RESEARCH ARTICLES

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MEASUREMENT OF EFFECTIVE DIFFUSION COEFFICIENTS IN MIXTURES OF ACID AND BASE

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Summary

Effective diffusion coefficients have been measured for sodium hydroxide-hydrochloric acid mixtures at various concentration ratios and temperatures. The measurements were made in a simple diffusion cell. By applying a moving plane interface technique to the data, diffusivities were calculated. Effective Schmidt numbers of the mixtures were also evaluated. Dependency of effective Schmidt number on temperature was found to agree well with the theory.

Introduction

Diffusion coefficients are normally reported for binary mixture, such as HCl in H_2O and NaOH in H_2O, etc. There are cases when more than two components are involved and diffusion coefficients of such systems are called effective diffusion coefficients. An example of such system is an acid—base reaction which is always used in mass transfer and mixing studies.

First consider the diffusion of a passive or non-reacting mixture of two liquids in one dimensional geometry. Initially, on one side of the boundary is found a liquid containing a tracer material of concentration C_{Ao}, while the other side is filled with the same substance without tracer. For one dimensional diffusion, Fick's second law of diffusion can be written as:—

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \qquad (1)$$

The concentration distribution after a time t has elapsed is given by Crank[1] as:

$$C_A = \tfrac{1}{2}\, C_{Ao} \operatorname{erf}\left(\frac{\bar{x}}{2\sqrt{D_A t}}\right) \tag{2}$$

where C_A = concentration of the tracer at any point which is a function of distance $\bar{x}$ and time t

D_A = diffusion coefficient of the tracer material in the liquid

The boundary between fluid of concentration greater than C_A and fluid of concentration less than C_A moves according to:

$$\bar{x} = 2\sqrt{t}\,\sqrt{D_A}\,\operatorname{erf}^{-1} 2\left(\frac{C_A}{C_{Ao}}\right) \tag{3}$$

To be more specific, the equation above could describe the distribution of a dilute acid in water.

Assume that water on the other side of the boundary is replaced by a aqueous solution of base of concentration C_{Bo}. The reaction between A and B is instantaneous and irreversible

$$A + B \longrightarrow \text{Product} \tag{4}$$

and A and B cannot coexist on either side of the reaction zone. This case has been examined by Danckwerts[2], and Arrowsmith and Smith[3], who have shown that the boundary between acidic and basic fluid will move according to

$$\bar{x} = 2\sqrt{t}\,\sqrt{D_{eff}}\,\operatorname{erf}^{-1} 2\left(\frac{C_{Bo}}{C_{Ao} + C_{Bo}}\right) \tag{5}$$

The term D_{eff} will be called the effective diffusion coefficient of the reacting system and therefore is equivalent to the diffusion coefficient of the passive scalar being modelled. For a given mixture, the terms on the right hand side of equation (5) are constant except for $\sqrt{t}$.

Hence $\bar{x} = 2\sqrt{t}\,\lambda$

or $$\lambda = \frac{\bar{x}}{2\sqrt{t}} \tag{6}$$

in which $$\lambda = D_{eff}\operatorname{erf}^{-1} 2\left(\frac{C_{Bo}}{C_{Ao} + C_{Bo}}\right) \tag{7}$$

The effective diffusivity is related to the diffusivities of the individual species involved in the reaction and in principle, it should be possible to calculate them. Danckwerts[2] has provided the following relationship between the initial concentrations of the reactants, their diffusivities and the term λ:

$$\exp\left[-\lambda^2\left(\frac{1}{D_B} - \frac{1}{D_A}\right)\right] = \frac{C_{Ao}}{C_{Bo}}\sqrt{\frac{D_A}{D_B}}\left[\frac{1 - \operatorname{erf}\dfrac{\lambda}{\sqrt{D_B}}}{1 + \operatorname{erf}\dfrac{\lambda}{\sqrt{D_A}}}\right] \tag{8}$$

As part of this work λ has been measured experimentally and the results compared with equation (8).

Equations (7) and (8) hold for cases where the reaction is between molecules of A and molecules of B. In the case of the neutralization reaction where the reaction is ionic, the diffusion is more complicated. There is the added restraint of the ionic equilibrium for the acid, the base and the products of the reaction. Ions rather than molecules are diffusing. Therefore, the diffusivities of the reacting ions rather than the diffusivities of the acid and the base should be considered. An equation for the ionic diffusivity is given by Moore[4].

$$D_i = \frac{RT\gamma_i}{F^2 |z_i|} \tag{9}$$

where γ_i = equivalent ionic conductance, coulomb $\cdot$ cm^2 s^{-1} V^{-1}
z_i = electronic charge
F = Faraday's number, 94, 479 coulomb
R = constant, 8.31432 J K^{-1}
T = temperature, K

Tables of ionic conductivities are also available in Moore[4].

Methods

In order to obtain the effective diffusion coefficient of an acid-base solution, the apparatus shown in Fig. 1 and 2 was designed and set up. The basic requirement of the cell was that diffusion should be along one axis only with a minimum of convection effects. An acidic solution was filled in one side of the capillary cell and basic solution in the other side. Both solutions contained equal concentrations of the indicator Bromocresol Green. The blocks holding the two tubes were turned about the bolt bringing the axes of the tubes in line. The diffusion was observed by following the movement of the boundary between acidic and basic solutions. A travelling microscope was used to measure the displacement of the moving reaction zone as a function of time.

The experiments were divided into two parts, the measurement of the effect of concentration and the effect of temperature on effective diffusion coefficients. In the first part, experiments were carried out at 25 °C but at varied HCl/NaOH ratio from 2.18 to 4.12. This was done by fixing the concentration of NaOH at 0.0300 N and varying the concentration of HCl from 0.0655 N to 0.1235 N. In the second part, the temperature was varied from 18 °C to 50 °C.

Results and Discussion

Fig. 3 shows typical plots of experimental data for run number 1 and 6. The plot of the boundary displacement against the square root of time showed good linearity and reasonable extrapolation back to the origin. The reaction zones for all runs were well defined at all time and definite values could be obtained. Hence, D_{eff} values could be calculated with confidence.

Effective Diffusion Coefficient of HCl-NaOH Mixtures at Various Concentrations

In mass transfer study, Schmidt number is frequently used instead of diffusion coefficient. Schmidt number is a dimensionless group and is defined as:—

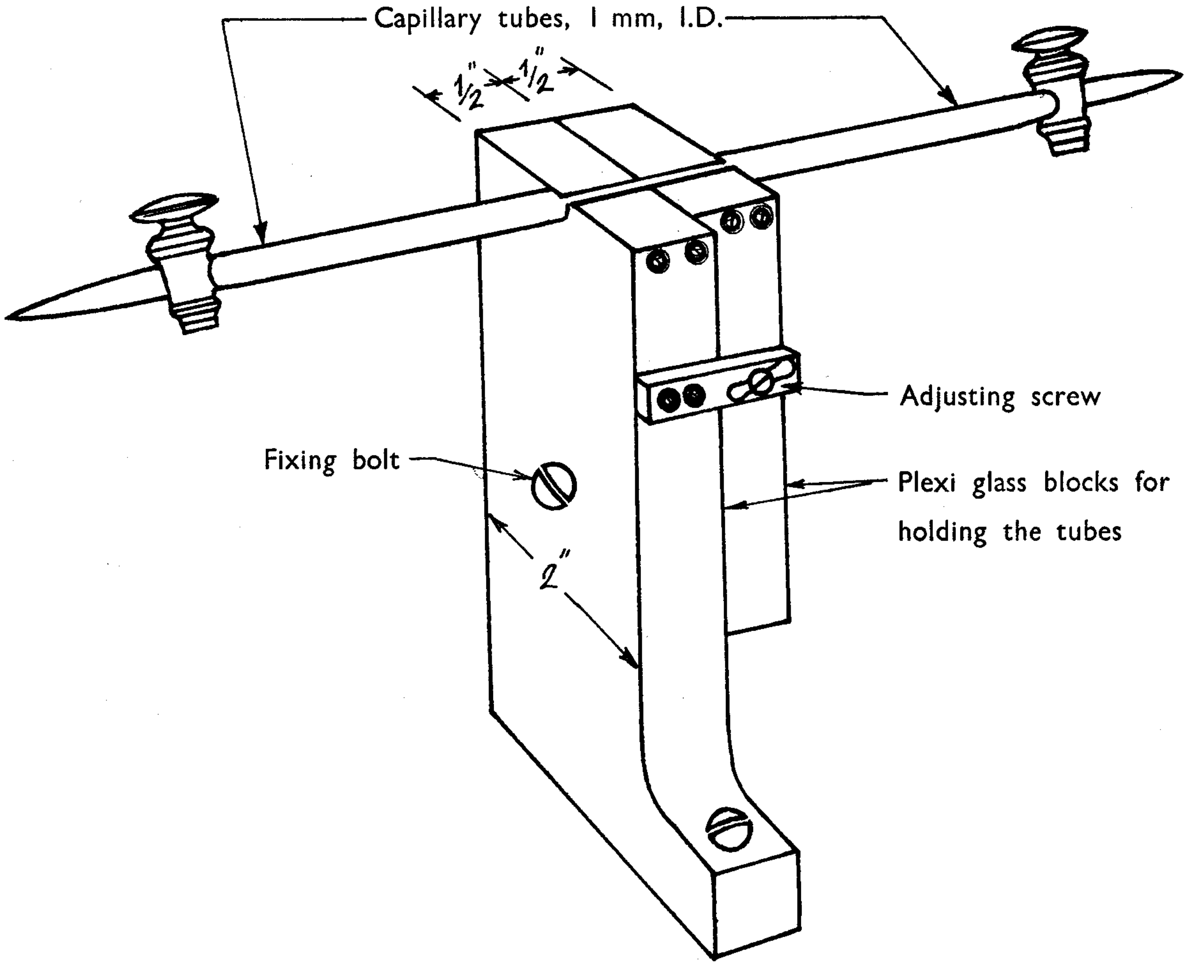

Fig. 1. Sketch of the diffusion cell.

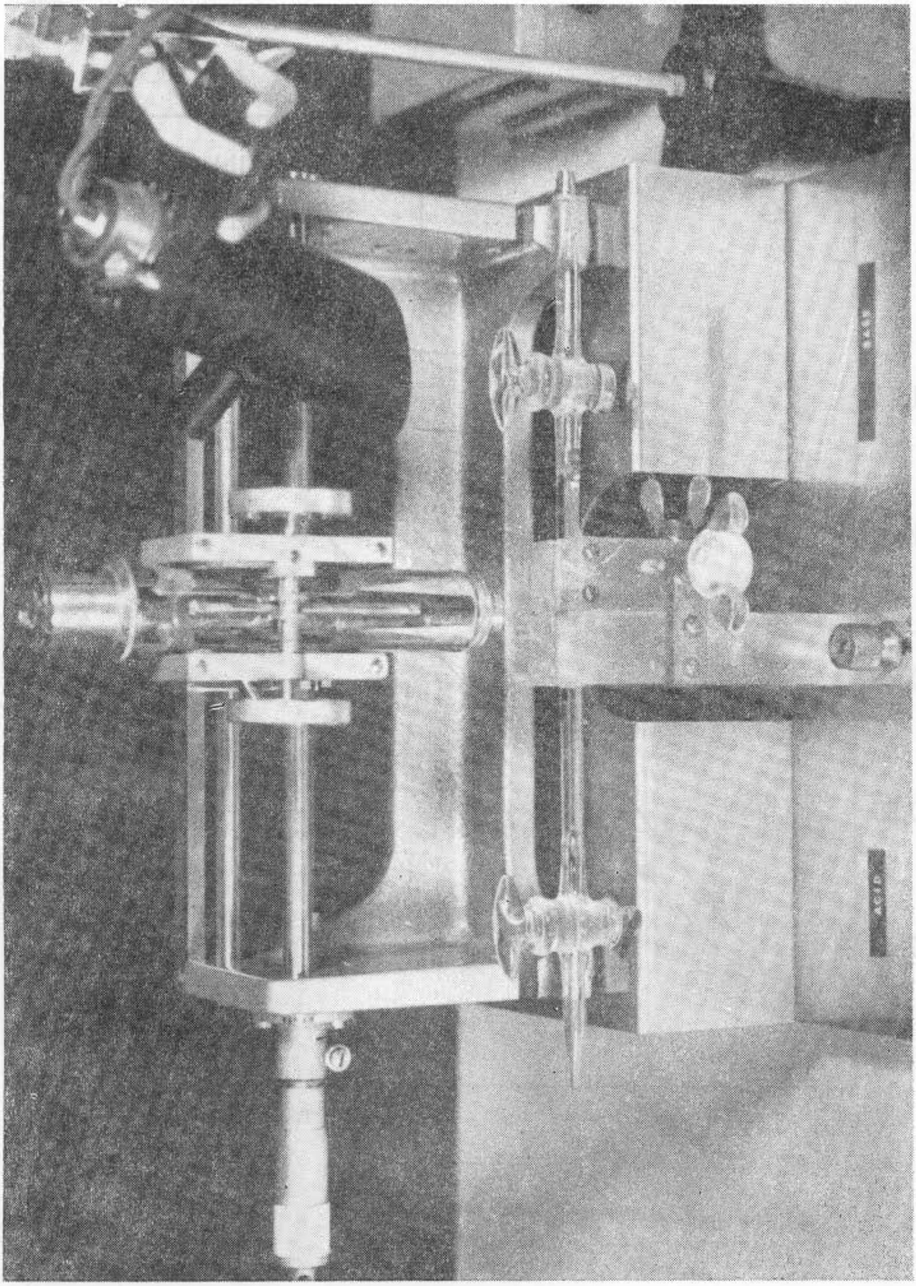

Fig. 2. Diffusion cell set-up.

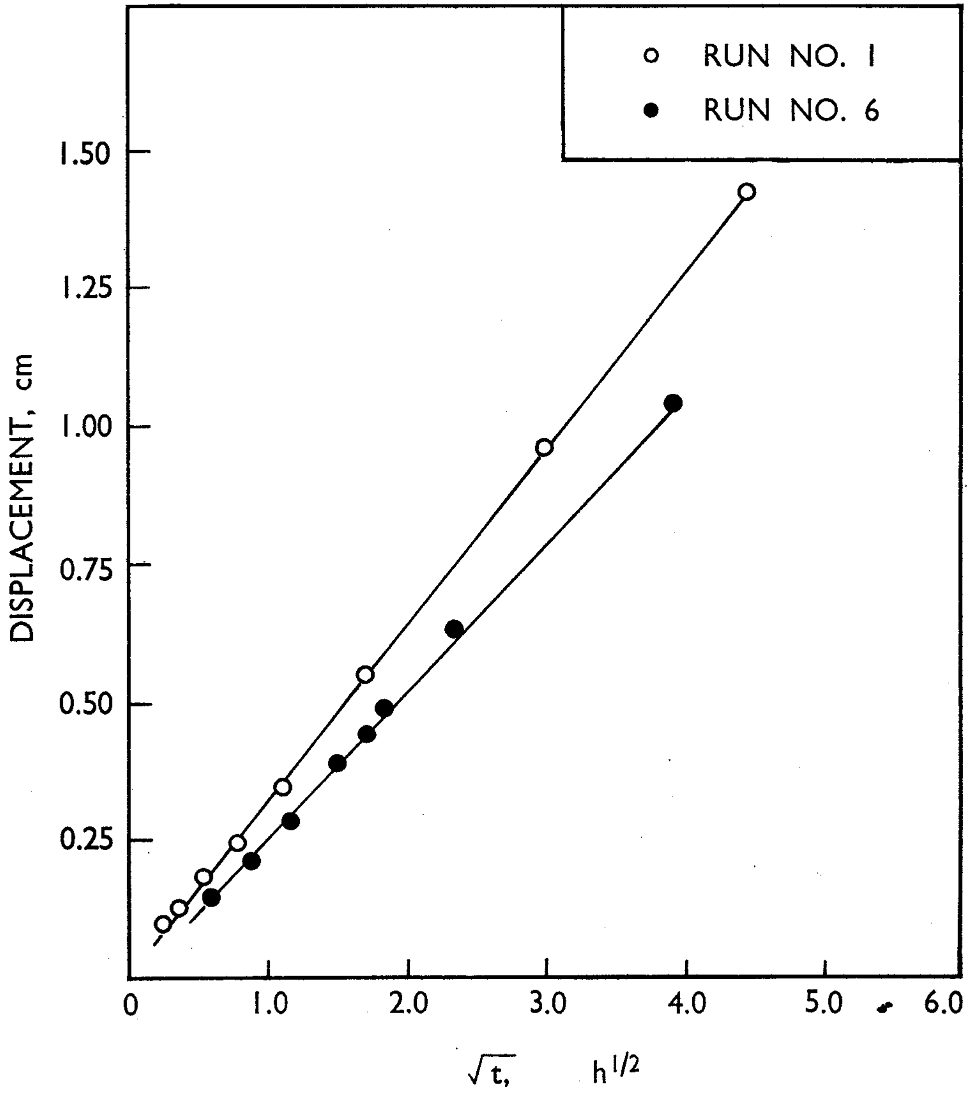

Fig. 3. Plot of displacement vs. $\sqrt{t}$.

$$Sc = \frac{\mu}{\rho D}$$

where μ = viscosity

ρ = density

The results of this study are also expressed in terms of Sc and are shown in Table I. It is clear that D_{eff} or Sc_{eff} varies little within the concentration range studied. No systematic relation between D_{eff} and C_{Ao}/C_{Bo} was found. This might be due to the low concentration range used. It was concluded that D_{eff} and Sc_{eff} under the concentration range used at 25 °C were approximately constant and had average values of 0.576×10^{-4} cm²/sec and 155, respectively.

TABLE I: D_{eff} AND Sc_{eff} AT 25 °C

Run No.	HCl N	NaOH N	HCl/NaOH	$D_{eff} \times 10^4$ cm²/s	Sc_{eff}
1	0.0655	0.0300	2.18	0.591	151
2	0.0734	0.0300	2.45	0.597	150
3	0.0900	0.0300	3.00	0.543	165
4	0.0975	0.0300	3.25	0.561	159
5	0.1235	0.0300	4.12	0.588	152

D_{eff}(ave.) = 0.576×10^4 cm²/s

Sc_{eff}(ave.) = 155

Effective Diffusion Coefficients of HCl-NaOH Mixtures at Various Temperatures

The results are shown in Table II. Temperature was varied at six different values from 18 °C to 50 °C. A plot of D_{eff} and Sc_{eff} vs. temperature is shown in Fig. 4.

TABLE II: D_{eff} AND Sc_{eff} AT VARIOUS TEMPERATURES

Run No.	HCl N	NaOH N	Temperature °C	$D_{eff} \times 10^4$ cm²/s	Sc_{eff}
6	0.0555	0.0300	18	0.488	217
1	0.0655	0.0300	25	0.591	151
7	0.0555	0.0300	30	0.643	125
8	0.1235	0.0300	35	0.704	103
9	0.1000	0.0555	40	0.770	85
10	0.1260	0.0600	50	1.130	49

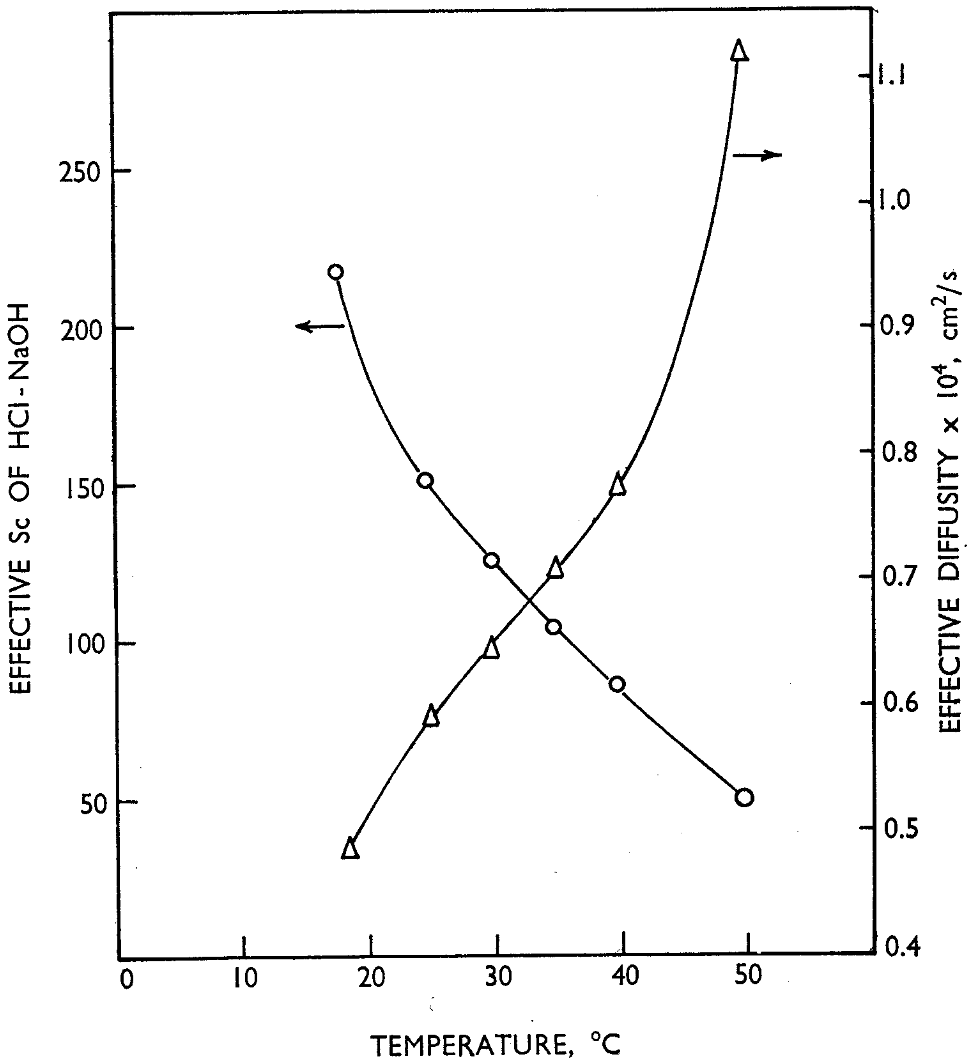

Fig. 4. Influence of temperature on effective diffusivity and effective Schmidt number of HCl-NaOH mixtures.

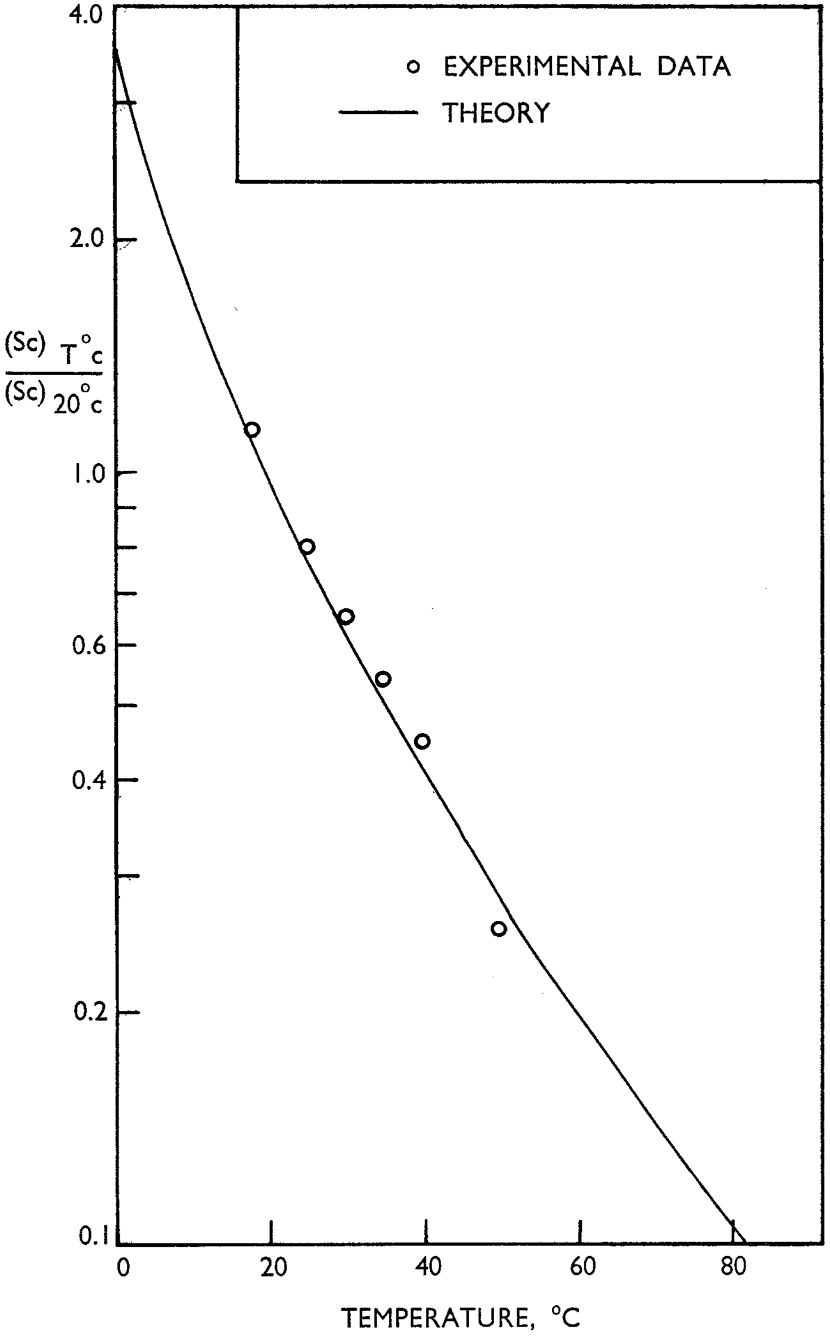

Fig. 5. Comparison between theoretical prediction and experimental work of the influence of temperature on Schmidt number of liquids.

For the diffusion of dilute solutions of non-reacting substances in Newtonian liquids, it is possible to predict theoretically the change of Sc with temperature. The calculation has been done by Spalding[5]. To compare the results of this work with the prediction of Spalding, a plot of the ratio of Sc at temperature T °C and 20 °C vs. T °C is shown in Fig. 5. It is identical with the calculated curve within experimental error.

To check the accuracy of the results and verify equation (8), the left-hand side and the right-hand side of equation (8) were calculated. This was done by substituting values of D_{H^+} and D_{OH^-} as calculated from equation (9), and the values of λ, C_{A_0}, C_{B_0} as found experimentally, into equation (8). The difference between the left-hand side and the right-hand side was found to be less than 8% for all runs. There appears to be good agreement between the theory and the experimental results.

References

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บทคัดย่อ

ได้ทำการวัดค่าสัมประสิทธิ์การแพร่ของของผสมระหว่างโซเดียมไฮดรอกไซด์และกรดเกลือที่ความเข้มข้นในอัตราส่วนและอุณหภูมิต่าง ๆ โดยใช้เครื่องมือแบบง่าย ๆ และได้คำนวณโดยใช้เทคนิคที่เรียกว่า moving plane interface นอกจากนี้ยังได้คำนวณค่า Schmidt number ของของผสมด้วยและได้พบว่า ค่านี้มีความสัมพันธ์กับอุณหภูมิตรงตามทฤษฎี.