

EXPERIMENTAL DETERMINATION OF DIFFUSION COEFFICIENTS IN LIQUID MIXTURES IN A LABORATORY OF TRANSPORT PHENOMENA

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ABSTRACT

The diffusion coefficient is a variable present in the operations of mass transfer, since it is part of many correlations. For this reason it is necessary to know its value or to determine it through experiments. This article presents a diffusion cell that has been used by students of Chemical Engineering in the laboratory of Transport Phenomena in the Faculty of Chemistry at the Universidad Nacional Autónoma de México (UNAM).

KEYWORDS: Coefficient of Diffusion, Experimental Determination, Transport Phenomena

INTRODUCTION

The diffusion coefficient is a very important variable in the mass transfer operations, since it is inside of many correlations implicitly or explicitly. Therefore knowing its value is essential and when this is not the case it must be obtained experimentally.

The Coefficient of Diffusion in Liquids

The diffusion is the mechanism through which mass is transferred from one place to another by molecular motion. This mechanism of diffusion is much slower in liquids than in gases (near thousand times less), but it is always present in the liquid mass transfer and it in many cases causes 90 percent of the inter-phase mass transfer resistance.

The transfer of mass by diffusion is governed by Fick's law.

$$\mathcal{J}_A = -D_{AB} \frac{d\tilde{c}_A}{dz} \quad (1)$$

Fick's law indicates that the mass of the component A flows in the direction of the decreasing of concentration. Where \tilde{J}_A is the mass molar flow of substance A in the direction z , and it is only due to molecular motion. D_{AB} is the coefficient of diffusivity or diffusion. It has been observed that when two solutions of different concentrations are put in contact there is spontaneously a concentration gradient between them, creating in this way a molar flux density, from regions of high concentration to areas of low concentration.

It can be considered that Eyring theory about the liquid state is the best approach that we have to describe the behavior in the liquid state. The model proposed by Eyring and collaborators [1], [2] indicates that the molecules of the liquid in a closed settlement form a continuous phase, where the molecules are kept within the array due to intermolecular forces, so that the clearances between the molecules are very small. In a liquid the mass transport occurs when a molecule

trek to a hollow, this implies that the transported molecule has the energy needed to break the barrier of energies that hold it in place and jumps into a hole, and when they leave they will leave or create a new hollow. Mass transport is accompanied by energy and momentum transport.

When experimental data are lacking, empirical correlations are used to predict the diffusivity coefficient. An empirical correlation is a mathematical model that tends to represent the behavior of a system with a certain accuracy. Most correlations developed try to reproduce the experimental data of diffusion coefficients in an approximation of 5-10% range.

The diffusion coefficient for dilute solution of non electrolytes can be obtained using the empirical correlations of Wilke [3], Othmer [4], Sheibel [5], Sehmel [6] and Sitaram [7]

In liquids:

$$D_{AB} \neq D_{BA} \quad (2)$$

The coefficient of diffusion in liquids varies with the concentration, so to obtain the coefficient in non-diluted and ideal solutions must be:

$$D_{AB} = (D_{AB}^o)^{\tilde{x}_B} (D_{BA}^o)^{\tilde{x}_A} \quad (3)$$

Where D_{AB} is the coefficient of diffusion to the concentration \tilde{x}_A

$$D_{AB}^o = \text{coefficient of diffusion concentration } \tilde{x}_A = 0$$

$$D_{BA}^o = \text{coefficient of diffusion concentration } \tilde{x}_A = 1$$

For non-ideal mixtures:

$$D_{AB} = (D_{AB}^o)^{\tilde{x}_B} (D_{BA}^o)^{\tilde{x}_A} \alpha_{AB} \quad (4)$$

$$\alpha_{AB} = \left(\frac{d \ln \gamma_A}{d \ln \tilde{x}_A} + 1 \right) \quad (5)$$

$$\gamma_{AB} = \text{coefficient of activity.}$$

Obtaining Experimental Diffusion Coefficients in Liquid Mixtures

In the laboratory of Transport Phenomena in the Faculty of chemistry at the University National Autonoma de Mexico the students can obtain, through experimentation, the behavior of systems used in the engineering and the properties needed to evaluate the mass transfer coefficients. Among the necessary variables are the diffusion coefficients.

Diffusion cell

The cell used to obtain the diffusion coefficients was proposed by Valiente [8] and Ortiz [9]. It is an horizontal cell with a horizontal diaphragm that prevents damage to the cell. The cell is made of Pyrex glass and is equipped with a 3 mm thick of sintered glass diaphragm. The cell is covered with a jacket that keeps a constant temperature during the

experiments. See figure.1

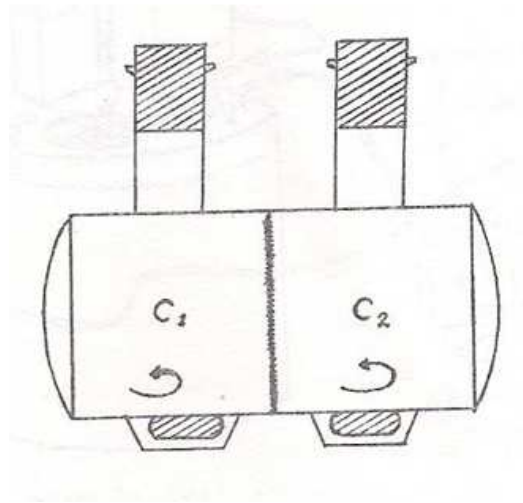


Figure 1

In the laboratory there are two of the mentioned cells the diffusion cells are enclosed in a jacket of glass, through which water circulates at a constant temperature and it is controlled by a thermostat Bath. The magnetic stirrers are covered with teflon. The characteristics of the volume of each compartment and the diaphragm of the cells are given in table 1.

Table 1

Cell	IRIS Pore Diameter	Thickness of the Diaphragm	Diameter	Volume V1 in Ml	V2 Volume in Ml
I	15 microns	3 mm	40 mm	46.5	50.35
II	Fine	3 mm	40 mm	42.5	43.5

At the bottom of the unit, directly under the agitators is placed a motor magnet (magnetic) to perform the movement of agitators, figure (2).

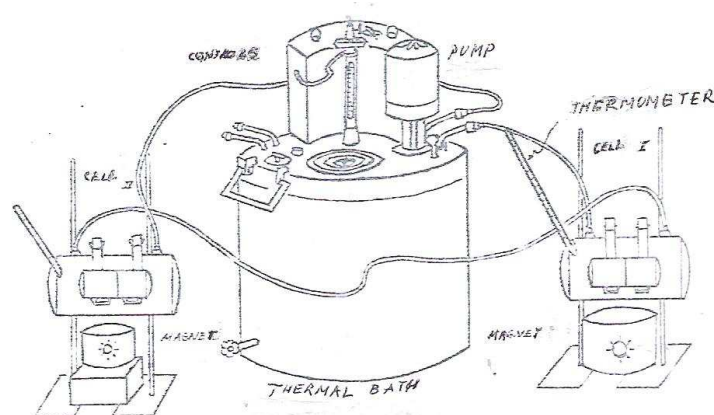


Figure 2: Experimental Arrangement

Experimental Development

So that students can make the required experiments they should follow the steps:

- Two solutions, one concentrated and the other diluted must be prepared.
- Remove the diaphragm gas passing the solution concentrated from one compartment to another by means of a vacuum pump.
- Remove the concentrated solution washing it by means of a diluted solution.
- Fill the two compartment of the cell with the respective solutions.
- Adjust the water bath temperature.
- Connect the agitators
- It takes 48 hours to obtain proper results..
- At the end of the experiment the cell samples are taken for analysis.
- After the analysis of the solutions calculate the coefficient of diffusion through the formula of Barnes (8).

$$D_{AB} = \frac{\ln \frac{\Delta C_i}{\Delta C_f}}{Bt} \quad (6)$$

Where B is a constant of the cell.

$$B = \frac{A}{l} \left(\frac{1}{V_2} + \frac{1}{V_1} \right) \quad (7)$$

A is the transversal area of the diaphragm, l is the width of the diaphragm, t is time, and V1 and V2 are volumes of each compartment of the cell.

Experimental Data

The experimental data obtained by some students are shown in the following table where they are compared with the data predicted by some correlations:

Table II: Diffusion Coefficients at Infinite Dilution for the Systemmethanol in Water at 25° C

Author	$D_{AB}^0 \times 10^5 \text{ Cm}^2/\text{S}$	$D_{AB}^0 \times 10^5 \text{ Cm}^2/\text{S}$
Shemel (experimental)	1.445	2.17
Wilke	1.737	2.73
Scheibel	1.45	2.45
Otmer and Thakar	1.61	2.78
Sitaraman	0.65	0.92
Experimental (students)	1.76	2.5

Table III: Diffusion Coefficients at Infinite Dilution of the System Acetone- Water at 25 ° C

Author	$D_{AB}^0 \times 10^5 \text{ Cm}^2/\text{S}$	$D_{AB}^0 \times 10^5 \text{ Cm}^2/\text{S}$
Anderson, Hall and Babb	1.292	5.16
Wilke	1.28	3.95
Scheibel	1.2	5.43
Otmer	1.19	3.61
Experimental (students)	1.21	4.32

CONCLUSIONS

The proposal cell to obtain coefficients of diffusion in liquid mixtures is simple, cheap and easy to operate. The experimental results obtained by the students are consistent with those reported in the literature. This cell also allows to obtain the coefficients of diffusion of binary mixtures of liquids at all concentrations and at high temperatures with a special adaptation.

REFERENCES

1. Gladstone, Laidler, Eyring - The theory of rate processes, Chap. IX, Mc. Hill, 1941
2. Hirsschfelder, Curtis, Bird-Moleculat Theory of gases and liquids.P.624.Wiley, 1964.
3. Wilke, C.R. and Chang, p. - J.Phys. Chem, p.592, 1955.
4. Scheibel, E.G-Ind. Eng. Che., 46, p.2007, 1954.
5. Othmer, D.F. and Thaker, M.S.-Ind. Eng. Chem., 45, p.58, 1953.
6. Sehmel, g. and Babb, Al-Chem. Revs, 12, p.441, 1956.
7. Sitaraman, r., Ibrahim, S.H. and Kullor, N.R.-J. Chem. & Eng. Data., 9.p.198, 1963.
8. Valiente, B, A-Diffusivity in binary liquid mixtures at elevated temperatures-Thesis, Loughborough University of Technology - 1970.
9. Ortiz, S.A. Determinación experimental de los coeficientes de difusión de mezclas binarias líquida.-Thesis Universidad Nacional Autonoma de Mexico - 1973.
10. Barnes, C-Physics., p.5. 1934.

