

# Mathematical modeling of solvent parameters' relevant contribution to the alpha-amino acid (valine, alpha-alanine) solvation in H<sub>2</sub>O–MeOH, H<sub>2</sub>O–EtOH and H<sub>2</sub>O–PrOH-2

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## Abstract

The regression correlative analysis of the aqueous–organic solvents' (water–methanol, water–ethanol and water–propan-2-ol) effect on the strength of amino acids ( $\alpha$ -alanine, valine) has been provided at 298.15 K. Energetic contributions of acceptor  $\Delta\Delta G_{d,1}^0(E_T^N)$  and cohesion  $\Delta\Delta G_{d,1}^0(\delta_N^2)$  properties of water–organic solvents into amino acid strength with carboxylic groups change  $\Delta\Delta G_{d,1}^0$ , and energetic contributions of acceptor  $\Delta\Delta G_{d,2}^0(E_T^N)$ , cohesion  $\Delta\Delta G_{d,2}^0(\delta_N^2)$  and dielectric  $\Delta\Delta G_{d,2}^0(\epsilon_N^{-1})$  properties of water–organic solvents into amino acid strength with amino groups change  $\Delta\Delta G_{d,2}^0$  are evaluated.

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## 1. Introduction

The principle of linear free-energy (LFE) is the basis of quantitative correlations between the thermodynamic characteristics of equilibrium processes of dissociation, complex-formation, association and various properties of a media — dielectric, donor–acceptor and cohesion (empirical solvent parameters) [1–3].

In solution chemistry, four concentration scales are widely used — molarity ( $c$ ), molality ( $m$ ), mole fraction ( $X$ ) and solvomolality ( $C_{sm}$ ) [4]:

$$C_{sm} = \frac{m \cdot 55.51 \cdot M_1}{1} = \frac{c \cdot M_1 \cdot 55.51}{\rho \cdot c M_2} = \frac{X_2 \cdot 55.51}{X_1}, \quad (1)$$

where  $M_1$  and  $M_2$  — molecular mass of the solvent and of the dissolved substance respectively,  $\text{kg mol}^{-1}$ ;  $\rho$  — density of solution,  $\text{kg dm}^{-3}$ ;  $C_{sm}$  — solvomolality, (mole of the dissolved substance)/(mole of the solvent, it equals 55.51 for water);  $m$  — molality,  $\text{mol (1 kg of solvent)}^{-1}$ ;  $c$  — molarity,  $\text{mol dm}^{-3}$ ;  $X$  — mole fraction.

Therefore the choice of the standard state for chemical equilibria and reagents at the correlative analysis of media

influence on chemical equilibria is of great importance. The equilibria constant ( $K$ ) does not depend on the choice of concentration scale only in the case when the stoichiometry of initial substances ( $\sum \nu_{i,\text{in}}$ ) and reaction products ( $\sum \nu_{i,\text{pr}}$ ) remains constant  $\Delta \nu = 0$  [5,6]:

$$K_{C_{sm}} = K_m (M_{W-S}/M_W)^{\Delta \nu} = K_c \left( \frac{M_{W-S}}{\rho_0 M_W} \right)^{\Delta \nu} = K_X (1/M_W)^{\Delta \nu}, \quad (2)$$

where  $M_W$  and  $M_{W-S}$  — molecular mass of water and of water–organic solvent respectively,  $\rho_0$  — density of the solvent.

If this condition is not fulfilled ( $\Delta \nu \neq 0$ ), the standard thermodynamic functions of reactions and reagents in molarity and molality scales are non-comparable in the comparative quantitative analysis of aqueous–organic solvent effect on the thermodynamic parameters of equilibria because of the dependence on molecular mass and density of solvent:

$$\mu_2^0(c) = \mu_2^0(C_{sm}) - RT \ln(\rho_0 M_W / M_{W-S}), \quad (3)$$

$$\mu_2^0(m) = \mu_2^0(C_{sm}) + RT \ln(M_{W-S} / M_W), \quad (4)$$

$$\mu_2^0(X) = \mu_2^0(C_{sm}) - RT \ln M_W. \quad (5)$$

where  $\mu_2^0$  — standard chemical potential of reagent.

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Table 1  
Physico-chemical and donor–acceptor properties of methanol–water, ethanol–water, propan-2-ol–water solvents and dissociation Gibbs energy of amino acids with carboxylic,  $\Delta G_{d,1}^0$ , and with amino groups,  $\Delta G_{d,2}^0$ , (solvomolal scale)

| Mole fraction of alcohol | $E_T^{N*}$ | $B_{KT}^{**}$ | $B_{KT}^*$ | $\delta_N^{2*}$ | $\delta_N^{2**}$ | $\varepsilon_N^{-1}$ | Valine             |                    | $\alpha$ -Alanine  |                    |
|--------------------------|------------|---------------|------------|-----------------|------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                          |            |               |            |                 |                  |                      | $\Delta G_{d,1}^0$ | $\Delta G_{d,2}^0$ | $\Delta G_{d,1}^0$ | $\Delta G_{d,2}^0$ |
| <i>Methanol–water</i>    |            |               |            |                 |                  |                      |                    |                    |                    |                    |
| 0.00                     | 1.00       | 0.47          | 0.19       | 1.00            | 1.00             | 1.00                 | 13.1               | 54.0               | 13.4               | 56.4               |
| 0.10                     | 0.92       | 0.46          | 0.26       | 0.68            | 0.87             | 1.10                 | 14.8               | 56.3               | 15.1               | 55.7               |
| 0.20                     | 0.88       | 0.56          | 0.36       | 0.55            | 0.77             | 1.20                 | 15.8               | 56.6               | 16.7               | 55.0               |
| 0.30                     | 0.84       | 0.64          | 0.43       | 0.49            | 0.69             | 1.30                 | 16.8               | 55.8               | 17.4               | 54.3               |
| 0.40                     | 0.82       | 0.70          | 0.50       | 0.44            | 0.62             | 1.42                 | 18.0               | 54.7               | 18.5               | 53.7               |
| 0.50                     | 0.81       | 0.73          | 0.53       | 0.40            | 0.57             | 1.55                 | 18.3               | 54.1               | 20.0               | 53.3               |
| 0.60                     | 0.80       | 0.70          | 0.54       | 0.37            | 0.52             | 1.68                 | 19.3               | 54.8               | 20.5               | 53.3               |
| 0.70                     | 0.79       | 0.68          | 0.55       | 0.34            | 0.48             | 1.84                 | 21.1               | 57.7               | 21.0               | 53.2               |
| 0.80                     | 0.78       | 0.65          | 0.54       | 0.32            | 0.44             | 1.97                 |                    |                    |                    |                    |
| 0.90                     | 0.77       | 0.64          | 0.60       | 0.31            | 0.41             | 2.14                 |                    |                    |                    |                    |
| 1.00                     | 0.77       | 0.64          | 0.62       | 0.29            | 0.39             | 2.32                 |                    |                    |                    |                    |
| <i>Propan-2-ol–water</i> |            |               |            |                 |                  |                      |                    |                    |                    |                    |
| 0.00                     | 1.00       | 0.47          | 0.19       | 1.00            | 1.00             | 1.00                 | 13.1               | 54.0               | 13.4               | 56.4               |
| 0.10                     | 0.77       | 0.59          | 0.49       | 0.42            | 0.77             | 1.15                 | 14.6               | 54.4               | 14.2               | 55.9               |
| 0.20                     | 0.70       | 0.66          | 0.60       | 0.35            | 0.62             | 1.68                 | 16.1               | 54.4               | 15.7               | 55.5               |
| 0.30                     | 0.67       | 0.68          | 0.65       | 0.32            | 0.51             | 2.11                 | 17.3               | 54.1               | 17.9               | 54.9               |
| 0.40                     | 0.66       | 0.70          | 0.69       | 0.30            | 0.44             | 2.57                 | 18.2               | 53.8               | 19.3               | 54.9               |
| 0.50                     | 0.64       | 0.71          | 0.72       | 0.29            | 0.38             | 2.97                 | 19.2               | 53.7               | 20.6               | 55.0               |
| 0.55                     | 0.63       | 0.72          | 0.73       | 0.29            | 0.36             | 3.32                 | 19.4               | 53.9               | 20.5               | 53.9               |
| 0.60                     | 0.62       | 0.74          | 0.75       | 0.28            | 0.34             | 3.34                 |                    |                    |                    |                    |
| 0.70                     | 0.60       | 0.77          | 0.79       | 0.27            | 0.31             | 3.69                 |                    |                    |                    |                    |
| 0.80                     | 0.58       | 0.80          | 0.83       | 0.26            | 0.28             | 3.92                 |                    |                    |                    |                    |
| 0.90                     | 0.56       | 0.82          | 0.89       | 0.25            | 0.26             | 4.06                 |                    |                    |                    |                    |
| 1.00                     | 0.54       | 0.84          | 0.88       | 0.24            | 0.24             | 4.12                 |                    |                    |                    |                    |

Where  $E_T^{N*}$  and  $B_{KT}^*$  — data from the work of Krygowski et al. [13],  $B_{KT}^{**}$  — data from the work of Marcus [14],  $\delta_N^{2*}$  — calculated from surface tension, data on surface tension are from [15],  $\delta_N^{2**}$  — calculated on vapor pressure data in [11], and  $\varepsilon_N^{-1}$  — data from [15–18].

In this work for the quantitative interpretation of aqueous–organic solvent influence (water–methanol, water–ethanol and water–propan-2-ol) on dissociation Gibbs energy of valine and  $\alpha$ -alanine ( $\Delta v = 1$ ) at 298.15 K standard solvomolality (aqua-

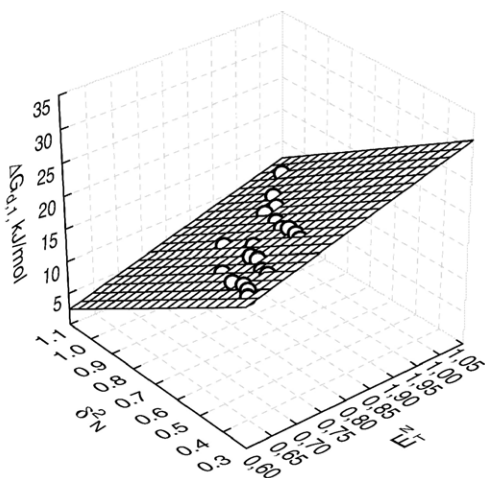


Fig. 1. Standard Gibbs energy  $\Delta G_{d,1}^0$  of dissociation of  $\alpha$ -alanine with carboxylic groups in water–methanol, water–ethanol and water–propan-2-ol systems as a function of  $E_T^N$ ,  $\delta_N^{2*}$  and  $\varepsilon_N^{-1}$ .

molality) scale is used. The aim is to reveal the regularities of the connection between the thermodynamics of processes, i.e. the energetics of solvation of reagents in solutions of biologically active substances and the solvent properties.

## 2. Multiple regression analysis of water–organic solvent effect of water–methanol, water–ethanol, water–propan-2-ol on $\alpha$ -alanine and of water–methanol, water–propan-2-ol on $\alpha$ -alanine and valine strength at 298.15 K

Dissociation constants of amino acids are taken from these works: [7] — valine–water–methanol, [8] — valine–water–propan-2-ol, [8] —  $\alpha$ -alanine–water–methanol, [9] —  $\alpha$ -alanine–water–propan-2-ol, and [10] —  $\alpha$ -alanine–water–ethanol.

For the treatment with means of correlation analysis the normalized data on Dimroth–Reichardt parameter  $E_T^N$ , Kamlet–Taft donicity parameter  $B_{KT}^N$ , density of cohesion energy  $\delta_N^{2*}$ , reciprocal dielectric

Table 2

Coefficients of Eqs. (9) and (10) of dissociation Gibbs energy of  $\alpha$ -alanine with carboxylic groups in water–methanol, water–ethanol, water–propan-2-ol systems and amino groups in water–methanol, water–propan-2-ol systems, dissociation Gibbs energy of valine with carboxylic and with amino groups in water–methanol, water–propan-2-ol,  $T = 298.15$  K

| $\Delta G_{d,1}^0 = \Delta G_{d,1,in}^0 + A_1 E_T^N + A_2 \delta_N^{2*}$                                                                       |                |           |                      |      |       |                 |                    |  |  |
|------------------------------------------------------------------------------------------------------------------------------------------------|----------------|-----------|----------------------|------|-------|-----------------|--------------------|--|--|
| <i>Valine–methanol–water and valine–propan-2-ol–water</i>                                                                                      |                |           |                      |      |       |                 |                    |  |  |
|                                                                                                                                                | $A_i$ , kJ/mol | $s_{A_i}$ | $t_{obs}(12)/t_{cr}$ | $s$  | $r$   | $F_{obs}(2,12)$ | $F_{cr}(v_1, v_2)$ |  |  |
| $\Delta G_{d,1,in}^0$                                                                                                                          | 16.6           | 0.71      | 23.2/2.18            | 0.28 | 0.993 | 448             | 3.88               |  |  |
| $A_1$                                                                                                                                          | 15.1           | 1.47      | 10.3/2.18            |      |       |                 |                    |  |  |
| $A_2$                                                                                                                                          | −18.3          | 0.86      | −21.2/2.18           |      |       |                 |                    |  |  |
| <i><math>\alpha</math>-Alanine–methanol–water, <math>\alpha</math>-alanine–propan-2-ol–water and <math>\alpha</math>-alanine–ethanol–water</i> |                |           |                      |      |       |                 |                    |  |  |
|                                                                                                                                                | $A_i$ , kJ/mol | $s_{A_i}$ | $t_{obs}(19)/t_{cr}$ | $s$  | $r$   | $F_{obs}(2,19)$ | $F_{cr}(v_1, v_2)$ |  |  |
| $\Delta G_{d,1,in}^0$                                                                                                                          | 15.1           | 0.66      | 23.0/2.09            | 0.27 | 0.995 | 932             | 3.88               |  |  |
| $A_1$                                                                                                                                          | 21.9           | 1.38      | 15.8/2.09            |      |       |                 |                    |  |  |
| $A_2$                                                                                                                                          | −23.5          | 0.79      | −29.7/2.09           |      |       |                 |                    |  |  |
| $\Delta G_{d,2}^0 = \Delta G_{d,2,in}^0 + B_1 E_T^N + B_2 \delta_N^{2*} + B_3 \varepsilon_N^{-1}$                                              |                |           |                      |      |       |                 |                    |  |  |
| <i>Valine–methanol–water</i>                                                                                                                   |                |           |                      |      |       |                 |                    |  |  |
|                                                                                                                                                | $B_i$ , kJ/mol | $s_{B_i}$ | $t_{obs}(4)/t_{cr}$  | $s$  | $r$   | $F_{obs}(3,4)$  | $F_{cr}(v_1, v_2)$ |  |  |
| $\Delta G_{d,2,in}^0$                                                                                                                          | 49.9           | 0.82      | 60.6/2.78            | 0.04 | 0.999 | 1527            | 6.59               |  |  |
| $B_1$                                                                                                                                          | −119.3         | 3.4       | −35.0/2.78           |      |       |                 |                    |  |  |
| $B_2$                                                                                                                                          | 96.1           | 2.2       | 43.3/2.78            |      |       |                 |                    |  |  |
| $B_3$                                                                                                                                          | 30.3           | 0.59      | 51.7/2.78            |      |       |                 |                    |  |  |
| <i>Valine–propan-2-ol–water</i>                                                                                                                |                |           |                      |      |       |                 |                    |  |  |
|                                                                                                                                                | $B_i$ , kJ/mol | $s_{B_i}$ | $t_{obs}(3)/t_{cr}$  | $s$  | $r$   | $F(3,3)$        | $F_{cr}(v_1, v_2)$ |  |  |
| $\Delta G_{d,2,in}^0$                                                                                                                          | 47.8           | 0.72      | 66.1/2.78            | 0.12 | 0.998 | 246             | 9.28               |  |  |
| $B_1$                                                                                                                                          | −20.4          | 3.0       | −6.9/2.78            |      |       |                 |                    |  |  |
| $B_2$                                                                                                                                          | 26.7           | 2.9       | 9.3/2.78             |      |       |                 |                    |  |  |
| $B_3$                                                                                                                                          | 2.84           | 0.38      | 7.6/2.78             |      |       |                 |                    |  |  |
| <i><math>\alpha</math>-Alanine–methanol–water and <math>\alpha</math>-alanine–propan-2-ol–water</i>                                            |                |           |                      |      |       |                 |                    |  |  |
|                                                                                                                                                | $B_i$ , kJ/mol | $s_{B_i}$ | $t_{obs}(11)/t_{cr}$ | $s$  | $r$   | $F(3,11)$       | $F_{cr}(v_1, v_2)$ |  |  |
| $\Delta G_{d,2,in}^0$                                                                                                                          | 52.3           | 0.73      | 72.0/2.20            |      |       |                 |                    |  |  |
| $B_1$                                                                                                                                          | −10.3          | 0.89      | −11.6/2.20           | 0.16 | 0.991 | 208             | 3.59               |  |  |
| $B_2$                                                                                                                                          | 12.9           | 0.54      | 24.0/2.20            |      |       |                 |                    |  |  |
| $B_3$                                                                                                                                          | 1.42           | 0.13      | 11.3/2.20            |      |       |                 |                    |  |  |

$s_{A_i}$ ,  $s_{B_i}$  and  $s$  — standard errors of regression coefficients and of approximation respectively;  $r$  — correlation coefficient.

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