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Thermogravitational Column as a Technique for Thermal Diffusion Factor Measurement in Liquid Mixtures

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Abstract

Thermogravitational thermal diffusion separations are studied for benzene-*n*-heptane, benzene-*n*-hexane, toluene-*n*-heptane, toluene-*n*-hexane, carbon tetrachloride-*n*-hexane, and cyclohexane-*n*-hexane mixtures at a mean temperature of 37.5°C. The column used was of 90 cm length with a 0.095 cm gap. Despite its length, this column can be used as a standard for the value of α_T extraction when the separation factor is extrapolated to $\Delta T = 0°C$. Thermal diffusion factors are calculated for benzene-*n*-heptane and benzene-*n*-hexane mixtures in different concentrations. For the rest of the systems investigated, $\alpha_T D_{12}$ values (D_{12} being the ordinary diffusion coefficient) are calculated.

INTRODUCTION

At present there is increasing interest in the study of the thermal and transport properties of liquid and gaseous mixtures (*1*, *2*). A good knowledge of the transport coefficients is necessary for the technical

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design of separation plants (*3–5*). Besides the study of their dependence on temperature, valuable information can be obtained about the molecular interactions, which allows discussion of different theoretical models proposed in the literature. Among all transport properties, thermal diffusion is the most sensitive. However, the experimental determination of the thermal diffusion factor, α_T, which characterizes this phenomenon, is a delicate problem due to the smallness of the effect. In general, two methods have traditionally been used: the "pure thermal diffusion cell" method (*6*) and the "flow-cell" method (*7*) which lead to α_T values which are not always reliable enough because it is difficult to control convection in the cell and also because the values found for separation are extremely small, especially for small concentrations of one of the components of the mixture (*8*, *9*).

For these reasons, the Clusius-Dickel thermal diffusion column has been used recently to get a better determination of α_T values (*10–12*). In this technique the separation is strongly enhanced by the advantage of convection currents. The theory of the operation of the column which connects the separation factor with the thermal diffusion factor was proposed by Horne and Bearman (*13*, *14*). In this theory the equilibrium separation is inversely proportional to the fourth power of the distance between the cylinders or the "gap." Therefore, the columns used for the determination of α_T are of short lengths (<30 cm) in order to maintain this gap as uniform as possible. These lengths strongly limit the advantages inherent in the method (great separation), since the separation is proportional to the column length.

Recently, and after the method successfully followed by Savirón et al. (*15*) for gaseous systems, some attempts have been made to use longer columns in order to get values of α_T through a previous calibration (*16*, *17*). The good results attained seem to confirm the theoretical predictions about the influence of the so-called "forgotten effect" in equilibrium situations which can be rejected, at least for the mixtures used there. Likewise, the possible parasite currents and disturbances in convectional flow due to geometrical faults need not be considered.

The aim of this work is to study the possibility of using columns of approximately 1 meter length to determine α_T with no previous calibration. The values of the separations in these columns led to values of α_T which were more accurate that those obtained by conventional procedures.

2. EXPERIMENTAL METHOD

In this work a thermogravitational column of the Clusius-Dickel type was designed and built. It consists of two concentric cylinders of stainless steel with a total length $L = 90$ cm and an available or work space between them of $\delta = 0.095$ cm. In Table 1 and Fig. 1 the geometrical dimensions and an outline of the column can be found.

Although the mechanical construction of the column was very carefully done, it must be kept in mind that for such a great length, full cylindricity and uniformity in the gap is not always possible.

The sampling ports are designed, as previously reported (*16*), with Viton septums which are drilled with a syringe when an extraction is carried out. In this way, the dead volume of the column is reduced to a minimum. The column walls were thermostatized by means of circulating baths at 15 L/min, thus the hot wall corresponds to the inner cylinder. With this steady circulating flow of thermostatized water, the vertical temperature gradient in the column is lower than 0.3°C/m. The mean temperature, T_m, can be measured as the arithmetic average between the hot and cold wall temperature, T_H and T_C, respectively. In this work, we chose T_m to be 311.5 ± 0.5 K. The experimental procedure is completely similar to that presented in previous work (*16*).

The measurement of the separation factor is defined as usual:

$$q = \frac{c_T(1 - c_B)}{c_B(1 - c_T)}$$

where c_T and c_B are the concentrations at the top and the bottom of the column, respectively, and were obtained in the steady-state, q_∞. The determination of mass-concentration was realized with a Zeiss refractometer, with a nominal accuracy of 2×10^{-5} in the range of the present measurements. The separation factor was measured for several concentrations of the systems benzene-*n*-heptane, benzene-*n*-hexane, toluene-

TABLE 1
Basic Dimensions of Our Thermogravitational Column

Inner diameter of the outer cylinder: $2r_C = 60.94 \pm 0.02$ mm
Outer diameter of the inner cylinder: $2r_H = 59.04 \pm 0.02$ mm
Annulus width (gap): $\delta = r_C - r_H = 0.95 \pm 0.02$ mm
Total length: $L = 900$ mm
Effective length: $L_e = 791 \pm 1$ mm

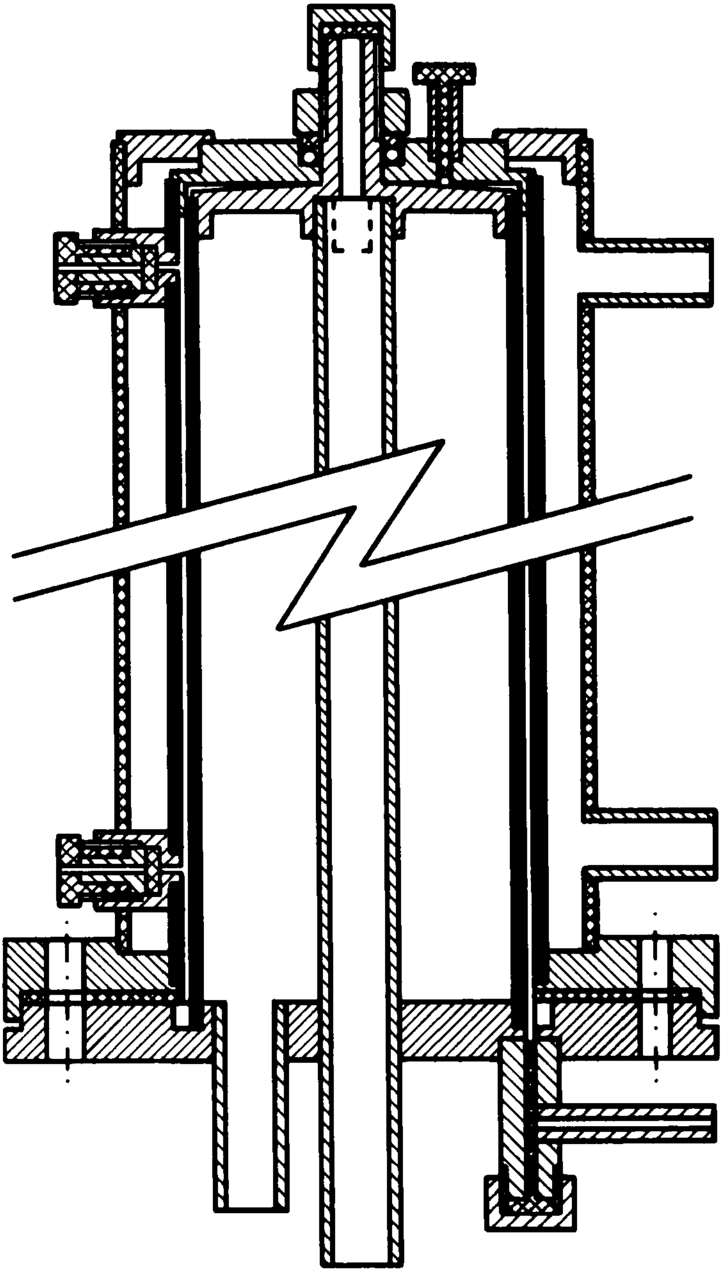

FIG. 1. Cross-sectional view of our thermal diffusion column showing the work space and auxiliary connecting tubes for thermostated baths.

n-heptane, toluene-*n*-hexane, carbon tetrachloride-*n*-hexane, and cyclohexane-*n*-hexane. The reproductibility in the logarithm of the separation factor was estimated to be better than 5%.

3. RESULTS AND DISCUSSION

In accordance with the Horne and Bearman theory (*13*, *14*), the steady-state separation factor logarithm for the thermogravitational diffusion in liquid mixtures of nonelectrolytes is defined as

$$\ln q_\infty = \frac{504L_e}{g(2\sigma r_0)^4 T_m} \frac{\alpha_T \eta D_{12}}{\rho} \tag{1}$$

where ρ, η, and D_{12} are the density, the viscosity, and the diffusion coefficient of the liquid mixture, respectively, β is the expansion coefficient, and g is the acceleration of gravity. The σ and r_0 values are defined as

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

where r_C and r_H are the cold and hot wall radii. T_m is the mean temperature to which the physical properties must be related. For the temperature gradients employed in this work, it can be considered that $T_m = (T_H + T_C)/2$. Equally, the gap between the concentric columns (δ) is small enough to assume that $(2\sigma r_0)^4 \approx \delta^4$. Equation (1) allows us to relate the values of the separation obtained in the column with the terminal diffusion factor α_T.

According to this theory, the separation must be essentially independent of the temperature difference between the walls of the column, ΔT. Thus, for carbon tetrachloride-*n*-hexane mixtures, this theory predicts that $\ln q_\infty$ does not depend on ΔT within a precision of 0.1% in the range $0.28°\text{C} < \Delta T < 56.8°\text{C}$ (*18*, *19*, *21*). However, Beyerlein and Bearman (*19*) experimentally found a slight dependence of about 1% of the increase in the $\ln q_\infty$ value per each degree centrigrade of increase in ΔT in a column with reservoirs. This dependence, although small, is much larger than the one predicted by the theory. The theory–experience discrepancy can essentially be due to the fact that Horne and Bearman took no account of the remixing currents which take place at the extremities of the column, neither of the dead spaces nor of the reservoirs. Ecenarro et al. (*20*) established that the temperature difference effects in a column without reservoirs can also be due to local remixing at the extremities of a thermal diffusion column, and they are inversely proportional to the column length. This dependence explains the small negative ΔT dependence found by Stanford and Beyerlein in short columns (of about 0.25%/°C) (*21*). For the column used in this work, with an approximate length of 1 m and small dead spaces, the effect of the remixing currents on the value of separation must be, in accordance with Ref. *20*, so small as to be disregarded.

These predictions were experimentally tested with different compositions of the systems studied in this work. The dependence of the separation factor on ΔT, at a mean constant temperature T_m equal to 37.5°C, was studied. The results obtained for the benzene-*n*-heptane and benzene-*n*-hexane systems are shown in Fig. 2. Analogous results were obtained for the rest of the mixtures. It is observed that the dependence of $\ln q_\infty$ on ΔT is stronger than the one predicted previously in Ref. *20* and, moreover, for an increase in ΔT, an increase in $\ln q_\infty$ is obtained. This result means that the strong dependence of the separation on ΔT is not due to remixing in the possible dead spaces, but, on the contrary, could be

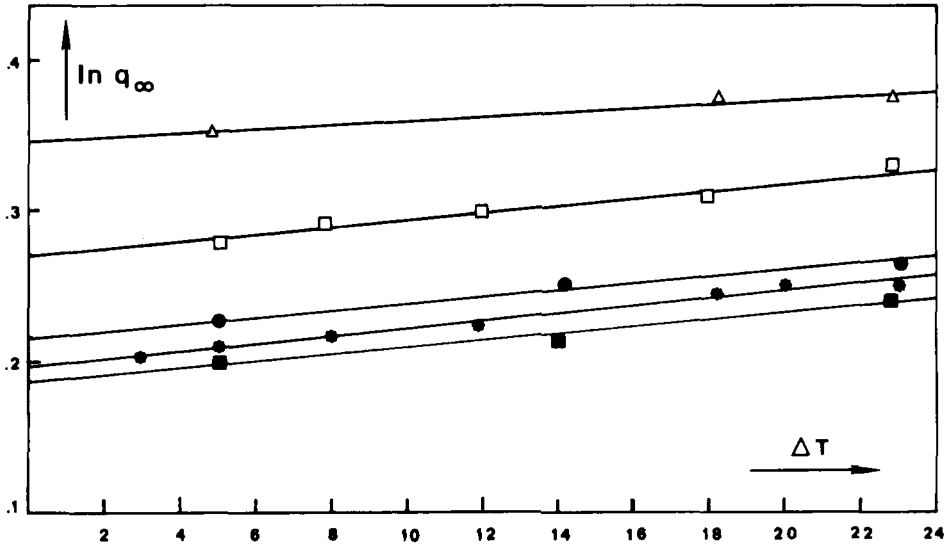

FIG. 2. Dependence of the steady-state separation factor logarithm on ΔT for some different concentrations of benzene (x_0) in benzene-*n*-hexane (BHX) and benzene-*n*-heptane (BHP) systems. (△) BHX, $x_0 = 0.84$; (□) BHX, $x_0 = 0.72$; (●) BHX, $x_0 = 0.52$; (*) BHP, $x_0 = 0.56$; (■) BHX, $x_0 = 0.37$.

due to deformations produced by thermal dilatations of the column which modify the "gap." These deformations have been shown by direct observation of the volume variation of a liquid mixture into our column at a constant mean temperature for a direct and inverse gradient. Nevertheless, this geometrical deformation cannot wholly explain the strong dependence of ln q_∞ on ΔT, because we suspect that the physical properties of the mixture are also important in this behavior. Summarizing, in spite of reducing the dead spaces and taking off the reservoirs, a considerable temperature difference effect can exist due to inherent design problems (welds between cylinders, etc.), the column material constituents, and possible effects on the hydrodynamics of the thermogravitational circulation due to the vertical concentration gradient.

Nevertheless, the errors resulting from a lack of accuracy in knowledge of the "gap" due to the temperature difference effect can be removed by correcting the logarithm of the separation factor to $\Delta T \simeq 0°\text{C}$, say ln q^0_∞. Values for the separation factor logarithm in the steady-state, corrected in this way and obtained for mixtures of benzene-*n*-heptane, benzene-*n*-hexane, toluene-*n*-heptane, toluene-*n*-hexane, carbon tetrachloride-*n*-hexane, and cyclohexane-*n*-hexane, are given in Fig. 3. When these values are used in Eq. (1) for ln q, we are able to employ the geometrical dimensions of the column measured without thermal gradients (L = 79.1 cm, δ = 0.095 cm) and to determine the value of α_T if the values of the auxiliary magnitudes (η, ρ, β, D_{12}) which appear in this expression are known. In the different mixtures of benzene-*n*-heptane, the values used for these auxiliary magnitudes were the same as in previous works. For the diffusion coefficients D_{12}, those measured by Sanni et al. (*22*) were used, whereas for the calculation of ρ and η, a method analogous to the one of Navarro (*23*) was used, in accordance with the specific volumes of the pure constituents. Finally, the viscosities were measured by us at the work temperature (*24*). In Fig. 4 we show the α_T values obtained together with those taken from other authors. As can be seen, the agreement between α_T values obtained in our thermogravitational column and those obtained by Korsching (*25*) at T = 308.5 K from the pure thermodiffusion effect, especially from the middle concentration zone, is highly satisfactory, and the deviations between both groups do not exceed 3%. The largest deviations are observed in benzene at low concentrations, i.e., low separations, and for these the results obtained in the elementary cell can be affected by strong errors. On the other hand, agreement can be considered to be excellent according to what was obtained by Navarro at T = 313 K from a thermogravitational column through calibration.

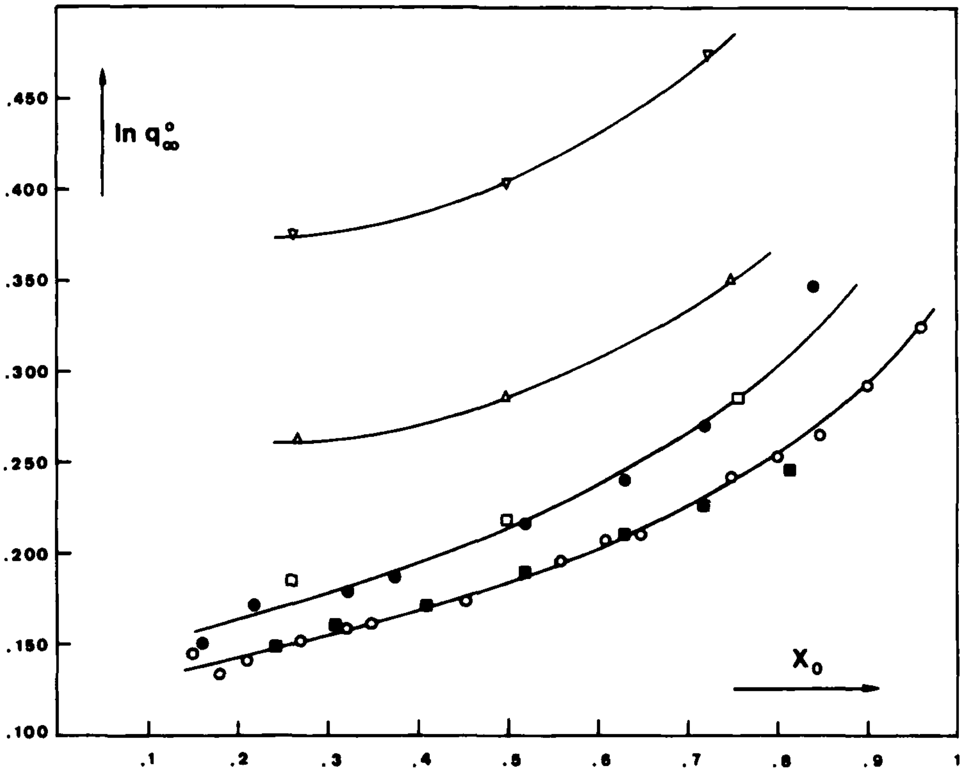

FIG. 3. Extrapolated steady-state separation factor logarithm to ΔT = 0°C vs molar fraction of the first component named for benzene-*n*-heptane (○), benzene-*n*-hexane (●), toluene-*n*-heptane (■), toluene-*n*-hexane (□), cyclohexane-*n*-hexane (△), *n*-hexane-carbon tetrachloride (▽) systems.

Another system used as a reference to check the reliability of our thermal diffusion column for α_T measurements was made of benzene and *n*-hexane because of many reported data on the auxiliary properties which are necessary to make use of Eq. (1). In the actual case of the ordinary diffusion coefficients D_{12}, values calculated from those already determined by Harris et al. (*28*) through Goüy diffusiometry, as well as those recently obtained by Krahn et al. (*29*) for dilute mixtures by quasielastic light scattering, were used. The viscosity values were determined by us at the work temperature. Regarding the values of ρ and β, the same procedure as for the first system was used. The values of α_T obtained by this method are shown in Fig. 5 together with those obtained

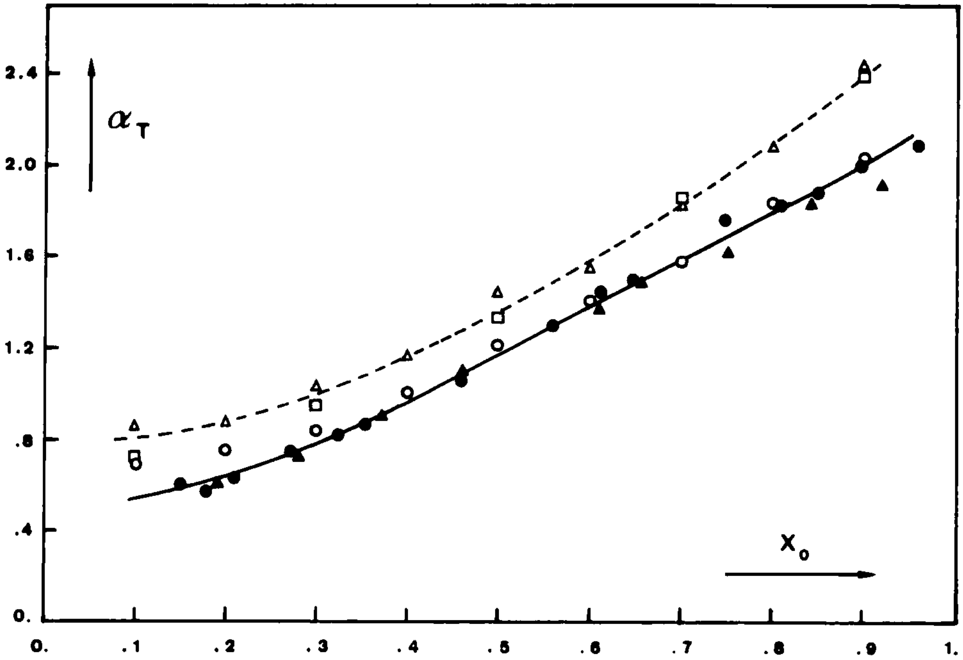

FIG. 4. Thermal diffusion factor of benzene-*n*-heptane system vs molar fraction of benzene. (●) This work, at 37.5°C; (○) Korsching, at 35.5°C (*25*); (▲) Navarro et al., at 40°C (*16*); (□) Korsching, at 25°C (*26*); (△) Demichowicz-Pigoniowa et al., at 25°C (*27*); (- -) fitting of experimental values at 25°C.

by Korsching (*25*) at T = 308.5 K in the elementary thermodiffusion cell. We again note excellent agreement between these sets of results.

Unfortunately, for the rest of the systems studied in this work, it was not possible to obtain α_T values because of the lack of reported D_{12} and α_T values. Nevertheless, for these systems we chose to calculate the product $\alpha_T D_{12}$. From Eq. (1), we can write

$$\alpha_T D_{12} = \frac{\rho\beta}{\eta} \frac{\ln q_\infty^0}{\Psi_s}$$

where Ψ_s includes the geometrical and thermal characteristics of the column. The values of $\ln q_\infty^0$ employed in the calculation were obtained from a study of the dependence of $\ln q_\infty$ with ΔT, extrapolating to ΔT = 0°C, and they are shown in Fig. 3. The viscosity values for all these

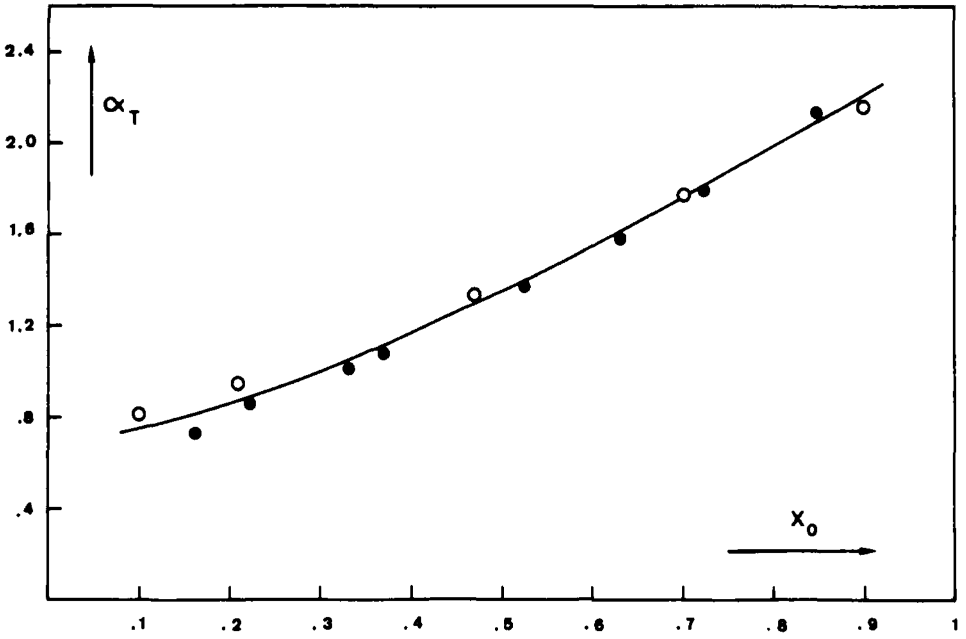

FIG. 5. Thermal diffusion factor of benzene-*n*-hexane system vs molar fraction of benzene. (●) This work, at 37.5°C; (O) Korsching, at 35.5°C.

mixtures were also determinated by us. The density and the expansion coefficient values have been taken from the *International Critical Tables* (*30*), following a procedure analogous to that described for benzene-*n*-heptane and benzene-*n*-hexane.

The results obtained for $\alpha_T D_{12}$ are shown in Figs. 6 and 7. First, one can check that the product $\alpha_T D_{12}$, which is an important number in material transport, has similar values for the benzene-*n*-heptane and toluene-*n*-heptane systems when there is a high concentration of the common component in the mixture. The same occurs in the case of benzene-*n*-hexane and toluene-*n*-hexane systems for rich *n*-hexane mixtures. On the other hand, for higher concentrations in benzene and toluene, it is observed that the $\alpha_T D_{12}$ value for the system containing benzene is higher than for the system containing toluene. This means that the different molecular structures of benzene and toluene decisively affect the mass transport.

From the results obtained for benzene-*n*-heptane and benzene-*n*-hexane systems, we can say that our column behaves as a standard one,

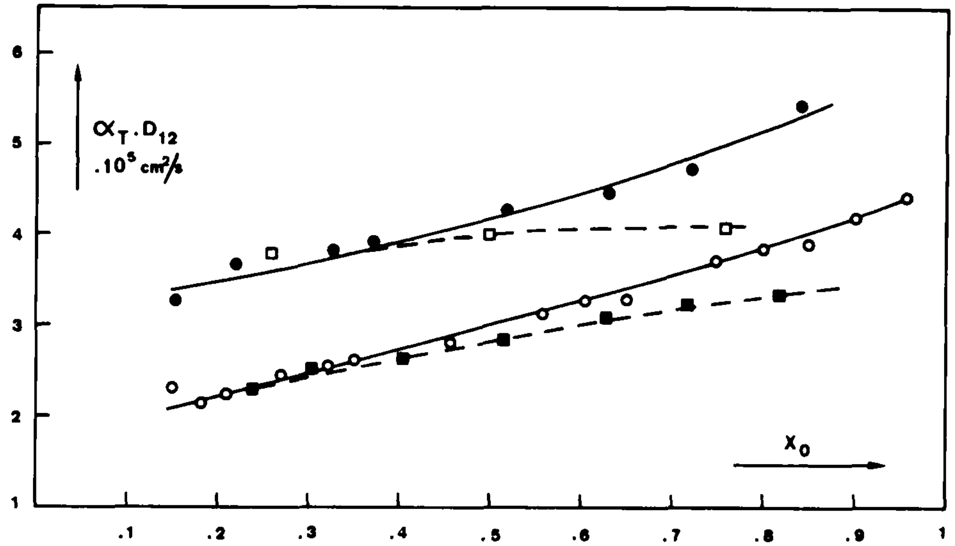

FIG. 6. Values for $\alpha_T D_{12}$ vs molar fraction of benzene (toluene) for benzene-*n*-hexane (●), benzene-*n*-heptane (○), toluene-*n*-hexane (□), and toluene-*n*-heptane (■) systems at 37.5°C.

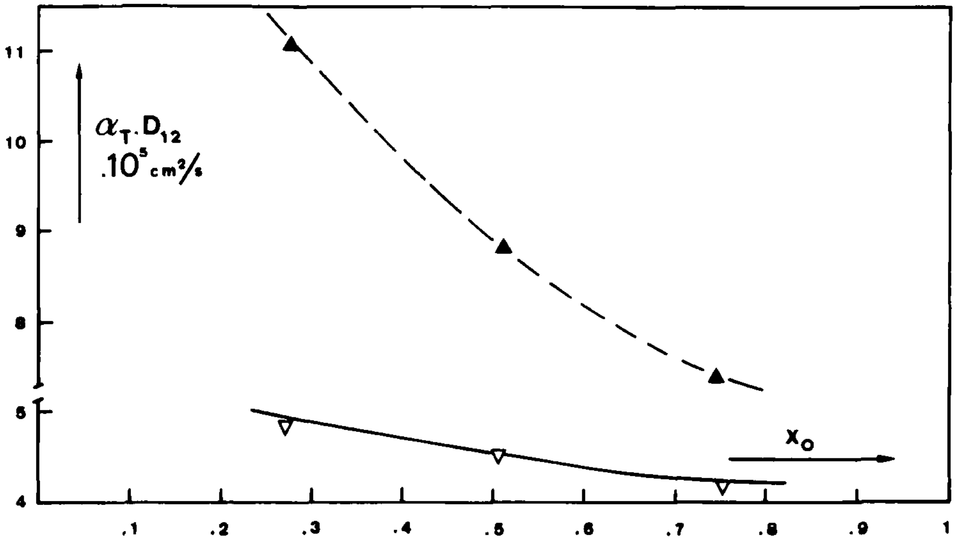

FIG. 7. Values for $\alpha_T D_{12}$ vs molar fraction of carbon tetrachloride (cyclohexane) for carbon tetrachloride-*n*-hexane (▲) and cyclohexane-*n*-hexane (▽) systems at 37.5°C.

and therefore it is able to yield reliable values of α_T without any need for previous calibrations, at least for the quasi-ideal or moderately nonideal mixtures studied. The only precaution is that we must use the value of ln q_∞ extrapolated to $\Delta T = 0°C$, ln q_∞^0, in order to avoid the possible geometrical deformations inherent to our experimental design and the dependence on the mixture used. This conclusion is very interesting for the design of thermal diffusion columns, since up to now, only columns of small lengths (10–30 cm) have been used for the determination of α_T because of trying to get carefully designed geometries in order to apply the Horne and Bearman theory. This limit in the length leads to some excessively small values of the separation, which are very difficult to measure, and therefore increase the experimental error. Besides, in these short columns the relative influence of the nonactive volumes in the most distant points is large, and the extraction volume can bring important deviations from the real ones in the measured separation value. Therefore, the initial advantages of the use of a thermal diffusion column remain strongly limited.

SYMBOLS

c	mass concentration
D_{12}	ordinary diffusion coefficient
g	gravitational acceleration
L	total column length
L_e	effective column length
q	separation factor
q_∞	steady-state separation factor
q_∞^0	steady-state separation factor extrapolated to $\Delta T = 0°C$
r	radius of the tubes
r_0	mean radius
T	temperature of the walls
T_m	mean temperature
x	molar fraction

Greek

α_T	thermal diffusion factor
β	thermal expansion coefficient
δ	gap, or work space width

η	dynamic viscosity of the mixture
ρ	density of the mixture
σ	addimensional constant, defined by Eq. (1)
Ψ_s	constant including thermal and geometrical characteristics

Subscripts

T	top
B	bottom
C	cold
H	hot

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