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Diffusion Coefficients and Viscosities of $CO_2 + H_2O$, $CO_2 + CH_3OH$, $NH_3 + H_2O$, and $NH_3 + CH_3OH$ Liquid Mixtures

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To evaluate quantitatively the results of gas−liquid absorption experiments, accurate liquid-phase diffusion coefficients and viscosities are needed. In this paper experimental values of these quantities will be reported for the binary systems carbon dioxide + water, carbon dioxide + methanol, ammonia + water, and ammonia + methanol. The diffusion coefficients have been measured using the Taylor−Aris dispersion method, and the viscosities have been measured with a falling ball viscometer at temperatures from 293 to 333 K. The ammonia mole fraction ranged from 0 to 0.312. The results have been correlated using Arrhenius-type equations and have been compared with literature data, where available. Furthermore, the measured diffusion coefficients are compared with values predicted by the modified Stokes−Einstein equation and the Wilke−Chang equation.

1. Introduction

Liquid-phase mass transfer coefficients determined from absorption experiments in a stirred cell with a smooth gas−liquid interface using a pure slightly soluble gas can be correlated using a Sherwood correlation as shown, among others, by Versteeg (1986). The main physical properties influencing the mass transfer coefficient are the diffusion coefficient of the solute in the solvent and the viscosity of the solvent. In cases of absorption of pure highly soluble gases, it is expected that convective transport mechanisms will become important and as a consequence that the mass transfer coefficient will become a function of the solubility of the gas. The convective transport contribution (i.e., drift) can be described on the basis of the Maxwell−Stefan theory for mass transport. To demonstrate the validity of the Maxwell−Stefan theory for describing liquid-phase mass transport, both qualitatively and quantitatively, gas−liquid absorption experiments have previously been carried out in a stirred cell where the following gas + liquid systems have been studied: carbon dioxide + water, ammonia + water, carbon dioxide + methanol, and ammonia + methanol. As diffusion coefficients, which are necessary for the validation of the theory, on these systems, except for carbon dioxide + water, are scarce, show a large scatter, or are not available, these have been measured in the present work using the Taylor−Aris dispersion method (Snijder *et al.*, 1993; 1995). This method gives diffusion coefficients of dissolved gases, salts, and liquids in liquids with an accuracy of 1−2% within relatively short measuring times (2−3 h). Furthermore, calibration of the apparatus is not required, and measurements can be fully automated, resulting in a 24-h-a-day availability. Viscosities, which are also necessary for the validation of the theory, of the pure solvents are well known, but results on mixtures with ammonia are scarce. Therefore, these have also been measured using a falling ball viscometer.

2. Experimental Section

2.1. Theory of the Taylor−Aris Dispersion Method. When a pulse of solute is introduced into a solvent flowing through a straight narrow tube, dispersion of this pulse will occur due to the radial velocity profile and the process of radial and axial molecular diffusion. If the dimensionless time $\tau = Dt/R^2$ exceeds 5, where D is the diffusion coefficient, t is the time, and R is the inner tube radius, radial concentration profiles are virtually absent and the following analytical expression is valid for the solute concentration (Snijder, 1992):

$$C = \frac{N_{\mathrm{inj}}}{2\pi R^2(\pi K t)^{1/2}} \exp\left[-\frac{(x - ut)^2}{4Kt}\right] \qquad (1)$$

In this expression C is the solute concentration in the solvent, N_{inj} is the amount of solute introduced into the solvent, x is the distance from the tube inlet, u is the average liquid velocity, and K is given by

$$K = u^2R^2/48D + D \qquad (2)$$

Equation 1 describes axial dispersion around position $x = ut$ in the tube with dispersion coefficient K. As evident from inspection of eq 2, K is a function of the diffusion coefficient, the average velocity, and the inner tube radius. By measuring the solute concentration C at the outlet of the tube as a function of time, N_{inj}, u, and K can be calculated by fitting the experimental concentration versus time curve using eq 1. The diffusion coefficient D can then be calculated from u and K using eq 2.

Equation 1 is valid in cases where a δ-Dirac injection pulse is used and the fluid is flowing in a straight tube. In the experimental setup errors are introduced as the solute pulse has a finite length and the tube is curved. Baldauf and Knapp (1983) demonstrated that as long as $\delta L/L < 0.01$, where δL and L are, respectively, the length of the pulse and the tube length, the error in the measured diffusion coefficient is less than 1% (in our case $\delta L/L = 0.006$). Flow through a curved tube causes development of secondary flow. Janssen (1976) derived that the apparent diffusion coefficient increases when the dimensionless group De^2Sc (Sc is the Schmidt number and De is the Dean number ($=(Re)(R/R_c)^{-0.5}$ where Re is the Reynolds number and R_c is the coil radius)) is larger than a critical value. This critical value can be determined by varying the liquid velocity. For sufficiently low velocities the apparent diffusion coefficient will obtain a constant value which is the true diffusion coefficient.

2.2. Experimental Procedure. The flow scheme of the experimental setup for measuring the diffusion coefficients is given in Figure 1. For a detailed description of the

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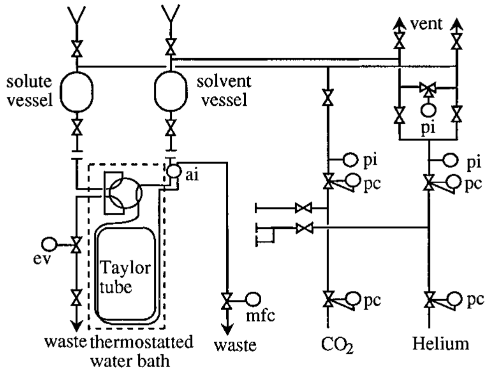

pi: pressure indicator
pc: pressure controller
mfc: liquid mass flow controller
ev: electrical valve
ai: differential refractometer

Figure 1. Experimental setup of the Taylor–Aris dispersion technique for measuring diffusion coefficients.

Table 1. Characteristics of the Taylor–Aris Dispersion Experimental Setup

tube length	L	15.085 m
tube inner radius	R	5.57×10^{-4} m
smallest coil radius	R_c	0.1 m
injector volume	V_{inj}	8.76×10^{-8} m^3
detector volume	V_{det}	8×10^{-9} m^3

equipment see Snijder *et al.* (1993, 1995). The dimensions of the setup are given in Table 1.

The following chemicals have been used: deionized water, methanol (Merck, p.A.), methanol (Merck, p.A.) saturated with NH_3 (Hoekloos), 25% and 32% NH_4OH (Merck, respectively p.A. and pure), and CO_2 (Hoekloos).

For the binary systems $CO_2 + H_2O$ and $CO_2 + CH_3OH$ the solvent and the solute vessels were filled with pure solvent prior to an experiment. Subsequently the liquids were degassed by stripping with helium and additionally the liquid in the solute vessel was saturated with CO_2. The solvent and solute vessels were pressurized to 4 bar with, respectively, He and CO_2. For the binary systems $NH_3 + H_2O$ and $NH_3 + CH_3OH$, the solvent vessel was filled with the pure solvent or solvent with a known mole fraction of NH_3. The solute vessel was filled with the same liquid containing a small extra amount (N_{inj}) of ammonia ($\Delta x_1 = 0.01-0.03$). Both vessels were stripped with He for a short time and pressurized with He. The ammonia mole fraction was determined by titration with 0.1 N HCl. Stripping the liquid mixtures with He resulted in a negligible change of the ammonia mole fraction: $\Delta x < 0.005$. The liquid flow rate was controlled by means of a mass flow controller (Rosemount Flowmega 5881). The (excess) solute concentration at the outlet was measured using a differential refractometer (Varian, RI-4). For each binary system the effect of pressure, initial excess solute concentration, and liquid velocity on the experimental diffusion coefficient was determined. The pressure showed no influence on the experimental value, and the initial excess solute concentration and liquid velocity were chosen sufficiently low to show negligible influence on the experimental diffusion coefficient. This indicates that disturbances due to density gradients and secondary flow are negligible (Snijder, 1992). Experiments with $CO_2 + H_2O$ were conducted to determine the accuracy of the method and the present experimental setup.

Liquid-phase viscosity measurements were made with a Haake falling ball microviscometer. Times needed for a sphere (diameter 3.175 mm and density 7800 kg/m^3) to fall a certain distance through a narrow tube filled with the liquid were measured. Calibration with water at 20 °C provides the viscosity of the liquid. The accuracy of the setup is estimated to be within ±2%.

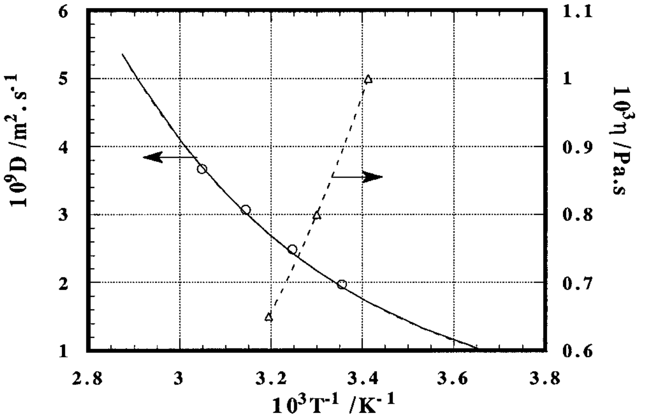

Figure 2. Comparison between experimental data and literature data for the diffusion coefficients (○, own data; —, Versteeg (1986)) and viscosities (△, own data; - - -, interpolation of data from White and Twining (1913), Weber (1955, 1963), and Swindells et al. (1952, 1954)) of the $CO_2 + H_2O$ system.

3. Results

The diffusion coefficients and viscosities have been presented in, respectively, Tables 2 and 3. The data have been correlated using Arrhenius-type equations (eq 3) and

$$Y = Y_o \exp(-E_a/RT) \tag{3}$$

are shown in Table 4. For reference purposes the available literature data have been included in Tables 2 and 3. For the binary system $CO_2 + H_2O$ Versteeg (1986) correlated a vast amount of literature diffusion data, and therefore his correlation is presented instead of the original data.

3.1. $CO_2 + H_2O$. The diffusion coefficients and the viscosities for the $CO_2 + H_2O$ system are shown in Figure 2. Our experimental data, represented by the symbols, are in good agreement with literature data, the differences for the diffusion coefficients being smaller than 2.5% and those for the viscosities being smaller than 1%. It can be concluded that diffusion coefficients and liquid viscosities can be measured with the equipment used in the present study.

3.2. $CO_2 + CH_3OH$. The results for $CO_2 + CH_3OH$ are shown in Figure 3. The diffusion coefficients found in the literature show a large scatter: at $T = 298$ K reported values vary from 4.54×10^{-9} up to 8.37×10^{-9} m^2/s. Taking this fact into account, our data agree well with the values reported by Chen and Chen (1985) who also used the Taylor–Aris dispersion method (within 10–15%). The energy of activation (E_a in eq 3) for diffusion of the $CO_2 + CH_3OH$ system is remarkably low compared to the one found for the $CO_2 + H_2O$ system: respectively 9.3 and 17 kJ/mol (see Table 4).

The average deviation between our experimental viscosity data and the reference data for pure methanol is about 4%. The energy of activation of the liquid-phase viscosity is also lower than the one found for the $CO_2 + H_2O$ system: respectively 13 and 16 kJ/mol (see Table 4).

3.3. $NH_3 + H_2O$. The solubility of ammonia in water is very high, $x_{NH_3} = 0.34$ at 25 °C and $P = 1$ bar, and therefore the diffusion coefficient and viscosity can be measured as functions of the ammonia concentration. Figure 4a shows a deviation plot of the fit correlation for this binary system (see Table 4), the experimentally

Table 2. Experimental and Reference Data on the Diffusion Coefficients of the Binary Systems $CO_2 + H_2O$, $CO_2 + CH_3OH$, $NH_3 + H_2O$, and $NH_3 + CH_3OH$ as a Function of the Molar Solute Fraction x_1 and Temperature T

system	x_1	T/K	$10^9D/(m^2 \cdot s^{-1})$ this work	$10^9D/(m^2 \cdot s^{-1})$ lit.
CO_2 (1) + H_2O (2)	0	298	1.97	*o*
		308	2.49	
		318	3.07	
		328	3.67	
CO_2 (1) + CH_3OH (2)	0	279		4.29[a]
		293	4.75	6.12[b]
		298	5.13	5.55,[a] 8.37[c]
		298		4.54,[d] 4.95[e]
		298		8.02[f]
		303	5.36	
		308	5.78	
		313	6.11	6.89[a]
		318	6.53	
		323	6.90	
		328	7.10	
		333	7.54	8.44[a]
		348		9.89[a]
NH_3 (1) + H_2O (2)	0 ($\Delta x_1 = 0$)	293	1.51	
		298		2.10,[g] 2.50[h]
		303	1.90	
		313	2.41	
		323	2.86	
		333	3.39	
	0 ($\Delta x_1 = 0.03$)	293	1.71	
		303	2.20	
		313	2.75	
		323	3.32	
		333	3.95	
	<0.02	277		1.23[i]
		281		1.08[j]
		284		1.16[j]
		285		1.64[k]
		286		1.21[j]
		287		1.22[j]
		288		1.29,[j] 1.78[l]
		290		1.84[m]
		293		1.46[n]
NH_3 (1) + H_2O (2)	0.053	293	1.94	
		303	2.45	
		313	3.05	
		323	3.72	
		333	4.41	
	0.105	293	2.02	
		303	2.56	
		313	3.18	
		323	3.87	
		333	4.61	
	0.157	293	2.20	
		303	2.76	
		313	3.43	
		323	4.19	
		333	4.97	
	0.209	293	2.37	
		303	2.97	
		313	3.69	
		323	4.50	
		333	5.31	
	0.312	293	2.64	
		303	3.30	
		313	4.06	
		323	4.94	
NH_3 (1) + CH_3OH (2)	0	293	2.12	
		303	2.54	
		313	3.03	
	0.02	293	2.11	
		303	2.58	
		313	3.23	
	0.04	293	2.18	
		303	2.69	
		313	3.33	
	0.16	293	2.66	
		303	3.25	
		313	3.94	
	0.22	293	2.97	
		303	3.58	
		313	4.31	
	0.23	293	2.99	
		303	3.47	
		313	4.28	

[a] Chen and Chen (1985). [b] Vitovec (1968). [c] Won et al. (1981). [d] Takahashi and Kobayashi (1982). [e] Takeuchi et al. (1975). [f] Hikita et al. (1959). [g] Leaist (1985). [h] Godfrey (1973). [i] Scheffer (1888). [j] Hüfner (1897, 1898). [k] Arrhenius (1892). [l] Abegg (1893). [m] Gyunter and Pfeifer (1964). [n] Voigtländer (1889). [o] Versteeg (1986). $D = 2.35 \times 10^{-6} \exp(-17600/RT)$.

determined diffusion coefficients, and the available literature values. For this binary system it turned out that the experimentally determined diffusion coefficient in pure water, $x_1 = 0$, depends on the initial excess solute concentration Δx_1. In Figure 4a both the results for $\Delta x_1 = 0.03$ and the results obtained from a linear extrapolation to $\Delta x_1 = 0$ are shown. The data with $x_1 > 0$ could be fitted using an Arrhenius-type equation where the preexponential factor Y_o (see eq 3) is a linear function of the ammonia fraction. It can be seen from the figure that the fit correlation does not represent the experimentally determined diffusion coefficients in pure water. A possible explanation for this phenomenon is the dissociation of aqueous ammonia, which becomes more pronounced at low fractions of NH_3. Landolt Börnstein (1969) summarizes diffusion coefficients from the literature. Most of the data are from before 1900 and have validity for diluted systems ($x_1 < 0.02$). They either coincide with our experimental data for $x_1 = 0$ with $\Delta x_1 = 0$ or are close to the values calculated with the fit correlation. The values reported by Leaist (1985) and Godfrey (1973) are, respectively, 20% and 40% higher than our experimental values at $x_1 = 0$ and 5% and 25% higher than the values calculated with the fit correlation.

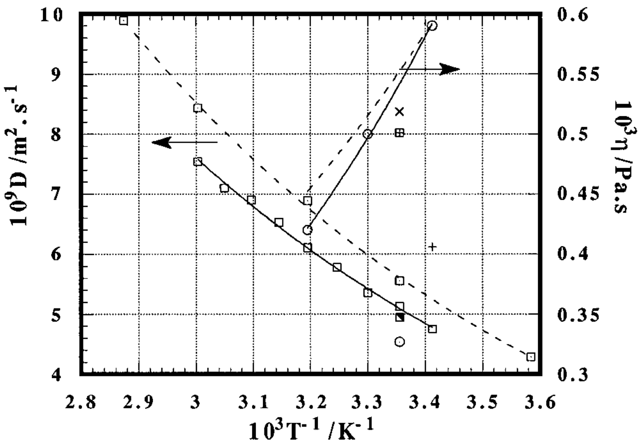

Figure 3. Diffusion coefficients (□, own data; ⊡, Chen and Chen (1985); ×, Won et al. (1981); +, Vitovec (1968); ⊙, Takahashi and Kobayashi (1982); ◪, Takeuchi et al. (1975); plus sign inside box, Hikita et al. (1959)) and viscosities (○, own data; - - -, interpolation of data from Isakowa and Oznewa (1966), Bridgman (1949), and Bridgman (1925)) of the $CO_2 + CH_3OH$ system.

It can be seen from Table 3 and Figure 4b that the viscosities reported by Kanitz (1891) and Blanchard and

Table 3. Experimental and Reference Data on the Viscosities of the Binary Systems $CO_2 + H_2O$, $CO_2 + CH_3OH$, $NH_3 + H_2O$, and $NH_3 + CH_3OH$ as a Function of the Molar Solute Fraction x_1 and Temperature T

system	x_1	T/K	$10^3\eta$/(Pa·s)	
			this work	lit.
CO_2 (1) + H_2O (2)	0	293	1.00	1.00^{a-c}
		303	0.80	$0.80^{b,c}$
		313	0.65	$0.65^{b,c}$
CO_2 (1) + CH_3OH (2)	0	293	0.59	0.59^{d}
		303	0.50	$0.52^{e,f}$
		313	0.42	0.45^{d}
NH_3 (1) + H_2O (2)	0	293	1.00	
		298		0.89^{g}
		303	0.80	
		313	0.65	
	0.02	298		0.91^{g}
	0.04	298		$0.93^{g,h}$
	0.053	293	1.09	
		303	0.86	
		313	0.69	
	0.08	298		0.96^{h}
	0.105	293	1.16	
		303	0.92	
		313	0.72	
	0.157	293	1.21	
		303	0.97	
		313	0.75	
	0.16	298		1.04^{h}
	0.209	293	1.26	
		303	1.00	
		313	0.79	
NH_3 (1) + CH_3OH (2)	0	293	0.59	
		303	0.50	
		313	0.42	
	0.16	293	0.57	
		303	0.48	
		313	0.40	
	0.23	293	0.55	
		303	0.48	
		313	0.39	

[a] White and Twining (1913). [b] Weber (1955, 1963). [c] Swindells et al. (1952, 1954). [d] Isakowa and Oznewa (1966). [e] Bridgman (1949). [f] Bridgman (1925). [g] Kanitz (1891). [h] Blanchard and Pushee (1904, 1912).

Table 4. Correlations of the Experimental Data on the Diffusion Coefficients and Viscosities of the Binary Systems $CO_2 + H_2O$, $CO_2 + CH_3OH$, $NH_3 + H_2O$, and $NH_3 + CH_3OH$ Using Eq 3

system	correlations
$CO_2 + H_2O$	$D = 1.81 \times 10^{-6} \exp(-16900/RT)$
	$\eta = 1.18 \times 10^{-6} \exp(16400/RT)$
$CO_2 + CH_3OH$	$D = 2.22 \times 10^{-7} \exp(-9340/RT)$
	$\eta = 2.91 \times 10^{-6} \exp(12900/RT)$
$NH_3 + H_2O$	$D = (1.65 + 2.47x_{NH_3}) \times 10^{-6} \exp(-16600/RT)$
	$\eta = (0.67 + 0.78x_{NH_3}) \times 10^{-6} \exp(17900/RT)$
$NH_3 + CH_3OH$	$D = (0.96 + 1.74x_{NH_3}) \times 10^{-6} \exp(-15000/RT)$
	$\eta = (2.52 - 0.64x_{NH_3}) \times 10^{-6} \exp(13300/RT)$

Pushee (1904, 1912) are somewhat lower (3−4%) than our values, but they show the same dependency of the viscosity with respect to the ammonia fraction.

3.4. NH_3 + CH_3OH. The solubility of ammonia in methanol is also very high, $x_{NH_3} = 0.28$ at 25 °C and $P = 1$ bar, and the diffusion coefficient and viscosity can be measured again as functions of the ammonia concentration. The results are shown in parts a and b of Figure 5. For all ammonia mole fractions the diffusion coefficient was independent of the initial excess solute concentration. Both the diffusion data and the viscosity data could be correlated with the same type of equation as used for the $NH_3 + H_2O$ system. No literature data have been found for this binary system with $x_1 > 0$.

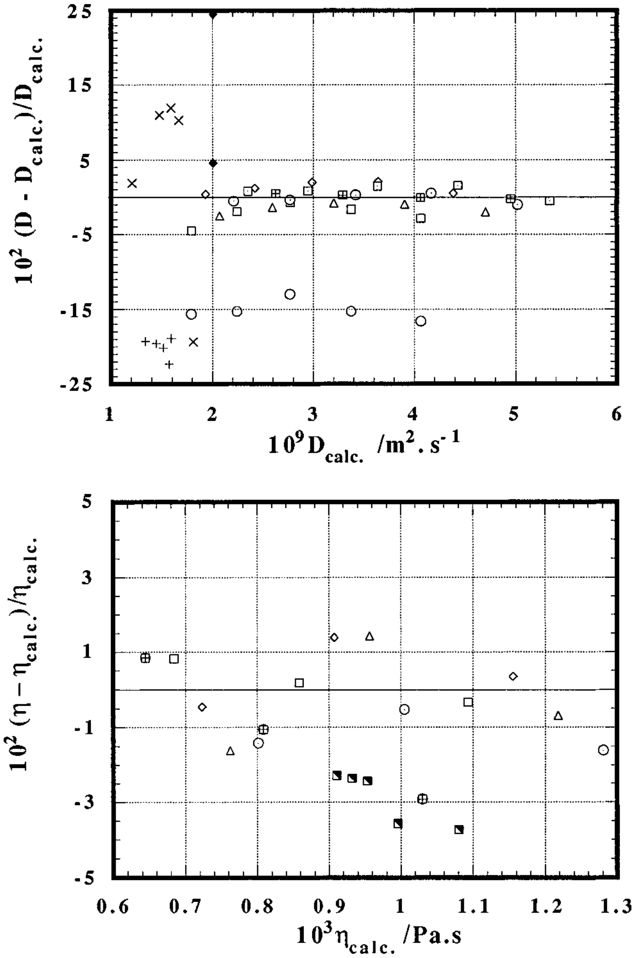

Figure 4. Deviation plots of (a, top) the diffusion coefficients (○, $x_1 = 0$, $\Delta x_1 = 0$; □, $x_1 = 0$, $\Delta x_1 = 0.03$; ◇, $x_1 = 0.053$; △, $x_1 = 0.105$; ⊙, $x_1 = 0.157$; ⊡, $x_1 = 0.209$; plus sign inside box, $x_1 = 0.312$; ×, results from Scheffer (1888), Arrhenius (1892), Abegg (1893), Gyunter and Pfeifer (1964), and Voigtländer (1889); +, results from Hüfner (1897, 1898); ◆, results from Leaist (1985) and Godfrey (1973)) and (b, bottom) the viscosities (○, $x_1 = 0$; □, $x_1 = 0.053$; ◇, $x_1 = 0.105$; △, $x_1 = 0.157$; ⊙, $x_1 = 0.209$; plus sign inside box, results from White and Twining (1913), Weber (1955, 1963), and Swindells et al. (1952, 1954); ◪, results from Kanitz (1891) and Blanchard and Pushee (1904, 1912)) and their fit correlations from Table 4 of the $NH_3 + H_2O$ system.

4. Discussion

In the case of diffusion of a solute molecule in a pure solvent, two equations for estimating the diffusion coefficient are very popular (a good overview is given by Rutte (1992)): the modified Stokes−Einstein equation

$$D_{i\ \mathrm{in}\ j} = \frac{kT}{n_{SE}\pi\eta_j R_i}\left[\frac{R_j}{R_i}\right] \tag{4}$$

where $D_{i\ \mathrm{in}\ j}$ is the diffusion coefficient of solute i in pure solvent j, k is the Boltzmann constant, T is the temperature, n_{SE} is the Stokes−Einstein number, η_j is the solvent viscosity, R_i is the radius of the solute molecule, and R_j is the radius of the solvent molecule, and the Wilke−Chang equation

$$D_{i\ \mathrm{in}\ j} = n[(xM_{wj})^{1/2}T/\eta_n V_{bi}^{\ 0.6}] \tag{5}$$

where $D_{i\ \mathrm{in}\ j}$ is given in cm^2/s, n is the Wilke−Chang parameter, x is the association parameter, M_{wj} is the molar mass of the solvent in g/mol, η_j is given in cP and V_{bi} is the volume of the solute at its normal boiling point in cm^3/mol.

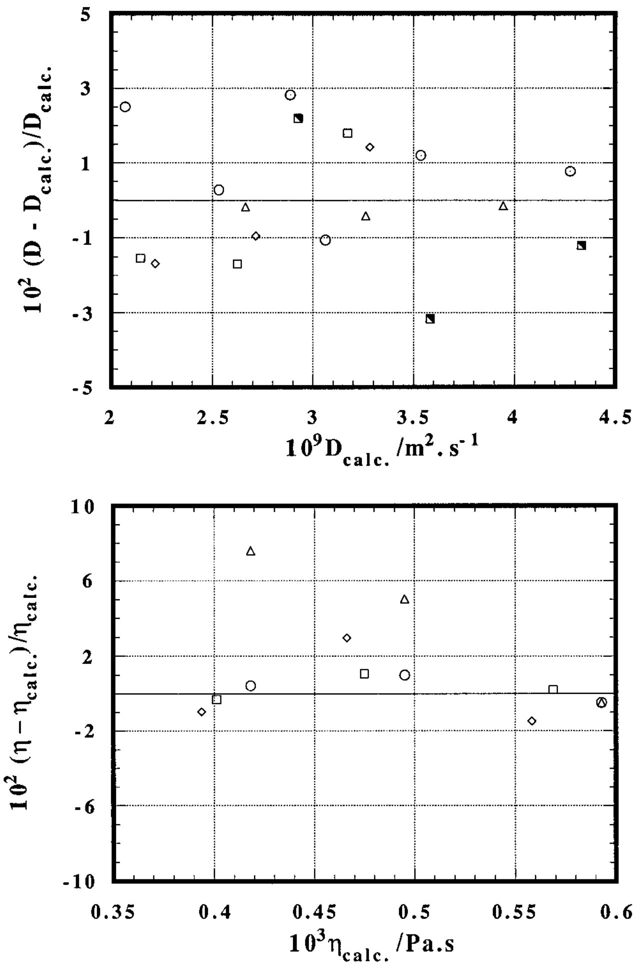

Figure 5. Deviation plots of (a, top) the diffusion coefficients (○, $x_1 = 0$; □, $x_1 = 0.02$; ◇, $x_1 = 0.04$; △, $x_1 = 0.16$; ⊙, $x_1 = 0.22$; ◩, $x_1 = 0.23$) and (b, bottom) the viscosities (○, $x_1 = 0$; □, $x_1 = 0.16$; ◇, $x_1 = 0.23$; △, results from Isakowa and Oznewa (1966), Bridgman (1949), and Bridgman (1925)) and their fit correlations from Table 4 of the $NH_3 + CH_3OH$ system.

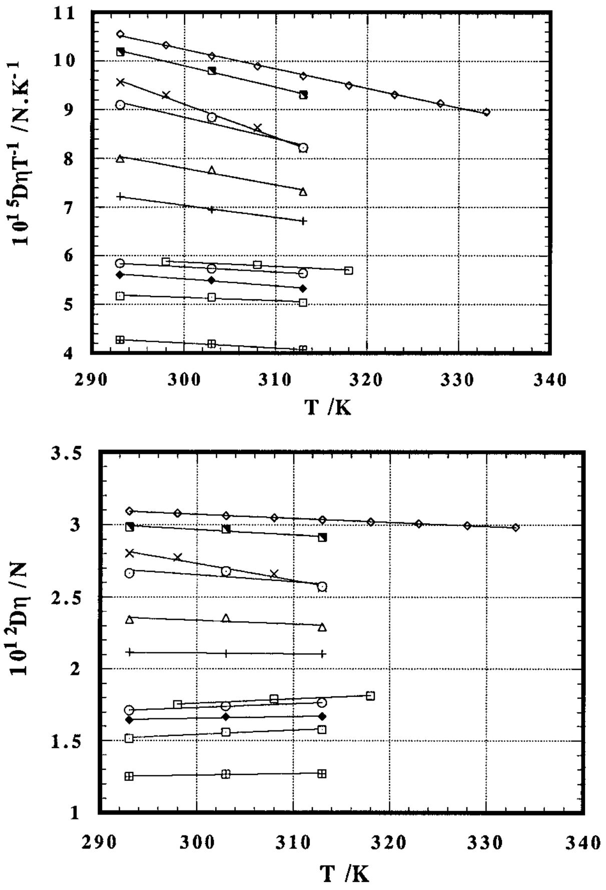

Figure 6. Correspondence between the viscosity and diffusion coefficient for all investigated binary gas + liquid systems presented as (a, top) $D\eta/T$ and (b, bottom) $D\eta$ as functions of temperature (◇, $CO_2 + CH_3OH$, literature data; ◩, $NH_3 + H_2O$, $x_1 = 0.053$; ×, $CO_2 + CH_3OH$, own data; ⊙, $NH_3 + H_2O$, $x_1 = 0.157$; △, $NH_3 + H_2O$, $x_1 = 0.105$; +, $NH_3 + H_2O$, $x_1 = 0.053$; ○, $CO_2 + H_2O$, literature data, □, $CO_2 + H_2O$, own data; ◆, $NH_3 + CH_3OH$, $x_1 = 0$; ⊡, $NH_3 + CH_3OH$, $x_1 = 0.16$; plus sign inside box, $NH_3 + CH_3OH$, $x_1 = 0.23$).

n is independent of temperature and the solute−solvent system. n_{SE}, R_i, R_j, x, M_{wj}, and V_{bi} depend on the solute + solvent system, but are independent of temperature. So both equations predict the following dependency of the diffusion coefficient with respect to temperature:

$$D_{i\ \mathrm{in}\ j}(T) = (\mathrm{constant})T/\eta_j(T) \qquad (6)$$

For the four dilute gas + liquid systems ($x_1 = 0$) presented in this paper the values predicted by the modified Stokes−Einstein equation (4) and the Wilke−Chang equation (5) have been calculated and presented in Table 5. Generally speaking both equations show a similar degree of correspondence with our experimental data and have a typical accuracy of 30%. In the case of the $NH_3 + CH_3OH$ system, however, the Wilke−Chang equation shows an unacceptably high deviation.

Equation 6 has been evaluated by plotting $D(T)\ \eta(T)/T$ for all investigated binary systems versus the temperature T, which should be a constant according to eq 6. It can be seen from Figure 6a that all lines show a decrease with increasing temperature, with a maximum change of about 10% per 20 K. Compared to the changes in viscosity and diffusion coefficient of about 40% per 20 K, eq 6 can be considered as good. If however the temperature T is left out of eq 6, as is mentioned in, e.g., Landolt Börnstein (1969), resulting in

$$D_{i\ \mathrm{in}\ j}(T) = \mathrm{constant}/\eta_j(T) \qquad (7)$$

the results will improve as can be seen from Figure 6b. The maximum change is now about 5% per 20 K. Equation 7 implies that, for the investigated binary systems, the molecular forces playing a role in the liquid viscosity are

Table 5. Prediction of the Diffusion Coefficients in Pure Solvents Using the Modified Stokes−Einstein Equation (mSE) and the Wilke−Chang Equation (WC) and Their Deviation from the Experimental Values[a]

system	T/K	10^9D_{exp}/ ($m^2 \cdot s^{-1}$)	10^9D_{mSE}	10^9D_{WC}	dev- (mSE)/%	dev- (WC)/%	$10^{10}R_i$/m	$10^{10}R_j$/m	x	V_{bi}/ ($m^3 \cdot kmol^{-1}$)
$CO_2 + H_2O$	298	1.97	2.21	1.86	12	−6	1.98	2.14	2.6	0.09400
$CO_2 + CH_3OH$	298	5.13	3.56	3.57	−30	−30	1.98	2.05	1.9	0.09400
$NH_3 + H_2O$	293	1.51	1.60	2.08	6	38	2.18	2.14	2.6	0.07247
$NH_3 + CH_3OH$	293	2.12	2.20	4.15	4	96	2.41	2.05	1.9	0.07247

[a] $n_{SE} = 3.5$ and $n = 7.4 \times 10^{-8}$, whereas the parameters R_i, R_j, and x have been given values according to the theory as described in Rutte (1992).

the same as those determining the diffusion coefficient. If eq 7 is better than eq 6, then, for a certain class of binary systems, the modified Stokes−Einstein equation and the Wilke−Chang equation can be improved by removing the parameter T.

5. Conclusions

It has been shown that the equipment used in this paper provides accurate diffusion coefficients and liquid viscosities. The dependency of both quantities with respect to temperature was correlated using Arrhenius-type equations. In the case of the ammonia mixtures the preexponential factor was a linear function of the ammonia fraction. The correlations describing the experimental results for the diffusion coefficients and the viscosities are given in Table 4.

The correlation between the diffusion coefficient and the viscosity as functions of temperature was described best by eq 7 and can therefore be very useful for extrapolating known diffusion coefficients to other temperatures by using liquid viscosities, which can be measured more easily. The modified Stokes−Einstein equation and the Wilke−Chang equation show typical errors up to 30% for estimating diffusion coefficients in diluted systems. They can, however, produce deviations which are much larger, as was shown in this paper, and care must therefore be taken when using these equations.

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