

Measurement of negative Soret coefficients in a vertical fluid layer with an adverse density gradient

M. M. Bou-Ali, O. Ecenarro,* J. A. Madariaga, and C. M. Santamaría

Departamento de Física Aplicada II, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

J. J. Valencia

Departamento de Ingeniería Mecánica, Energética y de Materiales, Universidad Pública de Navarra, Pamplona, Spain

(Received 17 December 1999)

Using a thermogravitational cell, we have measured the Soret coefficient of the binary liquid systems formed by benzene and toluene with methanol and ethanol. The existing data in the literature present large deviations, particularly in the low alcohol concentration range in which the Soret coefficient is negative. It is shown that the thermal gradient maintains an adverse density gradient in the vertical fluid layer. When the thermal gradient is suppressed, the density gradient reverses, and recovers the adverse initial value when the thermal gradient is reestablished.

PACS number(s): 47.20.Bp, 47.27.Te, 66.10.Cb

In previous work [1], we analyzed the stability of the thermogravitational steady state with an adverse density gradient. The results obtained open the possibility of measuring negative values of the Soret coefficient of binary liquid mixtures in a thermogravitational cell. In this work, we exploit these results to determine the Soret coefficient of the binary systems formed by benzene and toluene with methanol and ethanol. In particular, for the benzene-methanol system many attempts have been made to determine the Soret coefficient as a function of the concentration. However, the data found in the literature [2] from at least six independent groups of researchers report large deviations, particularly in the low methanol concentration range in which the Soret coefficient seems to be negative. Such discrepancies have been attributed to the presence of parasitic convective currents in the thermal diffusion cells used in the experiments. To avoid such perturbations, experiments under microgravity conditions have recently been performed [3] and although the results are not conclusive, they do seem to point to important differences from the values obtained on Earth. In view of this confusing situation we were prompted to measure the Soret coefficient of the benzene-methanol system using the thermogravitational method. Precise values of the Soret coefficient are needed in analysis of the phenomena of hydrodynamic instability [4]. In liquid theory, they are needed to test the predictions for nonequilibrium fluctuations in mixtures [5] and for comparison with molecular dynamic simulations [6] and kinetic theory models [7].

In the thermogravitational method, the liquid mixture is placed between two vertical walls at different temperatures. Under these conditions, the vertical convective currents combine with the horizontal separation due to the Soret effect, giving rise to a steady-state vertical concentration gradient and hence to a certain degree of solute separation between the ends of the cell. According to thermogravitational theory [8], the Rayleigh number for the solute in this separation is given by

$$Ra = 504S, \quad (1)$$

where Ra and S are the Rayleigh number and the buoyancy ratio, respectively, defined by

$$Ra = \frac{\gamma g d^4 \Delta c}{\nu D h}, \quad S = \frac{S_T c (1-c) \gamma}{\beta}. \quad (2)$$

Here c is the concentration (mass fraction) of the less dense component and Δc is the concentration difference between the upper and lower ends of the cell; d and h are, respectively, the gap width and the height of the cell; β is the coefficient of thermal expansion; g is the acceleration of gravity; γ is the coefficient of variation of density with concentration; D is the ordinary diffusion coefficient; and ν is the kinematic viscosity. S_T is the Soret coefficient, which we take as positive when the less dense component migrates to the hotter region.

For the concentration difference Δc , Eqs. (1) and (2) yield

$$\frac{\Delta c}{c(1-c)} = \Psi \frac{S_T \nu D}{\beta}, \quad (3)$$

where Ψ is a factor related to the geometrical characteristics of the cell according to $\Psi = 504h/d^4g$. Equation (3) is the working equation in the thermogravitational method. It allows one to determine S_T from steady-state separation measurements Δc . According to this equation, the separation is independent of the temperature difference ΔT between the vertical walls.

For mixtures with positive Soret coefficient, the less dense component is enriched in the upper part of the cell, giving rise to a stable density stratification. However, in mixtures with a negative Soret coefficient, it is the denser component that becomes enriched in the upper part of the column, giving rise to an adverse density gradient along the fluid layer. The stability of such a situation has been analyzed in previous work [1]. Experimentally, we have found

*Author to whom correspondence should be addressed.

TABLE I. Values for the concentration difference (Δc), thermal expansion (β), kinematic viscosity (ν), ordinary diffusion coefficient (D), and Soret coefficient (S_T) of binary systems including benzene (B), toluene (T), methanol (Mt), and ethanol (Et). The molar fraction (x) and the mass fraction (c) correspond to the first-named component and the temperature is $T=298$ K.

System	x	c	$10^2\Delta c$	$10^3\beta$ (K^{-1})	ν (cm^2/s)	10^5D (cm^2/s)	10^3S_T (K^{-1})
B-Mt	0.050	0.114	+0.145	1.210	0.699 ^a	2.40 ^b	+2.58
	0.100	0.213	+0.261	1.211	0.701	2.13	+3.15
	0.225	0.414	+0.341	1.215	0.698	1.59	+3.65
	0.300	0.511	+0.295	1.217	0.695	1.35	+3.87
	0.400	0.619	+0.204	1.219	0.688	1.11	+3.45
	0.500	0.709	+0.132	1.220	0.680	0.94	+3.05
	0.570	0.764	+0.072	1.222	0.674	0.89	+2.01
	0.700	0.850	-0.036	1.223	0.663	0.84	-1.51
	0.750	0.879	-0.078	1.224	0.661	0.88	-3.86
	0.800	0.907	-0.111	1.224	0.661	0.98	-6.31
	0.850	0.932	-0.111	1.225	0.660	1.16	-7.08
	0.900	0.956	-0.096	1.225	0.665	1.50	-7.15
	0.930	0.970	-0.076	1.226	0.672	1.89	-6.34
	0.950	0.979	-0.050	1.226	0.677	2.26	-4.90
B-Et	0.050	0.820	+0.108	1.102	1.350 ^a	2.17 ^c	+1.37
	0.100	0.158	+0.138	1.110	1.240	1.95	+1.20
	0.200	0.297	+0.131	1.128	1.063	1.62	+1.00
	0.300	0.421	-0.051	1.144	0.951	1.37	+0.43
	0.550	0.674	-0.132	1.179	0.771	1.00	-2.31
	0.650	0.759	-0.136	1.191	0.716	0.95	-3.25
	0.800	0.871	-0.114	1.207	0.662	1.05	-4.46
	0.900	0.938	-0.085	1.217	0.657	1.46	-4.73
T-Mt	0.050	0.131	+0.193	1.195	0.697 ^a	2.25 ^d	+3.25
	0.075	0.189	+0.250	1.189	0.700	2.10	+3.32
	0.100	0.242	+0.316	1.183	0.704	1.98	+3.69
	0.150	0.336	+0.374	1.173	0.704	1.74	+4.06
	0.200	0.418	+0.383	1.165	0.707	1.53	+4.26
	0.250	0.489	+0.335	1.157	0.703	1.35	+4.09
	0.300	0.552	+0.301	1.150	0.701	1.20	+4.19
	0.400	0.657	+0.188	1.138	0.686	0.97	+3.62
	0.500	0.742	+0.081	1.129	0.669	0.85	+2.11
	0.550	0.778	+0.010	1.124	0.662	0.83	+0.27
	0.650	0.842	-0.103	1.117	0.649	0.90	-3.75
	0.725	0.883	-0.137	1.112	0.640	1.07	-5.47
	0.775	0.908	-0.148	1.108	0.636	1.26	-6.21
	0.825	0.931	-0.090	1.106	0.632	1.55	-6.74
0.900	0.963	-0.095	1.103	0.627	2.21	-5.33	
T-Et	0.050	0.095	+0.073	1.198	1.478 ^a	2.04 ^e	+0.85
	0.100	0.181	+0.086	1.190	1.376	1.48	+0.86
	0.150	0.261	+0.093	1.186	1.298	1.29	+0.84
	0.200	0.333	+0.076	1.174	1.230	1.12	+0.74
	0.250	0.400	+0.054	1.167	1.169	0.98	+0.57
	0.400	0.571	-0.022	1.148	1.002	0.71	-0.36
	0.450	0.620	-0.054	1.142	0.958	0.67	-1.04
	0.500	0.666	-0.072	1.137	0.912	0.63	-1.62
	0.550	0.710	-0.092	1.132	0.869	0.63	-2.36
	0.625	0.769	-0.111	1.125	0.810	0.65	-3.36
	0.675	0.806	-0.118	1.121	0.775	0.69	-4.03
	0.750	0.857	-0.117	1.115	0.732	0.81	-4.56
	0.800	0.888	-0.096	1.111	0.709	0.93	-4.12
	0.850	0.919	-0.061	1.108	0.693	1.14	-2.92

TABLE I. (Continued).

System	x	c	$10^2 \Delta c$	$10^3 \beta$ (K ⁻¹)	ν (cm ² /s)	$10^5 D$ (cm ² /s)	$10^3 S_T$ (K ⁻¹)
B-Mt	0.875	0.933	-0.047	1.106	0.688	1.25	-2.49
	0.960	0.979	+0.013	1.101	0.681	2.85	+0.96

^aReference [10].

^bReference [11].

^cReference [11], extrapolated.

^dReference [12].

^eReference [13].

that it remains stable for Grashof numbers exceeding a critical value which in terms of the buoyancy ratio of the mixture is given by

$$(\text{Gr})_c = 965|S|. \quad (4)$$

For the benzene-methanol system $\beta \approx 10^{-3}$ and $\gamma \approx 10^{-1}$. By taking $S_T = 10^{-2} \text{ K}^{-1}$ for a mass fraction of 0.1 of methanol, the corresponding value of the buoyancy ratio is $S \approx 0.1$. Thus, from Eq. (4) the critical Grashof number is of the order of 10^2 . For a cell with a gap width of $1.5 \times 10^{-1} \text{ cm}$, and using for kinematic viscosity the value of $0.8 \times 10^{-2} \text{ cm}^2/\text{s}$, the critical value of ΔT for stability is about 1 K. We shall take a temperature difference of 5 K in the experiments, thus being well inside the stability region.

Experiments were performed in an annular slot arranged between two stainless-steel coaxial cylinders with a height of 52 cm, and inner and outer diameters of 9.53 mm and 12.60 mm, respectively. The annular gap width was thus 1.53 mm. The concentration difference is of the order of 10^{-3} , and thus it was determined from the difference in the refractive indices of samples removed from the upper and lower ends of the cell, 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 mixture by adjusting the measurements of the refractive index with concentration. A Pulfrich-type refractometer with a nominal accuracy of 5×10^{-6} was used. More details about the apparatus and the experimental method can be found in Ref. [9].

Using steady-state separation measurements, from Eq. (3) we determined the Soret coefficient of the systems considered as a function of the concentration at a temperature of 25 °C. The values of the required thermophysical properties appearing in this equation were taken from the literature. The density and the thermal expansion coefficients were determined from the corresponding values of the pure components assuming ideal behavior, since the excess volume is negligible in all cases.

The experimental values of the steady-state concentration difference and the Soret coefficient at 25 °C are given in Table I. Each value of the separation represents the average value over four runs, yielding a mean accuracy of about 3%. This table also shows the values we used of the kinematic viscosity and diffusion coefficient taken from the literature [10–13]. The accuracy of the values of the Soret coefficient is determined by the accuracy of the thermophysical properties used in the calculations.

Figure 1 shows the experimental results for the Soret coefficient of the benzene-methanol and benzene-ethanol systems as a function of the molar fraction of benzene. As can be seen, the Soret coefficient of both systems depends strongly on the concentration, and changes sign at the benzene molar fraction of 0.66 for benzene-methanol and 0.32 in the case of benzene-ethanol. At lower concentrations, the Soret coefficient is positive and therefore the denser component—the benzene—becomes enriched at the bottom of the cell. By contrast, at higher concentrations, the Soret coefficient is negative and benzene becomes enriched at the top. Figure 1 also includes the values obtained by Farsang and Tyrrell [14] in a thermal diffusion cell for the two systems under consideration. As can be seen, the agreement with our data is excellent. The Soret coefficient of the system benzene-methanol has been previously measured by at least six independent research groups. The results obtained reveal strong deviations, as can be seen in Ref. [2]. The only data that coincide with our results throughout the concentration range are those of Farsang and Tyrrell. This agreement between two data sets measured with different techniques is proof of the reliability of the obtained values of the Soret coefficient for the two systems considered.

Figure 2 shows the experimental results for the Soret coefficients of the systems toluene-methanol and toluene-ethanol as a function of the molar fraction of toluene. As can be seen the trend is similar to that of the homologous systems considered above. This figure also offers the data reported by Belton and Tyrrell [15] for mixtures of toluene-ethanol. As can be seen, the agreement with our data is excellent for this system also. The toluene-methanol system

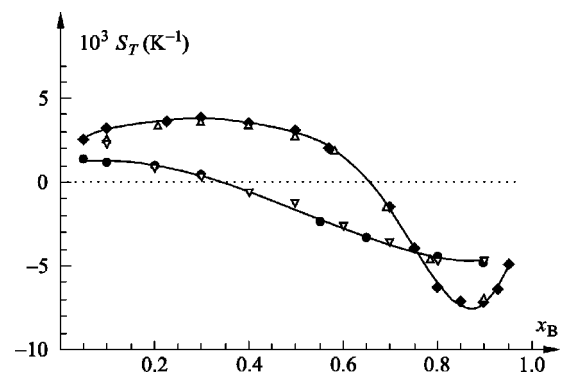


FIG. 1. Soret coefficient at 25 °C vs benzene molar fraction for the mixtures benzene-methanol (\blacklozenge , this work; \triangle , Ref. [14]), and benzene-ethanol (\bullet , this work; ∇ , Ref. [14]).

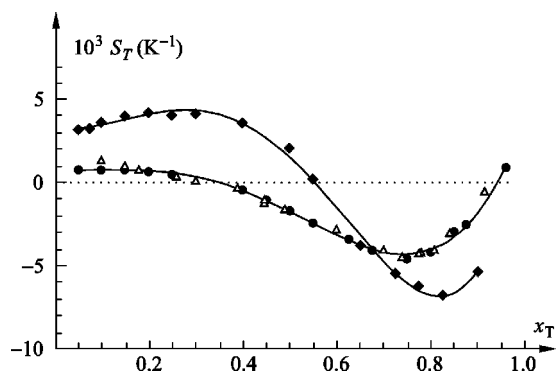


FIG. 2. Soret coefficient at 25 °C vs toluene molar fraction for the mixtures toluene-methanol (\blacklozenge , this work), and toluene-ethanol (\bullet , this work; \triangle , Ref. [15]).

has not been considered previously.

As we reported in previous work [1], negative values of the Soret coefficient can be measured in a thermogravitational cell because convection and thermal diffusion stabilize adverse density gradients that would otherwise be unstable. This stabilizing effect can be appreciated in the next experiment, which we performed with a mixture of toluene-ethanol at a toluene molar fraction of 0.625, for which the Soret coefficient is negative. The results obtained are shown in Fig. 3. When a thermal gradient is established across the initially uniform mixture, after about 15 min a thermogravitational steady state with an adverse density gradient is reached, and it remains stable [Fig. 3(a)]. According to Eqs. (1) and (2), the Rayleigh number corresponding to this situation is $Ra = 33$. If the thermal gradient is suppressed, the density gra-

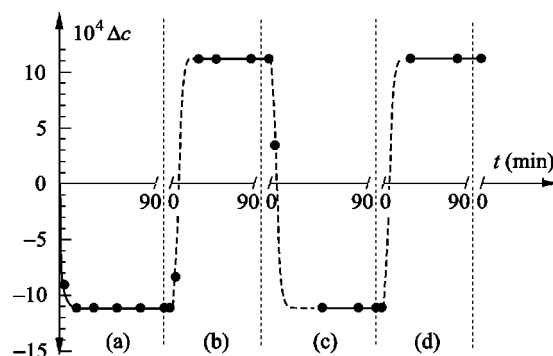


FIG. 3. Time evolution of the separation in the presence of a thermal gradient [(a) and (c)], and when the thermal gradient is suppressed [(b) and (d)].

dent becomes unstable. Indeed, according to Wooding [16], the critical Rayleigh number for a quiescent fluid layer and for the dimensions of our cell is $Ra_c = 0.12$. Consequently, the more dense fluid at the top of the cell descends to the bottom and after about 10 min the separation is reversed as is shown in Figure 3(b). When the thermal gradient is reestablished, a thermogravitational steady state is again reached after about 15 min [Fig. 3(c)]. This flip-flop effect shows that a thermal gradient in a mixture can stabilize situations with relatively large adverse density stratifications.

The results obtained show that the thermogravitational method can be successfully extended to determine negative values of the Soret coefficient. In a thermogravitational cell, an apparatus easy to construct, convection favors the stability of an adverse concentration gradient along the vertical fluid layer.

- [1] M. M. Bou-Ali, O. Ecenarro, J. A. Madariaga, C. M. Santamaría, and J. Valencia, *Phys. Rev. E* **59**, 1250 (1999).
- [2] J. C. Legros, P. Goemaere, and J. K. Platten, *Phys. Rev. A* **32**, 1903 (1985); S. Schechter, M. G. Velarde, and J. K. Platten, *Adv. Chem. Phys.* **26**, 265 (1974); J. C. Johnson and A. Beylerlein, *J. Phys. Chem.* **82**, 1430 (1978).
- [3] S. van Vaerenbergh and J. C. Legros, *J. Phys. Chem. B* **102**, 4426 (1998).
- [4] H. Touiri, J. K. Platten, and G. Chavepeyer, *Eur. J. Mech. B/Fluids* **15**, 241 (1996); P. Kolodner, *Phys. Rev. E* **50**, 2731 (1994); J. K. Platten and J. C. Legros, *Convection in Liquids* (Springer, Berlin, 1984).
- [5] K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. V. Sengers, *J. Chem. Phys.* **104**, 6881 (1996); W. B. Li, K. J. Zhang, J. V. Sengers, R. W. Gammon, and J. M. Ortiz de Zárate, *Phys. Rev. Lett.* **81**, 5580 (1998).
- [6] S. Sarman and D. J. Evans, *Phys. Rev. A* **45**, 2370 (1992); B. Hafskjold, T. Ikeshoji, and S. Ratkje, *Mol. Phys.* **80**, 1389 (1993); R. Vogelsang and C. Hoheisel, *Phys. Rev. A* **38**, 6296 (1988).
- [7] R. Castillo and J. Orozco, *J. Chem. Phys.* **106**, 8204 (1997).
- [8] O. Ecenarro, J. A. Madariaga, J. Navarro, C. M. Santamaría, J. A. Carrión, and J. M. Savirón, *J. Phys.: Condens. Matter* **1**, 9741 (1989); O. Ecenarro, J. A. Madariaga, C. M. Santamaría, M. M. Bou-Ali, and J. Valencia, *Entropie* **198/199**, 71 (1996); H. J. V. Tyrrell, *Diffusion and Heat Flow in Liquids* (Butterworths, London, 1961).
- [9] M. M. Bou-Ali, O. Ecenarro, J. A. Madariaga, C. M. Santamaría, and J. Valencia, *J. Phys.: Condens. Matter* **10**, 3321 (1998).
- [10] J. B. Irving, Glasgow National Engineering Laboratory (NEL) Report No. 631, 1977 (unpublished).
- [11] K. Mckeigue and E. Gulari, *J. Phys. Chem.* **88**, 3472 (1984).
- [12] L. W. Schemilt and R. Nagarajan, *Can. J. Chem.* **45**, 1142 (1967).
- [13] H. Lemonde, *Ann. Phys. (Paris)* **9**, 539 (1938).
- [14] G. Farsang and H. J. V. Tyrrell, *J. Chem. Soc. A*, 1839 (1969).
- [15] P. S. Belton and H. J. V. Tyrrell, *Z. Naturforsch. A* **26**, 48 (1971).
- [16] R. A. Wooding, *J. Fluid Mech.* **7**, 501 (1960).