An alternative reference fluid for the COSMO-SAC model

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In the COSMO-SAC [1] model of Lin and Sandler, the *activity coefficient* of a segment Γ_m is obtained using a reference fluid where all segments have an identical chemical potential $\mu^0(0)$. In the present work we show a new derivation for the activity coefficient of a segment using the reference of an *ideal* fluid with zero interaction energies but not identical chemical potentials.

We start from the Eq. (9) of [1], which is also similar to the one originally derived by Klamt[2]:

$$\frac{\mu_m}{kT} = -\ln\left[\sum_n \exp\left(\frac{-E_{m,n}+\mu_n}{kT}\right)\right] + \ln p_m \tag{1}$$

where μ_m is the chemical potential of a segument m; $E_{m,n} = E_{n,m}$ is the interaction energy for the contact between the segments m and n; p_m is the probabylity of finding a segment m in the mixture; and T is the temperature.

Now let us consider an *ideal* fluid where all the interations are zero, $E_{m,n} = 0$, resulting in:

$$\frac{\mu^0_m}{kT} = -\ln\left[\sum_n \exp\left(\frac{\mu^0_n}{kT}\right)\right] + \ln p_m \tag{2}$$

One could argue that, if there is no interaction, the chemical potential of a segment μ^0_m should not depend on the chemical potential of other segments μ^0_n. Indeed, since $\sum_n p_n = 1$, one can verify that $\mu^0_m/kT = \ln p_m$ is a solution of Eq. (2).

Then, if we subtract $\mu^0_m/kT = \ln p_m$ from Eq. (1) and define the activity coefficient of a segment as $\ln\Gamma_m \equiv (\mu_m - \mu^0_m)/kT$, we get:

$$\ln\Gamma_m = -\ln\left[\sum_n \exp\left(\frac{-E_{m,n}+\mu_n}{kT}\right)\right] \tag{3}$$

Finally, if we use $\mu_n/kT = \ln\Gamma_n + \mu^0_n/kT = \ln\Gamma_n + \ln p_n$, it is possible to show that:

$$\ln\Gamma_m = -\ln\left[\sum_n p_n\Gamma_n \exp\left(\frac{-E_{m,n}}{kT}\right)\right] \tag{4}$$

which is equivalent to Eq. (10) of [1].

With this derivation it is more clear that many contributions can be added directly to the interaction energy $E_{m,n}$, not only the usual electrostatic and hydrogen bond contributions. Further, that the activity coefficient of a segment $\ln\Gamma_m$ can be used to compute the residual Helmholtz energy, with respect to a non-interacting fluid.

References

[1] S.-T. Lin, S. I. Sandler, A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model, Ind. & Eng. Chem. Res. 41 (5) (2002) 899–913.

[2] A. Klamt, Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena, The Journal of Physical Chemistry 99 (7) (1995) 2224–2235.

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