APPROXIMATE CHARGE-POTENTIAL RELATIONSHIP FOR CYLINDRICAL PARTICLE IN ARBITRARY SALT MEDIUM

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ABSTRACT

Article presents accurate charge-potential relationship for cylindrical particle in arbitrary salt medium, applicable down to molecular size. For the case of arbitrary mixture of 1:1, 2:1, 1:2, and 2:2 electrolytes, this relationship is given by analytical expression. The application of the cylindrical diffuse layer model to calculation of chemical equilibria in polyelectrolytes is considered in details.

INTRODUCTION

If the curvature of the solid-water interface is negligible, the charge-potential relation is defined by Gouy-Chapman equation (below all numerical values of constant factors are valid for $25^{o}C$ and aqueous medium):

$$\sigma, C/m^2 = (2000RT\varepsilon_o\varepsilon)^{0.5}\times I^{0.5}\times Q = 0.0587\times I^{0.5}\times Q \quad , \text{or} \tag{1}$$

$$\sigma, \mu eq/m^2 = 0.608\times I^{0.5}\times Q \tag{1a}$$

$$Q = \{1/I^{0.5}\}\times sgn(y_d)\times\{\sum c_i[exp(-z_iy_d) -1]\}^{0.5} \tag{2}$$

$$y_d = F\varphi_d/RT \tag{3}$$

$$I = 0.5\times\Sigma z_i^2 c_i \tag{4}$$

Here φ_d is potential in the head of diffuse layer, y_d is scaled potential, $sgn(y_d)$ is sign of y_d, I is molar ionic strength, c_i is molar concentration of ion in the bulk solution (moles per dm^3), z_i is charge of ion, F is Faraday constant (96484.6 C/mol), R is gas constant (8.3144 $J\times mol^{-1}\times K^{-1}$), T is absolute temperature, ε_o is dielectric constant of free space (8.8541878×10^{-12} $C\times V^{-1}\times m^{-1}$), ε is relative dielectric constant of medium (78.47 for water at $25^{o}C$).

The Eq (2) may be rearranged as (Pivovarov 2010):

$$Q = \{I_{eff}/I\}^{0.5}\times(P_d^{0.5} - 1/P_d^{0.5}) \tag{5}$$

$$P_d = exp(F\varphi_d/RT) = exp(y_d) \tag{6}$$

$$I_{eff} = 0.5\{[A^-] + [An^{2-}](2 + 2P_d) +\dots [An^{n-}](n + 2(n-1)P_d +\dots2P_d^{n-1}) +$$
$$+ [M^+] + [Me^{2+}](2 + 2/P_d) +\dots [Me^{n+}](n + 2(n-1)/P_d +\dots2/P_d^{n-1})\} \tag{7}$$

Here $[A^-]$, $[An^{2-}]$, and $[An^{n-}]$ are molar concentrations of mono-, bi- and n-valent anions, $[M^+]$, $[Me^{2+}]$, and $[Me^{n+}]$ are molar concentrations of mono-, bi- and n-valent cations.

For symmetric z:z electrolytes, the Eq. 2 is reduced to

$$Q = (2/z)sh(zy_d/2) \qquad (8)$$

Here $sh(x) = 0.5\{exp(x)-exp(-x)\}$ is hyperbolic sinus.

The Gouy-Chapman equation is exact charge-potential relationship for flat interface, and it may be applied if the curvature of interface is negligible. For cylindrical particles, accuracy of planar approach is 1 % at $\kappa a = 50$, and 10 % at $\kappa a = 5$, where a is radius of cylinder and κ is inversed Debye length:

$$\kappa = (2000F^2I/RT\varepsilon_o\varepsilon)^{0.5} \text{ or} \qquad (9)$$

$$\kappa^{-1}, \text{Å} = 3.04/I^{0.5} \qquad (9a)$$

The exact analytical charge-potential relation for infinite cylinder is not known. For low values of surface potential, it may be derived analytically from the Poisson-Boltzmann equation:

$$\sigma, \text{C/m}^2 = \varepsilon_o\varepsilon\varphi_d\kappa/\beta \ , \text{ or} \qquad (10)$$

$$\sigma, \mu eq/\text{m}^2 = 0.608 \times I^{0.5} \times y_d/\beta \qquad (10a)$$

Here $\beta = K_0(\kappa a)/K_1(\kappa a)$, where $K_0(\kappa a)$ and $K_1(\kappa a)$ are modified Bessel functions of second kind, of zero and first order.

As may be found from formula for electrical capacity of cylindrical condenser, $\beta \sim \kappa a \times ln(1+1/\kappa a)$ (maximum error 2.7 %). More accurate approximation is (maximum error 0.002 %):

$$\beta \approx \kappa a \times ln(1+1/\kappa a)\} + \{ln(2) - C\} \times \kappa a/(1 + 6.023(\kappa a)^{0.94} + 8.48(\kappa a)^2 + 2.78(\kappa a)^3) \quad (11)$$

Here $C = 0.5772156649\dots$ is Euler constant.

At high values of surface potential, the Eq. (10) is not applicable. However, based on perturbation analysis of Poisson-Bolmzmann equation, variety of first-order relationships may be deduced. One was deduced by Ohshima et al. (1982, Eq. A14). For symmetric z:z electrolyte it is:

$$\sigma, \mu eq/\text{m}^2 = 0.608 \times I^{0.5} \times (2/z)sh\{zy_d/2\}[1+(\beta^{-2}-1)/ch^2\{zy_d/4\}]^{0.5} \qquad (12)$$

Here $ch(x) = 0.5\{exp(x)+exp(-x)\}$ is hyperbolic cosine. The uncertainty of this relation is 1 % at $\kappa a = 0.5$, and 10 % at $\kappa a = 0.1$. At smaller size of cylinder, error increases to infinity.

At $\kappa a \rightarrow \infty$, the factor $(\beta^{-2}-1)$ approaches to $1/\kappa a$, and Eq. 12 may be reduced to:

$$\sigma, \mu eq/\text{m}^2 = 0.608 \times I^{0.5} \times [(2/z)sh\{zy_d/2\}+ 0.5 \times \{1/\kappa a\} \times (4/z)th\{zy_d/4\}] \qquad (13)$$

Here $th(x) = \{exp(x)-exp(-x)\}/\{exp(x)+exp(-x)\}$ is hyperbolic tangent. The uncertainty of Eq. (13) is 1 % at $\kappa a = 3.3$, and 10 % at $\kappa a = 1$; at smaller particle size, error increases to infinity. Both Eqs (12) and (13) are asymptotically exact at $\kappa a \rightarrow \infty$. Note also that the last

term in Eq. (13) is simply 2 times smaller than that in Loeb-Overbeek-Wiersema equation (see Eq. 4.50 in Loeb et al. 1961) for sphere with radius a. In other words, the charge-potential relationship coincides for large cylinder with radius a, and for sphere with radius 2a.

Similarly to Loeb-Overbeek-Wiersema equation for sphere, the Eq. (13) may be extended to arbitrary salt medium (see Eq. 20 in Ohshima, 1995, but multiply the second term by the factor 0.5):

$$\sigma, \mu eq/m^2 = 0.608 \times I^{0.5} \times \{Q + 0.5 \times \{1/\kappa a\} \times (2U/Q)\} \tag{14}$$

$$U = \int_0^{y_d} Q dy_d \tag{15}$$

Here Q is that defined by Eqs. (2), or (5), or (8). For the symmetric z:z electrolytes, the function U is

$$U = (4/z^2) \times \{ch(zy_d/2)-1\} = (8/z^2) \times sh^2(zy_d/4) \ , \qquad \text{and} \tag{16}$$

$$2U/Q = (4/z)th(zy_d/4) \tag{17}$$

The function U may be also solved analytically for arbitrary $(M^+, Me^{2+})(A^-, An^{2-})$ salt mixture (Pivovarov, 2013):

$$U = 2\{I_{eff}/I\}^{0.5}(P_d^{0.5} + 1/P_d^{0.5}) - 4 + U_{Me} + U_{An} \tag{18}$$

$$I_{eff} = N + [An^{2-}]P_d + [Me^{2+}]/P_d \tag{19}$$

Here $N = [M^+] + 2[Me^{2+}] = [A^-] + 2[An^{2-}]$ is total normality of solution, and P_d is that defined by Eq. (6). The function U_{Me} is zero at $[Me^{2+}] = 0$; at $[Me^{2+}]>0$, it is defined by:

$$U_{Me} = 1 - \left(\frac{I_{eff}}{I \times P_d}\right)^{0.5} + 0.5\left(\frac{[M^+]}{(I \times [Me^{2+}])^{0.5}}\right) \ln\left\{\frac{2\left(I_{eff}[Me^{2+}]/P_d\right)^{0.5} + 2([Me^{2+}]/P_d) + N}{2(I[Me^{2+}])^{0.5} + 2[Me^{2+}] + N}\right\} \tag{20}$$

Similarly, U_{An} is zero at $[An^{2-}] = 0$; at $[An^{2+}]>0$, this function is defined by:

$$U_{An} = 1 - \left(\frac{I_{eff} P_d}{I}\right)^{0.5} + 0.5\left(\frac{[A^-]}{(I \times [An^{2-}])^{0.5}}\right) \ln\left\{\frac{2\left(I_{eff}[An^{2-}]P_d\right)^{0.5} + 2[An^{2-}]P_d + N}{2(I[An^{2-}])^{0.5} + 2[An^{2-}] + N}\right\} \tag{21}$$

The Eq. (12) also may be extended to arbitrary salt mixture (see Eqs. 10, 11, 23, and 24 in Ohshima, 1998):

$$\sigma, \mu eq/m^2 = 0.608 \times I^{0.5} \times [Q^2 + 2(\beta^{-2} -1)U]^{0.5} \tag{22}$$

The available analytical relations are applicable to very fine crystalline particles (Eq. 13, 14), or down to the upper limit of high-molecular colloids (Eqs. 12, 22). However, most important application of cylindrical model of diffuse layer is that in the molecular range (radius of chain of the polymeric acid is few angstroms). In the present study, the accurate approximation was deduced, applicable down to molecular size.

THEORY

As may be seen from Eq. (14), the exact charge-potential relationship for may be expressed as

$$\sigma, \mu eq/m^2 = 0.608 \times I^{0.5} \times \{Q + \{0.5/\kappa a\} \times \Phi\}$$

$$(23)$$

Here Φ is some unknown function.

In Fig. 1, the function Φ for 1:1 electrolyte is shown. Points are results of numerical integration of the Poisson-Boltzmann equation, taken from Ohshima (1998). The limiting slope of the function Φ is defined by Eq. (10), which gives the following relation:
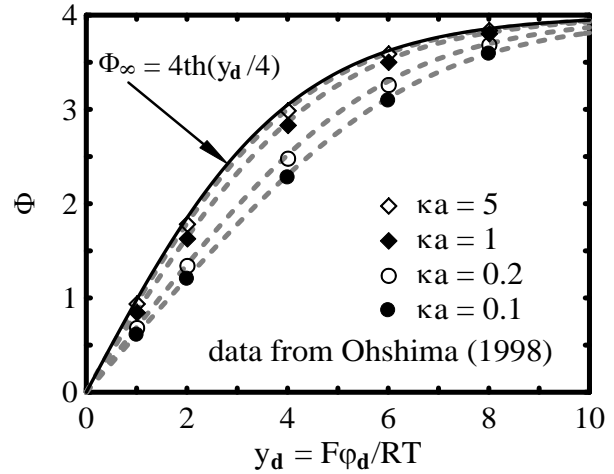

Fig. 1. The function Φ (see Eq. 23) for cylindrical particle in 1:1 electrolyte. Points are results of numerical integration of Poisson-Boltzmann equation (Ohshima, 1998). Dashed curves: Eq. 30.

$$\Phi \text{ (at } y_d \rightarrow 0, \text{ arbitrary salt medium)} = \{2\kappa a/\beta - 2\kappa a\} y_d \qquad (24)$$

Further, as may be guessed from Fig. 1, this function has asymptote at high surface potentials and any size of particle:

$$\Phi \text{ (at } \varphi_d \rightarrow \infty, \text{ 1:1 electrolyte)} = 4 \qquad (25)$$

Based on Eqs. (24, 25), variety of close approximations may be deduced. For symmetric z:z electrolytes, most accurate approximation is:

$$\Phi \approx (2b_1/z) \times \ln[\{\exp(-2/b_1) + \exp(zF\varphi_d/2RT)\}/\{1 + \exp(-2/b_1)\exp(zF\varphi_d/2RT)\}] \quad (26)$$

In accordance with Eq. (24), parameter b_1 is defined by:

$$b_1 \times th(1/b_1) = 2\kappa a/\beta - 2\kappa a \qquad (27)$$

Eq. (27) may be solved iteratively, or the following approximation may be used (maximum error 0.0024 %):

$$b_1 \approx \{x/(1-x)^{0.5}\}\{1-0.5x+5.232x^2+11.065x^3+2.95x^4\}/\{1+5.385x^2+13.193x^3+14.624x^4\}$$

$$(28)$$

$$x = 2\kappa a/\beta - 2\kappa a \qquad (29)$$

Down to $\kappa a = 0.1$, maximum error of Eq. (23 with 26) is 0.1 % (in surface charge), i.e., it is almost exact relation. However, Eq. (26) cannot be extended to arbitrary salt mixture. Less accurate, but more universal correlation is:

$$\Phi \approx (2U) \times y_d/\{(y_d Q)^4 + b_2 \times (2U)^4\}^{1/4} \qquad (30)$$

The power factor 4 (and 1/4) is fitting parameter, Q is that defined by Eq. (2), or (5), or (8), U is that defined by Eq. (15), or (16), or Eqs. (18-21). In accordance with Eq. (24), factor b_2 is:

$$b_2 = 1/\{2\kappa a/\beta - 2\kappa a\}^4 - 1 \qquad (31)$$

Down to $\kappa a = 0.1$, maximum error of Eq. (23 with 30) is 0.65 % (in surface charge). The Eq. (23 with 30) deviates from Eq. (23 with 26) by 1.8 % in maximum at κa down to 0.01, and by 15 % in maximum in the limit $\kappa a \to 0$. Because Eq. (23 with 26) is much more accurate, these values may be considered as estimates of accuracy of Eq. (23 with 30) at $\kappa a < 0.1$.

EXTENSION TO STERN MODEL

In accordance with the Stern model, the head of diffuse layer is separated from the surface by some distance λ (familiarly, it is radius of counter ion), and all above relations are valid for imaginary cylinder with radius $a + \lambda$. Thus the charge of diffuse layer, related to the surface area at the head of diffuse layer is defined by:

$$\sigma_d, \mu eq/m^2 = - 0.608 \times I^{0.5} \times \{Q + \{0.5/\kappa(a+ \lambda)\} \times \Phi\} \qquad (32)$$

The relations for Q (Eq. 2, or 5 or 8) and for Φ (Eq. 26 or 30) stand the same, whereas parameters b_1 and b_2 should be recalculated for larger radius of particle. For clarity, let us follow approximation given by Eq. (30). In that case, parameter b_2 is defined by

$$b_2 = 1/\{2\kappa a_d/\beta_d - 2\kappa a_d\}^4 - 1 \qquad (33)$$

$$a_d = a + \lambda \ , \quad \text{and} \qquad (34)$$

$$\beta_d \approx \kappa a_d \times \ln(1+1/\kappa a_d)\} + 0.1159315 \times \kappa a_d/(1 + 6.023(\kappa a_d)^{0.94} + 8.48(\kappa a_d)^2 + 2.78(\kappa a_d)^3) \qquad (35)$$

The charge of cylindrical particle (in Coulombs) is equal by modulus to total charge of diffuse layer. In terms of surface charge, this balance equation may be expressed as

$$\sigma_s = - (1+\lambda/a)\sigma_d \qquad (36)$$

In accordance with the formula for cylindrical capacitor, the surface potential is related with potential at the head of diffuse layer as
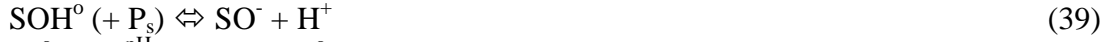
$$\varphi_s = \varphi_d + \{\sigma_s/\varepsilon_o\varepsilon\} \times a \times \ln(1+ \lambda/a) = \varphi_d + \sigma_s/C \qquad (37)$$

Here C ($C \times m^{-2} \times V^{-1} = F/m^2$) is electric capacitance, related to the surface of particle. Consequently, the factor $P_s = \exp(F\varphi_s/RT)$ is related with P_d as

$$P_s = P_d\exp[\{F\sigma_s/RT\varepsilon_o\varepsilon\} \times a \times \ln\{1+\lambda/a\}] \ , \text{ or} \qquad (38)$$
$$P_s = P_d\exp[(1/1.85) \times [\sigma_s, \mu eq/m^2] \times [a, Å] \times \ln\{1+\lambda/a\}] \qquad (38a)$$

If the surface charge is generated by dissociation of some acidic surface site, it may be simulated by reaction:

$$SOH^o (+ P_s) \Leftrightarrow SO^- + H^+ \tag{39}$$
$$K_a^o = 10^{-pH}[SO^-]/([SOH^o]P_s) \tag{40}$$

Traditionally, the factor $P_s^z = \exp(zF\varphi_s/RT)$ is considered as an "activity coefficient" of surface species with charge z (in present case, SO^-), and this leads to a willing to follow a common way for calculation of activity coefficients (speciation → activity coefficients → speciation → etc). However, this algorithm is not too convenient, taking into account for huge magnitude of this variable (from zero to infinity). From the other hand, as may be seen from Eq. (39-40), the factor P_s acts as a component of reaction, and thus, it may be calculated on a manner of activity of some component, together with activities of all other species, i.e. within a single iteration cycle. To apply this algorithm, it is necessary to introduce the charge balance equation (if to follow the common way, it is satisfied automatically). For this purpose, let us split the total charge of diffuse layer (Eq. 32) into positive and negative branches:

$$\sigma_d = \theta_M - \theta_A \tag{41}$$

It should be noted that θ_M and θ_A are operational variables. The values θ_M and θ_A should be positive, and they should satisfy the Eq. (41). Variety of functions complies with these conditions. The convenient variant is a following:

$$\theta_M, \mu eq/m^2 = 0.608\{I_{eff}/P_d\}^{0.5} + \{1.85/[a+\lambda, \text{Å}]\}\times\{(\Phi^2/4 + 1)^{0.5} - \Phi/2\} \tag{42}$$
$$\theta_A, \mu eq/m^2 = 0.608\{I_{eff}\times P_d\}^{0.5} + \{1.85/[a+\lambda, \text{Å}]\}\times\{(\Phi^2/4 + 1)^{0.5} + \Phi/2\} \tag{43}$$

Thus, the charge balance equation (see Eq. 36) may be rearranged as

$$[SO^-] + (1+\lambda/a)\times\theta_A = (1+\lambda/a)\times\theta_M \tag{44}$$

Because θ_M and θ_A are positive variables, Eq (44) may be used similarly to any other balance equation.

APPLICATION

Polyacrylic acid $(C_3H_4O_2)_n$ has apparent molecular weight 72.064 grams per carboxylic group. The distance C-C is about 1.54 Å and angle [C-C-C] is about 109.28^o (tetrahedral angle), which gives segment length about $l = 2.51$ Å (note that one carbon per segment is located outside the chain). Thus, the specific surface area of polyacrylic acid is $2\pi al$ per carboxylic group or

$$s, m^2/g = 1318\times[a, \text{Å}] \tag{45}$$

From the other hand, radius of cylinder is related with its density and specific area as

$$a, \text{Å} = 20000\times[\rho, g/cm^3]^{-1}\times[s, m^2/g]^{-1} \tag{46}$$

Combining Eqs (45, 46), the following estimates may be obtained:

$$s, m^2/g = 5134/[\rho, g/cm^3]^{0.5} \qquad (47)$$

$$a, Å = 3.895/[\rho, g/cm^3]^{0.5} \qquad (48)$$

$$TS, \mu mol/m^2 = 2.703 \times [\rho, g/cm^3]^{0.5} \qquad (49)$$

Fig. 2 shows degree of dissociation of polyacrylic acid (data from Nagasawa et al., 1965) in comparison with model calculations. The value $\rho = 1$ g/cm^3 seems to be realistic, whereas radius $a \sim 3.9$ Å is close to length of C-C-O-H branch. Thus, the values 5134 m^2/g, TS = 2.703 μmol/m^2, and $a = 3.895$ Å were used in model calculations. The values of pK_a^o = 4.2 and radius of counter ion $\lambda = 0$ Å were adjusted. The overlap of diffuse layers was not considered, and curves correspond to zero concentration of polyacrylic acid. For clarity, the difference in temperature (i.e., between 15 and 25°C) was neglected, because the factor $\varepsilon \times T$ (see Eq. 1) is almost constant over wide range of temperatures. As may be seen, this primitive model gives
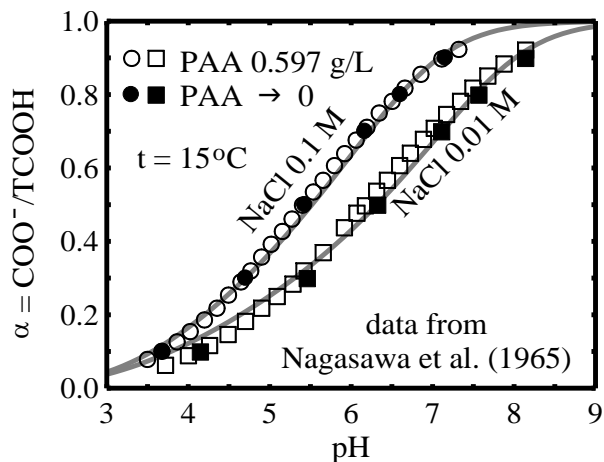

Fig. 2. Degree of dissociation of the polyacrylic acid (PAA) as function of pH. Data from Nagasawa et al. (1965). Curves: cylindrical model of diffuse layer.

reasonable agreement with experimental data. The only strange result is that the "radius of counter ion" $\lambda = 0$ Å is unrealistic. Perhaps, this reflects the invasion of diffuse layer in-between the charged groups of molecule of polyacrylic acid. It should be also noted that the approximation given by Eqs (23, 30) is accurate, and deviation of the cylindrical diffuse layer model from the experiment is objective reality and not uncertainty of calculations.

The algorithm of calculations at given pH, $[M^+]$, $[Me^{2+}]$, $[A^-]$, $[An^{2-}]$, K_a^o, radius of cylinder a (Å), radius of counter ion λ (Å), site density TS (μmol/m^2), specific surface area s (m^2/g):

Calculate: $I = 0.5\{[M^+] + 4[Me^{2+}] + [A^-] + 4[An^{2-}]\}$; $N = [M^+] + 2[Me^{2+}]$; κ, Å^{-1} = $I^{0.5}/3.04$; $a_d = a + \lambda$; β_d = (see Eq. 35); b_2 = (see Eq. 33)
Define: $P_s = 1$, $P_d = 1$, $I_{eff} = I$, $B = 0$, $U_{Me} = 0$, $U_{An} = 0$
Cycle. Calculate:

$P_d = P_s \times exp(-B)$; $y_d = ln(P_d)$; I_{eff} = (see Eq. 19); Q = (see Eq. 5)
If $[Me^{2+}] > 0$, U_{Me} = (see Eq. 20)
If $[An^{2+}] > 0$, U_{An} = (see Eq. 21)
U = (see Eq. 18)
$\Phi = y_d/(1+b_2)^{1/4}$
If $|y_d| > 0.01$, Φ = (see Eq. 30)
θ_M = (see Eq. 42); θ_A = (see Eq. 43)
$[SO^-] = K_a^o \times TS \times P_s \times 10^{pH}/(1 + K_a^o \times P_s \times 10^{pH})$
$PLUS = (1 + \lambda/a) \times \theta_M$
$MINUS = [SO^-] + (1 + \lambda/a) \times \theta_A$
$P_{s1} = P_s \times PLUS/MINUS$

$$P_s = (P_{s1} \times P_s)^{0.5}$$

Compare P_s and P_{s1}; if necessary, repeat cycle

Calculate $B_1 = \{1/1.85\} \times a \times \ln(1+\lambda/a) \times \{ - [SO^-]\}$

$B = \{B_1 + 3 \times B\}/4$

Compare B_1 and B; if necessary, repeat cycle

Calculate σ_s , $\mu eq/m^2 = - [SO^-]$, or $\alpha = [SO^-]/TS$, or COO^-, meq/g $= 0.001 \times [SO^-] \times s$

CONCLUDING REMARKS

The correction of the diffuse double layer model on curvature of cylindrical particles is not too complex. In arbitrary $(M^+, Me^{2+})(A^-, An^{2-})$ salt medium, and for particles of arbitrary size, it may be performed analytically.

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