



## Liquid Diffusion - Measurement and Correlation of Diffusion Coefficient in Acetic acid - Carbon tetra chloride System

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**Abstract :** The diffusion experiment was conducted involving the study of diffusivities of associating solute (Acetic Acid) in non associating solvent ( Carbon Tetra Chloride ), A New model equation for predicting diffusivities at infinite dilution has been derived for the case of associating solutes diffusing as dimmer. This model equation satisfactorily explains the wide discrepancy in predicting the diffusivities of such associating solutes by the conventional correlations proposed in the literatures. The model equation  $D_{AB} = [D_{A1} + D_{A2} [\sqrt{(1 + 4KX_A)} - 1]]/\sqrt{(1+4KX_A)}$ . The model parameter K remains nearly constant for the range of concentrations ( up to 5%) studied, and that a mean value of K (290.85) could be used satisfactorily in the proposed model equation. The results also indicates that the conventional diapharm cells could be used satisfactorily for experimental determination of liquid diffusivities up to a concentration of 5%. The Cell constant is 0.3624. The experimental diffusivity is  $1.4945 \times 10^{-5} \text{ cm}^2/\text{sec}$ .

**Keywords :** Diffusivity, Acetic Acid - Carbon Tetra Chloride system, diapharm Cell, Associating solute, Model Parameter.

### 1. Introduction

Estimation of liquid diffusivities is of considerable interest in understanding the mechanism of solute transport in liquids specially in liquid liquid extraction, distillation, crystallization, absorption and chemical reaction.

If a solute is partitioned between two immiscible solvents, there is diffusion in liquids was clarified by Thomas Graham, even though he has failed to put his experiments on a quantitative basis. Following graham's work Fick has described diffusion on the same mathematical basis as Fourier's law of heat conductance or ohm's law of electrical conduction. This analogy is still a useful pedagogical tool.

Fick has defined the total one dimensional flux  $J_1$  as  $J_1 = -D (\partial c_1 / \partial x)$  where  $c_1$  is the concentration of the solute and  $x$  is the distance. The term  $D$ , which Fick calls "the constant depending on the nature of the substances" is of course, the diffusion coefficient.

Diffusion coefficient for liquids are at least one thousand times smaller than those in gases. Theoretical estimation of diffusion in liquids are much less accurate than those for gases.

The various theoretical approaches to diffusion in liquid mixtures have helped to provide a greater insight into the diffusion process. The intermolecular forces, the shape and size of molecules are all important

factors. However, these attempts have not been very successful when complex interactions between the molecules in the liquid state occur. In view of the difficulties in formulating the exact theory, model approaches such as cell model, free volume model and hard sphere model have been resorted to.

However, correlations based on experimental measurements predicts diffusivities better than those by theoretical predictions. Owing to the complex nature of liquids correlations based on semi theoretical considerations also do not always give satisfactory predictions on account of complex molecular interactions as in high viscous solutes / solvents as also association tendencies in the solute – solvent systems.

## Theories of Diffusion

### 2.1 General

Notwithstanding a great deal of difficulty encountered in the formulation of a satisfactory theoretical equation to explain the phenomenon of diffusion, attempts have been made to explain the mechanism of diffusion on the basis of the following theories :

- 1.Hydrodynamic theory, 2.Eyring's absolute reaction rate theory,3.Statistical mechanical theory
- 4.Theory of irreversible thermodynamics.

### 3.1 Semi Empirical Correlations

There are number of semi empirical correlations reported for the prediction of diffusivities in liquids. Most of the correlations do not take association or complex formation between solute and solvent molecule into consideration. Recently some of the investigators have studied systems involving simple binary solute solvent interaction. Studies involving semi empirical correlations are discussed in some where else<sup>54</sup>

### 3.5 Conclusions from Literature Review

The above literature review indicates that little attention has been paid towards studying systems, where solute association affect diffusivity values, as for example in the case of acetic acid solute where association may occur.

Hence it would be of interest to study diffusivities of solute systems which exhibit solute association, and to check the applicability of the correlation of Laddha – Smith for water as solute ( a highly associating solute ) and that of Lysis. A new attempt at deriving a model to take into account the solute association will be useful.

### Scope of Present Work

The earlier investigations viz., that of Kamal and Canjar<sup>22</sup>, Lysis and Ratcliff<sup>30</sup>, Sitaraman etal<sup>43</sup>, Laddha and Smith<sup>27</sup>, Reddy and Duraiswamy<sup>38</sup>, Schiebel<sup>42</sup> with the exception in Wilke and Chang<sup>51</sup> have not given much importance to the effect of association on diffusivity predictions though the deviations from experimental measurements for such systems involving association were high. Wilke and chang have introduced a parameter for association of the solvent molecules in their correlation. They have not, however, taken into account, these systems which show association of the solute molecules or complex formation between solute and solvent molecules. Ratcliff and Lysis<sup>37</sup>, considered those systems which have shown complex formation between the solute and solvent molecules. Kuppuswamy and Laddha<sup>25</sup> have reported an improved correlation of Ratcliff and Lysis by studying the diffusivities with systems which have shown simple binary complexes between solute and solvent molecule.

A careful review of diffusion literature indicated that there has been no attempt at investigating association in the solute in non associating solvents. An attempt is made in this work to study the diffusivities of an associating solute ( viz. acetic acid ) into non associating solvent.

## Experimental Techniques

### 5.1 General

Available experimental diffusivity data for associating solutes in non associating solvents are meagre and there is need for reliable data in view of the inadequacies in the various semi empirical and empirical correlations. Diffusion coefficients are not difficult to measure out. Sophisticated equipment and accessories are needed for accurate determination within 1% accuracy. However, results within 5% accuracy can be accomplished with less sophisticated and conventional diaphragm cells. Diffusion coefficients at various concentrations of the solute could be obtained using Diaphragm cell with reasonable accuracy under pseudo steady state conditions.

### 5.2 Pseudo steady state Diffusion

The establishment of a steady concentration gradient across a porous diaphragm separating two miscible solutions of different compositions constitutes Pseudo steady state diffusion. After a known period of diffusion the concentration of the two solutions are analysed to determine the diffusivity. Because of its simplicity and efficiency, the method is widely used.

#### 5.2.1 Experimental Techniques

Almost all methods employ Fick's Law for determining diffusion coefficients. The difference between the methods lies mainly in the boundary conditions and in the analytical procedures used. Four types of techniques are in practice and they are discussed briefly here.

#### Diaphragm Cell technique

First developed by Northrup and Auron<sup>33</sup> later improved by Gordon and Stokes, the diaphragm cell technique has been recognized as a satisfactory method for measurement of diffusion coefficients. This technique and its application have been discussed at length in succeeding chapters.

#### Isotope Effects

Intra diffusion coefficients have been measured using radioactive isotope methods but an elaborate and complicated apparatus is necessary for successful utilization. One advantage of these tracers is that they can be assayed accurately even when they are present in very small concentration. Very precise determination of radiotracer concentrations has not been possible until the development of liquid scintillation counter.

#### Nuclear Magnetic Resonance Method

The discovery of NMR phenomenon has found its successful use for diffusivity measurements. This method can be used only when the system contain certain atomic nucleus with both magnetic momentum and angular momentum. Diffusion coefficients, which were beyond the scope of steady gradient method, have been measured down to the order of  $10^{-10}$  cm<sup>2</sup>/sec.

#### Some of the Application of Diffusion :

Carbon dioxide capture is mainly by diffusion process<sup>56</sup>, Penetration of water Absorption by blended Concrete<sup>58</sup>, Chromizing of steel<sup>60</sup>, Removal of Dyes<sup>69</sup>, Adsorption of Fluoride<sup>71,63</sup>, Removal of Heavy metal ions<sup>67</sup>, Synthesis of Copper Nano particles<sup>65</sup> are some of the papers published based on the diffusion.

#### Diaphragm Cell and Cell Equation

### 6.1 Diaphragm cell

Experimental determination of diffusion coefficients are accomplished to a great extent by the diaphragm cell technique. The solution of Fick's Law has been used with varying boundary conditions for this purpose. Diaphragm cell technique was now recognized as an exact method for diffusivity determination. This technique was first developed by Northrup and Auron (33) and subsequently improved by others. This technique is undergoing various modifications from time to time incorporating the latest design and accessories.

Gorden has reviewed the use of diaphragm cell with reference to the following

1.The cell volume 2.The assumption of quasi steady state in the diaphragm 3.Mechanism of transport in the diaphragm 4.Calibration of the diaphragm cell, and 5.The relationship between the integral and differential diffusion coefficients.

The diaphragm eliminates error due to convection which often arise during diffusion in liquids. It offers an effective cross sectional area,  $A_e$ , and a path length  $l_e$ , to the diffusing medium which must be determined experimentally by studying a system whose diffusivity is known. Thus the cells are calibrated. Appropriate equations developed from Fick's Law ( which assumes a linear concentration gradient across the diaphragm) are used to calculate diffusivity. A. lvarez<sup>1</sup> has shown that the influence of non linear concentration gradient is small and is, in effect, corrected by calibration. Gardon , in his review, has ruled that the measured integral coefficient could be taken to be equal to the true differential coefficient at very low concentrations.

So as far as the diffusion coefficient measurements are concerned, diaphragm cell technique presents an elegant method.

## 6.2 Cell Equation

For binary diffusion and unidirectional transfer, Fick's law gives

$$J_A = - D_{AB} \frac{dc}{dz} \quad \text{--- (26)}$$

$$J_A = \frac{ds}{A_e dt} \quad \text{--- (27)}$$

Where  $J_A$  is the mass flux of solute

$dc/dz$  is the concentration gradient

$$\text{And } ds = - D_{AB} A_e \frac{dc}{dt} / dz \quad \text{---- (28)}$$

Here  $s$  is the moles of solute diffusing and  $A_e$  is the total effective cross sectional area of pores.

For quasi – steady state and linear concentration gradient

$$\frac{dc}{dz} = \frac{\Delta c}{l_e} = (c_1 - c_2) / l_e \quad \text{----(29)}$$

substituting equation

$$ds = - D_{AB} A_e (c_1 - c_2) \frac{dt}{l_e} \quad \text{----(30)}$$

Here  $l_e$  is the effective pore length of the diaphragm and subscripts 1 and 2 refer to the two compartments of the cell, top and bottom respectively.

A material balance of component A yields

$$V_1 \frac{dc_{1A}}{dt} = - V_2 \frac{dc_{2A}}{dt} = ds \quad \text{---(31)}$$

Combining Equation, we have

$$D_{c_{1A}} = - D_{AB} A_e (c_{1A} - c_{2A}) \frac{dt}{(V_1 l_e)} \quad \text{---(32)}$$

$$D_{c_{2A}} = - D_{AB} A_e (c_{1A} - c_{2A}) \frac{dt}{(V_2 l_e)} \quad \text{---(33)}$$

Addition of the above two equation yields

$$D_{c_{1A}} - D_{c_{2A}} = - D_{AB} A_e (1/V_1 + 1/V_2)(c_{1A} - c_{2A}) \frac{dt}{(l_e)} \quad \text{---(34)}$$

$A_e$  and  $l_e$  are not available directly but  $A_e, l_e, V_1$  and  $V_2$  are constants for a given cell.

Putting  $A_e(1/V_1 + 1/V_2) = \beta$  and  $c_{1A} - c_{2A} = c^0$

$$\text{We get } d_{c1A} - d_{c2A} = -D_{AB} C^0 dt \quad \text{----(35)}$$

Integrating the above equation between the limits  $\Delta C^0$  and  $\Delta C^F$ , We obtain

$$\text{Int } d(C^0) / C = - \text{Int } 0 \text{ to } t \beta D_{AB} dt \quad \text{---- (36)}$$

$$\text{Or } D = (1/\beta t) \ln \Delta C^0 / \Delta C^F \quad \text{---- (37)}$$

Here  $\Delta C^0$  is the initial concentration difference =  $C_1^0 - C_2^0$

$\Delta C^F$  is the final concentration difference =  $C_1^F - C_2^F$

The assumption involved in the working equation (36) are -

1.The unidirectional form of diffusion has been shown to be valid by Toor if  $Ae / le$  depends only upon the internal diffusion path of the diaphragm.

2.Barnes has provided the assumption of quasi – steady state to be quite valid so long as the following two conditions are met.

a) The total pore volume should be less than 1% of the total cell volume, and

b) The preliminary period of diffusion is sufficient enough to disappear the original constant concentration gradient, which is about 4 to 5 hours.

A cell of normal dimensions satisfies the first condition. The ratio of the effective cross sectional area to the volume of the cell should be minimum or else quasi steady state condition is not valid. It is essential to note that the solute transfer is only by diffusion and not due to bulk flow or surface transport. The solutions are assumed to be of uniform concentration.

The diffusion of the cell factor suggests that as long as the volume of each solution is the same during the calibration and actual runs, the actual solution volume on either side of the diaphragm are immaterial. For low concentrations Gordon has shown that the time averaged integral diffusion coefficient is not different from the ordinary integral diffusion coefficient, the error being only 0.3%.

## Experimental Set up and Procedure

### 7.1 Experimental setup:

The diaphragm cell used for this investigation consists of a sintered silica diaphragm of pore size 4 – 5 microns. The cell is divided into two compartments with the diaphragm at the center. Each compartment has a volume of about 50 ml and is provided with independent inlet and outlet connections. Through the outer surrounding jacket, water at constant temperature was circulated from a thermostat. (fig 1)

### 7.2 Calibration of Diaphragm cell :

The calibration and standardization of the diaphragm cell constitutes an important part of the experiment. There are two methods, in practice, principally used for the calibration of cells. One method is using 0.1 kcl as the solute species diffusing into pure water. The other is 0.1N Hcl solution diffusing into pure water with a reported<sup>28</sup> diffusivity value of  $3.078 \times 10^{-5}$  cm<sup>2</sup>/sec at 30°C. The latter method was used here for the calibration of the cell.

### Procedure

Initially the cell compartments are flushed with acetone to clean the pores and the inside of the cell. The cell is dried in a vacuum drier. Initially pure water is filled in the bottom compartment by applying vacuum in the top compartment. Water is withdrawn through the pores of the diaphragm to the top compartment so as to drive out all the entrapped air. Then the top compartment is drained and filled with 0.1N Hcl after rinsing it well. Care is taken to avoid air bubbles in both the compartments. All the stop cocks are closed air tight.

**Fig1 :****Diaphragm cell Used for the determination of diffusion coefficient**

The cell was clamped vertically. Water at the required temperature is circulated through the outer jacket of the diaphragm cell. After the preliminary period of diffusion, lasting about four to five hours, the cell was taken out carefully and the contents drained off.

The cell is again filled up with the respective solutions and clamped. The run was allowed for 36 to 72 hours after which the contents were taken out and analysed quantitatively for their concentrations. From the analysis of initial and final concentrations the cell constant  $\beta$  was calculated by using the cell equation<sup>36</sup>

Five runs were made under identical conditions and the mean value of the cell constant  $\beta$  was evaluated. In this manner the cell constant for all the five cells used in this study were obtained. Their values are given in Table 1 at the end of the result chapter with their respective 98% confidence limit, which have been calculated.

**Table 1 : Cell Constant  
System : 0.1N Hcl – Water****Temperature : 30°C**

S.No	Time $T \times 10^{-5}$ sec	C1	$C_1^F$	$C_2^F$	$\Delta C$	$\Delta C^F$	$D_{AB} \times 10^5$ $\text{cm}^2/\text{sec}$	Cell Constant B
1	1.707	0.1050	0.0590	0.0430	0.1050	0.0160	3.078	0.3581
2	1.716	0.1050	0.0600	0.0450	0.1050	0.0150	3.078	0.3684
3	1.719	0.1040	0.0600	0.0450	0.1040	0.0150	3.078	0.3659
4	1.518	0.1030	0.0600	0.0410	0.1030	0.0190	3.078	0.3618
5	1.758	0.1040	0.0590	0.0440	0.1040	0.0150	3.078	0.3578

Concentration in gmoles /litre

Mean  $\beta = 0.3624$

### 7.3 Experimental Method

Initially one percent solution of the solute in solvent was prepared, on volume basis. As before the cell was first filled with the solvent. The one percent solution was taken in the top or bottom compartment depending on whether the solute is heavier or lighter than the solvent respectively.

After the preliminary period of diffusion the cell was taken out, emptied and filled after rinsing both the compartments with the respective solutions. The run was continued with circulating water being maintained at 30°C

After the stipulated time the contents of the top compartment and the bottom compartment were analysed accurately as given in section 7.4

The above procedure was repeated for studying the diffusivities at various solute concentrations. In each case the top and bottom compartments were analysed and the diffusivities are calculated.

### 7.4 Analytical procedure

Estimation of Acetic acid

Reagents : 1. Standard NaOH Solution  
2. Phenolphthalein Indicator.

Procedure : 10 ml of the sample solution are pipetted out into the Iodine flask. A few drops of Phenolphthalein indicator is added. It is titrated against the standard sodium hydroxide. The end point is the appearance of pale pink colour. In the course of the titration, we have a two phase solution. However, this does not affect the results.

### Result and Discussions

The system of Acetic acid – Carbon tetra chloride is chosen. Acetic acid is strongly associating solute and the solvent carbon tetra chloride fall in the class V category of solvents.

Table 2 gives the experimental values of the diffusion coefficients obtained with the use of conventional diaphragm cells for the systems Acetic acid – Carbon tetra chloride respectively covering concentration up to 5 %

**Table 2 : Diffusivities of Acetic Acid in Carbon Tetra Chloride System At 30°C**

S.No	Conc %	Time $T \times 10^{-5}$ sec	Concentration gmoles/litre				Cell Constant B	Diffusion Coefficient $D_{AB} \times 10^5$ $\text{Cm}^2/\text{sec}$
			Top Compartment		Bottom Compartment			
			Initial	Final	Initial	Final		
1	0.3	1.728	0.05241	0.04473	0.000	0.009939	0.1525	1.5275
2	0.5	1.584	0.08735	0.07842	0.000	0.017540	0.1525	1.4945
3	0.8	1.728	0.13980	0.10100	0.000	0.045480	0.3624	1.4722
4	1.0	1.728	0.17470	0.14410	0.000	0.024960	0.1525	1.4516
5	2.0	1.779	0.34940	0.25170	0.000	0.088920	0.3033	1.4149
6	5.0	1.850	0.87010	0.67530	0.000	0.217500	0.2499	1.3889

**8.1 Comparison of Experimental diffusivities with Predicted values using conventional Correlations :**

Table 3 shows a comparison of the diffusivity data predicted by three conventional correlations

- 1) Laddha – Smith ( both correlations, covering water as solute and non aqueous solute system)
- 2) Wilke chang (taking into account the solvent association parameter to be unity)

3) Lulis ( Incorporating the latent heats of vaporization of solute and solvent. It is seen from the error analysis given in table 3 that the calculated diffusivities by the conventional Lulis, Wilke chang, Laddha – Smith equations are less adequate in predicting the diffusivities of acetic acid in Carbon tetra chloride. This could be attributed to the associating nature of the solute in non associating solvent and hence requires further analysis based on a more satisfactory equation involving sound theoretical principles.

**Table 3 : Comparison of Experimental Data with other Correlations**

S.No	D <sub>exp</sub> x 10 <sup>5</sup> cm <sup>2</sup> / sec	D <sub>wc</sub> x 10 <sup>5</sup> cm <sup>2</sup> /sec	% Error	D <sub>LS</sub> x 10 <sup>5</sup> cm <sup>2</sup> /sec	% Error	D <sub>L</sub> x 10 <sup>5</sup>	% Error	D <sub>Predict</sub> x 10 <sup>5</sup> by equation 8.9	% Error
Solute : Acetic Acid				Solvent : Carbon Tetra Chloride					
1	1.4945	1.780	19	(1.773)	(18.63)	1.8307	22.5	1.4964	+0.13

D<sub>exp</sub> = Experimental Diffusivity

D<sub>wc</sub> = Wilke – Chang

D<sub>LS</sub> = Laddha – Smith

D<sub>L</sub> = Predicted by Lulis

% Error = [D<sub>exp</sub> – D<sub>predict</sub> ] x 100 / D<sub>exp</sub>

**8.2 Derived model to account for solute association**

Let us consider a case where the solute gives a dimer in solution due to association as follows :



Where A1 represents the monomer and A2 represents the dimer. From Fick’s law, diffusional flux is given by

$$J_A = - D_{AB} \Delta C_A$$

Writing the above equation for the monomer and dimer

$$J_{A1} = - D_{A1} \Delta C_{A1}$$

$$J_{A2} = - D_{A2} \Delta C_{A2}$$

D<sub>AB</sub>, the diffusion coefficient of the solute may be affected by the diffusion of the monomer as well as the dimer. Hence we may write

$$D_{AB} = D_{A1} dx_{A1} / dx_A + D_{A2} dx_{A2} / dx_A \quad \text{---- (39)}$$

Where x<sub>A1</sub> is the mole fraction of monomer and x<sub>A2</sub> is the mole fraction of dimer. From equation (38) one may write the following on the basis of Law of Mass Action

$$K = X_{A2} / X_{A1}^2 \quad \text{---- (40)}$$

$$X_{A2} = K X_{A1}^2$$

Since the initial solute concentration X<sub>A</sub> may be written in terms of the monomer and dimer concentration X<sub>A1</sub> and X<sub>A2</sub> we may write

$$X_A = X_{A1} + X_{A2} = X_{A1} + KX_{A1}^2 \quad \text{----(41)}$$



From equation

$$D_{AB} dX_A = D_{A1} dX_{A1} + D_{A2} dX_{A2} \quad \text{---- (42)}$$

Substituting for XA from equation (39) and (40)

$$D_{AB} d ( X_{A1} + KX_{A1}^2 ) = D_{A1} dX_{A1} + D_{A2} d(KX_{A1}^2)$$

$$D_{AB} (d X_{A1} + 2 KX_{A1} d X_{A1}) = D_{A1} dX_{A1} + 2 KX_{A1} D_{A2} dX_{A1}$$

$$D_{AB} d X_{A1} ( 1 + 2 KX_{A1} ) = dX_{A1} ( D_{A1} + 2 KX_{A1} D_{A2} )$$

$$D_{AB} = ( D_{A1} + 2 KX_{A1} D_{A2} ) / ( 1 + 2 KX_{A1} ) \quad \text{---- (43)}$$

Where  $D_{AB}$  = Actual diffusivity of solute

$D_{A1}$  = Diffusivity of monomer solute ( without association )

$D_{A2}$  = Diffusivity of dimer solute ( from association)

From equation (41) it follows that

$$KX_{A1}^2 + X_{A1} - X_A = 0$$

This is a quadratic equation in  $X_{A1}$  and solving

$$X_{A1} = [-1 \pm \sqrt{1 + 4KX_A}] / 2K$$

Since  $X_{A1}$  Cannot be negative, we have

$$X_{A1} = [\sqrt{1 + 4KX_A} - 1] / 2K \quad \text{--- (44)}$$

$$2KX_{A1} = [\sqrt{1 + 4KX_A} - 1] \quad \text{--- (45)}$$

substituting for  $X_{A1}$  by equation 44 we get

$$D_{AB} = [D_{A1} + D_{A2} [\sqrt{1 + 4KX_A} - 1]] / \sqrt{1 + 4KX_A} \quad \text{--- (46)}$$

### 8.3 Evaluation of Model Parameter K from Experimental Data

From Equation 46 we get

$$D_{AB} \sqrt{1 + 4KX_A} = D_{A1} + D_{A2} [\sqrt{1 + 4KX_A} - 1]$$

$$D_{AB} \sqrt{1 + 4KX_A} = D_{A1} + D_{A2} \sqrt{1 + 4KX_A} - D_{A2}$$

$$D_{AB} \sqrt{1 + 4KX_A} - D_{A2} \sqrt{1 + 4KX_A} = D_{A1} - D_{A2}$$

$$(D_{AB} - D_{A2}) \sqrt{1 + 4KX_A} = D_{A1} - D_{A2}$$

$$\sqrt{1 + 4KX_A} = (D_{A1} - D_{A2}) / (D_{AB} - D_{A2})$$

$$(1 + 4KX_A) = [(D_{A1} - D_{A2}) / (D_{AB} - D_{A2})]^2 \quad \text{--- (47)}$$

From the above equation the value of K can be evaluated from a knowledge of the experimental diffusivity  $D_{AB}$  and the predicted values of  $D_{A1}$  and  $D_{A2}$

By the following correlation based on Laddha – Smith Model for the monomer and modified Kuppuswamy – Laddha model for dimmer respectively.

$$D_{A1} = 2 \times 10^{-5} T(1/V_A)^{0.33} (V_B/V_A)^{0.16} / \eta_B \quad \text{--- (48)}$$

$$\text{And } D_{A2} = 2 \times 10^{-5} T(1/2V_A)^{0.33} (V_B/2V_A)^{0.16} / \eta_B \quad \text{-- (49)}$$

#### 8.4 Application of the above model for the case of Acetic acid Diffusion

The Experimental diffusivity values were used for estimation of the constant K, of the model equation (47). The values of K obtained for the various concentrations of the Carbon tetra chloride solvent studied are shown in table 4. It is seen that the constant K does not vary widely over the concentration range studied and hence one could use the mean value of K for data analysis.

**Table 4 : Model Parameter K                      System : Acetic Acid – Carbon Tetra Chloride**

S.No	Concn %	Concn in mole fraction $X_A$	$D_{AB} \times 10^5$ $\text{cm}^2/\text{sec}$	K
1	0.3	0.00505	1.5275	329.4
2	0.5	0.00840	1.4945	298.4
3	0.8	0.01343	1.4722	256.7
4	1.0	0.01676	1.4516	287.4
5	2.0	0.03329	1.4149	307.5
6	5.0	0.08128	1.3889	265.7

Mean K = 290.85

**Table 5 : Comparison of Predicted Values of Diffusion Coefficient by the Present Proposed Model System : Acetic Acid – Carbon Tetra Chloride**

S.No	Concn %	$D_{AB\text{exp}} \times 10^5$ $\text{cm}^2/\text{sec}$	$D_{AB\text{pred}} \times 10^5$ $\text{cm}^2/\text{sec}$	% Error
1	0.3	1.5275	1.5381	- 0.69
2	0.5	1.4945	1.4964	- 0.13
3	0.8	1.4722	1.4642	0.55
4	1.0	1.4516	1.4509	0.05
5	2.0	1.4149	1.4172	-0.16
6	5.0	1.3889	1.3864	0.18

**Table 6 : Properties of Chemical used**

S.No	Chemicals	Density gm/cc	Viscosity at 30°C Cp	Latent Heat of Vapourisation Kcal / gmole	Heat of	Molecular volume cc / gmole	Molecular weight
1	Acetic Acid	1.049	1.065	5.813	6.663	68.4	60.05
2	Carbon Tetra Chloride	1.5925	0.8418	7.117	7.7169	101.2	153.84

The experimental diffusivities are compared with the diffusivities predicted by the present proposed model<sup>46</sup> using an average value of K obtained for each case of the solvent used. These are shown in Tables 5 which show good agreement with experimental values.

Hence it may be observed that the proposed model is amply adequate in taking into account the dimmer formation in Acetic acid solute.

However, further work is necessary before a satisfactory method is developed for analyzing the model parameter K for different solvent systems with a view to predicting the same for use with equation in the absence of any experimental data. It may be observed from the present results that the diaphragm cell could be satisfactorily used for determining diffusivity values involving concentration range as upto 5%

## Conclusions

The Following conclusions are drawn based on the results of the present investigation involving the study of diffusivities of associating solute (Acetic Acid) in non associating solvent ( Carbon Tetra Chloride )

1. A New model equation for predicting diffusivities at infinite dilution has been derived for the case of associating solutes diffusing as dimmer. This model equation satisfactorily explains the wide discrepancy in predicting the diffusivities of such associating solutes by the conventional correlations proposed in the literatures.
2. The model parameter K remains nearly constant for the range of concentrations (upto 5%) studied, and that a mean value of K could be used satisfactorily in the proposed model equation.
3. It is noted that the model parameter K varies with the solvent used for a given solute. This requires further study involving a wide range of solute solvent systems.
4. The results also indicates that the conventional diaphragm cells could be used satisfactorily for experimental determination of liquid diffusivities up to a concentration of 5%.

## References:

1. A. Ivarez, R., Bueno, J. L., & Coca, J. (1980). Binary gaseous diffusion coefficients. I. Air with furan derivaties. Journal of Chemical and Engineering Data, 25(1), 27–28.
2. Ambrosini D, Paoletti D, Rashidnia N. (2008) Overview of diffusion measurements by optical techniques. Opt Lasers Eng. 46:852–864.
3. Asher WE, Litchendorf TM. (2009) Visualizing near-surface concentration fluctuations using laser-induced fluorescence. Exp Fluids. 46:243–253.
4. Bearman, R.J(1960),J.Chem.Phys., 65, 1308
5. Crimaldi JP(2008). Planar laser induced fluorescence in aqueous flows. Exp Fluids. 44:851–863.
6. Dani A, Guiraud P, Cockx A.(2007) Local measurement of oxygen transfer around a single bubble by planar laser-induced fluorescence. Chem Eng Sci. 62:7245–7252.
7. de Blok WJ, Fortuin JMH.(1981) Method for determining diffusion coefficients of slightly soluble gases in liquids. Chem Eng Sci. 36:1687–1694.
8. Eyring, H., and Hirschfelder, J.O.Phys.chem.,4,249 (1937)

9. Falkenroth A, Degreif K, Jähne B. Visualisation of oxygen concentration fields in the mass boundary layer by fluorescence quenching. In: Garbe CS, Handler RA, Jähne B, editors. *Transport at the Air-Sea Interface*. Environmental Science and Engineering. Berlin, Germany: Springer, 2007:59–72.
10. Feist, R., & Schneider, G.M. (1982). Determination of binary diffusion coefficients of benzene, phenol, naphthalene and caffeine in supercritical CO<sub>2</sub> between 308 and 333 K in the pressure range 80 to 160 bar with supercritical fluid chromatography (SFC).
11. Francois J, Dietrich N, Guiraud P, Cockx A. Direct measurement of mass transfer around a single bubble by micro-PLIFI. *Chem Eng Sci*. 2011;66:3328–3338.
12. Geddes CD, Lakowicz JR. *Topics in Fluorescence Spectroscopy—Part B—Advanced Concepts in Fluorescence Spectroscopy Macromolecular Sensing*, Vol. 10. Springer, 2005.
13. Geddes CD. Optical halide sensing using fluorescence quenching: theory, simulations and applications—a review. *Meas Sci Technol*. 2001;12:R53–R88.
14. Gordon, A.R., *Am. New York, Acad. sci.*, 46, 285 (1945)
15. He M, Guo Y, Zhong Q, Zhang Y. Determination of binary gas diffusion coefficients using digital holographic interferometry. *J Chem Eng data*. 2010;55:3318–3321.
16. Hébrard G, Zeng J, Loubiere K. Effect of surfactants on liquid side mass transfer coefficients: a new insight. *Chem Eng J*. 2009;148:132–138.
17. Herlina, Jirka GH. Application of LIF to investigate gas transfer near the air–water interface in a grid-stirred tank. *Exp Fluids*. 2004;37:341–349.
18. Ho CS, Ju LK, Baddour RF, Wang DIC. Simultaneous measurement of oxygen diffusion coefficients and solubilities in electrolyte solutions with a polarographic oxygen electrode. *Chem Eng Sci*. 1988;43:3093–3107.
19. Islam MA. Einstein–Smoluchowski diffusion equation: a discussion. *Phys Scr*. 2004;70:120–125.
20. Jamnongwong M, Loubiere K, Dietrich N, Hébrard G. Experimental study of oxygen diffusion coefficients in clean water containing salt, glucose or surfactant: consequences on the liquid-side mass transfer coefficients. *Chem Eng J*. 2010;165:758–768.
21. Jamshidi-Ghaleh K, Tavassoly MT, Mansour N. Diffusion coefficient measurements of transparent liquid solutions using Moiré deflectometry. *J Phys D: Appl Phys*. 2004;37:1993–1997.
22. Kamal MR, and Canjar, LN. (1962), 'Binary Liquid Diffusion coefficients', *AIChE Journal* 8 (3): pp . 329-334 .
23. Karthikeyan, K., M.tech Thesis, University of Madras, 1975.
24. King, Hauch and Mao, *J. Chem. Engg. Data* 10 308 (1965).
25. Kuppaswamy, M.tech Thesis, University Of Madras (1977).
26. Kutepov AM, Pokusaev BG, Kazenin DA, Karlov SP, Vyazmin AV. Interfacial mass transfer in the liquid–gas system: an optical study. *Theor Found Chem Eng*. 2001;35:213–216.
27. Laddha, G.S., and Smith, J.M. (1969), 'Chemical Reactor', *Ind. Chem. Engr.* 11(4), 109.
28. Lakowicz JR. Advanced topics in fluorescence quenching. In: Lakowicz JR, editor. *Principles of Fluorescence Spectroscopy*, 2nd ed. New York, NY: Plenum, 1999; 267–289.
29. Leahy-Dios A, Firoozabadi A. Unified model for non-ideal multicomponent molecular diffusion coefficients. *AIChE J*. 2007;53:2932–2939.
30. Lysis, M. A., & Ratcliff, G.A. (1968). Diffusion in binary liquid mixtures at infinite dilution. 'Canadian Journal of Chemical Engineering', 46, 385.
31. Malik VK, Hayduk W. A steady state capillary cell method for measuring gas–liquid diffusion coefficients. *Can J Chem Eng*. 1968;46:462–466.
32. Münsterer T, Jähne B. LIF measurements of concentration profiles in the aqueous mass boundary layer. *Exp Fluids*. 1998;25:190–196.
33. Northrup. J.A., and Aurnon, M.L., *Gen. Physiology*, 12, 543 (1949)
34. Olander, D.R., *A.I.Ch.E.J.* (1961), 'Olander, D.R., "The Diffusivity of Water in Organic Solvents', pp. 171-175.
35. Onsager, L. (1931), 'Reciprocal relations in irreversible processes', *Phys. Reviews*, 38 (12), pp. 2265-2279.
36. Perry, J.H. (1975), 'chemical engineering handbook', London and New York: McGraw-Hill Book, McGraw-Hill Book Perry, J.H., *Chem. Engr. Hand book*.
37. Ratcliff, G.A., and Lysis, M.A., and EC. (1971), 'Diffusion in Simple-Complex Forming Liquid Mixtures', *Ind. Eng. Chem. Fundamen.*, 10 (3), pp. 474–477.

38. Reddy, K.A., & Doraiswamy, L.K. (1967). Estimating liquid diffusivity. *Industrial and Engineering Chemistry Fundamentals*, 6(1), 77.
39. Reid, R. C., Prausnitz, J. M., & Poling, B. E. (1987). *The properties of gases and liquids* (4th Ed.). New York: McGraw-Hill.
40. Roetzel W, Blömker D, Czarnetzki W. Messung binärer Diffusionskoeffizienten von Gasen in Wasser mit Hilfe der holographischen Interferometrie. *Chemie Ingenieur Technik*. 1997;69:674–678.
41. Scheibel EG. *Physical chemistry in chemical engineering design*. *Ind Eng Chem*. 1954;46:1569–1579.
42. Scheibel, E. G. (1954). Liquid diffusivities. *Industrial and Engineering Chemistry*, 46(9), 2007.
43. Sitaraman, R., Ibrahim, S.H., and Kuloor, N.R., *J.Chem.Engg.Data* 8, 198(1963).
44. Slininger PJ, Petroski RJ, Bothast RJ, Ladisch MR, Okos MR. Measurement of oxygen solubility in fermentation media: a colorimetric method. *Biotechnol Bioeng*. 1989;33:578–583.
45. Sovova H, Prochazka J. A new method of measurement of diffusivities of gases in liquids. *Chem Eng Sci*. 1976;31:1091–1097.
46. Stöhr M, Schanze J, Khalili A. Visualization of gas–liquid mass transfer and wake structure of rising bubbles using pH-sensitive PLIF. *Exp Fluids*. 2009;47:135–143.
47. Takehara K, Etoh GT. A direct visualization method of CO<sub>2</sub> gas transfer at water surface driven by wind waves. In: Donelan M, Drennan WM, Saltzman ES, Wanninkhof R, editors. *Gas Transfer at Water Surfaces*. Washington, DC: American Geophysical Union, 2002:89–95.
48. Tham MJ, Bhatia KK, Gubbins KF. Steady-state method for studying diffusion of gases in liquids. *Chem Eng Sci*. 1967;22:309–311.
49. Variano EA, Cowen EA. Quantitative imaging of CO<sub>2</sub> transfer at an unsheread free surface. In: Garbe CS, Handler RA, Jähne B, editors. *Transport at the Air-Sea Interface*. Environmental Science and Engineering, Berlin, Germany: Springer, 2007:43–57.
50. Walker JW, Peirson WL. Measurement of gas transfer across wind-forced wavy air–water interfaces using laser-induced fluorescence. *Exp Fluids*. 2008;44:249–259.
51. Wilke CR, Chang P. Correlation of diffusion coefficients in dilute solutions. *AIChE J*. 1955;1:264–270.
52. Wolff LM, Hanratty TJ. Instantaneous concentration profiles of oxygen accompanying absorption in a stratified flow. *Exp Fluids*. 1994;16:385–392.
53. Wylock C, Dehaeck S, Cartage T, Colinet P, Haut B. Experimental study of gas–liquid mass transfer coupled with chemical reactions by digital holographic interferometry. *Chem Eng Sci*. 2011;66:3400–3412.
54. K. Bogeshwaran, Dr. B. Karunanithi, Manasa Tripuraneni, S. Jerin Ross 'Measurement and Correlation of Diffusion Coefficient In Hexane – Air System' *International Journal of Engineering Research and Development*, Volume 11, Issue 11 (November 2015), PP.19-31.
55. Ulfa Andayani, Jumina, Dwi Siswanta, Dandiah Mardiana 'Permeation of Acetone-Butanol-Ethanol (ABE) Using Blended Membrane PVA-Pectin' *International Journal of ChemTech Research*, Vol.8, No.4, pp 1626-1631, 2015.
56. Dao Sy Duc 'Carbon dioxide capture technologies' *International Journal of ChemTech Research* Vol.9, No.04 pp 539-546, 2016.
57. Kamal Kayed, 'The correlation between carbon tetrachloride Raman spectra and methanol configuration in CH<sub>3</sub>OH/CCl<sub>4</sub> mixtures' *International Journal of Chem Tech Research*, Vol.8, No.10 pp 187-193, 2015.
58. J. Srikanth, N. Chidambaram, B. Karthikeyan, and G. Dhinakaran 'Resistance to Deterioration and Water Absorption by Ternary Blended Concrete with Ceramic Powder and SiO<sub>2</sub>' *International Journal of Chem Tech Research* Vol.8, No.2, pp 696-703, 2015
59. Balwinder Saini, Ravi Sharma and R.C. Thakur 'Thermodynamics and transport properties of L-Proline in water and binary aqueous mixtures of acetonitrile at 303.15 K.' *International Journal of Chem Tech Research*, Vol.8, No.12 pp 395-402, 2015
60. S.C. Atul 'Investigation on Chromizing of C45 Steel using Response Surface Methodology' *International Journal of Chem Tech Research*, Vol.9, No.01 pp 82-91, 2016
61. Gupta S., Dutta G., Mondal D. 'Mechanism of Fluoride Mobilization in an Alluvial Aquifer: a Kinetic Approach' *International Journal of Chem Tech Research* Vol.9, No.04 pp 270-278, 2016
62. Rubila. S and Ranganathan T.V. 'Effect of Allium Sativum paste against Antimicrobial, Antioxidant and Cytotoxicity activity' *International Journal of Pharm Tech Research*, Vol.9, No.3, pp 328-332, 2016
63. Davoud Balarak 'Kinetics, Isotherm and Thermodynamics Studies on Bisphenol A Adsorption using Barley husk' *International Journal of ChemTech Research*, Vol.9, No.05 pp 681-690, 2016.

64. Kaushita Banerjee, Mouli Mukherjee, Ruchi Chaudhry, Niharika Pandey, Padma Thiagarajan,' Characterization and Antibacterial Activity of Hydroxyapatite nanoparticles' International Journal of Pharm Tech Research, Vol.9, No.3, pp 452-459, 2016.
65. S.Devasenan<sup>1</sup>, N.Hajara Beevi , S.S.Jayanthi,' Synthesis and characterization of Copper Nanoparticles using Leaf Extract of Andrographis Paniculata and their Antimicrobial Activities' International Journal of Chem Tech Research, Vol.9, No.04 pp 725-730, 2016.
66. R.Prithvirajan, S. Jayabal, S.Kalayana Sundaram and A. Pravin Kumar,' Hybrid Bio Composites from Agricultural Residues: Mechanical and Thickness Swelling Behavior' International Journal of ChemTech Research, Vol.9, No.03 pp 609-615, 2016.
67. Shanmugam. S and Arabi Mohammed Saleh M.A,' An Overview of Research Trends in Remediation of Heavy Metal Ion from Polluted Water' International Journal of PharmTech Research Vol.9, No.1, pp 90-96, 2016.
68. Nisha Chhetri, S. A. Bhoite,' Study of Solvent Effects on Hydrolysis of Mono-m-toluidine Phosphate' International Journal of ChemTech Research, Vol.9, No.02 pp 106-109, 2016.
69. Alaa R. Omran , Maysam A. Baiee , Sarab A. Juda , Jasim M. Salman, Ayad F. AlKaim,' Removal of Congo red dye from aqueous solution using a new adsorbent surface developed from aquatic plant (Phragmites australis)' International Journal of ChemTech Research Vol.9, No.04 pp 334-342, 2016.
70. S.R. Premkartikkumar,' Enhancing diesel engine combustion using hydrogen enriched fuels – A Review', International Journal of ChemTech Research, Vol.9, No.01 pp 01-06, 2016.
71. V. Durga Praveena , K. Vijaya Kumar,' Eco-Friendly Silver Nano Films for the Adsorption of Fluoride Ions Based on Light Scattering Phenomenon, International Journal of ChemTech Research, Vol.9, No.04 pp 288-295, 2016.

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