Critical Coagulation Concentration of Counterions

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The minimum concentration of electrolyte to initiate the coagulation of a stable dispersion of charged entities is defined as the critical coagulation concentration (CCC). For some dispersed entities, the CCC for counterions of various valences was found to be inversely proportional to the sixth power of its valence, the so-called Schulze-Hardy rule. As an example, for cations of valences 3, 2, and 1, the corresponding CCC ratio is 3^{-6}:2^{-6}:1^{-6}, or roughly 1:11:729. The Schulze-Hardy rule was interpreted successfully on the basis of the DLVO (Deryaguin, Landau, Verwey, and Overbeek) theory (Hunter, 1989) which assumed the following: (a) symmetric electrolyte; (b) planar surface; (c) two interacting surfaces are separated far enough; (d) high absolute surface potential. Under the first two assumptions, the Poisson-Boltzmann equation governing the electrical potential distribution for an isolated surface can be solved analytically. Information about this distribution is essential to the evaluation of the electrical interaction energy between two surfaces Vr (J). If assumption (c) is satisfied, the linear superposition approximation is applicable. In this case, the electrical potential at the midplane between two surfaces is twice that of an isolated surface at this plane. This makes V_r readily estimable. The last assumption was employed to recover an analytical expression for CCC. Although experimental evidence which supports the Schulze-Hardy rule exists, laboratory data which deviate appreciably from this rule are also not uncommon. For example, the CCC ratio for As_2S_3 particles is about 1:7.65:588, and is about 1:34:2,000 for AgI particles (Overbeek, 1952). The latter may be due to the violation of the experimental conditions from some of the assumptions listed above. Apparently, a more rigorous deviation for CCC is desirable for practical applications. In a recent study (Hsu and Kuo, 1995) analytical expressions for the CCC ratio for asymmetric electrolytes was estimated under limiting levels of surface potential. If the absolute surface potential is high, it was shown that for a common monovalent anion, the CCC ratio of cations of valences 3, 2, and 1 is about 1:15:1,118 (Hsu and Kuo, 1995). In this note the CCC of counterions is discussed for the case that the assumptions (c) and (d) are not necessarily true, and we consider spherical surfaces.

Modeling

The analysis begins by considering two identical, parallel planar surfaces in a symmetric electrolyte solution. Without loss of generality, these surfaces are assumed to be positively charged. One of the two surfaces is located at $x = -L$, and the other at $x = L$. (x is the dimensionless variable, L is half the dimensionless separation distance between two particles, and L^* is half the dimensionless separation distance between two spheres at CCC.) The distribution of the dimensionless electrical potential Ψ is described by

$$\frac{d^2\Psi}{dx^2} = \frac{\sinh(a\Psi)}{a}, \qquad -L \le x \le L, \tag{1}$$

where $\Psi = e\phi/KT$, $x = \kappa\tilde{x}$, $\kappa^2 = 2e^2a^2n_0/\epsilon_r\epsilon_0 KT$. In these expressions, $\tilde{x}$ is the position variable (m), ϕ represents the electrical potential, K and e are the Boltzmann constant (1.38×10^{-23} J/k) and the elementary charge (1.6×10^{-19}C), respectively, T is the absolute temperature (K), a and n_0 are, respectively, the valence and the concentration of the ion species in the bulk liquid phase (No. /m^3), ϵ_r and ϵ_0 are the relative permittivity of solution and the permittivity of the vacuum (8.85×10^{-12}C^2/J/m), respectively, and κ is the reciprocal Debye length (1/m). For surfaces remaining at a constant potential, the boundary condition associated with Eq. 1 is

$$\Psi = \Psi_s \quad \text{at} \quad x = -L \quad \text{and} \quad x = L, \tag{2}$$

where Ψ_s is the dimensionless surface potential. Solving Eq. 1 subject to Eq. 2 yields (Chan et al., 1980)

$$|x| = \int_{y/y_m}^{1} \frac{2y_m}{\sqrt{(v^2-1)(y_m^4v^2-1)}}dv = \int_{\sin^{-1}(y/y_m)}^{\pi/2} \frac{2y_m}{\sqrt{1-y_m^4\sin^2\theta}}d\theta, \tag{3}$$

where $y = \exp(-a\Psi/2)$, and $y_m = \exp(-a\Psi_m/2)$, Ψ_m is the dimensionless potential at $x = 0$. The value of y_m can be estimated by

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$$L = \int_{y_s/y_m}^{1} \frac{2y_m}{\sqrt{(\upsilon^2-1)(y_m^4\upsilon^2-1)}}\,d\upsilon$$

$$= \int_{\sin^{-1}(y_s/y_m)}^{\pi/2} \frac{2y_m}{\sqrt{1-y_m^4\sin^2\theta}}\,d\theta, \tag{4}$$

where $y_s = \exp(-a\Psi_s/2)$. Solving Eq. 4 for y_m and substituting the resultant expression into Eq. 3 gives the potential distribution between two surfaces. On the basis of Eq. 4, we have

$$y_m = y_m(a\Psi_s, L) \tag{5}$$

For surfaces remaining at a constant dimensionless surface charge density σ_s, Eq. 1 needs to be solved subject to

$$\frac{d\Psi}{dx} = \sigma_s \quad \text{at} \quad x = -L, \quad \text{and} \quad \frac{d\Psi}{dx} = -\sigma_s \quad \text{at} \quad x = L, \tag{6}$$

where y_s, y_m, and σ_s are related by

$$-a\sigma_s = [y_s^2 + y_s^{-2} - (y_m^2 + y_m^{-2})]^{1/2}. \tag{7}$$

Since $0 < y_s < 1$ and $y_s \le y_m$, we have

$$y_s = \sqrt{\frac{(a\sigma_s)^2 + y_m^2 + y_m^{-2} - \sqrt{\left((a\sigma_s)^2 + y_m^2 + y_m^{-2}\right)^2 - 4}}{2}}. \tag{8}$$

Substituting $y_s(a\sigma_s, y_m)$ into Eq. 4 and solving the resultant expression yields

$$y_m = y_m(a\sigma_s, L). \tag{9}$$

The electrical repulsion force between two surfaces F can be calculated by (Hunter, 1989)

$$F = 2KTn_0(\cosh a\Psi_m - 1)$$

$$= 2KTn_0\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right). \tag{10}$$

The corresponding electrical interaction energy V_r is

$$V_r = \int_L^{\infty} F(L')\,d(2\kappa^{-1}L')$$

$$= \int_L^{\infty} 4\kappa^{-1}KTn_0\left(\frac{y_m(L')^2 + y_m(L')^{-2}}{2} - 1\right)dL'. \tag{11}$$

The van der Waals interaction energy between two surfaces V_a (J) can be calculated by (Hunter, 1989)

$$V_a = -\frac{A}{12\pi(2L)^2\kappa^{-2}}, \tag{12}$$

where A is the Hamaker constant (J). The total interaction energy V_t is

$$V_t = V_r + V_a \tag{13}$$

At the CCC

$$V_t = 0 \tag{14}$$

and

$$\frac{\partial V_t}{\partial L} = 0. \tag{15}$$

Substituting Eqs. 11 and 12 into Eqs. 13–15 leads to

$$\int_{L^*}^{\infty}\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right)dL' = \frac{L^*}{2}\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right) \tag{16}$$

and

$$\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right) = \frac{A}{96\pi KTn_0^* L^{*3}\kappa^{-3}}, \tag{17}$$

where L^* is the value of L at which coagulation occurs, and n_0^* (No./m^3) is the corresponding n_0. Substituting L^* and $y_m(L^*)$ into Eq. 17 gives the CCC of counterions.

The simulated variation in the ratio (CCC of a:a electrolyte/CCC of 3:3 electrolyte) for various a at several levels of dimensionless surface potential is shown in Table 1. The result shown in this table reveals that, depending upon the

Table 1. Simulated CCC Ratio*

a	L^*	$y_m(L^*)$	CCC Ratio
		$\Psi_s = 0.5$	
1	1.113	0.863	10.530
2	1.112	0.750	2.491
3	1.106	0.659	1
4	1.091	0.584	0.484
		$\Psi_s = 1$	
1	1.101	0.748	16.647
2	1.079	0.581	3.235
3	1.051	0.476	1
4	1.022	0.410	0.367
		$\Psi_s = 2$	
1	1.080	0.582	50.130
2	1.020	0.410	5.656
3	0.973	0.340	1
4	0.953	0.314	0.234
		$\Psi_s = 10$	
1	0.938	0.302	684.967
2	0.935	0.297	11.409
3	0.934	0.297	1
4	0.930	0.296	0.177

*CCC of a:a electrolyte/CCC of 3:3 electrolyte for various a at selected levels of dimensionless surface potential Ψ_s.

level of surface potential, various CCC ratio for counterions can be assumed. If $\Psi_s \to \infty$, Eq. 4 reduces to

$$L = \int_0^{\pi/2} \frac{2y_m}{\sqrt{1 - y_m^4 \sin^2\theta}} d\theta. \tag{18}$$

Since $y_m = y_m\,(a\Psi_s,\, L)$, if $\Psi_s \to \infty$, y_m becomes independent of a. According to Eq. 18, L^* is also independent of a. In this case, Eq. 17 leads to the Schulze-Hardy rule. Note that the linear superposition approximation employed in the conventional analysis is redundant. In other words, assuming that two charged surfaces to separate far enough is unnecessary.

For spherical particles V_r can be estimated by employing the Derjaguin approximation (Hunter, 1989), we have

$$V_r = 8\pi KTRn_0\kappa^{-3}\int_L^{\infty}\int_z^{z+R}\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right) \times\left(1 - \frac{L'}{R} + \frac{z}{R}\right) dL'dz, \tag{19}$$

where $R = \kappa R_t$ (R is the dimensionless radius of sphere and R_t the radius of sphere (m)), $2L$ is the dimensionless surface-to-surface distance between two particles. The van der Waals interaction energy for two identical spherical particles can be calculated by (Lyklema, 1991)

$$V_a = -\frac{A}{6}\left[\frac{2R^2}{4L^2 + 8RL} + \frac{2R^2}{4L^2 + 8RL + R^2} + \ln\left(\frac{4L^2 + 8RL}{4L^2 + 8RL + R^2}\right)\right] \tag{20}$$

L^* and n_0^* can be determined by substituting Eqs. 19 and 20 into Eqs. 13–15 and solving the resultant expressions. Given a, T, and R, we suggest using the following numerical scheme:

Step 1. For constant potential surfaces, $y_m(a\Psi_s, L)$ is calculated by Eq. 4; for constant charge density surfaces, $y_m(a\sigma_s, L)$ is estimated by Eqs. 4 and 8.

Step 2. The following expression is solved for L^*

$$\frac{V_r(L)}{dV_r(L)/dL} = \frac{V_a(L)}{dV_a(L)/dL}. \tag{21}$$

We have

$$\frac{\int_L^{\infty}\int_z^{z+R}\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right)\left(1 - \frac{L'}{R} + \frac{z}{R}\right)dL'dz}{-\int_L^{L+R}\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right)\left(1 - \frac{L'}{R} + \frac{L}{R}\right)dL'} = \frac{V_a(L)}{dV_a(L)/dL} \tag{22}$$

Step 3. Solving $dV_r(L)/dL + dV_a(L)/dL = 0$ for n_0^*, yields

$$n_0^* = \left(\frac{8\pi KTR\int_L^{L+R}\left(\frac{y_m^2 + y_m^{-2}}{2} - 1\right)\left(1 - \frac{L'}{R} + \frac{L}{R}\right)dL'}{e^3a^3\sqrt{\frac{2}{\epsilon_r^3\epsilon_0^3K^3T^3}}\,dV_a(L)/dL}\right)^2_{|L = L^*} \tag{23}$$

Step 4. Calculate κ by using the n_0^* obtained in Step 3.

Step 5. Rescale R and return to Step 2.

The simulated CCC ratio for spherical particles of various sizes are summarized in Table 2 for the case of constant potential, and in Table 3 for the case of constant charge density. As can be seen from these tables, appreciable deviation from the Schulze-Hardy rule is possible. Tables 2 and 3 show that, for a fixed surface condition, the CCC ratio is insensitive to the variation in particle size. This is because that for the values of the parameters assumed ($T = 298$ K, $\epsilon_r = 78.54$, and $A = 1.2 \times 10^{-20}$ J.), the Debye length ($1/\kappa$) is small at the critical coagulation concentration of electrolyte, κR_t is large for the range of particle size considered, and, therefore, the behavior of a spherical surface can be approximated by that of a planar surface. This is consistent with the experimental observation of Ottewill and Shaw (1966). Tables 2 and 3 also suggest that, for a fixed particle size, the CCC ratio

Table 2. Simulated CCC Ratio for Various Sizes of Spherical Particles, R_t, at Constant Dimensionless Surface Potential Ψ_s^*

R_t (m)	Ψ_2, 0.1	Ψ_2, 0.8	Ψ_2, 1.5	Ψ_2, 2.2	Ψ_2, 2.9	Ψ_2, 3.6	Ψ_2, 5.0	Ψ_2, 20.0
1.000E-07	1:2.26:9.03	1:2.79:12.83	1:4.14:25.60	1:5.56:51.17	1:7.44:96.17	1:8.96:159.3	1:10.56:319.8	1:11.24:708.9
1.750E-06	1:2.24:8.95	1:2.78:12.78	1:4.12:25.60	1:5.60:51.54	1:7.51:97.32	1:9.05:161.7	1:10.68:326.9	1:11.36:725.5
3.400E-06	1:2.26:8.94	1:2.79:12.78	1:4.12:25.61	1:5.61:51.58	1:7.52:97.43	1:9.06:161.9	1:10.69:327.5	1:11.37:726.8
5.050E-06	1:2.26:8.97	1:2.79:12.78	1:4.12:25.61	1.5.61:51.59	1:7.52:97.47	1:9.07:162.0	1:10.69:327.7	1.11.38:727.3
6.700E-06	1:2.27:8.99	1:2.79:12.78	1:4.12:25.61	1:5.61:51.60	1:7.52:97.50	1:9.07:162.0	1:10.69:327.8	1:11.38:727.6
8.350E-06	1:2.27:9.00	1:2.79:12.78	1:4.12:25.61	1:5.61:51.61	1:7.52:97.51	1:9.07:162.0	1:10.70:327.9	1:11.38:727.8
1.000E-05	1:2.27:9.00	1:2.79:12.78	1:4.12:25.61	1:5.61:51.61	1:7.52:97.52	1:9.07:162.1	1:10.70:328.0	1:11.38:727.9

*The entry denotes the ratio (CCC of 3:3 electrolyte):(CCC of 2:2 electrolyte):(CCC of 1:1 electrolyte). Key: $T = 298$ K, $\epsilon_r = 78.54$, and $A = 1.2 \times 10^{-20}$ J.

Table 3. Simulated CCC Ratio for Various Sizes of Spherical Particles, R_t, at Constant Dimensionless Surface Charge Density σ_s^*

R_t (m)	Ψ_2, 0.1	Ψ_2, 0.8	Ψ_2, 1.5	Ψ_2, 2.2	Ψ_2, 2.9	Ψ_2, 3.6	Ψ_2, 5.0	Ψ_2, 20.0
1.000E-07	1:1.70:2.29	1:3.88:11.14	1:5.56:26.50	1:7.45:55.80	1:9.03:103.4	1:10.07:167.6	1:10.94:332.2	1:11.23:708.6
1.750E-06	1:1.71:2.45	1:3.86:11.09	1:5.61:26.59	1:7.53:56.33	1:9.13:104.8	1:10.18:171.3	1:11.06:340.0	1:11.36:725.7
3.400E-06	1:1.71:2.45	1:3.86:11.08	1:5.62:26.60	1:7.54:56.38	1:9.14:104.9	1:10.19:171.6	1:11.07:340.6	1:11.37:727.1
5.050E-06	1:1.71:2.44	1:3.86:11.08	1:5.62:26.60	1.7.54:56.40	1:9.15:105.0	1:10.20:171.7	1:11.08:340.8	1.11.38:727.6
6.700E-06	1:1.71:2.44	1:3.86:11.08	1:5.62:26.61	1:7.54:56.41	1.9.15:105.0	1:10.20:171.7	1:11.08:341.0	1:11.38:727.9
8.350E-06	1:1.71:2.44	1:3.86:11.08	1:5.62:26.61	1:7.54:56.42	1:9.15:105.0	1:10.20:171.8	1:11.08:341.1	1:11.38:728.1
1.000E-05	1:1.71:2.44	1:3.86:11.08	1:5.62:26.61	1:7.54:56.42	1:9.15:105.1	1:10.20:171.8	1:11.08:341.1	1:11.38:728.2

*The entry denotes the ratio (CCC of 3:3 electrolyte):(CCC of 2:2 electrolyte):(CCC of 1:1 electrolyte). The dimensionless surface potential Ψs is the undisturbed potential corresponding to σ_s. Key: same as Table 2.

approaches to a constant value. This is because that as $\Psi_s \rightarrow \infty$, the CCC ratio becomes 1:11.39:729, the ratio predicted by the Schulze-Hardy rule, grant no. NSC85-2214-E002-023.

Acknowledgment

This study is supported by the National Science Council of the Republic of China.

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Manuscript received Jan. 5, 1996, and revision received Apr. 16, 1996.