Prediction of mutual diffusion coefficients in non-ideal binary mixtures from PFG-NMR diffusion measurements

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In ideal solutions, binary, or mutual, diffusion is well described by Fick's law, which describes the driving force for diffusion in terms of a concentration gradient. However, from a thermodynamic perspective, the driving force is more correctly considered to be a gradient of chemical potential. The simplest analysis for a binary mixture suggests that the molar flux can be written as [1]:

$$j_1 = -D_{12}c\frac{dx_1}{dz} = -D^*_{12}\frac{cx_1}{RT}\frac{d\mu_1}{dz} \tag{7}$$

Here D_{12} is the mutual diffusion coefficient and D^*_{12} is a different diffusion coefficient defined for a chemical potential gradient. The gradient of chemical potential can be written as:

$$\mu_1 = \underline{G}_1 + RT\ln x_1\gamma_1 \tag{8}$$

Substitution of (2) in (1) yields the following expression:

$$D_{12} = D^*_{12}\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right] \tag{9}$$

In equation (3) D^*_{12} may be identified as some sort of molecular mobility, whilst the term in square brackets is a thermodynamic correction factor, taking account of the "force" on the diffusing molecules due to the gradient of excess chemical potential. The main critic to equation (3) is that it systematically underpredicts measured mutual diffusivities in non-ideal binary mixtures, especially those with a consolute point; however, there is no general agreement about the appropriate form of an improved equation. Other equations have been developed [2, 3], containing one or more adjustable parameters, which give better predictions near the consolute point but seems to fail far from it and do not give accurate predictions for non-ideal solutions without a consolute point.

Based on scaling laws [4], an improved form of equation (3) has been developed and successfully validated for non-ideal liquid mixtures with and without a consolute point. According to our model, the mutual diffusion coefficient can be written as:

$$D_{12} = D^*_{12}\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right]^\alpha \tag{10}$$

where α is a parameter grounded in scaling law theory, expected to be around two thirds.

In this work we demonstrate the practicality of calculating mutual diffusion coefficients using equation (4) for the non-ideal mixture nitrobenzene/n-hexane, which shows an upper consolute point. The PFG-NMR method is used to measure the tracer diffusion coefficients, which are then used to calculate the collective mobility term D^*_{12}. Vapour liquid equilibrium (VLE) thermodynamic data are then used to quantify the thermodynamic correction factor. The required non-thermodynamic parameter ($\alpha = 0.64$) is consistent with that reported by Wu *et al.* [5] for the temperature dependence of the diffusion coefficient in the same system, and with the theoretical value expected from semi-empirical scaling laws, describing the influence of dynamic concentration fluctuations.

Besides the mixture studied in this work, equation (4) has been tested on a wide range of non-ideal binary mixtures [6, 7, 8] and in all cases it has shown excellent predictions. Therefore, its use seems to be of general validity and this could have significant applications, notably in measuring diffusion coefficients in practical situations such as porous catalysts or packed beds, where conventional methods can be challenging.

References

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