Mutual Diffusion Coefficients of the Systems $C_6H_5Br + C_2H_3N$, $C_6H_5Br + C_6H_{14}$, and $C_6H_5Br + C_2H_6O$

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Mutual diffusion coefficients of the systems $C_6H_5Br + C_2H_3N$, $C_6H_5Br + C_6H_{14}$, and $C_6H_5Br + C_2H_6O$ have been measured at 20 °C by the quasi-elastic light scattering technique as a function of composition. Data of the refractive index of these mixtures are also reported.

The use of the quasi-elastic light scattering technique for measuring mutual diffusion coefficients in binary liquid mixtures has been described in the works of Gulari et al. (*1*), Czwornlak et al. (*2*), and Krahn et al. (*3*). Some recent measurements by this technique were reported by Siddiqi et al. (*4*). In this work the method is used to provide diffusion data for the binary mixtures of bromobenzene with acetonitrile, *n*-hexane, and ethanol. To our knowledge, no experimental data of diffusion coefficients have yet been published for these mixtures.

Experimental Method

We use the experimental setup described by Krahn et al. (*3*) with some minor modifications. The basic formula from which the binary diffusion coefficient D_{AB} is evaluated reads

$$F_D(\mathbf{K},t) = F_{0,D} \exp(-D_{AB}\cdot\mathbf{K}^2\cdot t) + C \qquad (1)$$

where the autocorrelation function F_D is expressed in terms of its amplitude $F_{0,D}$, the scattering wave vector **K**, and time t. Equation 1 is valid for mixtures in which the thermal diffusivity is much larger than D_{AB}.

The magnitude of the scattering wave vector **K** is given by

$$K = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right) \qquad (2)$$

where n_0 is the refractive index, λ the laser wavelength, and θ the observation angle of the scattered light. A helium–neon laser with λ = 632.8 nm was used with a maximum output of 30 mW. The scattered light was recorded at an angle of 7°. A photomultiplier, EMI 9863 KB 100, was used with an anode voltage of 1500 or 1700 V. With sampling times between 40 and 100 μs, the digital correlator (Malvern K 7025) produced optimum results. The measuring time was between 5 and 45 min.

A double-wall cylindrical Hellmar optical cell, Model 165, with a path length of 5 cm, was used for the measurements. The temperature of the sample in the cell was maintained at 20 ± 0.1 °C with the help of a precision circulation constant-temperature bath. The mixtures investigated were produced by weighing appropriate portions of components on a precision scale (Satorius, Type 2842), filling the cell, and shaking vigorously for about 5 min to achieve homogeneity. A period of about 10 h of sedimentation was allowed before reproducible experimental results were obtained. A series of five to ten individual measurements were performed for each sample. The refractive index was measured after each light scattering experiment by an Abbe refractometer (Zeiss, Type B).

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Table I. Diffusion Coefficient and Refractive Index of the System Bromobenzene (1) + Acetonitrile (2) at 20 °C

x_1	D_{AB}/ (10^{-5} cm^2/s)	ΔD_{AB}/ (10^{-5} cm^2/s)	ΔD_{AB}/%	n_0
0				1.345
0.05	2.26	0.13	5.8	1.365
0.10	1.86	0.05	2.7	1.382
0.15	1.62	0.02	1.2	1.400
0.20	1.40	0.02	1.4	1.416
0.25	1.31	0.02	1.9	1.430
0.30	1.19	0.01	0.8	1.442
0.35	1.16	0.01	0.9	1.456
0.40	1.07	0.02	1.9	1.471
0.45	1.06	0.02	1.8	1.480
0.50	1.04	0.02	1.9	1.490
0.55	1.04	1.02	1.9	1.500
0.60	1.06	0.02	1.9	1.507
0.65	1.10	0.02	1.8	1.516
0.70	1.17	0.02	1.7	1.522
0.75	1.20	0.02	1.3	1.530
0.80	1.28	0.03	2.4	1.538
0.85	1.37	0.08	5.9	1.543
0.90	1.5	0.15	10.0	1.549
0.94	1.57	0.20	12.8	1.552
1				1.559

Table II. Diffusion Coefficient and Refractive Index of the System Bromobenzene (1) + *n*-Hexane (2) at 20 °C

x_1	D_{AB}/ (10^{-5} cm^2/s)	ΔD_{AB}/ (10^{-5} cm^2/s)	ΔD_{AB}/%	n_0
0				1.375
0.05	3.71	0.58	15.5	1.383
0.10	3.43	0.26	7.6	1.391
0.15	2.96	0.14	4.7	1.400
0.20	2.66	0.16	6.0	1.410
0.25	2.22	0.19	8.5	1.417
0.30	2.02	0.07	3.5	1.426
0.35	1.85	0.07	3.8	1.434
0.40	1.72	0.07	4.0	1.443
0.45	1.59	0.07	4.4	1.452
0.50	1.47	0.03	2.1	1.460
0.55	1.41	0.04	2.7	1.470
0.60	1.38	0.05	3.6	1.480
0.65	1.30	0.03	2.3	1.490
0.70	1.28	0.03	2.3	1.500
0.75	1.25	0.03	2.4	1.509
0.80	1.23	0.04	3.6	1.518
0.85	1.27	0.04	3.1	1.528
0.90	1.30	0.05	3.8	1.539
0.95	1.44	0.04	2.5	1.550
1				1.560

Results

The experimental results for the mutual diffusion coefficients and refractive indices are summarized in Tables I–III. Each of the reported data points for the diffusion coefficient is the average of five to ten individual measurements of D_{AB}. This procedure allows one to compute an error bound ΔD_{AB}, defined so that $D_{AB} \pm \Delta D_{AB}$ includes all of the measured results. Figure 1 demonstrates the stabilization of the experimental result for the system bromobenzene (1) + ethanol (2) at x_1 =

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Table III. Diffusion Coefficient and Refractive Index of the System Bromobenzene (1) + Ethanol (2) at 20 °C

x_1	D_{AB}/ (10^{-5} cm^2/s)	ΔD_{AB}/ (10^{-5} cm^2/s)	ΔD_{AB}/%	n_0
0.136	4.78	0.1	2.1	1.409
0.259	3.49	0.07	1.9	1.439
0.333	3.25	0.11	3.6	1.456
0.399	2.88	0.19	6.5	1.470
0.517	2.17	0.04	1.8	1.492
0.686	2.30	0.13	6.0	1.520
0.767	2.58	0.07	2.6	1.535
0.797	2.65	0.06	2.2	1.535
0.842	1.65	0.06	2.5	1.541
0.866	3.06	0.09	3.1	1.545
0.927				1.551
0.941	3.8	0.2	5.3	1.552

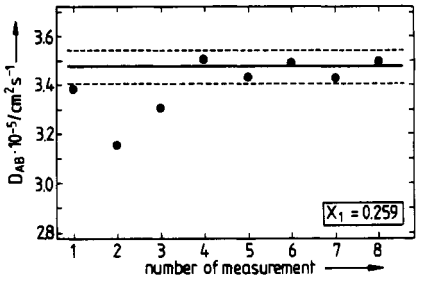

Figure 1. Stabilization of the experimental diffusion coefficient within ±2% with increasing time at 20 °C (system bromobenzene (1) + ethanol (2) at x_1 = 0.259).

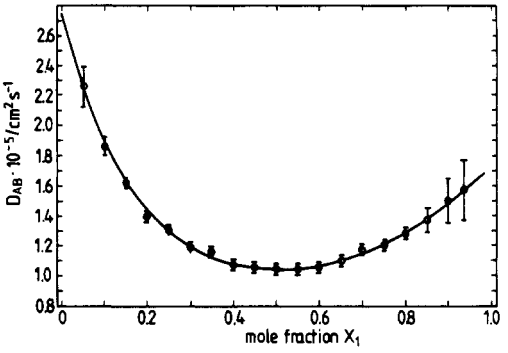

Figure 2. Mutual diffusion coefficient for the bromobenzene (1) + acetonitrile (2) system at 20 °C: Φ, experimental result; —, eq 3 [n = 4; x_0 = 0; C_1 = 1.009; C_2 = -4.3; C_3 = 5.58; C_4 = -1.74].

0.259 with increasing time. Experimental results were only accepted after stabilization; i.e. the first measurements were not included in the calculation of ΔD_{AB}. The individual measurements were made about every 2 h. The results of the diffusion coefficients are displayed graphically in Figures 2–4. The curves are calculated from the equation

$$D_{AB} = \exp[\sum_{i=1}^{n} C_i (x_1 - x_0)^{i-1}] \qquad (3)$$

and the constants n, x_0, and C_i are given in the figure captions. It should be noted that the use of eq 3 outside of the concentration range of the measurements may yield unreliable results.

Discussion

The measured diffusion coefficients show a satisfactory degree of internal consistency. In all cases, the relative amplitude of the correlation function is rather small at extreme concentrations, resulting in considerable experimental noise. To some extent, this effect could be compensated for by increasing the time of a measurement, for which a maximum of 45 min was chosen. To check the influence of laser-induced heating effects of the sample, measurements were performed with various laser outputs. No significant effects were observed. The dominant source of imprecision of these measurements is lack of quality of the sample, e.g. dust, or uncertainties in composition due to different evaporation rates of the components during the preparation.

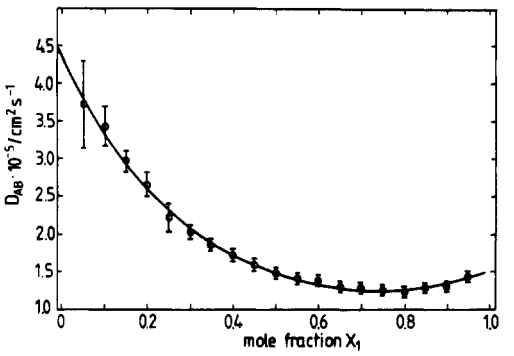

Figure 3. Mutual diffusion coefficient for the bromobenzene (1) + n-hexane (2) system at 20 °C; Φ, experimental result; —, eq 3 [n = 4; x_0 = 0; C_1 = 1.47; C_2 = -2.74; C_3 = 6.5; C_4 = -1.05].

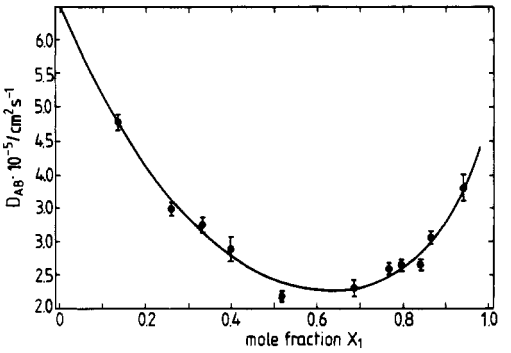

Figure 4. Mutual diffusion coefficient for the bromobenzene (1) + ethanol (2) system at 20 °C; Φ, experimental result; —, eq 3 [n = 4; x_0 = 0; C_1 = 1.87; C_2 = -2.16; C_3 = -1.06; C_4 = 2.92].

Glossary

C_i	constant in eq 3
D_{AB}	mutual diffusion coefficient
F_D	autocorrelation function
K	scattering wave vector
n_0	refractive index
t	time
x_1	mole fraction of component 1
x_0	constant in eq 3
λ	wavelength
θ	observation angle of scattered light

Registry No. C_2H_3N, 75-05-8; C_6H_5Br, 108-86-1; C_6H_{14}, 110-54-3; C_2H_6O, 64-17-5.

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