DIFFUSION COEFFICIENTS OF WATER IN WHEAT KERNELS[1]

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ABSTRACT

The diffusion coefficients of four varieties of wheat, Ponca (HRW) and Vernum (durum) wheats representing hard wheats and Seneca (SRW) and Brevor (SWW) wheats representing soft wheat, were measured under previously untried conditions (maximum temperature, 98.3°C. and maximum diffusion time, 8 hours). The theoretical treatment and the experimental techniques proposed by previous investigators were found to be valid under the conditions of the present investigation.

The values of the diffusion coefficients ranged from 2.7×10^{-8} cm^2/sec (26.7°C.) to 245.6×10^{-8} cm^2/sec (98.3°C.) for Ponca wheat, 2.2×10^{-8} cm^2/sec (30°C.) to 75.2×10^{-8} cm^2/sec (86°C.) for Vernum wheat; 3.1×10^{-8} cm^2/sec (26.7°C.) to 140.9×10^{-8} cm^2/sec (98.3°C.) for Seneca wheat; and 2.7×10^{-8} cm^2/sec (30°C.) to 89.2 cm^2/sec (86°C.) for Brevor wheat.

The effective surface moisture content is independent of temperature, and the diffusion coefficients at temperatures below about 65°C. are practically independent of variety. The diffusion coefficients, and therefore the activation energies for diffusion, increase sharply above this temperature for four varieties of wheat.

The diffusion coefficient of water in wheat kernels is of practical importance in the drying and tempering of wheat, since these processes involve the transport of water in and out of wheat kernels.

Although the problem of water diffusion into wheat kernels has been studied for some time, most of the previous studies have been qualitative in nature. The study of mechanism and the quantitative treatment of data of water diffusion into wheat kernels, however, have been initiated only recently (1,2,3,5). Grosh and Milner (5) investigated the mechanism of water diffusion by visual and X-ray methods. They found that crack formation precedes the diffusion of water at the initial stage. Becker and his co-workers (1,2,3) developed a mathematical model based on Fick's Law of diffusion which correlates both absorption and desorption data.

The diffusion coefficients of water in four varieties of wheat, Ponca and Vernum representing hard wheat, and Seneca and Brevor representing soft wheat, measured at various temperature levels, are reported in this paper. The maximum temperature of 98.3°C. at which the measurement was made was considerably higher than that of 70.5°C. attained in previous measurements (1,2).

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Theoretical Aspect

The diffusion coefficient is defined by Fick's Law as (6):

$$D\left(\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2}\right)=\frac{\partial c}{\partial \theta} \qquad (1),$$

where D is the diffusion coefficient, c is the concentration of diffusing substance at a point in a solid, x, y, and z are Cartesian coordinates of the point under consideration, and θ is the diffusion time. Becker (1) demonstrated that equation 1 is integrated for the particle of arbitrary shape under the assumption that the surface-to-volume ratio, S/V, remains constant as:

$$\overline{C}=1-\frac{2}{\sqrt{\pi}}X+BX^2 \qquad (2),$$

where $\overline{C}=\frac{\bar{c}-c_s}{c_o-c_s}$ in which $\bar{c}$ is the average concentration, c_o the initial concentration, and c_s the concentration at bounding surface, $X = S/V\sqrt{D\theta}$, and B = a dimensionless constant. If the concentration term is represented by the moisture content on a weight basis:

$$\overline{C}=\overline{M}=\frac{\overline{m}-m_s}{m_o-m_s} \qquad (3),$$

in which $\overline{m}$ is the average moisture content at the given immersion time, m_s is the effective surface moisture content, and m_o is the initial moisture content (moisture contents expressed in g/g). Equation 2, then, can be written as follows:

$$\overline{M}=1-\frac{2}{\sqrt{\pi}}X+BX^2 \qquad (4).$$

For small values of X, equation 4 approximates to:

$$1-\overline{M}=\frac{2}{\sqrt{\pi}}X \qquad (5),$$

or, in terms of experimental variables:

$$\overline{m}-m_o=K\sqrt{\theta}$$

$$\text{where } K=\frac{2}{\sqrt{\pi}}(m_s-m_o)\frac{S}{V}\sqrt{D} \qquad (6).$$

Becker (1,2) demonstrated that this equation was valid up to a moisture level of 0.57 g/g in wheat kernels.

Materials and Methods

The varieties of wheat used in this study were Ponca (hard wheat), Vernum (hard wheat), Seneca (soft wheat), and Brevor (soft wheat). The pycnometer method was applied to measure the initial densities of wheat. A 50-cc. pycnometer with toluene as the fluid was used with

5-g. samples of wheat. Densities of Ponca, Vernum, Seneca, and Brevor wheats used were 1.357, 1.315, 1.312, and 1.345 g/cc respectively. Protein contents of Ponca, Vernum, Seneca, and Brevor were 12.7, 13.85, 10.5, and 9.63% respectively.

The initial moisture contents were 15.6% (dry basis) for Ponca, 14.72% (dry basis) for Vernum, 13.4% (dry basis) for Seneca, and 11.05% (dry basis) for Brevor.

To estimate the sphericity, the porosity was calculated by using the bulk and true densities of wheat. After the porosity was known, sphericity was estimated from the plot of sphericity as a function of porosity (4). The estimated sphericities were approximately 0.91 for Ponca, 0.90 for Vernum, 0.84 for Seneca, and 0.91 for Brevor. The values of the sphericity of Ponca, Vernum, and Brevor were identical with that of Thatcher wheat estimated by Becker (1,2).

The volume-to-surface-area ratio was then evaluated by using the formula (1), $V/S = \psi r_v/3$, where ψ is the sphericity, and r_v is the radius of a sphere with volume equal to that of the wheat kernel. The values of the volume-to-surface-area ratio, V/S, for Ponca, Vernum, Seneca, and Brevor wheats were found to be 0.0547, 0.0607, 0.0504, and 0.0597 cm. respectively.

Twenty-gram samples of wheat were placed in wire gauze baskets and immersed in a stirred water bath controlled within 0.5°C. of the set temperature. The pH of the steeping water used in this study ranged from 7.5 to 8.0. Experiments were carried out with temperatures ranging from 26.7° to 98.3°C., and for immersion periods from several minutes to 8 hours. At the end of each immersion period, each sample was quickly removed from the water bath and superficially dried on a large filter paper (2). After the surface water on the wheat kernels was removed, the weight of the sample was determined.

To evaluate the effective surface moisture content, samples were prepared with initial moisture contents ranging from 15.6 to 52.4% (dry basis) for Ponca, from 14.7 to 38.4% (dry basis) for Vernum, from 13.4 to 42.7% (dry basis) for Seneca, and from 11.05 to 34.5% for Brevor. Samples were immersed in water at 30° and 70°C. and their final moisture values were measured after 15 minutes.

Results and Discussion

The relation between moisture gain and the square root of the immersion period is shown in Fig. 1 for Vernum wheat. Results for other wheats were similar to those of Fig. 1 for Vernum wheat. There was a rapid moisture pick-up by capillary action at the moment wheat kernels contact water. This moisture pick-up by capillary action, m_i, increased slightly and linearly with increasing temperature. The increase was approximately 2% at 30° and 4% at 90°C. for each variety of wheat. As indicated in Fig. 1, m_i was subtracted from the total moisture gain since m_i was due to a phenomenon other than diffusion (2).

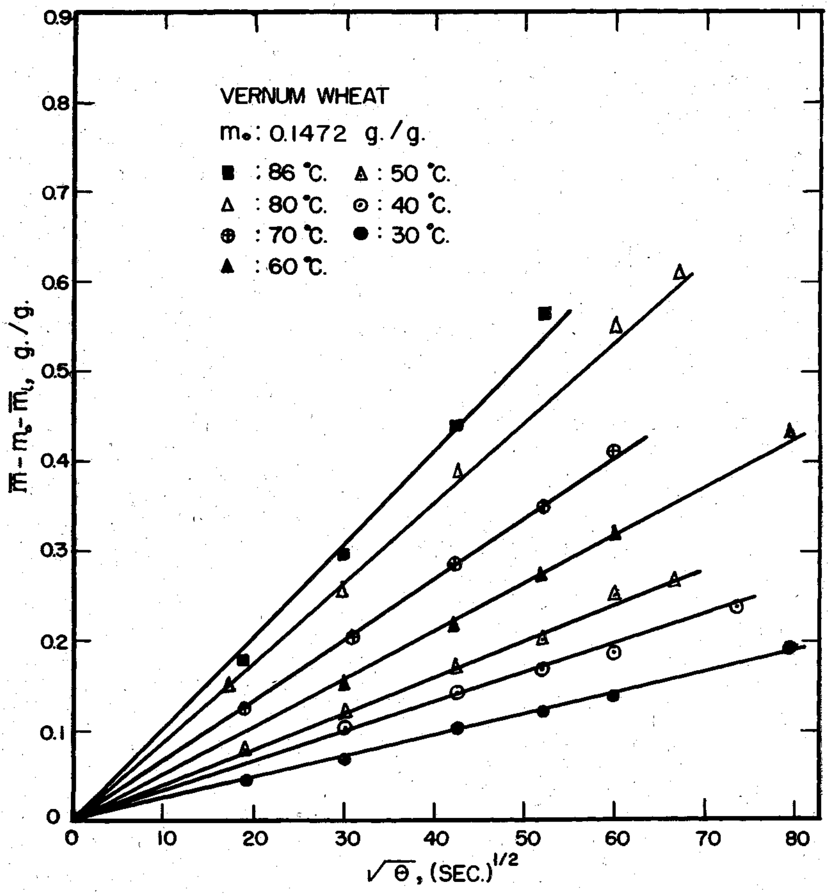

Fig. 1. Linear relation between moisture gain and square root of absorption time for Vernum wheat.

Ranges of validity of equation 6 were different for hard wheat and soft wheat. It was smaller for the latter, especially at high temperatures. The slopes of curves in Fig. 1 and similar figures for other wheats were obtained by the method of least squares.

The values of effective surface moisture content, m_s, required in evaluating the diffusion coefficients were measured at two temperature levels as shown in Fig. 2 for Vernum and Ponca wheat (2). A similar figure was obtained for Seneca and Brevor wheat. The effective surface moisture content for Ponca wheat was in close agreement with that for Thatcher wheat as measured by Becker (2). This result indicates that the effective surface moisture content is, for all practical purposes, independent of temperature level. These values of effective surface moisture contents, which are equilibrium moisture contents for the diffusion process, should also indicate that the applicability of equation 5 or 6 above those moisture contents is empirical in nature. The applicability of Fick's Law ceases above the equilibrium moisture content. The equilibrium moisture content may actually change continually with progress of water absorption owing

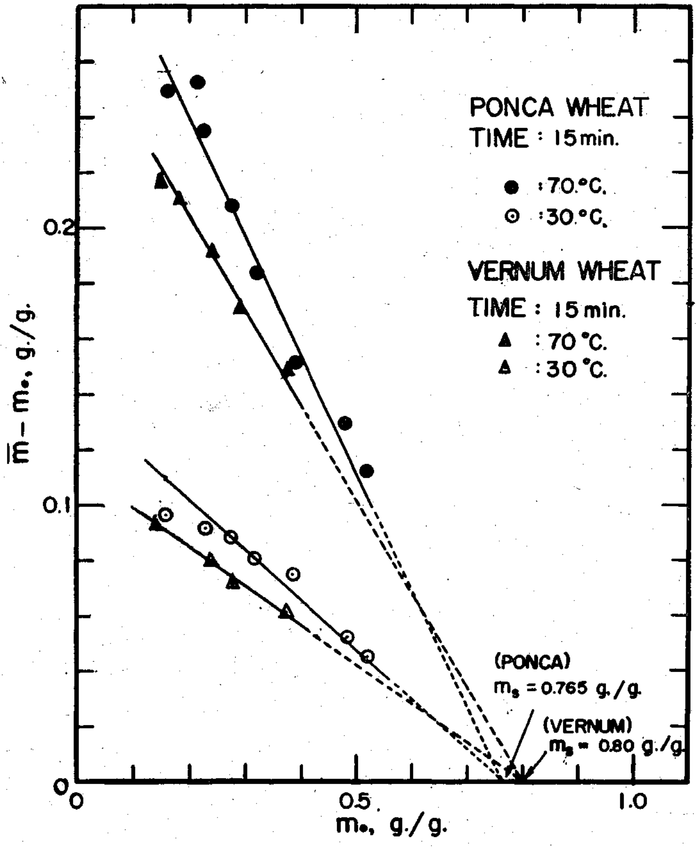

Fig. 2. Moisture gain as a function of initial moisture content at 70° and 30°C., showing the linear regression on effective surface moisture contents for Ponca and Vernum wheat.

to the considerable structural change of wheat kernels.

The diffusion coefficients, D, could be evaluated from equations 5 and 6 after the effective surface moisture contents were known.

$$D = \left[\frac{\sqrt{\pi}}{2} \frac{V}{S} \frac{K}{(m_s - m_o)} \right]^2$$

The diffusion coefficients obtained are listed in Table I. Figure 3 for Vernum and Brevor wheat shows the diffusion coefficients calculated from experimental data as a function of the reciprocal of absolute temperature. A similar figure was also obtained for Ponca and Seneca wheat. These figures show Arrhenius relation for the diffusion coefficients, $D = D_0 \exp\left(-\frac{E}{RT}\right)$, in which E is the activation energy, and D_0 is the constant. The constant (frequency factor), D_0, and the slope, (E/R), of the linear regression of the Arrhenius relation were estimated by the method of least squares.

TABLE I

DIFFUSION COEFFICIENTS

TEMPERATURE	VARIETY OF WHEAT			
	Ponca	Vernum	Seneca	Brevor
°C	$D \times 10^8$ cm^2/sec	$D \times 10^8$ cm^2/sec	$D \times 10^8$ cm^2/sec	$D \times 10^8$ cm^2/sec
26.7	2.7		3.1	
30.0		2.2		2.7
32.2	4.4			
37.8	6.0		6.0	
40.0		5.0		5.3
48.9	10.3		12.8	
50.0		7.2		8.2
54.4	13.8			
60.0	18.2	14.6	22.3	16.3
65.6	27.5			
69.4			30.0	
70.0	41.1	23.3		26.2
76.7	75.4			
80.0		48.1		53.8
81.7	118.6			
82.2			61.8	
86.0		75.2		89.1
98.3	245.6		140.9	

It can be seen that a poor correlation by the Arrhenius relation results when the diffusion coefficients are correlated in a single linear regression for each variety of wheat. D at high temperature deviates markedly from a single regression. Careful inspection indicates that every plot of the Arrhenius relation shows consistently concave curvatures. The best linear correlation, however, is obtained when the

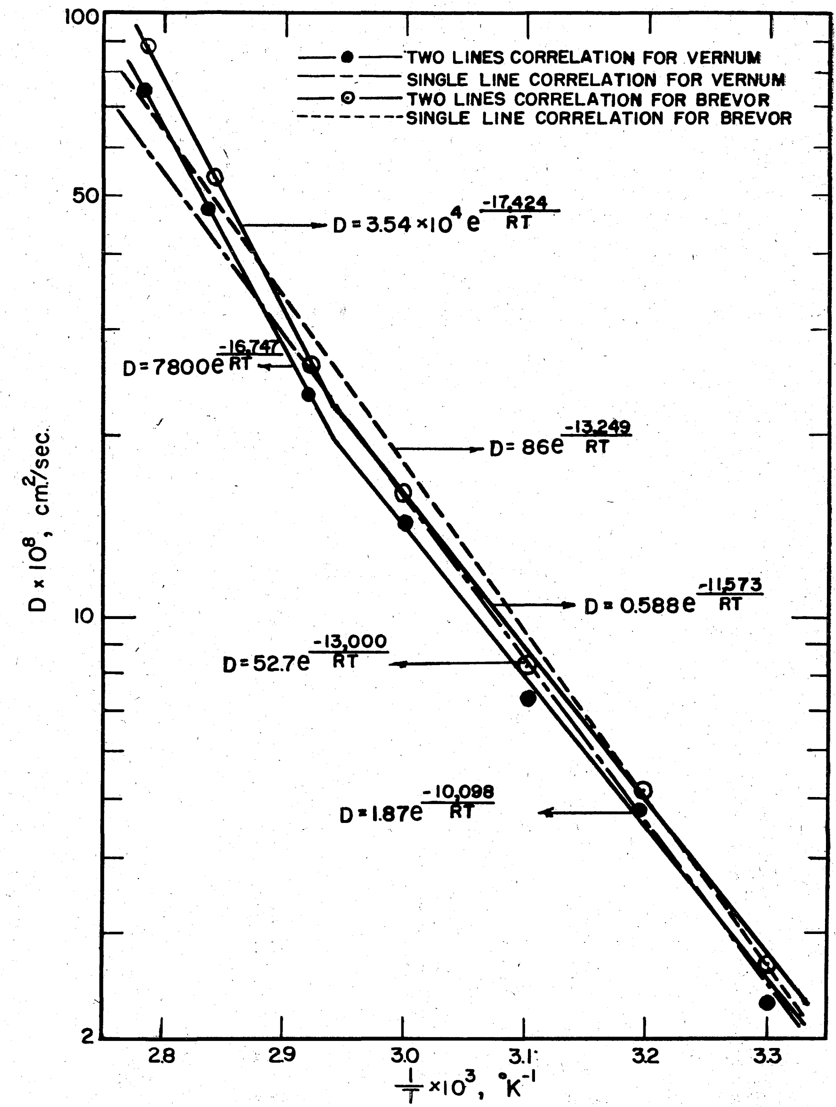

Fig. 3. Diffusion coefficient as a function of the reciprocal of absolute temperature for Vernum and Brevor wheat.

data are divided into two parts as shown in Fig. 3.

Activation energies, E, and constants, D_0 in a single regression line and two regression lines of the Arrhenius relation are presented in Tables II and III.

TABLE II

THE CONSTANTS, D_0, AND ENERGIES OF ACTIVATION, E, IN SINGLE LINE CORRELATION OF THE ARRHENIUS RELATION

VARIETY OF WHEAT	D_0	E
	cm²/sec	*kcal/mol*
Ponca	142	13.3
Vernum	52.7	13
Seneca	6.3	11.4
Brevor	86	13.3

TABLE III

THE CONSTANTS, D_0, AND ENERGIES OF ACTIVATION, E, IN TWO-LINE CORRELATION OF THE ARRHENIUS RELATION

VARIETY OF WHEAT	RANGE OF TEMPERATURE	D_0	E	ΔE
	C°	*cm²/sec*	*kcal/mol*	*%*
Ponca	Below 65	4.7	11.2	71.0
	Above 65	5.7×10^5	19.2	
Vernum	Below 65	1.9	10.1	63.2
	Above 65	7.8×10^3	16.5	
Seneca	Below 65	1.0	10.2	39.3
	Above 65	390	14.3	
Brevor	Below 65	0.59	11.6	50.6
	Above 65	3.5×10^4	17.4	

The diffusion coefficients and activation energies at temperatures below about 65°C. fall within the range of the diffusion coefficients and the activation energy evaluated by Becker (2) for Thatcher wheat. The diffusion coefficients at temperatures below this are almost independent of variety of wheat in contrast to Fraser and Haley's results (2).

The activation energies at temperatures above 65°C., however, markedly increase for each variety of wheat. The increase is from 40 to 70% of the values below 65°C., with hard wheats generally showing greater increase than the soft wheats.

It appears that the rise in the value of E may be associated with thermal change of the molecular structure of wheat, specifically due to the starch gelatinization and protein denaturation (3; and personal communication from H. A. Becker). Gross changes in the macro structure which would affect the diffusion properties also could cause the change in activation energies. Gelatinization of starch and protein denaturation are complex problems. In fact, there is still no clear picture of the mechanism of granule gelatinization and protein denaturation. It can be expected, however, that the gelatinization of starch and protein denaturation take place rapidly above 65°C.

Acknowledgment

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