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Thermogravitational measurement of the Soret coefficient of liquid mixtures

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Abstract. We have designed and constructed a thermogravitational column for determining the Soret coefficient of liquid mixtures. The excellent agreement of the results obtained for toluene and *n*-hexane mixtures with recent accurate measurements performed by optical methods shows the validity of the thermogravitational method when a column with the correct geometry is used. We have applied this technique to determine the Soret coefficient of the binary systems benzene–*n*-heptane and carbon tetrachloride with cyclohexane, methanol and ethanol. Comparison with the literature data allows us to determine the reliability of the existing measurements of thermal diffusion for these mixtures.

1. Introduction

The phenomenon of thermal diffusion consists in the appearance of a concentration gradient when a mixture is subjected to a temperature gradient. The magnitude of the effect depends on the so-called Soret coefficient. This coefficient is usually measured using thermodiffusion cells or using thermogravitational columns. In the first case, the mixture is placed between two horizontal walls at different temperatures and the resulting concentration gradient is measured in the absence of convection. In the case of thermogravitational columns, the two walls are vertical. Under these conditions the elementary effect of separation by thermal diffusion is combined with vertical convective currents, giving rise to an enhanced separation between the two ends of the column. Measurement of the stationary separation achieved allows one to determine the Soret coefficient of the mixture.

Although much attention has focused on measuring the Soret coefficient of different binary liquid mixtures, the results available in the literature differ considerably. It thus seems that new measurements should be performed using different techniques to obtain reliable data. Precise values of the Soret coefficient are needed, for example, in the analysis of the phenomena of hydrodynamic instability (Platten and Legros 1984, van Vaerenbergh *et al* 1991, Velarde and Schechter 1971) and in the design of separation set-ups (Lin *et al* 1991). In liquid theory they are needed for comparing the results with those of molecular simulations (Vogelsang and Hoheisel 1988, Sarman and Evans 1992) and as a test of the theory of non-equilibrium fluctuations in liquid mixtures (Segrè *et al* 1993).

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The measurements carried out in thermal diffusion cells may be affected by the presence of convective perturbations arising from hydrodynamic instability or the existence of lateral temperature gradients. With a view to avoiding such perturbations, attempts have recently been made to measure the Soret coefficient of different mixtures under conditions of microgravity (see for example van Vaerenbergh *et al* 1995). Although the results are not conclusive, they do seem to point to important differences from the values obtained on Earth. At the same time, non-convective experimental devices have been improved and optical analytical methods have been refined (Zhang *et al* 1996, Khöler and Müller 1995).

The discrepancies found in thermogravitational measurements could be due to the presence of parasitic convection currents caused by irregularities in the geometry of the column or by a lack of uniformity in the temperature of the column walls. In very short columns, the return currents at the ends may also give rise to deviations from the behaviour predicted by the theory (Chavepeyer *et al* 1995, Ecenarro *et al* 1985).

In a previous investigation (Ecenarro *et al* 1990) we used the thermogravitational method to measure the Soret coefficient of the toluene–*n*-hexane system and other organic mixtures at 38 °C. Recent measurements made independently by Zhang *et al* (1996) and by Khöler and Müller (1995) for the toluene–*n*-hexane system, using non-convective techniques, are consistent with each other and are about 20% higher than those reported by us. We suspect that this difference could be due to distortions in the gap geometry of the column used, which arise from thermal expansion of the inner tube, which is clamped at its ends, when it is brought to the working temperature of 40 °C.

To circumvent such difficulties and to demonstrate the validity of the thermogravitational method, we designed and constructed a new column that is smaller as regards the length and radius of the tubes comprising it. The column is easy and simple to construct and one can thus have several units available, to check in advance their correct functioning with mixtures of well known Soret coefficient.

Using this column, we determined the Soret coefficients of different organic mixtures for which data are available in the literature. Here, we only considered mixtures with positive Soret coefficient values. Other systems with negative coefficient values will be addressed in a forthcoming work.

The results obtained show that the thermogravitational method affords reliable Soret coefficient values for binary liquid mixtures using a simple and easy to construct set-up.

2. Experimental method

According to the theory of the thermogravitation effect (Tyrrell 1961, Ecenarro *et al* 1989, Horne and Bearman 1968), the stationary separation, Δc , between the two ends of a column is given by

$$\frac{\Delta c}{c_0(1 - c_0)} = \Psi \frac{S_T \eta D}{\rho \beta} \quad (1)$$

where c_0 is the initial concentration in fraction of mass; S_T is the Soret coefficient; η is the dynamic viscosity; D is the ordinary diffusion coefficient; ρ is the density; β is the thermal expansion coefficient; and ψ is a factor related to the geometric characteristics of the column according to $\psi = 504L/g\sigma^4$, where L is the length, g is the acceleration due to gravity and σ is the width of the gap in which the liquid is confined. The physical properties are for the mean column temperature, T .

In principle, this equation can only be applied to the case of plane columns. In the case of cylindrical columns in which the mixture is placed between two coaxial cylinders, a shape

factor, ε , must be applied to equation (1); this is a function of the ratio of the external radius to the internal radius, r . For r -values close to unity, the expression $\varepsilon = 1 + 0.039(\ln r)^2$ was obtained for this correction factor (Navarro *et al* 1983). In the column that we used in this work, $r = 1.3$. Accordingly, the correction for cylindricality is 0.3% and was not further considered.

Another correction term for equation (1) comes from the so-called 'forgotten effect', which appears when the dependence of density on concentration is considered in the theory. This effect has been exhaustively addressed in other work (Ecenarro *et al* 1994, 1996, Navarro *et al* 1982). In the light of the results obtained and for the mixtures considered here, the correction due to this effect lies within the experimental error and therefore will not be taken into account.

Apart from the separation, another variable to be considered in the design of a column is the relaxation time of the process. According to theory, this time is given by

$$t_r = \frac{9!L^2}{(\pi \Delta T g)^2 \sigma^6} \left(\frac{\eta}{\rho\beta} \right)^2 D \quad (2)$$

where ΔT is the temperature difference between the walls.

Equations (1) and (2) show that both the separation and the relaxation time increase with length and strongly decrease with gap width, σ . It is therefore not possible to achieve large separations in short times. On designing the column we choose a length and gap width that were sufficiently large for the relaxation time to be small and for the separation to be sufficiently large to be measured with precision.

Taking the above considerations into account, we designed and constructed a column of concentric tubes measuring 52 cm long with a gap width of 1.53 mm. Calibrated stainless steel tubes were used, the diameter of the inner tube being 9.53 mm and that of the outer tube 12.60 mm. Small-diameter tubes were chosen because they are easier to construct with precision and it is easier to maintain a uniform temperature in the column walls. An additional advantage is that only a relatively small volume of mixture is required. The lower end of the gap was sealed off with a piece of stainless steel soldered to the tubes and with a 1 cm high centring ring. The upper end was closed with a 0.5 cm Teflon stopper. The tubes were thus perfectly centred. Figure 1 shows a vertical section of the column.

The temperatures of the cold and hot walls are maintained by circulating water flowing at a rate of 15 l min⁻¹; the water comes from two thermostatted baths and circulates rapidly through the refrigeration and heating jackets, which are made small in section so that the temperature variations along the column are less than 0.1 K. The temperatures of the water flowing in and that flowing out are monitored with 0.01 K precision thermometers. As detailed below, precise knowledge of the temperature difference between the walls is not required.

The upper and lower sampling ports are located at a distance of 42 cm from each other and are closed off with viton septa, which are pierced with a syringe for sample removal. The volume of liquid taken from each port is 1 cm³. The separation is of the order of 10⁻³ and thus is determined from the difference in refractive indices of the samples removed, using the value of the derivative of the index with respect to the concentration at the temperature of the refractometer. This derivative was determined for each binary system from the quadratic adjustment of the measurements of the refractive index with concentration. The agreement in the values obtained for toluene-*n*-hexane mixtures with the values reported in the literature (Li *et al* 1994) was better than 1%. A Pulfrich-type refractometer with a nominal accuracy of 5 × 10⁻⁶ was used.

To prepare the mixtures, each component was weighed on a digital balance with a

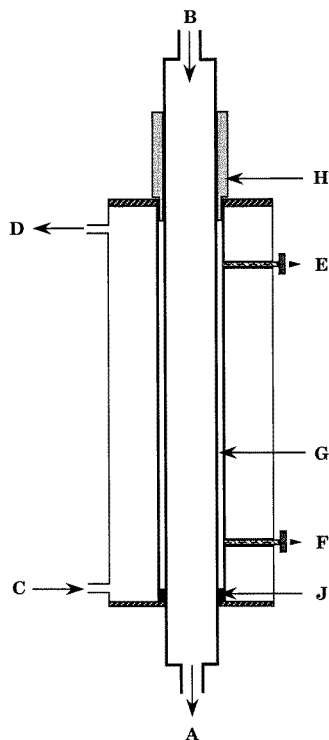


Figure 1. A line drawing of the thermogravitational column. Key: (A), (B) the inlet and outlet of the hot water; (C), (D) the connection to the circulating cooling water; (E), (F) sampling ports; (G) the working space; (J) a centring ring; and (H) a Teflon stopper.

resolution of 0.01 g. The purities of the liquids were greater than 99% and they were used without further purification. The components were mixed in a clean dry flask shaken gently but firmly at intervals for 10 min.

In each operation, once the samples have been removed, the column is emptied and the refractive index of the mixture is determined. Agreement with the index of the initial mixture is proof of the absence of contamination arising, for example, from chemical reactions between the liquids and the column materials (Ma *et al* 1983, Kuppers 1978).

According to equation (1), the separation is essentially independent of ΔT . This is a consequence of the assumption of a pure conduction regimen in the column, which can only be achieved in well constructed set-ups. In fact, we noted that small deviations in the centring of the tubes, for example, led to a significant dependence of the separation on ΔT . Therefore, to check the correct construction of the device we carried out separation measurements for different values of ΔT with an equimolar mixture of toluene-*n*-hexane whose physical properties, including the Soret coefficient, were known with precision (see below). The results obtained are shown in figure 2 in terms of the differences in refractive index among the samples. As may be seen, the fitting of the experimental values to the theoretical straight line is excellent. In view of these results, it may be concluded that our experimental device can be used to reliably determine the Soret coefficient for organic liquid mixtures.

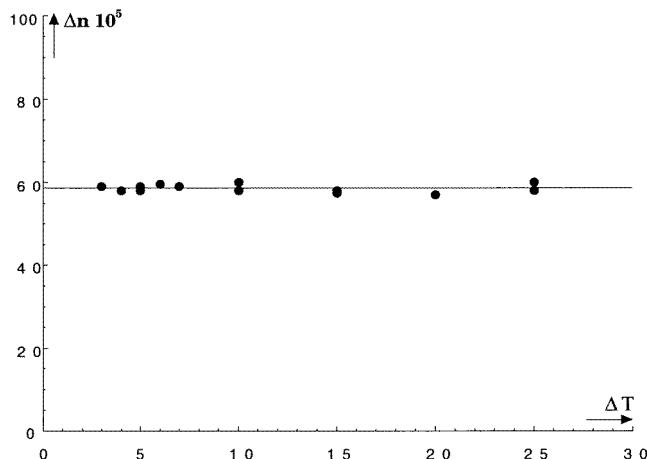


Figure 2. The dependence of the separation, Δn (the difference in refractive index), on ΔT for an equimolecular mixture of toluene-*n*-hexane at 25 °C. ●: from this work; —: the theoretical straight line.

In what follows, we worked with a temperature difference between the column walls of 5 K. Under these conditions, the relaxation time for an equimolar mixture of toluene-*n*-hexane is about 15 min. According to equation (2), this time is longer for mixtures with greater kinematic viscosity.

Determination of the Soret coefficient from separation measurements requires knowledge of the thermophysical properties appearing in equation (1). The viscosity and diffusion coefficient were taken for all of the binary systems considered from the literature. The density and thermal expansion coefficient were determined from the corresponding values of the pure components assuming ideal behaviour—that is, neglecting excess volume, which in all cases was lower than 1%.

3. Results and discussion

We first considered the toluene-*n*-hexane and carbon tetrachloride-cyclohexane systems, for which reliable experimental data related to the Soret coefficient are available in the literature. In this sense, for both systems, measurements made by different authors using different techniques are in agreement and therefore we can have a high degree of confidence in them.

3.1. Toluene-*n*-hexane

The Soret coefficient of toluene-*n*-hexane mixtures has been measured exhaustively as a function of temperature and concentration by Zhang *et al* (1996) using the technique of laser beam deviation in a carefully designed thermodiffusion cell, and by Khöler and Müller (1995) using the forced Rayleigh scattering method. The results obtained by both sets of authors are in agreement within the experimental error. Table 1 shows the data reported by Zhang *et al* (1996) for temperatures of 25 °C and 35 °C at the five concentrations considered by this author.

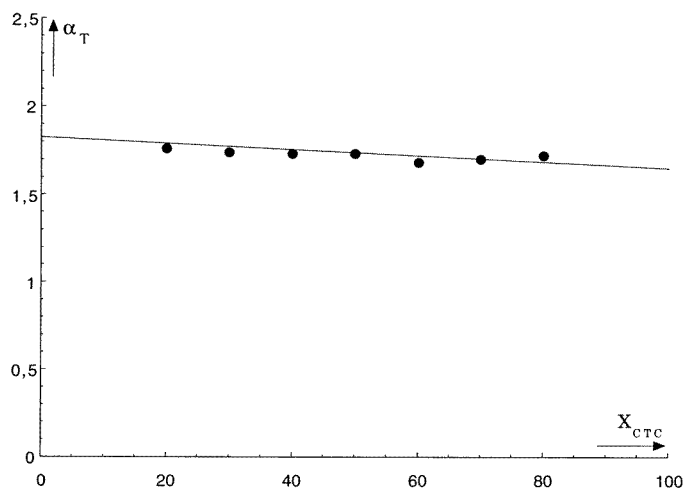
Using measurements of the stationary separation in the column described, we determined

Table 1. Soret coefficients S_T of mixtures of toluene-*n*-hexane (in 10^{-3} K^{-1}); X_T is the molar fraction of toluene.

	X_T (%)	S_T This work	S_T Zhang <i>et al</i> (1996)	δ (%)
$t = 25 \text{ }^\circ\text{C}$	5	3.21	3.17	-1.3
	25	3.82	3.98	4.0
	50	4.76	4.92	3.2
	75	5.43	5.56	2.3
	95	5.87	5.96	1.5
$t = 35 \text{ }^\circ\text{C}$	5	3.20	3.12	-2.5
	25	3.80	3.85	1.3
	50	4.48	4.64	3.4
	75	5.09	5.20	2.1
	90	5.29	—	—
	95	5.65	5.53	-2.1

the Soret coefficient at the above temperatures and concentrations. For $25 \text{ }^\circ\text{C}$, the data of Ghai and Dullien (1974) were used for the diffusion coefficient and viscosity, and for $35 \text{ }^\circ\text{C}$ the Zhang *et al* (1996) data for diffusion and the viscosity were measured by us using an Ubbelohde viscosimeter. The reproducibility of the separation measurements was 3% for mid-level concentrations and 5% for very high and very low concentrations. Table 1 shows the results obtained for the separation and the Soret coefficient. As may be seen, the agreement with the data of Zhang *et al* (1996) is excellent. Preliminary results obtained in a set-up with a brass column of similar geometrical characteristics were also in the same good agreement with those of Zhang *et al*.

As mentioned above, the Soret coefficient of this system was also measured in a previous investigation (Ecenarro *et al* 1990). The results of that work were about 20% lower than

**Figure 3.** The thermal diffusion factor at $25 \text{ }^\circ\text{C}$ for mixtures of carbon tetrachloride-cyclohexane versus the molar fraction of carbon tetrachloride (X_{CTC}). ●: from this work; —: from the fitting of Anderson and Horne (1971) experimental values.

those shown in table 1. This difference seems to be due to the effects of thermal expansion of the hot wall of the column. The earlier results show that these problems had been satisfactorily solved in the new set-up.

3.2. Carbon tetrachloride–cyclohexane

For the carbon tetrachloride–cyclohexane system, the literature also includes reliable data obtained at 25 °C concerning the so-called thermal diffusion factor α_T , related to the Soret coefficient by $\alpha_T = S_T T$. Thus, it includes reports of the data of Turner *et al* (1967) measured using a flow cell, the data of Anderson and Horne (1971) measured using a thermodiffusion cell and those of Stanford and Beyerlein (1973) obtained for a thermogravitational column. All of these data are coincident within a deviation of a few per cent and fit a straight line as a function of the concentration of carbon tetrachloride. Figure 3 shows the straight line proposed by Anderson and Horne (1971).

Using column separation measurements we determined the thermal diffusion factor α_T of this system at different concentrations. The values of the necessary thermophysical properties were taken from Sanni *et al* (1971) for the diffusion coefficient and from Hammond and Stokes (1956) for the viscosity. The results are shown in figure 3. As may be seen, the fitting of the points to the straight line is excellent, with deviations of less than 2% even though the separations obtained in the mixtures considered were relatively small, the precision of the measurements thus being around 5%.

The results obtained with these two systems on the one hand underscore the validity of the thermogravitational method when operating with an appropriate set-up and, on the other, lend additional support to the existing data on the Soret coefficient. Below, we analyse the benzene–*n*-heptane, carbon tetrachloride–methanol and carbon tetrachloride–ethanol systems, for which inconsistent data can be found in the literature.

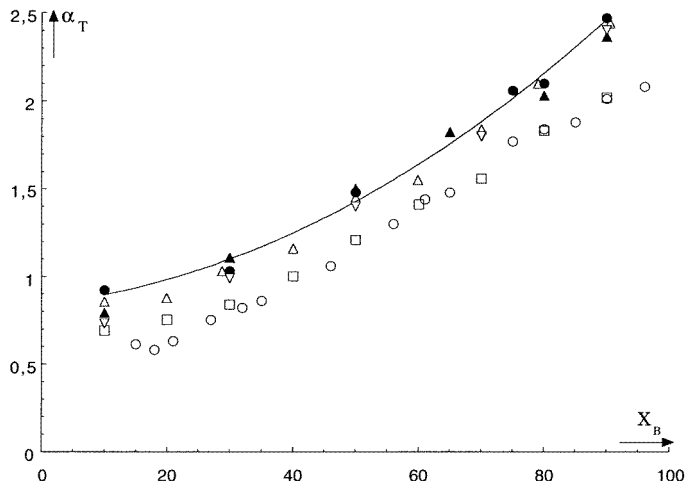


Figure 4. The thermal diffusion factor of the benzene–*n*-heptane system as a function of the molar fraction of benzene (X_B). ●: from this work for 25 °C; ▲: from this work for 35 °C; ○: from the work of Ecenarro *et al* (1990) for 37.5 °C; △: from Demichowicz-Pigoniowa *et al* (1971) for 25 °C; ▽: from Korsching (1974) for 25 °C; □: from Korsching (1969) for 35 °C; —: the fitting of experimental values obtained in this work at 25 °C.

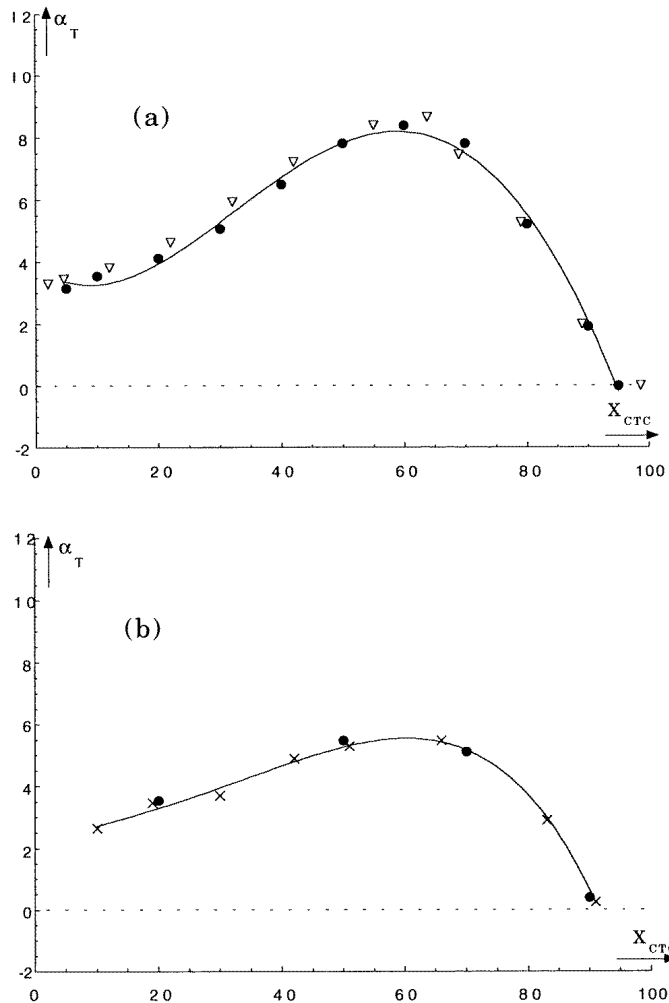


Figure 5. The thermal diffusion factors of carbon tetrachloride–methanol and carbon tetrachloride–ethanol systems against the molar fraction of carbon tetrachloride (X_{CTC}). (a), (b) The $\text{CCl}_4\text{-CH}_3\text{OH}$ system. (a) 25 °C; (b) 35 °C. (c), (d) The $\text{CCl}_4\text{-C}_2\text{H}_5\text{OH}$ system. (c) 25 °C; (d) 35 °C. ●: from this work; ▽: from Story and Turner (1969); ×: from Whitaker and Pigford (1958); △: from Poty *et al* (1974); ○: from Beyerlein and Bearman (1968); □: from Sánchez and Mahenc (1976).

3.3. Benzene–*n*-heptane

The thermal diffusion factor α_T of the benzene–*n*-heptane mixture has been measured independently by Demichowicz-Pigoniowa *et al* (1971) and by Korsching (1974) at 25 °C and by Korsching (1969) at 35 °C using the thermodiffusion cell technique. The results given by these authors are plotted in figure 4 as a function of the benzene concentration. As can be seen, for 25 °C the two data sets are in agreement with each other except at the point of the lowest concentration.

Using column separation measurements and making use of equation (1) together with the viscosity data of Mato and Coca (1970) and those for the diffusion coefficient of Sanni *et al*

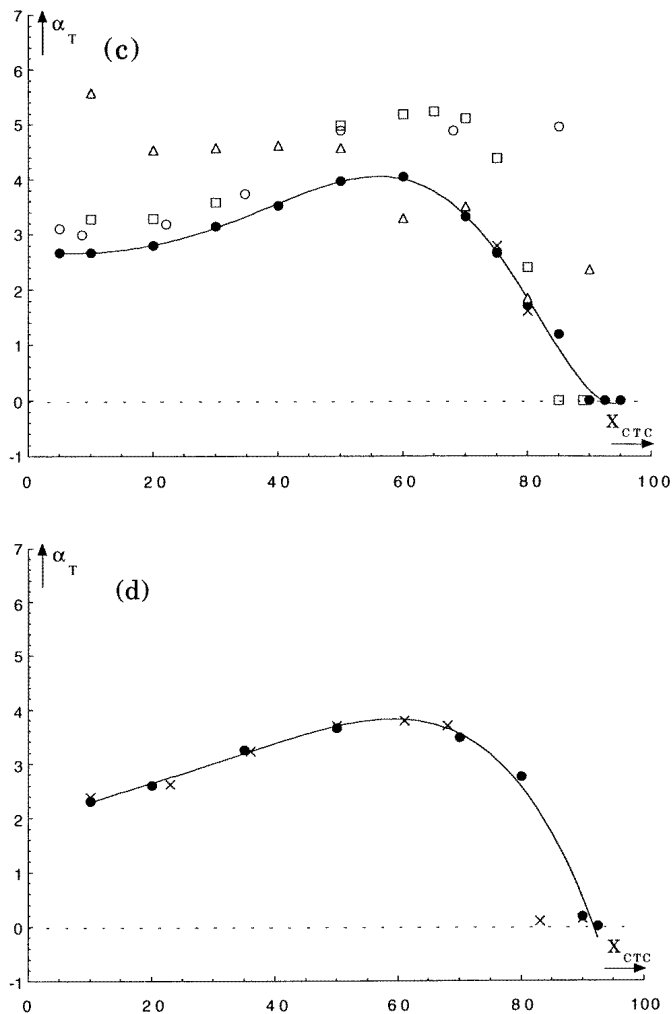


Figure 5. (Continued)

(1971), we determined the thermal diffusion factor of this system at different concentrations and at the temperatures given above. As can be seen in figure 4, the results obtained at 25 °C are in close agreement with those of Demichowicz and Tyrrell. However, our data for 35 °C are more than 20% higher than those of Korsching obtained at the same temperature and differ little from those obtained at 25 °C, in agreement with the small dependence of the Soret coefficient on temperature observed in ideal or quasi-ideal mixtures.

Figure 4 plots the results obtained by us at 37.5 °C in the aforementioned earlier work (Ecenarro *et al* 1990). As may be seen, they agree fairly well with the data reported by Korsching for 35 °C. However, and despite this agreement, these results should be considered to be incorrect as they were obtained using a column with distortions in the gap geometry. Unfortunately, this agreement was used in the earlier work (Ecenarro *et al* 1990) to support the thermal diffusion measurements of different organic mixtures. A review of these measurements is shortly to be published.

3.4. Carbon tetrachloride–methanol

For the carbon tetrachloride–methanol system, the literature contains the data on thermal diffusion measured by Story and Turner (1969) at 25 °C using a flow cell and by Whitaker and Pigford (1958) at 35 °C using a thermal diffusion cell. Figures 5(a) and 5(b) show the data of both sets of authors together with the values obtained by us from column separation measurements. The required physical properties were taken from the literature. For 25 °C, the data of Anderson and Babb (1963) were used for the diffusion coefficient and those of Jones (1948) for the viscosity. For 35 °C, the thermophysical data were taken from Rathbun (1965).

As may be seen in figure 5(a), the agreement between our results on the thermal diffusion factor, α_T , and those of the above authors is good, the deviations being within the experimental error. At concentrations higher than 90% the thermal diffusion factor changes sign, since negative values are obtained for the separation. However, the absolute values are very small and it is not possible to reliably determine the value of α_T .

3.5. Carbon tetrachloride–ethanol

For the carbon tetrachloride–ethanol system the literature reports many experimental data on the thermal diffusion factor at 25 °C, measured by different techniques. Figure 5(c) shows the data obtained by Poty *et al* (1974) using a flow cell, those of Beyerlein and Bearman (1968) for a thermogravitational column and those of Sánchez and Mahenc (1976) for a thermodiffusion cell. The same figure shows the values for α_T obtained by us from column separation measurements making use of the data on viscosity and the diffusion coefficient reported by Hammond and Stokes (1956). As can be seen, in general our data do not agree with those of any of these authors, although partial agreement is reached with some of the data of Poty *et al* at high carbon tetrachloride concentrations, while at low concentrations they follow the same trend as those reported by Sánchez and Beyerlein, although they are 15% lower and hence far outside the experimental error. As a test of the reliability of our results, we determined the thermal diffusion factor of this system at 35 °C, taking the required thermophysical properties from Rathbun (1965). Whitaker and Pigford (1958) measured this factor at the same temperature using a thermodiffusion cell. Figure 5(d) shows that the agreement between the two sets of data is excellent. Although this agreement supports our results for 25 °C, new measurements made with a different technique would be helpful in order to definitively confirm their correctness.

4. Summary

In previous sections, on the one hand, we have proved the validity of the thermogravitational method operating on mixtures of toluene–*n*-hexane and carbon tetrachloride–cyclohexane for which reliable values of the Soret coefficient exist in the literature. On the other hand, we have applied this method to measure this coefficient for the binary systems benzene–*n*-heptane and carbon tetrachloride with methanol and ethanol. The agreement found with values from the literature measured with other techniques constitutes an additional proof of the reliability of the thermal diffusion data obtained for these systems.

As may be seen from figures 3–5, the Soret coefficient for associated mixtures, such as those in which one of the components is an alcohol, strongly depends on concentration in the region of relatively low alcohol concentrations. By contrast, for ideal or quasi-ideal mixtures, this dependence is small. Also, the dependence of the Soret coefficient on

temperature is much more pronounced in associated mixtures.

From the results obtained, it may be concluded that when a column with a good geometry is employed, the thermogravitational technique affords precise values of the Soret coefficient for binary liquid mixtures. The quality of the geometry should be checked from steady-separation measurements as a function of the temperature difference between the column walls for a mixture of well known physical properties

References

- Anderson D K and Babb A L 1963 *J. Phys. Chem.* **67** 1362
 Anderson T G and Horne F H 1971 *J. Chem. Phys.* **55** 2831
 Beyerlein A and Bearman R J 1968 *J. Chem. Phys.* **49** 5022
 Chavepeyer G, Platten J K and Bada M B 1995 *Appl. Sci. Res.* **55** 1
 Demichowicz-Pigoniowa J, Mitchell M and Tyrrell H J V 1971 *J. Chem. Soc. A* 307
 Ecenarro O, Madariaga J A, Navarro J L, Santamaría C M, Bou-Ali M M and Valencia J 1996 *Entropie* **32** 71
 Ecenarro O, Madariaga J A, Navarro J, Santamaría C M, Carrión J A and Savirón J M 1989 *J. Phys.: Condens. Matter* **1** 9741
 ———1990 *J. Phys.: Condens. Matter* **2** 2289
 Ecenarro O, Madariaga J A, Navarro J L and Savirón J M 1985 *J. Non-Equilib. Thermodyn.* **10** 185
 Ecenarro O, Madariaga J A, Santamaría C M, Bou-Ali M M, Carrion J A and Savirón J M 1994 *Entropie* **30** 68
 Ghai R K and Dullien F A L 1974 *J. Phys. Chem.* **78** 2283
 Hammond B R and Stokes R H 1956 *Trans. Faraday Soc.* **52** 781
 Horne F H and Bearman R J 1968 *J. Chem. Phys.* **49** 2457
 Irving J B 1977 *Glasgow National Engineering Laboratory (NEL) Report* No 631
 Jones W J 1948 reported in Irving (1977)
 Khöler W and Müller B 1995 *J. Chem. Phys.* **103** 4367
 Korsching H 1969 *Z. Naturf. a* **24** 444
 ———1974 *Z. Naturf. a* **29** 1914
 Kuppers J R 1978 *J. Electrochem. Soc.* **125** 97
 Li W B, Segrè P N, Gammon R W, Sengers J V and Lamvik M 1994 *J. Chem. Phys.* **101** 5058
 Lin J L, Taylor W L, Rutherford W M and Millat J 1991 *Measurement of the Transport Properties of Fluids* (Oxford: Blackwell Scientific)
 Ma N R, Stanford D J and Beyerlein A L 1983 *J. Non-Equilib. Thermodyn.* **8** 207
 Mato F and Coca J 1970 *Studia Chem. Salamanca* **4** 141
 Navarro J L, Madariaga J A and Savirón J M 1982 *J. Phys. A: Math. Gen.* **15** 1683
 ———1983 *J. Phys. Soc. Japan* **52** 478
 Platten J K and Legros J C 1984 *Convection in Liquids* (Berlin: Springer)
 Poty P, Legros J C and Thomaes G 1974 *Z. Naturf. a* **29** 1915
 Rathbun R E 1965 *PhD Thesis* University of Washington, Seattle, WA
 Sánchez V and Mahenc J 1976 *J. Chim. Phys.* **73** 485
 Sanni S A, Fell C J D and Hutchinson H P 1971 *J. Chem. Eng. Data* **16** 424
 Sarman S and Evans D J 1992 *Phys. Rev. A* **45** 2370
 Segrè P N, Gammon R W and Sengers J V 1993 *Phys. Rev. E* **47** 1026
 Stanford D J and Beyerlein A 1973 *J. Chem. Phys.* **58** 4338
 Story M J and Turner C R 1969 *Trans. Faraday Soc.* **65** 1523
 Turner J C R, Butler B D and Story M J 1967 *Trans. Faraday Soc.* **63** 1906
 Tyrrell H J V 1961 *Diffusion and Heat Flow in Liquids* (London: Butterworth)
 Van Vaerenbergh S, Colinet P and Legros J C 1991 *Capillarity Today (Springer Lecture Notes in Physics 386)* (Berlin: Springer) p 276
 Van Vaerenbergh S, Legros J C and Dupin J C 1995 *Adv. Space Res.* **16** 8
 Velarde M G and Schechter R S 1971 *Chem. Phys. Lett.* **12** 312
 Vogelsang R and Hoheisel J 1988 *J. Chem. Phys.* **89** 1588
 Whitaker S and Pigford R L 1958 *Indust. Eng. Chem.* **50** 1026
 Zhang K J, Briggs M E, Gammon R W and Sengers J V 1996 *J. Chem. Phys.* **104** 6881