

## Accepted Manuscript

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PII: S0167-7322(17)36273-6  
DOI: doi:[10.1016/j.molliq.2018.02.035](https://doi.org/10.1016/j.molliq.2018.02.035)  
Reference: MOLLIQ 8677  
To appear in: *Journal of Molecular Liquids*  
Received date: 31 December 2017  
Revised date: 5 February 2018  
Accepted date: 9 February 2018

Please cite this article as: Mihalj Poša , Introduction of the novel coefficient of interaction in the micellar co-solubilisation of the binary mixture of structurally different solubilizates: Thermodynamic of the micellar co-solubilisation – A pseudophase approximation. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Molliq(2017), doi:[10.1016/j.molliq.2018.02.035](https://doi.org/10.1016/j.molliq.2018.02.035)

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Introduction of the novel coefficient of interaction in the micellar co-solubilisation of the binary mixture of structurally different solubilizes: thermodynamic of the micellar co-solubilisation – a pseudophase approximation

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Abstract

The mutual influence of the different molecules of solubilizes in the micellar co-solubilisation of their binary mixture is expressed with the excess Gibbs energy ( $G^E$ ). In the literature, for describing the  $G^E$  mainly symmetrical function is used (related to the molar fraction of a solubilizer,  $x = 0.5$ ) that originates from the Regular Solution Theory (RST), i.e. Margules function of the first order. However, experiments of the micellar co-solubilisation are implemented on the certain molar mixture of the binary mixture of solubilizes, so it is impossible to get a dependence of the  $G^E$  on  $x$  in the wider range of the composition of the binary mixture of solubilizes (it is not possible to graphically check the symmetry of the  $G^E$ ). If the  $G^E$  is described with the asymmetric function, the mutual synergistic effect of solubilizes in the process of the micellar co-solubilisation cannot be expressed exclusively with the one interaction coefficient ( $\beta_{ij}$ ). It can be showed that the thermodynamic stabilisation of some solubilize from the micellar pseudophase in the solubilisation of the binary mixture of solubilizes of the certain composition is expressed through the ratio between the molar fraction of examined solubilize in the micellar phase that contains only one, monocomponent solubilize ( $x_{i(m)}$ ), and the molar fraction of the same solubilize from the micellar pseudophase with the binary mixture of solubilizes ( $\hat{x}_{i(m)}$ ):  $\varphi_i = x_{i(m)} / \hat{x}_{i(m)}$  - the novel coefficient of interaction. If the  $G^E$  is a symmetric function, with  $\varphi_i = x_{i(m)} / \hat{x}_{i(m)} \wedge \varphi_j = x_{j(m)} / \hat{x}_{j(m)}$  next condition should be met  $\beta_{ij} = \left(1 / (1 - x_i)^2\right) \ln \left(x_{i(m)} / \hat{x}_{i(m)}\right) = \beta_{ji} = \left(1 / (1 - x_j)^2\right) \ln \left(x_{j(m)} / \hat{x}_{j(m)}\right)$ , contrary the  $G^E$  is described with the asymmetric function as the Margules function of the second order:  $g^E = RT \left(a_{ij} x_j + a_{ji} x_i\right) x_j$ . The coefficient of the interaction in the limit state, when in the micellar pseudophase of the binary mixture the molecule of solubilize of a certain structure is surrounded with the molecules of solubilizes of the different structure is:  $(\ln \varphi_i)^\infty = a_{ij}$  i.e.  $(\ln \varphi_j)^\infty = a_{ji}$ .

Keywords: thermodynamic equilibrium, the excess Gibbs energy, Margules functions, spatial ecraning, Regular Solution Theory

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