Diffusivities of some organic amines in alcohols

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ABSTRACT

Experimental data on diffusivities involving organic amines diffusing in alcohols have been reported using the diaphragm cell technique. Experimental values have been compared with the predicted values by the generalized correlation proposed by Laddha and Smith.[6]

NOMENCLATURE

A_e Effective cross-sectional area of all pores in the diaphragm

C_{1A} Concentration of component 1 in compartment *A* from which component 1 diffuses, g mole/litre

C_{1B} Concentration of component 1 in compartment *B* to which component 1 diffuses, g mole/litre

$\triangle C_1$ Molar concentration differences of component 1

D Diffusion coefficient, calculated from the diaphragm cell equation, cm^2/sec

D_L Estimated value of diffusion coefficient by Laddha-Smith correlation, Equation (2)

l_e Effective pore length

t Time, sec.

T Absolute temperature, deg K

V_1, V_2 Molecular volumes of components 1 and 2

V_A, V_B Volume of compartments *A* and *B* of the diaphragm cell

Greek letters

    β Cell factor

    η viscosity, poise

Superscripts

o Initial

F final

1. INTRODUCTION

A KNOWLEDGE of liquid diffusivities is essential in mass transfer operations such as gas absorption, distillation, leaching, liquid-liquid extraction and crystallization. Attempts made to relate transport properties to molecular properties with the help of kinetic theory and absolute reaction rate theory have not been successful in obtaining a generalized correlation for estimation of liquid diffusivities and it is often necessary to obtain reliable diffusivity data by experimental techniques. The present investigation reports experimental data on diffusivities for organic amines at 30° C using the diaphragm cell technique.

2. EXPERIMENTAL

An improved type of diaphragm cell with magnetic stirring arrangement within the cell compartments was used. A sketch of the cell is shown in figure 1. The cell consisted of two equal compartments separated by a No. 4 sintered glass diaphragm about 30 mm in diameter and 2·3 mm in thickness. The whole cell was provided with an outside jacket with a narrow annulus for flow of water at constant temperature (at 30° C from a thermostat) during the experimental runs. Each compartment of the cell was provided with a glass encapsulated iron needle which could be rotated without touching the diaphragm or the side walls in a plane parallel to that of the diaphragm at a distance 5 mm away from it by means of an external rotating arm carrying bar magnet. The stirring speed was maintained at 120 rpm as recommended by Lewis.[1]

In the present investigation two identical cells were used for diffusion measurements. These were standardised using HCl-water system, with 0·1 N HCl diffusing into distilled water at 30° C. Using the reported diffusivity of $3·078 \times 10^{-5}$ cm^2/sec for HCl diffusion into water,[2] the value of the cell constant β was obtained according to the following cell equation:

$$D = \frac{1}{\beta t} \ln \frac{(\triangle C_1)^\circ}{(\triangle C_1)^F} \qquad (1)$$

where

β = cell constant representing the cell geometry, $\frac{A_e}{l_e}\left(\frac{1}{V_A} + \frac{1}{V_B}\right)$

$(\triangle C_1)^\circ$ = initial concentration difference = $C_{1A}^\circ - C_{1B}^\circ$

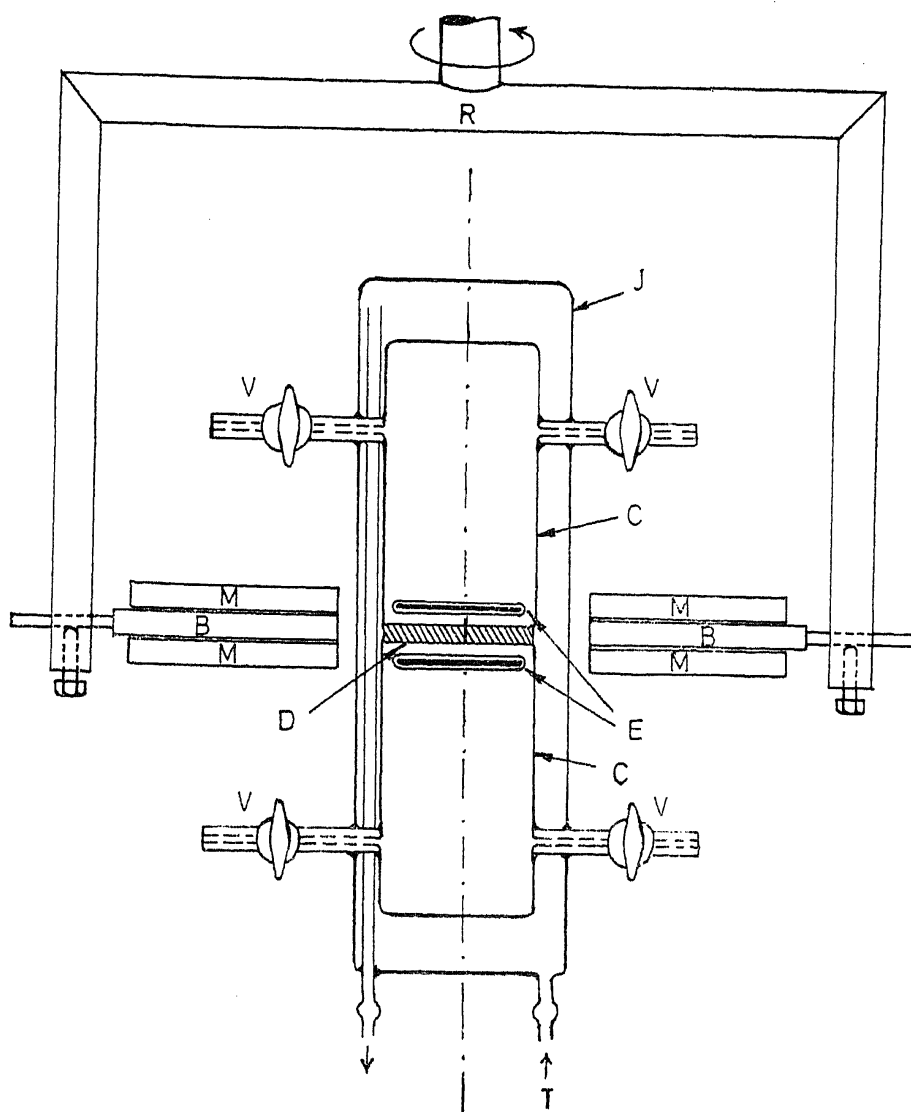$(\triangle C_1)^F$ = final concentration difference = $C_A^F - C_{1B}^F$

Figure 1. Jacketted diaphragm cell with magnetic stirrer arrangement. B. brass supports: C. cell compartments; D. sintered glass diaphragm; E. encapsulated iron needles; J. jacket; M. bar magnets; R. rotating arm; T. thermostatic liquid inlet; V. vacuum-proof stop-cocks.

a nd

$$D = \text{the diffusion coefficient.}$$

The above equation has been shown to give the time averaged integral diffusion coefficient by Gordon,[3] provided, quasi-steady state conditions were established within the pores of the diaphragm.[4] Barnes[5] has shown that these conditions are usually met by conducting a preliminary diffusion experiment lasting about 4 to 5 hours sufficient to set up the quasi-steady state making the original concentration within the pores of the diaphragm to disappear, when a diaphragm of proper dimensions (porosity 5–10 μ) are used. In the present standardisation experiments preliminary runs were conducted

Table 1. Physical properties of solutes and solvents used*

	B. pt. °C	Density at 30°C g/cm³	Viscosity at 30°C poise	Molecular volume by Kopp's Law cc/g mole	Latent heat vaporization at B. pt. g cal/gm
Benzyl amine	184·0 (184·5)	0·9800 (0·9820)	0·01672 (0·01680)	132·4	150·00
Dimethyl aniline	193·0 (193·5)	0·9580 (0·9560)	0·01200 (0·01170)	159·7	80·84
Ethyl aniline	203·0 (204·7)	0·970 (0·9580)	0·01680 (0·01700)	156·1	82·78
Diethyl amine	55·0 (55·5)	0·708 (0·7120)	0·0034 (0·00346)	111·9	91·01
n-butyl amine	73·0 (73·14)	0·738 (0·739)	0·0068 (0·0068)	110·4	91·00
Methanol	65·0 (64·7)	0·7950 (0·7920)	0·00512 (0·00515)	42·0	263·35
Isopropanol	82·0 (82·3)	0·8060 (0·8040)	0·0172 (0·0173)	81·4	160·57
n-butanol	118·0 (117·0)	0.8110 (0·8110)	0·0220 (0·0227)	103·6	141·12
isobutanol	107·0 (106·9)	0·804 (0·8099)	0·0285 (0·02864)	103·6	138·34
iso-amyl alcohol	131·0 (130·2)	0·8090 (0·8130)	0·0332 (0·0334)	125·8	105·40

* Figures in brackets represent the values reported in literature for pure liquids.

Table 2. Diffusivity data at 30° C

Solute	Solvent	Cell constant	Concentration difference ΔC_1°	ΔC^F_1	$t \times 10^{-5}$ sec	$D \times 10^5$ expt. cm²/sec	$D_L \times 10^5$ cm²/sec	% error
Benzyl amine	Methanol	0·4303	0·09081	0·02745	1·692	1·644	1·830	−11·30
Benzyl amine	Isopropanol	0·4303	0·08870	0·05913	1·692	0·5569	0·5845	− 4·95
Benzyl amine	n-butanol	0·3535	0·08764	0·06652	1·728	0·4517	0·4764	− 5·46
Benzyl amine	Isobutanol	0·3535	0·08659	0·06758	1·692	0·4144	0·3792	8·49
Benzyl amine	Isoamyl alcohol	0·4303	0·08870	0·06969	1·692	0·3315	0·3334	− 0·57
Dimethyl aniline	Methanol	0·4303	0·09142	0·02803	1·728	1·590	1·668	− 4·9
Dimethyl aniline	Isopropanoi	0·4303	0·11337	0·05973	1·800	0·5875	0·5522	6·00
Dimethyl aniline	n-butanol	0·4303	0·08533	0·06095	1·764	0·4433	0·4343	2·03
Dimethyl aniline	Isobutanol	0·3535	0·08728	0·07216	1·608	0·3347	0·3457	− 3·28
Dimethyl aniline	Isoamyl alcohol	0·4303	0·08167	0·06460	1·707	0·3192	0·3040	4·76
Ethyl aniline	Methanol	0·3535	0·09569	0·03719	1·692	1·581	1·688	− 6·76
Ethyl aniline	Isopropanol	0·3535	0·12312	0·08411	1·728	0·5769	0·5584	3·20
Ethyl aniline	n-butanol	0·3535	0·11336	0·08412	1·785	0·4735	0·4393	7·22
Ethyl aniline	Isobutanol	0·4303	0·09386	0·07192	1·728	0·3600	0·3497	2·88
Ethyl aniline	Isoamyl alcohol	0·3535	0·11580	0·09387	1·728	0·3439	0·3040	10·15
Diethyl amine	Isobutanol	0·4303	0·10670	0·0803	1·602	0·4126	0·4121	0·121
n- butyl amine	Isobutanol	0·3535	0·11220	0·0902	1·440	0·4288	0·4305	− 3·96
n-butyl amine	Isoamyl alcohol	0·4303	0·10340	0·0814	1·596	0·3482	0·3677	− 5·60

for 4 to 5 hours for quasi-steady state to be reached within the pores of the diaphragm before the actual experiments lasting about 48 hours were started. The average values of β thus obtained from an analysis of four independent runs for each cell used are

Cell (1) $\beta = 0 \cdot 353$

Cell (2) $\beta = 0 \cdot 4303$

The estimation of diffusivities for the various amines in different organic solvents were carried out in a similar manner as follows. After initial flushing of the two compartments of the diaphragm cell, the solution containing the solute is filled in the top compartment and the pure solvent in the bottom compartment. After attainment of quasi-steady state in the diaphragm the solutions were discarded and again filled up with fresh solutions. The experiment was conducted for about 48 hours after which the solutions were taken out and analysed for the solute concentration.

3. CHEMICALS USED

The various chemicals used were of BDH Analar quality. The solvents were purified by fractional distillation. Table 1 gives the list of solutes and solvents used and their physical properties.

4. RESULTS

The experimentally obtained diffusion coefficient data for 18 binary systems involving diffusion of amines in alcohols as solvents are reported in table 2 and compared with the predicted values according to the following generalized correlation of Laddha and Smith.[6]

$$\frac{D_L \eta_2}{T} (V_1)^{1/3} = 1 \cdot 892 \times 10^{-9} \left(\frac{V_2}{V_1} \right)^{0.16} \tag{2}$$

The maximum deviation of the experimental data from the predicted diffusivity values was found to be $\pm 12\%$.

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