

tive viscosity, the diffusion coefficient would be independent of the volume fraction of added third component, if Stokes' law were applicable. Instead, the data show a linear regression with volume fraction of addend to within $\pm 0.16\%$. The slope of this line, following the form of equation 1, is 1.66, compared to Wang's value of 1.5 for large unhydrated spheres. This suggests the possibility that an obstruction-effect theory may be devised to account for experiments in which the presence of small molecules slows the diffusion of other small molecules. It is further suggested that the hydrodynamic portion of the concentration dependence of diffusion, which has been treated as a question of

solution viscosity,^{38,39} may possibly be reinterpreted as a self-obstruction of diffusion by the small diffusing molecules.⁴⁰

Acknowledgment.—This study was made possible through support by U. S. Public Health Service Research Grant RG-3449, entitled "Sedimentation and Diffusion of Low Molecular Weight Substances."

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(39) C. L. Sandquist and P. A. Lyons, *THIS JOURNAL*, **76**, 4641 (1954).

(40) A similar suggestion has been made by R. H. Stokes, *Austral J. Science*, **19**, 35 (1957).

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAINT LOUIS UNIVERSITY]

Etherates of Lithium Borohydride. I. The System Lithium Borohydride-Dimethyl Ether¹

BY GEORGE W. SCHAEFFER, THADDEUS L. KOLSKI² AND DONALD L. EKSTEDT

RECEIVED APRIL 27, 1957

Pressure-composition isotherms for the system lithium borohydride-dimethyl ether at 20.0, 0.0, -45.2 , -63.5 and -78.6° show that the three solid dimethyl etherates, $\text{LiBH}_4 \cdot 2(\text{CH}_3)_2\text{O}$ (I), $\text{LiBH}_4 \cdot (\text{CH}_3)_2\text{O}$ (II) and $(\text{LiBH}_4)_2 \cdot (\text{CH}_3)_2\text{O}$ (III), exist. Values for the heats, free energies and entropies of dissociation of these compounds per mole of dimethyl ether evolved at 25° are $\Delta H_d^\circ =$ (I) 10.42, (II) 11.13 and (III) 12.25 kcal.; $\Delta F_d^\circ =$ (I) -0.145 , (II) 1.66 and (III) 2.21 kcal.; and $\Delta S_d^\circ =$ (I) 35.4, (II) 31.7 and (III) 33.7 e.u. The heats and free energies of formation and absolute entropies of the etherates at 25° are $\Delta H_f^\circ =$ (I) -157.1 , (II) -102.4 and (III) -149.3 kcal./mole; $\Delta F_f^\circ =$ (I) -87.1 , (II) -60.0 and (III) -91.0 kcal./mole; and $S^\circ =$ (I) 77.4, (II) 49.1 and (III) 66.3 e.u.

Introduction

In recent years, lithium borohydride has come into widespread use because of its unique properties as a reducing agent for both organic³ and inorganic^{3,4} compounds. The reactivity of lithium borohydride places serious restrictions on the media which may be used to facilitate its reactions and useful solvents have been generally found among the ethers. In some reactions of lithium borohydride, the ether acts not merely as a solvent, but must play a more direct role in the chemical process. A striking example⁵ is the effect of diethyl ether on the rate of production of diborane in the reaction between copper(I) chloride and lithium borohydride. The reaction rate increases with the amount of diethyl ether until the mole ratio of ether to borohydride is one to one; more than this amount of diethyl ether is not reflected by a further increase in the rate of production of diborane. This fact has been interpreted to indicate that the reacting species may be the one to one adduct of lithium borohydride and diethyl ether rather than

lithium borohydride itself. Such a diethyl etherate of lithium borohydride has been described by Schlesinger and his co-workers,⁶ who found that it is formed when diethyl ether and lithium borohydride are brought together at 0° .

The present paper describes an investigation of the binary system lithium borohydride-dimethyl ether and subsequent papers will describe similar investigations of systems of lithium borohydride with diethyl ether and with tetrahydrofuran. It is hoped that the information obtained in these studies will prove helpful in extending the usefulness of lithium borohydride-ether systems and in elucidating the role of the ether in reactions of lithium borohydride.

Results and Discussion

Pressure-composition isotherms for the system lithium borohydride-dimethyl ether at 20.0, 0.0, -45.2 , -63.5 and -78.6° clearly show the existence of three solid dimethyl etherates of lithium borohydride: an hemi-(dimethyl etherate), $(\text{LiBH}_4)_2 \cdot (\text{CH}_3)_2\text{O}$; a dimethyl etherate, $\text{LiBH}_4 \cdot (\text{CH}_3)_2\text{O}$; and a bis-(dimethyl etherate), $\text{LiBH}_4 \cdot 2(\text{CH}_3)_2\text{O}$. Experimentally determined pressures at various mole fractions of lithium borohydride (n_2) are given in Table I and plots of these data are shown in Fig. 1.

In each of these phase diagrams, the uppermost plateau indicates the constant vapor pressure of a saturated solution in equilibrium with the solid

(1) Presented at the 132nd meeting of the American Chemical Society, New York, N. Y., September, 1957.

(2) Taken in part from a thesis presented by T. L. Kolski to the Graduate School of Saint Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1957.

(3) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

(4) (a) G. W. Schaeffer, J. S. Roscoe and A. C. Stewart, *THIS JOURNAL*, **78**, 729 (1956); (b) A. C. Stewart and G. W. Schaeffer, *J. Inorg. Nuc. Chem.*, **3**, 194 (1956); (c) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).

(5) R. H. Toeniskoetter, M.S. thesis, Saint Louis University, February, 1956.

(6) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *THIS JOURNAL*, **75**, 199 (1953).

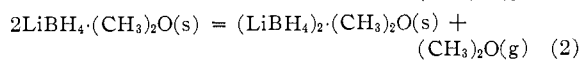
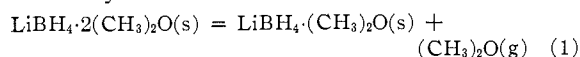
TABLE I

DATA FOR PRESSURE-COMPOSITION ISOTHERMS AT VARIOUS TEMPERATURES FOR THE SYSTEM LITHIUM BOROHYDRIDE-DIMETHYL ETHER

-78.6°		-63.5°		-45.2°		0.0°		20.0°	
Comp., n_2	Press., mm.	Comp., n_2	Press., mm.	Comp., n_2	Press., mm.	Comp., n_2	Press., mm.	Comp., n_2	Press., mm.
0.000	34.3 ^a	0.000	98.5 ^a	0.000	286.4 ^a	0.000	1986 ^{a,b}	0.493	76.7
.034	31.8	.034	94.2	.034	271.9	.331	423.9	.529	33.3
.102	32.0	.103	94.4	.113	272.6	.334	354.2	.588	33.0
.176	31.8	.178	93.9	.274	272.8	.351	193.7	.653	33.2
.259	32.1	.262	93.8	.323	264.9	.407	193.8	.678	29.8
.325	32.0	.329	89.4	.333	129.9	.493	193.8	.679	20.8
.334	16.0	.333	65.3	.333	5.8	.550	165.3	.686	12.7
.382	0.1	.335	29.3	.364	4.0	.500	97.0	.772	13.0
.458	.1	.356	0.5	.469	4.1	.518	8.3	.851	12.6
.508	.0	.458	.5	.500	3.1	.569	7.9	.974	13.0
.547	.0	.508	.1	.541	0.1	.636	7.9		
		.547	.0	.634	.1	.672	5.8		
				.678	.0	.679	2.9		
				.741	.0	.809	2.8		
				.969	.0	.968	2.9		

^a R. M. Kennedy, M. Sagankahn and J. G. Aston, THIS JOURNAL, 63, 2267 (1941). ^b Extrapolated from data which cover the range -83.2 to -24.2°.

phase, an interpretation which was corroborated by visual observation. The next three plateaus correspond, in order, to the dissociation pressures of the bis-(dimethyl etherate), the dimethyl etherate and the hemi-(dimethyl etherate). The dissociations of these three compounds may be represented by



It is evident that the hemi-(dimethyl etherate) is the lowest stable etherate formed in this system at temperatures up to 20°, for the isothermal constancy of the pressure of the system between $n_2 = 0.667$ and $n_2 = 1.000$ shows that lithium borohydride hemi-(dimethyl etherate) dissociates directly into lithium borohydride and dimethyl ether. Also, in view of the constancy of the saturated solution plateau up to $n_2 = 0.333$, there are no higher stable dimethyl etherates of lithium borohydride than the bis-(dimethyl etherate) at temperatures as low as -78.6°.

TABLE II

DISSOCIATION PRESSURES OF THE DIMETHYL ETHERATES OF LITHIUM BOROHYDRIDE

A. $\text{LiBH}_4 \cdot 2(\text{CH}_3)_2\text{O}$

Temp., °C.	-63.5	-45.2	-22.9	0.0	17.1
Press., mm. (obsd.)	0.5	4.1	33.6	194.5	601.9
Press., mm. (calcd.)	0.6	4.3	33.6	104.4	601.9

B. $\text{LiBH}_4 \cdot (\text{CH}_3)_2\text{O}$

Temp., °C.	-45.2	-22.9	0.0	20.0	29.6	57.3
Press., mm. (obsd.)	0.1	1.2	8.0	33.2	60.9	286.9
Press., mm. (calcd.)	0.1	1.3	8.2	33.2	60.9	286.9

C. $(\text{LiBH}_4)_2 \cdot (\text{CH}_3)_2\text{O}$

Temp., °C.	-22.9	0.0	20.0	38.0	56.2
Press., mm. (obsd.)	0.4	2.9	12.8	43.6	129.9
Press., mm. (calcd.)	0.4	2.8	12.9	43.5	129.9

The dissociation pressures of the etherates at various temperatures are given in Table II. Table III gives empirical relations which best describe

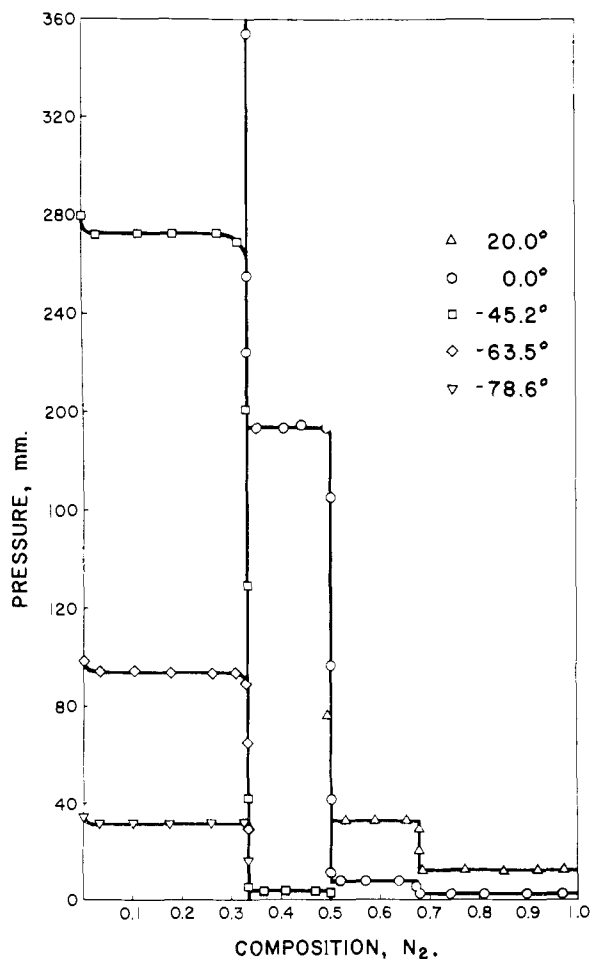


Fig. 1.—Pressure-composition isotherms for the system lithium borohydride-dimethyl ether.

TABLE III

THERMODYNAMICS OF DISSOCIATION AT 25° FOR THE DIMETHYL ETHERATES OF LITHIUM BOROHYDRIDE

Process	$\log P_{\text{mm.}} = A - \frac{B}{T}$		ΔH , kcal.	ΔF , kcal.	ΔS , e.u.
	A	B			
$\text{LiBH}_4 \cdot 2(\text{CH}_3)_2\text{O}$ to $\text{LiBH}_4 \cdot (\text{CH}_3)_2\text{O}$ (equation 1)	10.6212	2276.5	10.42	-0.145	35.4
$2\text{LiBH}_4 \cdot (\text{CH}_3)_2\text{O}$ to $(\text{LiBH}_4)_2 \cdot (\text{CH}_3)_2\text{O}$ (equation 2)	9.8159	2431.9	11.13	+1.66	31.7
$(\text{LiBH}_4)_2 \cdot (\text{CH}_3)_2\text{O}$ to 2LiBH_4 (equation 3)	10.2378	2676.1	12.25	+2.21	33.7
$\frac{1}{2}\text{LiBH}_4 \cdot 2(\text{CH}_3)_2\text{O}$ to $\frac{1}{2}\text{LiBH}_4$			11.06	+0.90	34.1
$\text{LiBH}_4 \cdot (\text{CH}_3)_2\text{O}$ to LiBH_4			11.69	+1.94	32.7

the dissociation pressure-temperature relationship and the derived thermodynamic quantities for the dissociation processes at 25°. Standard heats of formation, free energies of formation and absolute entropies at 25° for the three dimethyl etherates of lithium borohydride which were calculated from the thermodynamic properties of lithium borohydride, dimethyl ether and the values of Table II are listed in Table IV.

TABLE IV

HEATS AND FREE ENERGIES OF FORMATION AND ABSOLUTE ENTROPIES OF THE DIMETHYL ETHERATES OF LITHIUM BOROHYDRIDE AT 25°

Compound	ΔH_f° , kcal./mole	ΔF_f° , kcal./mole	S° , e.u.
$\text{LiBH}_4 \cdot 2(\text{CH}_3)_2\text{O}(s)$	-157.1	-87.1	77.4
$\text{LiBH}_4 \cdot (\text{CH}_3)_2\text{O}(s)$	-102.4	-60.0	49.1
$(\text{LiBH}_4)_2 \cdot (\text{CH}_3)_2\text{O}(s)$	-149.3	-91.0	66.3
$\text{LiBH}_4(c)^a$	-46.36	-30.74	18.13 ^a
$(\text{CH}_3)_2\text{O}(g)^b$	-44.3	-27.3	63.72

^a "Thermodynamic Properties of Boron Compounds at 25°C.," National Bureau of Standards, Washington 25, D.C., April, 1954. ^b F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards 500, p. 128, U.S. Government Printing Office, Washington 25, D. C., 1952.

Because of the limitations imposed by the experimental system, it was not possible to extend the observations into the range of dilute solution, but it was visually noted that at the lowest concentration measured at -45.2° ($n_2 = 0.0344$) the amount of solid phase remaining was extremely small. The solubility of lithium borohydride in dimethyl ether might be estimated to be approximately 1.6 g./100 g. at -45.2°

Experimental

The reactivity of lithium borohydride with air and moisture and the nature of the measurements involved necessitated the use of high vacuum techniques. These are adequately described in Sanderson's monograph.⁷

Apparatus.—The essential components of the apparatus include a sample tube with its connected manometer and a system of calibrated volumes for measuring amounts of dimethyl ether added to or withdrawn from the sample attached to the usual high vacuum apparatus. Mole fractions were corrected for the amount of gaseous dimethyl ether contained in this volume. In regions of composition where an appreciable amount of liquid phase was present in the sample tube, the liquid volume was computed from the density of dimethyl ether at the temperature concerned

(7) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

and subtracted from the determined volume of the vapor space.

Materials.—Lithium borohydride of 95% purity was obtained from Metal Hydrides, Inc. Purification was accomplished by solution in diethyl ether and filtration of the solution in an enclosed filtration apparatus. Samples prepared in this manner showed a purity of 99.0-100.0% on the basis of hydrogen evolution, amount of acid consumed during hydrolysis, or boric acid titration.

Dimethyl ether was fractionated slowly at -78.6, -140 and -196°. The fraction held at -140° was condensed on an excess of lithium borohydride which had been pumped for several hours to remove adsorbed gases. The complex formed had a dissociation pressure of about 8 mm. at 0°. Assuming that all non-ether gaseous impurities would be in vapor phase above the complex, the vapor was successively pumped off and allowed to build up several times. Pure dimethyl ether was then collected by decomposing the remaining etherate. After degassing, the following vapor tensions were noted: 1.5 mm. at -111.8° (lit. 1.5 mm.), 34.1 mm. at -78.6° (lit. 34.3 mm.) and 284.2 mm. at -45.2° (lit. 286.4 mm.).

Introduction of Lithium Borohydride into the Apparatus.—An 8 mm. glass tube with one closed end was prepared which fit closely into a 10 mm. side arm sealed to the sample tube at an angle of approximately 20° above the horizontal. The side arm was sealed off at the end to allow the system to be thoroughly pumped and "baked out" prior to introduction of the sample. The 8 mm. inner tube was charged with purified lithium borohydride in the dry-box, stoppered and weighed. Dry, deoxygenated nitrogen was slowly admitted through the vacuum apparatus into the sample tube and when the nitrogen pressure in the system was somewhat above atmospheric, the end of the side arm was cracked off. With nitrogen flushing through the sample tube and out of the side arm, the charging tube was opened in the nitrogen stream and inserted in the side arm. The charge was transferred into the sample tube by gentle tapping, after which the charging tube was carefully withdrawn and re-stoppered. The side arm on the sample tube was then sealed off, great care being taken not to allow any sucking back of air into the system. It was essential for the side arm to be of sufficient length to prevent water vapor from the torch from finding its way into the system. Immediately after sealing off the side arm the apparatus was evacuated and pumping was continued for several hours to remove any adsorbed gases from the solid. The weight of the lithium borohydride introduced into the system was taken as the difference in weight of the charging tube before and after the addition.

Determination of Isotherms.—Composition of the sample was varied by both additions and withdrawals of dimethyl ether, liquid nitrogen being used to condense the dimethyl ether portion in either the sample tube or the vapor-measuring system. The amount of each increment or decrement was measured in the system of calibrated volumes by application of the ideal gas relationship. After each addition or withdrawal, the sample tube was maintained at the desired temperature until the observed pressure of the system reached a constant value. This usually required several hours. In most cases the equilibrium pressure was determined by approaching from both a higher and a lower temperature to assure that the measured pressure was associated with true equilibrium.

Constant Temperature Baths.—The ordinary low temperature slush baths or a small constant temperature bath, arranged so that it could be elevated about the sample tube

and which would maintain the temperature constant to within 0.1° were found adequate. In the event that equilibrium was not reached before the bath was nearly spent, a

fresh bath could be substituted for the depleted one rapidly enough so that the sample tube did not warm.
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Acid-Base Equilibria in Glacial Acetic Acid. V. The Effect of Water on Potentiometric and Indicator End-Points in Acid-Base Titrations in Acetic Acid

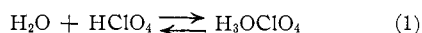
BY S. BRUCKENSTEIN AND I. M. KOLTHOFF

RECEIVED JUNE 14, 1957

The effect of water on acid-base equilibria in acetic acid can be calculated quantitatively for titrations carried out potentiometrically or with indicators. The equations governing the shape of potentiometric titration lines of bases in acetic acid as a function of water concentration have been derived and experimentally verified. These relationships have been used to calculate the change in e.m.f. in the vicinity of, at and after the equivalence point for bases of different concentration and strength. They predict that titration to an equivalence potential, which is independent of concentration of base, will be an accurate procedure. The relationships determining the ratio of acid to basic color of an indicator base over the titration range in water containing acetic acid also have been established and tested and used to predict the color change of *p*-naphtholbenzein (PNB) in a sodium perchlorate solution.

Water is an undesirable contaminant in the titration of bases in acetic acid.¹⁻⁶ With increasing water concentration the magnitude of the first derivative in a potentiometric titration of a base and the sharpness of the color change of an indicator in the region of the equivalence point decreases. Furthermore³ the potentiometric end-point is found after the equivalence point, and the titration error increases with the water content of the acetic acid. Water is a weak base in acetic acid, and it is possible to calculate quantitatively its effect upon titration curves in acetic acid^{7d} and particularly upon the break in potential and the sharpness of the color change of an indicator near the equivalence point, using the various equilibrium constants for acids, bases and salts reported in previous papers.^{7a-c}

Water reacts with perchloric acid to form hydronium perchlorate according to equation 1. The equilibrium constant for the reaction as written, $K_{\text{H}_3\text{OClO}_4}$,



is 34.^{7b} In order to account quantitatively for the effect of water over the entire region of a titration curve it is necessary to know the over-all dissociation constant of water as a base, $K_{\text{H}_2\text{O}}$, and the over-all dissociation constant of hydronium perchlorate, $K_{\text{H}_3\text{OClO}_4}$. One simple way of determining these constants is to study the change in hydrogen ion concentration of a perchloric acid solution as a function of the water concentration, using

a chloranil electrode as the hydrogen ion indicator electrode. Since the acetate ion concentration is negligible in such a solution, we can write

$$[\text{H}^+] + [\text{H}_3\text{O}^+] = [\text{ClO}_4^-] \quad (2a)$$

From the expressions of the various equilibrium constants we find $[\text{ClO}_4^-] = K_{\text{HClO}_4} C_{\text{HClO}_4} / [\text{H}^+]$ and $[\text{H}_3\text{O}^+] = K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} [\text{H}^+] / K_s$. After rearrangement, equation 2a may be written as

$$C_{\text{H}_2\text{O}} = \frac{K_s K_{\text{HClO}_4}}{K_{\text{H}_2\text{O}}} \frac{C_{\text{HClO}_4}}{[\text{H}^+]^2} - \frac{K_s}{K_{\text{H}_2\text{O}}} \quad (2b)$$

The symbol C refers to the equilibrium concentration of the species indicated by the subscript and $K_s = [\text{H}^+][\text{Ac}^-]$.⁸ From the stoichiometric concentrations of perchloric acid and water added, $(C_{\text{HClO}_4})_t$ and $(C_{\text{H}_2\text{O}})_t$, respectively, and $K_{\text{H}_3\text{OClO}_4}$ it is possible to calculate equilibrium concentrations of water and perchloric acid. Thus, if $C_{\text{H}_2\text{O}}$ is plotted *versus* $C_{\text{HClO}_4} / [\text{H}^+]^2$, a straight line of slope $K_s K_{\text{HClO}_4} / K_{\text{H}_2\text{O}}$ and intercept $-K_s / K_{\text{H}_2\text{O}}$ should result. Such a plot of the experimental results yielded a straight line, and $K_{\text{H}_2\text{O}}$ was calculated from the intercept using the previously determined value of $K_s = 3.55 \times 10^{-15}$.^{7c} $K_{\text{H}_3\text{OClO}_4}$ could then be calculated from the relationship $K_{\text{H}_3\text{OClO}_4} = K_{\text{HClO}_4} K_{\text{H}_2\text{O}} / K_s K_{\text{H}_3\text{OClO}_4}$,^{7a,d} in which the dissociation constant of hydronium perchlorate is the only unknown.

The Effect of Water on *pH* over the Entire Region of an Acid-Base Titration Curve. Solutions of Water and a Pure Base.—The *pH* of a mixture containing water and another base, B, in acetic acid can be calculated by substituting into the electroneutrality rule equation 3a

$$[\text{H}^+] + [\text{BH}^+] + [\text{H}_3\text{O}^+] = [\text{Ac}^-] \quad (3a)$$

the expressions $[\text{BH}^+] = K_B C_B [\text{H}^+] / K_s$, $[\text{H}_3\text{O}^+] = K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} [\text{H}^+] / K_s$ and $[\text{Ac}^-] = K_s / [\text{H}^+]$ to yield

$$[\text{H}^+]_w = \frac{K_s}{\sqrt{K_s + K_B C_B + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}}} \quad (3b)$$

(8) The nomenclature used in the present paper is the same as in the preceding papers in this series.

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