for the osmotic coefficient and the activity coefficients for various mixture compositions are given in Table VI.

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Glossary

A	symbols subscripted A refer to $NaClO_4$
B	symbols subscripted B refer to $Ba(ClO_4)_2$
m	molal concentration, mol/kg
I	total ionic strength, mol/kg
y	ionic strength fraction
ϕ	molal osmotic coefficient
$\gamma_\pm$	mean molal activity coefficient
$a(n)$	parameters (n = 1–4) in Scatchard equations for single electrolytes, see ref *1*
$b(pq)$	parameters (pq = 01, 02, 03, 12, 13) in Scatchard equations for electrolyte mixtures, see ref *1*
$\sigma(\phi)$	standard deviation for osmotic coefficients

Registry No. $NaClO_4$, 7601-89-0; $Ba(ClO_4)_2$, 13465-95-7.

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Binary Gaseous Diffusion Coefficients. 7. Tetrachloroethene and 1,1,1-Trichloroethane with Methane and Tetrafluoromethane at 100 kPa and 283–343 K

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Binary gaseous diffusion coefficients D_{12} for tetrachloroethene diffusing in methane and tetrafluoromethane and for 1,1,1-trichloroethane diffusing in tetrafluoromethane were measured at about 283, 298, 313, 328, and 343 K and at 100 kPa by the capillary-tube method of Stefan. In addition, D_{12} for tetrachloromethane in methane and in tetrafluoromethane were determined at 283 and 298 K, respectively. The experimental results are compared with diffusion coefficients calculated via the first-order Chapman–Enskog approximation. For the gases, effective Lennard-Jones [6,12] pair potential parameters were taken from recent literature; for the heavy chlorinated hydrocarbons the parameters were obtained from semitheoretical extended-corresponding-states correlations. Agreement is satisfactory throughout.

Introduction

The measurements reported in this paper are a sequel to our recent study of diffusion in air of chlorinated hydrocarbons of practical, industrial importance (*1*), and continue our systematic investigations of binary gaseous diffusion coefficients D_{12} via the Stefan capillary-tube method (*1–6*). Specifically, we now report D_{12} of tetrachloroethene (C_2Cl_4) diffusing in methane (CH_4) and tetrafluoromethane (CF_4) and of 1,1,1-trichloroethane (1,1,1-$C_2H_3Cl_3$) diffusing in tetrafluoromethane. All experiments were conducted at atmospheric pressure in the temperature range 283–343 K. In addition, D_{12} was determined for tetrachloromethane (CCl_4) diffusing in methane at 283 K and in tetrafluoromethane at 298 K, respectively. The results are compared with diffusion coefficients calculated via the first-order Chapman–Enskog approximation (*7*, *8*) in conjunction with effective pair-potential parameters from two popular extended-corresponding-states correlations (*1*, *6*, *9*, *10*).

Experimental Section

The apparatus and procedure for measurements by the capillary-tube method have been described in detail in our earlier papers (*1–6*). Each solvent/gas pair was run in duplicate at a pressure of approximately 100 kPa at 283, 298, 313, 328, and 343 K, with the exception of CCl_4/CH_4 and CCl_4/CF_4, which were investigated only at 283 and 298 K, respectively. Temperature was controlled to better than ±0.01 K over the entire measurement periods and was measured with a calibrated platinum resistance thermometer on IPTS-68. The total system pressure was controlled to better than ±0.5 kPa by a mercu-

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Table I. Experimental and Calculated Binary Gaseous Diffusion Coefficients D_{12}, at $P_{ref} = 10^5$ Pa, of Tetrachloromethane, Tetrachloroethene, and 1,1,1-Trichloroethane (Components 1) Diffusing in Tetrafluoromethane and Methane (Components 2)

T/K	D_{12}/cm^2·s^{-1} exptl	D_{12}/cm^2·s^{-1} calcd[a]
	$CCl_4 + CF_4$	
298.20	0.0404	0.0388
	$C_2Cl_4 + CF_4$	
283.10	0.0350	0.0321
298.20	0.0384	0.0356
313.17	0.0403	0.0392
328.13	0.0445	0.0429
343.14	0.0483	0.0468
	1,1,1-$C_2H_3Cl_3 + CF_4$	
283.10	0.0392	0.0373
293.15	0.0417	0.0413
313.17	0.0472	0.0454
328.13	0.0506	0.0498
343.14	0.0569	0.0543
	$CCl_4 + CH_4$	
283.15	0.0786	0.0805
	$C_2Cl_4 + CH_4$	
283.14	0.0737	0.0741
298.14	0.0815	0.0822
313.12	0.0896	0.0905
328.15	0.0983	0.0993
343.14	0.1066	0.1084

[a] Calculated via eq 4 in conjunction with eq 9 and 10. The pure-component Lennard-Jones parameters are given in Table III.

Table II. Parameters $D_{12}(T_{ref},P_{ref})$ and s of Eq 3, where $T_{ref} = 273.15$ K and $P_{ref} = 10^5$ Pa, and the Average Percent Deviation[a] d of the Experimental Diffusion Coefficients from Those Calculated with Eq 3

system	$D_{12}(T_{ref},P_{ref})$/cm^2·s^{-1}	s	d
$C_2Cl_4 + CF_4$	0.03290	1.645	0.9
$C_2Cl_4 + CH_4$	0.06883	1.928	0.1
1,1,1-$C_2H_3Cl_3 + CF_4$	0.03594	1.949	1.5

[a] $d = N^{-1}\sum_N|\Delta_i|$, where $\Delta_i = 100\,[D_{12}(\text{exptl}) - D_{12}(\text{smoothed})]/D_{12}(\text{smoothed})$ is the percent deviation of an individual data point. N is the number of data points, and D_{12}(smoothed) is obtained from eq 3 with parameters given in this table.

ry-filled Cartesian manostat. Diffusion path lengths were determined with a reproducibility of ±0.05 mm, and corresponding diffusion times to ±5 s.

Routine comparison measurements on water diffusing in nitrogen yielded an average value of $D_{12} = 0.276$ cm^2·s^{-1} at 313.15 K and 100 kPa, which is in close agreement with the most reliable literature data (*11*), i.e., 1.8% below the result of O'Connell et al. (*12*), and 1.6% above that of Schwertz and Brow (*13*). The imprecision of our measured diffusion coefficients is about ±1%, while the inaccuracy is considered to be less than ±2%.

All solvents, that is, tetrachloromethane, tetrachloroethene, and 1,1,1-trichloroethane, were from the Fluka Chemical Co. with purities of 99.0 mol % or better. They were dried with molecular sieve and used without further purification. Water was purified by reverse osmosis followed by distillation. Methane (99%) and tetrafluoromethane (99.7%) were from Matheson Gas Products.

Results

Binary gaseous diffusion coefficients $D_{12}(T,P)$ at thermodynamic temperature T and total pressure P (which was always close to 100 kPa) were obtained as before from the following expression:

$$D_{12}(T,P) = (l_\theta^2 - l_0^2)RT\rho_1^L/\{2\theta PM_1 \ln [P/(P - P_{s,1})]\} \qquad (1)$$

Here, l_0 and l_θ are the measured diffusion paths at the start of the experiment and at time θ, respectively, R is the gas constant, ρ_1^L is the mass density of the liquid, M_1 is the molar mass of the liquid, and $P_{s,1}$ is its vapor pressure at T. Liquid densities and vapor pressures were obtained from reliable literature sources (*14*–*18*).

Diffusion coefficients obtained at any experimental pressure were converted to $P_{ref} = 10^5$ Pa by making use of the fact that at low to moderate pressures (and at constant temperature) the product $PD_{12}(T,P)$ is practically independent of pressure, whence

$$D_{12}(T,P_{ref}) \equiv D_{12} = D_{12}(T,P)(P/P_{ref}) \qquad (2)$$

These pressure corrections were always small, that is to say, less than 2%. The results shown in Table I are corrected diffusion coefficients $D_{12} \equiv D_{12}(T,P_{ref})$, at the indicated temperatures, of CCl_4, C_2Cl_4, and 1,1,1-$C_2H_3Cl_3$ (components 1) diffusing either in CH_4 or CF_4 (components 2).

At low to moderate pressures and over not too large a temperature range, D_{12} varies as T^s, where s usually lies between 3/2 and 2 (*7*, *11*, *19*). Accordingly, the data of Table I may be represented by an expression of the form

$$D_{12} = D_{12}(T_{ref},P_{ref})(T/T_{ref})^s \qquad (3)$$

Table II contains the values of s and $D_{12}(T_{ref},P_{ref})$ for three of the systems investigated, with $T_{ref} = 273.15$ K and $P_{ref} = 10^5$ Pa, as obtained from fitting $\ln D_{12}$ vs $\ln (T/T_{ref})$. The average percent deviations d of the experimental diffusion coefficients from those calculated with eq 3 are also given. For (C_2Cl_4 + CH_4) we find the smallest average percent deviation, $d = 0.1\%$; for (C_2Cl_4 + CF_4) $d = 0.9\%$, and for (1,1,1-$C_2H_3Cl_3$ + CF_4) $d = 1.5\%$. No literature data could be found for comparison.

Discussion

The first-order Chapman–Enskog approximation in the theory of dilute simple gases (*7*, *8*) provides the following expression for the binary diffusion coefficient:

$$D_{12}(T,P) = {}^3\!/_8(N_Ak_BT)^{1/2}/[(2\pi M_{12})^{1/2}n^V\sigma_{12}^2\Omega_{12}^{(1,1)*}(T^*_{12})] \qquad (4)$$

Here, N_A is Avogadro's constant, $k_B = R/N_A$ is Boltzmann's constant, $M_{12} = M_1M_2/(M_1 + M_2)$, M_1 and M_2 denote the

Table III. Values of Some Bulk Properties and Molecular Parameters of the Pure Substances: Molar Mass M, Critical Pressure P_c, Critical Molar Volume V_c, Critical Temperature T_c, Acentric Factor ω, and Effective Lennard-Jones [6,12] Parameters σ and ϵ/k_B

substance	10^3M^a/kg·mol^{-1}	$10^{-6}P_c$/Pa	10^6V_c/m^3·mol^{-1}	T_c/K	ω	$10^9\sigma$/m	ϵ/k_B/K
CCl_4	153.823	4.56 (*15*)	276 (*15*)	556.4 (*15*)	0.194 (*15*)	0.5407[b]	458.7[b]
C_2Cl_4	165.834	4.46 (*15*)	290 (*15*)	620 (*15*)	0.211 (*1*)	0.5643[b]	512.9[b]
1,1,1-$C_2H_3Cl_3$	133.405	4.30 (*18*)	283[c]	545 (*18*)	0.216 (*18*)	0.5154[d]	488.9[d]
CH_4	16.043	4.604 (*26*)	99 (*26*)	190.6 (*26*)	0.012 (*26*)	0.3706 (*23*)	159.7 (*23*)
CF_4	88.005	3.74 (*26*)	140 (*26*)	227.6 (*26*)	0.177 (*26*)	0.4662 (*24*)	134.0 (*24*)

[a] From IUPAC, *Pure Appl. Chem.* 1984, 56, 653. [b] TGS estimates, eq 5 and 6. [c] Estimated by Lydersen's method. [d] ST estimates, eq 7 and 8.

molar masses of the two components, σ_{12} is a characteristic molecular interaction size parameter, and n^V is the number density. To a good approximation (*7*, *8*, *11*) n^V may be expressed as P/k_BT. The details of the collision dynamics are contained in the reduced collision integral $\Omega_{12}^{(1,1)*}(T^*_{12})$ at a reduced temperature $T^*_{12} = k_BT/\epsilon_{12}$, where ϵ_{12} is a characteristic molecular interaction energy parameter.

For the Lennard-Jones [6,12] pair potential, the reduced collision integral has been tabulated, as a function of T^*, by several authors (*8*, *20*, *21*). An empirical analytical representation for $0.3 \leqslant T^* \leqslant 100$ is due to Neufeld et al. (*22*). It allows the direct calculation of $\Omega^{(1,1)*}(T^*)$ with an accuracy comparable to that of the best tables to date.

The key to the actual use of eq 4 is the selection of appropriate effective pair potential parameters of the pure components and the subsequent calculation of the corresponding interaction quantities. σ and ϵ/k_B of the pure gases CH_4 and CF_4 were taken from Clifford et al. (*23*) and from Svehla (*24*), respectively. The parameters for tetrachloromethane and tetrachloroethene were obtained from a dimensionless form (*1*, *6*) of a correlation originally suggested by Tee, Gotoh, and Stewart (TGS) (*9*)

$$\sigma(P_c/k_BT_c)^{1/3} = 0.45767 - 0.01698\omega \tag{5}$$

$$\epsilon/k_BT_c = 0.7915 + 0.1693\omega \tag{6}$$

where P_c is the critical pressure, T_c is the critical temperature, and ω is the acentric factor. For the polar 1,1,1-trichloroethane (with gas-phase dipole moment $\mu = 5.94 \times 10^{30}$ C·m (*25*)) we used a dimensionless form of the Stiel–Thodos (ST) correlation (*10*)

$$\sigma(N_A/V_c)^{1/3} = 0.6629 \tag{7}$$

$$\epsilon/k_BT_c = 0.897 \tag{8}$$

where V_c is the critical molar volume. Table III shows the potential parameters σ and ϵ/k_B used in this work, together with critical properties and the acentric factors.

For the estimation of the interaction quantities σ_{12} and ϵ_{12}, adequate combining rules must be selected (*27*–*30*). In view of the approach outlined above, with its inherent uncertainties, only the rather approximate conventional Lorentz–Berthelot prescription

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \tag{9}$$

$$\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2} \tag{10}$$

was used.

Diffusion coefficients calculated via eq 4 have been included in Table I. Considering the relatively complex systems, agreement between experimental and calculated D_{12}'s is quite satisfactory, i.e., within a few percent throughout, which is in line with the previous findings (*1*, *6*, *31*). The experimental results are on the average 4.1% high for CF_4 and 1.3% low for CH_4.

Application of the TGS correlation to methane and tetrafluoromethane yields $\sigma = 0.3797 \times 10^{-9}$ m and $\epsilon/k_B = 151.2$ K for the former and $\sigma = 0.4290 \times 10^{-9}$ m and $\epsilon/k_B = 187.0$ K for the latter. The corresponding theoretically calculated D_{12}'s differ only slightly from the values given in Table I, the differences being generally smaller than 1%. This is just another manifestation of the relative insensitivity of the product $\sigma_{12}^2\Omega_{12}^{(1,1)*}(T^*_{12})$ to the details of the intermolecular potential.

Registry No. 1,1,1-$C_2H_3Cl_3$, 71-55-6; C_2Cl_4, 127-18-4; CH_4, 74-82-8; CF_4, 75-73-0.

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