p, T Dependence of the Self Diffusion Coefficients and Densities in Liquid Silicone Oils

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Z. Naturforsch. 51 a, 192–196 (1996); received January 26, 1996

Self diffusion coefficients and densities from a series of commercial silicones have been studied in the temperature range between 290 and 410 K at pressures up to 200 MPa. The densities are fitted to a modified Tait equation. The self diffusion coefficients are discussed in terms of the rough hard sphere model and tested against the Rouse-model.

Key words: Self diffusion, densities, silicones.

Introduction

Technical silicones have been applied in many fields of science and industry because of their chemical stability and their unique combination of useful properties [1, 2]. In the following the densities $\rho$ and self diffusion coefficients $D$ for a small series of low molecular weight silicones have been measured in a wide temperature and pressure range. The aim of this study is to compare the density and temperature dependence of $D$ in this class of compounds to the one observed in a similar series of long liquid $n$-alkanes [3]. In comparison to the alkanes the silicones possess much lower melting pressure curves and offer the possibility to study the liquid state in a significantly larger temperature range, thus providing more stringent tests for the applicability of models for the molecular dynamics.

Experimental

Substances

The silicones are commercial products (Bayer, Leverkusen, FRG) with molecular weight distributions as given in Figure 1. In the following they will be characterized by their average chain length $\bar{L}$ given as the number of $-\text{Si}(-\text{CH}_3)_2-\text{O}-$ segments. $\bar{L} = 13.7$ corresponds to an experimental low temperature oil; $\bar{L} = 23.5$, $\bar{L} = 165$ and $\bar{L} = 695$ correspond to the commercial Baysilones M3, M50 and M500, respectively (the mass distributions were provided by Dr. Grape, Bayer, Leverkusen). These products were used without further treatment. The densities $\rho$ of these silicones were determined in a piston-cylinder type densimeter described in detail in [4]. The temperatures given are accurate to ± 0.2 K. The pressures were determined with two precision Bourdon gauges (Heise, Erie / Pennsylvania / USA). At pressures up to 90 MPa they are accurate to ± 0.2 MPa; in the range...
Silicone Reference point $L$ $13.7$ $297.8$ $20$ $882$ $0.1036$ $259$ $-0.9$ $7.8 \cdot 10^{-4}$ $L = 23.5$ $294$ $10$ $898$ $0.1010$ $274$ $-0.9$ $8.6 \cdot 10^{-4}$ $L = 165$ $293.9$ $10$ $969$ $0.0973$ $240$ $-0.7$ $6.2 \cdot 10^{-4}$ $L = 695$ $261.1$ $10$ $975$ $0.0965$ $208$ $-0.6$ $4.8 \cdot 10^{-4}$

between 90 and 200 MPa the maximum error is ± 0.8 MPa. The overall maximum error of the densities is ± 0.4 %.

The self diffusion coefficients $D$ were measured by the pulsed field gradient technique [5] of Bruker MSL 100 and MSL 300 spectrometers in home built probe heads. Strengthened glass cells, as introduced by Yamada [6], were used as high pressure cells. Our versions of this design and details of the fitting procedure and the NMR experiments have been described in [7, 8]. The self diffusion coefficients are judged accurate to ± 5 %.

Results and Discussion

Densities

In Figs. 2 and 3 isotherms of the densities for the silicone $L = 13.7$ and $L = 695$ are given.

The densities for each silicone could be fitted by a modified Tait equation [9]:

$$\frac{\rho - \rho_0}{\rho} = A \ln \left( \frac{B + P}{B + P_0} \right). \quad (1)$$

$\rho_0$ is the density at the lowest temperature and pressure studied. $A$ is a temperature independent parameter, while $B$ can be given by

$$B = b_0 + b_1 T + b_2 T^2. \quad (2)$$

The parameter for the four substances are compiled in Table 1. The full experimental densities are contained in the diploma thesis of Thern [10] and are available upon request.

In Fig. 4 the isotherms of the self diffusion coefficients $D$ for the silicone $L = 165$ are given. In the log $D$ vs. $p$ plot they all reveal a pronounced curvature indicating that the pressure coefficient of $D$ is itself a function of $p$. The magnitude decreases with rising pressure.
Fig. 4. Isotherms at the self diffusion coefficient $D$ for the silicone oil $L = 23.5$.

Fig. 5. Arrhenius plot of the isobars of the self diffusion coefficient $D$ for the silicone oil $L = 165$ compared to a polyethylene wax with $L = 152$ [3].

The log $D$ vs. $1/T$ plots are straight lines, the slope being independent of pressure. It is customary to calculate from the slope Arrhenius activation energies $E_a$ [$E_a(L = 13.5) = 14.3 \pm 1$ (kJ/mol), $E_a(L = 23.5) = 14.9 \pm 1$ (kJ/mol), $E_a(L = 165) = 16.3 \pm 1$ (kJ/mol)]. These appear to increase slightly with increasing chain length. The same trend is also seen in the n-alkane series [11], where $E_a$ increases from 16 kJ/mol for n-hexadecane to 23 kJ/mol for a polyethylene wax with $L = 78$. The smaller compounds in the n-alkane series show, contrary to the silicones, a significant increase of $E_a$ with pressure. The experimental $D$’s for all four oils are compiled in Table 2.

The $D$ for $L = 695$ show a very peculiar $p, T$ dependence that is not expected from an extrapolation of the data for the silicones with a lower average molecular weight. Inspection of Fig. 1 shows that this oil has the widest distribution of molecular masses. It is thus to be suspected that the experimental $D$ is disproportionately influenced by the lower molecular mass fraction in the mixture. Similar conclusions have been drawn previously from the ambient pressure study of a series

### Table 2. Experimental self diffusion coefficients $D$ ($10^{-11}$ m$^2$s$^{-1}$) for four liquid silicones.

<table>
<thead>
<tr>
<th>$L$</th>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>SVP</th>
<th>77(K)</th>
<th>2611</th>
<th>2936</th>
<th>3233</th>
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of silicones [12]. The data for \( L = 695 \) will thus not be included in the general discussion given in the following.

In previous studies of self diffusion on several classes of liquids, reviewed in [13], it was shown that the rough hard sphere (RHS) treatment as proposed by Chandler [14, 15] and the interacting sphere (IS) model by Speedy [16] can describe the \( \rho, T \) dependence of \( D \) for most liquids including conformationally flexible chain molecules [3, 17]. In the following we will apply the RHS model for a comparison of the data obtained for the silicones here to the corresponding results for n-alkanes [3].

In this model, \( D(T, \rho) \) can be expressed in terms of the hard sphere diffusion coefficient by

\[
D(T, \rho) = A \cdot D_{\text{HSS}}(T, \rho, \sigma(T)) = A \cdot (D_0/n) \cdot P(n).
\]

(3)

\[
P(n) = (1 - n/1.09) 
\cdot [1 + n^2 \cdot (0.4 - 0.83 \cdot n^2)]
\]

(4)

with \( D_0 \) the Boltzmann diffusion coefficient for a dilute gas \((D_0 = (3/8) \cdot (k_B/T\rho n)^1/2)\), \( P(n) \) is a polynomial in the packing fraction \((n = \rho\sigma^3, \sigma; \text{hard-sphere diameter})\) derived from a fit of all reliable results obtained from molecular dynamics simulations [18]. \( P(n) \) accommodates manybody corrections and backscattering effects, that must occur at liquid like densities.

Chandler [14, 15] argues that the difference between the predicted hard sphere diffusion coefficient and the self diffusion coefficient is due to a coupling of rotational and translational modes and is taken into account by introducing the parameter \( A = D_{\text{exp}}/D_{\text{SHS}} \). By definition this parameter must be independent of \( T \) and \( \rho \).

A non-linear least-squares fit to the density dependence of \( D \) on each isotherm yields an approximately temperature independent hard sphere diameter \( \sigma \) and an \( A \)-value which decreases strongly with falling temperature.

In Fig. 6 the results of this fitting process are given for the silicone \( L = 165 \). The fit parameter obtained for this and the other two silicones are given in Table 3. In rigid molecules \( \sigma \) decreases slightly with increasing temperature, while for these silicones and also for octamethylocyclotetrasiloxane (OMCTS) [19], a \( \sigma \) that increases slightly with \( T \), respectively as for OMCTS is independent of \( T \), is derived. The comparison to the n-alkane [13] data shows similar tendencies, although the trend of increasing \( \sigma \) with \( T \) is not evident in the data, most probably because of the smaller temperature range accessible for this class of compounds.

The viscoelastic properties of linear polymers are usually well described by the Rouse [20] or reptation model [21, 22]. The data obtained here are clearly within the range where the Rouse model should apply. The Rouse model predicts

\[
D \sim M^{-\alpha}
\]

(5)

with the theoretical exponent \( \alpha = 1 \). The data for one temperature are given in Fig. 7 and compared to the results obtained for n-alkanes [3]. In experiments
Table 4. Exponents of the $D \sim M^\alpha$ plot in Figure 7 (T: 423 K).

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Alkanes [3]</th>
<th>Silicones</th>
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<tr>
<td>SVP</td>
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<td>-1.41</td>
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<tr>
<td>100 MPa</td>
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<td>400 MPa</td>
<td>-2.14</td>
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</table>

$\alpha > 1$ is often found. Table 4 compiles the $\alpha$ for the lines given in Figure 7.

The slopes derived for the silicones are significantly smaller and show a weaker pressure dependence. The deviation of $\alpha$ from the Rouse result ($\alpha = 1$) to larger values is usually explained by the influence of the free volume upon the translational mobility [23, 24]. The log $D$ vs. log $M$ graphs given in Fig. 7 provide an excellent method for the interpolation of self diffusion coefficients for compounds with intermediate chain lengths.

Acknowledgement

The expert technical support by Mr. R. Knott and G. Niesner made this study possible. Their contribution is gratefully acknowledged. Generous financial support was provided by the Fonds der Chemie.