MUTUAL DIFFUSION COEFFICIENTS OF SOME BINARY LIQUID SYSTEMS: XYLENE-*n*-ALKYL ALCOHOL

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Key Words:

The mutual diffusion coefficients for binary liquid systems of Xylene-*n*-alkyl alcohol at various compositions have been determined by the diaphragm cell method at 28°C. All the alcohols used from methanol to octanol were *n*-alkyl alcohols. The maximum possible experimental error was estimated to be 14%. The data were smoothed with a generalized correlation, giving the deviation from the experimental data to within 3.3% on average.

The present article reports experimentally determined mutual diffusion coefficients for the binary systems of Xylene-*n*-alkyl alcohol. Alcohols used were the first eight members of the homologous series of normal paraffinic alcohols.

1. Experimental

The diaphragm cell method (Stokes, 1950) was used to measure the integral diffusion coefficients, as it is the only successful method based on Fick's first law and combines experimental simplicity with accuracy. A G-4 grade diaphragm was used in the present work. A diagram of the apparatus is given in Fig. 1. The volume of each compartment was 70 ± 1 ml. The liquid layers adjacent to the two faces of the diaphragm were stirred by magnetic stirrers which were operated by rotating bar magnets fitted outside the cell. In each rotation of the magnets, the diaphragm was wiped twice.

The diaphragm cell was calibrated at 25°C by diffusing 0.1 N potassium chloride solution (kept in the bottom compartment) into double-distilled water. The equation used to calculate the integral diffusion coefficients is

$$D_{AB} = \frac{1}{\beta t} \ln \frac{C_{i,B} - C_{i,T}}{C_{f,B} - C_{f,T}} \quad (1)$$

For the water - 0.1 N KCl system, the diffusion coefficient, D_{AB} , to be used in equation 1 is obtained from

$$D_{AB} = \frac{\bar{C}_B D_{C,B} - \bar{C}_T D_{C,T}}{\bar{C}_B - \bar{C}_T} \quad (2)$$

where

$$\bar{C}_B = \frac{1}{2} (C_{i,B} + C_{f,B}) \quad (3)$$

and

$$\bar{C}_T = \frac{1}{2} (C_{i,T} + C_{f,T}) \quad (4)$$

where $\bar{C}_B$ and $\bar{C}_T$ are the averages of the initial and

Scale: 1:1

Item no.	Name	Specifications
1	Cell	Pyrex
2	Magnetic stirrers	Glass
3	Diaphragm	Porcelain no. 4
4,5	Stoppers	Ground glass B-24

Fig. 1. Diaphragm Cell

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Table 1.

Chemical	Purity	Density at 20°C in gcm ⁻³		Refractive index at 20°C		Viscosity
		literature*	measured	literature*	measured	kg/m.sec
Xylene**	—	—	0.8680	—	1.4980	0.731
Methanol	99.8	0.7917	0.7918	1.3312	1.3313	0.652
Ethanol	—	0.7893	0.8019	1.3624	1.3639	1.484
<i>n</i> -Propanol	99.00	0.8044	0.8040	1.3854	1.3848	2.176
<i>n</i> -Butanol	99.00	0.8098	0.8120	1.3993	1.4000	2.907
<i>n</i> -Pentanol	99.00	0.8144	0.8145	1.4099	1.4102	3.931
<i>n</i> -Hexanol	99.00	0.8166	0.8187	1.4179	1.4183	5.061
<i>n</i> -Heptanol	99.00	0.8219	0.8233	1.4241	1.4249	6.616
<i>n</i> -Octanol	99.00	0.8246	0.8233	1.4292	1.4293	8.397
Potassium chloride	99.5					
Silver nitrate	99.5					

* Handbook of Chemistry and Physics, 58th Edition, CRC Press, Cleveland (1978).

** Xylene available in the market is a mixture of *o*-, *m*- and *p*-xylene. The density of the xylene is close to that *m*- and *p*-xylene in the literature.

final concentrations in the bottom and top compartments, respectively.

The parameter $D_{C,B}$ is the integral diffusion coefficient which would be obtained in a run of vanishingly short duration with the initial concentrations, C_B and zero, on the bottom and top sides of the diaphragm respectively. Similarly, $D_{C,T}$ is also defined for the initial concentrations, C_T and zero. The values of $D_{C,B}$ and $D_{C,T}$ were obtained from the literature (Woolf and Tilley, 1967).

The cell constant, β , was measured after every 240 hours of usage, and the freshly determined β was used for the calculation of diffusion coefficients in subsequent runs. It was observed that after 960 hours of usage, the value of β changed by 2.5% of its initial value, which was 1917.9 m^{-2} .

In the diffusion runs, each of which lasted for over 24 hours, the bottom compartment was always filled with the solution having higher density. The temperature of the thermostat was kept at $28 \pm 0.05^\circ\text{C}$.

All the chemicals used in the present work were analytical reagent grade. All except ethanol were used without further purification; the ethanol was purified as described by Vogel, 1975. The refractive index and density of each of them, determined at 20°C , are given in Table 1 along with the literature value for comparison. Potassium chloride solutions were analysed volumetrically by freshly prepared silver nitrate solution.

Compositions of the xylene-alcohol solutions were analysed by Abbe refractometer with a resolution of 0.0001 refractive index (RI) units. The calibration of the refractive index data was done by measuring the refractive index at various known compositions of the respective mixture at 28°C .

2. Results

Table 1 lists the density, refractive index and viscosity of the pure components used in this study as well as those given in the literature.

The experimental diffusion coefficients for the xylene-*n*-paraffinic alcohol systems at various compositions are given in Table 2. Each datum is an average of three runs. The maximum possible error in each of the parameters affecting the diffusion coefficient (Eq. 1) is as follows:

for each of the composition parameters, $C_{i,B}$, $C_{i,T}$, $C_{f,B}$ and $C_{f,T}$, the maximum error is $0.5 \times 10^2 \text{ mol m}^{-3}$; for the cell constant, β , it is 5.0 m^{-2} .

The maximum error in the determination of time, t , is several orders of magnitude less than that for other parameters and hence is not reckoned in the calculation of overall accuracy. The resultant maximum possible error in the diffusion coefficient, D_{AB} , could then be as high as 14%.

We could not find any report on the experimental determination of diffusion coefficients of these systems in the literature and hence no comparative analysis could be made.

3. Correlation

The diffusion coefficient data for all compositions of any binary system under study were fitted in the generalized expression

$$(D_{AB})_i = \frac{1}{2}k_{1i} + k_{2i}\bar{x}_A + k_{3i}\cos(2\cos^{-1}\bar{x}_A) + k_{4i}\cos(3\cos^{-1}\bar{x}_A) \quad (5)$$

where $(D_{AB})_i$ is the diffusion coefficient of the i -th binary system; k_{1i} etc. are the adjustable constants for the i -th system; $\bar{x}_A = 2x_A - 1.0$, where x_A is the mole

Table 2. Integral diffusion coefficient at 28°C

Sl.No.	System	Mol fraction of xylene	Diffusion coefficient $\times 10^9$, m^2/sec	
			Experimental	Calculated Eqn.7
1.	Xylene-Methanol	0.0000	1.169	1.144
		0.0926	1.030	1.000
		0.1820	0.933	0.894
		0.3217	0.873	0.834
		0.5731	0.984	0.951
2.	Xylene-Ethanol	0.0000	1.070	1.057
		0.1067	0.924	0.916
		0.2400	0.812	0.801
		0.4162	0.800	0.767
		0.6590	1.007	0.971
3.	Xylene-Propanol	0.0000	0.917	0.962
		0.1461	0.783	0.806
		0.2983	0.674	0.704
		0.5015	0.670	0.713
		0.7128	0.889	0.966
4.	Xylene- <i>n</i> -Butanol	0.0000	0.799	0.870
		0.1555	0.698	0.732
		0.3250	0.606	0.625
		0.5209	0.637	0.636
		0.7340	0.919	0.919
5.	Xylene- <i>n</i> -Pentanol	0.0000	0.764	0.766
		0.1921	0.624	0.630
		0.3791	0.518	0.525
		0.5815	0.577	0.577
		0.7922	0.977	0.973
6.	Xylene- <i>n</i> -Hexanol	0.0000	0.672	0.666
		0.1978	0.561	0.556
		0.3912	0.447	0.440
		0.6048	0.489	0.499
		0.7967	0.921	0.896
7.	Xylene- <i>n</i> -Heptanol	0.0000	0.582	0.567
		0.2363	0.528	0.458
		0.4263	0.400	0.344
		0.6364	0.469	0.434
		0.8161	0.850	0.879
8.	Xylene- <i>n</i> -Octanol	0.0000	0.463	0.466
		0.2468	0.336	0.379
		0.4714	0.236	0.244
		0.6757	0.414	0.394
		0.8346	0.885	0.873

fraction of xylene.

Each of the four constants, k_1 , k_2 , k_3 and k_4 , thus obtained, was linearly correlated with a property P , which is defined as

$$P = \left[10.3 + \left(\frac{\eta_B}{\eta_A} \right)^{0.6} \right] / \left[0.731 + \left(\frac{V_B}{V_A} \right)^{0.6} \right] \quad (6)$$

where η_A and η_B are the viscosity of xylene and alcohol, respectively, and V_A and V_B are the molar volume at normal boiling point of xylene and alcohol.

The final generalized correlation of the diffusion coefficient with the property P for all the binary systems of xylene-alcohol is given by

$$D_{AB} \times 10^5 = 1.322 - 0.044P[1 - 0.372\bar{x}_A] + 0.300\bar{x}_A + [0.015P + 0.258] \cos [2 \cos^{-1} \bar{x}_A] + [0.016P - 0.052] \cos [3 \cos^{-1} \bar{x}_A] \quad (7)$$

The correlated data, given in Table 2, show good agreement with the experimental results, with an average deviation of about 3.3%.

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Nomenclature

$C_{i,B}, C_{i,T}$	= initial concentration of solven (xylene) in the bottom and top compartments, respectively	[mol m ⁻³]
$C_{f,B}, C_{f,T}$	= final concentration of solvent (xylene) in the bottom and top compartments respectively,	[mol m ⁻³]
D_{AB}	= mutual diffusion coefficient when A diffuses into B or vice versa	[m ² s ⁻¹]
$D_{C,B}, D_{C,T}$	= integral diffusion coefficient in a vanishingly short duration with initial concentrations being C_B in the bottom compartment and zero in the top compartment, or C_T in the top and zero in the bottom compartment	[m ² s ⁻¹]
$(D_{A,B})_i$	= diffusion coefficient in the i th binary system	[m ² s ⁻¹]
$k_{1i}, k_{2i}, k_{3i}, k_{4i}$	= constants in Eq. 1 for the i th binary system	[m ² s ⁻¹]
V_A, V_B	= molar volume of solvent (xylene) and alcohol used in the binary system, respectively	[m ³]
x_A	= mole fraction of solvent (xylene)	
β	= cell constant	[m ⁻²]
η_A, η_B	= viscosity of xylene and alcohol used in the binary system, respectively	[kg m ⁻¹ s ⁻¹]

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