisfactory method than is commonly employed was devised for treating the experimental measurements of potential.*

One of the many applications of the recently developed cation-sensitive glass electrodes is to determine mean activity coefficients, $\gamma_{\pm}$, of salts, singly or in mixtures, in aqueous solution. At least for monoelectrolyte solutions of univalent-cation salts, we believe that the accuracy of such values thus derived rivals that by more classical methods. Moreover, the cation-sensitive glass electrode stands alone in convenience. We now report $\gamma_{\pm}$ values for KCl at 10°, 18°, 25°, 38°, and 50°C. Our purpose is twofold: to check the accuracy of the technique at 25°C (at which temperature, data by classical methods are plentiful) and to present values for $\gamma_{\pm KCl}$ at other temperatures, at which earlier data are more meagre.

Our cell is without liquid junction and consists of a potassium-sensitive glass electrode, the aqueous KCl solution to be measured, and a Ag–AgCl electrode; it is represented as:

K-sensitive glass electrode, KCl (molality, m), Ag–AgCl

The potassium-sensitive electrode used was a Beckman 39137, the glass membrane of which has the recommended composition (*1*). The Ag–AgCl electrode was produced by electrolytic deposition of chloride on a silver-billet electrode (*2*).

Potential measurements were made with a vibrating-capacitor, high-impedance electrometer (Vibron 33B) and a potentiometer. Solutions were maintained to within 0.1°C of the desired temperature in a constant-temperature bath and were stirred magnetically. Individual measurements of potential were read to within 0.02 mv.

The potential developed by our cell may be expressed as:

$$E = E' + S(T) \log (\gamma m) \qquad (1)$$

where $(\gamma m) = (\gamma_{\pm} m_{\pm})_{KCl}$, $S(T) = 2(2.303\ RT)/F$, R is the gas constant, T is the absolute temperature, F is the Faraday, and m is the molality of the KCl solution. The quantity E' is a complex function of the glass and the particular construction of the K-sensitive electrode, and of the Ag–AgCl electrode. By comparing the potential E_s of a standard solution, of molality m_s and of known γ_s, with the potential E_x of a solution of molality m_x to determine γ_x, E' may be eliminated, and Eq. 1 yields

$$[(E_x - E_s)/S(T)] - \log (m_x/m_s) + \log \gamma_s = \log \gamma_x \qquad (2)$$

This method, which is analogous to that employed in determinations of *p*H, was used (*1*) to determine $\gamma_{\pm NaCl}$ over a molality range of approximately 0.13 to 6.1; 1.0-molal NaCl was used as the standard solution.

In deriving Eq. 2 one assumed that E' is constant; however, the value of E'