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PART 4

DIFFUSION STUDIES

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#### 4.1 INTRODUCTION

As mentioned in the general introductory section, the process of diffusion of substances is important in order for elucidation of the changes in the structural arrangements of the solvent upon dissolution of solutes. The process of diffusion in a mixture, as distinct from convection, implies a relative motion of the components, that is, a difference in the mean velocities of each species of molecule. Diffusion is most frequently associated with a non-uniformity of composition, but it can also arise from non-uniformity of other properties, in particular, of temperature and pressure.

The driving force for diffusion is the difference in the chemical potential of the diffusing substance which has, in general, the same sign as the difference in its concentrations, in the same phase, and at uniform and constant temperature all over the system. Such diffusion is termed isothermal diffusion in order to differentiate this from thermal diffusion which is caused by a difference in temperature.

The available methods for the diffusion study may conveniently be grouped into (i) steady-state methods, based on the Fick's first law equation, namely,

$$J = - D \frac{\delta C}{\delta x} \quad (4.1.1)$$

where  $J$  is the flux of the solute,  $\frac{\delta C}{\delta x}$  the concentration gradient and  $D$ , the diffusion coefficient, and (ii) those based on the equation of continuity in matter - transport (i.e., Fick's second law).

The fundamental idea of the method, used in the present determination, and developed by Stokes<sup>1</sup>, is to eliminate the disturbing effects of vibrations and of small temperature fluctuations by confining the diffusion process to the capillary pores of a sintered glass diaphragm. The theoretical background of the process, as well as the various quantitative formulations based thereon, have been well-documented in literature<sup>2</sup>, and need not be repeated here. The usual procedure to calculate the diffusion coefficient D has been to utilise the "simple logarithmic formula", given by,

$$D = \frac{1}{\beta t} \ln \frac{C_1 - C_2}{C_3 - C_4} \quad (4.1.2)$$

where, D is the (double-average) diaphragm-cell integral diffusion coefficient,  $\beta$  is the cell constant, t is the time of diffusion, and  $(C_1 - C_2)$  and  $(C_3 - C_4)$  are the initial and final (i.e., after time t) concentration differences between the cell compartments.

Well-compiled reviews for diffusion processes have already been given, among others, by Jost (1952, 1957)<sup>3,4</sup>, Robinson and Stokes (1959)<sup>2</sup>, Tyrrell (1961)<sup>5</sup>, Frank-Kamenetskii (1969)<sup>6</sup> and Erdey-Grúz (1974)<sup>7</sup>. Each of these gives an elaborate account of the methodology of such diaphragm diffusion cell, and the results obtained by using the technique.

## 4.2 EXPERIMENTAL DETAILS

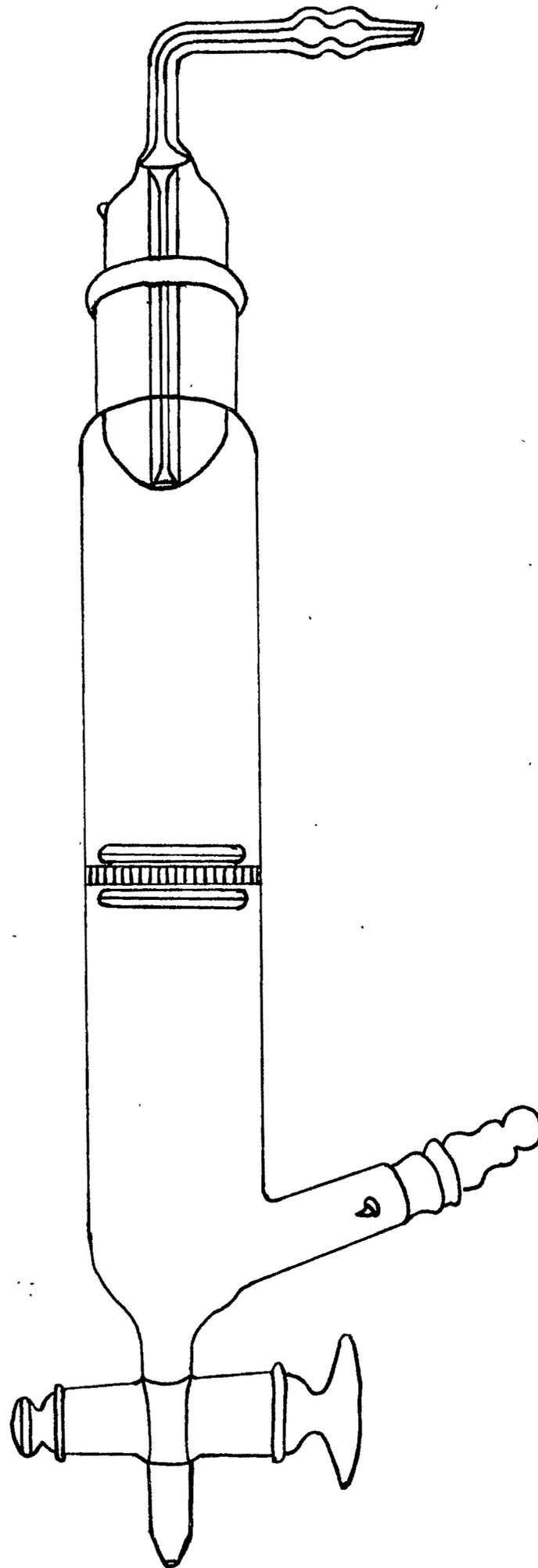
### (A) APPARATUS

#### (i) DIFFUSION CELL

Diaphragm cells with arrangements for magnetic stirring of the type close to that designed by Stokes<sup>1</sup>, (vide. figure 4.2.1) were used. The cell is made from a glass tubing of internal diameter 2.3 cm. The vertical cell is divided into two compartments by a pyrex G-4 sintered glass disc. The compartments above and below this diaphragm have volumes of 45.8 and 48.0 ml, respectively. The upper compartment is provided with a standard joint-glass stopper. Rear of the lower compartment has a burette fitting. The lower compartment is also provided with a side-tube having a standard joint-stopper at the end. Sealed glass tubes, containing encased iron wires, having lengths slightly shorter than the diameter of the diaphragm, are used as stirrers. The weights of the stirrers are so adjusted that the upper one sinks while the lower one floats in the respective solutions.

#### (ii) AIR THERMOSTAT

The thermostat is an air-tight closed wooden box (90x60x60 cm) with arrangements for keeping the inside temperature constant within  $\pm 0.05^{\circ}\text{C}$  by means of a relay circuit, having as components, an electric bulb (100 W), an electric fan (REMI) situated inside the thermostat, and an electrical contact thermometer inserted through a hole into the thermostat. The box is insulated from the surroundings with polystyrene foam on the inside of the front wall which can be opened whenever necessary. The relay circuit can be operated from outside. Once the thermostat starts working,



DIFFUSION CELL

Fig.4.2.1

automatic regulation through make-and-break of the relay circuit occurs maintaining the temperature constant over a long period of time, as indicated by the precision thermometer inserted into the thermostat.

A pair of bar magnets, located face to face across the diaphragm of the diffusion cell, on a circular ring of a metallic frame work (fixed inside the thermostat), is driven by a synchronous motor ( operated from a variable frequency generator ) which rotates the entire frame work. Such rotating magnets keep, in turn, the glass-sealed stirrers of the diffusion compartments in motion, the diffusion cell having been mounted with clamps vertically at the centre of the circular ring mentioned above. While thus mounting the diffusion cell in the appropriate position inside the thermostat, due care is taken so as to maintain the diaphragm within  $1^\circ$  of the horizontal position.

(B) METHOD OF FILLING THE DIAPHRAGM CELL

Out of the three types of cases, namely solvent-filled, gradient-filled and solution-filled, the solution-filled methodology seems to be the most convenient as it eliminates a long pre-diffusion period for establishing the steady state in the diaphragm<sup>8</sup>. The upper compartment was filled with the solution and pumped through the diaphragm pores into the lower compartment with the aid of a vacuum pump attached to the side tube of the lower compartment. This operation was repeated several times in order to ensure complete removal of the entrapped air bubbles from inside the diaphragm pores. The solution from the diffusion cell was then rejected, and the cell was refilled with the solution afresh, again by pumping through the diaphragm pores.

(C) CHEMICALS

The chemicals used have been the organic electrolytes such as the alkyl carboxylates, namely, sodium formate, sodium acetate, sodium propionate, sodium-n-butyrate, sodium-n-pentanoate and sodium trichloroacetate prepared by the method described earlier in connection with viscosity experiments, while the non-electrolytes studied (eg. phenols and benzyl alcohol) were used after purification of the commercially best available sample, by distillation or recrystallisation from suitable solvents, as the case may be.

(D) CALIBRATION OF THE DIAPHRAGM CELL

For the determination of the cell constant, as well as for the confidence that the diaphragm diffusion technique gives reproducible data for the diffusion coefficients of the present solutes, calibration experiments were conducted where solutions of KCl (concentration 0.05 M in each case) were allowed to diffuse into pure water at 30°C until four successive such experimental runs afforded identical results within the limits of experimental error. After estimating the chloride ion concentration in each compartment, conductometrically (against standard  $\text{AgNO}_3$  solution), the cell constant was evaluated with the help of equation 4.1.2 and using the literature<sup>1</sup> value of D of KCl at the appropriate concentration and temperature. The cell constant thus obtained was utilised in determining the diffusion coefficients for another two KCl solutions, and the diffusion coefficients thus obtained were compared with the literature value<sup>1</sup> of D. A satisfactory concordance between the experimental and the literature D is taken to indicate that the methodology adopted for determining the diffusion coefficient, using the Stokes type of diaphragm

diffusion cell, was adequately appropriate for giving accurate results.

(E) EXPERIMENTAL PROCEDURE

(i) After filling the diaphragm and both the compartments with fresh air-freed solution (i.e, the solution-filled methodology followed), the diffusion cell was placed in the air thermostat for thermal equilibration and allowed to attain the steady-state in the diaphragm for about one to two hours (although the solution-filled diaphragm does not necessarily require a pre-diffusion period, which may be of importance in solvent-filled or gradient-filled methodology). Next, the solution of the bottom compartment was replaced by pure distilled water after rinsing the compartment five to six times with the water while the cell was still kept inside the thermostat, and all the operations were completed within a few minutes in order that the temperature fluctuations could not interfere much with the diffusion process. The experiment was timed from this instant. The diffusion was allowed to continue for two days.

(ii) After the requisite diffusion periods, solutions from both the compartments were withdrawn and their concentrations measured. For alkyl carboxylates, a given volume of the solution was titrated conductometrically with standard solutions of HCl. Two solutions of HCl were used for titration, one for titrating the upper compartment solution and the other for lower compartment one. The concentrations of the solution were calculated from the corresponding acid equivalent required for neutralisation at the inflexion points.

(iii) For non-electrolytes, spectrophotometric (in the UV region)

method was adopted for the determination of concentrations using a Carl Zeiss spectrophotometer (Germany). For the purpose, a calibration curve, showing the variation of absorbance (measured at  $\lambda_{\max}$  of the particular system) with concentrations, was plotted (Beer's law curve), and a straight-line passing through the origin drawn. The concentration of the unknown (experimental) solution was then obtained by measuring the corresponding absorbance (using the same spectrophotometric cell), followed by interpolation from the calibration curve.

(iv) The initial concentration ( $C_1$ ) of the solution in the upper compartment may not be equal to that of the original solution because during the preliminary period of diffusion (1-2 hrs.), that has been allowed in the present case, the concentration may change while the diaphragm is being brought into the steady state.  $C_1$  can, however, be obtained in an indirect manner. Thus, starting with a zero initial concentration ( $C_2$ ) in the lower compartment (i.e., with pure water), and measuring the "after-diffusion" concentrations of the solutions in both the compartments, along with a knowledge of the volumes of the compartments themselves, and that of the diaphragm pores,  $C_1$  can be calculated by a method as given by Stokes<sup>2</sup>.

(v) The stagnant layer of the solute that may accumulate on the surface of the diaphragm changing the rate of diffusion (and thereby leading to erroneous measurements of diffusion coefficients) was continuously wiped out by the process of magnetic stirring so that a uniform concentration can always be maintained throughout the whole bulk of the solution in each compartment.

### 4.3 RESULTS

#### (i) CALIBRATION RESULTS

The calibration experiments were run at 30°C while the literature D for KCl was the value at 25°C. Hence, this value of D was converted to that at 30°C by using the Stokes-Einstein equation which reads,

$$D = \frac{k T}{6 \pi \eta r} \quad (4.3.1)$$

where, D = diffusion coefficient,

k = Boltzmann constant,

T = absolute temperature,

$\eta$  = coefficient of viscosity of solution (at T)

r = radius of the diffusing entity

Comparing the diffusion coefficients  $D_1$  and  $D_2$  at two temperatures  $T_1$  and  $T_2$ , one obtains,

$$\frac{D_1}{D_2} = \frac{\eta_2}{\eta_1} \times \frac{T_1}{T_2} \quad (4.3.2)$$

Thus, the values of the diffusion coefficients at 30°C can be calculated from the literature<sup>1</sup> D (at 25°C), and the corresponding viscosity coefficients of the same KCl solutions at temperatures  $T_1$  and  $T_2$ .

Table 4.3.1 records the values of the cell constants for four runs as well as the mean cell constant.

#### (ii) RESULTS ON DIFFUSION COEFFICIENTS

(a) The cell constant obtained in this way is utilised to calculate the diffusion coefficients of KCl solutions having the same concentrations as that used in the calibration experiments. Table 4.3.2

reports such D values.

(b) Using the same cell constant the diffusion coefficients of the various solutes (electrolytes and non-electrolytes) in aqueous solutions have been determined and the data are recorded in tables 4.3.3 and 4.3.4.

The conductometric titration curves for the analysis of compartment solutions after diffusion<sup>of</sup> sodium trichloroacetate are shown in figures 4.3.1 and 4.3.2, as representative plots for the present electrolytes.

For the non-electrolytes studied, the validity of the Beer's law is shown in figure 4.3.3 (calibration curve) by taking phenol as the representative member.

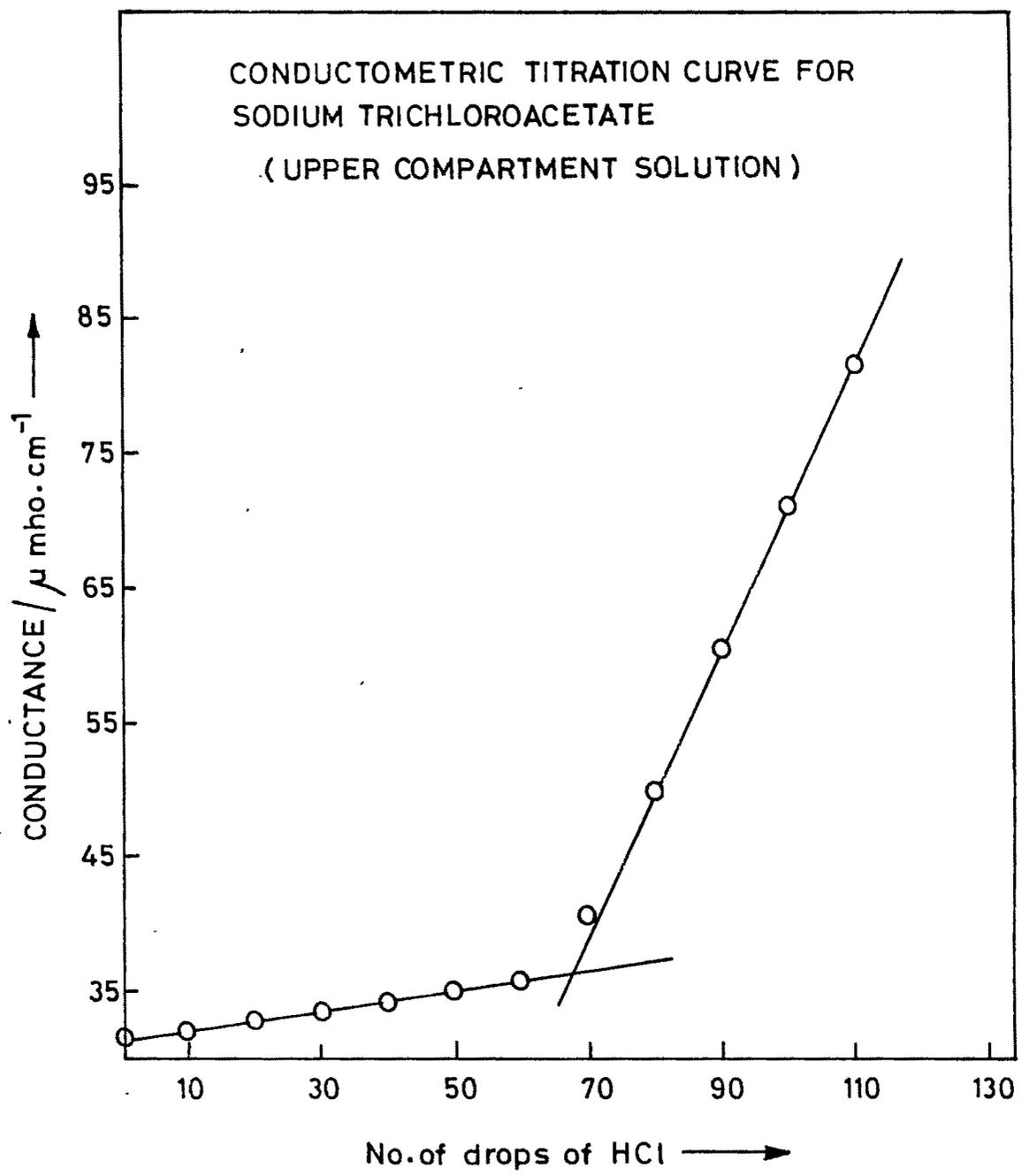


Fig.4-3.1

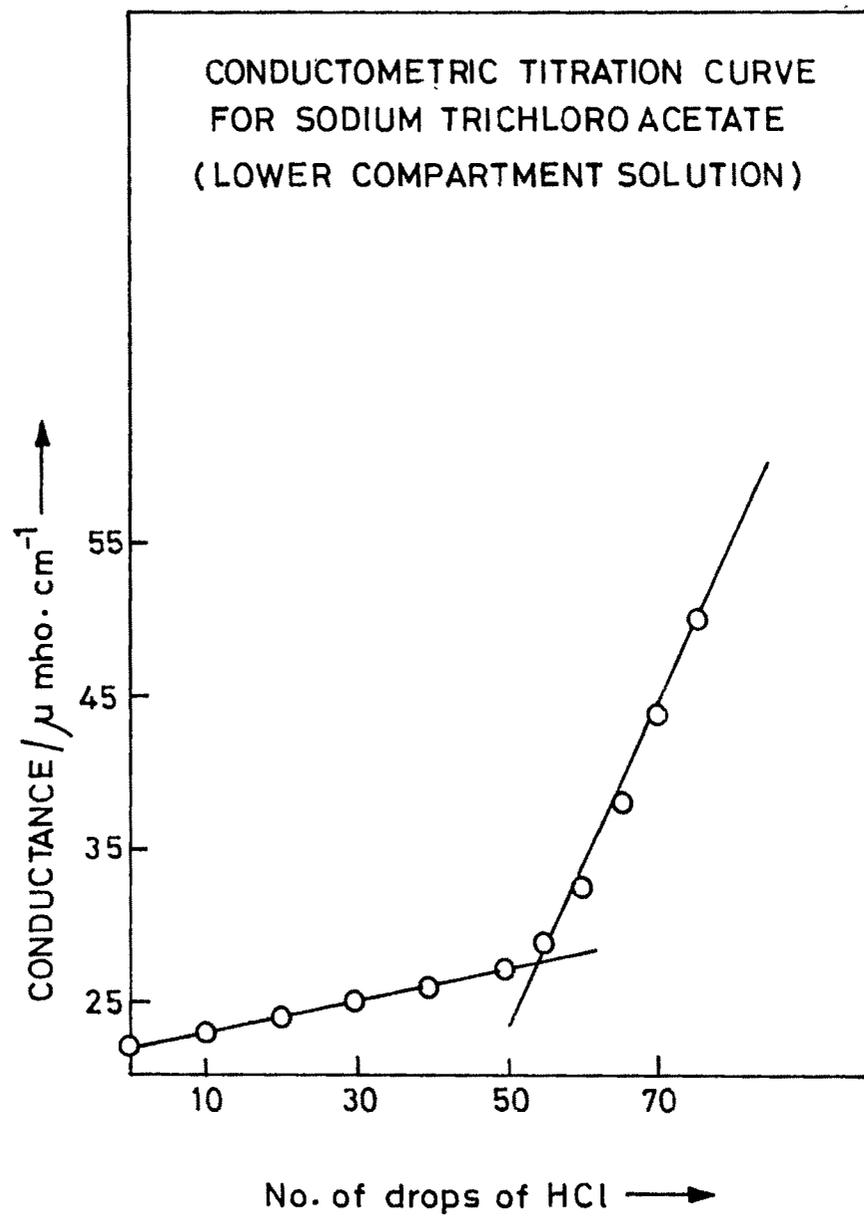


Fig-4.3.2

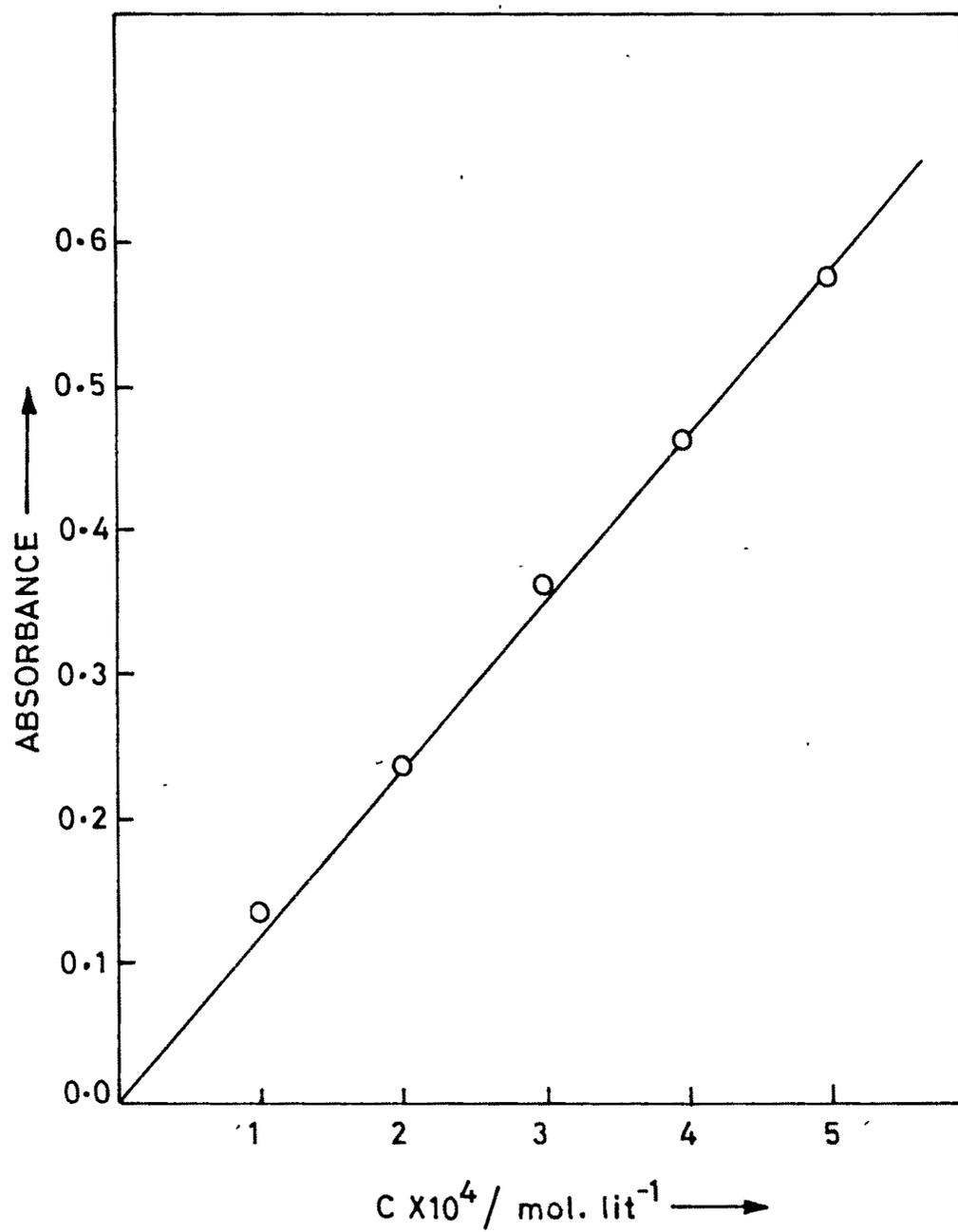


Fig. 4.3.3

TABLE 4.3.1

DATA AT 30°C

| Set | Molar concentration<br>C/M | $\beta / \text{cm}^{-2}$ | Mean $\beta / \text{cm}^{-2}$ |
|-----|----------------------------|--------------------------|-------------------------------|
| 1   | 0.05                       | 0.085                    |                               |
| 2   | 0.05                       | 0.082                    |                               |
| 3   | 0.05                       | 0.084                    | 0.083                         |
| 4   | 0.05                       | 0.081                    |                               |

TABLE 4.3.2

DATA AT 30°C

| Set | $\beta / \text{cm}^{-2}$ | Molar concentration<br>C/M | $10^5 D_{\text{obs}} / \text{cm}^2 \text{ s}^{-1}$ | $10^5 D \text{ (Stokes)} / \text{cm}^2 \text{ s}^{-1}$ |
|-----|--------------------------|----------------------------|--|--|
| 1   | 0.083                    | 0.05                       | 2.205  | 2.217  |
| 2   | 0.083                    | 0.05                       | 2.227  | 2.217  |

TABLE 4.3.3

DATA AT 30°C

| Solution                | Molar<br>concentration<br>G/M | $10^5 D_{\text{obs}} /$<br>$\text{cm}^2 \text{s}^{-1}$ |
|-------------------------|-------------------------------|--|
| Sodium formate          | 0.05                          | 1.74   |
| Sodium acetate          | 0.05                          | 1.32   |
| Sodium propionate       | 0.05                          | 0.64   |
| Sodium-n-butyrate       | 0.05                          | 0.56   |
| Sodium-n-pentanoate     | 0.05                          | 0.41   |
| Sodium trichloroacetate | 0.05                          | 1.18   |

TABLE 4.3.4DATA AT 30°C

| Solution       | Molar<br>Concentration<br>G/M | $10^5 D_{\text{obs}} /$<br>$\text{cm}^2 \text{ s}^{-1}$ | $10^5 D^* /$<br>$\text{cm}^2 \text{ s}^{-1}$ |
|----------------|-------------------------------|---|--|
| Phenol         | $5.0 \times 10^{-4}$          | 0.71  | 0.87   |
| Resorcinol     | $5.0 \times 10^{-4}$          | 0.51  | 0.77   |
| p-cresol       | $2.5 \times 10^{-4}$          | 0.95  | 0.83   |
| Benzyl alcohol | $5.0 \times 10^{-3}$          | 1.15  | 1.06   |

\* Diffusion data taken for the purpose of comparison from the reference 9, obtained for 0.1 M aqueous solutions by using a flow-cell technique to study thermal diffusion.

#### 4.4 ESTIMATION OF ERRORS

The common experience on diffusion experiments shows that it is very difficult to have reproducible data with insignificant errors. The trouble seems to arise primarily from temperature fluctuations while manipulating the operational technique with the diaphragm diffusion cell. Mechanical vibrations also disturb the measurements. Before presenting the diffusion data, it is thus necessary to have an idea about the error associated with the various measurements. Wherever possible, a comparison with the literature data is also desirable for ascertaining the relative error.

In the calibration experiments for the determination of the cell constant ( $\beta$ ), the individual error relative to a mean value of four reproducible observations was found to be less than  $\pm 2.5\%$ .

The diffusion coefficients of KCl solutions (0.05 M) at 30°C determined by the present method was compared with Stokes' determination<sup>1</sup> after converting the latter values (at 25°C) to those at 30°C by using equation 4.3.2. The maximum relative error for the D values of KCl was found to be  $\pm 0.5$  percent, showing that the methodology followed furnished diffusion coefficient values that are comparable with the Stokes' determination.

The determination of relative error for the D values of the present solutes was not convenient owing to either the non-availability of the literature data (eg., for the alkyl carboxylates), or the fact that the literature<sup>9</sup> values, if at all available, were at concentrations widely different from those used in the present case (eg., phenols and benzyl alcohol). However, the

accuracy of the diffusion coefficient values for the present solutes in aqueous solutions at 30°C have been ascertained by ensuring reproducibilities of the data within  $\pm 0.5$  percent.

Although the porous diaphragm cell technique can not claim to be more precise a method than the available absolute ones for studying the diffusion process, the advantage of greater operational simplicity in the former with reasonable precision as well as its adaptability, leads to its wide applicability.

#### 4.5 DISCUSSION

An attempt has been made to interpret the diffusion coefficient data (vide. tables 4.3.3 and 4.3.4) of the present solutes in terms of the classical hydrodynamic theory for diffusion, as developed by Sutherland<sup>10</sup> and Einstein<sup>11</sup>, and further suggested by Stokes, by considering the frictional resistance acting on a spherical body moving in a continuum. Such frictional resistance ( $f_s$ ) is function of the radius ( $r$ ) of the sphere (i.e., the diffusing entity), viscosity of the solution ( $\eta$ ) and the extent of sliding friction ( $\beta$ ) of the Stokes law equation :

$$f_s = 6\pi\eta r \frac{1 + \frac{2\eta}{\beta r}}{1 + \frac{3\eta}{\beta r}} \quad (4.5.1)$$

( $\beta$  may assume the extreme values of either  $\infty$  or zero depending, respectively, on whether the liquid entirely wets the sphere moving in it or does not adhere to the sphere). From the Stokes-Einstein equation (eq.4.3.1), which results from the above considerations, it is seen that the diffusion coefficient is inversely related to both the coefficient of viscosity ( $\eta$ ) and the radius ( $r$ ) (the latter being directly proportional to the frictional

resistance); and hence with increasing number of methylene groups in the molecule from formate to n-pentanoate (i.e., an increase in size), the diffusion coefficient decreases. The trend in the decreasing D values from formate to n-pentanoate is also consistent with the trend in the increasing viscosity B coefficient values (and hence in increasing  $\eta$  ; see table 1.4.3 for B values) at a temperature, say 30°C. As the solute molecules become progressively larger and larger, their diffusion and thermal strolling takes place with a relatively low velocity, decreasing gradually the diffusion coefficient by the "obstruction (hindering) effect" which tends to be the function of the volume fraction  $\phi$  , as well as the shape and size of the solute<sup>12</sup>. Moreover, the solute molecules are hydrated by water molecules, and the larger hydrated entity so formed hinders the rate of diffusion by enhancing further the obstruction effect<sup>12</sup>.

For trichloroacetate, the important contributory factor, for making the D value somewhat higher than those for propionate, n-butyrate and n-pentanoate (eventhough the corresponding size may be considerably larger), is probably the structure-breaking effect of the solute which operates in a direction opposite to the obstruction and hydration effects<sup>12</sup>. Hence, the diffusion coefficient of the trichloroacetate is not as low as the "obstruction effect" would have caused it (similar to that in the case of propionate, n-butyrate and n-pentanoate), due possibly to a partial cancellation of the obstruction effect by the known structure-disruptive influences of the chlorine groups in aqueous medium<sup>13</sup>.

Among the non-electrolytes, resorcinol shows a lower diffusion coefficient than phenol which may perhaps be the result of an increased obstruction effect in the formation of a larger solvated

species involving the two weakly polarising phenolic hydroxyl groups (in place of one for phenol) and, decreasing thereby the mobility of the solute molecule. Thus, in resorcinol the greater degree of solvation seems to play the predominating role in characterising the diffusion coefficient.

The introduction of an electron-repelling methyl group in the p-position of the hydroxyl group of phenol (i.e., in p-cresol) will presumably suppress the ionisation of the hydroxyl group (i.e., the formation of phenoxide type of ion which would have the effect of being strongly hydrated), and as a result the solvation effect on diffusion coefficient is smaller in p-cresol than that in phenol and resorcinol. Hence, the hydroxyl group in p-cresol will be more effective as a structure breaker by contributing its share to a greater extent towards structure-disruption in water (unlike that in phenol and resorcinol). Such structure-breaking effect, as said before<sup>12</sup>, will be in favour of an increased D value for p-cresol.

Benzyl alcohol, with its structure-making ( $\text{CH}_2$ ) and structure-breaking (OH) groups in close proximity, presents a rather complicated situation in regard to the relative efficiencies of these groups to influence the different factors that are responsible for characterising the diffusion coefficient.

Although a direct comparison between the diffusion data for phenols and benzyl alcohol, as obtained in the present study, and those reported in the literature<sup>9</sup>, is not possible because of different concentration ranges used (as mentioned above), nevertheless it is satisfying to note that both sets of D values (which are quite insensitive to concentration changes<sup>9</sup>) agree as far as

the order of magnitude and the qualitative trends are concerned (vide. last two columns of table 4.3.4).

The solutions of the present study (especially the non-electrolytes) being dilute (and therefore, ideal), the Hartley and Crank's equation<sup>14</sup> becomes identical for both mutual and self-diffusion coefficients of the components present at low concentrations, and hence the latter would be expected to follow the same trend, as discussed here, for the present solutes.

It is worth mentioning in this connection that the main difficulty lies in the fact that the diffusion data available in the literature are not sufficient for an unequivocal decision. However, in absence of any convenient quantitative formulations for studying the relationship between diffusion and structural changes in presence of the solutes, the above mode of analysis of the diffusion coefficient data, even though qualitative, may provide some insight into the understanding of such a complex transport phenomenon as diffusion.

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