

**Authors' reply to the comment of P. M. Mathias**

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We thank P. M. Mathias for his interest and time to read the paper. In the following paragraphs, we attempt to respond to his concern and hope that this will be to his satisfaction.

We do agree that a well-defined model like Redlich-Kwong-Soave equation of state (SRK EOS)/van der Waals mixing rule (VDW MR) used in the paper would provide unique and unambiguous predictions of vapor/liquid phase equilibria and the relevant thermodynamic properties of a binary mixture, when the model parameters are well-defined (including the unlike mixture parameter k_{12} as used in this work). However, it may be noted that EOS/MR model may be analytical but the calculation of phase equilibria is always numerical. The latter is based on the numerical method used. It depends on the numerical method to provide phase equilibrium results from the assumed model. Although, the final results can be no better than the model itself, a numerical method that fails to provide sufficient criteria for Gibbs minimization can yield incorrect results which is not the fault of the model.

Therefore, we checked the performance of the three numerical methods, called fugacity method FM, Gibbs minimization method GM and area method AM, which were used to generate vapor/liquid phase equilibria in binary mixtures modeled by SRK EOS/VDW MR using the same set of parameters. Initially, the experimental data were used as guidelines for the existence of the vapor/liquid equilibria over a range of temperature and pressure. We found that AM converged and predicted vapor/liquid equilibria (with the different compositions at a given temperature T and pressure P) up to the critical loci of the mixtures, while FM

failed to converge and resulted into the trivial solutions (with the same compositions at a given T and P) close to the critical regions of the mixtures. GM predictions were found to lie in between as discussed in the paper. Note that our major emphasis was on the critical region of the mixtures. Once we found that AM converged better than the other two numerical methods, we finally used the area method to predict phase equilibria over the whole range of T and P of the mixtures and compared those predictions with experimental data in checking the accuracy of the model. In our opinion, once the reliability of the numerical method has been established one has to use experimental data to check the accuracy of the EOS/MR model over the whole range of temperature and pressure of the mixture. We could establish that AM was the most reliable numerical method (compared to other two methods investigated in this work) to predict the vapor/liquid phase equilibria. Then, the remaining discrepancy between the SRK EOS/VDW MR model using AM and experiment might naturally lie in the model itself. Similar observations were also made by Eubank *et al.* [*Ind. Engng Chem. Res.* **31**, 942 (1992)] as referenced in the paper.

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