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Inter- and Intradiffusion in Liquid Mixtures of Methane and *n*-Decane[1]

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The interdiffusion coefficient, D_{12}, has been measured by Mach–Zehnder interferometry for liquid mixtures of methane and *n*-decane at 303 K. The mole fraction of methane was from 0.11 to 0.96 and the pressure was from 30 to 60 MPa. This includes measurements in the critical region, the critical locus being approached from supercritical pressures to within 0.4 MPa. The accuracy in D_{12} is estimated to be from 3 to 10%, depending on the composition. Our data are compared with the Sigmund correlation, which is widely used to estimate diffusion coefficients in hydrocarbons at high pressures. The deviation between estimate and measurement is one order of magnitude for some of the states. We have also compared with a more recent correlation used by Erkey, but this one is not found to be applicable to the compositions studied in the present work. Our data were related to recently measured intradiffusion coefficients, D_1 and D_2, at the same state points. On this basis, we have evaluated different mixing rules for obtaining the interdiffusion coefficient from intradiffusion coefficients, both close to and away from the critical region. It is found that the so-called Darken and Adamson relations have the right qualitative behavior.

KEY WORDS: alkanes; diffusion; high pressure; mixtures.

1. INTRODUCTION

Diffusion data for hydrocarbon systems at high pressure are rather sparse, despite the fact that many industrial and natural processes where diffusion is important occur at high pressure. Two examples are heterogeneous catalysis and migration of hydrocarbons in oil reservoirs. Increased use of supercritical extraction has increased the need for diffusion data at high

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pressure and in the critical region of the mixture. Measurements of the mutual diffusion coefficient is not an easy task if the pressure is higher than a few megapascals, let alone the interpretation of the data if the mixture contains more than two components.

A number of measurements have been made, however, Akgerman and co-workers [1–3] have measured the interdiffusion (mutual diffusion) coefficient for several binary mixtures of alkanes at infinite dilution up to 3.5 MPa, using a Taylor dispersion technique. Lüdemann and co-workers [4–8] have measured the intradiffusion (self-diffusion) coefficient in pure hydrocarbons and their mixtures up to 200 MPa, using nuclear magnetic resonance (NMR). Interdiffusion coefficients for hydrocarbon mixtures at high pressures have also been derived from pressure–time measurements [9–11].

Correlations for diffusion coefficients in liquids are usually developed for atmospheric pressure. When applied to high pressure, they often give very different results [12], and lack of experimental data makes it difficult to assess the quality of the correlations. Most correlation and prediction schemes either disregard the difference between inter- and intradiffusion or deal only with intradiffusion.

In this paper, we report some recent measurements by Mach–Zehnder interferometry of the interdiffusion coefficient for liquid methane/*n*-decane mixtures at 303.2 K and pressures up to 60 MPa over the entire composition range. The data are used in the present context to discuss the application of two existing correlations to high pressure. Some of the state points were chosen as close as possible to those used by Helbæk in a recent series of intradiffusion measurements by NMR [12]. We can thus relate the two sets of data to examine relationships between them.

2. THEORETICAL BACKGROUND

2.1. Interdiffusion

Our analysis of interdiffusion is based on Fick's law for isothermal systems (written here for a two-component system):

$$J_1 = -cD_{12}\nabla x_1 \tag{1}$$

where x_1 is the mole fraction of component 1, taken to be methane, J_1 is the molar flux of component 1 with respect to the volume-fixed reference frame, D_{12} is the interdiffusion coefficient, and $c = c_1 + c_2$, where c_i is the molar concentration of component i. In our interdiffusion experiments the concentration gradient was one-dimensional (in the z-direction). Since the diffusion coefficient is concentration dependent (see Fig. 2), the following diffusion equation was used for analysis:

$$q\frac{\partial x_1}{\partial t}=\frac{\partial}{\partial z}\left[D_{12}q\frac{\partial x_1}{\partial z}+c_1\int_{z_0}^{z}dz'\frac{D_{12}q^2}{v_2c_2}\frac{\partial v_1}{\partial c_1}\left(\frac{\partial x_1}{\partial z'}\right)^2\right] \tag{2}$$

where z_0 is a position outside the diffusion zone, $q=v_2c^2$, and v_i, is the partial molar volume of component *i*.

The thermodynamic driving force is the gradient in chemical potential, $\nabla\mu_1$, which implies that the diffusion coefficient depends on the system's thermodynamic properties as well as the dynamic properties. This suggests splitting the interdiffusion coefficient into a thermodynamic factor, B_x, and a kinetic factor, D^K:

$$D_{12}=B_x\cdot D^K, \qquad B_x=\frac{x_1}{RT}\left(\frac{d\mu_1}{dx_1}\right)_{T,p} \tag{3}$$

The thermodynamic factor equals 1 for ideal systems and at infinite dilution. The kinetic factor, D^K. is closely connected to the diffusion coefficients used in kinetic theory, nonequilibrium thermodynamics, the Maxwell–Stefan description, and the Green–Kubo relations. Using the Green–Kubo relations it may be expressed as

$$D^K=-\left(\frac{x_1M_1+x_2M_2}{M_1M_2}\right)^2\frac{N_0}{3Vx_1x_2c}\int_0^{\infty}dt\,\langle\mathbf{J}_1(0)\cdot\mathbf{J}_2(t)\rangle \tag{4}$$

The variables V, N_0, M_i, and $\mathbf{J}_i$, are the volume, Avogadro's number, molar mass, and microscopic mass current of component *i*, respectively.

The intradiffusion coefficient of component *i*, D_i, may be expressed by the Einstein relation and in terms of the velocity autocorrelation function,

$$D_i=\frac{1}{6t}\langle(\mathbf{r}_i(t)-\mathbf{r}_i(0))^2\rangle=\frac{1}{3}\int_0^{\infty}dt\,\langle\mathbf{u}_i(0)\cdot\mathbf{u}_i(t)\rangle \tag{5}$$

where $\mathbf{r}_i(t)$ is the position and $\mathbf{u}_i(t)$ the velocity of particle *i* at time *t*. The mean square displacement is measured by a pulsed-gradient spin-echo technique [12]. In this case, there is no external force or inhomogeneity in the system, and the method measures the Brownian motion of the particles.

2.2. The Relation Between Inter- and Intradiffusion

Much effort has been put into relating inter- and intradiffusion of liquid mixtures [13]. Equations (4) and (5) express both D^K and D_i as velocity time–correlation functions. Since the intradiffusion coefficients are defined purely by autocorrelation, while D^{K} contains correlations between different particles, one cannot in general expect to obtain D^{K} from D_1 and D_2 only. Nonetheless, several forms of the kinetic factor have been suggested, for example, the Adamson relation $D^{\mathrm{K}}_{\mathrm{A}} = \phi_2 D_1 + \phi_1 D_2$ [14], where ϕ_i is the volume fraction of component i, and the Darken relation $D^{\mathrm{K}}_{\mathrm{D}} = x_2 D_1 + x_1 D_2$ [15]. The $D^{\mathrm{K}}_{\mathrm{A}}$ reduces to $D^{\mathrm{K}}_{\mathrm{D}}$ for thermodynamically ideal mixtures (and therefore at infinite dilution). Tyrrell [16] has shown, based on the formalism of resistance coefficients, that there is no a priori reason why the Darken relation should be valid even for ideal mixtures. Hertz and Leiter [17] have defined reference cross-correlation functions that have been used extensively to study deviation from "ideality" of diffusive motion. The search for an "ideal" or reference cross-correlation function is effectively the same as defining an ideal kinetic factor, $D^{\mathrm{K}}_0(D_1, D_2)$. The reference functions of Hertz and Leiter incorporate the same assumption as the Darken relation [18]. Other modeling attempts for D^{K} have been based on kinetic theory (e.g., Al-Chalabi and McLaughlin [19]), but there is as yet no generally accepted definition of the ideal composition dependence of $D^{\mathrm{K}}(D_1, D_2)$.

3. EXPERIMENTS

The interdiffusion coefficients were measured with a high-pressure Mach–Zehnder interferometer. The basic components of this apparatus have been described by Killie et al. [20], but several modifications have improved its accuracy. The method is transient, nonintrusive, and absolute, based on the relaxation of an initial, preferably step-like concentration profile. A description of the modified apparatus and method of analysis will be published separately [21].

The *n*-decane used was produced by Merck with a stated purity of 99.5% and the methane was from AGA and had a stated purity of 99.9995%.

At the start of each experiment, the cell contained an equilibrated liquid mixture of methane and *n*-decane. A new mixture, which contained 0.2–1.5 mol% more decane, was injected through inlets in the bottom of the cell. The heavier mixture displaced the lighter in such a way that a steep concentration profile was maintained. The cell was then left to equilibrate over a period of several hours, the first 1–12 of which (depending on the diffusion rate) were used to record light intensities from the interferometer. The content of the diffusion cell was analyzed after the experiments and the concentration was then determined to within ±0.3%.

The precision of the data presented here, taken as the reproducibility of results under nominally identical conditions, is estimated to ±1%. Measurements of D_{12} of NaCl in water had a reproducibility of ±0.6% and agreed with the compiled data fit of Rard and Miller [22] within ±0.3%. The location in state space of each measurement represents an uncertainty in D_{12} when assigned to a specific state point. The temperature never varied more than ±0.1 K, the typical standard deviation being 0.03 K. The largest difference between two individual experiments was 0.3 K. The pressure usually decreased during an experiment due to volume change on mixing, but never more than 0.3 MPa. During experiments in the "critical region" (at pressures below 40 MPa) the pressure was adjusted as never to vary more than ±0.03 MPa.

For the data at mole fractions of methane of 0.91 or less, the resulting accuracy of the interdiffusion coefficients is estimated to ±3%. At the highest methane concentrations a change of mole fraction of 0.3% changes the diffusion coefficient by 10%, which is the reason for the large uncertainty in our data at the highest methane concentrations. The interdiffusion experiments reported here were all performed at 303.2±0.2 K and at pressures and compositions shown in Fig. 1. Included are also the

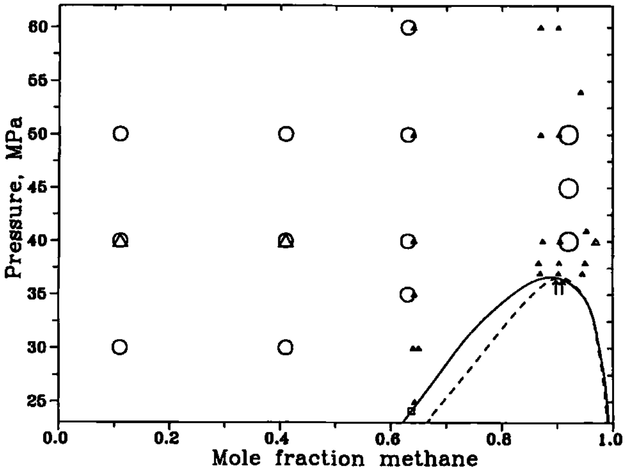

Fig. 1. State points of interdiffusion (triangles) and intradiffusion (circles) experiments together with the phase envelope from experiment (solid line) and from the PR EOS (dashed line). The sizes of the symbols reflect the individual accuracy of the concentration determination. The arrows indicate the critical compositions from experiments [27] (lower composition) and the PR EOS. Also shown is the state point used by Reamer et al. [9] (square).

compositions and pressures of the intradiffusion experiments of Helbæk [12]. Helbæk's data had to be interpolated in temperature before comparison with the interdiffusion data.

4. RESULTS AND DISCUSSION

The measured interdiffusion coefficients are given in Table I and plotted as functions of mole fraction in Fig. 2 and as function of pressure in Fig. 3. The lines between the points indicate the trends in the data. One observes that when approaching the critical point, the diffusion coefficient tends to zero. For compositions in the range $0.64 < x_1 < 0.93$, D_{12} increases with increasing pressure. For $x_1 = 0.64$, D_{12} is independent of pressure to within experimental accuracy. The data point from Reamer et al. [9] shown in Fig. 2 was measured at 310.9 K at the composition and pressure indicated in Fig. 1. We believe that the deviation of 55% relative to our data is due to the general problem of extracting diffusion coefficients from pressure–time measurements.

A theory for crossover of transport coefficients in binary mixtures from the classical region to the asymptotic critical region has recently been developed [23–25]. It is customary to split the diffusion coefficient into the background, D^{b}, and critical enhancement, ΔD: $D_{12} = D^{b} + \Delta D$. The two parts scale approximately as $D^{b} \sim B_x$ and $\Delta D \sim B_x^{1/2} \cdot \Omega$, where Ω is a crossover function tending to zero in the classical region and to unity in the asymptotic critical region [25]. It is outside the scope of this paper to analyze our data in this context, and we do not know if our measurements are in the region where ΔD is significant. To investigate this further one needs accurate values for B_x.

The thermodynamic factor B_x was determined from the Peng–Robinson (PR) equation of state (EOS). The PR equation was chosen because it is reported to give the best predictions for the methane/*n*-decane system [26]. The binary interaction parameter was adjusted to the value 0.0265 to get the experimental critical pressure, and the resulting phase envelope and critical composition is shown in Fig. 1. Reamer et al. [27] have measured the critical line at temperatures from 310.9 to 510.9 K. Extrapolating their data to 303.2 K, we find the corresponding critical point at $p_c = 36.63$ MPa and $x_c = 0.899$. We also tried to build a model from published data on volumetric properties in the region of interest. This did not give consistent results, a problem that has been reported previously [28].

The intradiffusion data of Helbæk have a stated accuracy of 5%. The data of Helbæk for pure *n*-decane and pure ethane agree with those of Lüdemann and co-workers [4, 6] within 2%. But the data for pure

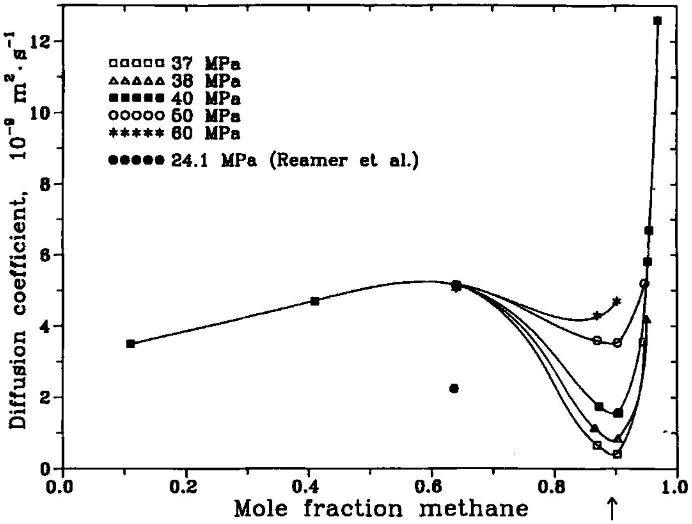

Fig. 2. Interdiffusion coefficients at 303.15 ± 0.2 K as a function of mole fraction at 37 to 60 MPa. Also shown is the result of Reamer et al. [9] at 310.9 K.

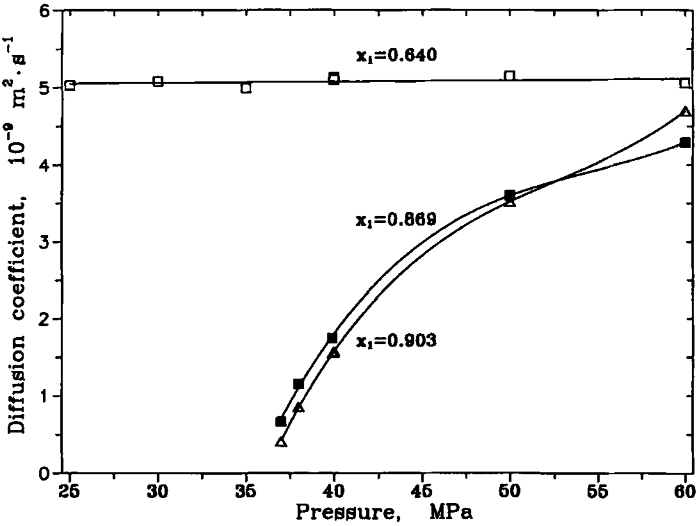

Fig. 3. Interdiffusion coefficients as a function of pressure at mole fractions of 0.640 ± 0.002 (open squares), 0.869 ± 0.002 (filled squares), and 0.903 ± 0.001 (open triangles).

Table I. Experimental Interdiffusion Coefficients

Mole fraction x_1	Press. (MPa)	Temp. (°C)	D_{12} ($10^{-9} \cdot m^2 \cdot s^{-1}$)
0.11	40.0	30.02	3.5
0.41	39.3	29.88	4.7
0.643	25.0	30.07	5.0
0.650	30.0	30.15	4.9
0.642	35.0	30.09	5.0
0.640	40.0	30.12	5.0
0.640	50.0	30.12	5.2
0.640	60.0	30.12	5.1
0.869	37.0	30.14	0.67
0.866	38.0	30.13	1.11
0.873	39.9	30.23	1.64
0.870	50.0	30.20	3.2
0.870	60.0	30.14	4.3
0.902	37.0	30.24	0.39
0.903	38.0	30.28	0.86
0.904	39.5	30.30	1.55
0.905	40.0	30.27	1.52
0.903	50.0	30.30	3.5
0.902	60.0	30.31	4.7
0.945	37.0	30.42	3.6
0.950	38.0	30.42	4.3
0.952	41.0	30.47	6.0
0.942	53.5	30.11	4.4
0.97	40.0	30.00	12.6

methane is 28% too high with respect to those of Harris [29] and Greiner-Schmid et al. [4]. The cause of this discrepancy is nonideal gradient pulses for short pulse lengths.[4] We have fitted the temperature-interpolated data of Helbæk together with the pure methane data of Harris to calculate D_A^K and D_D^K as functions of composition and pressure. The fit has a standard deviation of 2%, but between the measured compositions and at $x_1 > 0.65$ it may be regarded as reliable only to -5 to $+15$%.

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[4] The gradient coil used by Helbæk has been recalibrated and the data corrected. The data used for Figs. 4 and 5 are 6% too high at $x_1 = 0.11$ and 0.41, correct at $x_1 = 0.63$, and 15% too high at $x_1 = 0.92$. This does not, however, alter the qualitative comparisons made, and numbers given in the text are corrected.

Figure 4 shows the Adamson and Darken relation predictions $D_A = D_A^K B_x$ and $D_D = D_D^K B_x$ together with the measured D_{12}. In the region of the critical composition both D_A and D_D show the same trend as the interdiffusion data, the main cause of deviation is the shift of the minimum due to the erroneous critical composition of the EOS. At $x_1 = 0.41$, D_A is 17% and D_D is 36% lower than D_{12}. At $x_1 = 0.64$ the deviations range from +8 to +20% for D_A and from −18 to −27% for D_D. With the available information it is impossible to decide whether the deviations for $x_1 < 0.65$ are due to the two D^K models, the EOS model for B_x, or both. This is a general problem in most investigations on inter-/intradiffusion relationships: The B_x factor has a low accuracy or the accuracy is not stated at all.

Figure 5 shows all recent methane/*n*-decane diffusion data together with the Sigmund correlation [30, 31]. The densities used here were obtained by interpolation in the data tables of Reamer et al. [27]. The Sigmund correlation is widely used in the oil industry for estimation of diffusion coefficients [32]:

$$\frac{\rho D}{\rho^0 D^0} = \sum_i a_i \rho_r^i \tag{6}$$

where ρ is the density, $\rho_r = \rho/\rho_c$, with ρ_c being the critical density and $\rho^0 D^0$ the density-diffusion product in the dilute gas limit. The parameters a_i were fitted to both intra- and interdiffusion data compiled until 1976 of mostly hydrocarbons in both the gas and the liquid phase. An ad hoc extension for $\rho_r > 3$ was later proposed by daSilva and Belery [32]. The open circles in Fig. 5 are D_D^K, from the measurements by Helbæk, times the density divided by the dilute gas density–diffusion product. One observes that the open circles are grouped together in four groups (mole fraction, top to bottom: 0.92, 0.63, 0.41, 0.11). Inside each group the trend from changing temperature and pressure is the same as that of the Sigmund correlation. From this one may infer that the correlation describes the temperature and pressure dependence qualitatively right, whereas the concentration dependence of the kinetic factor is totally wrong. There are several reasons for this discrepancy, one being the expansion in reduced density, ρ_r, instead of in some close-packed density. Another main defect of the correlation is that it does not discriminate between intra- and interdiffusion.

Christoffersen et al. [11] have done pressure–time measurements on mixing (gas/oil) hydrocarbons and calculated diffusion coefficients from this by using the Sigmund correlation to model the pressure and composition dependence. Their results may be used in reservoir simulators

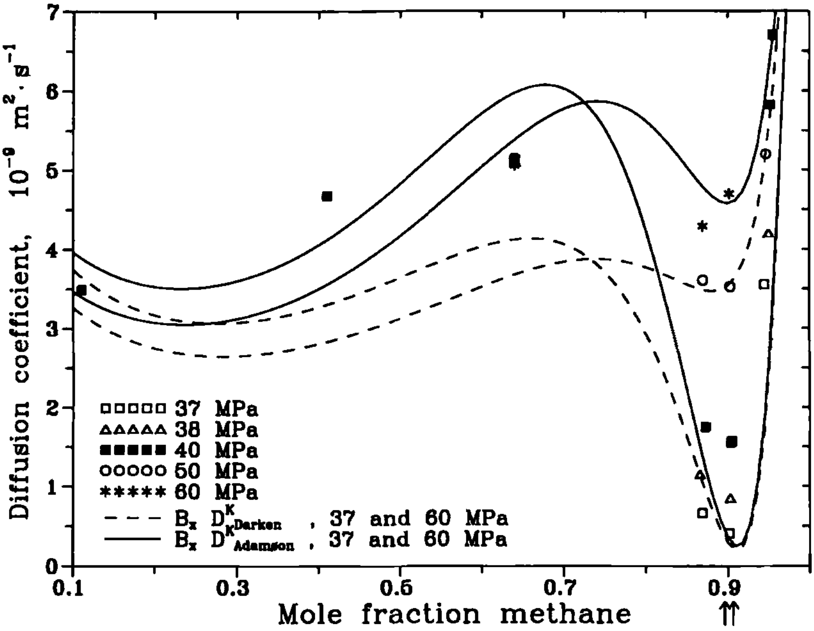

Fig. 4. Interdiffusion coefficients as a function of mole fraction. Darken [15] and Adamson [14] relations are obtained with thermodynamic factor from PR EOS and experimental intradiffusion data [12]. The arrows indicate the critical composition from experiments [27] and PR EOS.

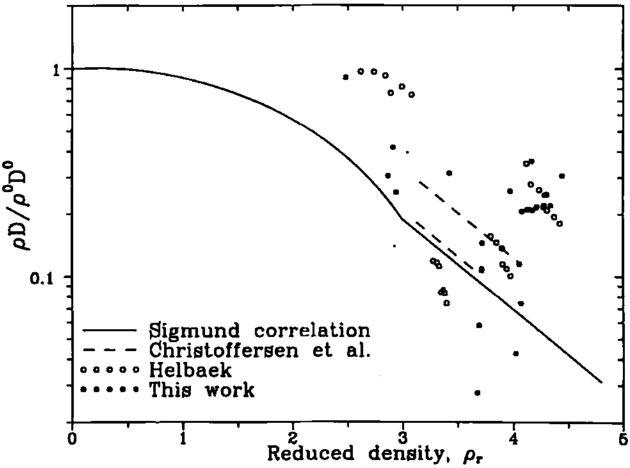

Fig. 5. The product of the density and the diffusion coefficient (relative to the zero-density limiting value) versus the reduced density. The graph shows a comparison between the Sigmund correlation [30, 31] (including the daSilva and Belery extension [32]) and experimental data in the high-pressure regime.

based on the same model but may not be interpreted as Fickian diffusion coefficients.

Erkey et al. [3, 33] have modeled certain infinitely diluted mixtures of *n*-alkanes by extracting translational–rotational parameters from measurements. They have included the effect of B_x and proposed but not tested a mixing rule. In an attempt to generalize their findings [34] they have constructed a correlation for interdiffusion in *n*-alkane mixtures at infinite dilution, where D_{12} is proportional to $(V - bV_0)$, V is the molar volume, V_0 a close-packed volume of the solvent, and b a solute–solvent factor. For methane in *n*-decane at infinite dilution the correlation agrees with an extrapolation from our data, but attempting to extrapolate their model to other compositions leads to negative D_{12}. The cause is probably that their model is based on infinite dilution data only.

The most recent and coherent effort at constructing correlation formulae for dense fluid transport coefficients is that of Assael et al. [35–38]. They use an expansion in reduced volume, $V_r = V/V_0$, that was fitted to data over a wide volume range. They have recognized the difficulty of the composition dependence of diffusion coefficients and have yet (to our knowledge) treated only intradiffusion in pure fluids.

5. CONCLUSIONS

We have presented new data for interdiffusion in mixtures of methane and *n*-decane at 303.2 K and supercritical pressures. The accuracy of the data is ±3%, except for methane mole fractions higher than 0.91, where it is ±10% due to the uncertainty of the compositions reported and the strong dependency of the diffusion coefficient on the composition in this region. We have not found any existing correlation that agrees with our data in the composition range we have measured. The available models for both the thermodynamic and the kinetic contributions to interdiffusion are not sufficiently accurate to predict interdiffusion in supercritical mixtures of methane and *n*-decane.

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