A local composition model for the prediction of mutual diffusion coefficients in binary liquid mixtures from tracer diffusion coefficients

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A local composition model is proposed based on cluster diffusion theory for prediction of mutual diffusion coefficients (D_{12}) in binary liquid mixtures from tracer diffusivities (D_1^* and D_2^*):

$$D_{12} = (x_{11}D_2^* + x_{22}D_1^*)\left[1 + \frac{dln\gamma_1}{dlnx_1}\right]^{0.64} \quad (1)$$

In this equation, the effect of strong molecular association in mutual diffusion is accounted by using the local mole fractions (x_{11} and x_{22}). γ_1 and x_1 are the activity coefficient and mole fraction. The thermodynamic correction factor in bracket is scaled by 0.64 on the basis of critical point theory with which the concentration-dependence of diffusion driven by the chemical potential gradient is assumed to be similar to the transient concentration fluctuations near the consolute point.

Equation 1 was validated for prediction of mutual diffusion coefficients for binary liquid mixtures in a wide range of non-ideality. Particular interest lies in the prediction for mixtures containing one self-associating component and on non-polar component for which most of the existing models can not accurately predict the mutual diffusion coefficients (example shown in Figure 1).

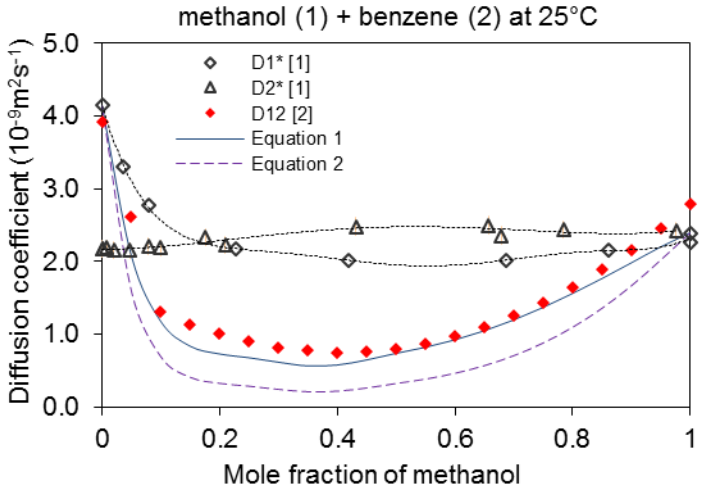

Figure 1: Prediction of mutual diffusion coefficients of methanol-benzene at 25 ^{0}C

Equation 2 in Figure 1, developed by [3], is expressed as:

$$D_{12} = (x_{11}D_2^* + x_{22}D_1^*)\left[1 + \frac{dln\gamma_1}{dlnx_1}\right] \quad (2)$$

References

[1] P.A. Johnson, A.L. Babb: *Self-diffusion in liquids. I. concentration dependence in ideal and non-ideal binary solutions*. Journal of Physical Chemistry **60**, 14–19 (1956).

[2] C.W. Caldwell, A.L. Babb: *Diffusion in the system methanol-benzene*. Journal of Physical Chemistry **59**, 1113-1114 (1955).

[3] J. Li, H. Liu, Y. Hu: *A mutual diffusion coefficient model based on local composition*. Fluid Phase Equilibria **187-188**, 193–208 (2001).