Restricted Diffusion in Binary Organic Liquid Mixtures

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Restricted diffusion has been used to determine the mutual diffusion coefficients of binary organic systems. The concentration difference between two fixed points in the cell was measured by holographic interferometry. After a short description of this method, the results of a test at 25 °C with the mixture CCl_4–C_6H_{12} are presented. The differential diffusion coefficients determined at temperatures of 15, 20, 25, and 30 °C are given for the four following systems: CCl_4–C_2HCl_3, CCl_4–1,2-$C_2H_4Cl_2$, CCl_4–C_2H_5OH, C_2HCl_3–1,2-$C_2H_4Cl_2$. For each mixture, the relationship $[\ln D = A + B/T]_N$ has been verified and the activation energy for diffusion has been calculated at the mean temperature of 25 °C.

The restricted diffusion method of Harned and French (10) is commonly used for the determination of mutual diffusion coefficients in dilute solutions; in a recent article, Newman and Chapman (12) have extended its range to concentrated electrolyte solutions. In concentrated solutions, the differences in concentration are no longer measured by conductometry, but by the optical method of Rayleigh interferometry; the results obtained for aqueous solutions of potassium chloride are excellent.

This method, which allows the differential, mutual, diffusion coefficients to be obtained directly, has been extended in the present work to organic mixtures. Holographic interferometry, which we earlier used in a study of free diffusion (7, 18), has here been adapted to the measurement of concentration differences. After an explanation and analysis of the experimental method, the mutual diffusion coefficients are presented for four different temperatures and the entire range of concentration for the following systems: tetrachloromethane–trichloroethene; tetrachloromethane–1,2-dichloroethane; 1,2-dichloroethane–trichloroethane; carbon tetrachloride–ethanol.

Simplified Analysis of Restricted Diffusion

In binary organic mixtures, the molar diffusion flux of the component i with respect to the mean molar velocity v is (3)

$$J_i = c_i(v_i - v) \tag{1}$$

where c_i is the molar concentration and v_i is the velocity of the component i with respect to stationary axes.

The fundamental law controlling the diffusion phenomenon in a chosen x direction may be expressed for this reference system as

$$J_i = -cD\frac{dN_i}{dx} \tag{2}$$

with c the molar density of the solution, D the mutual diffusion coefficient, and N_i the concentration expressed as a mole fraction.

Consider a cell of height a, in which diffusion is taking place between two mixtures of similar concentration. Equation 2 may be integrated by considering the diffusion coefficient as constant and by taking into account the continuity equation

$$-\text{div } J_i = c\frac{\partial N_i}{\partial t} \tag{3}$$

with the boundary conditions

$$\frac{\partial N_i}{\partial x} = 0 \tag{4}$$

for $x = 0$ and $x = a$. A derivation analogous to that of Harned and French leads to the following expression for the difference in concentration, after a sufficient length of time, between a point at $x = a/6$ and one at $x = 5a/6$:

$$\Delta N = N\left(\frac{a}{6}\right) - N\left(\frac{5a}{6}\right) = 2B \exp\left(-\frac{Dt\pi^2}{a^2}\right) \tag{5}$$

A graph of $\ln(\Delta N)$ as a function of time should give a straight line, the slope of which may be used to calculate D provided that the exact height of the cell is known. Furthermore after a sufficiently long period of time the concentration gradient approaches a zero value and it is then possible to determine the differential diffusion coefficient of a mixture whose composition is equal to the mean concentration of the liquid in the cell. This calls for an extremely precise technique to measure the difference ΔN.

Experimental Apparatus

Several similar cells were used, of various sizes (3–4 cm in height, 0.8–1 cm in width and 0.8–2 cm in optical path length), the size being chosen to suit the particular mixture. Each cell consists of a glass frame clamped between two brass side-walls, the temperature of which may be controlled to within ±0.01 °C. Furthermore, the experiments at 25 °C were performed within a constant-temperature room.

Two methods were used in superposing the two mixtures of similar concentrations. The first (7) consists in initially placing the denser mixture in the bottom of the cell, then adding the less dense by means of a hypodermic syringe. In the second method (16), the cell is completely filled with the less dense mixture and a certain volume of the denser mixture is then introduced into the bottom of the cell by means of a peristaltic pump and a hypodermic needle. In every case, the liquids are at the experimental temperature.

The various steps in the filling procedure are checked, in real time, by holographic interferometry. This makes it possible to see that the mixtures are correctly superposed, with no parasitic convection currents, so that the validity of the results is assured. In the cells used, the superposition becomes difficult when the difference in density of the two diffusing mixtures is less than 2×10^{-3}.

Measurement of the Concentration Difference

The difference in concentration between the points $a/6$ and $5a/6$ is determined by holographic interferometry, of which the principles and the applications are well known (4, 5, 19). It is enough to say that this is a method in which two different states of the same cell are compared: firstly when filled with a liquid of uniform composition, and secondly while containing the diffusing system under consideration. This is a great advantage because the faults in the cell (imperfectly flat walls, slight variations in the thickness of the liquid contained, etc.) are eliminated by difference, which is not at all the case in classical interferometry.

Table I. Differential Diffusion Coefficients of Various Authors for the CCl₄-C₆H₁₂ System at 25 °C

% mol CCl₄			$10^5 D$, cm² s⁻¹				
% initial		% mean	This work	(Ref 2)	(Ref 17)	(Ref 11)	(Ref 9)
0.0	5.6	2.8	1.48	1.476	1.481	1.481	1.483
0.0	14.7	7.3	1.47	1.467	1.475	1.476	1.477
22.2	26.6	24.4	1.43	1.437	1.443	1.432	1.453
50.2	54.2	52.2	1.38	1.387	1.389	1.367	1.399
100.0	90.0	95.0	1.29	1.310	1.287	1.290	1.281
100.0	90.0	95.0	1.29	1.310	1.287	1.290	1.281
100.0	95.2	97.6	1.28	1.305	1.280	1.285	1.273

When a holographic interferometer is operated in real time, as in our experiments, a reference state corresponding to a liquid of uniform composition is stored in the form of a hologram. The light wave reconstituted by the hologram is then made to interfere with the wave which has passed through the cell during the diffusion process. This method makes it possible to follow directly the progress of the phenomenon to be recorded. One can then form, by means of a suitable device (6), a system of auxiliary interference fringes, the profile of which shows directly the variation in refractive index of the mixture at each point in the cell.

The number of fringes, k, observed between two points is related to the difference in refractive index, Δn, in the following manner:

$$k = \frac{e\Delta n}{\lambda} \tag{6}$$

where e is the optical path length in the cell and λ is the wavelength of the light.

In order to convert the difference Δn into ΔN, the difference in concentration, it is necessary to know how the refractive index varies with concentration at the wavelength of the laser (λ 6328 Å). The measurements were carried out for each mixture and for each temperature either by using a differential refractometer or directly by holographic interferometry (13), with a mean error

of the order of $\pm 2 \times 10^{-6}$. In the narrow range of concentration between the two superposed mixtures the refractive index varies linearly with concentration. Under these circumstances, a knowledge of the function $\Delta N = f(\Delta n)$ is not needed for the determination of the diffusion coefficient. It is enough simply to know the number of fringes k_0 initially observed between the two mixtures under consideration, as well as the difference in their concentrations, ΔN_0.

Accuracy of the Method

Holographic interferometry allows the formation of a very stable system of fringes. Moreover, the points $a/6$ and $5a/6$ may be located on each photograph with such precision that the number of fringes k between the two points may be measured with an error of about one-tenth of a fringe. The experimental points on the straight line showing ln (Δn) as a function of time are collected by taking a photograph every 2 h throughout the course of the experiment (1–3 days). A statistical analysis indicates an error of the order of 0.5% in the gradient when the experiment is carried out with a separation of about ten fringes. When other sources of error have been taken into account (viz., temperature, height of the cell, random errors), the error contained in the value for the diffusion coefficient may be estimated as being definitely less than 1.5%.

This technique was tested at 25 °C using the mixture CCl₄-C₆H₁₂ in the cell with the smallest optical path length. The results obtained, with a reproducibility of 0.6%, are compared in Table I with those presented by other authors. The agreement is satisfactory.

Experimental Results

Differential diffusion coefficients were determined for the mixtures already mentioned, throughout the entire range of concentrations and at four temperatures: 15, 20, 25, and 30 °C. The difference in concentration between the superposed mixtures at the beginning of each experiment depends on the rate of variation of refractive index with concentration. The difference was always between 1 and 5 mole %.

The results are shown in Table II. The values of the diffusion

Table II. Differential Diffusion Coefficients for Binary Systems

N₂	$10^5 D$, cm² s⁻¹				$10^{-4} E_d$ (J mol⁻¹)	N₂	$10^5 D$, cm² s⁻¹				$10^{-4} E_d$ (J mol⁻¹)
	15 °C	20 °C	25 °C	30 °C			15 °C	20 °C	25 °C	30 °C	
	(1) CCl₄-C₂HCl₃ (2)						(1) CCl₄-C₂H₄Cl₂-1,2 (2)				
0	1.28	1.39	1.50	1.62	1.14	0	1.11	1.27	1.43	1.60	1.77
10	1.35	1.46	1.57	1.69	1.09	10	1.08	1.24	1.41	1.58	1.85
20	1.42	1.53	1.65	1.76	1.05	20	1.06	1.22	1.39	1.57	1.90
30	1.49	1.60	1.72	1.83	1.00	30	1.05	1.21	1.39	1.56	1.92
40	1.55	1.67	1.78	1.90	0.96	40	1.05	1.21	1.38	1.55	1.91
50	1.63	1.74	1.86	1.97	0.93	50	1.06	1.22	1.39	1.56	1.87
60	1.70	1.81	1.92	2.04	0.89	60	1.08	1.24	1.40	1.57	1.82
70	1.78	1.89	2.01	2.13	0.86	70	1.11	1.27	1.43	1.60	1.77
80	1.85	1.96	2.08	2.19	0.83	80	1.15	1.32	1.48	1.64	1.71
90	1.92	2.04	2.16	2.29	0.80	90	1.20	1.36	1.52	1.70	1.65
100	2.00	2.11	2.23	2.34	0.78	100	1.28	1.44	1.60	1.77	1.59
							(1) CCl₄-C₂H₅OH (2)				
						0	—	—	—	—	—
	(1) C₂HCl₃-C₂H₄Cl₂-1,2 (2)					1	0.88	1.10	1.44	1.90	—
0	1.70	1.91	2.12	2.34	1.55	5	0.71	0.85	0.99	1.14	—
10	1.70	1.90	2.12	2.33	1.54	10	0.61	0.72	0.84	0.97	2.25
20	1.69	1.90	2.11	2.33	1.55	20	0.50	0.60	0.72	0.85	2.63
30	1.68	1.89	2.10	2.32	1.56	30	0.43	0.54	0.66	0.79	2.94
40	1.66	1.87	2.09	2.30	1.59	40	0.43	0.54	0.66	0.79	2.95
50	1.63	1.84	2.06	2.28	1.62	50	0.50	0.61	0.74	0.86	2.67
60	1.60	1.81	2.03	2.25	1.65	60	0.61	0.73	0.85	0.97	2.25
70	1.55	1.77	1.98	2.20	1.69	70	0.74	0.86	0.98	1.10	1.92
80	1.50	1.72	1.94	2.15	1.74	80	0.90	1.01	1.13	1.26	1.64
90	1.45	1.66	1.88	2.09	1.79	90	1.05	1.17	1.30	1.42	1.45
100	1.39	1.60	1.82	2.04	1.85	100	1.23	1.34	1.45	1.58	1.21

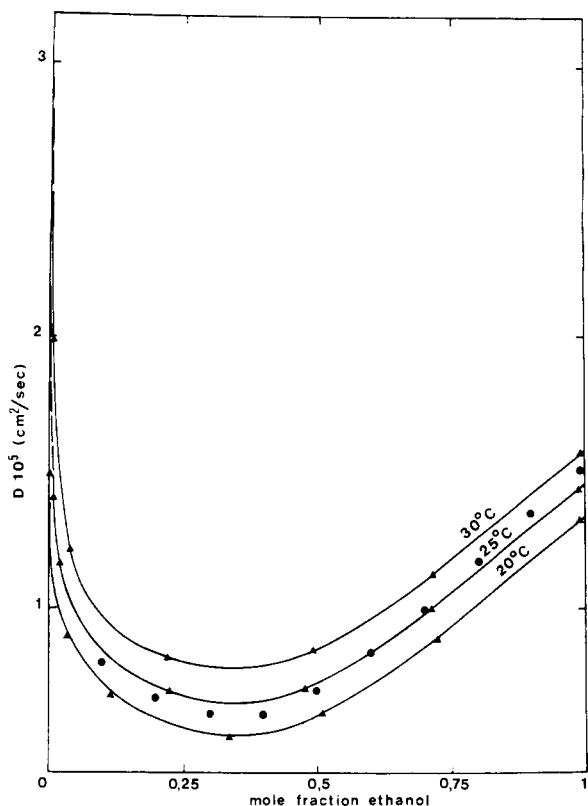**Figure 1.** Differential diffusion coefficients for carbon tetrachloride–ethanol mixture compared with data of other authors: ▲, this work; ●, Hammond and Stokes.

coefficients at infinite dilution were obtained by graphical extrapolation of the experimental curves while the values corresponding to other concentrations were derived by interpolation. The average deviations of individual data points from the smoothed curve amounted to no more than ±1% for all experimental systems.

In Figure 1, the values obtained at 25 °C for the mixture CCl_4–C_2H_5OH are compared with those obtained by Hammond and Stokes (9) using a diaphragm cell. Their results do not depart from those of this work by any more than ±4.5%. The disagreement observed undoubtedly arises from the difference in methods of measurement used, such a disagreement having already been noted in other systems by previous workers (14).

For this mixture, in the range of concentrations weak in ethanol, the diffusion coefficient rises very steeply, making an extrapolation to infinite dilution very difficult. This sharp rise, which is observed in other binary mixtures containing an alcohol, is due to a variation with concentration in the degree of association of the ethanol in the tetrachloromethane.

In the range of temperature considered and for a mixture of a particular composition, the variation of the diffusion coefficient with temperature has been analyzed using a formula of the type (1, 8):

$$\left[\ln D = A + \frac{B}{T} \right]_N \tag{7}$$

in which B is related to the activation energy of the system by the relationship:

$$B = -E_d/R \tag{8}$$

The validity of this law has been checked for all the mixtures shown in Table II (13).

The results show the same trend as those obtained previously by ebulliometry (15). In fact, it is found that the excess activation

energy of the system CCl_4–C_2HCl_3 is practically zero (ideal mixture), for the two systems CCl_4–1,2-$C_2H_4Cl_2$ and C_2HCl_3–1,2-$C_2H_4Cl_2$ it is small (regular mixture), while for the system CCl_4–C_2H_5OH it is quite large (associated mixture).

Conclusion

The limited-diffusion method used in this work is perfectly suited to the measurement of mutual diffusion coefficients in binary organic mixtures. For each mixture studied, the accuracy is always better than 1%.

The use of holographic interferometry offers important advantages: experimental accuracy is not harmed by using a cell which would not meet the standards required for classical interferometry; the transfer of matter is made visible throughout the whole of the cell. This condition makes it possible to measure exactly the differences in concentration not just between two specific points, but between the preferred planes located at $a/6$ and $5a/6$. Moreover, the appearance of convection currents may be detected at any point in time so that experiments affected by this fault may be discarded. Finally, it is possible to work at different temperatures without altering the experimental apparatus.

Glossary

a	height of the cell, cm
c_i	molar concentration of species i, mol cm^{-3}
D	mutual diffusion coefficient, cm^2 s^{-1}
E_d	diffusional activation energy, J mol^{-1}
e	thickness of the diffusion cell in the direction of the light beam, cm
J_i	molar flux of species i, mol cm^{-2} s^{-1}
k	number of interference fringes between two given points
$N_i; N$	mole fraction
n	refractive index of the solution
R	ideal gas constant, J K^{-1}
T	absolute temperature, K
t	time, s
v	mean molar velocity with respect to fixed axes, cm s^{-1}
v_i	velocity of component i with respect to fixed axes, cm s^{-1}
x	vertical space coordinate, cm
λ	wavelength of laser light, Å

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