

Enhanced Molecular Separation in Inclined Thermogravitational Columns

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We show in this paper that the molecular separation (or the difference in mass fraction) between the top and the bottom in a thermogravitational column can be substantially increased by inclining the column by an angle θ . This increase is almost given by $1/\cos \theta$. This view is supported by experiments performed on the water–ethanol system.

1. Introduction

In binary fluid mixtures submitted to temperature gradients, the thermodiffusion effect (usually called the Soret effect) will induce molecular migration and subsequently a mass fraction gradient. In the mass flux J of one of the components, besides the usual isothermal contribution (given by the Fick law) there is an additional contribution proportional to the temperature gradient.¹

$$J = \rho D \text{grad} C - \rho D_T C_0 (1 - C_0) \text{grad} T \quad (1)$$

In eq 1, ρ is the density of the mixture, C the mass fraction of the reference component (we usually take the denser component but the opposite choice could equally well be made) with initial value C_0 , D the isothermal diffusion coefficient, and D_T the thermodiffusion coefficient. The two contributions to the mass flux are of opposite sign: the temperature gradient is responsible for thermomigration, thus molecular separation, while isothermal diffusion tends to homogenize the solution. There exists a convectionless steady state where these two contributions are of equal intensity ($J = 0$), and the resulting mass fraction gradient is then proportional to the temperature gradient.

$$\text{grad} C = -\frac{D_T}{D} C_0 (1 - C_0) \text{grad} T \quad (2)$$

The ratio D_T/D is called the Soret coefficient and ranges usually from 10^{-3} to 10^{-2} K^{-1} (in some exceptional cases the Soret coefficient is negative, but we shall not be concerned with such situations in this paper). Therefore the difference in mass fraction per unit temperature difference is typically on the order of 10^{-3} or 0.1%, i.e., small. However, this is not always the case in the presence of convection. Absence of convection (for eq 2 to be valid) means a temperature gradient parallel to the gravity vector: the liquid layer is horizontal and heated from above to avoid convection. When the liquid layer is enclosed in a vertical slot, heated from one side and cooled from the other, the component that migrates to the hot is advected to the top, and the component that goes to the cold wall is advected to the

bottom of the cell. Thus a vertical mass fraction gradient will be created due to the interplay between Soret effect and convection, even if initially this gradient is horizontal since the temperature gradient is horizontal. The difference in mass fraction ΔC between the top and the bottom of the column, which we call the molecular separation, is given by the Furry–Jones–Onsager–Majumdar theory.^{2–4} We will not outline here the main features of this well-known theory, but we want for the sake of simplicity to recall some useful equations. The separation is given by

$$\Delta C = \frac{(q^{C_0} - 1)(q^{1-C_0} - 1)}{(q - 1)} \quad (3)$$

where

$$q = e^{(H/K)L_z} \quad (4)$$

and

$$\frac{H}{K} = \frac{\frac{\alpha \rho g D_T \Delta T^2 L_x^3}{6! \nu D}}{\frac{\alpha^2 \rho g^2 \Delta T^2 L_x^7}{9! \nu^2 D} + L_x \rho D} \quad (5)$$

In these equations, q is the factor that really governs the separation, and the constants H and K (the numerator and the denominator of eq 5) are called the “column constants”. In these constants, α is the thermal expansion coefficient of the mixture, g the acceleration due to gravity, ν the kinematic viscosity, and ΔT the applied temperature difference between the two lateral walls of the column, and L_i are characteristic lengths in the i -directions; in particular L_x will be the gap between the two walls (x is thus the horizontal direction) and L_z the height of the column (z is the vertical direction). Thus one recognizes that the separation is due to the interplay between buoyancy, convection, and thermodiffusion. It was noticed for a long time that there is an optimal separation for some particular value of the gap since $H/K \rightarrow 0$ (or equivalently $\Delta C \rightarrow 0$) when $L_x \rightarrow$

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0 or $L_x \rightarrow \infty$. This optimal gap L_x^{opt} is easily derived and found to be

$$L_x^{\text{opt}} = \left(\frac{9!}{2}\right)^{1/6} \left(\frac{\nu D}{\alpha g \Delta T}\right)^{1/3} \quad (6)$$

and gives the optimal value of H/K .

$$\left(\frac{H}{K}\right)^{\text{opt}} = \frac{(9!4)^{1/3}}{3.6!} \left(\frac{\alpha g}{\nu}\right)^{1/3} \left(\frac{\Delta T}{D}\right)^{4/3} D_T \quad (7)$$

Thus, for a given system characterized by α , ν , D and D_T , $(H/K)^{\text{opt}}$ can be made as large as we want simply by increasing the applied temperature difference ΔT . And when $(H/K) \gg 1$, then $q \gg 1$ and from eq 3, $\Delta C \rightarrow 1$. The separation is almost complete. However the optimal gap is usually rather small. As an example, for the water–ethanol system that we will study in this paper (see later for the physicochemical properties) and for a temperature difference of only 5 °C (a quite reasonable value), $L_x^{\text{opt}} \approx 235 \mu\text{m}$! It is rather difficult to maintain constant such a small gap over the height of the column (typically 50 cm, sometimes 1 m); moreover the volume of the liquid is rather small, making the sampling process necessary to measure ΔC even more difficult. Thus in practice, the spacing between the two walls of a thermogravitational column is typically several millimeters (for the experiments that we have done and described later, we have used a 1.58 mm spacing). In such conditions the spacing L_x is far from optimal and the separation remains small. Thus in many situations L_x is much larger than the optimal value, and the first term proportional to L_x^7 in the expression of the constant K (see denominator of eq 5) is dominant, while the second proportional to L_x is negligible. To be concrete, for the water–ethanol system discussed later, K may be evaluated for $\Delta T = 1$ °C:

$$K \approx (0.479 \times 10^{14}) L_x^7 + (0.404 \times 10^{-6}) L_x \quad (8)$$

and for $L_x = 1/2$ mm, the two terms are of the same order of magnitude, whereas for $L_x = 1.58$ mm the first term is 2000 times greater than the second. In such conditions, the ratio H/K reduces to

$$\frac{H}{K} = 504 \frac{\nu}{\alpha g} D_T \frac{1}{L_x^4} \quad (9)$$

and H/K remains much smaller than 1; for example, $H/K \approx 0.04$ for water–ethanol and a 1.58 mm spacing. Thus we may expand the q factor (see eqs 3 and 4),

$$q = \exp\left(\frac{H}{K} L_z\right) \approx 1 + \frac{H}{K} L_z; \quad q^{C_0} = \exp\left(\frac{H}{K} L_z C_0\right) \approx 1 + \frac{H}{K} L_z C_0; \text{ etc.} \quad (10)$$

and the separation becomes

$$\Delta C = 504 \frac{\nu}{\alpha g} D_T C_0 (1 - C_0) \frac{L_z}{L_x^4} \quad (11)$$

The separation is independent of the applied temperature difference, which could appear strange at first sight to nonspecialists in the field, but on the other hand it is the signature that the approximation made in the constant K is valid. This equation is of practical importance in all the experiments using thermogravitational columns to determine the thermodiffusion coefficient^{4–7} and shows that the separation is only on the order of

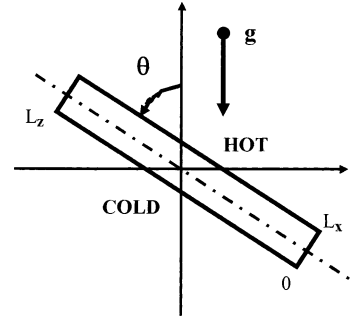


Figure 1. The inclined cell. Gap L_x : 1.58 mm. Height L_z : 530 mm.

1% (more precisely 0.49% for water–ethanol with $L_x = 1.58$ mm and $L_z = 530$ mm). On the other hand, all situations that tend to decrease the convective velocity amplitude (high viscosity, small expansion coefficient, small gap) increase the separation. Inversely, low viscosity, high thermal expansion coefficient, large gap L_x will increase the convection amplitude and decrease the separation. Since it is not easy to work with gaps on the order of 200–300 μm , Lorenz and Emery⁸ proposed to use larger gaps (e.g., 5 mm) but filled with a porous medium next saturated with the binary mixture. The use of a porous medium slows down the velocity amplitude to the level of a few $\mu\text{m/s}$ instead of several hundreds. As a matter of fact, large separations may be obtained with large gaps. In a porous medium eq 11, giving the separation, is almost unchanged and reads

$$\Delta C = 10 \frac{\nu}{\alpha g} D_T C_0 (1 - C_0) \frac{L_z}{L_x^2 k} \quad (12)$$

The changes result from the use of Darcy's law instead of the Navier–Stokes equation to describe the flow field. Thus the constant 504 has been changed to 10 and L_x^2 to the permeability k of the porous medium. Since we use a permeability k on the order of 10^{-10} m^2 instead of, for example, $4 \times 10^{-6} \text{ m}^2$ for L_x^2 , much larger separations can be obtained in a porous medium with the same gap. We also see from eq 11 that another possibility to obtain large molecular separations is to reduce the gravity level supported by a free fluid. This is the subject of the present paper.

2. Inclined Thermogravitational Cells

Let us consider a thermogravitational column inclined by an angle θ with respect to the gravity vector (Figure 1). As usual the column has an aspect ratio L_z/L_x (we keep the same notations for the characteristic lengths) much larger than unity (e.g., 335 as in the experiments described in section 4). Therefore we consider a one-dimensional velocity field with one nonzero velocity component parallel to the larger side of the cell (it would be a misuse to say a “vertical velocity” in the present case). We are thus doing the same kind of assumptions as in the classical Furry–Jones–Onsager–Majumdar theory, and what we need is the component of the body force per unit mass along the axis that supports this velocity component, i.e., $\rho g \cos \theta$. Thus the only thing we have to change in eq 5 is to replace g by its effective value $g \cos \theta$,

$$\frac{H}{K} = \frac{\alpha \rho g \cos \vartheta D_T \Delta T^2 L_x^3}{6! \nu D} \frac{1}{\alpha^2 \rho g^2 (\cos \vartheta)^2 \Delta T^2 L_x^7 + L_x \rho D} \quad (13)$$

and this shows that at constant L_x there is an optimal separation for a particular angle θ^{opt} . When θ is not too close to 90° (the meaning of “not too close to 90° ” will be quantified soon), i.e., when $\cos \theta$ is not too close to zero and in usual conditions ($L_x \approx 1\text{--}2\text{ mm}$), the second term in the denominator of eq 13 may once again be neglected, and the separation reduces to

$$\Delta C = 504 \frac{\nu}{\alpha g \cos \vartheta} D_T C_0 (1 - C_0) \frac{L_z}{L_x} \quad (14)$$

This last equation shows that the separation increases when the angle θ increases. When θ approaches 90° (or when $\cos \theta \rightarrow 0$), the separation remains of course finite because the second term in the denominator of eq 13 is dominant, and we find then

$$\frac{H}{K} = \frac{\alpha \rho g \cos \vartheta D_T \Delta T L_x^2}{6! \rho \nu D^2} \quad (15)$$

which shows that the separation goes to zero for horizontal layers ($\theta = 90^\circ$). The separation we are speaking of is, of course, a “longitudinal” separation, perpendicular to the applied temperature gradient, that is to say between top and bottom when the layer is vertical, but when inclining the layer, it is between the small boundaries, or between left and right boundaries when the layer is horizontal. When the layer is horizontal, there is a separation, but parallel to the temperature gradient, i.e., between top and bottom, or between hot and cold walls, and given by eq 2, but we are not dealing with this separation.

At constant L_x the optimal angle can be easily found.

$$\vartheta^{\text{opt}} = \cos^{-1} \left(\frac{\sqrt{9!} \nu D}{\Delta T \alpha g L_x^3} \right) \quad (16)$$

A rough order of magnitude can be very quickly obtained for this optimal angle. Let us take a kinematic viscosity of 10^{-2} St (that of water at 20°C), a diffusion coefficient of $10^{-5}\text{ cm}^2/\text{s}$, a temperature difference of 5°C , an expansion coefficient of $2 \times 10^{-4}\text{ K}^{-1}$ (that of water), a spacing of 10^{-1} cm , and finally a g of $\sim 1000\text{ cm/s}^2$. We get immediately

$$\vartheta^{\text{opt}} = \cos^{-1}(\sqrt{9!} \times 10^{-4}) \sim \cos^{-1}(0.06) \sim 86.5^\circ$$

The optimal separation for this angle may be as close to 1 as we want simply by increasing the applied temperature difference. Clearly the separation cannot be made greater than 1, neither in the vertical position by reducing the gap nor at large gap by inclining sufficiently the cell. The message of the paper, also in the title, is that for practical gaps of several millimeters inclining the cell may increase the separation. The price we have to pay for that is the relaxation time of the process. For a vertical layer it is given by^{3,4}

$$\tau = \frac{9! L_z^2 \nu^2 D}{(\pi \Delta T g \alpha L_x^3)^2} \quad (17)$$

and each factor that decreases the velocity (large viscosity, small temperature difference, small expansion coefficient, small gap) will increase the relaxation time. In fact for the water–alcohol system reported below in section 3 and for $\Delta T = 5^\circ\text{C}$, the relaxation time is less than 0.5 h, which is quite reasonable. In a porous medium where the velocity is extremely small, the relaxation time is typically one month! It is safe to wait 5 times the relaxation time before starting the measurements! In inclined columns, since g has to be replaced by $g \cos \theta$, the relaxation

TABLE 1: Properties of the Mixture Water (60.88 wt %)—Ethanol (39.12 wt %) at a Mean Temperature of 22.5°C and Characteristics of the Column

properties of the mixture	units	numerical value
water mass fraction	C_0	0.6088
density	ρ kg/m ³	935.17
thermal expansion coefficient	α °C ⁻¹	7.86×10^{-4}
mass expansion coefficient	β	0.212
isothermal diffusion coefficient	D m ² /s	$(4.32 \pm 0.26) \times 10^{-10}$
thermodiffusion coefficient	D_T m ² /s °C	$(1.37 \pm 0.08) \times 10^{-12}$
kinematic viscosity	ν m ² /s	$(2.716 \pm 0.010) \times 10^{-6}$
Characteristics of the Column		
length	L_z m	0.53 ± 0.001
gap	L_x m	0.00158 ± 0.00002

time diverges when the column approaches horizontality.

$$\tau^{\text{inclined layer}} = \frac{\tau^{\text{vertical layer}}}{(\cos \vartheta)^2} \quad (18)$$

For an angle of 84° , the relaxation time is 91 times greater than in a vertical column, i.e., 45 h with $\Delta T = 5^\circ\text{C}$, but only 5 h with $\Delta T = 15^\circ\text{C}$. For the last angle that we have investigated in the experimental part, namely, 88° , the relaxation time is 821 times greater than in a vertical column, i.e., 400 h with $\Delta T = 5^\circ\text{C}$, but only 2 days with $\Delta T = 15^\circ\text{C}$, and this is such that the experiment can be completed in one week. As a matter of fact, increasing ΔT will increase the optimal angle, up to more than 89.9° , which is excellent if we want to work with an 88° angle. But before working with large temperature differences, we have to verify that the separation in vertical layers remains independent of ΔT , 5°C or 15°C , to be sure that the assumptions are correct, and when dealing with temperature differences as high as 15°C , we think about the Boussinesq approximation that was made in the theory. We shall come back to this point in the experimental part.

3. Properties of the Water–Ethanol System

We decided to investigate the water–ethanol system simply because the thermodiffusive properties are well known: this system was investigated by several groups, namely, ourselves,⁴ Kolodner et al.,⁹ Zhang et al.,¹⁰ Köhler and Müller,¹¹ and Bou-Ali et al.¹² with coherent values between the five groups (see ref 4 for a comparison). We give in the Table 1 the properties of this system taken from our contribution⁴ and reproduced here for the sake of simplicity, together with the characteristics of the experimental column, by the way exactly the same as used before.⁴

Moreover, for this system the Soret coefficient is positive. As we said before in the Introduction, we exclude from the present study the case of negative Soret coefficients (this happens to be the case for water-rich systems, e.g., 90 wt % water–10 wt % alcohol). In that case the denser component would migrate to the hot plate and then would be advected to the top of the column, creating an adverse concentration gradient responsible for possible instability phenomena. We are currently examining this case in a vertical column, without definitive answer, and it would be outside the scope of this paper to discuss possible instabilities in inclined columns. By the way this is also the reason, when we incline the column, the hot plate is the upper plate to avoid any problem with free convection.

With the values of Table 1, we have tabulated (see Figure 2) the separation given by eqs 3, 4, and 13 for two temperature differences: 1 and 15°C . There are no noticeable differences for angles below 80° , and this finally defines what we called

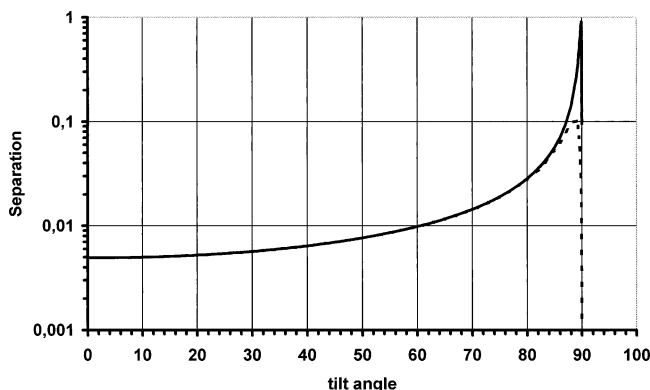


Figure 2. Variation of the separation with the tilt angle. Solid line: $\Delta T = 15$ °C. Dotted line: $\Delta T = 1$ °C.

TABLE 2: Variation of the Density with Position in the Column for Different Tilt Angles ($\Delta T = 15$ °C)

position z in the column (in cm)	$\theta = 0^\circ$ $\tau = 158$ s	$\theta = 75^\circ$ $\tau = 2361$ s	$\theta = 82^\circ$ $\tau = 8165$ s
3.5	0.936380	0.937193	0.938854
13	0.936207	0.936611	0.937763
26	0.935980	0.935749	0.936123
40	0.935690	0.934840	0.934378
50	0.935526	0.934146	0.932913

before “not too close to 90°”. Then eq 14 is a sufficient approximation. For an angle of 89° (close to the optimal), the separations are respectively 10% for $\Delta T = 1$ °C and 27% for $\Delta T = 15$ °C, instead of 0.5% for the vertical layer. We want now to test this enhanced separation in an experimental session described below.

4. Experiments

The experiments described below were performed in the same thermogravitational column as the one used before in order to determine the thermodiffusion coefficient.⁴ Therefore no details concerning the column and its use will be given here, except that the useful dimensions are given in Table 1. Evidently the column has been mounted on a rotating disk. Let us recall that along one of the sides of the column we have managed 5 sampling taps in order to remove samples, later analyzed to find their composition: this gives the variation of the mass fraction with position in the column, and thus we experimentally have access to the separation. The removed samples are analyzed by taking their densities with the quartz vibrating U-tube densimeter DMA5000 manufactured by Anton Paar, having an accuracy of 2×10^{-6} g/cm³. Of course we need the relation between density and mass fraction, i.e., a calibration curve. This calibration curve is Figure 5 of ref 4 and will not be reproduced here. However let us say that in a not too large range of variation of mass fraction (say $\sim 10\%$ around the mean mass fraction) this curve is linear, and we recall in Table 1 the value of the mass expansion coefficient $\beta = (1/\rho_0)(\partial\rho/\partial C)$. We give in Table 2 and in Figure 3 the variation of the density as directly given by the Paar densimeter, with position in the column ($z = 0$ is the bottom and $z = 53$ cm is the top) for three values of the tilt angle θ (0° , 75° , and 82°), but more cases were investigated.

We also give in Table 2 the relaxation time τ in seconds given by eqs 17 and 18. We usually wait 5 times the relaxation time before removing the samples. To keep the relaxation time to a reasonable value, in particular when approaching horizontality ($\theta = 88^\circ$), we impose a temperature difference of 15 °C. But before, we have checked for the vertical layer that the separation was independent of ΔT , that is to say that non-Boussinesq effects

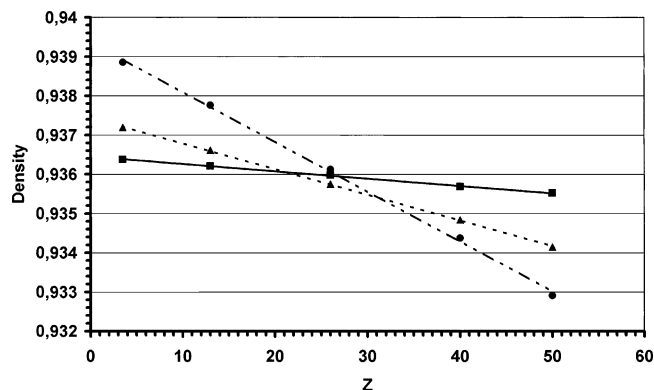


Figure 3. Variation of the density with position in the column for three tilt angles, $\Delta T = 15$ °C. Squares: $\theta = 0^\circ$. Triangles: $\theta = 75^\circ$. Circles: $\theta = 82^\circ$.

TABLE 3: Variation of the Separation with the Tilt Angle

θ (deg)	ΔC (exptl)	ΔC (theory)	$\Delta C_\theta/\Delta C_0^\circ$ (exptl)	$\Delta C_\theta/\Delta C_0^\circ$ (theory)	difference (%)
0	0.00480	0.004926	1	1	
25	0.00433	0.005435	0.90	1.10	18
50	0.00663	0.007663	1.38	1.56	12
60	0.00843	0.009851	1.77	2.00	12
70	0.01340	0.014400	2.79	2.92	4
75	0.01752	0.019028	3.65	3.86	5
80	0.02770	0.028352	5.77	5.76	
82	0.03400	0.035366	7.08	7.18	9
84	0.04394	0.047061	9.15	9.55	4
88	0.13397	0.139728	27.91	28.37	2

were absent. Figure 3 shows that the variation of the density (and therefore of the mass fraction) remains linear even for large separations. Thus from Table 2 we are able to calculate the slope $\partial\rho/\partial z$, to linearly extrapolate to find the difference in density $\Delta\rho$ between the bottom and the top of the column $\Delta\rho = (\partial\rho/\partial z)L_z$, and finally to find the separation $\Delta C = \Delta\rho/\rho_0\beta$. For example, concerning the results presented in Figure 3, we have found by a linear fit the variations of the density with the position in the column:

$$\theta = 0^\circ: \rho(z) = 0.936449 - (1.8567 \times 10^{-5})z \text{ (cm)}; \\ R^2 = 0.9990$$

$$\theta = 75^\circ: \rho(z) = 0.937445 - (6.5554 \times 10^{-5})z \text{ (cm)}; \\ R^2 = 0.9997$$

$$\theta = 82^\circ: \rho(z) = 0.939377 - (12.721 \times 10^{-5})z \text{ (cm)}; \\ R^2 = 0.9988$$

There are of course errors on each individual measurement of the density of a removed sample, mainly due to possible evaporation of the most volatile component during the handling of the sample. Therefore, to calculate ΔC , we do not take the densities at the two extreme positions ($z = 3.5$ cm and $z = 50$ cm), in which case the benefits of a 5-point sampling process would be lost. We use the linear fits given here above, and owing to the values of R^2 very close to 1 (the worst value is $R^2 = 0.9988$), it is safe to say that ΔC is determined with an accuracy better than 1%. This is not the case for $\Delta C(\text{theory})$ listed in column 3 of Table 3. Indeed $\Delta C(\text{theory})$ is calculated from eq 13 or 14, and we need the values of α , ν , and D_T , reproduced in Table 1, together with experimental uncertainties discussed in detail in ref 4.

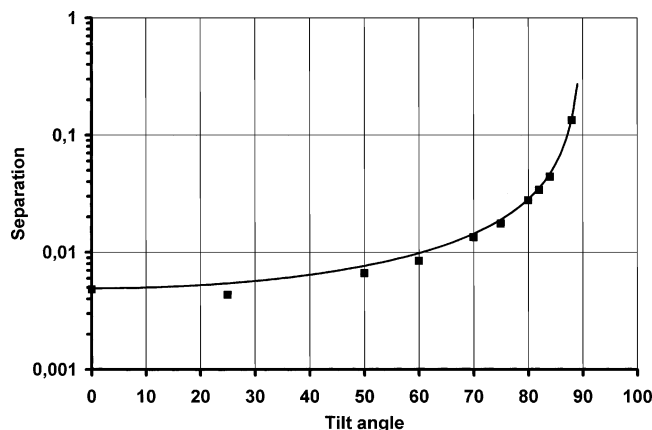


Figure 4. Variation of the separation with the tilt angle. $\Delta T = 15\text{ }^{\circ}\text{C}$. Solid line: theory. Squares: experiments.

Table 3 and Figure 4 give the experimental and theoretical separations (given by eqs 3, 4, and 13) for all the cases that we have investigated.

In columns 4 and 5 of Table 3, we give the increase of the separation relative to the vertical column. Let us mention here that $\Delta C_{\theta}/\Delta C_0$ (theory) is, in contradistinction with ΔC (theory), independent of the physicochemical parameters of the mixture, since it is merely the tabulation of $1/\cos \theta$ according to eq 14. In the last case however ($\theta = 88^{\circ}$), the full eq 13 has to be used, but experimental errors on α , ν , D , D_T , etc., which are included in small correcting terms, are of no practical significance, and in any case we prefer to use the value 28.37 instead of $1/\cos 88^{\circ} = 28.65$.

The experimental point at $\theta = 25^{\circ}$ is abnormal: the separation is smaller than in the vertical layer. But the experiment has been redone, and again we have found the same anomaly. By the way, looking at Figure 4, even if the general tendency to an increase of the separation with inclination is obvious, the first three experimental points ($\theta = 25^{\circ}$, 50° , and 60°) are clearly below the theoretical curve for some yet unexplained reasons, but certainly not related to experimental error: the experimental separation for $\theta = 25^{\circ}$ is below that of the vertical layer ($\theta = 0^{\circ}$) and is reproducible.

In the last column of Table 3 we give the difference between experiments and theory. Except for the three first angles ($\theta = 25^{\circ}$, 50° , and 60°), it is our opinion that the agreement with the $1/\cos \theta$ increase of the separation is demonstrated. The remaining discrepancy could be linked (maybe?) to the exact position of the center of mass of the removed samples when

the layer is inclined, supposed not to vary in our approach. But this is difficult to quantify.

5. Conclusions

We have clearly demonstrated that when inclining a thermogravitational column, the molecular separation is increased. A very simple reformulation of the old Furry–Jones–Onsager–Majumdar theory, in which the effective body force $g \cos \theta$ is introduced, agrees fairly well with the experiments. The use of longer columns (say 1 or 2 m), higher temperature differences, and tilt angles close to the optimal could result in separations close to 1, even if the relaxation time diverges. Thus the present study could be of practical interest for industrial processes.

On the other hand, as far as the measurement of thermodiffusion coefficients is concerned by thermogravitational techniques and the use of eq 11, we recommend inclining the cell in order to increase the separation. This is especially interesting when the separation is small or when using densimeters having a smaller resolution, e.g., 10^{-5} g/cm^3 instead of $2 \times 10^{-6}\text{ g/cm}^3$ (or when employing any other analyzing apparatus, e.g., measuring the index of refraction with only four digits). Inclining the cell when the dominant error is on ΔC would result in a better accuracy on D_T , rendering sometimes possible the measurement of D_T when impossible in vertical columns. Of course when the error on D_T is mostly determined by the experimental error on α , ν , and L_x and not by that on ΔC , inclining the cell will not be of particular interest.

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