Thermogravitational separation and the thermal diffusion factor near critical points in binary liquid mixtures

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Abstract. The thermogravitational separation for each of the binary liquid systems nitrobenzene + n-hexane and isobutyric acid + water, as a function of composition, was measured at temperatures above and near to their critical conditions. The first system, in which the component densities are very different, presents large separations near the critical composition. In contrast, in the second one, with similar densities of the pure components, no separation is observed. The extension to high Soret numbers of our previously developed thermogravitational theory, which takes into account the effect of the bouyancy-driven convection induced by the density composition dependence allows us to obtain values of thermal diffusion factors of binary liquid mixtures in the vicinity of consolute points from separation measurements.

1. Introduction

In recent papers [1, 2], we have developed the theory of thermogravitational operation in binary liquid mixtures which takes into account the effect on separation of the buoyancy-driven convection induced by the density composition dependence (the forgotten effect). According to this theory, the quantity which describes the magnitude of the effect is the Soret parameter (see below). For moderate values of this parameter, we have shown that the influence of density effects on the stationary separation is small. In contrast, the non-stationary operation is notably affected, giving rise to an increased time to approach equilibrium.

By using the above-mentioned theory, we have obtained reliable values of the ordinary diffusion coefficient, D, and the thermal diffusion factor, α, of several ideal or quasi-ideal binary liquid mixtures from stationary and non-stationary separation measurements [1–3]. These results show that this theory correctly describes the column thermogravitational operation for mixtures with moderate values of the Soret parameter.

The present paper deals with the analysis of the thermogravitational thermal diffusion effect in mixtures near critical conditions in which the Soret parameter can take high values. We have measured the stationary separation as a function of composition of the liquid systems nitrobenzene + n-hexane and isobutyric acid + water above the critical temperature.

When a critical point of mixtures is approached, the ordinary diffusion coefficient tends towards zero [4, 5] and it has been also observed that the thermal diffusion factor increases,

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the thermal diffusion coefficient D' ($D' = \alpha D/T$) remaining, nevertheless, approximately constant [6–8]. According to the standard column theory for liquid mixtures, the steady separation factor is proportional to the pure thermal diffusion coefficient, D' [9], and the ordinary diffusion or Fickian coefficient, D, determines the time evolution of the separation factor [10, 11]. Therefore, one would expect normal equilibrium separations and small relaxation times in the vicinity of critical points. However, the increase of the thermal diffusion factor in this region makes the Soret parameter unusually high and thus density effects must be taken into account.

In section 2 of this paper, we analyse the results of our column theory for the case of large values of the Soret parameter. The derived equations show that density effects considerably enhance the stationary separation producing at the same time a strong delay in the time to approach equilibrium. The experimental results presented in section 3 confirm these predictions.

Finally, from the separation measurements we have extracted the thermal diffusion factor of the mixture nitrobenzene $+ n$-hexane. As it is well known, the analysis of the divergences of transport properties near critical conditions have achieved great interest in recent years. In this respect, data of thermal diffusion scarcely exist.

2. Theory

2.1. The steady state

We shall consider a binary liquid mixture in a closed thermogravitational column of length L and annular gap width $2w$. The column walls are placed at $x = \pm w$ and are kept at temperatures T_1 and T_2, with $T_1 > T_2$.

According to the previously developed thermogravitational column theory [1], which takes into account density effects, the stationary separation is given by

$$R = (63S/2)h/k \tag{1}$$

R and S being the Rayleigh number based on the vertical composition gradient and the Soret parameter, respectively, defined by

$$R = \rho\gamma g w^4 \Delta c/\eta DL \qquad S = \alpha c(1 - c)\gamma/\beta T \tag{2}$$

where ρ is the density, η the viscosity, D the ordinary diffusion coefficient, α the thermal diffusion factor, g the gravitational acceleration, c the initial mass fraction of the less dense component, Δc the separation between the column ends, β and γ, the coefficients of thermal expansion and density variation with composition, respectively, T the mean temperature of the fluid, w the annular gap semi-width, and L the column length. Finally, the quantities h and k in (1) are correction factors to be applied to the standard column transport coefficients which reduce to unity when the density coefficient γ tends to zero. They are complicated functions of R and S given by

$$h = (1 + S)\alpha_1(R) \qquad k = (1 + S)^2\alpha_2(R) \tag{3}$$

where

$$\alpha_1 = (6!/2^6\mu^4)\{1 - (1/\mu)[\cosh(2\mu) - \cos(2\mu)]/[\sinh(2\mu) + \sin(2\mu)]\}$$

$$\alpha_2 = (9!/2^{13}\mu^8)\{2 + 2\sinh(2\mu)\sin(2\mu)/[\sinh(2\mu) + \sin(2\mu)]^2$$

$$- (5/2\mu)[\cosh(2\mu) - \cos(2\mu)]/[\sinh(2\mu) + \sin(2\mu)]\}$$
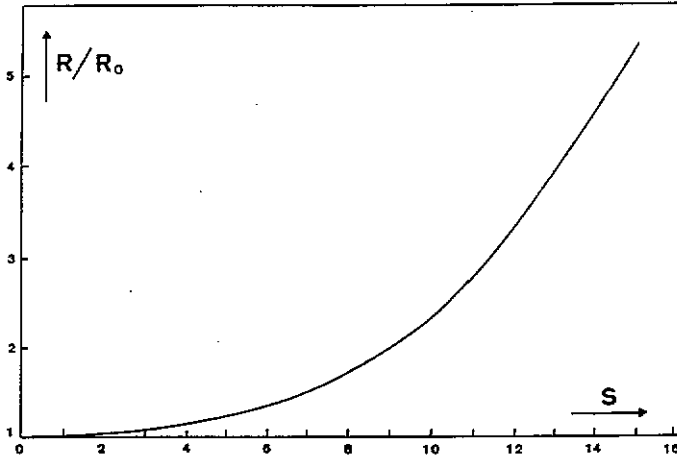
$$\mu = (R/4)^{1/4}.$$

Figure 1. Dependence of reduced Rayleigh number, R/R_0, on the Soret number.

The solution of (1)–(3) gives the stationary value of R as a function of the Soret parameter, $R = R(S)$. By using this solution one can obtain from the expression for the Rayleigh number the separation Δc in terms of the S parameter.

For small values of S, the solution for R, which we shall denote by R_0, is simply $R_0 = 63S/2$, and then, from (2), the corresponding separation is given by

$$\Delta c = 504 Lc(1 - c)/g(2w)^4 (\eta/\rho\beta)(\alpha D/T) \tag{4}$$

which coincides, as expected, with the solution of the standard column theory [9] in which the density composition dependence is ignored. In [1], we have shown that this solution can be considered as a good approximation in the wide range $S \leqslant 2$. As this range covers the major part of the ordinary liquid mixtures, it means that the forgotten effect usually does not affect the steady separation. However, as we shall see below, this is not the case for higher values of S. High values of S could be found, for instance, in mixtures near critical conditions in which it seems that the thermal diffusion factor increases considerably.

In particular, for $S \geqslant 8$ an asymptotic solution of (1) can be found. In this case, the coefficients h and k reduce to

$$h = (1 + S)(\mu - 1)/\mu^5 \qquad k = [(1 + S)^2/\mu^8](2 - 5/2\mu) \tag{5}$$

and the solution for $R(S)$ is

$$R = (S + 5)^4/4^3 \tag{6}$$

the separation being consequently given by

$$\Delta c = (\eta DL/\rho\gamma gw^4)(S + 5)^4/4^3 \tag{7}$$

which presents a much higher dependence on α than that shown in (4) and demonstrates the strong influence of density effects on the separation for high values of the Soret parameter. For intermediate values of S, (1) may be solved numerically.

Figure 1 displays the calculated values of R/R_0 obtained from (1) as a function of the Soret parameter. This quantity gives the ratio $(\Delta c)/(\Delta c)_0$ and thus the magnitude of the forgotten effect. As it can be seen, for instance, for $S = 11$, the separation is amplified by a factor of three with respect to the value given by the standard column theory.

2.2. The approach to equilibrium

As for the non-steady-state column operation, we have shown in [1] that the final stages of the process show an exponential decay with a characteristic relaxation time, t_r, given by

$$t_r = (t_r)_0/D^*$$

where $(t_r)_0$ is the relaxation time corresponding to the standard theory

$$(t_r)_0 = \mu' L^2/\pi^2 K_0$$

μ' being the mass of fluid per unit length of column, K_0 the remixing column coefficient and D^* a desorption-like coefficient quoted in [1]. Omitting details, which can be found in [1], for small values of S, we demonstrate that D^* is simply given by

$$D^* = (1 + S)^{-1}$$

which shows that the approach to equilibrium is notably influenced by density effects even in this case. This influence considerably increases for higher values of S. In particular, for $S \geqslant 8$, taking into account the D^* expression of [1], one obtains for D^*

$$D^* = 4 \times 9!(1 + S)/(S + 5)^8$$

which clearly shows the strong delay in the equilibrium time caused by density effects.

3. Experimental results and discussion

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 [3]. 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 1 min^{-1}) thermostatted baths. The temperature difference across the annulus is considered as the temperature difference between the two water baths corrected for the conductivity of the stainless-steel walls ($\Delta T = 4$ K). Determination of mass concentration was carried out with a Zeiss refractometer. The experimental procedure and the preparation and manipulation of the liquid mixture have been described elsewhere [3].

We have measured the stationary separation as a function of composition in the supercritical region of the binary liquid systems nitrobenzene + n-hexane and isobutyric acid + water. In the first system the density of nitrobenzene is about twice the density of n-hexane and consequently the separation parameter, S, could take high values. In contrast, in the second system the densities of the pure components are nearly equal ($\sim 4\%$ difference at 20 °C) [5], and thus the values of the separation parameter can be expected to be small at the considered temperatures. In consequence, and according to the previous theory, the thermogravitational behaviour of the two systems has to be very different.

The critical temperature T_c and the critical concentration c_c of the nitrobenzene + n-hexane system are $T_c = 20.29$ °C and $X_c = 42.20 \pm 0.05$ mol% of nitrobenzene ($c_c \sim 50\%$ in mass fraction of nitrobenzene) [12]. Separation measurements have been made at the mean temperature $T = 32$ °C, i.e. at about 12 °C above the critical temperature. This temperature has been chosen to assure the cold wall temperature to be above the critical one. Figure 2 displays the obtained results. Each Δc value is the arithmetic mean of at least three experimental determinations. As can be seen, unusually high separations of about
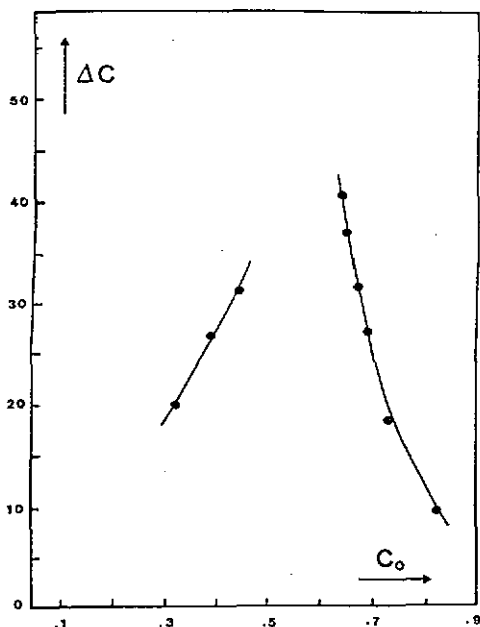
Figure 2. Thermogravitational separation versus mass concentration of nitrobenzene for the nitrobenzene–*n*-hexane system.
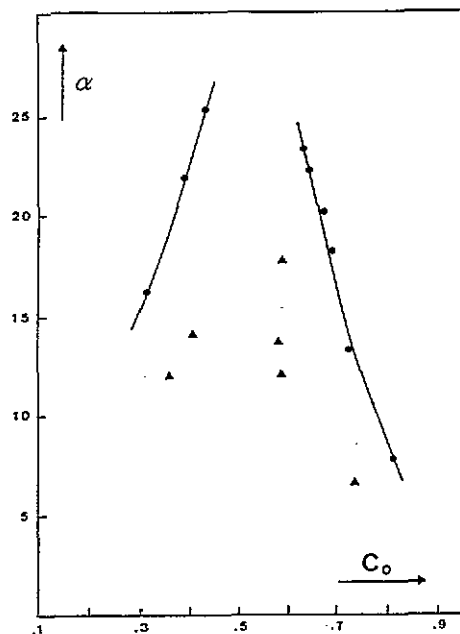
Figure 3. Thermal diffusion factor of the nitrobenzene–*n*-hexane system against the mass concentration of nitrobenzene. Experimental values: ●, this work; ▲, [8].

40% between the column ends are measured near the critical composition despite the mean temperature being considerably higher than T_c.

Introducing separation data in (2) for the Rayleigh number, we determine, from (1) the Soret parameter at the different concentrations considered. In this way, Soret parameters as high as $S = 10$ are obtained near the critical composition. The required thermophysical properties have been extracted from the literature. The density and density coefficients were calculated from experimental density data of pure components [13] assuming ideal mixing. The viscosity was estimated at the working temperature by extrapolating the data in the literature [13] using the Arrhenius equation. Finally, the data of Haase and Siry [14] were used for the ordinary diffusion coefficient.

From the values of the Soret parameter, we determine the thermal diffusion factor as a function of composition. The values so obtained are displayed in figure 3. As it can be seen, this quantity increases considerably at the neighbourhood of the critical composition, despite the fact that the working temperature of the column is 12 °C above the critical temperature. In contrast, the values of $D' = \alpha D/T$, calculated by using the Haase and Siry values for D [14], remain practically constant in the range of concentrations around the critical composition ($D' = 2.3 \times 10^{-7}$ cm^2 s^{-1} K^{-1}) and their magnitude is of the same order as the value determined in non-critical organic mixtures [3]. Moreover, Giglio and Vendramini [6] found for the consolute critical mixture aniline + cyclohexane that the value of D' stays almost constant and practically coincident with our results for nitrobenzene + *n*-hexane. This behaviour seems to indicate that D', which determines material transport by thermal diffusion, does not exhibit any singularity in the critical region.

Figure 3 also shows the data of Thomaes [8] obtained by using a different technique

for the thermal diffusion factor of this mixture at the same temperature. As can be seen, although the quantitative differences with our values are high, a similar trend is observed in both cases. In any case, more experimental work is required to elucidate the disagreement between the two sets of data.

Although in this work we have not made systematic non-steady separation measurements, we mention here that near the critical composition the separation times are very large (about one month), according to the obtained theoretical predictions for large values of S. This fact causes experimental measurements near critical composition to be very tedious.

In respect of the isobutyric acid + water system, with our experimental set-up we have not detected any separation at the working mean temperature of 10 K above the critical point ($T_c = 300$ K) in the range of concentrations 5–90% of mass fraction of water. For this mixture, the density of both components being very similar, the Soret parameter S will be small and thus the standard column formulation can be used. Then according to (4) the thermal diffusion coefficient D' is zero within experimental error, as we have shown in a previous paper, also occurs for non-critical organic mixtures with components of similar density [15]. It seems therefore, that the thermal diffusion coefficient D' does not present any anomaly in the critical region for this critical mixture, at least at the mean temperature considered.

We can conclude that the forgotten effect in a thermogravitational column can produce a high enhancement of the steady separation in the vicinity of critical points. The column theory developed for high Soret numbers allows one to obtain values of the thermal diffusion factor in this region. However, more experimental work is required to confirm the validity of the proposed method and the obtained thermal diffusion values.

Acknowledgment

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