The Kinetics of Spreading

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A theoretical formulism has been presented on the spreading of a spherical droplet onto a smooth, rigid surface. It is based on the assumption that spreading is impelled by the surface tensions at the interface and retarded by the viscous flow of the droplet. Equations have been derived to predict the rate of spreading and the change of contact angle with time. The kinetic criterion for spreading to occur has also been defined.

Introduction

The formation of an adhesive bond requires the attainment of interfacial contact between the adhesive layer and the substrate. Whereas the thermodynamics of wetting had long been defined by Young[1] in terms of contact angle and surface energetics, the kinetics of spreading which describes the rate of attainment to equilibrium wetting remains largely unknown. Schonhorn, Frisch, and Kwei[2] studied the spreading of sessile drops of molten polymers on high and low surface energy substrates. They observed that the droplet retained its shape of a spherical cap with decreasing contact angle throughout the spreading process. However, the physical mechanism of spreading remained unclarified. Recently, Newman[3] incorporated the concept of a time-dependent contact angle into the classical Poiseuille's law of capillary flow. He suggested that measurements on the rate of penetration of liquids into capillaries and slits can be used as experimental models for the kinetic studies of spreading.

We wish to propose a formulism on the spreading[4] of a spherical droplet onto a smooth, horizontal surface. Instead of the capillary forces, it has been assumed that spreading is promoted by the net surface tensions at the interface only and retarded by the viscous flow of the entire liquid volume.

Theoretical Treatment

Consider a droplet in the process of spreading onto a smooth, rigid surface (Figure 1). It retains the shape of a spherical cap and achieves a circular interfacial contact area with the surface. The spreading force (in the direction of $+r$) is

$$\vec{f} = 2\pi r S_\phi \tag{1}$$

where

$$S_\phi = \gamma_s - \gamma_{sl} - \gamma_l \cos\phi \tag{1a}$$

= instantaneous spreading coefficient

ϕ = instantaneous contact angle, γ_s, γ_l, γ_{sl} = surface tensions of the surface, the spreading liquid, and their interfacial tension, respectively (dyn/cm), and r is the radius of the instantaneous contact area (cm). The resisting force (in the direction of $-r$) is

$$\overleftarrow{f} = -(\pi r^2 \eta)\frac{\mathrm{d}v}{\mathrm{d}h} \tag{2}$$

where η is the viscosity of the spreading liquid (poise) and $\mathrm{d}v/\mathrm{d}h$ is the velocity gradient of the *viscous flow* with respect to the h direction (1/sec). The use of total differential in the present case implicitly ignores the gravitational stress and the velocity gradient with respect to r.

For steady-state spreading, (1) = (2)

$$2\pi r S_\phi = -(\pi r^2 \eta)\frac{\mathrm{d}v}{\mathrm{d}h}$$

$$\mathrm{d}v = -\frac{2S_\phi}{r\eta}\mathrm{d}h \tag{3}$$

The instantaneous rate of spreading, in terms of area per unit time, is

$$\left\langle \frac{\mathrm{d}A}{\mathrm{d}t} \right\rangle = \int 2\pi r \mathrm{d}v = -\frac{4\pi}{\eta}\int S_\phi\, \mathrm{d}h \tag{4}$$

and the integral is to be evaluated from the contact base of the spherical cap where $h = 0$ and $\phi = \phi$, to the top where $h = h$ and $\phi = 0$.

We proceed to express h in terms of ϕ through the geometrical relationships shown in Figure 2.

$$h = r \tan\frac{\phi}{2} \tag{5}$$

$$r = R \sin\phi \tag{6}$$

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(1) T. Young, *Phil. Trans.*, **95**, 65, 82 (1805).

(2) H. Schonhorn, H. L. Frisch, and T. K. Kwei, *J. Appl. Phys.*, **37**, 13, 4967 (1966).

(3) S. Newman, *J. Colloid Interfac. Sci.*, **26**, 209 (1968).

(4) The terms "wetting" and "spreading" have been used interchangeably in the adhesion literature to describe the phenomenon of interfacial contact. It is suggested here to differentiate "wetting" as the thermodynamic state of interfacial contact and "spreading" as the kinetic process which leads to the enlargement of the interfacial contact area.

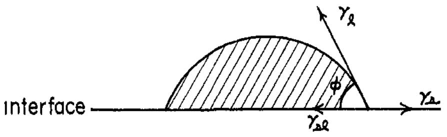

Figure 1. Profile and surface tensions of a spreading droplet.

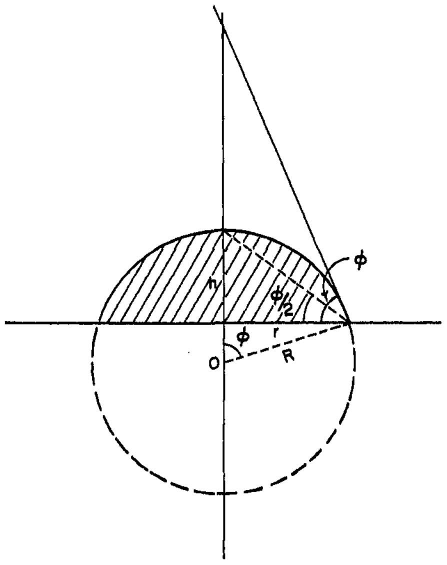

Figure 2. Geometrical relationships of a spherical cap.

Let $\phi/2 = x$ and substitute (6) into (5)

$$h = 2R \sin^2 x \tag{7}$$

R is the radius of the hypothetical volume sphere with the spreading droplet as the spherical cap. It is related to h and V_0, the volume of the droplet, by

$$V_0 = \pi h^2\left(R - \frac{h}{3}\right) = \text{constant} \tag{8}$$

Rearrange (8) and substitute into (7)

$$h^3 = \left(\frac{V_0}{\pi}\right)\left(\frac{6 \sin^2 x}{3 - 2 \sin^2 x}\right) \tag{9}$$

and

$$\frac{\mathrm{d}h}{\mathrm{d}x} = \left(\frac{3V_0}{\pi}\right)^{1/3}\left[\frac{4 \sin x \cos x}{(2 \sin^2 x)^{2/3}(3 - 2 \sin^2 x)^{4/3}}\right] \tag{10}$$

Let $y = 2 \sin^2 x$. Therefore

$$\mathrm{d}h = \left(\frac{3V_0}{\pi}\right)^{1/3}\left[\frac{\mathrm{d}y}{y^{2/3}(3 - y)^{4/3}}\right]$$

or

$$\mathrm{d}h = \left(\frac{3V_0}{\pi}\right)^{1/3} F(y)\mathrm{d}y \tag{11}$$

Substitute (11) into (4)

$$\left\langle\frac{\mathrm{d}A}{\mathrm{d}t}\right\rangle = -K_1 \int(\gamma_s - \gamma_{sl} - \gamma_l \cos 2x)F(y)\mathrm{d}y$$
$$= K_1S_0\int_0^y F(y)\mathrm{d}y + K_1\gamma_l\int_0^y yF(y)\mathrm{d}y$$

Therefore the instantaneous rate of spreading, in terms of area per unit time, is

$$\left\langle\frac{\mathrm{d}A}{\mathrm{d}t}\right\rangle = K_1(S_0I_1 + \gamma_lI_2) \tag{12}$$

where

$$K_1 = \left(\frac{4\pi}{\eta}\right)\left(\frac{3V_0}{\pi}\right)^{1/3} \tag{12a}$$

$$y = 2 \sin^2 \frac{\phi}{2} \tag{12b}$$

$$S_0 = \gamma_s - \gamma_{sl} - \gamma_l \tag{12c}$$
$$= \text{spreading coefficient at } \phi = 0$$

$$I_1 = \int_0^y (y)^{-2/3}(3 - y)^{-4/3}\,\mathrm{d}y \tag{12d}$$

$$I_2 = \int_0^y (y)^{1/3}(3 - y)^{-4/3}\,\mathrm{d}y \tag{12e}$$

Alternatively, the spreading kinetics can be expressed in terms of the instantaneous contact angle with spreading time. We return to (12) and find that

$$\left\langle\frac{\mathrm{d}A}{\mathrm{d}t}\right\rangle = 2\pi r\left(\frac{\mathrm{d}r}{\mathrm{d}y}\right)\left(\frac{\mathrm{d}y}{\mathrm{d}t}\right) = K_1(S_0I_1 + \gamma_lI_2)$$

Eliminate $r\left(\frac{\mathrm{d}r}{\mathrm{d}y}\right)$ through (5) and (9)

$$r = h \cot x$$

$$r\left(\frac{\mathrm{d}r}{\mathrm{d}x}\right) =$$
$$\left(\frac{V_0}{\pi}\right)\left[\frac{2 \cos x\,(6 \sin^2 x \cos^2 x - 3 \cos^2 x + 6 \sin^4 x - 9 \sin^2 x)}{(6 \sin^2 x)^{1/3}(3 - 2 \sin^2 x)^{5/3}(\sin x)}\right]$$

Substitute

$$\cos^2 x = (1 - \sin^2 x); \quad y = 2 \sin^2 x$$

$$r\left(\frac{\mathrm{d}r}{\mathrm{d}y}\right) = -\left(\frac{3V_0}{\pi}\right)^{2/3}\left[\frac{1}{y^{4/3}(3 - y)^{5/3}}\right] \tag{13}$$

Therefore

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -\left(\frac{2}{\eta}\right)\left(\frac{\pi}{3V_0}\right)^{1/3} y^{4/3}(3 - y)^{5/3}(S_0I_1 + \gamma_lI_2) \tag{14}$$

or

$$t = \frac{K_2\int_y^2 (y)^{-4/3}(3 - y)^{-5/3}\,\mathrm{d}y}{(S_0I_1 + \gamma_lI_2)} \tag{15}$$

where

$$K_2 = \left(\frac{\eta}{2}\right)\left(\frac{3V_0}{\pi}\right)^{1/3} \tag{15a}$$

At the initial spreading time $t = 0$, $\phi = 2\pi$ and $y = 2$.

Discussion

1. The Model. We have treated spreading as an interfacial phenomenon. The spreading force is derived entirely from the surface tensions of the liquid–substrate pair at the interface. This is in contrast to the formulism suggested by Newman[3] in which the capillary pressure from the micro-irregularities of the substrate surface has been considered the driving force. The capillary pressure P_c is defined as

$$P_c = \gamma_1\left(\frac{1}{G_1} + \frac{1}{G_2}\right)$$

where G_1 and G_2 refer to the radii of curvature of the liquid in the capillary. It appears that in the limiting case when the substrate is perfectly smooth, both G_1 and G_2 would approach infinity and P_c would become zero. Hence the driving force disappears with the surface irregularities.

A number of assumptions have been incorporated into our model.

(1) It is assumed that steady-state spreading occurs throughout the process so that the liquid always retains the shape of a spherical cap. This has been experimentally verified by Schonhorn, *et al.*,[2] throughout their measured contact angles from about 90° to near zero. On the other hand, Dettre[5] has observed that if the polymer melt is very viscous and ultimately attains a low equilibrium contact angle with the substrate, then the spherical profile shows degeneration during spreading with an extended foot near the contact area. This would be expected from a nonsteady-state process when the interfacial spreading force is greater than the bulk resisting force.

(2) The velocity gradient in the r direction has been ignored; *i.e.*, the horizontal flow velocity (v_r) is assumed constant. This is not exactly true. Since v_r at $r = 0$ must be zero to satisfy the requirement of circular symmetry, whereas v_r at $r \neq 0$ becomes finite, it is therefore unlikely that

$$\left(\frac{\partial v_r}{\partial r}\right) = 0$$

However, this velocity gradient would only contribute to the vertical force field (in the h direction) so that it should not alter the horizontal force balance assumed in eq 3.

(3) The gravitational stress in the vertical direction has also been ignored. As pointed out by Schonhorn, *et al.*,[2] if capillary stress is involved in spreading, then the gravitational stress can be neglected only when the lineal dimension of the liquid droplet l_0 ($\sim V_0^{1/3}$) is smaller than

$$l_0 = \left(\frac{2\gamma_1}{\rho g}\right)^{1/2}$$

where ρ is the density of the liquid and g is the gravitational acceleration. In their experiments, some droplets were large enough so that the above criterion was no longer valid, yet no appreciable effect in spreading rate was observed even when one of the large droplets was studied in the normal and inverted positions. Hence, this may be considered as experimental evidence that the capillary stress is not the prime driving force in spreading and that the exclusion of gravitational stress in our formulism is justified.

(4) Fowkes[6] has modified Young's equation of thermodynamic wetting with a correction term π_e which represents the equilibrium film pressure of the adsorbed vapor on the substrate

$$\gamma_s = \gamma_{s1} + \gamma_1 \cos\theta + \pi_e$$

This correction has not been included in our present definitions for the spreading coefficients S_0 and S_ϕ.

2. Applications. (1) The instantaneous rate of spreading can now be estimated from eq 12. The equation contains two definite integrals, I_1 and I_2, which are functions of the instantaneous contact angle only. They have been numerically integrated throughout the entire range from $\phi = 180$ to 0°, as shown in Figure 3. These curves can be used directly to compute the spreading rate of any given liquid–substrate pair with the specific values of S_0 and γ_1 as the weighting factors, and with known η and V_0.

It is interesting to note that even when $S_0 = 0$, *i.e.*, the Cooper–Nuttall[7] spreading coefficient is zero, $\gamma_1 I_2$ in eq 12 would remain finite and the instantaneous spreading rate is now governed by the profile of the I_2 curve in Figure 3. Physically this corresponds to the spreading of a liquid droplet onto a substrate of the same chemical composition

The change of contact angle, cos ϕ, with time can be estimated from eq 15. The equation has been numerically integrated with five ratios of the weighting factor, γ_1/S_0 from 100 to 0.01 (Figure 4). Although all the curves share a very similar shape, they may not be superimposed exactly into one throughout the range of contact angle from 180 to 0° This is inevitable since the integrals, I_1 and I_2, would contribute differently under various γ_1/S_0 ratios. In view of this complication, Figure 4 may not be as generally useful as Figure 3 although eq 15 can always be integrated for each specific case, including $S_0 = 0$.

(2) Based on eq 12, the criterion for spreading to occur can also be defined. Let

$$\left\langle\frac{\mathrm{d}A}{\mathrm{d}t}\right\rangle = K_1(S_0 I_1 + \gamma_1 I_2) > 0$$

when both I_2 and I_1 are evaluated at the initiation angle

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(5) R. H. Dettre, private communication.

(6) F. M. Fowkes, "Treatise on Adhesion and Adhesives," R. L. Patrick, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 9, p 351.

(7) W. A. Cooper and W. H. Nuttall, *J. Agr. Sci.*, 7, 219 (1915).

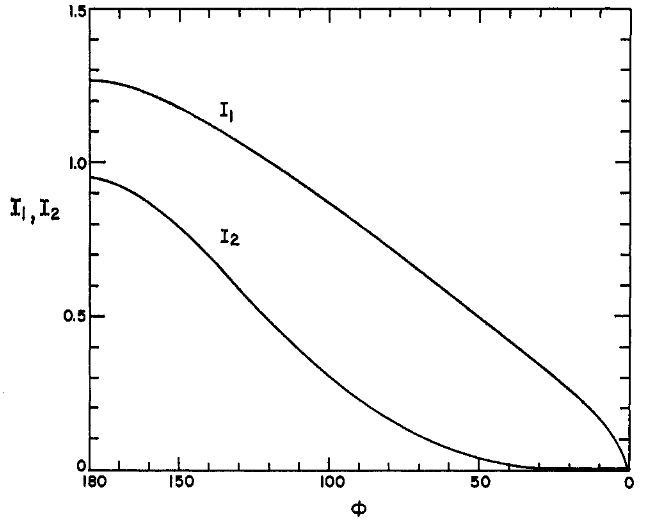

Figure 3. The definite integrals, I_1 and I_2, in the spreading equations (12) and (15) *vs.* instantaneous contact angle ϕ.

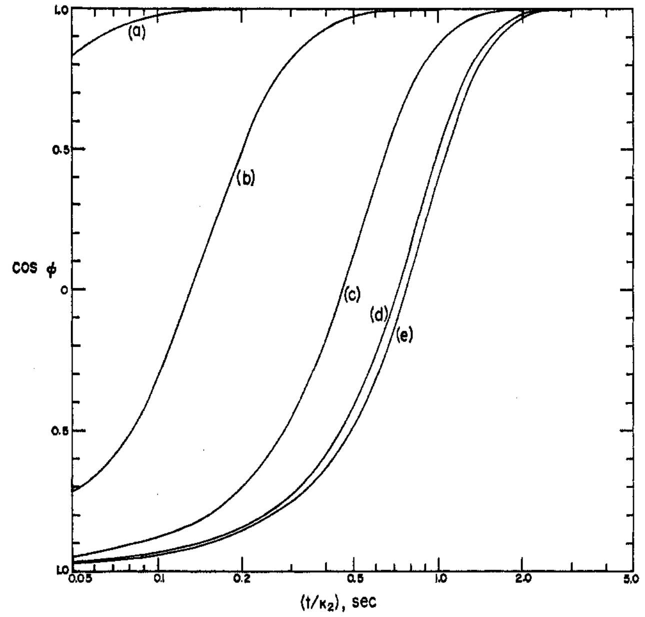

Figure 4. Spreading rate profiles with cos ϕ *vs.* (t/K_2) at five ratios of γ_1/S_0 = 100 (a), 10 (b), 1 (c), 0.1 (d), and 0.01 (e).

of $\phi = 180°$, which corresponds to the two intercepts at the ordinate in Figure 3. Therefore

$$1.260S_0 + 0.952\gamma_1 > 0$$

or

$$S_0 > -0.756\gamma_1 \tag{16}$$

Hence spreading would occur even when S_0 is negative; however, its absolute magnitude must be less than $0.756\gamma_1$.

(3) In the case when equilibrium wetting will be reached with a finite contact angle, the equilibrium contact angle θ can also be predicted from eq 12. Let

$$\left\langle \frac{\mathrm{d}A}{\mathrm{d}t} \right\rangle = K_1(S_0I_1 + \gamma_1I_2) = 0 \text{ for } 180° > \theta > 0$$

$$\frac{I_2}{I_1} = \frac{-S_0}{\gamma_1} \tag{17}$$

With known values of S_0 and γ_1, θ can be directly read off from Figure 5.

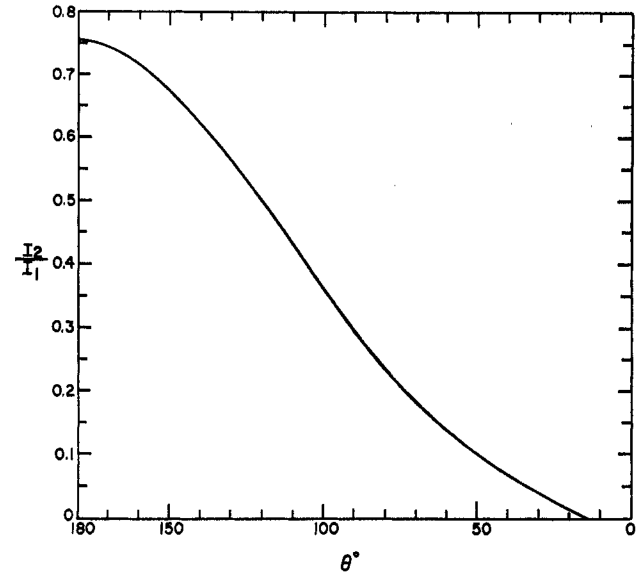

Figure 5. The ratio I_2/I_1 *vs.* equilibrium contact angle θ.

3. Comparison with Experimental Results. Schonhorn, *et al.*,[2] had conducted studies on the kinetics of spreading under experimental conditions comparable to the assumptions made in the present work. They measured the spreading rates of spherical droplets onto rigid, horizontal substrates and found that the results correlate with the surface tension of the polymer melt γ_1 and inversely with the viscosity η. Furthermore, all the spreading data from different polymer–substrate pairs, drop sizes, and temperatures could be superimposed into a single curve by only shifting the time scale with a characteristic function a_T; the latter has been defined as

$$a_T = \frac{\gamma_1}{L_w\eta}$$

where L_w is the "characteristic length" and assumed to be a property of the polymer–substrate system.

The rate equations, (12) and (15), can now be compared with the general observations made above. The predicted rate dependence on η is present. $(V_0)^{1/3}$ can be identified with L_w in terms of linear dimensions although the surface properties of the polymer–substrate pair are found in the expression $(S_0I_1 + \gamma_1I_2)$ which becomes a function of the liquid surface tension alone only when $S_0I_1 \ll \gamma_1I_2$. Since the rate profiles in Figure 4 are so similar to each other, it becomes feasible to superimpose the curves into one if the range of variables covered in the experimental studies is more limited.

Therefore it appears that the proposed rate equations are in qualitative agreement with the available experimental results.

4. Comparison with Flow. We hope that the present formulism also helps to clarify the conceptual difference between spreading and flow. Spreading occurs at the interface only whereas flow assumes the liquid layer adjacent to the substrate to be stagnant. Hence, the surface properties are dominant in spreading and become irrelevant in flow.

The mechanics and the physical variables which control the two transport processes are also different. This can be seen when eq 12 is compared with Poiseuille's law for the flow of Newtonian liquid through cylindrical tubes

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\pi R^4 P}{8\eta l}$$

where $\mathrm{d}V/\mathrm{d}t$ is the rate of flow in terms of volume per unit time, R is the radius, l is the length of the tube, and P is the applied pressure. Therefore the driving force is supplied externally for viscous flow whereas the spreading force is intrinsic; the dimensions of the confining walls are always present in the flow equation whereas only the inherent volume of the droplet is pertinent to spreading.

Both the spreading and flow rates are inversely proportional to the viscosity of the liquid. Temperature exerts an enormous effect on the rates through viscosity. In addition, the surface properties of the liquid–substrate pair are temperature dependent.

Acknowledgment. I am indebted to Dr. H. Schonhorn of the Bell Telephone Laboratories who alerted me to his publication. Mrs. Phyllis Gilmore of the Du Pont Engineering Department programmed the evaluation of the definite integrals.

The Partial Molal Volume of Ions in Various Solvents[1]

by Frank J. Millero

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The partial molal volumes of ions in the solvents methanol, water, and N-methylpropionamide (NMP) have been examined by using the Frank and Wen model for ion–solvent interactions. The partial molal volume of an ion is assumed to be due to three major components, $\bar{V}^0$(int), the intrinsic partial molal volume (equal to the crystal volume), $\bar{V}^0$(disord), the disordered partial molal volume (void space effects), and $\bar{V}^0$(elect), the electrostriction partial molal volume. The results of fitting the $\bar{V}^0$(ions) in these solvents to various semiempirical equations indicate that $\bar{V}^0$(disord) is related to the structure of the solvent. This disordered effect may be visualized as the void space caused by the solvated ion rather than improper packing in the electrostricted region. The $\bar{V}^0$(elect) of the ions in the various solvents is proportional to $1/r$ (r = crystal radius) and in the predicted order ($\bar{V}^0$(elect) of methanol > water > NMP).

Introduction

Using the Frank and Wen[2] model for ion–solvent interactions, the partial molal volume of an ion at infinite dilution can be attributed to the following components[3a]

$$\bar{V}^0(\text{ion}) = \bar{V}^0(\text{int}) + \bar{V}^0(\text{elect}) + \bar{V}^0(\text{disord}) + \bar{V}^0(\text{caged}) \quad (1)$$

where $\bar{V}^0$(int) is the intrinsic partial molal volume (the crystal volume), $\bar{V}^0$(elect) is the electrostriction partial molal volume (the decrease in volume due to ion–solvent interactions), $\bar{V}^0$(disord) is the disordered partial molal volume (normally attributed to void space effects), and $\bar{V}^0$(caged) is the caged partial molal volume (due to the formation of caged or structured water around ions with hydrocarbon tails).

Since the various components of eq 1 may be small when compared to the absolute size of the ion (*i.e.*, the crystal volume), it is difficult to determine the importance of the individual components of $\bar{V}^0$(ion) or

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(1) Paper presented at Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968.

(2) H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(3) (a) F. J. Millero, *J. Phys. Chem.*, **72**, 4589 (1968); (b) F. J. Millero and W. Drost-Hansen, *ibid.*, **72**, 1758 (1968).