

## Some phenomenological and thermodynamic aspects of diffusion in multicomponent systems

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**Abstract** - During the last twenty years diffusion coefficients have been primarily measured by light scattering and NMR techniques.

Optical interferometric techniques, such as those of Gouy or Rayleigh (ref. 1), allowing direct observation of the time evolution of a diffusing boundary are not very popular at present. However, they are the only ones that give a reasonably accurate measurement of the set of  $(n-1)^2$  diffusion coefficients describing the brownian transport process in a multicomponent system.

Experimental data on a variety of ternary systems indicate some aspects of diffusion in multicomponent systems:

(a) The thermodynamic stability conditions:

$$(i) \quad D_{11} + D_{22} > 0 \quad \text{and} \quad (ii) \quad D_{11}D_{22} - D_{12}D_{21} \geq 0$$

have been verified experimentally and the relevant contribution of cross terms, which cannot be ignored in describing the transport process, has been pointed out. Furthermore, it was also experimentally verified that on approaching a critical mixing point the determinant (ii) approaches zero.

(b) The main terms need not be necessarily positive; one of them may be negative.

(c) The presence of a binding equilibrium between solutes 1 and 2 affects the experimentally measured values of the four diffusion coefficients.

The equilibrium constant calculated from the experimental  $D_{ij}$ 's leads to values in very good agreement with those provided by direct thermodynamic techniques.

The binding equilibrium promotes conditions leading to the transport of one component against its own concentration gradient, or its own chemical potential gradient (passive transport).

(d) Diffusion measurements in three component systems provide a quantitative verification of the effect of the fluid-dynamics equations on the gravitational stability of diffusion boundaries or double diffusive convection, which is a convective transport process of great interest in several fields of pure and applied science.

### INTRODUCTION

The aim of this paper is to illustrate briefly some results of the research on brownian diffusion in ternary systems our group has been conducting at the Chemistry Department of University Federico II in Naples for several years.

Its main purpose has been the understanding of the phenomenological role the presence of one component has on the transport process of the others.

The phenomenological diffusion theory proposed by Onsager (ref. 2) describes the transport process in an  $n$ -component system by a set of  $n$  generalized Fick's equations:

$$(1) \quad J_i = - \sum_1^n D_{ij} \text{grad } C_j$$

However, neither the  $n$  concentration gradients nor the  $n$  flows are all independent. The relation among concentrations is:

$$(2) \quad \sum_1^n \bar{V}_i C_i = 1$$

In the absence of pressure gradients, this leads to:

$$(2a) \quad \sum_1^n \bar{V}_i \text{grad } C_i = 0$$

where  $\bar{V}_i$  is the partial molar volume of component  $i$ .

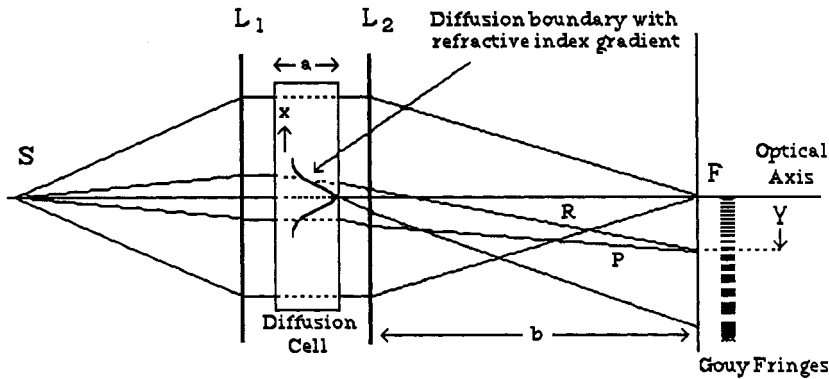


Fig. 1. Scheme of the Gouy Diffusometer showing the formation of interference fringes: S is the light source,  $L_1$  and  $L_2$  are two lenses that give the source image in F. Light passing through the diffusion boundary, where a vertical gradient of refractive index is present, deviates to form the source image at different levels in F. Light deviation Y, in F, is given by  $Y = ab(dn/dx)$ , where  $dn/dx$  is the refractive index gradient at level x into the diffusion cell. Light wave fronts R and P, passing through the diffusion boundary at different levels, but joining in F, have different optical paths and interfere on the focal plane F to form a fringe pattern.

The relation between flows arises from the continuity law and depends on the reference frame chosen to describe the transport process.

Experimental free diffusion measurements choose a *volume-fixed* reference frame defined by the following relation(ref. 3):

$$(3) \quad \nabla \cdot \sum_1^n \bar{V}_i J_i = 0$$

$\nabla$  being the local velocity of a volume element of the solution.

Sometimes it is preferable to describe the flow process in terms of the diffusional velocity of each component ( $v_i = J_i/C_i$ ) with respect to that of component n, generally assumed as the solvent:

$$(4) \quad J_i = C_i(v_i - v_n)$$

where  $J_i$  are the flows in the fixed-solvent reference frame,  $J_n$  being zero by definition. A set of  $n-1$  independent equations with a set of  $(n-1)^2$  independent coefficients, is obtained by introducing eq.(2) into eqs.(1) :

$$(5) \quad J_i = - \sum_1^{n-1} D_{ij} \text{grad } C_j$$

Onsager suggested the following arbitrary relations to define the  $n^2$  coefficients  $D_{ij}$  :

$$(6) \quad \sum_j D_{ij} C_j = 0 \quad (i = 1, 2, \dots, n)$$

eq.(6) includes the relation:

$$(7) \quad \sum_{i,j} \bar{V}_i D_{ij} C_j = 0$$

A further reduction of independent coefficients arises from the presence of Onsager reciprocity relations. However, their use requires knowledge of the thermodynamic properties of the solution, and this is very limited in multicomponent systems.

Experimental techniques, such as the Gouy interferometer (ref. 1) used in our research (see Fig. 1), give the  $(n-1)^2$  diffusion coefficients of a n-component system, at one mean concentration, from the analysis of the diffusion patterns of at least  $(n-1)$  diffusion runs with varying concentration differences of their components through the diffusion boundary. This technique has so far been employed only in the investigation of three component systems.

#### CHOICE OF COMPONENT n (the solvent)

In a 3-component system, equations (5) reduce to:

$$(8) \quad J_1 = - D_{11} \text{grad } C_1 - D_{12} \text{grad } C_2$$

$$(8) \quad J_2 = - D_{21} \text{grad } C_1 - D_{22} \text{grad } C_2$$

and four diffusion coefficients can be measured experimentally.



Table 1 collects the  $(D_{ij})_k$  for the **Acetic acid- Chloroform- Water** system at various compositions, the data for all three choices of component  $k$  are given. It can be seen that if components  $i$  and  $j$  are water and chloroform (salting out effect) the cross terms are positive; if they are water and acetic acid (attractive interactions), the cross terms are negative.

TABLE 1. Diffusion Coefficient for the System: Acetic Acid-Chloroform-Water at 25°C (ref. 7) and various compositions.  $X_i$  = mol fraction of component  $i$ .  $D$  units  $10^5$   $\text{cm}^2 \text{s}^{-1}$

Component $i \rightarrow$ Acetic Acid; Comp. $j \rightarrow$ Chloroform; Comp. $k \rightarrow$ Water					
$X_i$	$X_j$	$(D_{ii})_k$	$(D_{ij})_k$	$(D_{ji})_k$	$(D_{jj})_k$
0.8803	0.0496	1.296	0.011	-0.232	0.933
0.7811	0.0892	1.550	0.520	-0.548	0.367
0.6924	0.1288	1.547	0.545	-0.624	0.230
0.5405	0.1897	1.814	1.065	-0.939	-0.334
0.4199	0.2400	1.844	1.153	-1.095	-0.596

Component $i \rightarrow$ Water; Comp. $j \rightarrow$ Chloroform; Comp. $k \rightarrow$ Acetic Acid.					
$X_i$	$X_j$	$(D_{ii})_k$	$(D_{ij})_k$	$(D_{ji})_k$	$(D_{jj})_k$
0.0701	0.0496	0.970	0.130	0.073	1.259
0.1297	0.0892	0.782	0.194	0.172	1.135
0.1788	0.1288	0.672	0.236	0.196	1.105
0.2698	0.1897	0.498	0.321	0.295	0.983
0.3401	0.2400	0.309	0.368	0.344	0.939

Component $i \rightarrow$ Water; Comp. $j \rightarrow$ Acetic Acid; Comp. $k \rightarrow$ Chloroform					
$X_i$	$X_j$	$(D_{ii})_k$	$(D_{ij})_k$	$(D_{ji})_k$	$(D_{jj})_k$
0.0701	0.8803	0.941	-0.093	-0.002	1.288
0.1297	0.7811	0.738	-0.138	-0.117	1.178
0.1788	0.6924	0.619	-0.168	-0.122	1.158
0.2698	0.5405	0.426	-0.229	-0.239	1.055
0.3401	0.4199	0.226	-0.262	-0.258	1.022

### THERMODYNAMIC STABILITY CONDITIONS

Thermodynamic stability is ensured by the condition that any perturbation promotes an entropy absorption; namely, the entropy at equilibrium is a maximum; on the other hand, any spontaneous process occurs with a positive definite entropy production. For isothermal diffusion in an  $n$ -component system this condition is written as:

$$(13) \quad T \delta^2 S = - \sum_i \delta \mu_i \delta n_i \leq 0 \quad \text{where} \quad \delta \mu_i = \sum_k \frac{\partial \mu_i}{\partial n_k} \delta n_k$$

$\delta \mu_i$  being the perturbation of chemical potential of component  $i$ , and  $\delta n_k$  the possible arbitrary fluctuation in the number of moles of component  $k$ .

From eq.(13) one obtains the stability conditions with respect to diffusion:

$$(14) \quad \sum_{i,k} \mu_{ik} \delta n_i \delta n_k \geq 0 \quad \text{where} \quad \mu_{ik} = \frac{\partial \mu_i}{\partial n_k}$$

The conditions for the quadratic expression (14) to be positive or zero are that all  $\mu_{ii}$  must be positive and all the other minors, both odd and even order, constructed on the principal diagonal of the determinant of  $\mu_{ik}$  must be positive or zero. This condition is met by making the trace of the matrix of diffusion coefficients positive and the determinant positive or zero. In a ternary system:

$$(15) \quad D_{11} + D_{22} > 0 \quad \text{and} \quad D_{11} D_{22} - D_{12} D_{21} \geq 0$$

The equality sign corresponds to the boundary between stable (or metastable) and unstable systems. In the phase diagram this boundary is known as the spinodal curve. Any solution whose composition lies within this curve is unstable and concentration fluctuations always promote a phase separation.

The equality sign was confirmed in a set of experimental diffusion runs on the water-chloroform- acetic acid system (ref. 7) taken at various compositions approaching the plait-point, where the phase separation curve joins the spinodal curve; the results are shown in Fig. 2.

Conditions (15) do not require both main diffusion terms to be positive. Diffusion coefficients measured in a volume-fixed reference frame may give a negative main term. This was found in the system shown in Fig. 2. Table 1 collects the set of  $(D_{ij})_k$  obtained choosing each component as component  $k$  in turn.

It can be seen that when water is chosen the chloroform main diffusion coefficient is negative in a wide range of compositions approaching the plait-point.

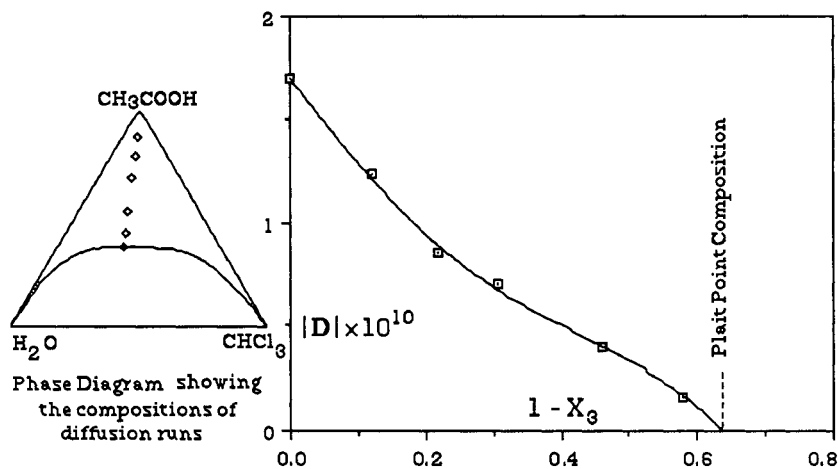


Fig. 2.

Fig. 2. System Acetic acid - Chloroform - Water at 25°C (ref. 7);  $|D|$  Determinant of Diffusion Coefficients;  $X_3$  mole fraction of acetic acid

### DIFFUSION IN THE PRESENCE OF A BINDING EQUILIBRIUM

While the size and sign of diffusion coefficients for systems with high solute concentrations are only understood in qualitative terms at present, a more detailed interpretation of data is possible for dilute solutions in which significant fractions of solute monomer species have combined to form associated species.

Let us consider a solution of monomer species A (1) and B (2) in equilibrium with a complex AB (3) according to the equation:



This is a quaternary system and diffusion eqs.(5) require nine coefficients,  $D_{ij}^*$  ( $i, j = 1, 2, 3$ ). However, if we are dealing with a dilute solution of both A and B, the cross diffusion terms are expected to be small as compared to the main terms, and they can reasonably be ignored in the flow equations (5).

Furthermore, in the presence of a fast equilibrium, the mass conservation law:

$$(17) \quad C_1 = C_1^* + C_3^*; \quad C_2 = C_2^* + C_3^*; \quad J_1 = J_1^* + J_3^*; \quad J_2 = J_2^* + J_3^*$$

(where  $C_i$  and  $J_i$  are the stoichiometric concentration and flow of component  $i$ ,  $i = 1, 2$ , and  $C_j^*$  and  $J_j^*$  are the concentration and flow of the actual species  $j$ ,  $j = 1, 2, 3$ ) and the mass action law:

$$(18) \quad K_c = C_3^* / (C_1^* C_2^*)$$

impose a restriction between concentrations and flows.

Because of eqs.(17) and (18) this system reduces to a ternary one having only four measurable diffusion coefficients which are related to the actual diffusion coefficients  $D_{ij}^*$  by the following expressions:

$$(19a) \quad D_{11} = (1/2)\{(D_{11}^* + D_{33}^*) + (D_{11}^* - D_{33}^*)[1 - K_c(C_2 - C_1)] R\}$$

$$(19b) \quad D_{12} = (1/2)\{(D_{33}^* - D_{11}^*) + (D_{11}^* - D_{33}^*)[1 + K_c(C_2 - C_1)] R\}$$

$$(19c) \quad D_{21} = (1/2)\{(D_{33}^* - D_{22}^*) + (D_{22}^* - D_{33}^*)[1 - K_c(C_2 - C_1)] R\}$$

$$(19d) \quad D_{22} = (1/2)\{(D_{22}^* + D_{33}^*) + (D_{22}^* - D_{33}^*)[1 + K_c(C_2 - C_1)] R\}$$

where:

$$(20) \quad R = \left( [1 + K_c(C_2 - C_1)]^2 + 4K_c C_1 \right)^{-\frac{1}{2}}$$

Eqs. (19) are a set of four equations allowing the three  $D_{ij}^*$  and  $K_c$  at each concentration to be computed from the experimental  $D_{ik}$ .

Eqs.(19-20) were verified for (a)  $\alpha$ -cyclodextrin-(L)phenyl alanine-water (ref. 8,9) and (b)  $\alpha$ -cyclodextrin-(D,L)norleucine-water (ref. 10) at 25°C and various amino acid concentrations. The  $K_c$  obtained from eqs.(19-20) was in very good agreement with that measured calorimetrically. Table 2 collects the diffusion data for (a) and (b) at one concentration and the average  $K_c$  from the diffusion and the calorimetry data (ref. 8-10).

TABLE 2. Diffusion data for (a)  $\alpha$ - cyclodextrin(1) - (L)phenyl alanine(2) - water and (b)  $\alpha$ -cyclodextrin(1) - (D,L)norleucine(2) - water at 25°C (ref. 8-10):

	$D_{11}$	$D_{12}$	$D_{21}$	$D_{22}$	( $10^6 \text{ cm}^2 \text{ s}^{-1}$ )	$D_{11}^*$	$D_{22}^*$	$D_{33}^*$
(a)	3.157	0.000	-1.630	6.332		3.157	6.510	3.157
(b)	3.142	-0.003	-2.178	6.270		3.163	6.432	3.128

The inclusion equilibrium drastically affects the value of the cross diffusion term responsible for aminoacid (A) transport under the concentration gradient of cyclodextrin (CD).

As can be seen from eq.(19b), the near equality of  $D_{11}^*$  and  $D_{33}^*$  is responsible for the very small cross-term diffusion coefficient  $D_{12}$ .

The cross-term  $D_{21}$  tends to be large and negative because the diffusion coefficient  $D_{22}^*$  of the faster moving A is much larger than  $D_{33}^*$  for the CD-A complexes. In this case, if there is a CD gradient and no gradient of A, the negative  $D_{21}$  causes A to move *uphill* towards the higher concentration of CD. This is because a higher concentration of CD means a lower concentration of unbounded A.

The transport of one component due to the concentration gradient of the other (passive transport) bears some similarity to the active transport that plays a substantial role in biological membrane processes.

Passive transport may also be of interest in membrane processes, the presence of cross terms can in fact lead to conditions for which one component diffuses against its own concentration gradient or even its chemical potential gradient, under the driving force of the other one.

**GRAVITATIONAL INSTABILITIES / IN FREE DIFFUSION BOUNDARIES**

In recent years, there has been a great interest in *double diffusive convection*, i.e. the convective motions which can arise in diffusive layers even if the top liquid system has a lower density than the bottom one. This phenomenon may appear in systems where at least two independent driving forces promote the transport process. Thus, it may appear in binary solutions when a temperature and a concentration gradient are present, or in isothermal ternary solutions in the presence of concentration gradients of two components (ref. 11).

An example is the heat and salt diffusion that gives rise to *fingering* or *layering* in oceans. Fig. 3 shows the temperature and salt concentration gradient conditions that may promote the growth of two different convective mechanisms in salty water.

Other examples include unwanted convection in lakes and solar ponds, rollover in liquid natural gas tanks, geology (crystallization and magma chamber processes), geophysics (mantle convection and vulcanism), astrophysics (inside stars at least 4 components may be involved in the process: angular momentum, heat, magnetic field, helium / hydrogen composition), metallurgy (morphology and crystallization).

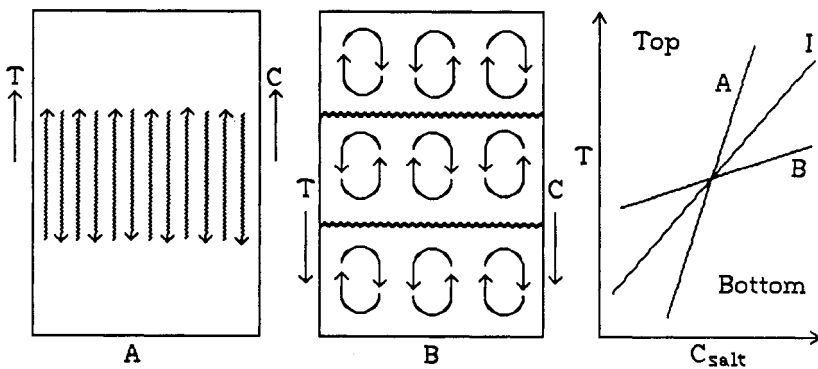


Fig. 3. Convection in sea water due to temperature and salt concentration gradients: I, isodensimetric line. A, Fingers growth. B, Formation of convection cells.

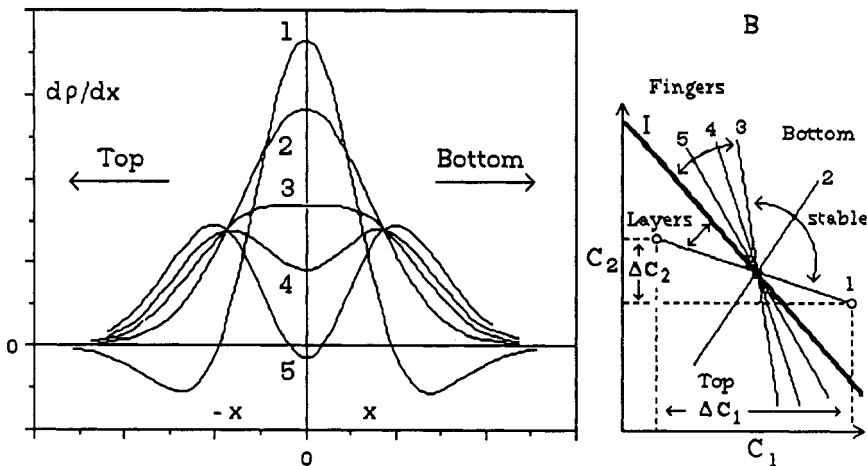


Fig. 4. Qualitative graph showing the density gradients through a diffusion boundary for various  $\Delta C_2 / \Delta C_1$  conditions. B: graph showing the average composition of a set of diffusion runs, the concentration differences between bottom and top solutions, and the fields of stable and unstable boundaries. 1 - convection at the borders of the boundary (*layering*). 2 - stable boundary. 3,4 - convection at the center of the boundary (*fingers*) with no density inversion inside the boundary due to diffusion. 5 - density inversion at the center of the boundary due to diffusion. I - isodensimetric line.

Free diffusion experiments can be performed in well-controlled conditions and have provided an accurate way of testing the fluid-dynamics theories concerned (ref. 4,12-14).

The profile of density ( $\rho$ ) gradient through the diffusion boundary is given by the sum of two gauss functions (ref.15). Its shape depends on the  $\Delta C_1$  and  $\Delta C_2$  concentration differences of components 1 and 2 across the diffusion boundary, and on the diffusion coefficients. Two different kinds of instabilities were observed in free diffusion boundaries:

(a) A dynamic instability arising at the center of the boundary, even in the absence of density inversions due to the diffusion process [Fig. 4 (3, 4)], for:

$$(21) \quad (\partial^2 \rho / \partial x^2)(1/x) \leq 0$$

In this case convection tends to destroy the boundary and the process is similar to the *fingering* in sea water (Fig. 3 A).

(b) A static instability, namely a density inversion, at the borders of the boundary, as shown in Fig. 4(1). In this case convection at the borders of the boundary promotes its apparent overstabilization and the diffusion boundary keeps itself sharp and narrow much longer than expected from the diffusion experiment (ref. 16). This process is similar to the layering effect in sea water, shown in Fig. 3 B.

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17. Owing to the limited space available for this note, the references are mainly limited to personal papers, in which an extensive bibliography can also be found.