

Testing the Cell for Measurement of Diffusivity in Liquids

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For the measurement of diffusion coefficients in liquids a method has been suggested, where the time dependence of the component concentration in a small volume of the solvent, which is in the contact with the solution inside the vertical bundle of capillaries plugged at the lower end, is monitored. This method has been tested using sulfuric acid, which diffusivity is published. It has been found that the calculated values of acid concentration are in good agreement with those obtained experimentally. The calculated values have been obtained by a numerical solution of Fick's second law, the concentration dependence of diffusivity of sulfuric acid in the capillaries being considered.

Keywords:

Sulfuric acid, diffusivity, diffusion cell

Introduction

In the solution of mass transfer through the interface, diffusivity of the component must be known. If only one component is transported, the problem can easily be solved, because all necessary data concerning binary mixtures are mostly at disposal. In the case of multicomponent transport, the data needed must be obtained experimentally, because these are published only scarcely.

A series of methods and procedures has been suggested for the measurement of diffusivity.^{1,2} The diaphragm method, where the diaphragm separates two solutions of the same composition but with different concentration and the time dependence of the concentration of component (or components) at both sides is monitored, belongs among very simple and favourite ones. The disadvantage of this method is the fact that it gives effective diffusivity, and the calibration using a system with known diffusivity is needed. With careful techniques, the capillary method, which is inexpensive, allows to achieve high accuracy. This method consists of the filling the capillary plugged at the lower end with the solution. Subsequently, it is immersed into a large volume of a pure solvent.³⁻⁵ The diffusion coefficients are then calculated from the changes in the concentration of the component inside the capillary. This method is mostly used for measurements with radioactive tracers — in this case, interpreting the data obtained can be difficult.

In order to study diffusion in ternary mixtures, we suggest a method based on a monitoring the concentration of the component in a small volume of the solvent, which is in the contact with the solu-

tion inside the bundle of capillaries plugged at the lower end.

The aim of this paper is the testing the diffusion cell using published data on diffusivity. As a test system the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ system was used as sulfuric acid is one of the components of mixtures separated by diffusion dialysis^{6,7} which is a subject of our research.⁸⁻¹⁰

Theory

Figure 1 schematically shows the capillary containing a component A and the solvent inside. The lower end of the capillary ($z = 0$) is plugged while the upper one ($z = l$) is brought into the contact with the pure solvent at the time $\tau = 0$. Under these conditions, unsteady diffusion in the direction

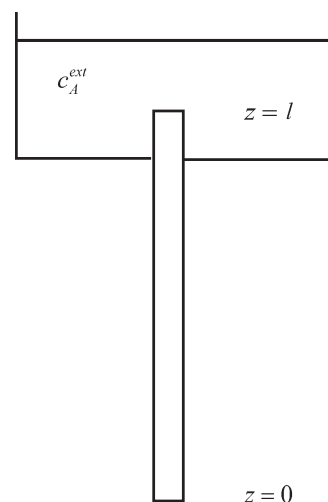


Fig. 1 – Scheme of capillary

of axis z exists. The concentration field inside the capillary is then described by Fick's second law

$$\frac{\partial c_A}{\partial \tau} = \frac{\partial}{\partial z} \left(D_A \frac{\partial c_A}{\partial z} \right) \quad (1)$$

with the initial

$$c_A = c_{A0} \quad \text{for } \tau = 0 \quad z \in \langle 0; l \rangle \quad (2)$$

and two boundary conditions

$$\frac{\partial c_A}{\partial z} = 0 \quad \text{for } \tau > 0 \quad z = 0 \quad (3)$$

$$c_A = c_A^{\text{ext}} \quad \text{for } \tau > 0 \quad z = l \quad (4)$$

where c_A^{ext} is the concentration of the component in the external solution.

Furthermore, the balance equation (5) must be added to Eqs (1) – (4)

$$\frac{d(V^{\text{ext}} c_A^{\text{ext}})}{d\tau} = -A_c D_A \frac{\partial c_A}{\partial z} \quad \text{for } z \rightarrow (l)^- \quad (5)$$

If diffusivity of the component A is known, then the basic differential equation can be solved, so that one can obtain the concentration of this component in the external solution at a given time. The calculated values of the concentration of the component A can be compared with those obtained experimentally — this is the principle of testing the cell for measurement of diffusivity. Generally, diffusivity of the component is dependent upon its concentration. If this concentration dependence is considered, the differential equation (1) must be solved numerically.

Experimental

The diffusion cell is schematically sketched in Fig. 2. Its main part was a vertical bundle of seven capillaries (the lower end of each capillary was plugged) which was attached to a partition wall. The length of each capillary was 0.07 m and its ID was 1.6×10^{-3} m. The capillaries were filled with degassed 2.0 mol dm^{-3} H_2SO_4 and after a precise thermostating (over night) 300 ml distilled water was poured into the upper compartment. The solution was mixed by a stirrer excentrically located, the rotational speed of stirrer was 2 s^{-1} . In the course of the experiment, samples were taken from the upper compartment at a given time and analysed, the acid concentration being determined by a coulometric titration. The decrease in the volume of the solution in the upper compartment was compensated by an addition of the solution of the same amount and

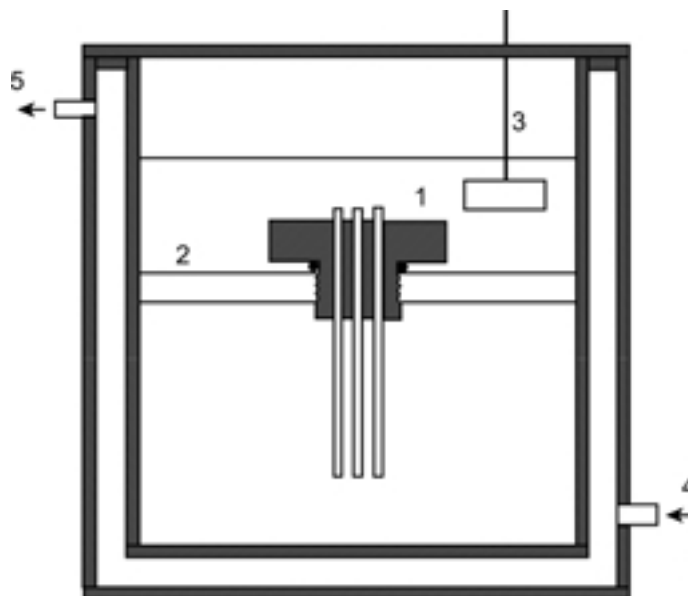


Fig. 2 – Diffusion cell: 1 – bundle of capillaries; 2 – partition; 3 – stirrer; 4 – thermostated water in; 5 – thermostated water out

concentration. During the experiment, which lasted 48 hours, the temperature was kept at a constant value of 20 ± 0.1 °C.

Results and discussion

With respect to the fact that the concentration dependence of diffusivity of sulfuric acid (component A) was considered, the basic differential equation (1) with the initial and boundary conditions (2) – (4) was solved numerically. In order to ensure the stability of the solution, the Crank–Nicolson method was used. In the calculation of the $(j + 1)$ -th concentration profile the following set of linear algebraic equations had to be solved

$$\begin{aligned} & \frac{1}{2h} (-3c_1^{i+1} + 4c_2^{i+1} - c_3^{j+1}) = 0 \quad i=1 \quad (6) \\ & -\frac{k}{4h^2} (D_{i-1}^{j+1} + D_i^{j+1}) c_{i-1}^{j+1} + \\ & + \left[1 + \frac{k}{4h^2} (D_{i-1}^{j+1} + 2D_i^{j+1} + D_{i+1}^{j+1}) \right] c_i^{j+1} - \\ & - \frac{k}{4h^2} (D_i^{j+1} + D_{i+1}^{j+1}) c_{i+1}^{j+1} = \frac{k}{4h^2} (D_{i-1}^j + D_i^j) c_{i-1}^j + \\ & + \left[1 - \frac{k}{4h^2} (D_{i-1}^j + 2D_i^j + D_{i+1}^j) \right] c_i^j + \\ & + \frac{k}{4h^2} (D_i^j + D_{i+1}^j) c_{i+1}^j \end{aligned} \quad (7)$$

$i = 2, 3, \dots, n-1$

$$c_n^{j+1} = c_{n+1}^{j+1} \quad i = n \quad (8)$$

$$\frac{kA_c}{2V^{\text{ext}}h} D_n^{j+1} (c_{n-2}^{j+1} - 4c_{n-1}^{j+1} + 3c_n^{j+1}) + c_{n+1}^{j+1} = c_{n+1}^j \quad (9)$$

$$i = n + 1$$

Equation (6) is an approximation of the boundary condition (3), Eqs (7) are obtained by a discretization of the basic differential equation (1), Eq. (8) is discretized the second boundary condition (4) and Eq. (9) is discretized balance equation (5). In Eq. (8) c_{n+1}^{j+1} is the calculated concentration of component A in the upper compartment of the cell, i.e. in the external solution. The matrix of coefficients of the set (6) – (9) is bandwise — for that reason a modified Thomas algorithm was used. In the calculation of the $(j + 1)$ -th concentration profile, it was necessary to correct iteratively diffusivity of the component, as it is dependent upon the concentration in this profile. The calculation of the concentration fields in the capillaries and that of the concentration of the component in the upper compartment, was realized with data found in literature.^{11,12} Diffusivities in the individual grid points, were determined by interpolating these data.

The comparison of the calculated and experimental values of the acid concentration in the upper part of the cell is presented in Fig. 3 and Table I where relative errors are given, too. From the graphical presentation and the error analysis in Table I it follows that a good agreement between the experiment and model (Eqs (1) – (5)) exists — the maximum error does not exceed 4 %.

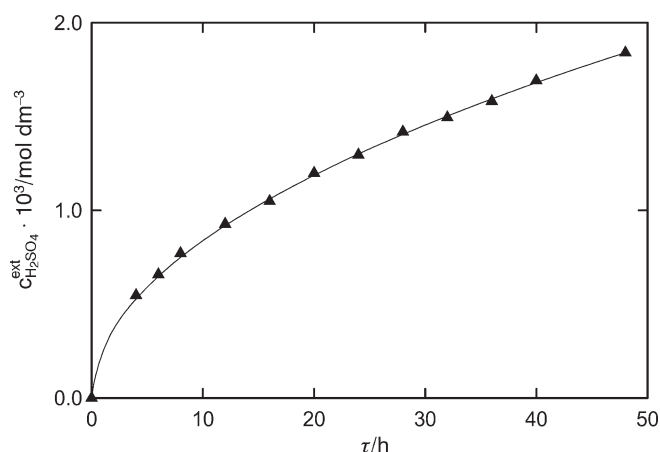


Fig. 3 — Comparison of calculated (—) and experimental (▲) concentration of sulfuric acid in external solution

Here, the data on diffusivity of the testing component (i.e. H_2SO_4) are considered to be very precise. In the case, if large differences between the calculated and experimental values of the acid con-

Table 1 — Comparison of calculated and experimental concentrations of sulfuric acid in external solution

τ/h	$c_{H_2SO_4, \text{calc}}^{\text{ext}} \times 10^3$, mol dm ⁻³	$c_{H_2SO_4, \text{exp}}^{\text{ext}} \times 10^3$, mol dm ⁻³	$\delta/\%$
0	0	0	—
4	0.5274	0.5473	3.77
6	0.6475	0.6585	1.70
8	0.7487	0.7710	2.98
12	0.9182	0.9268	0.94
16	1.061	1.049	-1.13
20	1.187	1.199	1.01
24	1.301	1.296	-0.38
28	1.405	1.419	1.00
32	1.503	1.495	-0.53
36	1.594	1.582	-0.75
40	1.681	1.692	0.65
48	1.841	1.841	0.00

$$\text{Note: } \delta = \frac{c_{\text{exp}} - c_{\text{calc}}}{c_{\text{calc}}} \times 100$$

centration in the upper compartment were found, it would mean that the method suggested fails. But good results were obtained, so that good quality of the method was proved and, consequently, very accurate values of diffusivity of the component in liquids can be expected using the procedure described above. If the time dependence of the component concentration in the upper compartment obtained experimentally is available, diffusivity of this component can be determined using the procedure based on numerical integration of the basic differential equation (1) followed by a suitable optimizing procedure. This computational procedure can be very similar to that used in the calculation of diffusivity of inorganic acids in an anion-exchange membrane.⁹

Conclusion

The cell consisting of a bundle of seven capillaries sealed at the lower end suggested, for the measurement of diffusivity coefficients in liquids was tested using sulphuric acid. At the beginning of the experiment, the solution inside the capillaries was brought into the contact with a small volume of

distilled water and acid concentration in it was monitored as a function of time. The experimental values of concentration were compared with those obtained by numerical integration of Fick's second law. As the data on diffusivity of the testing component are considered to be precise and no significant differences between the calculated and experimental acid concentrations were found, this test proved good quality of the method suggested. Moreover, very accurate experimental values of diffusion coefficients in liquids can be expected using the procedure described.

Nomenclature

- A – denotes component A, i.e. H₂SO₄
A_c – area of capillaries,
c – molar concentration, mol dm⁻³
D – diffusivity, m² s⁻¹
h – integration step in direction of axis *z*, m
k – integration step in direction of time, s
l – capillary length, m
n – number of grid points
V – volume, m³
z – length coordinate, m
 δ – relative error, %
 τ – time, s (h)

Subscripts and superscripts

- A – related to component A, i.e. H₂SO₄
 calc – calculated

- exp – experimental
 ext – external
i – index in direction of axis *z*
j – index in direction of axis *J*
 0 – initial

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