

Surface Tension of Molten Salts and Strong Electrolyte Solutions

by

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용융염과 강전해질용액의 표면장력

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ABSTRACT

A theory of surface tension developed by using the approximation that the surface of liquids consists of a monomolecular layer has been applied to the molten salts (NaCl, KCl, NaBr, KBr) and the strong electrolyte solutions.

By considering that the ionic forces are the long-range forces and with the use of the partition functions developed, the surface tension of molten salts and strong electrolyte solutions has been calculated.

The results show good agreement between theory and experiment at various temperatures and over a wide concentration ranges (0.1-4.0m)

I. Introduction

Up to now, a number of studies have been carried out concerning the experiments of molten salts and strong electrolyte solutions (1,2,3),

but a few approaches (4,5) have been offered theoretically toward an understanding of the surface tensions of them.

To evaluate the surface tensions of liquids, Kirkwood and Buff (6) used the radial distribution function method, whereas others (7-12)

used approximate models to simplify the calculations.

Chang et al (13) proposed the theory of surface tension on the basis of significant structure theory of liquid and calculated successfully the surface tensions of simple liquids by iteration method. On the other hand, Ree, Ree, and Eyring (14) developed a simple equation in closed form to calculate the surface tension by assuming a monomolecular layer approximation.

However, this equation includes the Lennard-Jones 6-12 potential, whose characteristic constants are only available for simple liquids.

Recently Lu, Jhon, Ree and Eyring (15) have derived a new simple equation of surface tension by introducing the monolayer approximation and applied to simple liquids, polar liquids, and molten metals. The applications of the above theories, however, result in very large deviation with the observations for the surface tension of molten salts and electrolyte solutions.

In this paper, with the use of the partition functions for the molten salts and electrolyte solutions, we evaluate the surface tensions by considering that the forces between ions are the long-range forces.

II. Theory

A. Partition Function of Bulk Liquid

According to the significant structure theory of liquids, the partition function for a bulk liquid (16-18) is given by

$$f_N = \left[f_s \left\{ 1 + n \left(\frac{V - V_s}{V_s} \right) \exp \left(- \frac{a E_s V_s}{(V - V_s) RT} \right) \right\} \right]^{N V_s / V} (f_g)^{N(V - V_s) / V} \quad (1)$$

where f_s and f_g are the partition functions of the solidlike and gaslike molecules, respectively, V is the molar volume of the liquid, V_s is that of the solid at the melting temperature, N is Avogadro's number, E_s is the sublimation energy per mole at the melting point, R is the gas constant, T is absolute temperature, n and a are the constants which are evaluated theoretically.

The partition functions, f_s and f_g , are written as follows;

$$f_s = \frac{\exp(E_s / RT)}{[1 - \exp(-\theta / T)]^3} \cdot J(T) \quad (2)$$

$$\begin{aligned} (f_g)^{N(V - V_s) / V} &= \left[\frac{(2\pi m k T)^{3/2}}{h^3} \cdot (V - V_s) \cdot J(T) \right]^{N(V - V_s) / V} \left[\left\{ \frac{N(V - V_s)}{V} \right\} ! \right]^{-1} \\ &= \left[\frac{(2\pi m k T)^{3/2}}{h^3} \cdot \frac{eV}{N} \cdot J(T) \right]^{N(V - V_s) / V} \quad (3) \end{aligned}$$

Here, $J(T)$ is the partition function for internal degrees of freedom, θ is the Einstein characteristic temperature, k is the Boltzmann constant, h is the Planck constant, and m is the mass of the molecule.

B. Partition Function Involving the Liquid Surface

In accordance with Ree, Ree, and Eyring(14), the partition function involving the liquid surface is given by

$$f'_N = f' \cdot f_B \quad (4)$$

where f' is the partition function for the surface molecules, and f_B is that for the bulk liquid molecules. The f' and f_B are written as follows;

$$f' = \left\{ f_s \left[1 + n' \left(\frac{V - V_s}{V_s} \right) \exp \left(- \frac{a'E_s V_s}{(V - V_s)RT} \right) \right] \right\}^{N'V_s/V} (f_s)^{N'(V - V_s)/V} \dots (5)$$

$$f_B = \left\{ f_s \left[1 + n \left(\frac{V - V_s}{V_s} \right) \exp \left(- \frac{aE_s V_s}{(V - V_s)RT} \right) \right] \right\}^{N_B V_s/V} (f_s)^{N_B(V - V_s)/V} \dots (6)$$

Here, N , the total number of liquid molecules is equal to N' , the number of surface liquid molecules plus N_B , the number of bulk liquid molecules and the prime denotes the values for surface liquid molecules.

From Eqs. (4) to (6), one obtains

$$\ln f'_N = N' \frac{V_s}{V} \left\{ \ln f'_s \left[1 + n'(V - V_s)/V_s \cdot \exp(-a'E_s V_s/(V - V_s)RT) \right] - \ln f_s \left[1 + n(V - V_s)/V_s \cdot \exp(-aE_s V_s/(V - V_s)RT) \right] \right\} + \ln f_N \dots (7)$$

C. Derivation of the Surface Tension Equation

According to the thermodynamic definition of surface tension,

$$\gamma = \left(\frac{\partial A}{\partial \Omega} \right)_{N, V, T} \dots (8)$$

where Ω is the surface area, and A is the Helmholtz free energy, i.e., $A = -kT \ln f'_N$

Assuming a random distribution of fluidized vacancies, N_c , the total number of sites available for molecules on the liquid surface, is given as $N_c = N' \left(\frac{V}{V_s} \right)$. Therefore, $\Omega = \omega N_c$, where ω is the area occupied by one molecule.

Then, Eq. (8) may be written as

$$\gamma = \omega^{-1} \left(\frac{\partial A}{\partial N_c} \right)_{N, V, T} = \omega^{-1} \left(\frac{V_s}{V} \right) \left(\frac{\partial A}{\partial N'} \right)_{N, V, T} \dots (9)$$

With Eqs. (2) through (9), one obtains

$$\gamma = \omega^{-1} \left(\frac{V_s}{V} \right)^2 kT [\ln f_s - \ln f'_s + \ln g_r] \dots (10)$$

where

$$\ln g_r = \ln \frac{\left\{ 1 + n \left(\frac{V - V_s}{V_s} \right) \exp \left(- \frac{aE_s V_s}{(V - V_s)RT} \right) \right\}}{\left\{ 1 + n' \left(\frac{V - V_s}{V_s} \right) \exp \left(- \frac{a'E_s V_s}{(V - V_s)RT} \right) \right\}} \dots (11)$$

Since a' and n' are not very much different from a and n , and g_r becomes quite close to unity, $\ln g_r$ is assumed to be zero.

Thus, Eq. (10) becomes

$$\gamma = \omega^{-1} \left(\frac{V_s}{V} \right)^2 kT [\ln f_s - \ln f'_s] \dots (12)$$

Introducing the partition function of the molten salts (19) into Eq. (12), the surface tension of the molten salts is given as

$$\gamma = \omega^{-1} \left(\frac{V_s}{V} \right)^2 kT \left[\frac{(E_s - E'_s) \left(\frac{V_s}{V} \right)^{1/3}}{RT} + 6 \ln \{1 - \exp(-\theta'/T)\} - 6 \ln \{1 - \exp(-\theta/T)\} \right] \dots (13)$$

Putting the partition function of electrolyte solution (20), and that of the first layer which considered the molecular orientation (See Eq. (14)), into Eq. (12),

$$f'_E = \left\{ \frac{\exp\left(-\frac{E_{s, \text{salt}}}{RT}\right)}{(1 - e^{-\theta/T})^3 (1 - e^{-\theta_s/T})^3} \right\}^{m'N} \left(K_1 \right)^{\frac{K_1 m' n_1 N}{1 + K_1}} \left(K_2 \right)^{\frac{K_2 m' n_2 N}{1 + K_2}} \cdot \left\{ \frac{\exp\left(-\frac{E_{s, H_2O}}{RT}\right)}{(1 - e^{-\theta/T})} \right\} \cdot f'_R \\ \cdot \left(K \right)^{\frac{K}{a(1+K)}} \left[1 + n \left(\frac{V - V_s}{V} \right) \exp\left(-\frac{a E_s V_s}{(V - V_s) RT}\right) \right] \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i/kT}} \left\{ 55.51 N \left(\frac{V_s}{V} \right) \right. \\ \cdot \left\{ \left(\frac{2\pi m k T}{h^3} \right)^{3/2} \cdot \frac{eV}{N} \cdot \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{2h^3} \cdot \frac{kT}{\mu X} \sinh \frac{\mu X}{RT} \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i/kT}} \right\}^{55.51 N \left(\frac{V - V_s}{V} \right)} \\ \cdot \exp \left\{ \frac{V}{8\pi} \left[\frac{1}{(1 + a\kappa)} \left(\kappa^3 - \frac{1}{a^3} \right) + \frac{1}{a^3} (1 + a\kappa) - \frac{2}{a^3} \ln(1 + a\kappa) \right] \right\} \\ \cdot \frac{(55.51N + 2m'N)!}{(55.51N)! [(m'N)!]^2} \dots (14)$$

where

$$f'_R = \frac{2\pi(2\pi I kT)^{1/2}}{2h} \cdot \frac{kT}{\mu X} \cdot \sinh \frac{\mu X}{kT}$$

The surface tension of the electrolyte solution becomes

$$\gamma = \omega^{-1} \left(\frac{V_s}{V} \right) kT \left\{ \frac{m'}{55.51 + m'} \left\{ \frac{E_s - E'_s}{RT} + 6 \ln(1 - \exp(-\theta'/T)) \right. \right. \\ - 6 \ln(1 - \exp(-\theta/T)) + \frac{55.51 - m'}{55.51 + m'} \cdot \left(\frac{V_s}{V} \right) \cdot \left\{ \frac{E_{s, H_2O} - E'_{s, H_2O}}{RT} \right. \\ + 5 \ln(1 - \exp(-\theta'/T)) - 5 \ln(1 - \exp(-\theta/T)) + \ln \frac{1}{1 - e^{-\theta/T}} \\ \left. \left. - \ln \frac{2\pi(2\pi I kT)^{1/2}}{2h} \cdot \frac{kT}{\mu X} \cdot \sinh \frac{\mu X}{kT} \right\} \right\} \dots (15)$$

In Eqs. (13) through (15), ω is represented by the following equation;

$$\omega = \frac{1}{2} \sqrt{3} b^3 = \frac{\sqrt{3}}{2} (V_s \sqrt{2}/N)^{2/3} \dots (16)$$

where b is the nearest-neighbor distance and is given by $(V_s \sqrt{2}/N)^{1/3}$ for close packing.

III. Calculations and Results

A. Determination of E'_s and θ'

In the molten salts and strong electrolyte solutions, the forces between ions are long-range forces.

Therefore, the potential energy can be determined by such sum of an infinite series as the calculation of the Madelung constants (21).

For the sodium chloride, the potential energy of the bulk liquid and the liquid surface are written as follows, respectively;

$$P.E_b = -\frac{e^2}{r} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} + \dots \right) \dots \dots \dots (17)$$

$$P.E_s = -\frac{e^2}{r} \left(5 - \frac{8}{\sqrt{2}} + \frac{4}{\sqrt{3}} - \frac{5}{2} + \frac{16}{\sqrt{5}} - \frac{12}{\sqrt{6}} + \dots \right) \dots \dots \dots (18)$$

The potential energies for other molten salts are evaluated by the same method as for the sodium chloride.

Accordingly, the quantities E' , and θ' (22) are then given by

$$E'_s = E_s \left(\frac{5 - \frac{8}{\sqrt{2}} + \frac{4}{\sqrt{3}} - \frac{5}{2} + \frac{16}{\sqrt{5}} - \frac{12}{\sqrt{6}} + \dots}{6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} + \dots} \right) \dots \dots \dots (19)$$

$$\theta' = \theta \left(\frac{5 - \frac{8}{\sqrt{2}} + \frac{4}{\sqrt{3}} - \frac{5}{2} + \frac{16}{\sqrt{5}} - \frac{12}{\sqrt{6}} + \dots}{6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} + \dots} \right)^{1/2} \dots \dots \dots (20)$$

B. Molten Salts

Using the experimental values of E_s , V_s , T and d for molten salts, the surface tension is calculated from Eq. (13).

The obtained values are compared with the observed values (1) in Table 1.

The results of calculation I are obtained from the assumption that the potential energy between ions are due to Van der Waal's force, while that of calculation II is obtained by considering the long-range forces.

C. Strong Electrolyte Solutions

In the calculation, the values of E' , and θ' obtained from the molten salts have been used. And using the experimental values of E_s , V_s , T , θ , and m' for the electrolyte solutions, the surface tensions are calculated from Eq. (15).

The obtained values are listed in Table II. Here, $\Delta\gamma$ is the difference between the surface tension of electrolyte solution and that of water, i.e., $\Delta\gamma = \gamma$.

IV. Discussion

As may be seen from the results given in Table I, the results of the calculation I show better agreement than that of the calculation II with the experimental values at the various temperatures.

The above facts confirm the correctness of our assumption that the ionic forces are long-range forces in molten salts and electrolyte solutions.

In the Table II, the calculated surface tension of strong electrolyte solutions are compared with the observations.

These results show again good agreement between theory and experiment over a wide concentration ranges (0-4.0m), and also agreement with the results by Onsager and Samaras' (5).

In very dilute concentration range, the validity of Jones and Ray's experiment (3) for

aqueous KCl and KBr solutions is not yet tested, but this may be explained by the negative hydration effect based on Samoilov's work (23).

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TABLE I. Surface Tension of Molten Salts

Molten Salts	T (°K)	d (g/cm ³)	V _s (cm ³)	E _s (Kcal/mole)	θ (°K)	γ _{obs.} (dyne/cm)	γ _{calc.I} (dyne/cm)	γ _{calc.II} (dyne/cm)
NaCl	1073	1.548(a)	30.19(b)	56.07(c)	215(e)	111.3(a)	369.8	86.0
	1273	1.448				98.0	329.4	74.5
NaBr	1023	2.334	36.02	51.91(d)	145(d)	99.4	314.9	75.0
	1173	2.217				91.0	284.4	67.0
KCl	1049	1.527	41.57	54.15(c)	170(e)	98.7	336.1	74.0
	1173	1.452				90.0	300.6	67.1
KBr	1008	2.214	48.06	51.53(d)	118(d)	89.3	290.0	66.0
	1073	2.073				85.0	270.7	61.5

(a) Data are taken from reference 1.

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TABLE II. Surface Tension of strion of Strong Electrolyte Solutions

Salts	T (°K)	$\Delta \gamma$ (dyne/cm)	Molality (m)				
			0.1	1.0	2.0	3.0	4.0
NaCl	293.16	Calcd (a)	0.25	1.45	3.02	4.72	6.35
		Obsd (a)	0.17	1.64	3.28	4.90	6.54
NaBr	288.16	Calcd (b)	0.19	1.44	3.00	4.62	6.07
		Obsd (b)	0.14	1.59	3.12	4.71	6.19
KCl	283.16	Calcd (b)	0.27	1.43	3.01	4.51	6.18
		Obsd (b)	0.18	1.55	3.13	4.72	6.31
KBr	293.16	Calcd (a)	0.20	1.27	2.51	3.75	5.26
		Obsd (a)	0.15	1.32	2.65	3.97	5.33

(a) Data are taken from reference 2.

(b) Data are taken from reference 24.

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