Pressure and Temperature Dependence of Self Diffusion in Fluid Binary Propane/Tetradecane Mixtures

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Self diffusion data were measured for both compounds of the binary propane/tetradecane mixture by the NMR pulsed gradient spin echo technique. A new autoclave for the investigation of binary gas/liquid mixtures in the fluid range up to pressures of 200 MPa is presented. The activation energies and volumes of both components are found to be identical for the mixtures under investigation (2.5 and 89 mole% propane).

Introduction

The p, T dependence of the self diffusion coefficient in simple nonassociating liquids can be remarkably well described by modifications of the hard sphere model [1–5]. It was shown that this treatment could also be used with good precision for neat alkanes [6, 7], although these molecules certainly deviate significantly from spherical shape. The molecular dynamics of the neat hard sphere liquid have been studied by computer simulations since the earliest days of this technique [8]. Speedy has compiled all existing data and described the density dependence of D by a polynomial [9] which was recently critically reviewed by Erpenbeck and Wood [10]. The comparison of real neat liquids to the computer simulation of hard sphere liquids thus rests on fairly safe grounds. Computer simulations of mixtures consisting of spheres differing in mass and diameter have been less popular, probably because the number of possible and meaningful combinations has deterred scientists thoroughly. A few attempts have recently been published [11], but the analysis with this theoretical tool is still hampered by the rarity of high pressure p, V, T data.

In the following a few self diffusion results on the system propane/tetradecane is given. We also describe an apparatus for the preparation and measurement of gas/liquid mixtures at fluid densities for use in a high resolution NMR instrument.

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Experimental

Substances

Propane (99.5%) was purchased from E. Merck (Darmstadt, FRG) and used after thorough drying over a 3 Å molecular sieve.

The proton spectra of propane and the methyl groups of tetradecane are too close in chemical shift at 300 MHz to allow a reliable quantitative integration of the signals. This tetradecane-d_6 $CD_3(CH_2)_{12}CD_3$ was synthesized from tetradecanoic acid diethylester (Aldrich, Steinheim, FRG) by the following standard procedures:

$$C_2H_5O_2C(CH_2)_{12}CO_2C_2H_5 \xrightarrow[(THF)]{LiAlD_4} HOCD_2(CH_2)_{12}CD_2OH\,,$$

$$HOCD_2(CH_2)_{12}CD_2OH \xrightarrow[(Methylcyclohexane)]{HJ\ aq.} JCD_2(CH_2)_{12}CD_2J\,,$$

$$JCD_2(CH_2)_{12}CD_2J \xrightarrow[(THF/D_2O)]{LiD/LiAlD_4} CD_3(CH_2)_{12}CD_3\,.$$

The deuterated substance was purified by fractionated destillation at 20 mbar. No impurities could be detected in the proton NMR-spectrum.

Apparatus

The propane was dried and degassed in a high pressure apparatus described previously [12, 13].

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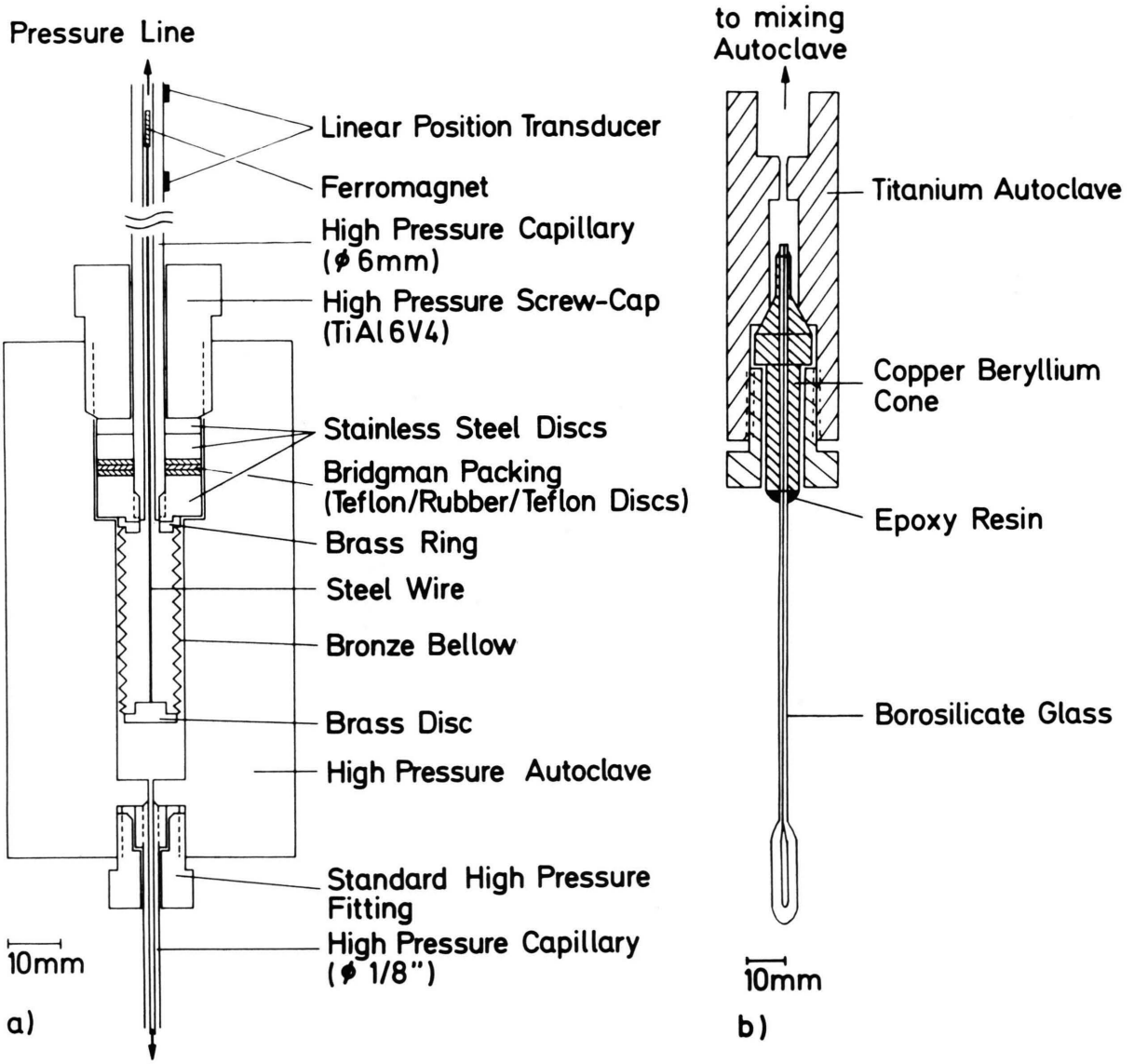

Fig. 1. a) High pressure autoclave for liquid/gas mixtures at fluid densities. The substances are filled into the bore of the autoclave by the technique described in the text. The bronze bellow separates the pressure liquid (inside the bellow) and the mixture (outside the bellow). The position of the bellow can be controlled with the linear position transducer in order to prevent damage by extreme compression or expansion. – b) Strengthened glass cell for diffusion measurements in the magnet of the NMR spectrometer. The cell is connected with the autoclave by a 1/8″ steel capillary.

The tetradecane/propane mixtures were prepared in the autoclave given in Figure 1 a. The autoclave was flushed with propane at atmospheric pressure. Then a defined amount of degassed tetradecane was given into the autoclave with a syringe and a hypodermic needle. The autoclave was closed immediately, and degassed propane was pressed into the autoclave with the lowest pressure used later in the experiments. The high pressure apparatus mentioned above was used for this filling procedure. During this process the bronze bellow had to be kept in a contracted position which was controlled by a linear position transducer and regulated by pressing standard pressure liquid into the bellow.

After filling, the autoclave was connected by a three way valve and an 1/8″ o.d. high pressure steel capillary

with the strengthened glass cell shown in Figure 1 b. This part of the system was evacuated and flushed with propane several times before the final filling in order to remove paramagnetic oxygen and other gaseous impurities.

After some pressure cycles between 25 and 200 MPa and after waiting for approximately 12 hours the concentrations in the glass cell were found to be stable. They were determined from the integral of the Fourier transformed proton NMR spectrum. This integration was reproducible to $\pm 0.5\%$. The determined concentrations are judged reliable to $\pm 1\%$. The concentration was determined frequently during the measurements in order to exclude changes in concentration in the strengthened glass cell. The concentration remained constant as long as a phase separation was avoided.

The measurements were performed in a Bruker MSL 300 Spectrometer operating at 7.05 Tesla in a home-built probehead. The pulsed field gradient method, proposed by Stejskal and Tanner [14], was used. Details of the experimental procedure and the probehead have been published [15]. The self diffusion coefficients were calculated from the Fourier transformed spin echoes.

The self-diffusion coefficients are judged reliable to $\pm 5\%$. They were reproducible to $\pm 2\%$.

Results and Discussion

In Fig. 2 the isobars of the self diffusion coefficients for neat propane and tetradecane are given. All values were taken from earlier data of our group [12, 16]. From the slope of the almost linear isobars the activation energies E_A at constant pressure can be calculated:

$$E_A = -R\left(\frac{\delta \ln D}{\delta T}\right)_p .$$

The pressure dependence of D yields the activation volume ΔV^*:

$$\Delta V^* = -RT\left(\frac{\delta \ln D}{\delta p}\right)_T .$$

These two quantities can be used for an empirical comparison of the T, p-dependence of self diffusion and other transport coefficients. Especially ΔV^* is clearly a function of pressure, and also $(E_A)_p$ becomes pressure dependent when sufficiently large ranges of the p, T-space are studied. These quantities should not be used for an extrapolation of the transport coefficients into regions not covered by the experiments, and their presentation here should not be taken as an indication of the applicability of the activated transition state theory to transport processes in simple liquids.

Because of the significant pressure dependence of ΔV^*, the data given in Table 2 were taken at 150 MPa, i.e. in a pressure range where the thermal expansivity of the neat substances and the mixtures should be similar.

In Fig. 3 the isobars of the self diffusion coefficients for a mixture containing 2.5 mole% propane are given. The same data are plotted as isotherms in Figure 4. Figure 5 gives the results collected for the binary mixture with 89 mole% propane.

From the slopes of the isobars and isotherms the activation energies and activation volumes are derived. They are collected in Tables 1 and 2. The data given there are considered reliable to $\pm 10\%$. They reveal some very remarkable general trends. Although the mass and size of the two constituents and also the p, T-dependence of the self diffusion of the neat liquids is quite different, all mixtures show for both components activation energies and volumes that are identical within experimental error. In our opinion this proves that diffusion of the two types of molecules cannot be described by the theory of the activated transition state, but is a collective property of the liquid. Polzin and Weiß [17] and Brüsewitz and Weiß [18] have shown that also the free volume model [19, 20] is not able to represent quantitatively the mixtures of tetramethyltin/cyclohexane [17] and n-hexane/benzene [18]. The test of this model with the data collected here as well as the applications of hard sphere treatments for mixtures [11] is impossible at the moment because of the lack of reliable high pressure ϱ, T-data.

The comparison of self diffusion data in the propane/tetradecane mixtures with older results on methane/tetradecane mixtures [16] and the two systems discussed above, however, shows that the behaviour described in the study presented here appears to be a general property of binary mixtures consisting of unpolar molecules, regardless of the size and mass ratios and the shape of the molecules of the constituents.

In order to evaluate the diffusion data in the framework of the various hard sphere models, p, V, T-measurements as well as more molecular dynamics simulations are needed. These studies are planned in our group for the near future.

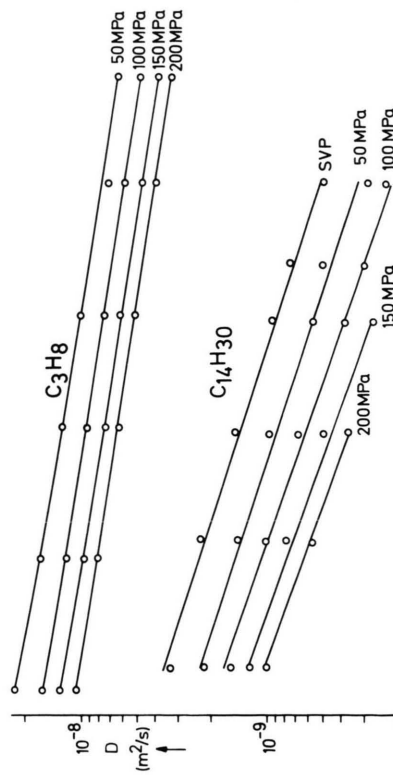

Fig. 2. Isobars of the self diffusion coefficient D of the neat propane and tetradecane [12, 16].

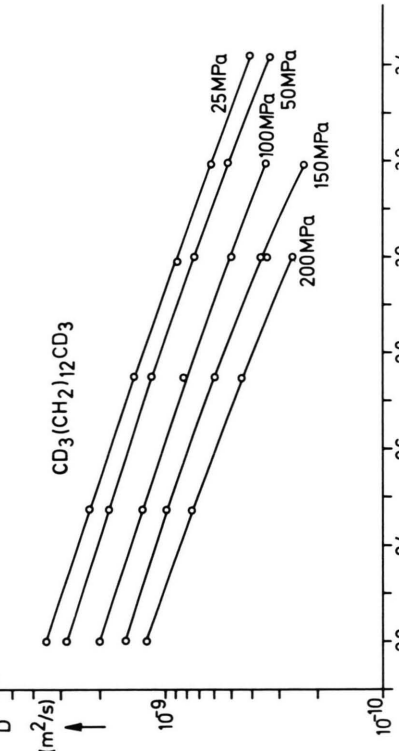

Fig. 3. Isobars of the self diffusion coefficient D of the propane/tetradecane-d_6 mixture with 2.5 mole% propane.

Table 1. Activation energies E_A [kJ/mole] of C_3H_8 and $CD_3(CH_2)_{12}CD_3$ and their mixtures.

p/MPa	Neat		Mixture 1 2.5 mole% C_3H_8		Mixture 2 89 mole% C_3H_8	
	C_3H_8	$CD_3(CH_2)_{12}CD_3$	C_3H_8	$CD_3(CH_2)_{12}CD_3$	C_3H_8	$CD_3(CH_2)_{12}CD_3$
25	6.8		15.0	14.7	8.8	9.7
50	7.4	14.3	14.1	13.3	8.6	7.6
100	7.1	15.2	14.2	13.8	7.2	7.5
150	7.1	15.7	13.6	13.4	6.3	7.4
200	6.8	16.1	14.1	15.6		

Fig. 4. Isotherms of the self diffusion coefficient D of the propane/tetradecane-d_6 mixture with 2.5 mole% propane.

Fig. 5. Isobars of the self diffusion coefficient D of the propane/tetradecane-d_6 mixture with 89 mole% propane.

Table 2. Activation volumes ΔV^* [10^{-6} m³/mole] at 150 MPa of C_3H_8 and $CD_3(CH_2)_{12}CD_3$ and their mixtures.

T/K	Neat		Mixture 1 2.5 mole% C_3H_8		Mixture 2 89 mole% C_3H_8	
	C_3H_8	$CD_3(CH_2)_{12}CD_3$	C_3H_8	$CD_3(CH_2)_{12}CD_3$	C_3H_8	$CD_3(CH_2)_{12}CD_3$
293	9.5		23.4	22.4	15.8	16.7
313	10.2		18.9	18.4	16.5	18.2
333	10.7	18.9	18.4	18.6	16.8	18.8
363	11.9	18.4	18.8	17.9	17.7	21.3
403	13.5	18.2	18.5	17.5	18.3	23.8
452	16.3	17.8			20.8	26.1

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