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THE COMPARATIVE EVALUATION OF COMPUTATIONAL AND EXPERIMENTAL APPROACHES TO THE DETERMINATION OF THE DIFFUSIVITY OF CARBON TETRACHLORIDE IN AIR

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ABSTRACT

The diffusivity of CCl_4 (component A) in air (component B) was determined by both experimental and estimation techniques. The experimental method was based on uni-directional steady state diffusion of CCl_4 vapour (A), from the graduated measuring cylinder containing liquid CCl_4, over which a current of air (B) was blown from a fan. The results obtained from the experiments showed that the CCl_4- air diffusivity (D_{AB}) at the fan speed of 3057 revolutions per minute (rpm) was $3.17 \times 10^{-9} m^2/s$; while the result for the fan speed of 3044 rpm was $6.38 \times 10^{-9} m^2/s$. On the other hand, the result of the CCl_4 – air diffusivity using the Wilke-Lee equation was $8.40 \times 10^{-6} m^2/s$; while the result from the Fuller et al equation was $8.47 \times 10^{-6} m^2/s$.

INTRODUCTION

The diffusivity, or diffusive coefficient, D is a property of a system dependent upon the temperature, pressure and nature of the components (1). Also, an advanced kinetic theory predicts that in binary mixtures there would be only a small effect of composition (1). Diffusivity measurements have been well developed in gaseous and liquid systems. For gases, the diffusivity or diffusive coefficients can be determined experimentally in the laboratory or field. However, in the absence of experimental data, the diffusivity for gases may be estimated from computations from equations and expressions developed from the kinetic theory of gases and from calculations from some empirical models or correlations.

According to Nnolim (2), the convective molar flux of

$$A = X_A N_T = X_A(N_A + N_B) \text{ .... } (1)$$

and the diffusional molar flux (Fick's first law) is :

$$D_{AB}\frac{\partial C_A}{\partial z} \text{ .... } (2)$$

Hence the molar flux of A, for diffusion in a binary system of components A and B is the addition of eqns (1) and (2) as:

$$N_A = X_A(N_A + N_B) - D_{AB}\frac{\partial C_A}{\partial z} \text{ ....}(3)$$

This equation (3) is consistent with assumption (f). Since component B is stagnant, $N_B = 0$; and considering carbon tetrachloride as an ideal gas [see assumption (d), $C = P_t / RT, X_A = {}^{C_A}\!/\!_{C} = {}^{p_A}\!/\!_{p}, \frac{dC_A}{c - c_A} = \frac{dp_A}{p - p_A}$, so that;

$$N_A(1 - X_A) = -\frac{D_{AB}}{RT}\frac{dp_A}{dz} \text{ ....}(4)$$

On integration and re-arrangement, yields

$$N_A = -\frac{D_{AB}P}{RTz}\ln\frac{p - p_{A1}}{p - p_{A2}} \text{ ....}(5)$$

or

$$N_A = \frac{D_{AB}P}{RTz}\ln\frac{p - p_{A2}}{p - p_{A1}} \text{ ....}(6)$$

Treybal (1) re-arranged eqn (6) as:

$$N_A = \frac{D_{AB}P}{RTz}\frac{p_{A1} - p_{A2}}{p_{B2} - p_{B1}}\ln\frac{p_{B2}}{p_{B1}} \text{ ....}(7)$$

where;

$p - p_{A2} = p_{B2}$, $p - p_{A1} = p_{B1}$, and
$p_{B2} - p_{B1} = p_{A1} - p_{A2}$

Introducing the concept of log mean partial pressure (P_{BM}) for carbon tetrachloride, eqn (7) becomes:

$$N_A = -\frac{D_{AB}P}{RTz}\frac{}{p_{bm}}(p_{A1} - p_{A2}) \quad \ldots\ldots\ldots\ldots\ldots(8)$$

where Treybal (1) shows that : (log mean partial pressure)

$$P_{BM} = \frac{p_{B2} - p_{B1}}{\ln\left(\frac{p_{B2}}{p_{B1}}\right)}$$

According to Nwosu *et al.* (3) the rate of carbon tetrachloride evaporation per unit area of the calibrated cylinder is

$$N_A = \frac{-\rho}{M}\frac{dz}{dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Equating eqns (8) and (9)

$$\frac{-\rho}{m}\frac{dz}{dt} = \frac{-D_{AB}P}{RTzp_{Bm}}\left(p_{A_2} - p_{A_1}\right) \quad \ldots\ldots(10)$$

$$Zdz = \left[\frac{D_{AB}PM}{RT\rho_{BM}}(p_{A2} - p_{A1})\right]dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

By letting $\frac{D_{AB}PM}{RT\rho P_{BM}}(p_{A2} - p_{A1}) = K$ then eqn (11) becomes

$$Zdz = kdt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

On integration of eqn (12), the following is obtained:

$$z\int_{z_0}^{z} dz = k\int_0^t dt$$

$$\frac{z^2 - z_0^2}{2} = kt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

$$z^2 - z_0^2 = 2kt$$

On expansion eqn (13) becomes: $(z-z_0)(z-z_0 + 2z_0) = 2kt$

or $$\frac{t}{z - z_0} = \frac{z - z_0}{2k} + \frac{z_0}{k} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

Thus; Nwosu et al [3] expresses that a graph of $\frac{t}{z - z_0}$ against $z - z_0$ will give a straight line from which D_{AB} can be obtained either from the slope, or the intercept.

Perry and Chilton (4) writes that when accurate estimates of gas diffusivities are desired, the Wilke-Lee modification of the equation by Hirschfelder, Bird and Spotz is recommended as :

$$D_{AB} = \frac{\left(0.00107 - 0.000246\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}\right) T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P(r_{AB})^2 \left[f\left(\frac{kT}{\epsilon_{AB}}\right)\right]} \quad \text{........(15)}$$

where:

$$r_{AB} = \frac{r_A + r_B}{2} \quad \text{.......................................(15a)}$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} \quad \text{............................(15b)}$$

$f\left(kT/\epsilon_{AB}\right)$= collision function

Treybal (1) recommends eqn (15) for mixtures of nonpolar gases, or of a polar with nonpolar gas.

Apart from the Wilke-Lee modification, another model for accurate estimation of gas diffusivities is the Fuller et al equation. Nnolim [2] expresses that the diffusivity of a vapour in a gas is given by the equation of Fuller et al as:

$$D_{AB} = \frac{1.013x10^{-7} T^{1.75} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{\frac{1}{2}}}{p\left[\left(\sum_A v_i\right)^{1/3} + \left(\sum_B v_i\right)^{1/3}\right]^2} \quad \text{..............(16)}$$

where the symbols and parameters are defined in the notation section.

Perry and Chilton (4) states that the accuracy of predictions from eqn (15) should be within ~7 to 8% for most systems; however, errors up to ~ 25% can be expected for binary systems involving highly polar and cigar-shaped molecules, halides, and metal vapours. A similar error range, i.e. ~ 7% average and 25% average maximum, is associated with eqn (16). For extrapolation over broad temperature ranges, eqn (15) probably is preferable (4).

Peters and Timmerhaus (5) writes that for linear regression of two variables where the theoretical least – square line is of the form

$$y = a + b\,(x - \bar{x}) \qquad \ldots\ldots\ldots\ldots(17)$$

then $a = \bar{y}$, the mean value of y

and $b = \dfrac{\sum(\bar{x}-x)(\bar{y}-y)}{\sum(\bar{x}-x)^2}$

Terms in the slope expression may be simplified in the following manner (5) :

$$\sum(\bar{x}-x)(\bar{y}-y)=\sum xy-\frac{\sum x\sum y}{n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(18)$$

$$\sum(\bar{x}-x)^2=\sum x^2-\frac{(\sum x)^2}{n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(19)$$

Equations 17, 18 and 19 provide the framework for regression analysis of data to be generated, with the aim of using it to enhance the determination of slope.

MATERIALS AND METHOD

The diffusive coefficient of carbon tetrachloride vapour in air was determined with experimental setup (Fig. 1). The experimental setup was maintained at a constant room temperature of 29^0C. The Stroboscope xenon-digital, model XE-H, made by Industrial Equipment and Control (IEC) Pty (6) was used to determine the speeds of rotation of the fan blades, which blew air current over the cylinder containing carbon tetrachloride. At two different fan speeds of 3044 and 3057 revolutions per minute (rpm) respectively, determine by the light stroboscope, an air stream was blown over the top of the carbon-tetrachloride-containing cylinder. The speeds of the air stream were sufficiently rapid to ensure that the partial pressure of the vapour in the system remained approximately zero. At intervals of 5 min., the change in the levels of carbon tetrachloride in the measuring cylinder were measured and recorded. These records are displayed (Tables I and II).

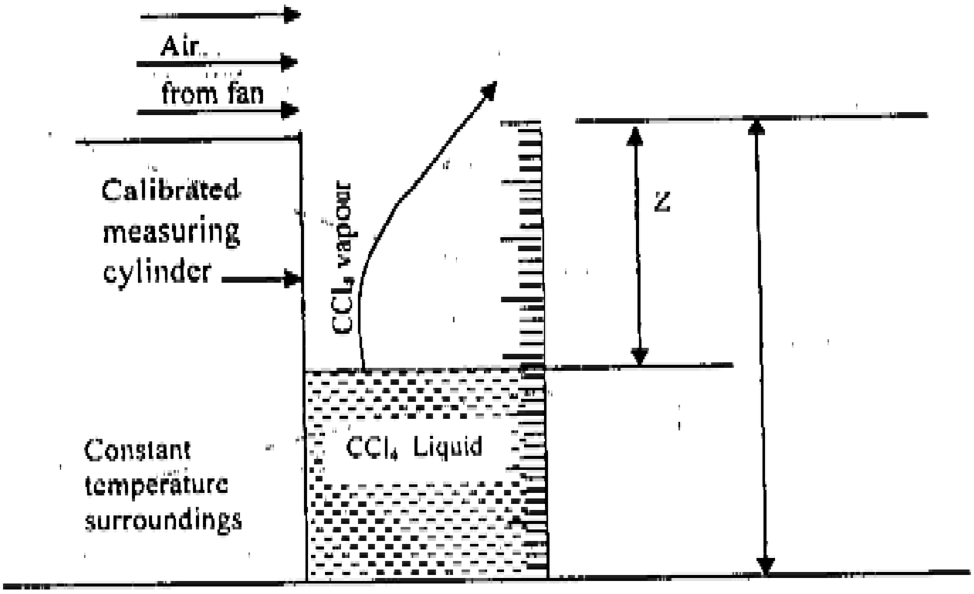

Fig. 1. Scheme of diffusion of Carbon tetrachloride vapour (A) through air (B)

The profile of the diffusion of carbon tetrachloride vapour (A) through stagnant air (B) is given (Fig. 2).

Using eqn (14) the data in (Tables I and II) were evaluated and displayed (Tables 3 and 4). Plots of eqn (14) were made with the data derived from the fan speed of 3044 and 3057 rpm, respectively (Figs. 3 and 4). Subsequently, the diffusive coefficients of carbon tetrachloride vapour in air were evaluated from these graphs by means of regression analysis employing equations 17, 18 and 19 The slopes of the regression lines determined the diffusion coefficients of carbon tetrachloride vapour in air at fan speeds for 3057 rpm and 3044rpm respectively (Figs. 3 and 4).

Also, the Wilke-Lee modification (eqn. 15), and the Fuller *et al.* equation (eqn 16) were applied in the estimations of the diffusive coefficients of carbon tetrachloride in air based on the experimental condition. The results obtained were compared with diffusivity values derived from the plots of eqn (14).

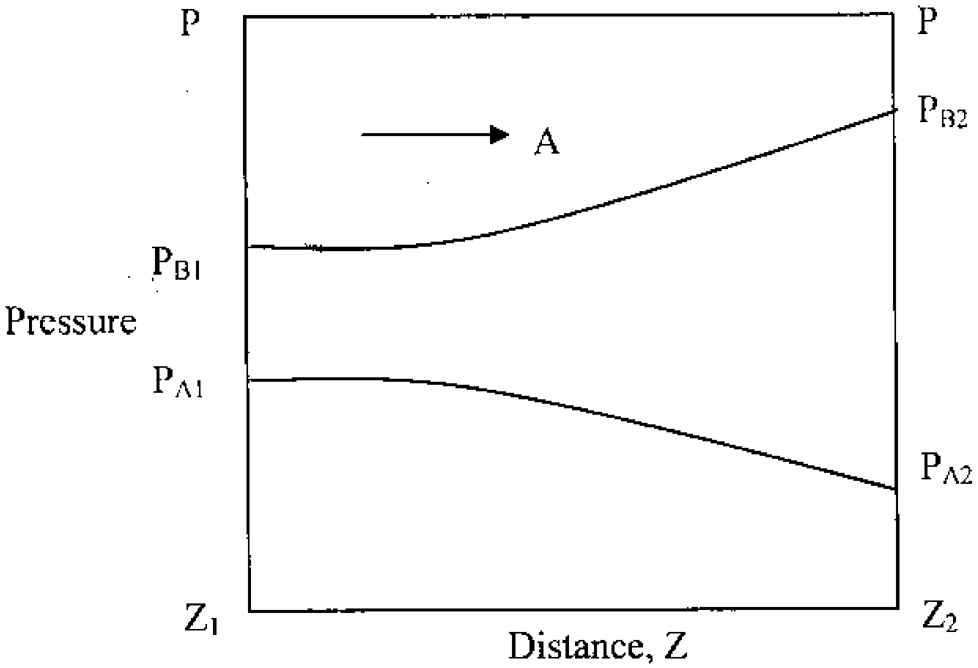

***Fig. 2.** Diffusion of carbon tetrachloride (A) through stagnant air (B)*

Table I. Time versus carbon tetrachloride level at fan speed at 3057 rpm

Time (minutes)	Carbon tetrachloride level (mm)
0	100
5	98
10	96
15	95
20	93
25	92
30	90
35	90
40	89
45	88
50	87
55	86
60	85

Table II. Time versus carbon tetrachloride level at fan speed of 3044 rpm.

Time (minutes)	Carbon tetrachloride level (mm)
0	100
5	98
10	97
15	96
20	95
25	94
30	93
35	93
40	92
45	91
50	90
55	90
60	89

RESULTS AND DISCUSSION

The results displayed were derived from the experimental records at various fan speeds, namely 3044 rpm and 3057 rpm, respectively (Tables III and IV).

At the fan speed of 3057 rpm the diffusivity of carbon tetrachloride vapour (A) through air (B), D_{AB} was the slope of the regression line (Fig. 3).

$$\text{Therefore, } D_{AB} = \frac{4.22 - 1.43}{15 - 0} = 0.19\text{mm}^2/\text{min}(3.17\text{x}10^{-9}\text{m}^2/\text{sec})$$

The fan speed of 3044 rpm D_{AB} is the slope of the regression line.

$$\text{Thus, } D_{AB} = \frac{6.01 - 1.50}{11 - 0} = 0.41\text{mm}^2/\text{min}(6.83\text{x}10^{-9}\text{m}^2/\text{sec})$$

Table III. Data derived from the measurements made at the Fan - blade speed of 3057rpm

S/N	Time, t (min)	CCl_4 level (mm)	Change in CCl_4 level $(Z-Z_0)$, mm	$\left(\frac{t}{z-z_0}\right)$ (min/mm)	$\left(\frac{t}{z-z_0}\right)'$ (min/mm)
1	0	100	0	0	1.43
2	5	98	2	2.50	1.81
3	10	96	4	2.50	2.19
4	15	95	5	3.00	2.38
5	20	93	7	2.86	2.76
6	25	92	8	3.13	2.95
7	30	90	10	3.00	3.33
8	35	90	10	3.50	3.33
9	40	89	11	3.64	3.52
10	45	88	12	3.75	3.71
11	50	87	13	3.85	3.90
12	55	86	14	3.93	4.09
13	60	85	15	4.00	4.28

Table IV. Data derived from the measurements made at the fan-blade speed of 3044rpm.

S/N	Time, t (min)	CCl_4 level (mm)	Change in CCl_4 level $(Z-Z_0)$, mm	$\left(\frac{t}{z-z_0}\right)$ (min/mm)	$\left(\frac{t}{z-z_0}\right)$ (min/mm)
1	0	100	0	0	1.50
2	5	98	2	2.50	2.32
3	10	97	3	3.33	2.73
4	15	96	4	3.75	3.14
5	20	95	5	4.00	3.55
6	25	94	6	4.17	3.96
7	30	93	7	4.29	4.37
8	35	93	7	5.00	4.37
9	40	92	8	5.00	4.78
10	45	91	9	5.00	5.19
11	50	90	10	5.00	5.60
12	55	90	10	5.50	5.60
13	60	89	11	5.46	6.01

Based on the experimental condition, the result obtained from the estimation of the diffusivity of CCl_4 through air using the Wilke-Lee equation was 8.40 x $10^{-6}m^2/s$. Also, the result obtained from the computation of the diffusivity of the same CCl_4 through air, based on the same experimental conditions, but using the Fuller et al equation was 8.47 x $10^{-6}m^2/s$. The comparison of these results (the Wilke-Lee and the Fuller *et al.* formulae) shows that they were consistent despite the 0.07 discrepancy between the two diffusivity values.

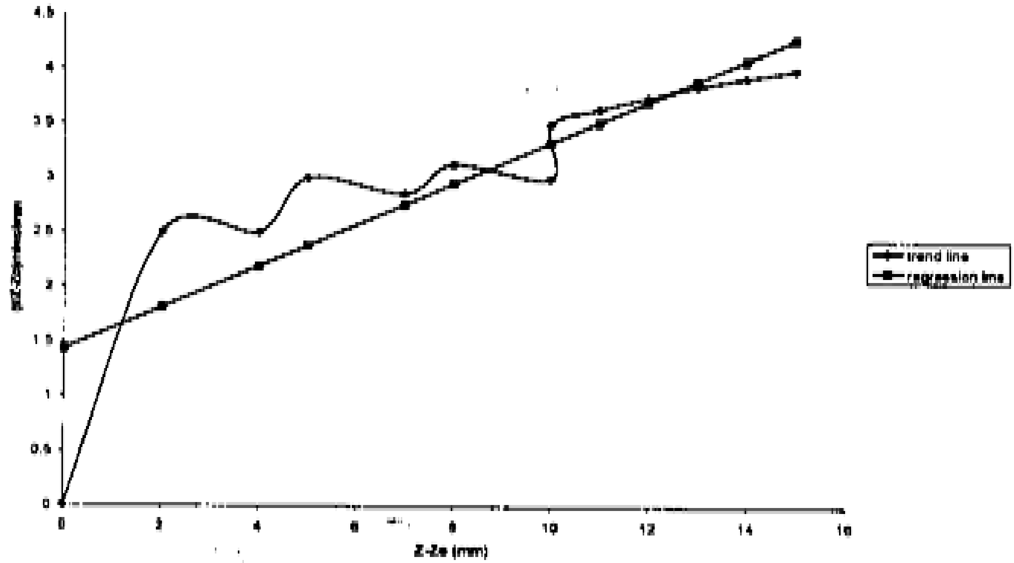

Fig. 3. Plot of (t/Z-Zo) min/mm vs (Z-Zo) mm at fan speed of 3057 rpm

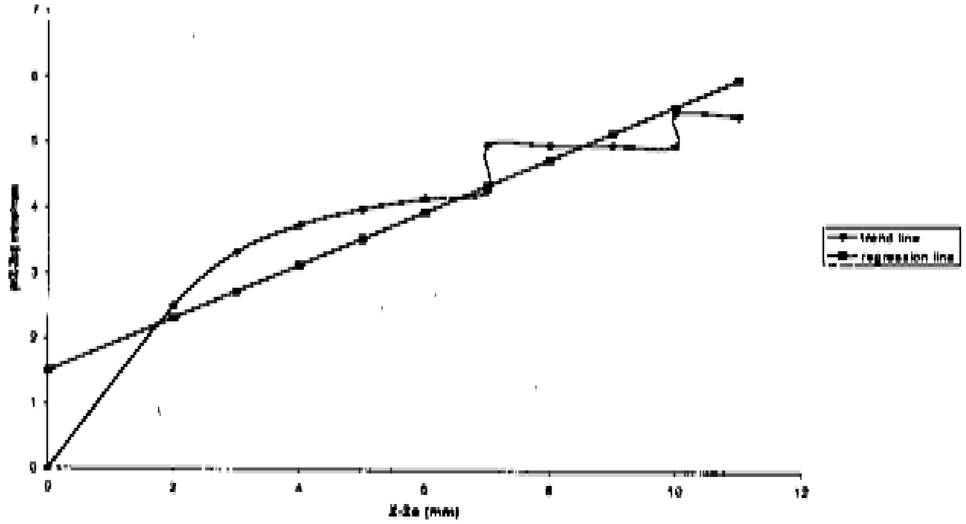

Fig. 4. Plot of (t/Z-Zo) min/mm vs (Z-Zo) mm at fan speed of 3044 rpm

However, these estimated values were widely inconsistent with the diffusive coefficients determined from the experimental approach (Figs. 3 and 4). The comparison between the estimated diffusivities and the experimentally-determined diffusivities show a 100% discrepancy for D_{AB} evaluated from the fan speeds of 3057 rpm and 3044 rpm respectively. This meant that the values of the experimentally-determined diffusivities were twice the values from estimations. These were suggestive of errors whose magnitudes overwhelm the approximately 7 to 25% prescribed (4).

For the experimentally-determined diffusivities, $6.83 \times 10^{-9} m^2/s$ determined from the fan speed of 3044 rpm was greater than $3.17 \times 10^{-9} m^2/s$ obtained from the fan speed of 3057 rpm. This suggests that in the experiment, the diffusivity decreased with increase in the fan speed since the diffusivity at the moderately high fan speed of 3044 rpm was greater than the diffusivity at higher fan speed of 3057 rpm. Thus, to enhance the system for improved results, it was suggested :

- that moderately lower fan speed should be applied in the course of the experiment.
- that calibrated solvent container with wider exposed surface area to air stream should be used in place of the graduated cylinder with very narrow exposed surface to air current.
- that solvents with boiling points lower than that of CCl_4 (76.8^0C) should be considered for the experimental condition of $T = 29^0C$ and $P = 1atm$.

CONCLUSION AND RECOMMENDATION

The experimentally-determined diffusivities for CCl_4 – air system proved not to be accurate method of diffusive coefficients measurements. The Wilke-Lee and Fuller *et al.* computational formulae techniques proved to be reliable methods as the diffusivities estimated from these models were almost consistent, with the deviation between them being in the negligible decimal range.

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