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Diffusion Coefficients of the Halocarbons CCl_2F_2 and $C_2Cl_2F_4$ with Simple Gases

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Binary diffusion coefficients for halocarbons CCl_2F_2 (R12) and $C_2Cl_2F_4$ (R114) with H_2, N_2, and He are reported, together with the corresponding temperature dependence coefficient in the 298–343 K region. Experimental results are obtained from the arrested-flow chromatographic method. The precision of the experimental diffusivities is within 2%, but predicted values with the equations of Fuller–Schetter–Giddings or Lennard-Jones differ substantially from those measured.

Introduction

Binary gaseous diffusion coefficients of halocarbons R12 (CCl_2F_2) and R114 ($F_2ClCCClF_2$) in the simple gases N_2, H_2, and He have been measured. The instrumental design has been verified by comparing with literature values the measured binary diffusion coefficients of ethane and ethene in nitrogen and hydrogen.

The diffusion coefficient of such compounds is of particular importance for the understanding of transport mechanisms and is relevant for particular chemical engineering applications.

Although various surveys of diffusion coefficients of gaseous organic molecules have been presented, little has appeared concerning mixtures of molecules such as halocarbons with a simple gas. Fuller et al. (*1*) have, however, measured the gaseous diffusion coefficients of halogenated hydrocarbons mixed with helium in the 428 K region.

Most experimental methods are derived from gas chromatographic (GC) techniques. Generally, a small gaseous pulse of compound A is introduced instantaneously into an unpacked column, where it diffuses in a flow of the carrier gas B. Maynard and Grushka (*2*) provide the corresponding theory of zone broadening by diffusion of a solute introduced in a carrier gas. Choudhary (*3*) reviews various GC techniques, of which the arrested-flow method has the advantages of simplicity of instrumental design and of rapidity of measurement. For these reasons, the method of arrested flow was chosen for the present study.

Experimental Section

As applications of the arrested-flow method are detailed by Ashraf et al. (*4*), only the modifications made in a conventional GC system are discussed here. The apparatus involved empty columns, injection and switching valves, a thermal conductivity detector, and measuring devices for gas flow, peak width, time, temperature, and pressure. The carrier gas was preheated in a helicoidal copper heat exchanger immersed in a water bath, which gave better control of column temperature than an oven. The two coiled stainless steel columns were immersed in the thermostated water bath. The diffusion column was 6.00 m long, with a coiling diameter of 0.20 m. By weighing the amount of an aqueous surfactant solution of known density necessary to fill the column the inside cross sectional area was accurately determined. Thus the section area, s_a, obtained was 1.28 × 10^{-4} m^2. An eight-port valve (Carle model) connected to the column with $^1/_{16}$-in. tubing was used to stop and switch the flowing gas to the catharometer. A six-port valve (Intersmat model) was used to take 0.4-cm^3 solute gas samples. The potentiometer recorder chart speed of 100 mm/min allowed accurate peak width measurement, better than 2%. As the pressure drop in the column was negligible, diffusion coefficients were measured at atmospheric pressure. This pressure was measured to 0.05 mmHg with a barometer. The bath temperature was controlled to 0.1 K, and no significant vertical temperature gradient could be observed. The thermistor thermometer was accurate to 0.1 K. Time was measured by a stopwatch. Gas flow, controlled by a Brooks flow controller (Model 8744), was measured by using a SGE digital flowmeter calibrated according to factory specifications to within 4% for the 5–20 mL/min range. The carrier gas was saturated by bubbling through a water saturator placed at the outlet of the GC equipment. Carrier gas flow rates were found to have no effect upon binary diffusion coefficients in the selected interval. Values corrected to the column temperature were in the range 5–20 mL/min. Solutes such as ethane (99.9% purity), halocarbons (99% purity), and carrier gases (H_2, N_2, He: 99% or higher purity) were supplied by Air Liquide.

Once temperature equilibrium was reached in the water bath, a typical experimental run was started while a constant carrier gas flow rate was maintained (measured flow varying within ±0.2 mL/min). Then a solute sample was injected into the column, and the retention time (t_A), i.e. the time interval between injection and elution, was recorded. In the following runs, after the pulse has reached the lower half of the column, the flow of the carrier gas was stopped. Repeatedly, during varying times ($t_{arrested}$), the flow was stopped and the arrest time recorded for a given gas velocity. At the end of each operation, the valve was rotated to its initial position to cause the solute to be eluted. Thus, the peak was recorded, the elution time corresponding to t_B.

Results

McCoy and Moffat (*5*) and Knox and McLaren (*6*) show that the final concentration profile of the elution peak has the form of the usual solution of the diffusion equation, where the spatial variance s_t is given by the following equation:

$$s_t = 2D_{axial}(t_A + t_B) + 2D_{AB}t_{arrested}$$

with the variance σ_t^2 in place of s_t, the binary diffusion coefficient D_{AB} is given by

$$d\sigma_t^2/dt = 2D_{AB}/v_l^2$$

where the variance σ_t^2 is calculated at half the height of the peak from

$$\Delta = 2.3548(\sigma_t^2)^{1/2}$$

A plot σ_t^2 versus $t_{arrested}$ (arrested time) should be a straight line of slope $2D_{AB}/v_l^2$, in which v_l is the carrier gas velocity given by the relation

$$v_l = F_c/s_a$$

where F_c is the corrected carrier gas flow rate at the conditions prevailing in the column, given by the relation

$$F_c = F_eT_c/T_a(P_{atm} - P_{H_2O})/P_{atm}$$

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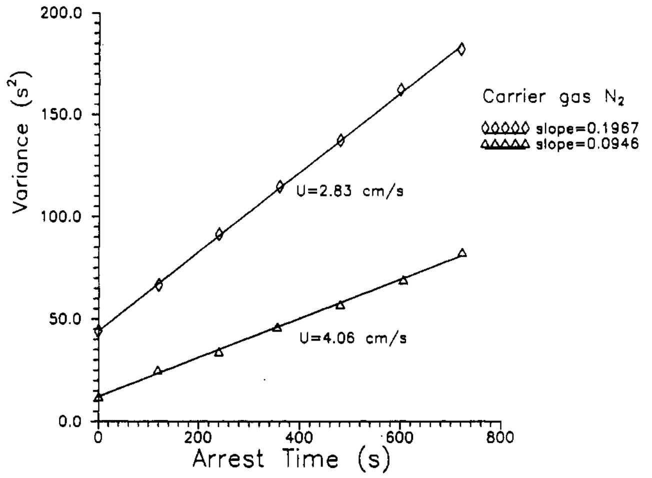

Figure 1. Effect of arrest time on variance for H_2-N_2 system.

Table I. Binary Diffusion Coefficients by the Arrested-Flow Method for Known Mixtures

gas pair			D_{AB}, cm²/s				
carrier	solute	temp, K	corrected to 101 kPa	calcd[a]		lit.	ref
H_2	N_2	304.2	0.806	0.808	0.786	0.797	8
H_2	N_2	307.2	0.831	0.821	0.802	0.879	8
N_2	C_2H_4	293.2	0.180	0.149	0.152	0.183	9
He	C_2H_6	322.7	0.582	0.531	0.588	0.556	7
He	C_2H_4	322.7	0.620	0.561	0.630	0.598	7

[a] First value calculated with FSG equation, second value calculated with the LJ equation, the parameters of which are taken from ref 10.

Table II. Temperature Coefficients *n* for H_2-N_2 and Halocarbon Carrier Gas Mixtures

gas pair			
carrier	solute	*n*	std dev, σ[a]
H_2	N_2	1.71[b]	0.998
N_2	R12	1.82	0.984
H_2	R12	1.47	0.997
He	R12	1.57	0.997
N_2	R114	1.27	0.991
H_2	R114	1.82	0.997
He	R114	1.41	0.998

[a] $\sigma = (\sum_i(D_{AB\,exp} - D_{AB\,calc})^2)^{1/2}/N - 1$ where N is the number of experimental points. [b] Literature values: 1.61 (*8*), 1.75 (*13*), and 1.69 (*14*).

A least-squares fit of the σ_t^2 data versus $t_{arrested}$ provides the slope and standard deviation. The reliability of the method was checked by measuring D_{AB} for the following well-known mixtures: nitrogen in hydrogen as carrier gas and mixtures of ethane and ethene with helium and nitrogen as carrier gases. A typical curve is shown in Figure 1 and comparisons with literature data are presented in Table I. Reproducibility of the measured peak variance was good. No influence of variable carrier gas velocity was observed for the low flow rates chosen for these experiments. Thus, the average deviation, 3.5%, and maximum value, 5.7%, between our data and literature data provide validation of the experimental method.

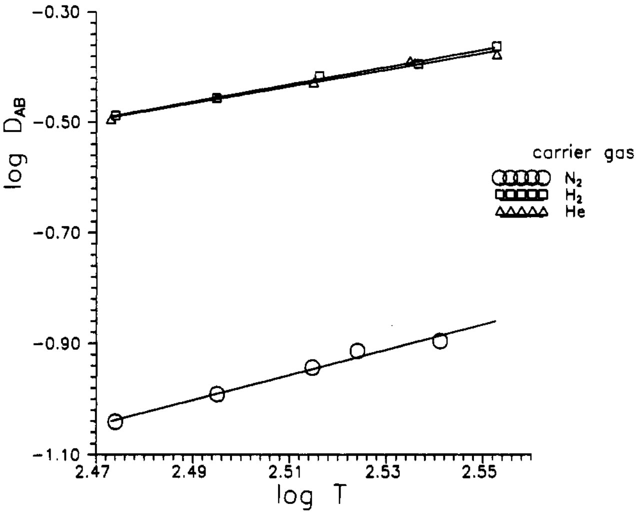

Figure 2. Effect of temperature on D_{AB} for the R12 mixtures.

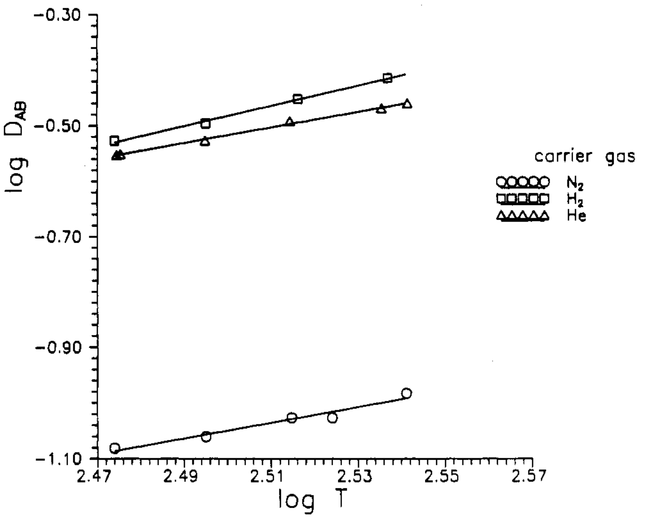

Figure 3. Effect of temperature on D_{AB} for the R114 mixtures.

Table III. Experimental and Calculated Values of D_{AB} for R12 and R114 Mixtures

gas pair			D_{AB}, cm²/s				
carrier	solute	temp, K	corrected to 101 kPa	calcd[a]		% deviation	
N_2	R12	297.65	0.091	0.089	0.094	2	3
H_2	R12	298.15	0.325	0.383	0.443	18	36
He	R12	298.05	0.320	0.320	0.403	0	26
N_2	R114	298.15	0.082	0.073	0.080	11	2
H_2	R114	298.15	0.297	0.317	0.417	7	40
He	R114	298.15	0.280	0.257	0.347	8	24

[a] First value calculated with FSG equation; second value calculated with the LJ equation; the parameters are taken from ref 10 for H_2, N_2, and He. For R12 and R114 halocarbons, the second virial coefficients have been fitted following the equation $B(T) = boB^*(T^*)$, where B^* is the reduced second virial coefficients and $bo = 2\prod\sigma^3/3$. The virial coefficients are given in ref 11. We obtained for R12 σ = 3.59 A and ϵ/k = 154.49 K and for R114 σ = 5.81 A and ϵ/k = 219.06 K. [b] % deviation = $|D_{exp} - D_{calc}|/D_{exp} \times 100$.

Dependence of binary diffusion coefficients upon temperature is generally described as a power dependence, AT^n, with n specific to each system, as reported by Katsanos (*7*), and A, a complex function involving various physical parameters. The exponent n can be determined from the slope of a logarithmic D_{AB} plot, presented in Figures 2 and 3. For the nitrogen in hydrogen as carrier gas and mixtures of the R12 and R114 hydrocarbons with various carrier gases, the values of n are shown in Table II. Experimental and calculated values of D_{AB} are shown in Table III. The calculated values are derived from the application of Fuller-Schetter-Giddings (FSG) and Lennard-Jones (LJ) equations (*10*). The average deviations between experimental and calculated values are larger than for hydrocarbon-simple gas mixtures. In particular, the calculated values with the FSG equation are slightly above the suggested accuracy, 5–10%, given by Reid et al. (*12*) for this correlation.

Conclusion

New binary diffusion coefficients for the halocarbons CCl_2F_2 and $C_2Cl_2F_4$, with H_2, N_2, and He, are presented together with the corresponding temperature dependence coefficients in the 298–343 K region. The arrested-flow method is easy to implement with a reasonable accuracy using simple equipment. The discrepancy observed between experimental and predicted values shows the necessity of experimental measurements to obtain reliable data.

Glossary

D_{AB}	binary diffusion coefficient, cm^2/s
D_{axial}	axial diffusion coefficient, cm^2/s
F_e, F_c	experimental flow rate and flow rate corrected to column conditions, cm^3/min
n	exponent of the temperature-dependent equation for D_{AB}
P_{H_2O}	vapor pressure of water at ambient temperature, mm Hg
s_t^2	spatial variance, m^2
s_a	cross-sectional area of the chromatographic column, m^2
$t_{arrested}$	time period corresponding to the flow arrest time, s
t_A	time period during convection of solute pulse to column midregion, s
t_B	time period during convection of solute pulse out of the column, s
T_a, T_c	ambient and column temperature, K
v_l	linear velocity of the carrier gas, cm/min
σ_t^2	standard deviation, s^2
Δ	width at half-height of a chromatographic peak, s

Registry No. R12, 75-71-8; R114, 76-14-2; H_2, 1333-74-0; N_2, 7727-37-9; He, 7440-59-7.

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Vapor–Liquid Equilibrium for the 2-Propanol–Methyl Acetate–Dichloromethane System at 298.15 K[†]

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Isothermal vapor–liquid equilibrium data were determined for the 2-propanol–methyl acetate–dichloromethane system at 298.15 K, by using a modified version of a Boublik–Benson still. The data proved to be thermodynamically consistent. Excess molar Gibbs energies G^E were calculated over the entire range of composition. Different expressions existing in the literature were used to predict G^E from the corresponding binary data. The empirical correlation of Cibulka resulted in being the best one for this system.

Introduction

Vapor–liquid equilibrium (VLE) data are necessary for the design of distillation processes. No experimental data have been reported in the available literature for the ternary 2-propanol + methyl acetate + dichloromethane system at 298.15 K. In previous papers we have published densities and viscosities (*1*), as well as molar excess Gibbs energies G^E for the corresponding binary mixtures (*2–4*). From the experimental VLE data, for this ternary system, activity coefficients γ_i and G^E can be calculated and compared with values predicted from different expressions in terms of the binary data (*5–11*).

Experimental Section

The methods used in our laboratory have already been described (*1–4*). Densities were determined with a digital densimeter AP, Model DMA 45. All weighings were made on an H315 Mettler balance. A thermostatically controlled bath (constant to 0.01 K) was used. Temperatures T were read from calibrated thermometers. Calibration was done with air and doubly distilled water. The accuracy in density ρ was 0.01%.

Equilibrium data, pressure P, and mole fractions x_i in the liquid phase and y_i in the vapor phase were determined by using a modified version of the still described by Boublik and Benson (*12*). The still and a water ebulliometer were attached to a large vessel that could be maintained at the required constant pressure. P was calculated from the boiling point of water in the ebulliometer. The later could be determined with an accuracy of 0.01 K with a Digitec digital thermometer. The temperature in the still was also measured to 0.01 K with a cali-

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