Indian J. Phys. 52B, 62–68 (1978)

On some correction on free energy of an assembly of charged paticles due to hard core potential

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(*Received* 27 *April* 1977, *revised* 22 *August* 1977)

The paper is an investigation of the physical properties of an assembly of charged particles in a continuous dielectric medium. Dutta's distribution formula (Dutta, 1952, 1953) is used to replace the Boltzmann formula in order to take into account the effect of hard core potential of the particles. The resulting non-linear Poisson equation is solved by the method of Onsager and Fuoss (1961) and the free energy and other functions associated with it are obtained. For experimental verification, the results are applied to the strong electrolytes in dilute solution.

1. INTRODUCTION

We shall consider an assembly of charged particles in a continuous medium where the effect of continuous medium is taken into account, through the dielectric constant. From the work of Dutta (1952, 1953), Bogolubov (1949), Sengupta (1954, 1956) and others it is well known that the long range Coulomb forces as well as short range forces are important in this system. One simple type of potential for the short-range forces is the hard core potential.

Distribution formula of Dutta (1952, 1953) which takes into account of the hard core potential i.e. the exclusion volumes in configuration space of particles, can be applied to any system of charged particles. In 1961, Onsager and Fuoss considered the above system in dielectric medium and obtained the free energy and other thermodynamic quantities associated with it using the Boltzmann distribution formula which does not take into account the hard core potential. We shall take into account the effect of the hard core potential in the said Onsager and Fuoss (1961) theory on replacing the Boltzmann distribution by Dutta's distribution (1951, 1952) formula for charged particles in dielectric medium. The results have been applied to the case of strong electrolytes in solution which is also an example of an assembly of charged particles in continuous medium. The agreement with experimental result is much better.

MATHEMATICAL CALCULATIONS

Here we take an assembly of ions in a continuous medium with dielectric constant D. The ions are supposed to be produced by complete dissociation of an acid or a salt in solution. The distribution of ions in the solution is given by Dutta's formula (1952, 1953)

$$n_{\pm,r} = \frac{\frac{1}{b_\pm}}{\exp\left(\nu_\pm + \frac{z_\pm \epsilon \psi_r}{kT}\right) + 1} \qquad \ldots (1)$$

where $n_{\pm,r}$ = number densities of positive and negative ions at distance from a reference ion and at that position potential is ψ_r;

$b_\pm$ = exclusion volumes of two like ions;

$z_\pm$ = valency of positive or negative ions;

$\nu_\pm$ = parameters of distribution;

ϵ, k, T have their usual significances.

For simplicity, we assume $|z_\pm| = 1$ and $b_+ = b_- = b$ (say), so that $\nu_+ - \nu_- = \nu$ (say). When $\psi_r \to 0$, the distribution is, on the average an uniform one, so that that $e^\nu = \frac{1-nb}{nb}$, where n = average number of ions per unit volume. Then the modified Poisson equation takes the form

$$\nabla^2 \psi_r = -\frac{4\pi\epsilon}{D}\left\{\frac{1}{1+e^{\nu+\epsilon\psi/kT}} - \frac{1}{1+e^{\nu-\epsilon\psi/kT}}\right\} \qquad \ldots (2)$$

We shall restrict ourselves to the case where the average concentration of ions per unit volume is small so that we can take $b_n << 1$. Neglecting higher order terms of bn, the eq. (2) becomes

$$\nabla^2 \psi_r = -\frac{4\pi\rho}{D} \qquad \ldots (3)$$

where $$\rho = -2\epsilon n(1-bn)\,\text{singh}\,\frac{\epsilon\psi}{kT}\left\{1-2bn\left(\cosh\frac{\epsilon\psi}{kT}-1\right)\right\} \qquad \ldots (3a)$$

is the average charge density at the distance r.

Proceeding along the line of Onsager and Fuoss (1961) we set, for short distances, i.e. for $r \leqslant \frac{\beta}{2}$ where $\beta = \frac{\epsilon^2}{DkT}$,

$$\psi_s = \frac{\epsilon}{Dr} + \Phi(r). \qquad \ldots (4)$$

In eq. (4) $\frac{\epsilon}{Dr}$ is the potential at a distance r from an isolated ion and $\Phi(r)$ is the perturbation in the Coulomb potential produced by neighbouring ions. From eqs. (4) and (3) one obtains

$$\nabla^2\Phi(r) = \frac{8\pi\epsilon n}{D}(1-bn)\sinh\left\{\frac{\epsilon}{kT}\left(\frac{\epsilon}{Dr}+\Phi\right)\right\}$$

$$\times\left\{1-2bn\left(\cosh\frac{\epsilon}{kT}\left(\frac{\epsilon}{Dr}+\Phi\right)-1\right)\right\}. \qquad \ldots (5)$$

We approximate $e^{\epsilon\Phi/kT} \simeq 1$. Due to spherical symmetry eq. (5) reduces to

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Phi}{\partial r}\right) = \frac{8\pi\epsilon n(1-bn)}{D}e^{\beta/r}(1+2bn-bne^{\beta/r}).$$

Integrating eq. (6) and substituting the result in eq. (4), we get

$$\psi_s = \frac{\epsilon}{Dr}+\frac{\kappa_1^2\epsilon\beta}{2D}\left\{-\frac{A\beta}{r}+B+(1+2bn)F_1(r)-bn\,F_2(r)\right\} \qquad (7)$$

where $\kappa_1^2 = 8\pi n\beta(1-nb) = \kappa^2(1-nb)$,

A and B are constants and

$$F_1(r) = e^{\beta/r}\left(\frac{r^2}{6\beta^2}+\frac{r}{3\beta}-\frac{1}{6}\right)+\left(\frac{\beta}{6r}-\frac{1}{2}\right)E_1\left(\frac{\beta}{r}\right)$$

$$F_2(r) = e^{2\beta/r}\left(\frac{r^2}{6\beta^2}+\frac{4}{3}\cdot\frac{r}{\beta}+\frac{2}{3}\right)+2\left(\frac{2}{3}\cdot\frac{\beta}{r}-1\right)E_2\left(\frac{\beta}{r}\right) \qquad \ldots (8)$$

where $E_i(x)$ is the positive exponential integral

$$E_i(x) = \int_{-\infty}^{x}\frac{e^{iu}}{u}\,du. \qquad \ldots (9)$$

For distance $r \geqslant \frac{\beta}{2}$, the long range potential ψ_L is obtained by integrating the equation

$$\nabla^2\psi_L = \kappa_1^2\psi_L+\frac{8\pi\epsilon^4 n}{D^3k^3T^3}\cdot\frac{1-7bn}{6}\cdot\psi_L^3 \qquad \ldots (10)$$

which is deduced from eq.(3) retaining up to cubic terms in ψ_L; this is justified by the fact that $\psi_L \to 0$ as $\frac{r}{a}\to\infty$, a = ionic radius.

We get with the boundary condition $\psi_L\left(\frac{r}{a}\to\infty\right)=0$

$$\psi_L = C.\frac{e^{-\kappa_1 r}}{r}+\frac{8\pi\epsilon^4 n}{Dk^3T^3}.\frac{1-7bn}{6}\left[2.\frac{e^{-\kappa_1 r}}{3r}E_4-\frac{e^{-\kappa_1 r}}{3r}E_2\right] \quad \ldots (11)$$

where $$E_n = \int^{\infty} \frac{e^{-u}}{a^n}\,du. \quad \ldots (12)$$

The integration constants A, B, C are evaluated by the following conditions;

$$-c = \int^{\infty} 4\pi\rho r^2 dr \quad (13a)$$

$$\psi_s\left(\frac{\beta}{2}-0\right) = \psi_L\left(\frac{\beta}{2}+0\right) \quad (13b)$$

and

$$\left(\frac{d\psi_s}{dr}\right)_{\frac{\beta}{a}-0} = \left(\frac{d\psi_L}{dr}\right)_{\frac{\beta}{a}-0}, \quad (13c)$$

From eqs. (3a) and (13a) we have

$$= D\int_a^{\infty} r^2\nabla^2\psi dr = -Da^2\left(\frac{d\psi_s}{dr}\right)_a, \text{ (using 13c)} \quad (14)$$

whence we obtain

$$\left(\frac{d\psi_s}{dr}\right) = -\frac{\epsilon}{Da^2}. \quad (15)$$

Differentiating eq. (7) and substituting in eq. (15),

$$A = \frac{F_3(p)}{p} \quad . \quad (16)$$

where

$$F_3(p) = (1+2bn)\left[\frac{e^p}{6p^2}(2)+p+p^2-\frac{p}{6}.E_1(p)\right]$$

$$-bn\left[\frac{e^{2p}}{3p^2}(1+3p-2p^2)-\frac{4}{3}pE_2(p)\right] \quad (17)$$

and

$$p = \frac{\epsilon^2}{aDkT} = \frac{\beta}{a}.$$

Eliminating C between eqs. (13b) and (13c) and substituting the value of A from eq. (16) we get

$$B = (1+\tau)^{-1}\Big[-\frac{1-bn}{\tau} - \frac{1-7bn}{6} G_3(\tau) - (1+2bn)F_3(2) + \frac{bn}{12}(55e^4+32E_2(2))$$

$$-(1+2bn)(1+\tau)F_1\left(\frac{\beta}{2}\right) + bn(1+\tau)F_3\left(\frac{\beta}{2}\right) - 2\tau\frac{F_3(p)}{p}\Big] \quad \ldots (18)$$

where

$$\tau = \frac{\kappa_1\beta}{2} \quad \ldots (19)$$

and

$$G_3(\tau) = \frac{2e^{-3\tau}}{3} - \frac{8\tau}{3}\cdot e^{\tau}E_4\left(\frac{\beta}{2}\right). \quad \ldots (20)$$

Now the potential ψ^* at the reference ion due to the presence of other ions is

$$\psi^* = \psi_s(a) - \frac{e}{Da}. \quad \ldots (21)$$

One may obtain ψ^* from eqs. (7), (16) and (18) as

$$\psi^* = \frac{\kappa_1^2\epsilon_j\beta}{2D}\Big[\frac{\beta}{ap}(1+2bn)\Big\{\frac{e^p}{6p^2}\cdot(2+p+p^2) - \frac{p}{6}\cdot E_1(p)\Big\}$$

$$-bn\Big\{\frac{e^{2p}}{3p^2}(1+3p-2p^2) - \frac{4}{3}pE_2(p)\Big\} - (1+\tau)^{-1}\Big\{-\frac{1-bn}{\tau}$$

$$-\frac{1-7bn}{6}G_3(\tau) - (1+2bn)F_3(2) + \frac{bn}{12}\cdot(55e^4+32E_2(2))$$

$$-(1+2bn)(1+\tau)F_1\left(\frac{\beta}{2}\right) + bn(1+\tau)F_3\left(\frac{\beta}{2}\right) - 2\tau\frac{F_3(p)}{p}\Big\} +$$

$$+(1+2bn)F_1(a) - bnF_2(a)\Big]. \quad \ldots (22)$$

The free electric energy is

$$G_e = \tfrac{1}{2}\sum_j n_j\epsilon_j\psi_j^* \quad \ldots (23)$$

Finally the relation $kT\ln f_j = \dfrac{\partial G_e}{\partial n_j}$ ... (24)

gives for the activity coefficient

$$-\ln f_j = \frac{\tau}{1+\tau} + O\left(\frac{\tau^2}{1+\tau^2}\right). \quad \ldots (25)$$

The above eq. (25) is similar to the eq. (34) of Fuoss and Onsager (1961), viz.

$$-\ln f_j' = \frac{\tau'}{1+\tau'} + O\left(\frac{\tau'^2}{1+\tau'^2}\right) \quad \ldots (26)$$

(τ' is written for τ in Onsager's equation only to distinguish it from our τ)

where $$\tau = \tau'\sqrt{1-bn} \quad (27)$$

Thus in our result, the volume correction i.e. the effect of hard core potential is introduced by the use of Dutta's (1952, 1953) distribution formula and the result reduces to that of Onsager & Fuoss (1961) when the volume correction is neglected.

3. Numerical Results

For verification with experimental data, we consider the case of strong electrolytes in dilute solution. For low concentrations, the equation (25) and (26) for activity coefficients become (retaining up to the leading terms in τ)

$$-\ln f_j = \frac{\tau}{1+\tau} \quad \ldots (28)$$

$$-\ln f_j' = \frac{\tau}{1+\tau'} . \quad \ldots (29)$$

The following gives a comparative study of the numerical values obtained from the present work and that of Onsager and Fuoss (1961) with the data of observed results (Harned and Owen, 1943).

The result (29) of Onsager and Fuoss (1961) does not contain any parameter. Our result (28) contains the parameter b which is the exclusion volume of two like ions and introduced through the distribution formula of Dutta (1952, 1953). This is related to the mean distance of closest approach a by the relation $b = \frac{4}{3}\pi a^3$

In the table

f' = activity coefficient as given by the work of Onsager and Fuoss (1961).

f = activity coefficient as given by the present work.

obs = observed results.

Here we have taken $D = 78.6$, $T = 25°C$ and the standard values of k and e.

c	NaCl $a = 4.4$Å			KCl $a = 4.1$Å			HCl $a = 4.6$Å		
	f'	f	obs	f'	f	obs	f'	f	
.001	.96486	.96487		.96486	.96486		.96486	.96487	.966
.005	.92626	.92635	.9283	.92626	.92632	.927	.92626	.92634	.929
.01	.90033	.90056	.9034	.90033	.90049	.901	.90033	.90033	.905
.02	.86737	.86797	.8726	.86737	.86780	—	.86737	.8679	.875
.05	.81237	.81445	.8221	.81237	.81384	.815	.81237	.81419	.830
.1	.76295	.76804	.778	.76295	.769	.769	·76295	.76740	.796
.2	.70890	.72097	.732	.70890	.71743	.719	.70890	.71946	.767
.5	.63553	.67190	.678	.63553	.66107	.651	.63553	.66553	.757

4. Conclusion

For comparison, we have given in the above table the values of activity coefficients of several 1—1 electrolytes in very dilute solution as given by our present work, the corresponding results of Onsager and Fuoss (1961) and the observed values (Harned and Owen, 1943). Better agreement as compared to the results of Onsager and Fuoss (1961) are obtained. The above result as well as the proceeding analysis shows that the modified distribution formula coupled with the above method of solving Poisson's equation can be fruitfully utilised for any system of charged particles.

5. Acknowledgments

The authors are very grateful to Professor M. Dutta, Professor-in-charge, S. N. Bose Institute of Physical Sciences, and Professor, Centre of Advanced Study in Applied Mathematics, C.U. for his kind help and valuable suggestions in preparing this paper and also wish to thank Dr. M. Sengupta, Reader, Department of Chemistry, C.U. for useful discussion. They also wish to thank the referee for his valuable suggestions.

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