# MEASUREMENT OF DIFFUSION IN BINARY NONELECTROLYTE SOLUTIONS BY THE DIAPHRAGM METHOD WITH *in situ* ANALYSIS. I. APPARATUS AND METHOD OF MEASUREMENT

I. SAMOHÝL

*Department of Physical Chemistry,*
*Institute of Chemical Technology, Prague 6*

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An apparatus and method of measurement of diffusion coefficients in binary solutions of nonelectrolytes is proposed. The upper compartment of a classical diaphragm vessel is supplemented by a differential refractometer cuvette serving as a sensing device for continual measurement of concentration. The concentration in the lower compartment is calculated from the mass balance. The apparatus was tested by measurements in the tetrachloromethane–benzene system at 25 and 40°C and in benzene–cyclohexane at 25, 35 and 40°C, where new data at the latter two temperatures were obtained. The accuracy of measurement is 1–2%.

The versatility of the classical diaphragm method[1–4] is improved by the diaphragm method with "*in situ*" analysis enabling continual measurement of concentration changes in the apparatus[5–9]. Thus, the measurement is made shorter and more accurate, the vessel can be filled under conditions different from those during the experiment, and the main advantages of the classical diaphragm method are preserved.

It is possible to determine continually the concentration in one compartment and to calculate that in the other one from the mass balance, as *e.g.* with electrolytes from conductivity measurements[5–7], or with nonelectrolytes from capacitance measurements[7]. It is also possible to determine directly the concentration difference between both compartments of the diaphragm cell as a function of time, as *e.g.* with electrolytes from electromotive force measurements[8], or with nonelectrolytes from interferometric measurements of the refractivity index[9].

In the present work an apparatus is described for measurement of diffusion coefficients in binary solutions of nonelectrolytes by continual "*in situ*" analysis with the use of a differential refractometer[10]. Although the measurement of the concentration difference in both compartments as function of time leads to a simpler calculation, *cf.* Eq. (*1*), we used analysis in only one compartment for the sake of simpler construction. As a result, the method is more complicated since the concentration in the other compartment has to be calculated from mass balance and the sensing device must be calibrated.

We used in the analysis an optical cuvette of a differential refractometer inserted

into the upper compartment of a horizontal diaphragm cell after Stokes[4]. The high sensitivity of the differential refractometer enables to shorten the measurements so that the logarithmic formula of the diaphragm method[12] in the differential form can be used. In this way the calculations and interpretation of results are simplified. The measurements were performed at a temperature of 25°C at which the cell was filled, and also at higher temperatures (during a short period of measurement the change in composition is small).

The method was verified on the tetrachloromethane–benzene system at 25 and 40°C and on benzene–cyclohexane at 25°C; for both combinations dependable data were obtained by interferometric methods of free diffusion[13,18]. These data were used in calculating the cell constant.

## THEORETICAL

If the concentration difference between both compartments is sufficiently small we can assume a linear dependence of the diffusion coefficient, $D$, on concentration, $c$, and neglect the change in volume by mixing. Then the so-called logarithmic formula in the differential form[12] holds in the pseudostationary state:

$$\mathrm{d}(c'' - c')/\mathrm{d}t = -\beta D(\bar{c})\,(c'' - c')\,, \tag{1}$$

where $c'$ and $c''$ denote concentrations of a component in the lower and upper compartments of the diaphragm cell, respectively, $D(\bar{c})$ diffusion coefficient at a mean concentration $\bar{c}$ (all at a time $t$),

$$\bar{c} = \tfrac{1}{2}(c' + c'')\,, \tag{2}$$

and $\beta$ the cell constant:

$$\beta = \frac{s}{l}\left(\frac{1}{V'} + \frac{1}{V''}\right). \tag{3}$$

Here $s$ denotes effective cross section of the diaphragm, $l$ its effective thickness, $V'$ and $V''$ volumes of the lower and upper compartments of the measuring cell. The mass balance of a component gives

$$(V' + \tfrac{1}{2}V''')\,c' + (V'' + \tfrac{1}{2}V''')\,c'' = M\,, \tag{4}$$

where $V'''$ means free volume in the diaphragm and $M$ total amount (in mol) of the component in the apparatus. Eq. (4) involves the assumption that the nonlinear concentration distribution in the diaphragm (resulting from the dependence of the $D$ value on concentration) can be in the mass balance replaced by a linear one. Use is made of the condition $V' \approx V'' \gg V'''$ usually involved in the construction of the

apparatus. Eq. (4) gives

$$c'' - c' = \frac{V' + V'' + V'''}{V' + \frac{1}{2}V'''} c'' - \frac{M}{V' + \frac{1}{2}V'''} . \tag{5}$$

Introducing Eq. (5) into (1) we obtain

$$\beta D(\bar{c}) = - \frac{\mathrm{d}c''}{\mathrm{d}t} \frac{1}{c'' - c'} \frac{V' + V'' + V'''}{V' + \frac{1}{2}V'''} . \tag{6}$$

This formula served in calculating the $\beta D(\bar{c})$ value. The volumes $V'$, $V''$ and $V'''$ were calibrated, the values of $\mathrm{d}c''/\mathrm{d}t$ and $c''$ determined by continual analysis "*in situ*". Eq. (5) gives us the value of $c'' - c'$ needed in (6). The $M$ value is determined in two ways. If the temperature of measurement is the same as during filling the apparatus (*e.g.* 25°C), then

$$M = M_{25} = (V' + V''') c'_0 + V'' c''_0 , \tag{7}$$

since the diaphragm and the lower compartment were filled with a solution of known concentration $c'_0$ and the upper compartment with a solution of known concentration $c''_0$. At a higher temperature $t$ we used the formula

$$M = M_t = M_{25} - \Delta M , \tag{8}$$

where $\Delta M$ is a small excess of the component removed from the apparatus during heating (due to dilatation).

The cell constant $\beta$, which depends only on the geometry of the fritted glass disc and on the volumes of both compartments, is determined by calibrating the cell with a solution of known diffusion coefficient. The calculated value of $D = D(\bar{c})$ corresponds to the mean concentration obtained from the known $c''$ and $c'' - c'$ values and Eq. (2).

In the case of nonelectrolytes the composition is expressed usually by their molar fraction $x$ rather than by their concentration $c$. These quantities are interrelated as follows:

$$c = \varrho x / \overline{M} , \tag{9}$$

where $\overline{M}$ for a binary mixture is given by the molar masses $M_1$ and $M_2$ of both components 1 and 2:

$$\overline{M} = M_1(1 - x) + M_2 x . \tag{10}$$

(We shall express the composition as the molar fraction of component 2.) Further the dependence of density on composition for the given system and temperature, $\varrho = \varrho(x)$, must be known.

The differential refractometer after Kratochvíl and Sedláček[11], used in our work, is shown schematically in Fig. 1. Its cuvette is dipped into the upper compartment of the diffusion cell containing a solution of refractivity index $n''$ changing during the experiment. The plane defined by the vectors $\boldsymbol{k}$ and $\boldsymbol{j}$ ($-\boldsymbol{k}$ has the same direction as the rays entering the cuvette) divides the cuvette into the measuring and the comparative parts. A standard solution of refractivity index $n_s$ is contained in the closed space of the measuring part. The rays coming from the latter have the direction $\boldsymbol{a}$, those coming from the comparative part have the direction $\boldsymbol{k}$ since on both sides of the refractive plane of the cuvette the solution has the same refractivity index $n''$. The signal of the sensing device, $y$ (the distance of the images of the slot originating from the measuring and comparative parts of the cuvette) is then proportional to the difference of the refractivity indices[11], $n'' - n_s$:

$$y = 2L(n'' - n_s) \operatorname{tg} \alpha \,, \tag{11}$$

where $L$ denotes focal distance of the lens and $\alpha$ refractive angle of the cuvette (the refractivity index of air is set equal to one).

Since in the narrow range of composition between the standard solution (molar fraction of component 2 is $x_s$) and the solution in the upper compartment (molar fraction $x''$, refractivity index $n''$) we can assume $\mathrm{d}x''/\mathrm{d}n'' = \text{const.}$, Eq. (*11*) gives

$$x'' = x_s + Gy \,, \tag{12}$$

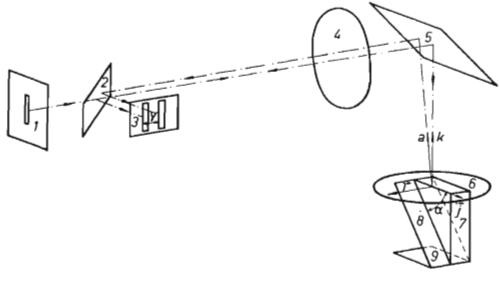


FIG. 1

Schematic View of the Optical Equipment

*1* Slot illuminated by sodium lamp, *2* semitransparent mirror, *3* view field of ocular micrometer with images of slot, *4* lens, *5* mirror, *6* upper glass of cuvette, *7* compartment with standard solution, *8* refracting plane of the cuvette, *9* mirror of the cuvette.

where

$$G = \frac{\mathrm{d}x''}{\mathrm{d}y} = \frac{\mathrm{d}x''}{\mathrm{d}n''} \frac{1}{2L \operatorname{tg} \alpha} . \qquad (13)$$

During a sufficiently short time of measurement $\mathrm{d}c''/\mathrm{d}x''$ is practically constant (*cf.* Eq. (*9*)), so that

$$\frac{\mathrm{d}c''}{\mathrm{d}t} = \frac{\mathrm{d}c''}{\mathrm{d}x''} G \frac{\mathrm{d}y}{\mathrm{d}t} . \qquad (14)$$

Here $\mathrm{d}y/\mathrm{d}t$ is the slope of the approximately linear dependence of $y$ on $t$ (in a short time interval), which is replaced by a straight regression line calculated by the least squares method. This yields $y$ values corresponding to the half-time of measurement and used in calculating the $c''$ value from Eqs (*9*) and (*12*); the $\mathrm{d}y/\mathrm{d}t$ value is used in calculating $\mathrm{d}c''/\mathrm{d}t$ from Eq. (*14*). The $\mathrm{d}c''/\mathrm{d}x''$ needed here is calculated from the derived Eq. (*9*) for the half-time of measurement. Thus the $c''$ and $\mathrm{d}c''/\mathrm{d}t$ values as well as the calculation according to Eq. (*6*) refer to the half-time of measurement.

The $G$ value is determined after every measurement by calibration as follows (its calculation from Eq. (*13*) is not accurate enough): The diaphragm is blocked by a mercury layer so that the solution in the upper compartment has a constant, although unknown concentration. The calibration is performed by measuring the distance $y_0$ at a composition of the standard solution in the cuvette $x_s = x_o''$ (the solution used in filling the upper compartment of the vessel; it is also used as standard during the measurement of diffusion) and by measuring the distance $y_s$ at a composition of the standard solution $x_s = x_{os}$ not too different from $x_o''$. The results are substituted in Eq. (*12*) and the constant unknown concentration of the solution in the upper compartment is eliminated to obtain

$$G = (x_o'' - x_{os})/(y_s - y_0) . \qquad (15)$$

The determination of the $G$ value at a higher temperature of measurement is analogous.

## EXPERIMENTAL

### Apparatus

Two variants of the apparatus were constructed differing only in details[10]. The typical variant used in most of the experiments will be described here.

The diffusion apparatus proper is shown schematically in Fig. 2. The diaphragm cell *8* after Stokes[4] (volume of each compartment about 27 ml, diameter of diaphragm 3 cm and thickness 0·155 cm, pore size about 5 μm) is placed in a thermostated vessel. In the upper compartment on the planely ground, strengthened end *10* of the cell is placed an optical cuvette *9* (shown in Fig. 1). Cuvette *9* is fixed by ring *17* to fitting *12* cemented on to the widened part *11*, which is cemented to the diffusion cell. To this purpose the high-temperature epoxy resin Araldit (Ciba,

Basel) was used. Both compartments are provided with mercury seals. Covering planparallel glasses *16* and *18* serve to diminish the temperature gradient; the lower one is provided with a diaphragm to control the passage of light. The stirrer after Stokes[4] has 130 r.p.m.; its ferrit magnets *7* are provided with a larger ball bearing *21* which together with transmission and motor is mounted on a vibration-free console *22*.

The manufacture of the optical cuvette *6*—*9* (Fig. 1) cemented by a pyroceramic cement was described elsewhere[15]. Its surface mirror *9* was covered with an evaporated film of aluminium in vacuum. The cuvette is provided with two ground glass joints (as inlets for solutions in the standard and upper compartments) protected by "Sial" glass tube *15* (Fig. 2) fastened with epoxy resin on upper glass *6* (Fig. 1) of the cuvette.

Other parts of the differential refractometer are mounted on an optical bench. Surface mirror *5* (Fig. 1) and simple lens *4* of focal distance 1 m are placed in a tube, which can be reproducibly

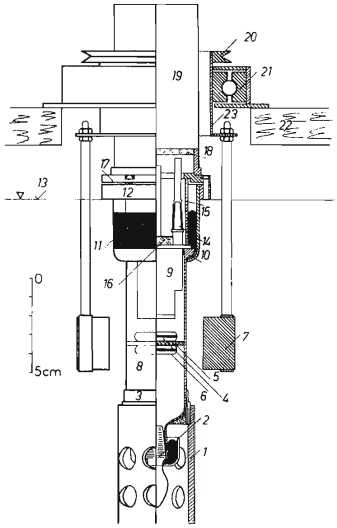


FIG. 2

Diffusion Apparatus

*1* Stand, *2* stopper of diffusion cell, *3* ring cemented onto the diffusion cell, *4* upper stirrer, *5* diaphragm, *6* lower stirrer, *7* ferrit magnet, *8* diffusion cell, *9* optical cuvette, *10* ground joint, *11* widened part of cell, *12* aluminium fitting, *13* water level in thermostat, *14* ground joint of cuvette with cap, *15* Sial glass tube, *16* cover glass with mask and holder, *17* contact ring, *18* cover glass in socket, *19* paper tube, *20* transmission, *21* bearing, *22* console, *23* rotating tube supporting the magnets of the stirrer.

inserted into the space above the diffusion cell. Slot 1, about 0·2 mm in width, is illuminated with a sodium lamp and its images are deflected by semipermeable mirror 2 into the field of vision of a micrometer ocular (Nachet, Paris) with 0·01 mm division and 10 mm range serving to measure the mutual distance $y$ of the images (usually was $y$ less than 4 mm).

Method of Measurement

Pure benzene, cyclohexane and tetrachloromethane for IR spectrography (Merck, Darmstadt, and UCB, Bruxelles), dried by molecular sieves and deaerated by boiling for half an hour, were used for preparation of the more dense lower solution of concentration $c'_0(x'_0)$, upper solution ($c''_0$ or $x''_0$) and standard ($x_{0s}$). The difference in concentration between the upper and lower solutions was 8—11 mol% cyclohexane in benzene or 15—30 mol% benzene in tetrachloromethane. For the standard, $x_{0s}$ was by 2—4% smaller than $x''_0$.

The lower compartment and diaphragm of the diffusion cell were filled in vacuum[10] by the solution of composition $x'_0$. At a lower temperature of measurement (25°C) the upper compartment was filled with a solution of composition $x''_0$ whose excess was expelled by inserting the optical cuvette containing the same solution as standard ($x''_0 = x_s$).

After attainment of a pseudostationary state (about 1 hour) the mutual distance $y$ of images of the slot was measured as a function of time (with an accuracy to 0·001 mm) for 2 hours at 5 min intervals (measured to 0·1 s). Afterwards the apparatus was heated to 35 or 40°C and the excess of liquid formed by dilatation was removed quantitatively with a special pipette filled with mercury[10], weighed and analyzed refractometrically. After attainment of a pseudostationary state the dependence of $y$ on time was measured analogously as before.

After cooling to a lower temperature the diaphragm was sealed by a mercury layer (about 4 mm in thickness), the concentration was allowed to reach a steady value and the sensing device

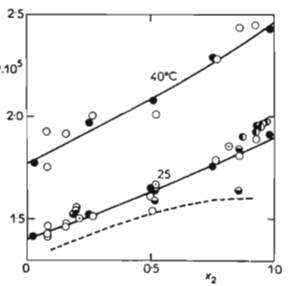


FIG. 3

Diffusion Coefficients $D$ ($cm^2\ s^{-1}$) for Tetrachloromethane (1)–Benzene (2) System

The cell constant was calculated from 5 measurements for $x_2 = 0·08$ and 0·15 at 25°C. ○ This work; ● ref.[13]; full lines are smoothed curves corresponding to ref.[13] (analytical expression *cf.*[16]); ◒ ref.[20]; ◐ ref.[21]; broken line after ref.[22]; ⊙ ref. [25].

was calibrated with two standard solutions ($x_o''$ and $x_{0s}$; the $y_0$ and $y_s$ values were measured repeatedly). The procedure was analogous at a higher temperature. The volumes of both compartments and of the diaphragm pores were determined by filling with water and weighing.

The dependences of density on composition for the tetrachloromethane–benzene system were obtained from smoothed curves calculated from the data of references[14,17], and for benzene–cyclohexane from references[18,19]. (The corresponding analytical expressions will be given in the next communication[16].)

From the $M_{25}$ and $\Delta M$ values obtained from Eq. (7) and from the amount and composition of the liquid expelled by heating we calculated after Eqs (5) and (6) the $\beta D$ value corresponding to a mean concentration $\bar{c}$. The dependence of $\beta D$ or $D$ on $\bar{c}$ was expressed with the aid of the dependence on the molar fraction (of component 2) related to concentration $\bar{c}$ by Eq. (9).

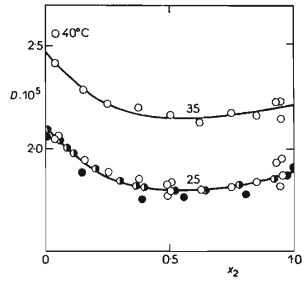


FIG. 4

Diffusion Coefficients $D$ ($cm^2\ s^{-1}$) for Benzene (1)–Cyclohexane(2) System

○This work (cell constant see Fig. 3), upper line represents the smoothed curve from data in Table I; ◑ ref.[18], lower line smoothed curve from data[18] (*cf.*[10,16] for analytical expression); ● ref.[23,24].

To judge the functioning of the apparatus, the $D$ values were calculated with the aid of the cell constants $\beta$ determined by calibrating our apparatus with 8–15 mol% benzene in tetrachloromethane at 25°C. For this system, $D$ values were obtained from smoothed curves calculated from data in the literature[13] (*cf.*[10,16] for the analytical expression).

## RESULTS AND DISCUSSION

The $D$ values determined by the described method are shown graphically in Figs 3 and 4 as functions of the molar fraction of component 2. The results of other au-

TABLE I

Diffusion Coefficients $D$ in Benzene (1)–Cyclohexane (2) System at 35 and 40°C

| $x_2$ | $D \cdot 10^5$, cm$^2$/s[a] | $x_2$ | $D \cdot 10^5$, cm$^2$/s[a] |
|---|---|---|---|
| 35°C | | 35°C | |
| 0·0361 | 2·430 | 0·8464 | 2·162 |
| 0·1494 | 2·286 | 0·9271 | 2·151 |
| 0·2478 | 2·202 | 0·9462 | 2·207 |
| 0·3730 | 2·161 | 0·9469 | 2·135 |
| 0·5009 | 2·168 | 40°C | |
| 0·6184 | 2·130 | 0·0388 | 2·556 |
| 0·7446 | 2·175 | | |

[a] Values calculated from Eq. (*16*).

thors[13,18,20–25] at the same temperatures and the smoothed curves from data in the literature[13,18] (*cf.*[10,16] for analytical expressions) are shown for comparison.

New data for the benzene–cyclohexane system at 35 and 40°C were calculated not only by the described method with results shown in Fig. 4 but also in the following, more exact manner. Let us assume that $\beta D$ is value measured at 35°C or 40°C for the mentioned system. Then the diffusion coefficient at this temperature is calculated as

$$D = [(\beta D)/(\beta D)_{25}]\, D_{25}\,, \qquad (16)$$

where $(\beta D)_{25}$ is the value measured at 25°C (with the same experiment) and $D_{25}$ the diffusion coefficient at 25°C obtained by correlation[10,16] from reference[18] (for the composition corresponding to $(\beta D)_{25}$). The data[18] can be considered as reliable; they are in good agreement with our results (Fig. 4) and their accuracy (0·2%) is of the same order as with the data for diffusion of potassium chloride in water, used often for calibration.

The new data for diffusion in the benzene–cyclohexane mixtures at 35 and 40°C obtained in the described way are summarized in Table I in dependence on the molar fraction of cyclohexane. This dependence at 35°C was correlated with a function[10,16] represented graphically in Fig. 4, from which it is seen that both modes of calculating the $D$ values give practically the same results.

It follows from Figs 3 and 4 that the results of our method of measurement are in good agreement with published data[13,18]. The mean deviations of measured values from the correlated curves in Figs 3 and 4 are about 1% for benzene–cyclohexane and 2% for tetrachloromethane–benzene mixtures. The $D$ values for the former system based on those for the latter[13] are evidence for the reliability of the

published data[13,18] and for a negligible systematic error of our apparatus. These conclusions are supported by a detailed analysis[10] of systematic and random errors.

In spite of the relative simplicity of our apparatus and short-termed measurement, the described method is complicated owing to the need of accurate mass balance and calibration of the differential refractometer. These difficulties would be overcome with an apparatus enabling to determine continually the concentration difference between both compartments. Its construction would be, however, substantially more complicated.

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