To the Editor:

In the article published in this issue of the *AIChE Journal* "Analysis of a concept for predicting missing group interaction parameters of the UNIFAC model using connectivity indices" by A Mohs, A Jakob, J Gmehling, the authors have examined the reliability of our method (González H E, Abildskov J, Gani R, Rousseaux P, Le Bert B. A method for prediction of UNIFAC group interaction parameters. *AlChE J*. 2007;53:1620–1633). We thank the authors for undertaking this work and appreciate their efforts to examine the reliability of our method. We do not question the accuracy of their calculations. We also agree with the authors that filling the group interaction parameters with experimental data is the best option. What we pointed out in our article, however, is that when the experimental data is not available, our UNIFAC-CI method provides a fast and simple estimation of the parameters. The accuracy, however, like the group contribution method itself, or the COSMO-RS method, can be good in some cases but not in every case.

What the Mohs et al. article has illustrated very well are the following two issues, (a) should the atom interaction parameters (AIPs) for functional groups be used for estimating the molecular group interaction parameters? and (b) which types of new groups can be created with the AIPs for the functional groups? From the examination made by Mohs et al. it is clear that the AIPs for functional groups should not be used to fill-out the interactions involving the molecular groups. This is also the reason why we provided separate AIP tables involving the molecular groups, water and methanol. We acknowledge that some confusion could have been created by case study 3 in our article where we considered the system 1-2 ethanediol-methanol (see Figure 9 in our article). For this case study, we actually used the AIPs for the methanol molecular group and not the functional AIPs. Also from the examination made by Mohs et al., it is clear that one should be careful about creating totally new groups. In our group parameter table for the reference UNIFAC model, we did not have groups 51 and above. Therefore, we did not also include any data for systems that required these groups. Also, we clearly pointed out in our article that we excluded the groups COO and CON (on page 1624; see also Table 2 on this page) from our correlation of the functional AIPs. It is unfortunate, therefore, that Mohs et al. used group 46 (CON) and group 57 (ACCN) for the evaluation of our UNIFAC-CI method. It, is, therefore, not surprising that our published AIPs did not give acceptable results for systems involving these groups.

As Mohs et al. also found, our method appears to perform well for the groups included in the parameter table of the reference UNIFAC model we used to develop the corresponding AIP tables. The AIPs we provided can be used mainly to fill the empty spaces in the reference UNIFAC model parameter table. Also, new groups can be created but these groups, in principle, should be combinations of existing groups — a point that we did not explicitly mention but implied through our case study 3. Totally new groups can be created with more confidence, if more representative data could be used in estimating the AIPs, which is also true for all group contribution based methods like UNIFAC. Again, the poor performance reported by Mohs et al. is not surprising. Clearly, we did not recommend (or expect) this kind of extrapolations of our published AIPs.

Since publication of our original AIPs, we have revised and enlarged our parameter tables by adding new atoms (González H E, Abildskov J, Gani R, Computer-aided framework for pure component properties and phase equilibria prediction for organic systems. *Fluid Phase Equilibria*. 2007;261:199–20). Just like Prof Gmehling and his group, we also regularly revise our parameter tables. With our latest parameter tables (not yet published) we can represent the four systems corresponding to Figure 18a–d of Mohs et al. very well (see Figure 1a–d). Here, we have used AIPs regressed for the molecular group DOH, as well as represented ethylene glycol with groups CH2 and OH (and used our AIPs for functional groups). For the two nitroethane systems, we also provide the calculated vapor compositions in the corresponding figures. In Table 1, we provide the corresponding group interaction parameters (GIPs) calculated from our latest AIPs.

In Figure 2a and b, we provide the correlation statistics for systems with C, H, O and N atoms. The systems with the highest errors relate to acetone-aniline (CH2, ACH, CH2CO, ACNH2), dimethylamine-n-hexane (CH2, C2NH), and acetonitrile-ethanol (CH2, OH, CCN). If one takes these systems and extrapolates the AIPs, the results may not be very good. The

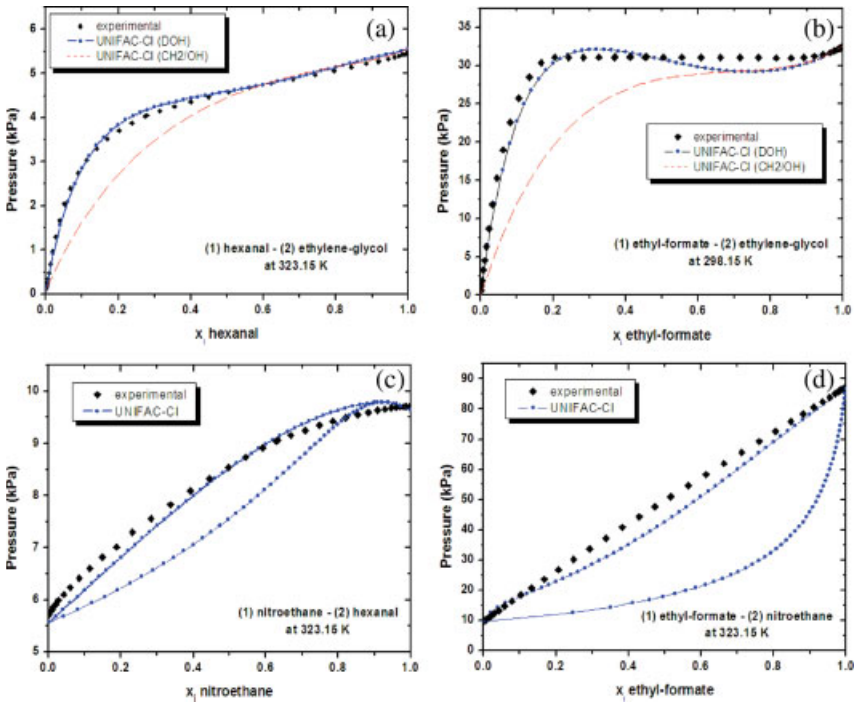

Figure 1. (a–d) Comparison of the UNIFAC-CI method calculations with VLE data (Mohs et al.) for ethylene glycol (top two figures) and nitroethane (bottom two figures) with 1-hexanal and ethyl formate.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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Table 1. The Calculated GIPs Estimated Through Our Latest AIPs With Our UNIFAC-CI Method (Used to Calculate the Phase Diagrams in Figure 1)

GIPs	Parameter a_{mn}	Parameter a_{nm}
CH2-CHO	292.37	32.67
CH2-HCOO	615.28	102.41
CH2-CNO2	−21.81	−151.18
CH2-DOH	1154.34	69.23
CHO-CNO2	7948.11	2510.69
CHO-DOH	813.73	−512.43
HCOO-CNO2	−360.04	34425.7
HCOO-DOH	53.19	377.14

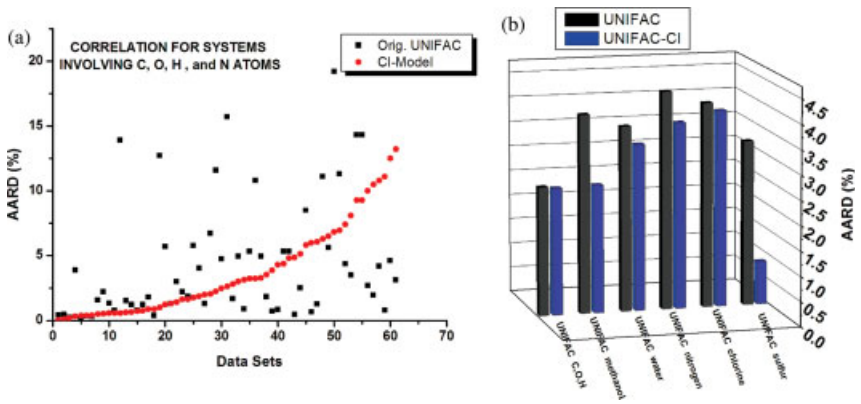

Figure 2. (a) Correlation for systems with C, H, O, and N atoms for the reference UNIFAC model and the UNIFAC-CI method. (b) Comparison of the reference UNIFAC model and the UNIFAC-CI method.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

same may also be true for the systems where the reference-UNIFAC model does not represent the data very well.

Finally, it is true that for molecular group interactions (pointed out by Mohs et al. for the water-methanol system), there can be two sets of generated parameters. That is why in our latest revision, we have forced these parameters to be the same. Also, just like a molecule can be represented differently by different groups, the same problem appears when representing groups with the atom-CI, therefore, this is not necessarily a limitation for only the atom-CI representation of groups. For this reason, we have developed rules for group as well as atom-CI representation, providing thereby, a unique representation.

Our current work is expanding the application of the UNIFAC-CI method to other reference UNIFAC models (such as UNIFAC-LLE and modified UNIFAC-Dortmund) as well as examining in more detail, the systems where the AIPs work and the systems where the AIPs do not work. We thank Mohs et al. for their interest in our UNIFAC-CI method and we hope they will find our method to perform better than they have experienced when they use our latest AIPs.

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