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On the calculation of nearest neighbors in activity coefficient models

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A B S T R A C T

Guggenheim proposed a theoretical expression for the combinatorial entropy of mixing of unequal sized and linear and branched molecules to improve the Flory-Huggins model. Later the combinatorial activity coefficient equation, which was derived from Guggenheim's model, was applied in the UNIQUAC, UNIFAC, and COSMOSAC models. Here we derive from Guggenheim's entropy theory a new function for the number of nearest neighbors of a compound in a multicomponent mixture for which the knowledge of the coordination number and a reference area are not needed. This new relation requires only the mole, volume and surface fraction of the compounds in the mixture. The benefit of the new relation is that both the combinatorial and the residual term in the aforementioned models can be made lattice-independent. We demonstrate that the proposed relation simplifies the Staverman-Guggenheim combinatorial model and can be applied with success to the UNIQUAC and COSMOSPACE model in the description of vapor-liquid phase equilibria and excess enthalpy. We also show that the new expression for the number of nearest neighbors should replace the relative surface area and the number of surface patches in the residual part of the UNIQUAC and the COSMOSPACE model, respectively. As a result a more rigorous version of the UNIQUAC and the COSMOSPACE model is obtained. This could serve as a better basis for predictive models like UNIFAC, COSMO-RS and COSMOSAC.

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1. Introduction

In the 1940s Huggins [1] and Flory [2] derived an expression for the combinatorial entropy of mixing of athermal mixtures consisting of unequally sized molecules. Guggenheim [3,4] showed that the FH model overestimates the combinatorial entropy of mixing, because the connectivity of sites in a molecule reduces the number of possible configurations. Consequently, Guggenheim derived a correction term on the Flory-Huggins (FH) model for molecules having no internal contacts, which can be linear or branched. Staverman [5] extended Guggenheim's entropy expression to more complicated molecules, i.e. molecules containing rings. Both theoretical models contain, besides the mole and volume fraction, the surface fraction and require as additional parameter the number of nearest neighbors for each compounds. Abrams and Prausnitz [6] and Magnussen et al. [7] derived from the Staverman-Guggenheim (SG) entropy expressions for the activity coefficient, which have been applied in the combinatorial term of the UNIQUAC [6], DISQUAC [8], UNIFAC [9,10], COSMOSAC [11], COSMOSPACE [12] and MOQUAC [13] models. In this paper we show that from the Guggenheim entropy of mixing an alternative expression for the combinatorial activity coefficient equation can be obtained, and thereby a new formula for the number of nearest neighbors. With this new equation for the number of nearest neighbors we revise the SG-corrected combinatorial activity coefficient as well as the residual activity coefficient of the UNIQUAC and the COSMOSPACE models. It makes the total activity coefficient, which is defined by the product of the combinatorial and the residual terms, for the UNIQUAC and COSMOSPACE model consistent. The new expression for the combinatorial activity coefficient equation is compared to the original form used in UNIQUAC and COSMOSPACE. In this comparison we will also consider the effect of the molecular size and shape defined by the Pauling bond lengths and the set of van der Waals radii, defined by Rowland and Taylor [14], respectively. Subsequently, the revised UNIQUAC and COSMOSPACE models are evaluated by comparing the description of vapor-liquid phase equilibria and excess enthalpy for alkane-alcohol binary systems.

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2. Theory

2.1. Guggenheim's entropy and the combinatorial activity coefficient

The mixing entropy ΔS for a binary mixture, consisting of molecules A and B, follows from Guggenheim's model [3] as

$$-\frac{\Delta S}{k_{\mathrm{B}}}=\left(1-\frac{z}{2}\right)\ln\frac{(r_{\mathrm{A}}N_{\mathrm{A}})!(r_{\mathrm{B}}N_{\mathrm{B}})!}{(r_{\mathrm{A}}N_{\mathrm{A}}+r_{\mathrm{B}}N_{\mathrm{B}})!}+\frac{z}{2}\ln\frac{(q_{\mathrm{A}}N_{\mathrm{A}})!(q_{\mathrm{B}}N_{\mathrm{B}})!}{(q_{\mathrm{A}}N_{\mathrm{A}}+q_{\mathrm{B}}N_{\mathrm{B}})!}. \tag{1}$$

Here N_{j}, r_{j}, q_{j} are the number, the relative volume and the relative area of molecules j in the mixture, z is the lattice coordination number and k_{B} Boltzmann's constant. For a multicomponent system, where M is the number of species, and applying Stirling's approximation, the equation of Guggenheim becomes

$$-\frac{\Delta S}{k_{\mathrm{B}}}=\left(1-\frac{z}{2}\right)\left[\sum_{\mathrm{j}=1}^{M}r_{\mathrm{j}}N_{\mathrm{j}}\ln(\phi_{\mathrm{j}})\right]+\frac{z}{2}\left[\sum_{\mathrm{j}=1}^{M}q_{j}N_{j}\ln(\theta_{\mathrm{j}})\right], \tag{2}$$

where ϕ_{j} and θ_{j} are defined as the volume and area fraction of molecule j in the mixture

$$\phi_{\mathrm{j}}=\frac{x_{\mathrm{j}}r_{\mathrm{j}}}{\sum\limits_{\mathrm{j}=1}^{M}x_{\mathrm{j}}r_{\mathrm{j}}}, \tag{3}$$

$$\theta_{\mathrm{j}}=\frac{x_{\mathrm{j}}q_{\mathrm{j}}}{\sum\limits_{\mathrm{j}=1}^{M}x_{\mathrm{j}}q_{\mathrm{j}}}, \tag{4}$$

and where x_{j} is the mole fraction of component j. These expressions contain the relative van der Waals volume, r_{j}, and area, q_{j}, which require an ad-hoc definition of a reference volume and area. We recommend to use the van der Waals volume and area of the molecule, which can be calculated from molecular data as we will demonstrate in the results section, because the reference volume and area cancel in these equations. Further, it would be better to use the quantity $z_{\mathrm{j}}q_{\mathrm{j}}$ instead of q_{j} in the expression of the area fraction, but since it is usually assumed that the lattice coordination number is the same for all molecules, it cancels in Eq. (4). Guggenheim introduced for the number of nearest neighbors of linear or branched molecules the formula

$$zq_{\mathrm{j}}=zr_{\mathrm{j}}-2\left(r_{\mathrm{j}}-1\right). \tag{5}$$

This can be rearranged into:

$$\left(1-\frac{z}{2}\right)r_{\mathrm{j}}=1-\frac{z}{2}q_{\mathrm{j}}. \tag{6}$$

Upon substituting Eq. (6) into Eq. (2) Guggenheim obtained:

$$-\frac{\Delta S}{k_{\mathrm{B}}}=\sum_{\mathrm{j}=1}^{M}N_{\mathrm{j}}\ln(\phi_{\mathrm{j}})+\frac{z}{2}\left[\sum_{\mathrm{j}=1}^{M}q_{\mathrm{j}}N_{\mathrm{j}}\ln\left(\frac{\theta_{\mathrm{j}}}{\phi_{\mathrm{j}}}\right)\right]. \tag{7}$$

To express the activity coefficient of compound k in a mixture, we subtract first the ideal entropy of mixing to obtain the excess entropy

$$-\frac{\Delta S^{\mathrm{E}}}{k_{\mathrm{B}}}=\sum_{\mathrm{j}=1}^{M}N_{\mathrm{j}}\ln\left(\frac{\phi_{\mathrm{j}}}{x_{\mathrm{j}}}\right)+\frac{z}{2}\left[\sum_{\mathrm{j}=1}^{M}q_{\mathrm{j}}N_{\mathrm{j}}\ln\left(\frac{\theta_{\mathrm{j}}}{\phi_{\mathrm{j}}}\right)\right], \tag{8}$$

and subsequently apply the thermodynamic relation

$$\ln\gamma_{\mathrm{k}}^{\mathrm{comb}}=-\frac{\partial\frac{\Delta S^{E}}{k_{\mathrm{B}}}}{\partial N_{\mathrm{k}}}. \tag{9}$$

This yields [7]:

$$\ln\left(\gamma_{\mathrm{k}}^{\mathrm{comb}}\right)=\left[\ln\left(\frac{\phi_{\mathrm{k}}}{x_{\mathrm{k}}}\right)+1-\frac{\phi_{\mathrm{k}}}{x_{\mathrm{k}}}\right]-\frac{zq_{\mathrm{k}}}{2}\left[\ln\left(\frac{\phi_{\mathrm{k}}}{\theta_{\mathrm{k}}}\right)+1-\frac{\phi_{\mathrm{k}}}{\theta_{\mathrm{k}}}\right]. \tag{10}$$

We recognize as first term the Flory-Huggins contribution and as second term the Staverman-Guggenheim correction [15,16]. Staverman [5] argued that Guggenheim's entropy equation (Eq. (7)) is not valid for more complicated molecules, such as for molecules containing one or more rings. Vera et al. [17] demonstrated, however, that Eq. (10) is still obtained for bulky molecules. In the derivation above the $\left(1-\frac{z}{2}\right)r_{\mathrm{j}}$ term was replaced by the $\left(1-\frac{z}{2}q_{\mathrm{j}}\right)$ term in Eq. (2), but we can also replace the $\frac{z}{2}q_{\mathrm{j}}$ term by $r_{\mathrm{j}}\left(\frac{z}{2}-1\right)+1$. This gives

$$-\frac{\Delta S^{\mathrm{E}}}{k_{\mathrm{B}}}=\sum_{\mathrm{j}=1}^{M}N_{\mathrm{j}}\ln\left(\frac{\theta_{\mathrm{j}}}{x_{\mathrm{j}}}\right)+\left(1-\frac{z}{2}\right)\left[\sum_{\mathrm{j}=1}^{M}r_{\mathrm{j}}N_{\mathrm{j}}\ln\left(\frac{\phi_{\mathrm{j}}}{\theta_{\mathrm{j}}}\right)\right]. \tag{11}$$

After applying Eq. (9) we get the alternative expression

$$\ln\left(\gamma_{\mathrm{k}}^{\mathrm{comb}}\right)=\left[\ln\left(\frac{\theta_{\mathrm{k}}}{x_{\mathrm{k}}}\right)+1-\frac{\theta_{\mathrm{k}}}{x_{\mathrm{j}}}\right]-\left(1-\frac{z}{2}\right)r_{\mathrm{k}}\left[\ln\left(\frac{\theta_{\mathrm{k}}}{\phi_{\mathrm{k}}}\right)+1-\frac{\theta_{k}}{\phi_{\mathrm{k}}}\right]. \tag{12}$$

This new expression for the SG-correction term no longer contains the number of nearest neighbors, zq_{k}, but the lattice coordination number times the number of sites, i.e. zr_{k}. Since Eq. (10) and Eq. (12) should yield the same activity coefficient for compound k, it follows

$$\begin{aligned}&\left[\ln\left(\frac{\phi_{\mathrm{k}}}{x_{\mathrm{k}}}\right)+1-\frac{\phi_{\mathrm{k}}}{x_{\mathrm{k}}}\right]-\frac{zq_{\mathrm{k}}}{2}\left[\ln\left(\frac{\phi_{\mathrm{k}}}{\theta_{\mathrm{k}}}\right)+1-\frac{\phi_{\mathrm{k}}}{\theta_{\mathrm{k}}}\right]\\&\quad=\left[\ln\left(\frac{\theta_{\mathrm{k}}}{x_{\mathrm{k}}}\right)+1-\frac{\theta_{\mathrm{k}}}{x_{\mathrm{k}}}\right]-\left(1-\frac{z}{2}\right)r_{\mathrm{k}}\left[\ln\left(\frac{\theta_{\mathrm{k}}}{\phi_{\mathrm{k}}}\right)+1-\frac{\theta_{k}}{\phi_{\mathrm{k}}}\right].\end{aligned} \tag{13}$$

With Eq. (5) we can reduce and rearrange the above expression to a property Q_j, which is half the number of nearest neighbors

$$Q_{\mathrm{k}}\equiv\frac{zq_{\mathrm{k}}}{2}=\frac{1-\frac{\theta_{\mathrm{k}}}{\phi_{\mathrm{k}}}-\frac{\phi_{\mathrm{k}}}{x_{\mathrm{k}}}+\frac{\theta_{\mathrm{k}}}{x_{\mathrm{k}}}}{2-\frac{\theta_{\mathrm{k}}}{\phi_{\mathrm{k}}}-\frac{\phi_{\mathrm{k}}}{\theta_{\mathrm{k}}}}=\frac{1-\frac{\phi_{\mathrm{k}}}{x_{k}}}{1-\frac{\phi_{\mathrm{k}}}{\theta_{\mathrm{k}}}}. \tag{14}$$

This new relation tells us that Q_{k} can be calculated from the mole, area and volume fraction, and that zq_{k} is not a free parameter anymore, as it was considered in the original UNIQUAC model. In Appendix A we show that Eq. (14) yields a constant, despite the fact that it contains functions of mole fraction. It has clear similarity with relation 5, which can be rearranged to

$$Q_{\mathrm{k}}\equiv\frac{zq_{\mathrm{k}}}{2}=\frac{1-r_{\mathrm{k}}}{1-\frac{r_{\mathrm{k}}}{q_{\mathrm{k}}}}. \tag{15}$$

In order to apply Eq. (15) one needs either a reference area and a lattice coordination number, or a reference volume and area in order to calculate the relative volume r_{k} and the relative area q_{k}, respectively. In the past this factor was obtained by setting $z=10$ and by calculating q_{k} using a reference area. We remark that the reference volume $V_{\mathrm{ref}}=25.17$ Å^3 was never changed after Abrams and Prausnitz [6] introduced it. The reference area, however, has been optimized several times in order to bring the activity models more in agreement with experimental results. Table 1 shows

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