Self-Diffusion in Compressed Dimethylether: The Influence of Dipole-Dipole Interaction and Hydrogen Bonding Upon Translational Diffusivity in Simple Fluids

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Self-diffusion coefficients of dimethylether have been measured as a function of temperature (185–458 K) and pressure (up to 200 MPa) by pulse-gradient field spin-echo NMR. Calculated activation volumes ($\Delta V^{\neq}$) fall from 15 (10^{-6} m^3/mole) at the highest temperature to 7 (10^{-6} m^3/mole) at the lowest. This trend is in keeping with values for other non-associating liquids. Comparison with self diffusion data for propane and ethanol reveals that the translational diffusivity in dimethylether is influenced by the substance's modest dipole moment (1.3 Debye). The effect is small but measurable and becomes more pronounced at lower temperatures.

Key words: Dimethylether, Diffusion, High Pressure.

Introduction

For the quantitative description of the self-diffusion coefficient D in simple fluids modifications of the hard sphere (HS) models as derived from early computer simulations [1] appear to be the most promising approach. The two most widely applied extensions of the simple hard sphere model ascribe the deviations of real liquids from the HS-liquid either to non-sphericity of the molecule [2–4] or by the neglection of attractive interactions (IS) [5]. A recent analysis of a series of simple liquids [6] showed that many systems can be described well by the rough hard sphere (RHS)-model, while the analysis of a series of liquids [7] yielded the result that attractive interactions as modelled by a spherical Lennard-Jones potential [5] account for most of the deviations of self-diffusion in real liquids from the ideal HS model. The present study of self-diffusion in dimethylether was initiated in order to collect more experimental data for a liquid consisting of strongly nonspherical molecules with a moderate dipole moment (1.3 Debye) and to compare these data with two neat liquids consisting of molecules of very similar geometry: unpolar propane [8] and hydrogen bond forming ethanol [9].

Experimental

Dimethylether (99.8%) was purchased from E. Merck, (Darmstadt, FRG). The substance was condensed directly from a steel bottle into a titanium autoclave and passed over a high pressure absorption column filled with dry silica gel in order to remove residual moisture. Oxygen and nitrogen were removed by several freeze-pump-thaw cycles. For details of the experimental design see [8].

The high pressure NMR cell used in our studies is a modification of the strengthened glass cell design introduced by Yamada [10]. Details of our version of this cell type and the filling and operating procedures have been described in [9, 11, 12].

The NMR measurements were performed on a Bruker MSL 300 spectrometer using a home built gradient probe. A commercial Bruker variable temperature unit was used for temperature regulation. Temperatures were measured by a metal sheathed chromel-alumel thermocouple (Philips, Kassel, FRG) before and after each experiment. The pulsed field gradient method, as introduced by Stejskal and Tanner [13] was used. In this experiment the decay of the echo amplitude is given by

$$A(2\tau)=A(0)\exp[-2\tau/T_2]\exp(-\gamma^2\delta^2 g^2 D(\Delta-\delta/3)],$$

where τ is the time between the 90°- and the 180°-pulse, D the self diffusion coefficient, δ the duration of the

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gradient pulse, Δ the time between the two gradient pulses, and g the gradient strength, given by $g = kI$. Here I is the current intensity and k the coil constant, which had been obtained from a calibration with the known diffusion coefficient of water at ambient pressure and 298 K [14] and controlled by benzene data, known from tracer measurements [15]. D was determined by recording 10–15 spin-echos with increasing g values while holding all other variables constant. The following Fourier transformation of the second half of the spin-echo improves apparently the S/N ratio. The temperatures are judged reliable to ± 1 K. The pressure was precise to ± 0.5 MPa. The measured diffusion coefficients are regarded as reliable to ± 5%. Their reproducibility was ± 1–3%.

Results and Discussion

All experimental self diffusion data are compiled in Table 1. Figure 1 gives the isobars of D in an Arrhenius plot. The isotherms are given in Figure 2. In Tables 2 and 3, second order polynomials that fit the experimental data well within the error limits are given, so that they may be used for interpolating the experimental results. The polynomials should only be used for a slight extrapolation of the data to ranges of pressure and temperature not covered by the experiments.

It is customary to use the energy of activation $(\Delta E_A)_p$ for the description of the slope of the isobars in Fig. 1, although the physical concepts underlying the model are certainly not applicable to diffusional transport in simple liquids. The isobars show a slight curvature, the slope increasing a little with rising pressure.

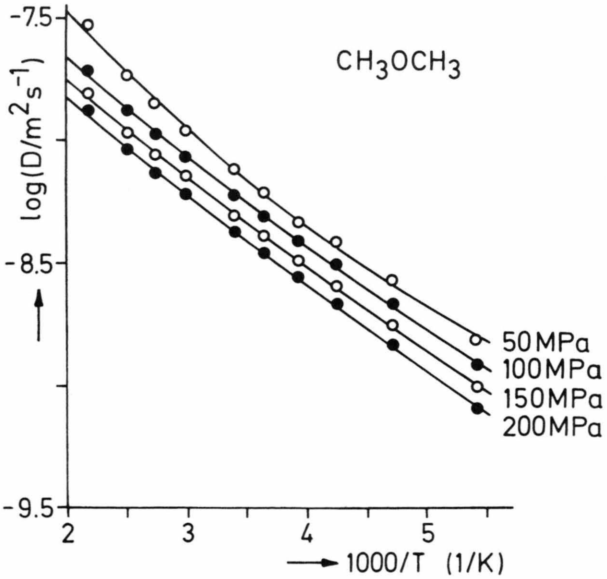

Fig. 1. Isobars of the self-diffusion coefficient D of fluid dimethylether. The lines drawn through the experimental points result from fitting the data to a second order polynomial. The parameters for the fits are given in Table 3.

Table 1. Experimental self-diffusion coefficients for dimethylether.

$D/10^{-10}$ m^2 s^{-1} Temp. (K)	50 MPa	100 MPa	150 MPa	200 MPa
458.0	297.1	192	156.7	133
398.5	185	132.7	107.9	92.3
365.5	141	106.3	87.1	73.9
334.0	110.1	86.5	71.6	60.8
294.0	76.3	59.8	49.6	42.6
274.0	61.4	49.1	40.6	35
254.5	46.7	39.1	32.3	27.7
235.5	38.5	31.1	25.6	21.6
212.0	26.8	21.6	17.6	14.7
184.5	15.3	12.1	9.8	8.1

Table 2. Coefficients for the isobars of a polynomial (2nd order) for the self-diffusion coefficient of dimethyl-ether (r^2 = correlation coefficient). $D = a_0 + a_1 T + a_2 T^2 + a_3 T^3$. T in K.

Pressure (MPa)	a_0	a_1	a_2	r^2
50	−6.2905	−0.66216	3.6875 e−2	0.998
100	−6.7572	−0.48326	1.6040 e−2	0.999
150	−6.8819	−0.46032	1.2894 e−2	0.999
200	−6.9851	−0.43827	9.4565 e−3	0.999

Table 3. Coefficients for the isotherms of a polynomial (2nd order) for the self-diffusion coefficient of dimethylether (r^2 = correlation coefficient). $D = a_0 + a_1 p + a_2 p^2 + a_3 p^3$; p in MPa.

Temp. (K)	a_0	a_1	a_2	r^2
458.0	−7.2987	−5.2450 e−3	1.1900 e−5	0.995
398.5	−7.5590	−3.8920 e−3	7.6000 e−6	0.999
365.5	−7.7082	−3.1290 e−3	5.1000 e−6	1.000
334.0	−7.8390	−2.5620 e−3	3.4000 e−6	1.000
294.0	−7.9930	−2.6880 e−3	4.0000 e−6	1.000
274.0	−8.0985	−2.4280 e−3	3.2000 e−6	1.000
254.5	−8.2435	−1.7780 e−3	1.0000 e−6	0.999
235.5	−8.3130	−2.1260 e−3	1.8000 e−6	1.000
212.0	−8.4698	−2.1170 e−3	1.5000 e−6	1.000
184.5	−8.7038	2.3210 e−3	1.9000 e−6	1.000

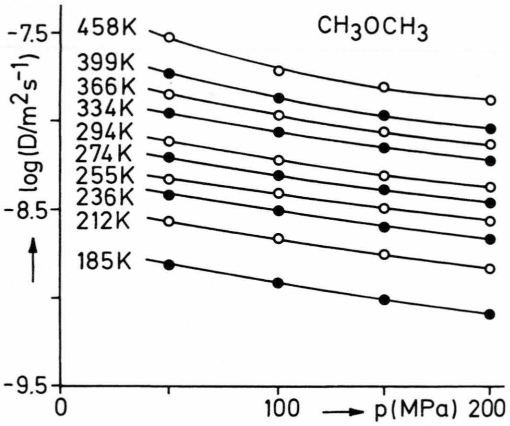

Fig. 2. Isotherms of the self-diffusion coefficients D of fluid dimethylether. The lines drawn through the experimental points result from fitting the data to a second order polynomial. The parameters for the fits are given in Table 3.

For a temperature of 230 K $(\Delta E_A)_p$ was derived to 6.5 ± 0.5 kJ/mole. An increase of $(\Delta E_A)_p$ with pressure is found, which however remains well within the experimental precision stated.

The isothermal pressure dependence can be characterized by the activation volume $\Delta V^{\neq}$ defined by

$$\Delta V^{\neq} = -RT\left(\frac{\mathrm{d}\ln D}{\mathrm{d}p}\right)_T . \tag{1}$$

All isotherms given in Fig. 2 have a small curvature, which decreases with falling temperature. This holds for most other simple liquids studied too. $\Delta V^{\neq}$ thus becomes smaller with rising pressure. At a medium pressure of 100 MPa, where the slope of the isotherms can be determined with the greatest precision, $\Delta V^{\neq}$ decrease from 15 $(10^{-6}\ \mathrm{m^3/mole})$ at 458 K to 7 $(10^{-6}\ \mathrm{m^3/mole})$ at 185 K. A decrease of $\Delta V^{\neq}$ with falling temperature is observed for most nonassociating liquids [12]. No simple explanation can be given for this finding.

The application of the RHS- and IS-model to the data is impossible for the time being because it demands reliable pVT data. For dimethylether no such data could be found in an extended literature search. A comparison of the data for the ether to the p, T-dependence of self diffusion in propane, where precise densities exist, reveals a qualitative similarity and leads to the conclusion that dimethylether can be certainly described by the RHS- as well as by the IS-model. Figure 3 gives the 100 MPa isobars for propane, dimethylether and ethanol. The slope of the isobars for the first two substances is very similar. The dipolar dimethylether reveals a slightly larger temperature dependence of D, which could result from the dipole-dipole interaction in the ether becoming more effective in retarding the molecular diffusivity with falling temperature.

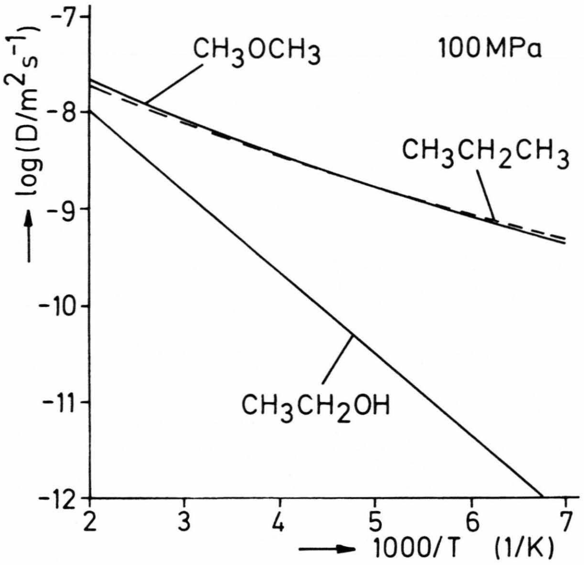

Fig. 3. Comparison of the 100 MPa isobars of dimethylether, propane, and ethanol. The data for propane and ethanol were taken from references [8] and [9], respectively. The lines drawn through the experimental points result from fitting the data to a second order polynomial. The parameters for the fits are given in Table 3.

The 100 MPa isobar of ethanol has a much steeper slope, characterized by an activation energy at constant pressure of 16 ± 1 kJ/mole. At the lowest temperature reached in these experiments the formation of transient hydrogen bonded two dimensional aggregates in the alcohol has slowed down the molecular diffusivity by more than two orders of magnitude when compared to the dipolar liquid consisting of molecules of similar geometry.

In conclusion one may state that the influence of a modest dipole moment of 1.3 Debye upon translational diffusivity is small under all conditions studied, but becomes more pronounced at lower temperatures.

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