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Mutual Diffusion Coefficients of Some Binary Liquid Systems: Benzene–*n*-Alkyl Alcohol

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The mutual diffusion coefficients for binary liquid systems of benzene–*n*-alkyl alcohol at various compositions have been determined by the diaphragm cell method at 28 °C. The alcohols used were the members of *n*-paraffinic alcohols ranging from C_1 to C_8. The maximum possible experimental error is 14%. The data were fitted with a generalized correlation, giving the deviation from the experimental data to within 2.75%, on average.

The present article reports the experimentally obtained diffusion coefficients for the binary systems of benzene–alcohols. The alcohols used were the first eight members of the homologous series of normal paraffinic alcohols.

Experimental Section

The diaphragm cell method (*1*) 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. The description of the apparatus is given in Figure 1. The volume of each compartment is 70 mL only, differing by not more than 1.0 mL. The liquid layers adjacent to the surfaces of the diaphragm were stirred by magnetic stirrers that were operated by rotating permanent bar magnets fitted outside the cell. In each rotation of the magnets, the diaphragm is wiped twice. The rate of rotation of the stirrers was kept constant at 40 rotations/min.

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

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

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

$$D_{AB} = \frac{C_B D_{C_B} - C_T D_{C_T}}{C_B - C_T} \quad (2)$$

where

$$C_B = \tfrac{1}{2}(C_{i,B} + C_{f,B}) \quad (3)$$

and

$$C_T = \tfrac{1}{2}(C_{i,T} + C_{f,T}) \quad (4)$$

The parameter D_{C_B} is an integral diffusion coefficient that would be found in a run of vanishingly short duration with the initial concentrations C_B and zero on two sides of the diaphragm, respectively. In a similar way D_{C_T} is defined for initial concentrations C_T and zero. The values of D_{C_B} and D_{C_T} were obtained from the work of Tilley and Woolf (*2*).

The cell constant, β, was measured after every 240 h of cell usage. The value of β after a period of 960 h of cell usage was found to have increased by about 2.5% of the initial value of 1917.9 m^{-2}.

In the diffusion runs, each of which was of about 24-h duration, the bottom compartment was always filled with higher density solutions. The temperature of the water bath was maintained at 28 ± 0.5 °C.

All the chemicals used in the present work were analytical reagent grade. All of them, except ethanol, were used without further purification, while the latter has been purified as described by Vogel (*3*). Potassium chloride solutions were analyzed by freshly prepared silver nitrate solution.

Compositions of the benzene–alcohol solutions were analyzed by an 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 mixture at 28 °C.

Results

Table I lists the densities, refractive indices, and viscosities of the pure components used in this study, as well as those given in the literature.

The experimental diffusion coefficients for the benzene–*n*-paraffinic alcohol systems at various compositions are given in Table II. Each datum is an average of three runs, the variations in diffusion coefficients obtained from individual runs being within 2% from the average. The mole fraction of benzene given in Table II, column 3, indicates the initial composition of the respective benzene–alcohol mixture in the top compartment, into which benzene from the bottom compartment (containing pure benzene) diffuses and from which the alcohol diffuses into the bottom compartment. The maximum 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 × 10^2 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 the other parameters. The resultant maximum possible error in the diffusion coefficient, D_{AB}, could then be as high as 14%.

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Table I. Physical Properties of Pure Components

chemical	purity	density at 20 °C, g cm^{-3}		refractive index at 20 °C		viscosity, kg/(m s)
		lit.[a]	measd	lit.[a]	measd	
benzene	99.8	0.8790	0.8784	1.5011	1.5006	0.646
methanol	99.8	0.7917	0.7918	1.3312	1.3313	0.652
ethanol		0.7893	0.8019	1.3624	1.3639	1.484
n-propyl alcohol	99.00	0.8044	0.8040	1.3854	1.3848	2.176
n-butyl alcohol	99.00	0.8098	0.8120	1.3993	1.4000	2.907
n-pentyl alcohol	99.00	0.8144	0.8145	1.4099	1.4102	3.931
n-hexyl alcohol	99.00	0.8166	0.8187	1.4179	1.4183	5.061
n-heptyl alcohol	99.00	0.8219	0.8233	1.4241	1.4249	6.616
n-octyl alcohol	99.00	0.8246	0.8233	1.4292	1.4293	8.397
potassium chloride	99.5					
silver nitrate	99.5					

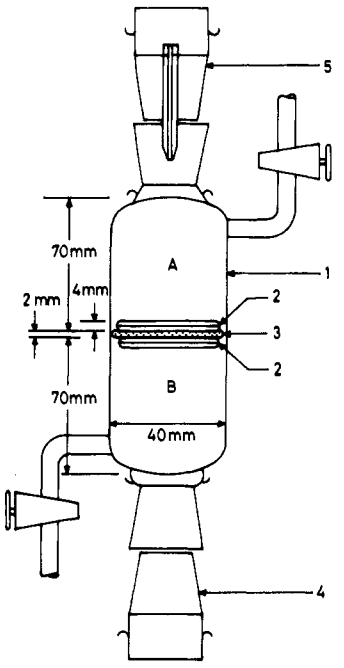
[a] *Handbook of Chemistry and Physics*, 58th ed.; CRC Press: Cleveland, OH, 1978.

Table II. Integral Diffusion Coefficients at 28 °C[a]

no.	system	$C_{i,B} - C_{i,T} \times 10^{-3}$, mol m^{-3}	mole fraction of benzene	diffusion coeff × 10^9, m^2/s	
				exptl	calcd (eq 7)
1	benzene–methyl alcohol	11.140	0.0000	1.289	1.278
			0.0742*	1.870*	
		8.860	0.1046	1.144	1.147
			0.1629*	1.560*	
		6.806	0.2244	1.045	1.038
			0.3123*	0.930*	
		4.508	0.4006	1.006	1.068
			0.4575*	0.700*	
			0.6449*	0.610*	
		2.206	0.6480	1.239	1.198
2	benzene–ethyl alcohol	11.140	0.0000	1.203	1.182
			0.0092*	1.650*	
		8.956	0.1366	1.039	1.044
			0.1629*	1.190*	
		6.968	0.2798	0.926	0.937
			0.3123*	0.920*	
			0.4911*	0.720*	
		4.410	0.4977	0.908	0.932
			0.7045*	0.820*	
		2.055	0.7417	1.268	1.295
3	benzene–*n*-propyl alcohol	11.140	0.0000	1.141	1.078
		8.933	0.1719	0.979	0.940
		6.532	0.3721	0.829	0.822
		4.203	0.5810	0.853	0.897
		2.048	0.7886	1.266	1.329
4	benzene–*n*-butyl alcohol	11.140	0.0000	0.928	0.963
		9.008	0.1952	0.818	0.842
		6.920	0.3847	0.722	0.725
		4.451	0.6064	0.818	0.808
		2.081	0.8171	1.335	1.327
5	benzene–*n*-pentyl alcohol	11.140	0.0000	0.838	0.865
		8.805	0.2437	0.717	0.736
		6.737	0.4426	0.624	0.628
		4.552	0.6376	0.754	0.750
		2.076	0.8415	1.345	1.348
6	benzene–*n*-hexyl alcohol	11.140	0.0000	0.755	0.757
		8.720	0.2798	0.599	0.631
		6.475	0.5022	0.508	0.527
		4.313	0.6891	0.724	0.733
		2.156	0.8538	1.277	1.324
7	benzene–*n*-heptyl alcohol	11.140	0.0000	0.658	0.648
		8.547	0.3244	0.518	0.514
		6.299	0.5488	0.449	0.434
		4.123	0.7293	0.752	0.726
		2.026	0.8769	1.328	1.375
8	benzene–*n*-octyl alcohol	11.140	0.0000	0.553	0.539
		9.142	0.2789	0.437	0.475
		6.998	0.5117	0.348	0.318
		4.690	0.7089	0.604	0.557
		2.207	0.8776	1.281	1.307

[a] Values marked with an asterisk are experimental data at 11 °C (ref 4).

Of the systems studied here, the only data available in the literature are for the diffusion coefficient of benzene–methanol and benzene–ethanol at 11 °C (*4*). These are included in Table II for comparison.



Scale 1:1

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

Figure 1. Diaphragm cell.

Correlation

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

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

where $(D_{AB})_i$ is the diffusion coefficient of the ith binary system, k_{1i}, etc., are the adjustable constants for the ith system, and $\bar{x}_A = 2x_A - 1.0$, where x_A is the mole fraction of benzene. All the k_1 values, thus obtained, were correlated with a property, P, of the respective binary system by a single linear equation. The same was done for all k_2's, k_3's, and k_4's, respectively. The property, P, for any binary system is defined as

$$P = [M_A^{0.5} + (\eta_B/\eta_A)^{0.6}]/[\eta_A(V_B/V_A)^{0.6}] \quad (6)$$

where M_A is the molecular weight of the solvent benzene and η_A, η_B, V_A, and V_B are the viscosities and molar volumes of benzene and alcohols, respectively.

The final generalized correlation of the diffusion coefficient with the property, P, for all the binary systems of benzene–alcohol is given by

$$D_{AB} \times 10^5 = 1.556 - 0.040P[1 - 0.323\bar{x}_A] + 0.423\bar{x}_A + [0.012P + 0.338]\cos(2\cos^{-1}\bar{x}_A) + [0.014P - 0.010]\cos(3\cos^{-1}\bar{x}_A) \quad (7)$$

The correlated data, given in Table II, show good agreement with the experimental results with an average deviation of about 2.5%.

Nomenclature

$C_{i,B}$, $C_{i,T}$ = initial concentration of solvent (benzene) at the bottom and top compartments, respectively, mol m^{-3}

$C_{f,B}$, $C_{f,T}$ = final concentration of solvent (benzene) at 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, respectively, m^2 s^{-1}

$(D_{AB})_i$ = diffusion coefficient in the ith binary system, m^2 s^{-1}

k_{1i}, k_{2i}, k_{3i}, k_{4i} = constants in eq 5 for the ith binary system, m^2 s^{-1}

M_A = molecular weight of solvent (benzene)

V_A, V_B = molar volume of solvent (benzene) and alcohol used in the binary system, respectively, m^3

x_A = mole fraction of solvent (benzene)

Greek Letters

β = cell constant, m^{-2}

η_A, η_B = viscosity of benzene and alcohol used in the binary system, respectively, kg m^{-1} s^{-1}

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; *n*-propyl alcohol, 71-23-8; *n*-butyl alcohol, 71-36-3; *n*-pentyl alcohol, 71-41-0; *n*-hexyl alcohol, 111-27-3; *n*-heptyl alcohol, 111-70-6; *n*-octyl alcohol, 111-87-5; benzene, 71-43-2.

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