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Self-Diffusion Coefficients of Methane or Ethane Mixtures with Hydrocarbons at High Pressure by NMR

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Self-diffusion coefficients have been measured in homogeneous mixtures of methane + hexane, ethane + hexane, methane + octane, ethane + octan, methane + decane, ethane + decane, and methane + hexane + benzene over the whole concentration range, at 303.2 K and 333.2 K and 30 MPa, 40 MPa, and 50 MPa. The experiments were performed in a glass cell by application of the NMR−PGSE technique. The estimated accuracy of the measurements is ±5%. Experimental self-diffusion coefficients were compared to the Sigmund correlation, which was found not to fit the experimental data.

Introduction

The main motivation for this work was the need for diffusion data in reservoir studies. Gas injection in heterogeneous or fractured reservoirs and gas diffusion through cap rock are processes where diffusion may play a significant role. Although these processes occur in porous oil- and water-saturated rock, diffusion data pertaining to bulk liquids are useful because the effect of the tortuosity of the rock can be represented by formation resistivity data (Matthews *et al*., 1987). Moreover, a diffusion model at the molecular level can include rock−fluid interactions.

For engineering purposes, correlations between the diffusion coefficients and pressure, temperature, and composition are useful. Several correlations exist, but when they are applied to reservoir conditions, their estimates may differ by several hundred percent. The Sigmund correlation (Sigmund, 1976) has been used with some success in reservoir simulations of fractured reservoirs, using an extension to the high pressures found in reservoirs at great depths (da Silva and Belery, 1989).

Studies of diffusion at reservoir conditions, such as diffusion of methane and ethane in crude oil contained in a porous rock, represents experimental difficulties leading to large uncertainties in the measured diffusion coefficients. Because inaccurate data will be of limited value, we have chosen to study self-diffusion in model gas/oil systems, by a technique providing results of high accuracy. The transformation of self-diffusion coefficients into mutual diffusion coefficients at reservoir conditions is not without problems (Dysthe and Hafskjold, 1995), but formal relationships in terms of velocity correlation functions exist (Hertz, 1977).

The NMR technique, by application of the pulsed field gradient spin echo technique (PGSE) (Stejskal and Tanner, 1965), has become the method of choice. To obtain liquid mixtures of methane or ethane with higher alkanes, high pressure must be applied. On the basis of the glass capillary technique described by Yamada (1974), high-pressure equipment has been constructed to prepare homogeneous gas/oil mixtures.

Diffusion data (both self-diffusion and mutual diffusion data) for hydrocarbon systems at high temperature and high pressure are in no respect complete at the moment. Erkey and Akgerman (1989) have measured mutual diffusion coefficients of methane, ethane, propane, pentane, heptane, decane, dodecane, and tetradecane infinitely diluted in octane, in the temperature range from 304 K to 435 K at 1.72 MPa. They used the Taylor dispersion technique (Tyrrell and Harris, 1984). Reamer *et al.* (1956) have measured the mutual diffusion of methane (gas phase) into liquid phases of methane + decane and methane + pentane mixtures in the temperature range from 258 K to 411 K, and at pressures up to 27.6 MPa. They used pressure−time measurements. Gavalas *et al.* (1968) have measured mutual diffusion in the system methane + propane at 344 K, and 3.93 MPa, using the pressure−time technique. Brow *et al.* (1984) have measured the mutual diffusion of gases in crude oils at temperatures up to 366 K, and pressures up to 20.7 MPa, by performing chromatographic analyses of samples from a diffusion cell. Atwood and Goldstein (1984) have measured the mutual diffusion of various hydrocarbon mixtures at 298 K, and pressures up to 21.0 MPa, by the Taylor dispersion technique. The techniques described in these references are suitable for rapid surveys, but their implementation often suffers from moderate accuracy.

Bachl and Lüdemann (1986) have measured self-diffusion coefficients in butane, pentane, hexane, decane, *trans*-2-butene, *cis*-2-butene, and 2-butyne at temperatures up to 450 K, and pressures up to 200 MPa. Vardag *et al.* (1990) have measured self-diffusion coefficients in methane, butane, pentane, hexane, decane, tetradecane, 2,2,3-trimethylbutane, and a mixture of methane + tetradecane at temperatures up to 450 K, and pressures up to 200 MPa. Vardag *et al.* (1991) have also measured self-diffusion coefficients in melts of *n*-alkanes with chain lengths between 16 and 154 carbon atoms, in the temperature range from 200 K to 500 K, and pressures up to 600 MPa. Greiner-Schmid *et al.* (1991) have measured self-diffusion coefficients in methane, ethane, and propane, in temperatures up to 450 K, and pressures up to 200 MPa. Brüsewitz and Weiss (1990) have measured self-diffusion coefficients in hexane + benzene mixtures, in the temperature range from 253 K to 368 K, and pressures up to 200 MPa. All these references used a NMR−PGSE technique. The data are regarded as reliable to ±5% by the authors.

Marbach (1995) has measured self-diffusion coefficients in mixtures of hexane + dodecane, hexane + octane, pentane + octane, and hexane + decane + dodecane at temperatures between 288 K and 318 K, and pressures up to 60 MPa. He used a steady field gradient NMR spin echo

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technique. Marbach regards the data as reliable to ±2%.

Harris and co-workers have measured self-diffusion in methane at temperatures between 223 K and 323 K, and pressures up to 180 MPa (Harris, 1978), in methane at temperatures between 110 K and 160 K, and pressures up to 220 MPa (Harris and Trappeniers, 1980), in hexane at temperatures between 223 K and 333 K, and pressures up to 400 MPa (Harris, 1982), in octane at temperatures between 248 K and 348 K, and pressures up to 361 MPa (Harris *et al*., 1993), and in hexadecane at temperatures between 298 K and 348 K, and pressures up to 300 MPa (Dymond and Harris, 1992). All these measurements were performed by applying NMR−PGSE techniques. All data are regarded as reliable to ±2% by the authors.

Theory

Diffusion. The mutual diffusion coefficient, D_{12}, is defined in a binary system with concentration gradient ∇c_i by Fick's first law (Fick, 1855):

$$J_i = -D_{12}\nabla c_i \tag{1}$$

where J_i is the molar flux of component i in the volume fixed reference frame. The mutual diffusion process is a net transport of matter due to the concentration gradient. In a homogeneous system the molecules undergo random Brownian motion. The self-diffusion coefficient D_i of species i is a measure of this motion. It may be expressed in terms of the mean square displacement or the velocity autocorrelation functions of the molecules:

$$D_i = \frac{1}{6t}\langle(r_i(t) - r_i(0))^2\rangle = \frac{1}{3}\int_0^\infty \mathrm{d}t\,\langle u_i(0)\cdot u_i(t)\rangle \tag{2}$$

where $r_i(t)$ is the position and $u_i(t)$ the velocity of particle i at time t. The three diffusion coefficients (D_1, D_2, D_{12}) of a binary fluid mixture are fundamentally independent except at infinite dilution of component i where the self-diffusion of component i and the mutual diffusion are indistinguishable, $\lim_{x_i\to 0} D_{12} = D_i$. Several attempts have been made, however, to establish practical relations among the three coefficients of the type $D_{12} = \mathrm{f}(D_1,D_2)$ (Darken, 1948; Hertz, 1977; Adamson, 1960; Friedman, 1986; Mills and Friedman, 1987). The most used one is probably the Darken relation (Darken, 1948):

$$D_{12} = B_2^{\,x}(x_1D_2 + x_2D_1) \tag{3}$$

which fulfills the exact infinite-dilution limits. Here x_i is the mole fraction of component i and $B_2^{\,x}$ represents the relation between the thermodynamic driving force (the chemical potential gradient) and the driving force used in the definition of the diffusion coefficient,

$$B_2^{\,x} = 1 + \left(\frac{\partial \ln f_2}{\partial \ln x_2}\right)_{T,P} \tag{4}$$

where f_2 is the activity coefficient of component 2 on mole fraction scale. $B_2^{\,x}$ equals unity for thermodynamically ideal mixtures. The conditions for fulfillment of the Darken relation (3) can be expressed in terms of frictional coefficients (Tyrrell, 1963) or a velocity−time correlation function (McCall and Douglass, 1967), but the conditions are not necessarily fulfilled even for thermodynamically ideal mixtures. Even so, the Darken relation is a good approximation for nearly ideal systems that show no tendency of specific chemical interactions such as solvation, compound formation, or polymerization (Carman, 1967, 1968a, 1968b). In particular, it has been shown to hold for a number of *n*-alkane mixtures (Van Geet and Adamson, 1964) and in lack of experimental mutual diffusion coefficients, the self-diffusion coefficients are the best basis for estimating D_{12} using the Darken relation. If one does find a relation $D_{12} = \mathrm{f}(D_1,D_2)$ that is valid for well-defined reference mixtures, the knowledge of all three coefficients can be used as a probe of liquid structure.

NMR. Self-diffusion coefficients reported here were determined by applying the pulsed field gradient spin-echo (PGSE) technique (Stejskal and Tanner, 1965). Dispersion and refocusing of the spins occur during the experiment. When two identical gradient pulses are applied, the refocusing becomes incomplete due to self-diffusion. The decay of the echo amplitude becomes

$$\frac{A(2\tau)}{A^0(2\tau)} = \exp\left[-\gamma^2 D\delta^2\left(\Delta - \frac{\delta}{3}\right)g^2\right] \tag{5}$$

where τ is the time between the 90° and 180° pulses, D is the self-diffusion coefficients, δ is the duration of the gradient pulse, Δ is the time between the two gradient pulses, and g is the gradient strength. The diffusion time Δ was kept constant while the gradient strength was increased by varying the current through the gradient coil. The gradient dead time was found to be less than 15 ms (Pfeifer, 1992). To ensure that the spin-echo attenuation was solely due to diffusion, the Δ values used were in the range from 40 ms and upward.

Due to erroneous results for short pulse lengths we suspect a finite, positive contribution to the area of the gradient pulse. To remedy this problem, we have performed a pulse length dependent calibration. The effect of a nonrectangular field gradient pulse has been discussed by Price and Kuchel (1991). They treated the Stejskal and Tanner pulse sequence algebraically for various forms of gradient raise and fall and showed numerically that the exact forms of the pulses were of minor importance. The area of the gradient pulse is, however, the crucial parameter in determining diffusion coefficients.

We apply a zero-order correction for the finite damping time of the field gradient pulses (due to eddy currents and image currents). The underlying assumption is that the form and time constant of the damping are constant with respect to the other variables. It is consistent with this approximation to treat the area of the gradient pulse,

$$\int_0^\delta g(t)\,\mathrm{d}t = \delta\cdot g \tag{6}$$

as a rectangular pulse of width $\delta = \delta_\mathrm{n} + \delta_0$ and height g, where δ_n is the nominal, applied pulse length and δ_0 is the constant, zero-order correction. Calibration experiments on water at atmospheric pressure were performed with δ_n varying from 0.2 to 2.0 ms. A linear fit of the results yielded $\delta_0 = 0.094 \pm 0.002$ ms.

The adequacy of this procedure was tested by comparing our results for pure alkanes obtained at varying δ_n with data from the literature. Figure 1 shows the relative deviation for methane, ethane, hexane, octane, and decane. The data from Harris *et al*. (Harris and Trappeniers, 1980; Harris, 1982; Harris *et al*., 1993) were interpolated by Harris using his hard-sphere-model fits with an estimated accuracy of ±2.5%. The data from Greiner-Schmid *et al*. (1991) and Bachl and Lüdemann (1986) were obtained by linear interpolation in T and p, which introduces an inaccuracy in addition to the stated accuracy of ±5% and ±10%, respectively. The mean deviation between our results and the literature data is −1.7%, the standard deviation is 3%, and all points are well within combined inaccuracies.

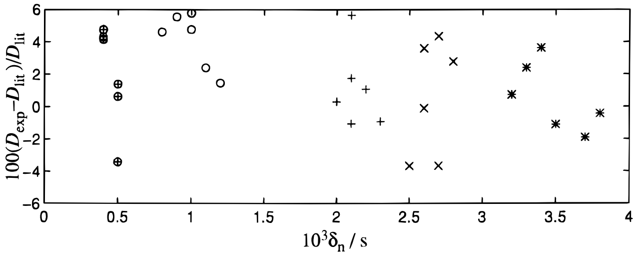

Figure 1. Relative deviation as a function of nominal gradient pulse length δ_n: (⊕) methane, D_{lit} from Harris (1978); (○) ethane, D_{lit} from Vardag *et al.* (1991); (+) hexane, D_{lit} from Harris and Trappeniers (1980); (×) octane, D_{lit} from Harris (1982); (*) decane, D_{lit} from Atwood and Goldstein (1984).

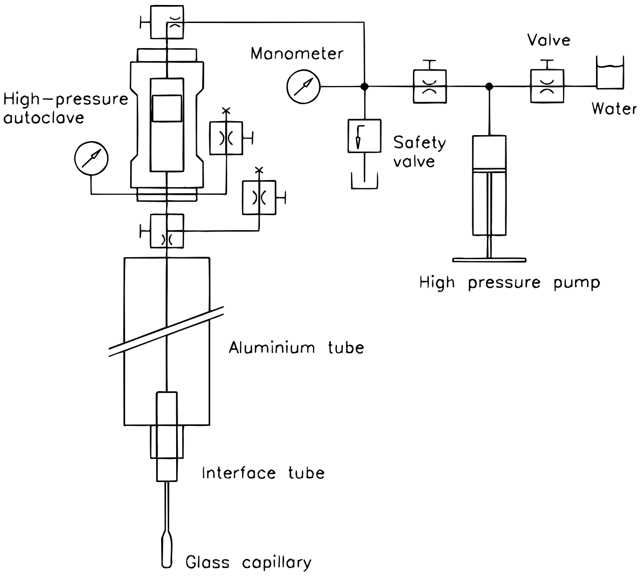

Figure 2. High-pressure experimental setup.

This simple procedure with one additional parameter, δ_0, is evidently sufficient to remove significant systematic errors due to a finite damping contribution to the gradient pulse area.

Experimental Section

Hexane (≥99%), octane (≥99%), decane (≥99%), and benzene (≥99%) were obtained from Merck (Darmstadt, FRG), and methane (≥99.9995%) and ethane (≥99.995%) were obtained from Aga (Tronheim, Norway). All chemicals were used without further purification.

The measurements were performed with a Bruker MSL 200 NMR spectrometer, with a magnetic field of 4.7 T. The home-built probe head for measuring self-diffusion coefficients by the PGSE technique contains Maxwell coil windings (i.e. anti-Helmholz coil) for setting up magnetic field gradients. The probe head was manufactured by the Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe. A pulse gradient unit, manufactured by the Institut für Biophysik und Physikalische Biochemie der Universität Regensburg was operated by the spectrometer to give gradient pulses to the probe. The temperature was regulated by a home-built temperature control system using the thermostating liquid Fluorinert FC77 (3M).

The high-pressure glass capillaries were drawn from Duran 50 glass and glued into the bore of a Cu/Be nipple with Torr Seal, low vapor pressure resin (Varian). This technique originally developed by Yamada (1974), was previously described by Vardag *et al.* (1990).

Table 1. Self-Diffusion Coefficients in Pure Components

comp	T/K	P/ MPa	10^9D/ m^2 s^{-1}	comp	T/K	P/ MPa	10^9D/ m^2 s^{-1}
methane	303.3	30	62	octane	303.3	30	1.90
		40	49			40	1.75
		50	43			50	1.67
	333.1	30	75		333.0	30	2.8
		40	60			40	2.6
		50	51			50	2.4
ethane	303.2	30	18.6	decane	303.3	30	1.10
		40	16.7			40	1.03
		50	15.2			50	0.95
	333.1	30	25		333.0	30	1.72
		40	21			40	1.57
		50	19.2			50	1.45
hexane	303.2	30	3.4				
		40	3.2				
		50	2.8				
	333.0	30	4.5				
		40	4.2				
		50	4.1				

The high-pressure equipment, shown in Figure 2, contains two parts, the high-pressure autoclave and the high-pressure pump. The lower part of the high-pressure autoclave is a titanium interface tube, connected to a $^1/_8$ in. stainless steel tube. The steel tube is about 80 cm long and is housed in a 90 mm aluminum tube. The aluminum tube, with the interface tube and the stainless steel tube, is placed in the NMR magnet with the sample part of the glass capillary positioned in the rf coil of the probe. It is possible to adjust the position of the aluminum tube in the magnet, to get the optimal position of the sample in the rf coil. At the top of the aluminum tube (over the magnet), two valves are connected to the stainless steel tube for the filling procedure. The stainless steel tube is also connected to a cylinder with a piston inside. The purpose of this arrangement is to make it possible to vary the pressure in the sample. Under the piston, the sample is filled all the way down to the glass capillary. Over the piston, a pressure transmitting liquid (water) is contained in a stainless steel tube down to a high-pressure pump. When the desired pressure is applied at the high-pressure pump, the piston in the cylinder will transfer this pressure to the sample side, and the desired pressure will be obtained in the glass capillary.

The composition was determined with the NMR spectrometer by integration of the signal. The filling procedure is therefore done in a quick and rather simple way. The entire sample containing part of the high-pressure equipment is evacuated (to about 10^{-3} mbar). The gas component is filled to a few bars, and the desired amount (approximately) of the liquid component is pumped in by a high-pressure hand pump. Then the rest of the desired gas component is pumped in from a pressure bottle. To obtain a homogeneous mixture, the pressure is changed a few times (2 to 3) in the sample, and the sample is left for about 24 h before measuring.

Results

The measured self-diffusion coefficients in the various mixtures at varying temperatures and pressures are listed in Tables 1−3. The measured self-diffusion coefficients are considered reliable to ±5%.

Discussion

As an example of the pressure, temperature, and composition dependencies, Figure 3 shows the self-diffusion coefficient of ethane as a function of composition at the six different combinations of temperature and pressure in the mixture ethane + octane. The main trend is that the diffusion coefficient increases with (1) increasing temperature, (2) decreasing pressure, and (3) increasing mole fraction of the lighter component. To analyze these trends

Table 2. Self-Diffusion in Mixtures as a Function of Temperature and Pressure

x_1	T/K	P/MPa	$10^9D_1/\mathrm{m^2\,s^{-1}}$	$10^9D_2/\mathrm{m^2\,s^{-1}}$	x_1	T/K	P/MPa	$10^9D_1/\mathrm{m^2\,s^{-1}}$	$10^9D_2/\mathrm{m^2\,s^{-1}}$
Methane (1) + Hexane (2)									
0.27	303.2	30	10.0	4.7	0.72	303.2	30	26	12.2
		40	9.1	4.3			40	23	11.1
		50	8.9	4.1			50	21	9.9
	333.0	30	13.6	6.3		333.2	30	34	16.4
		40	12.4	5.7			40	29	14.2
		50	11.0	5.3			50	26	13.2
0.52	303.3	30	16.5	7.7	0.88	303.2	30	41	18.5
		40	15.0	7.3			40	34	16.6
		50	14.0	6.6			50	30	15.6
	333.2	30	22	10.3		333.1	30	52	23
		40	19.5	9.4			40	40	19.2
		50	17.9	8.4			50	36	16.4
Ethane (1) + Hexane (2)									
0.33	303.3	30	7.2	4.7	0.60	303.3	30	10.2	6.4
		40	6.7	4.2			40	9.5	5.9
		50	6.2	4.0					
	333.1	30	9.7	6.2			50	8.9	5.6
		40	8.8	5.5		333.1	30	13.7	8.9
		50	8.6	5.4			40	12.3	7.8
0.49	303.2	30	9.1	5.5			50	11.5	7.2
		40	8.5	5.3	0.80	303.3	30	13.2	8.9
		50	7.9	5.0			40	12.1	7.9
	333.1	30	12.0	7.5			50	11.4	7.4
		40	11.2	6.9		333.0	30	17.2	11.6
		50	10.3	6.4			40	15.9	10.7
							50	15.6	9.8
Methane (1) + Octane (2)									
0.32	303.2	30	7.6	2.8		333.0	30	15.3	5.9
		40	7.0	2.7			40	14.4	5.3
		50	6.7	2.4			50	12.9	5.1
	333.1	30	10.4	3.9	0.70	303.6	30	15.8	6.2
		40	9.8	3.8			40	14.4	5.7
		50	9.5	3.5			50	13.0	5.3
0.48	303.2	30	9.1	3.3		333.0	30	21	8.3
		40	8.0	3.2			40	18.3	7.0
		50	7.5	2.8			50	16.8	6.6
	333.1	30	11.8	4.8	0.88	303.5	30	39	13.1
		40	10.6	4.1			40	32	12.6
		50	9.6	4.0			50	26	10.6
0.58	303.3	30	11.6	4.4		333.5	30	45	15.4
		40	10.6	4.2			40	37	13.4
		50	10.0	3.8			50	32	13.3
Ethane (1) + Octane (2)									
0.15	303.2	30	3.8	2.1	0.62	303.5	30	7.9	4.4
		40	3.3	2.0			40	7.3	4.0
		50	3.2	1.87			50	6.8	3.6
	333.0	30	4.9	3.0		333.0	30	10.0	5.7
		40	4.8	2.8			40	9.3	5.1
		50	4.4	2.6			50	8.6	5.0
0.44	303.1	30	5.8	3.2	0.81	302.9	30	11.7	6.0
		40	5.4	2.9			40	10.8	5.6
		50	5.0	2.7			50	10.1	5.5
	333.1	30	7.8	4.5		332.6	30	15.2	8.4
		40	7.3	4.0			40	13.6	7.6
		50	6.7	3.7			50	12.5	7.0
Methane (1) + Decane (2)									
0.11	302.7	30	3.8	1.22			40	9.5	2.7
		40	3.7	1.12			50	8.5	2.6
		50	3.3	1.05			60	8.0	2.3
	331.2	30	5.7	1.83		333.7	35	19.4	4.5
		40	5.5	1.66			40	14.0	4.3
		50	5.3	1.59			50	12.7	4.1
0.41	302.2	30	5.0	1.70			60	11.9	3.8
		40	4.7	1.57	0.92	298.9	40	31	10.6
		50	4.3	1.43			45	30	11.1
	331.0	30	7.3	2.5			50	28	9.8
		40	6.8	2.2		331.2	40	39	15.5
		50	6.3	2.1			45	37	14.8
0.63	294.7	35	9.9	2.8			50	35	13.6
Ethane (1) + Decane (2)									
0.12	302.7	30	2.6	1.21	0.66	302.6	30	6.8	3.0
		40	2.4	1.16			40	6.1	2.8
		50	2.3	1.09			50	5.8	2.6
	332.2	30	4.3	1.95		331.9	30	9.2	4.3
		40	3.6	1.63			40	8.6	4.0
		50	3.1	1.51			50	7.7	3.8
0.40	303.3	30	3.7	1.75	0.87	303.2	30	11.4	5.3
		40	3.5	1.49			40	10.5	5.0
		50	3.0	1.47			50	9.7	4.6
	331.8	30	5.0	2.3		331.8	30	15.1	7.2
		40	4.5	2.2			40	13.6	6.2
		50	4.2	2.0			50	12.3	5.7

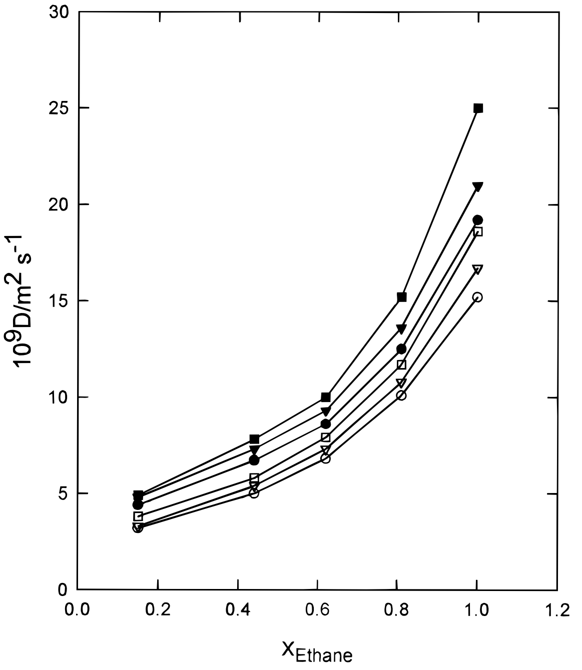

Figure 3. Self-diffusion coefficients of ethane versus mole fraction in the mixture ethane + octane: (■) at 30 MPa and approximately 333 K; (▼) at 40 MPa and approximately 333 K; (●) at 50 MPa and approximately 333 K; (□) at 30 MPa and approximately 303 K; (▽) at 40 MPa and approximately 303 K; (○) at 50 MPa and approximately 303 K.

Table 3. Self-Diffusion in Methane (1) + Hexane (2) + Benzene (3) Mixtures as a Function of Temperature and Pressure ($x_2 = x_3$)

x_1	T/K	P/MPa	10^9D_1/m^2 s^{-1}	10^9D_2/m^2 s^{-1}	10^9D_3/m^2 s^{-1}
0.00	303.2	30		2.9	3.0
		40		2.9	2.8
		50		2.7	2.8
	333.1	30		4.2	4.3
		40		3.8	4.0
		50		3.5	3.8
0.22	303.2	30	8.4	3.9	4.1
		40	7.9	3.6	3.9
		50	7.6	3.5	3.7
	333.1	30	11.8	5.3	5.8
		40	10.2	5.2	5.3
		50	9.6	4.5	5.0
0.32	303.1	30	10.0	4.8	4.9
		40	9.6	4.3	4.5
		50	8.5	4.1	4.2
	333.0	30	13.5	6.6	6.7
		40	12.4	5.8	6.1
		50	11.6	5.1	5.7
0.62	303.2	30	20	9.4	10.1
		40	18.8	8.8	8.9
		50	17.3	8.4	8.7
	333.1	30	27	13.3	13.3
		40	23	11.9	11.9
		50	22	10.5	11.5
0.70	303.2	30	23	12.1	11.9
		40	21	10.7	10.7
		50	18.5	9.9	9.7
	333.2	30	31	15.1	15.1
		40	27	13.8	13.8
		50	24	12.3	12.3
0.80	303.4	30	35	14.8	17.1
		40	30	14.4	15.7
		50	26	12.8	14.2
	333.2	30	45	19.9	23
		40	36	15.4	18.7
		50	30	13.1	15.9

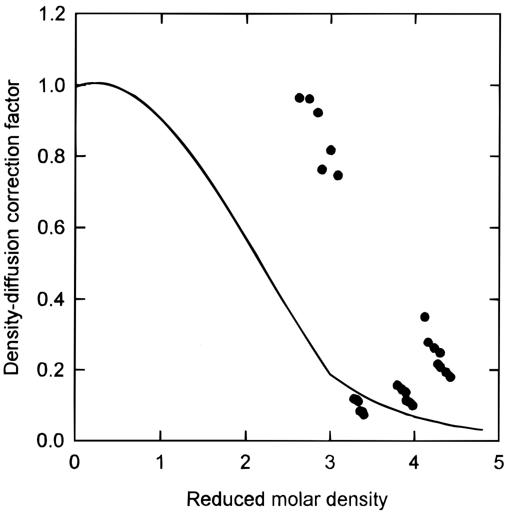

Figure 4. Variation of the density-diffusion correlation factor ($\rho D_{AB}/\rho^0 D^0_{AB}$) with the reduced density (ρ_r): (●) experimental data; (—) da Silva and Berery extended Sigmund correlation.

quantitatively, one needs both reliable density data and a model. Although much work has been done on modeling self-diffusion in pure, dense liquids (Dymond, 1985; Harris, 1995; Assael *et al.*, 1992a, 1992b), this is not the case for mixtures. The so-called Sigmund correlation (Sigmund, 1976) has, however, been used in reservoir engineering applications. The Sigmund correlation (Sigmund, 1976) is applied by the oil industry to determine mutual diffusion coefficients in binary mixtures. It is an empirical correlation based on diffusion data from both organic and inorganic substances. The correlation is an expansion in reduced density $\rho_r = \rho/\rho_c$ of the density-diffusion product divided by the infinite-dilution limit $\rho D_{AB}/\rho^0 D^0_{AB}$. Here ρ_c is the critical density of the pure fluid or mixture. The only mixture of those studied here, for which there exists reliable density data, is methane + decane.

To make sure that the measurements were performed at samples containing only one homogeneous liquid phase, phase diagrams ($P-x$ diagrams) for the measured systems were prepared from the Soave−Redlich−Kwong equation of state (Redlich and Kwong, 1949) and from the experimental data compiled by Knapp *et al.* (1982).

From the experimental self-diffusion coefficients for the system methane + decane, density-diffusion correlation factors have been calculated by adopting the Darken equation (Darken, 1948) and employing interpolated experimental density data from Reamer *et al.* (1956). These results are shown together with the da Silva and Belery extended Sigmund correlation (da Silva and Belery, 1989) in Figure 4.

The figure indicates that the Sigmund correlation does not predict the mutual diffusion coefficient very accurately for the system methane + decane. An increase in pressure represents an increase in reduced molar density, which can be seen in the figure by groups of three to four points forming short straight lines. An increase in temperature at constant composition and pressure leads to an increased diffusion coefficient because of increased thermal molecular motion and decreased density. This effect is qualitatively accounted for by the Sigmund correlation, but as can be seen from Figure 4, the temperature and pressure dependences are not consistent. The main defect of the correlation is that it fails to take into account the reduced density maximum for intermediate compositions at constant pressure and temperature. As the mole fraction of decane in the mixture methane/decane increases, the density-diffusion correction factor decreases, whereas the reduced density goes through a maximum. The diffusion coefficient is therefore not a unique function of the reduced density, as assumed in the Sigmund correlation.

Conclusions

Self-diffusion coefficients have been measured in homogeneous mixtures of methane + hexane, ethane + hexane, methane + octane, ethane + octane, methane + decane, ethane + decane, and methane + hexane + benzene, at 303.2 K and 333.2 K and 30 MPa, 40 MPa, and 50 MPa. The main trend is that the diffusion coefficient increases with increasing temperature, decreasing pressure, and increasing mole fraction of the lighter component. Due to the lack of density data only one of these systems could be used to test the Sigmund correlation. The correlation was found not to fit the experimental data.

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