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Thermal Diffusion Factor for Carbon Tetrachloride-Cyclohexane and Benzene-*n*-Heptane Mixtures from Thermogravitational Column Separation

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Abstract

Measurements of the separation of liquid mixtures of *n*-heptane/benzene and carbon tetrachloride/cyclohexane in a thermogravitational column are reported. The results show that thermal diffusion columns of little mechanical precision can furnish suitable thermal diffusion factors when the diffusion coefficient, viscosity, density, and compressibility factor for the mixture are known.

INTRODUCTION

A thermal diffusion column has recently been used with relative success in the determination of the thermal diffusion factor, α_T, in liquid mixtures (*1–5*). The column has the advantage over conventional methods in that the elemental effect of separation is strongly enhanced, thereby obviating most of the uncertainties inherent to the results obtained from pure thermal diffusion (henceforth abbreviated TD)

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experiments. The theory of column operation (*6*) connects the separation factor q, defined as usual, with α_T through

$$\ln \underset{\sim}{q} = \frac{504L}{g(2\sigma r_0)^4\bar{T}} \frac{\alpha_T \eta D}{\rho\beta} = \frac{504L}{g(2\sigma r_0)^4} \frac{1}{\bar{T}} \gamma\alpha_T \qquad (1)$$

where

$$\sigma = \tfrac{1}{2} \ln r_H/r_C \qquad \text{and} \qquad r_0 = (r_H r_C)^{1/2}$$

ρ, η, and D are the density, the viscosity, and diffusion coefficient of the liquid mixture, respectively; and β is the thermal expansion coefficient. The cold and hot wall radii are r_C and r_H, and the temperatures are T_C and T_H, respectively. L is the length of the column, g is the gravitational acceleration, and $\bar{T}$ is the mean temperature to which the physical properties must be related. In practice, under experimental conditions, temperature difference, $\Delta T = T_H - T_C$, and the gap between the two concentric tubes, $\Delta r = r_H - r_C$, are both small, and $\bar{T} = (T_H + T_C)/2$.

However, the theory that leads to Expression (1) assumes that the geometry of the column is perfect and also neglects the so-called "forgotten effect." There is evidence which indicates that the influence of this effect on $\ln q$ is very small (*7–9*). Nevertheless, the other condition is hardly ever achieved, at least in elevated separation performance columns. The imperfections of the column (irregular wall surfaces, eccentricity between the two tubes, i.e., unequal width of the gap, etc.) can lead to a disturbance in convectional flows (*10, 11*). Parasitic remixing also causes a decrease in the degree of separation, and consequently the real situation is more complex than that described by Expression (1).

In this article it is proposed that imperfections in the column can be included in a factor ψ_s so that Expression (1) becomes

$$\ln \underset{\sim}{q} = \psi_s \left\{ \frac{\eta D}{\rho\beta} \right\} \alpha_T = \psi_s \gamma \alpha_T \qquad (2)$$

In principle, it may be assumed that different liquid mixtures can influence ψ_s differently. However, we show empirically, i.e., from direct experimentation, that the ψ_s factor can be properly considered for fixed temperature conditions as a constant of the column. The existence of this factor leads automatically to the possibility of obtaining the ratio α_1/α_2 of TD factors from the ratio $\ln q_1/\ln q_2$ of the separations measured for two liquid mixtures if their physical properties (ρ, η, D, β) are known.

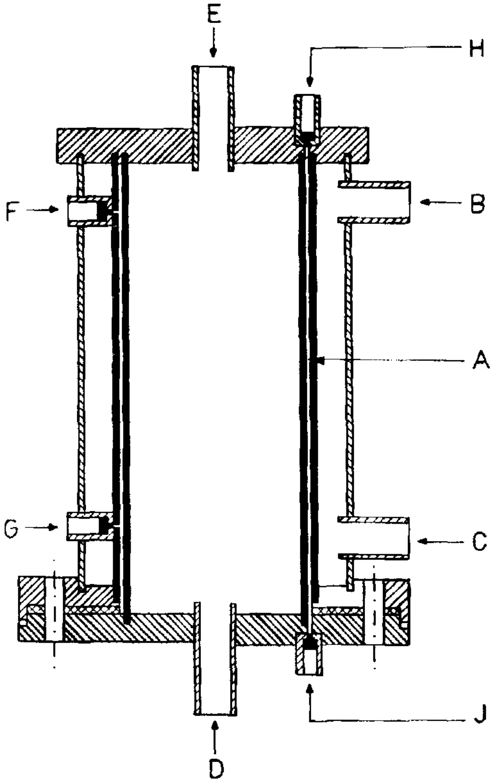

FIG. 1. A schematic drawing of the liquid thermal diffusion column. (A) working space, (B, C) connections to circulating cooling water, (D, E) oulet and inlet hot water, (F, G) sampling ports, (H, J) filling and draining connections.

This method is a natural extension for liquid mixtures of that previously reported for binary gaseous mixtures (*12, 13*) and also of the equivalent gap concept proposed by Bott and Romero (*11, 14*).

EXPERIMENTAL AND RESULTS

The liquid thermal diffusion column used in this work is a conventional stainless-steel concentric tube type and is shown schematically in Fig. 1. The total length of the column is 0.9 m and the active length or distance between the sampling ports is $L = 0.826$ m. These ports are

TABLE 1
Logarithm of the Separation and γ-Group Values for the n-Heptane-Benzene, Cyclohexane-Carbon Tetrachloride Mixtures

	System			
	C_7H_{16}/C_6H_6		C_6H_{12}/CCl_4	
X_0[a]	$\ln q_{exp}$	$10^{12}\gamma$[b] ($m^4 \cdot s^{-2} \cdot {}^\circ K$)	$\ln q_{exp}$	$10^{12}\gamma$[b] ($m^4 \cdot s^{-2} \cdot {}^\circ K$)
.190	—	—	.278	1.13
.278	.132	1.26	—	—
.288	—	—	.244	1.02
.362	—	—	.224	.95
.373	.151	1.13	—	—
.460	—	—	.202	.87
.463	.162	1.04	—	—
.529	—	—	.184	.83
.558	—	—	.182	.81
.614	.183	.93	—	—
.653	.196	.91	—	—
.682	—	—	.167	.73
.747	.205	.88	—	—
.840	.235	.89	—	—
.921	.252	.93	—	—

[a] X_0 is the initial molar fraction of the second component.
[b] $\gamma = \eta D/\rho\beta$ (see text).

closed with a viton's septum which is perforated with a syringe when an extraction of sample is performed, so the dead volume of the column is minimized. The liquid mixture is contained in the small annulus formed between the two stainless steel cylinders of radii $r_H = 3 \times 10^{-2}$ and $r_C = 2.9 \times 10^{-2}$m as indicated by the manufacturer.

The mechanical construction of the column cannot be considered as being of high mechanic precision, since it is not an easy task to ensure good precision in tooling over such a long geometry. Deviations from the nominal values of the gap ($\Delta r = r_C - r_H$) as large as 10% have been observed. This lack of uniformity in the gap value, together with the imprecisions in the radii values, prevent, in principle, the present experimental setup to be used to determine absolute values of α_T.

The cold and hot wall temperatures were maintained at constant values of $T_C = 303$ K and $T_H = 323$ K by using two circulating (15 L/m) thermostated baths. The vertical temperature gradient along the column was below 0.3 K. The mean temperature, in these conditions, can be estimated as the arithmetic mean between the hot and cold temperatures ($\bar{T} = 313$ K).

Steady-state separation measurements of carbon tetrachloride-cyclohexane and benzene-*n*-heptane mixtures have been performed. Mixtures were prepared volumetrically from pure grade reagents. Purification, when necessary, and handling were performed following the standard techniques reported in the literature (*15*). Experiments at very low values of the molar fractions of both components were not carried out.

The determination of mass concentration was implemented with a Zeiss refractometer (with a nominal accuracy of 2×10^{-5} in the range of the present measurements). Compositions derived from these refractive indices are believed to be accurate to about 0.2 wt%.

The separation data obtained and the α-group calculated for the two liquid systems are quoted in Table 1. The separation factor is defined, as usual, by

$$q = c_T(1 - c_B)/c_B(1 - c_T)$$

where c_T and c_B are the concentrations at the top and the bottom of the column, respectively. Each q value is the arithmetic mean of at least three experimental determinations. The reproductibility in the logarithm of the separation factor is estimated to be about 5%.

DISCUSSION

Because the independence of ψ_s with different types of mixtures is the basis for the procedure for α_T determination suggested in this work, we first checked it by using appropriate mixtures. We chose carbon tetrachloride-cyclohexane mixtures since the TD factors reported by different authors show unusually good agreement. The experimental α_T values obtained in a thermogravitational column by Stanford et al. (*5*) at 25°C and the values of Turner et al. (*15*) obtained by using flow cells agree, within experimental error, with the pure thermal diffusion values reported by Anderson and Horne (*16*).

The α_T values at 40°C used in this work were calculated according to Anderson and Horne's temperature dependence expression of the TD factor. The rest of the physical properties that appear in the parentheses of Expression (1) are taken directly from the literature (*17–19*) and were evaluated at $\bar{T} = (T_H + T_C)/2$ for the initial composition. In Fig. 2 the

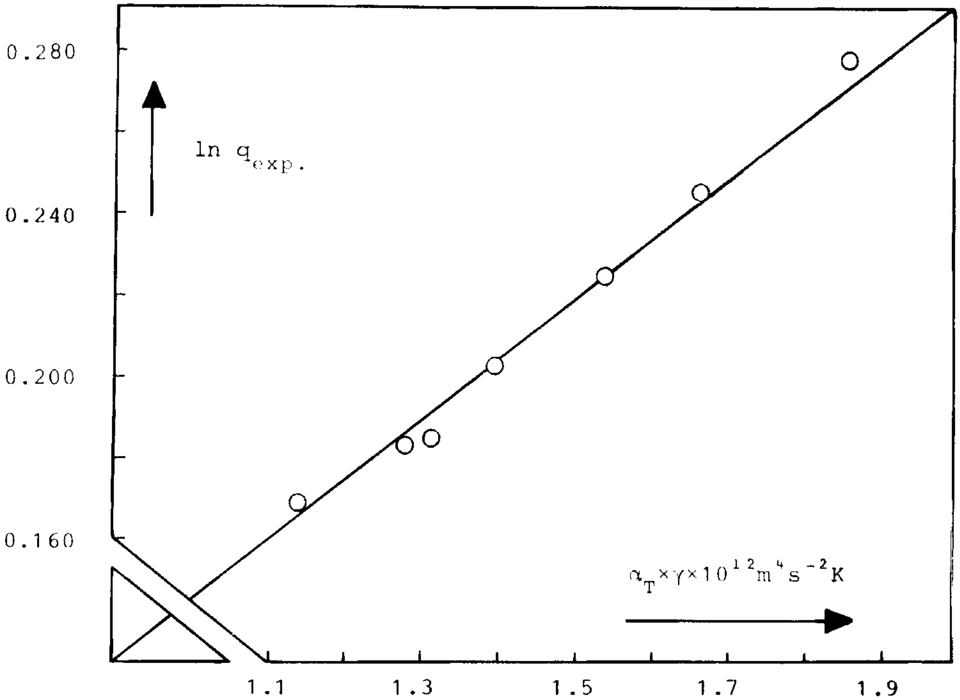

FIG. 2. Logarithm of the experimental separation factor vs group for the carbon tetrachloride–cyclohexane mixtures.

values of ln q_{exp} vs α_T are displayed. The linear relationship found between ln q_{exp} and γ indicates that there is a constant ψ_s characteristic of the column. The value of this constant is 0.145×10^{12} $s^2 \cdot m^{-4} \cdot K^{-1}$.

This empirical value of ψ_s is in good agreement with the theoretical one calculated from Expression (1) and the nominal value for the radii ($\psi_s = 0.136 \times 10^{12}$ $s^2 \cdot m^{-4} \cdot K^{-1}$). This agreement can be interpreted, in principle, as that, in spite of the constructional defects, the behavior of the column was quasi-ideal. Although we are aware of errors in the nominal radii values (about 5×10^{-4} m) and the possible thermal expansion effects on the walls, the direct ψ_s value calculated is affected by a large error since the gap value appears in the formulation as $(\Delta r)^4$, which impedes *a priori* the use of this theoretical value and prevents the extraction of conclusions in relation to the quasi-ideal behavior of the column based on the good agreement existing between the ψ_s empirical value and the theoretical one. In any case, with the empirical ψ_s value it should be possible to obtain, in principle, α_T values of any mixtures from

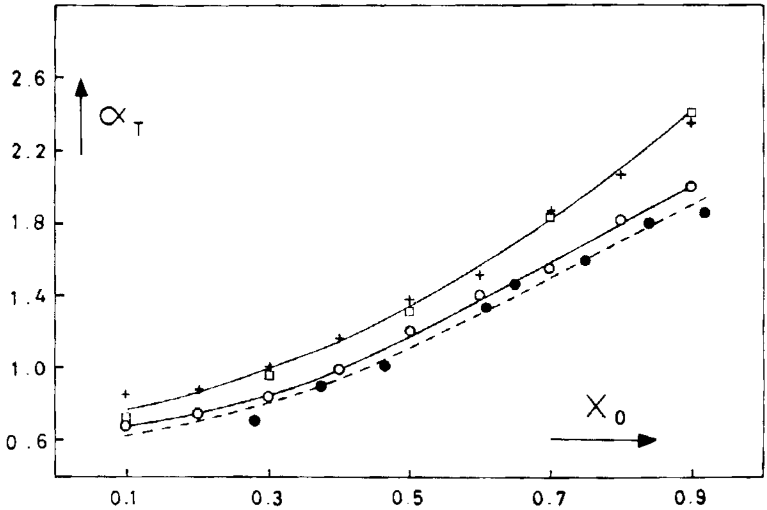

FIG. 3. Thermal diffusion factor of benzene-*n*-heptane mixtures as a function of the molar fraction of *n*-heptane. (●) This work at 40°C, (+) Demichowicz-Pigoniwa et al. (*21*) at 25°C, (□) Korsching (*22*) at 25°C, (O) Korsching (*23*) at 35.5°C. Dashed line: extrapolated α_T values to 40°C from experimental results at 25 and 35.5°C.

the ln q in the steady state once the physical properties, i.e., mutual diffusion coefficient (D), viscosity (η), density (ρ) and thermal expansion coefficient (β), are known for these mixtures. As a check of the procedure, we obtained α_T values for benzene-*n*-heptane mixtures from ln q measurements in the steady state, with D, η, β, and ρ taken from the literature (*17–20*) by using the $\psi_s = 0.145 \times 10^{12}$ $s^2 \cdot m^{-4} \cdot K^{-1}$ value. The results are shown in Fig. 3. Moreover, in this figure the experimental results obtained by Tyrrell et al. (*21*) at 25°C, Korsching (*22*) at 25°C, and Korsching (*23*) at 35°C are also displayed. Rather good agreement between our α_T calculated values and those measured by Korsching et al. at 35°C can be seen. This agreement is excellent when we compare our results with the α_T extrapolated to 40°C from the α_T values obtained by Tyrrell and Korsching at 25°C and the results of Korsching at 35°C (dashed line in Fig. 3).

It is important to point out that the thermal diffusion column constructed for the present experiments exhibits all the construction faults avoided in current work (*5*). However, the internal consistency of the results obtained is as high as those usually claimed for more elaborate measurements in TD columns or static cells. This suggests that nonideal construction does not allow absolute α_T values to be obtained; nevertheless, the ratio α_2/α_1 for two mixtures can be obtained from column separation with good precision. The accuracy limits are not determined by faults in the column construction but by the accuracy of the mixture composition measurement.

These results seem to indicate that the possible influence of the physical properties of a mixture on those effects due to the lack of column perfection are more or less compensated for or are negligible, at least for the quasi-ideal or moderately nonideal mixtures studied in this work. However, more measurements in systems with components with greater differentiated physical properties are necessary to generalize our hypothesis. Unfortunately, the lack of reliable data of α_T in the literature prevents us from checking the proposed method more extensively at the moment. Taking into account these limitations, a thermal diffusion column, in spite of constructional defects, can be a useful tool for obtaining relative α_T values for isotopic and nonisotopic liquid mixtures.

SYMBOLS

c	mass concentration
D	ordinary diffusion coefficient
g	gravitational acceleration
L	column length
q	separation factor
r	radius of the tubes
T	temperature of the walls
$\bar{T}$	average absolute temperature
x_0	initial molar fraction of specified component

Greek Symbols

α_T	thermal diffusion coefficient
β	thermal expansion coefficient
γ	defined in Eq. (1), $\gamma = \eta D/\rho\beta$
ρ	density of the mixture
η	viscosity of the mixture

Subscripts

T	top
B	bottom
C	cold
H	hot

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