## PHYSICAL CHEMISTRY OF SOLUTIONS

# Model for Calculating the Activity Coefficients of Electrolytes in the 0 to 16 mol/L Range of Concentrations

**B. B. Tanganov and I. A. Alekseeva**

*East Siberian State University of Technology and Management, Ulan-Ude, 670013 Russia*
*e-mail: tanganov@rambler.ru*
Received April 22, 2015

**Abstract**—Based on the plasma-like theory of electrolyte solutions, areas of concentration with minimum activity coefficients are found, and the predominance of association phenomena leading to the formation of ionic associates or molecular solvates is explained. Alternative nonempirical models for estimating the activity coefficients of electrolytes are developed that produce values close to or coinciding with the available literature data in the 0 to 16 mol/L range of concentrations.

## INTRODUCTION

In the chemistry of electrolyte solutions, theoretical models of the state of ions and molecules are valid only for the range of minor concentrations from 0 to 0.01 M, due to the Debye limit. Many attempts have been made to increase this range of concentrations for theoretical models by introducing adjustments and corrections that were in most cases unsubstantiated and unnecessary. In a broader range of concentrations, especially in the case of concentrated solutions, complex intermolecular interactions occur because of the close proximity to one another of particles, ions, and molecules, which is difficult to consider quantitatively. This is particularly true of ion–ion, ion–dipole, and dipole–dipole processes of interaction, which depend on the properties of the solute, and especially on the properties of the medium (i.e., the solvent).

Solvents differ in their parameters, individual properties, and nature. If some are clearly protophilic (e.g., liquid ammonia), others are protogenic (glacial acetic acid) or amphoteric (e.g., alcohols and ketones): the dielectric permittivity values (DP) of inert solvents (benzene, toluene) are close to 1, while others are distinguished by high or medium-high values of dielectric permittivity (e.g., 109.5 for formamide and 20.7 for acetone). Some solvents are polar (the dipole moment of propylene carbonate is 4.94) and some are nonpolar (again, benzene and toluene with $\mu \approx 0$). The autoprotolysis constants of some solvents are quite high (the ionic product of sulfuric acid is $K_s > 10^{-5}$), while dipolar aprotic solvents differ by rather negligible values of the ionic product (e.g., $K_s = 10^{-33}$ for dimethyl sulfoxide); and so forth.

The above examples demonstrate the difficulties in constructing a unified model for different processes in aqueous and nonaqueous electrolyte solutions that often proceed in opposite directions, making them complex, multidimensional phenomena.

In order to simplify the discussion and make it easier to calculate the physicochemical characteristics of an electrolyte, the activity coefficients for high concentrations of solutions are virtually ignored in the literature, due perhaps to the lack of suitable mechanisms and models. This leads to appreciable discrepancies between theoretical calculations and experimental data.

The activity coefficient is a measure of the deviation of actual (practical, experimental) parameters from ideal ones developed for dilute solutions of nonelectrolytes in the first approximation, where it is assumed there are no interactions [1, 2]. The activity coefficients for highly concentrated solutions are on the order of tens. Nevertheless, there are numerous empirical data on the dependence of activity coefficients on the concentrations of electrolytes, and minimum values are observed for them at certain concentrations. There are no clear explanations or substantiation for this abnormal behavior in the literature.
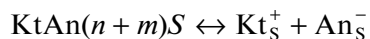
## ANALYTICAL APPROACH

In our opinion [1, 2], activity coefficients reflect the Boltzmann probability distribution of the ionic components of solutions:

$$\gamma = \exp(-\hbar\omega/k_B T), \tag{1}$$

$$\gamma = \exp[-(4\pi Z_{Kt} Z_{An} e^2 \hbar^2 C_i N_A / \mu 1000 k_B^2 T^2)^{1/2}], \tag{2}$$

where $\omega$ is the frequency of plasma-like "dissociation—recombination to neutral molecules or ionic associates" oscillations occurring according to the scheme

$$KtAn(n + m)S \leftrightarrow Kt_S^+ + An_S^-$$

in electrolyte solutions [3] and expressed by the formula

$$\omega = (4\pi Z_{Kt}Z_{An}e^2C_iN_A/\mu 1000)^{1/2},$$

where $\hbar$ is the Planck constant; $Z_ie$ is the ionic charge; $C_i$ is the ionic component of the electrolyte ($C_i = C\alpha$, where $C$ is the initial concentration of the electrolyte and $\alpha$ is its degree of dissociation); $N_A$ is the Avogadro number; $\mu$ is the reduced mass of nonsolvated electrolyte ions, determined with the formula $\mu = 1/m_{Kt} + 1/m_{An}$, where $k_B$ is the Boltzmann constant; and $T$ is temperature, K.

This work continues the development of model equations for calculating the optimum electrolyte concentrations corresponding to minimum activity coefficients and when they are increased to the level of concentrated solutions.

It was shown in [4, 5] that equalities $\hbar\omega = k_BT$ and $\omega = \omega_0$ are observed at the minimum point of function $\gamma = f(C)$ (1) at concentration $C_0$ that determines the value of $\gamma_{min}$, and this characterizes a special point where activity coefficient $\gamma$ has the minimum possible value in accordance with the equations

$$\gamma = 0.368\exp[-(245.467/T)(C_0/\mu)^{1/2}], \quad (3)$$

$$\gamma = 0.368\exp\{[(C_0)^{1/2} - (C)^{1/2}]/(C_0)^{1/2}\}. \quad (4)$$

At $\omega = \omega_0$ and at all values corresponding to $\omega > \omega_0$, a new structure forms in an electrolyte solution, and inter-ion interactions start to predominate as a result of the shorter free path length of solvated ions and molecules, giving rise to the preferential formation of ionic associates in solvents with high and medium-high dielectric constants, or to molecular solvates in nonpolar solvents with low values of dielectric permeability. Equation (4) is in this case transformed into

$$\gamma = 0.368\exp\{[(C)^{1/2} - (C_0)^{1/2}]/(C_0)^{1/2}\}. \quad (5)$$

Substituting universal constants into Eqs. (2)–(4) and converting units to the CGS system ($k_B = 1.38 \times 10^{-16}$, $e = 4.8 \times 10^{-10}$, $\hbar = 1.05 \times 10^{-27}$, $N_A = 6.023 \times 10^{23}$, and taking the conversion factor for the CGS unit of mass as equal to $1.67 \times 10^{-24}$, we obtain the following formula for any solvent:

$$C_0 = 1000\mu^2 1.67\times10^{-24}k_B^2T^2/64\mu_sZ_{Kt}Z_{An}e^2\hbar^2N_A,$$

$$C_0 = 1.02\times10^{-6}\mu^2T^2/\mu_sZ_{Kt}Z_{An}, \quad (6)$$

where $\mu_s$ is the reduced mass of the solvated electrolyte ions ($\mu_s = 1/m_{sKt} + 1/m_{sAn}$) in the solvent.

**Table 1.** Electrolyte concentrations $C_0$ (mol/L) at $\gamma_{min}$, according to Eq. (6)

| Ion | H$^+$ | Na$^+$ | K$^+$ | Ca$^{2+}$ | Cr$^{3+}$ | Al$^{3+}$ |
|---|---|---|---|---|---|---|
| OH$^-$ | 0.24 | 0.24 | 0.37 | 0.08 | 0.04 | 0.03 |
| Cl$^-$ | 0.30 | 1.26 | 1.68 | 0.41 | 0.31 | 0.12 |
| CH$_3$COO$^-$ | 0.31 | 0.59 | 1.26 | 0.27 | 0.30 | 0.10 |
| NO$_3^-$ | 0.32 | 1.52 | 2.17 | 0.48 | 0.34 | 0.11 |
| ClO$_4^-$ | 0.33 | 1.69 | 2.54 | 0.71 | 0.32 | 0.10 |
| SO$_4^{2-}$ | 0.30 | 0.49 | 1.01 | 1.04 | 0.51 | 0.18 |
| PO$_4^{3-}$ | 0.86 | 1.40 | 2.51 | 1.80 | 0.27 | 0.11 |

The obtained $C_0$ concentrations for 42 electrolytes at $\gamma_{min}$ are given in Table 1.

Let us derive throughput modeling equations for further calculations of the hydrogen ion concentration, degree of dissociation, and activity coefficient of the electrolyte in a wider range of concentrations, according to the formula

$$HA \leftrightarrow H^+ + A^-,$$

$$K = [H^+][A^-]/[HA].$$

This is a simplified initial equation for the dissociation constant that ignores the influence of the initial $[H^+]$, $\alpha$, and $\gamma_\pm$ parameters at high molarities, and produces only comparative and exploratory constants.

The formulas for calculating the $[H^+]$, $\alpha$, and $\gamma_\pm$ values are derived as

**1.** $K = [H^+][A^-]\alpha_{H^+}\alpha_{A^-}\gamma_{H^+}\gamma_{A^-}/C_{HA}(1 - \alpha)$
$$= [H^+]^2(\alpha_{H^+})^2\gamma_\pm^2/(C(1 - \alpha)),$$
$$[H^+]^2(\alpha_{H^+})^2\gamma_\pm^2 = KC - KC\alpha, \quad (7)$$
$$[H^+] = \{(KC - KC\alpha)/\alpha^2\gamma_\pm^2\}^{0.5},$$

**2.** $K = [H^+]^2\alpha^2\gamma_\pm^2/(C(1 - \alpha)),$
$$\alpha^2[H^+]^2\gamma_\pm^2 + \alpha KC - KC = 0,$$
$$\alpha = \{-KC + [K^2C^2 + 4K[H^+]^2\gamma_\pm^2C]^{0.5}/2[H^+]^2\gamma_\pm^2\}, \quad (8)$$

**3.** $\gamma_\pm^2[H^+]^2\alpha^2 = KC - K\alpha C,$
$$\gamma_\pm = \{(KC - K\alpha C)/\alpha^2[H^+]^2\}^{0.5}. \quad (9)$$

Such characteristics of hydrochloric acid as concentration, pH, H$^+$ ion concentrations (experimental and theoretical), degree of dissociation (calculated with Eq. (8)), and activity coefficients (tabulated and estimated with Eq. (9) and via multilevel modeling [6–8] with an MMLM coefficient of 0.9998) are given in Table 2 as examples.

As can be seen from Table 2, the activity coefficients calculated using modeling equation (9) and via multilevel modeling (the last two columns in Table 2)

**Table 2.** Characteristics of an aqueous solution of HCl and its mean ionic activity coefficients

| $C(HCl)$, mol/L | pH | $[H^+]$ | $[H^+]$ using Eq. (7) | $\alpha(HCl)$ using Eq. (8) | $\gamma \pm$ (lit.) | $\gamma \pm$ using Eq. (9) | $\gamma \pm$ via MMLM |
|---|---|---|---|---|---|---|---|
| 0.01 | 1.50 | 0.0316 | 0.0316 | 0.4949 | 0.904 | 1.435 | 0.756 |
| 0.05 | 1.15 | 0.0707 | 0.0707 | 0.4737 | 0.803 | 1.531 | 0.802 |
| 0.10 | 1.00 | 0.1000 | 0.1000 | 0.4750 | 0.796 | 1.525 | 0.806 |
| 0.30 | 0.76 | 0.1732 | 0.1732 | 0.4741 | 0.756 | 1.529 | 0.843 |
| 0.50 | 0.65 | 0.2236 | 0.2236 | 0.4921 | 0.757 | 1.448 | 0.844 |
| 1.00 | 0.50 | 0.3162 | 0.3162 | 0.5485 | 0.809 | 1.225 | 0.862 |
| 2.00 | 0.35 | 0.4472 | 0.4472 | 0.5979 | 1.010 | 1.060 | 1.041 |
| 3.00 | 0.26 | 0.5477 | 0.5477 | 0.5567 | 1.320 | 1.196 | 1.316 |
| 5.00 | 0.15 | 0.7071 | 0.7071 | 0.3760 | 2.380 | 2.100 | 2.270 |
| 7.00 | 0.077 | 0.8366 | 0.8366 | 0.2209 | 4.370 | 3.994 | 4.241 |
| 10.00 | 0.000 | 1.0000 | 1.0000 | 0.0957 | 10.440 | 9.927 | 10.424 |
| 11.00 | −0.020 | 1.0488 | 1.0488 | 0.0742 | 13.510 | 12.950 | 13.540 |
| 12.00 | −0.040 | 1.0954 | 1.0954 | 0.0583 | 17.250 | 16.643 | 17.313 |
| 13.00 | −0.057 | 1.1401 | 1.1401 | 0.0461 | 21.800 | 21.145 | 21.876 |
| 14.00 | −0.073 | 1.1832 | 1.1832 | 0.0369 | 27.300 | 26.596 | 27.362 |
| 15.00 | −0.088 | 1.2247 | 1.2247 | 0.0295 | 34.100 | 33.348 | 34.105 |
| 16.00 | −0.102 | 1.2649 | 1.2649 | 0.0237 | 42.400 | 41.599 | 42.300 |

virtually coincide with the activity coefficients in the literature that were determined empirically. The equation derived via MMLM has the form

$$\gamma_\pm = 0.2587C - 0.2295[H^+] + 2.2126\alpha + 0.9643\,\gamma_{\pm\text{by Eq. (9)}} - 1.7188,$$

$$K_{\text{MMLM}} = 0.9998.$$

The high multilevel modeling coefficient and the coincidence with the literature data testify to the high reliability of the mean ionic activity coefficients estimated via MMLM.

The acceptability of our models is confirmed by Figs. 1 and 2, in which the simulated activity dependences coincide with the literature functional dependences, often according to the same equations (Fig. 1). The behavior of the activities is linear (Fig. 2).
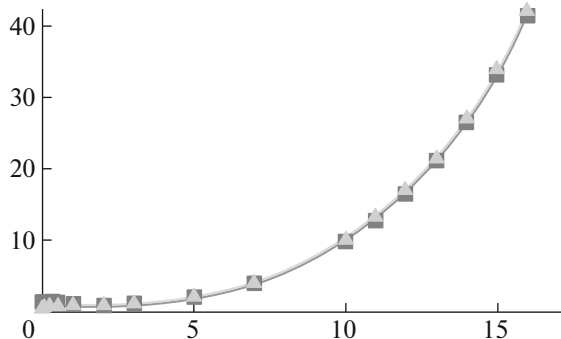


**Fig. 1.** Activity coefficients of HCl: (-♦-) calculated via MMLM; (-■-) calculated with Eq. (9); and (-▲-) from the literature (which coincide with the values calculated via MMLM). The HCl concentration (mol/L) is given on the abscissa axis; the values calculated with Eq. (9) and via MMLM on the ordinate axis.
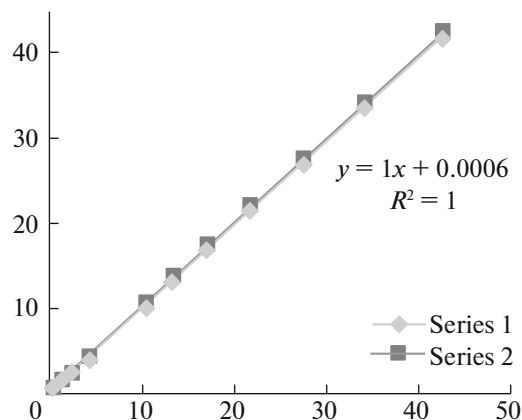


**Fig. 2.** Dependences of (series 1) the $\gamma\pm$ value according to Eq. (9) and (series 2) the $\gamma\pm$ value according to MMLM as functions of the $\gamma\pm$ (lit) values (the literature values are on the $X$ axis; those obtained via MMLM and with Eq. (9) are on the $Y$ axis).

$y = 1x + 0.0006$
$R^2 = 1$

Series 1
Series 2

## CONCLUSIONS

The range of electrolyte solution concentrations in which dissociation processes occur were theoretically substantiated. Minimum activity coefficients were observed at the point where rates of dissociation with the formation of solvated ions, and the reversible recombination of particles due to the predominant formation of ionic associates (or molecular solvates), were equal and mean ionic activity coefficient $\gamma_\pm$ subsequently grew.

Alternative nonempirical models for calculating electrolyte activity coefficients close to or coinciding with the available literature values in the 0 to 16 mol/L range of concentrations were developed. We propose using these model equations to study thermodynamics, equilibrium constants (see above), and mass transfer processes in aqueous and nonaqueous solutions of strong and weak electrolytes.

## ACKNOWLEDGMENTS

## REFERENCES

1. M. M. Baldanov, B. B. Tanganov, and M. V. Mokhosoev, Zh. Fiz. Khim. **64**, 88 (1990).
2. M. M. Baldanov, B. B. Tanganov, and B. D. Okhinov, Russ. J. Gen. Chem. **68**, 1672 (1998).
3. M. M. Baldanov, B. B. Tanganov, and M. V. Mokhosoev, Dokl. Akad. Nauk SSSR **308**, 397 (1989).
4. B. B. Tanganov, Vestn. VSGTU, No. **2**, 5 (2008).
5. B. B. Tanganov, in *Proceedings of the 4th International Forum on Natural Sciences*, Ch. 7: *Physical Chemistry* (Samara, 2008), p. 28.
6. B. B. Tanganov, *Interactions in Electrolyte Solutions: Simulation of Solvation Processes, Equilibriain Polyelectrolyte Solutions and Mathematical Forecasting of Chemical System Properties* (Ross. Akad. Estestvoznaniya, Moscow, 2009) [in Russian].
7. B. B. Tanganov, Mezhdunar. Zh. Prikl. Fundam. Issled., No. 4, 49 (2012).
8. B. B. Tanganov, Mezhdunar. Zh. Prikl. Fundam. Issled., No. 8, 136 (2012).

*Translated by O.N. Kadkin*