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Fickian and thermal diffusion coefficients from liquid thermogravitational columns

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Abstract. Experimental data on ordinary diffusion coefficients and thermal diffusion factors for binary liquid systems containing hexane, heptane, benzene, toluene and carbon tetrachloride are derived from steady-state and non-steady-state separation measurements in a thermal diffusion column. The data extraction method uses a time evolution theory previously developed by the authors that accounts for the *forgotten effect*. Comparison of the diffusion data with those of the literature provides a test of the derived thermal diffusion factors.

1. Introduction

Thermal diffusion (TD) is the transport of matter associated with a thermal gradient and may occur both in liquid and gaseous mixtures. Liquid thermal diffusion has recently aroused considerable interest in such diverse problems as the analysis of hydrodynamic instability in mixtures (Platten and Legros 1984), mass transport in living matter (Bonner and Sundelöf 1984), and some practical problems, such as the migration of minerals (Costeséque 1985). The quantity relevant in the description of the phenomenon is the thermal diffusion factor and considerable efforts have been devoted to determine its value in different kinds of mixture (Grodzka and Facemire 1977). However, the available data show large uncertainties and in some cases even the sign of the quantity is questionable (Legros *et al* 1985).

The TD separation occurring in a mixture is usually small. Higher separations can be achieved in a thermogravitational column where the pure effect is amplified to a considerable extent by countercurrent convection, the net result being the appearance of a stationary (steady-state) separation between the ends of the column. Owing to such relatively large separations, columns have been employed to determine thermal diffusion factors (Tyrrell 1961, Stanford and Beyerlein 1973, Rutherford 1987, Ecenarro *et al* 1989a). The theory describing the column stationary behaviour has been firmly established (Horne and Bearman 1968, Navarro *et al* 1982), at least in the case of mixtures far from its critical conditions and, in particular, it has been shown that the so-called 'forgotten effect' which accounts for the influence on separation of the density

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composition dependence, can be neglected. A large body of experimental work carried out with different types of column indicates that this theory correctly describes the column operation under stationary conditions.

Until now, data on non-stationary separation have scarcely been used to obtain information about the mass transport coefficients; this has mainly been due to the lack of a precise theory of the transient operation that includes the 'forgotten effect'. This theory for closed columns has been developed by us in a previous work and the preliminary experimental results have shown that it gives a good description of the non-stationary separation process in the column (Ecenarro *et al* 1989b).

According to the mentioned theories both steady-state and non-steady-state separation depends on the ordinary diffusion coefficient and the thermal diffusion factor. Consequently, both coefficients may, in principle, be derived from measurements in thermogravitational columns.

In the present work we report measurements of transient separation obtained in a thermogravitational column for five binary liquid systems. Analysis of the results shows that accurate values of both Fickian and non-Fickian diffusion coefficients can be extracted from column separation data. The practical importance of this conclusion stands in the fact that comparison of diffusion coefficients obtained in this way with those derived by conventional methods provides a stringent test of the validity of the theoretical treatment of column operation and thus of the values extracted for the thermal diffusion factor.

2. Theory

The theory of steady-state separation in a thermogravitational liquid column was developed by different authors. According to this theory the forgotten effect can be overlooked at steady state and hence separation is given by:

$$l_{\infty} = (504L/g\bar{T}\sigma^4)(\alpha\eta D/\rho\beta) \quad (1)$$

where l_{∞} is the natural logarithm of the steady-state separation factor; η , ρ and β are, respectively, the viscosity, density and the thermal expansion coefficient, \bar{T} is the mean temperature of the mixture, g is the acceleration due to gravity, α is the thermal diffusion factor that is considered to be positive when the less dense component migrates toward the hot wall, D is the ordinary diffusion coefficient and L and σ are the length and the annular gap width of the column, respectively.

Equation (1) allows one to determine the product αD of the two mass transport coefficients from steady-state separation measurements, if the remaining thermo-physical properties of the mixture present in this equation together with the column geometrical characteristics are known. In particular, due to the dependence of l_{∞} on σ , accurate values of the annular gap dimensions are required. Although according to equation (1) stationary separation does not depend on the difference in temperature between the walls of the column, experimentally it is seen that this dependence exists (Ecenarro *et al* 1985), mainly due to small changes in the dimensions of the gap caused by the effect of thermal expansion of the material used to construct the column. It has been shown (Ecenarro *et al* 1989a, Stanford and Beyerlein 1973), that the errors associated with this lack of accuracy in the knowledge of the dimensions of the gap can be removed by using in equation (1) the values of l_{∞} obtained by extrapolation of the experimental measurements of this quantity to zero thermal gradient. Following this

procedure reliable values of αD have been reported by Ecenarro *et al* (1989a) for the mixtures that we shall consider in the next section.

The theory describing non-stationary (non-steady-state) behaviour taking into account the forgotten effect was developed by us in a previous work (Ecenarro *et al* 1989b). From the numerical resolution of the partial differential equation (PDE) of the approach to equilibrium, the theory gives the time evolution of the quantity Ω defined by

$$\Omega(t) = 1 - l(t)/l_{\infty} \quad (2)$$

where t is the operating time of the column and $l(t)$ the corresponding natural logarithm of the non-stationary separation factor. To solve this equation, it is necessary to know the separation parameter of the mixture, defined by

$$S = \alpha c(1 - c)\gamma/\beta\bar{T} \quad (3)$$

where c is the mass fraction of the less dense component and γ is the isothermal coefficient of density variation with concentration. The separation parameter determines the magnitude of the forgotten effect. In particular, for $S = 0$, one has *ideal* column behaviour, corresponding to nil forgotten contribution. The range of S values for which the theory is valid is $0 \leq S \leq 2$, which covers most practical cases.

On the other hand, for a given value of S , the solution for Ω is given in terms of a non-dimensional time τ , related to time t through

$$\tau = \Gamma t \quad \Gamma = [\sigma^6(\Delta T)^2 g^2 / 9! L^2](\rho^2 \beta^2 / \eta^2 D) \quad (4)$$

where ΔT is the temperature difference between the column walls.

According to equations (1)–(4), to determine stationary and non-stationary separation, it is necessary to know the values of the coefficients α and D . Conversely, both coefficients can be extracted from measurements of $l(t)$ for different times and l_{∞} . The calculations necessary to do this can be performed if one takes into account that the dependence of Ω on separation parameter represents a correction to the ideal behaviour of the column ($S = 0$). Thus, an approximate value of Γ can be obtained by comparing the experimental Ω against t data with the theoretical solution Ω against τ for $S = 0$. From this value of Γ , equations (1), (3) and (4) give an approximate value of the separation parameter that in turn allows one to obtain a more reliable theoretical solution. With this latter solution one starts the calculation again, in the worst case three steps being required to determine correct values of Γ . The highest value of the forgotten correction to the values of Γ initially calculated proves to be approximately 30% and corresponds to values of the separation parameter $S = 2$. From the value of Γ thus obtained, equations (1) and (4) allow one to determine the coefficients α and D .

The strong dependence of Γ and σ in equation (4) may give rise to important errors in determining α and D when changes occur in the dimensions of the annular gap due to thermal expansion of the column walls. These errors may be reduced to acceptable limits using for Γ the equation

$$\Gamma = [7(\Delta T)^2 / 10\sigma^2 l_{\infty}^2] \alpha^2 D \quad (5)$$

obtained from equations (1) and (4) and where the measured values of l_{∞} must be introduced. In the above calculations, this equation should be combined with the values of the product αD corrected for temperature difference effects. In the column described in the following section, the changes in the annular width for a difference in temperature

of 4 °C, are less than 1.5%. Thus, the error bound introduced by this cause in equation (5) is 3%, which is within the range of experimental error.

We can also mention here that equation (5) suggests an alternative procedure to the one based on equation (1) for determining the thermal diffusion factor when reliable data for the ordinary diffusion coefficient exist. The advantage of this procedure lies in that by using only stationary and non-stationary measurements in the column it is possible to determine α without previous knowledge of the physical properties of the mixture, except for D , and via a formulation that is relatively insensitive to errors in the dimension of the annular gap and in the diffusion coefficient itself.

In the following section we offer results for the coefficients α and D of different binary mixtures obtained from measurements in the column following the method proposed here.

3. Experimental results

The liquid thermal diffusion column used in this work is a conventional stainless-steel, concentric-tube type closed at both ends, which has been described in detail in earlier publications (Ecenarro *et al* 1989a). The total length of the column is $L = 0.9$ m and the distance between the sampling ports at the ends is 0.791 m. The annular gap dimension is 0.95 mm. The temperatures of the walls were maintained at constant values using two circulating (15 l min^{-1}) thermostatically controlled baths. The temperature difference across the annulus is considered to be the temperature difference between the two water baths corrected for the conductivity of the stainless-steel walls ($\Delta T = 4$ K). The mean temperature under our experimental conditions is the arithmetic mean between the hot and cold temperatures, $\bar{T} = 311$ K. Determination of mass concentration was carried out with a Zeiss refractometer. A Pulfrich-type refractometer (with a nominal accuracy of 5×10^{-6}) has been used in some experimental runs when more precise determinations were required. The experimental procedure and the preparation and manipulation of the liquid mixture have been described elsewhere (Ecenarro *et al* 1989a). The reproducibility in the logarithm of the separation factor was estimated to be better than 5%.

Five binary systems comprising the following components were used: benzene (B), n-hexane (HX), n-heptane (HP), toluene (T) and carbon tetrachloride (CT). The systems considered, the working concentrations and the values of αD obtained from equilibrium measurements by Ecenarro *et al* (1989a) are shown in table 1. The same table also gives (where it has been possible to obtain these from the literature) the values of the ordinary diffusion coefficient and of the thermal diffusion factor of the different mixtures analysed.

For the B-HX and B-HP systems, there are reliable data on the two coefficients α and D which can be compared with those obtained by us. The thermal diffusion factor has been carefully measured by Korsching (1969) in an elementary cell and there are also reliable data from Sanni *et al* (1971), Krahn *et al* (1983) and Harris *et al* (1970) for the diffusion coefficient at different temperatures.

The results obtained for the T-HX and T-HP systems allow one to compare the different behaviour of ordinary diffusion and thermal diffusion when toluene is substituted by benzene in the mixtures with hexane and heptane. The literature only affords data on the ordinary diffusion coefficient of the T-HX system at 25 °C. Table 1 shows the values of this quantity at the working temperature obtained by extrapolation of data at 25 °C using the Wilke correlation (Tyrrell and Harris 1984).

Table 1. Comparison of the thermal diffusion factors, α , and ordinary diffusion coefficients, D , obtained in this work with those given in the literature. The mole fractions, x , correspond to the first-named component and S is the separation parameter. B = benzene, HX = n-hexane, HP = n-heptane, T = toluene, CT = carbon tetrachloride.

Mixture	x	αD ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	S	α		D ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	
				This work	Literat.	This work	Literat.
B-HP	0.32	2.56	0.096	0.85	0.88 ^a	3.01	3.12 ^b
	0.56	3.13	0.205	1.26	1.30 ^a	2.48	2.41 ^b
	0.80	3.85	0.228	1.84	1.83 ^a	2.09	2.09 ^b
B-HX	0.33	3.82	0.135	1.01	1.08 ^a	3.78	3.78 ^{+c}
	0.52	4.31	0.232	1.41	1.42 ^a	3.06	3.12 ^{+c}
	0.72	4.72	0.277	1.67	1.78 ^a	2.82	2.70 ^{+c}
T-HP	0.41	2.65	0.139	1.05	—	2.52	—
	0.63	3.11	0.212	1.29	—	2.42	—
	0.82	3.34	0.162	1.38	—	2.40	—
T-HX	0.26	3.82	0.114	0.94	—	4.06	3.94 ^{+d}
	0.50	3.98	0.198	1.14	—	3.49	3.25 ^{+d}
	0.76	4.03	0.190	1.31	—	3.08	2.90 ^{+d}
CT-HX	0.28	11.0	1.303	3.08	—	3.59	3.60 ^{+d}
	0.51	8.81	1.494	2.83	—	3.11	3.00 ^{+d}
	0.74	7.32	1.160	3.05	—	2.40	2.40 ^{+d}

† Extrapolated values at 37.5 °C

a Korsching (1969)

b Sanni *et al* (1971)

c Krahn *et al* (1983), Harris *et al* (1970)

d Ghai and Dullien (1974)

Finally, the CT-HX system was chosen in view of its high separation parameter mainly due to the large difference between the densities of the pure components. The data of Ghai and Dullien (1974) at 25 °C are available in the literature. The values shown in table 1 were extrapolated at the mean temperature of our experiments using the aforementioned correlation.

Following the procedure described in the previous section, we obtained the values of α and D shown in table 1. The required values of the density coefficients β and γ in calculating the separation parameter were derived from experimental density data of the pure components (Timmermans 1959) assuming an ideal mixture. As may be seen, the agreement with the data offered in the literature for B-HX and B-HP systems is well within 6% for all the concentrations considered. For the rest of the mixtures, for which only data on the ordinary diffusion coefficient are available, good agreement can also be seen between these data and those obtained by us.

With the values of α and D obtained the theoretical solution of Ω as a function of time, was calculated for each mixture. The results are shown as a continuous line in figures 1 and 2. The same figures show the experimental values for Ω against t obtained from measurements of stationary and non-stationary separation in the column. As may be seen, in all cases the non-stationary state theory developed by us correctly describes the operation of the column.

Incidentally, figure 3 shows the values of α and D obtained for the B-HP and T-HP systems as a function of composition. Figure 4 shows the same information for B-HX and

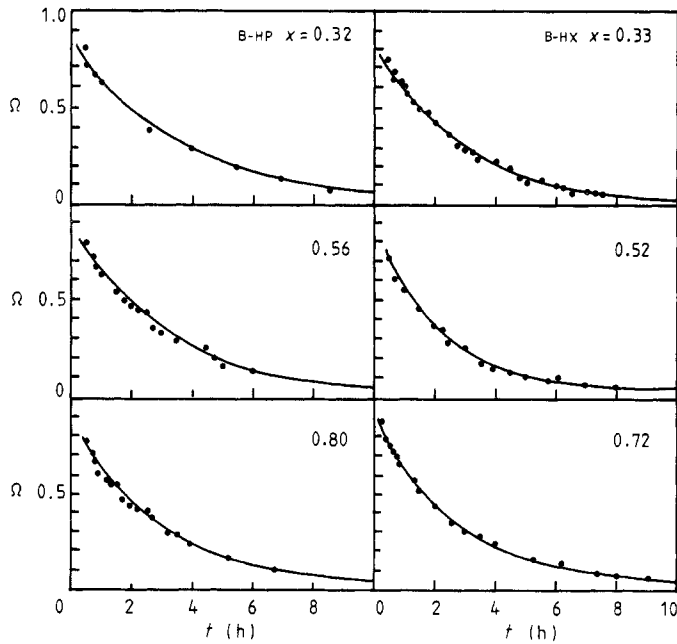


Figure 1. Dependence of Ω (equation (2)) versus time for different mixtures of B-HP and B-HX systems. ●, experimental results. The full curves represent the theoretical results. x is the initial mole fraction of the first-named component.

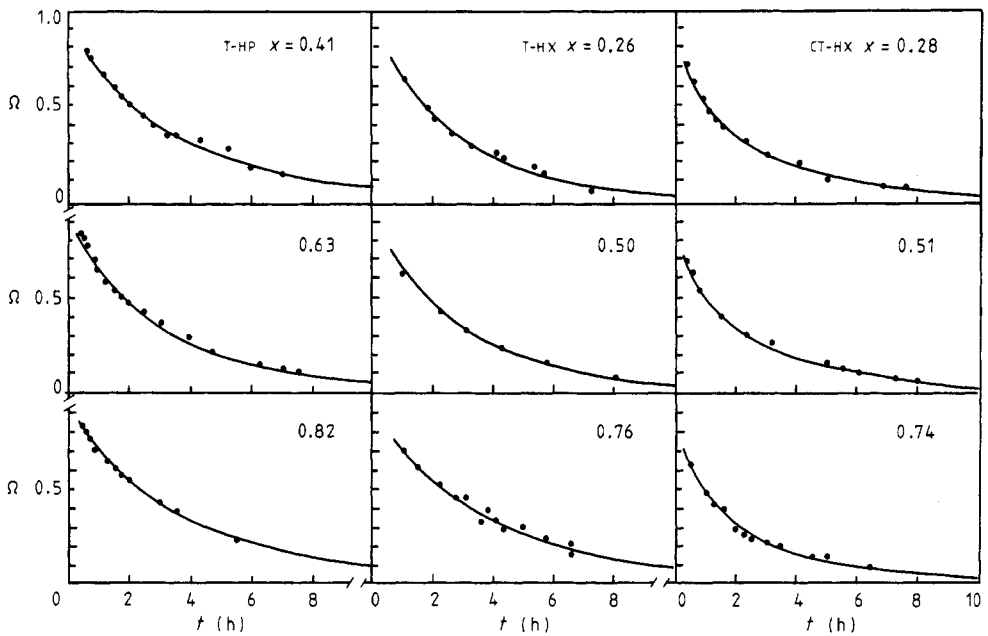


Figure 2. Dependence of Ω (equation (2)) versus time for different mixtures of the T-HP, T-HX and CT-HX systems. ●, experimental results. The full curves represent the theoretical results. x is the initial mole fraction of the first-named component.

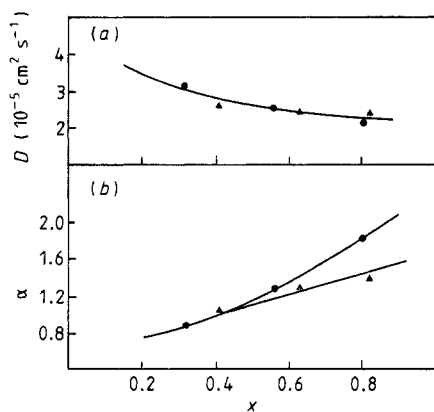


Figure 3. (a) Ordinary diffusion coefficient and (b) thermal diffusion factor versus mole fraction of benzene: ●, B-HP system; ▲, T-HP system.

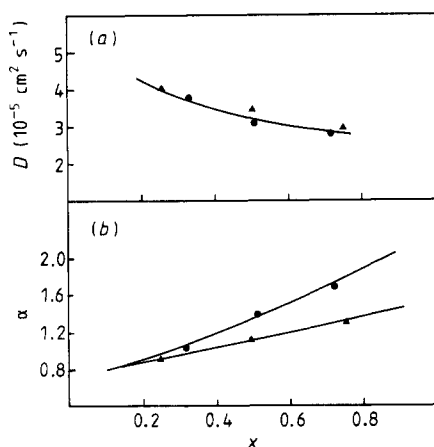


Figure 4. (a) Ordinary diffusion coefficient and (b) thermal diffusion factor versus mole fraction of benzene: ●, B-HX system; ▲, T-HX system.

T-HX systems. In both figures it may be seen that the ordinary diffusion coefficient changes very little when benzene is substituted by toluene in the mixture containing n-heptane or n-hexane. The same is true for other properties such as density and viscosity. However, the thermal diffusion factor differs considerably, in particular, in the case of mixtures rich in benzene or toluene. These results show that in liquid mixtures, as in gaseous ones, thermal diffusion is more sensitive than other properties to small modifications in the molecular characteristics of the components.

From the foregoing results, it may be concluded that it is possible to determine accurate values of the thermal diffusion factor and ordinary diffusion coefficient from measurements of stationary and non-stationary separation in a thermogravitational column when the correct theory is employed to describe the transient phenomenon. The agreement of the values of the ordinary diffusion coefficient with those found in the literature is a robust test of the validity of the values obtained for the thermal diffusion factor.

Although the mixtures studied here have separation parameter values in the range $0 \leq S \leq 2$, it would be expected that the thermogravitational method could be extended to mixtures with negative S values in which the data in the literature show great dispersion and to mixtures with large S values (critical mixtures). In all these cases, analysis of the

data on non-stationary separation may be the only route for extracting thermal diffusion factors from column measurements. Our efforts are directed towards extending the theory to S -values outside the range $0 \leq S \leq 2$, in order to interpret experiments currently under way with critical mixtures, in which large separations are obtained that cannot be interpreted using the above theory.

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