Self-Diffusion in Unpolar Binary Mixtures

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Self-diffusion coefficients and densities are reported for two binary systems tetramethylmethane/methane (TMM/M) and tetramethylmethane/tetramethyltin (TMM/TMT) at pressures up to 200 MPa. The experimental diffusion data are analyzed in the framework of the rough hard sphere (RHS) model under application of hard sphere (HS) molecular dynamics simulations for binary mixtures of hard spheres obtained recently in our group.

1. Introduction
In order to complete previous studies on neat liquids, self-diffusion coefficients (s.d.c.) $D_n$ and liquid densities have been studied for two binary model systems consisting of spherical unpolar molecules. The mixtures are tetramethylmethane/methane (TMM/M) and tetramethyltin/tetramethylmethane (TMT/TMM). The data are used as a test for the RHS model [1] in binary mixtures.

2. Experimental
Details of high pressure NMR setup [2] and the densimeter [3] have been published.

3. Results
In fig. 1 the densities of the system TMM/M at 150 MPa are given as function of the mole fraction. These curves show a very pronounced curvature. The decrease of the density becomes more pronounced with increasing $x_M$.

Fig. 2 gives one set of densities for TMT/TMM. For this mixture perfect regular mixing behaviour is observed.

Fig. 3 collects isotherm of the self-diffusion coefficients in the system TMM/M at a mole fraction $x_{TMM} = 0.395$ and compares them to the data found for the neat substances TMM and M. It is typical for these binary mixtures that the pressure and temperature coefficient of $D$ are almost identical for both compounds, although the neat compounds reveal significant differences in slope and curvature.

Fig. 1. Some isotherms of the density in the system TMM/M as function of composition at a pressure of 150 MPa.

Fig. 2. Isotherms of the density in the system TMT/TMM as function of composition at a pressure of 100 MPa.

Fig. 3. Isotherm of the self-diffusion coefficients in the system TMM/M at a mole fraction $x_{TMM} = 0.395$ and compares them to the data found for the neat substances TMM and M.
Fig. 3. Comparison of the self-diffusion coefficients $D_{ii}$ in the binary mixture TMM/M ($x_{\text{M}} = 0.395$) with self-diffusion data of the neat compounds [4, 5]. ◦ neat M, ■ neat TMM, ○ $D_{ii}$ (M) in mixture, □ $D_{ii}$ (TMM) in mixture.

Fig. 4. Arrhenius plot of isobars of $D_{ii}$ in the binary system TMM/M at a mole fraction $x_{\text{M}} = 0.544$. The surprising observation in this set of data is the small difference between $D_{ii}$ for the two compounds although the mass ratios of the molecules is $\approx 2.5$. The difference in $D_{ii}$ is even decreasing with falling temperature.

4. Simulations

To describe the $p$, $T$-dependence of the s.d.c. $D_{ii}$, molecular dynamic simulations were performed for hard sphere systems of 2000 and 4000 particles. We used the same diameter-, mass-ratios and mole fractions as in the real mixtures. The hard sphere diameters were derived from fitting the experimental s.d.c. $D$ for the neat liquids to the rough HS model. They are:

<table>
<thead>
<tr>
<th>component</th>
<th>M</th>
<th>TMM</th>
<th>TMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{rel}}$(nm)</td>
<td>0.345</td>
<td>0.552</td>
<td>0.552</td>
</tr>
</tbody>
</table>

5. The Rough Hard Sphere (RHS) Model [1]

In this model the lowering of the self-diffusion coefficient in real liquids when compared to the simulated behaviour of smooth hard spheres (SHS) is ascribed to the coupling between translational and rotational modes, by the introduction of a coupling parameter $A$, which by definition must be $A < 1$,

$$D_{\text{exp}} = D_{\text{RHS}} = A \cdot D_{\text{SHS}}.$$
Fig 6. RHS fit of the s.d.c. $D_{ii}$ for TMT + TMM mixture, $x_{\text{TMM}} = 0.544$ (points = experimental data, full symbols: TMT, lines and broken lines = RHS-fit)

$D_{ii} = A_{ii}(T) \cdot D_{ii}^{\text{HS}}(\sigma_i(T), \sigma_j(T)); \ A_{ii}(T) \leq 1.0$

with the same $\sigma_i(T)$ as the neat substances. Here the value of the rotation translation coupling parameter $A_{ii}(T)$ depends on the composition:

$A_i \leq A_{ii} \leq A_j, \ i, j = 1, 2$

The $A$-parameter obtained for the mixtures are at any given temperature in between the $A$-parameter derived for the neat substances, within the precision of the experimental data $A$ in these mixtures is identical for both compounds at any given composition and temperature. The best values obtained from fitting the individual isotherms are given below fig. 5 and 6.

Acknowledgment

Financial support for this work was obtained from the Deutsche Forschungsgemeinschaft and the Fonds der Chemie. Technical support by our faculty workshops, especially from Mrs. R. Knott, G. Niesner, and G. Wührl is gratefully acknowledged.

References