Fickian Diffusion in Binary Mixtures That Form Two Liquid Phases

Manfred Pertler and Eckhart Blass
Lehrstuhl A für Verfahrenstechnik, Technische Universität München, Arcisstr. 21, 80290 München, Germany

Geoffrey W. Stevens
Dept. of Chemical Engineering, University of Melbourne, Parkville 3052, Victoria, Australia

New data on the variation of the diffusion coefficient with concentration in binary nonideal liquid mixtures are presented. The diffusion coefficients were measured with laser holography with an improved analysis procedure and are primarily in systems that form two liquid phases. The results show that for such systems the diffusion coefficient is constant if a chemical-potential driving force is used. If, however, the miscibility gap is wide, the Schreiner equation (Schreiner, 1922) is shown to be more accurate than relations that consider the variation of viscosity. Cluster theories developed for diffusion behavior near critical points were found to explain the data well only in water-organic systems on the water-rich side.

Introduction

The objective of this investigation is to examine binary diffusion coefficients in concentrated solutions near saturated states. Such solutions, particularly those that exhibit two-phase formation, are highly nonideal and a number of authors, including Ghai et al. (1973), McKeigue and Gulari (1984) and Rutten (1992) have demonstrated significant concentration dependence of the binary Fickian diffusion coefficient D_{12}, calculated from Eq. 1.

$$j_1 = -D_{12}\frac{dc_1}{dz} \tag{1}$$

This investigation has been stimulated by the need to predict the rate of mass transfer from droplets in a liquid extraction column. There is much discussion in the literature regarding which hydrodynamic models should be used to predict the rate of mass transfer. However, these analyses are based on a constant diffusion coefficient with a concentration driving force as shown in Eq. 1. In liquid extraction the two liquid phases undergoing mass transfer are saturated or close to saturation (along the binodal line), however, not in equilibrium with each other and as a result the activity coefficient can vary significantly. Previous work has shown that the diffusion coefficient can vary significantly close to saturated or binodal states. Hampe et al. (1991) used a temperature-variation method to reach the saturated state and found a decrease of the diffusion coefficient of more than one order of magnitude. Clark and Rowley (1986) measured the same change of the diffusion coefficient by varying the concentration in the vicinity of the consolute point in the system methanol/*n*-hexane (Figure 8). Thus, diffusion coefficients in binary systems have been measured over a range of compositions and temperatures. These data, in addition to the new data obtained in this study, are used to assess the models available for the prediction of the variation of the Fickian diffusion coefficient with composition as the system approaches saturation.

Nernst (1888) derived the relationship between the diffusional driving forces and the thermodynamic potentials. Later this relationship was also obtained by Onsager (1931, 1945) based on the theory of the thermodynamics of irreversible processes, which proposes that the flux is proportional to the rate of entropy production in the system (Cussler, 1976). At constant pressure and temperature and in the absence of external forces, the one-dimensional flux for a binary system is proportional to the gradient of the chemical-potential, given by

$$j_1 = -\frac{D_0 c_1}{RT}\frac{d\mu_1}{dz} \tag{2}$$

Since

$$\mu = \mu^0 + RT \ln a \tag{3}$$

For constant density Eq. 2 can be expressed as

$$j_1 = -D_0 \left[\frac{d \ln a_1}{d \ln x_1} \right] \frac{dc_1}{dz} \tag{4}$$

Thus, the Fickian diffusion coefficient can be related to the diffusion coefficient based on a chemical-potential driving force by Eq. 5

$$D_{12} = D_0 \left(\frac{d \ln a_1}{d \ln x_1} \right) \tag{5}$$

This equation was derived by Schreiner in 1922 based on the theory of Bjerrum (1918). Gordon (1937) arrived at a similar result, with the addition of a viscosity correction term given in Eq. 6.

$$D_{12} = D_0 \left(\frac{d \ln a_1}{d \ln x_1} \right) \frac{\eta_0}{\eta} \tag{6}$$

The thermodynamic factor ($d \ln a / d \ln x$) can be predicted for many systems with thermodynamic models such as UNIQUAC or NRTL. The thermodynamic factors used in this investigation were calculated from activity coefficients predicted from the UNIQUAC equation of state (Taylor, 1993), the parameters of which were obtained from a regression of the liquid-liquid equilibrium data published in the DECHEMA Chemistry Data Series (Sørensen and Arlt, 1979) at the temperature of interest or were fitted to equilibrium data with the help of the Aspen Plus Simulator.

D_{12}, the mutual or interdiffusion coefficient, has been related theoretically and empirically to the infinite dilution values D^{0}_{12} and D^{00}_{12} (Table 1), and those in most cases are equal to the reference diffusion coefficient D_0. For a detailed description of the classical theories, we refer to the more complete reviews from Ghai et al. (1973), Ertl et al. (1974), Skelland (1974), or Tyrrell and Harris (1984).

Cussler (1980) and others suggest that the classical equations are inaccurate for concentrated nonideal solutions such as those that form two phases and in the proximity of critical and consolute points. In an attempt to develop a more accurate model for diffusion in concentrated solutions Cussler (1980) used statistical mechanical theory to develop a relationship between the reference diffusion coefficient D_0 and the correlation length ξ_0 for the fluid. This resulted in Eq. 6 which is similar (except for factor two) to the familiar Stokes–Einstein relationship.

$$D_0 = \frac{kT}{2\pi \eta \xi_0} \tag{7}$$

Using the results of Kirkwood and Buff (1951) who developed a relation between correlation length and chemical potential, Cussler (1980) developed the following relation

$$D_{12} = D_0 \left[1 + \frac{C}{x_1 x_2} \left(\frac{d \ln x_1}{d \ln a_1} - 1 \right) \right]^{-0.5} \tag{8}$$

where $D_0 = (kT/4\pi\eta\xi_0)$ is a reference diffusion coefficient and C is a characteristic of a given system and the correlation length varies with the square root of the thermodynamic factor.

This theory postulates that the change in chemical potential is related to a change in the structure through the formation of clusters in the fluid. Since these clusters are larger than the original diffusing molecules the correlation length is increased, thus reducing the diffusion coefficient. Cussler's equation has two empirical parameters which should be constant for a given system.

Cullinan (1985) extended this approach and was able to develop an explicit equation with no adjustable parameters for the prediction of the variation of diffusion coefficient with temperature and composition.

$$D_{12} = \frac{kT}{2\pi \eta V^{1/3}} \left[1 + \frac{1}{2\pi x_1 x_2} \left(\frac{d \ln x_1}{d \ln a_1} - 1 \right) \right]^{-0.5} \tag{9}$$

This relationship was tested on a series of ideal and nonideal mixtures by Rollins and Knaebel (1991) and found to be accurate. None of the systems tested formed two phases at the conditions investigated.

McKeigue and Gulari (1989) also recognized the importance of molecular associations or clusters and from a consideration of the molecular association parameter measured by Nath and Bender (1981) from vapor-liquid equilibrium data, they were able to develop an expression for the variation of the diffusion coefficient as a function of composition and temperature. This relation is shown in Table 1. Unfortunately, the analysis of McKeigue and Gulari has only been developed for one associating component and in many of the systems of interest, association may occur between both components in solution. Also, there is a limited amount of data on the degree of association available so this theory can only be used on a restricted number of systems.

In addition, a number of authors (Clark and Rowley, 1986; Wu et al., 1988; Matos Lopes et al., 1992) have examined the reduction in the rate of diffusion close to the critical or consolute point and found that in general Eq. 4 overpredicts the drop in diffusion coefficient, because of a divergence in the correlation length. These authors have used such theories as the renormalization-group theory or the mode coupling theory to develop scaling laws (Sengers, 1985; Jany, 1990). Two of these semi-empirical scaling laws are also presented in Table 1.

Experimental Technique for Diffusion Measurement

The measurement of diffusion coefficients was carried out by laser holographic interferometry, which is a very accurate and nonintrusive technique. Details of the holographic setup and the analysis are described by Hampe et al. (1991). A thermostated measuring cell in which the temperature can be controlled with a precision of ±0.02°C is shown in Figure 1. From a thermostated storage vessel, the two completely miscible solutions (1 and 2), which differ slightly in composition, are carefully fed from the top and the bottom into the measuring cell with the help of hydrostatic pressure. In the center of the cell the two solutions flow out through two 0.12 mm high horizontal slits which are placed opposite to each other. After 30 to 45 min of rinsing, a sharp concentration gradient is formed and if no disturbances are visible the flow rate of the liquids is reduced from 1–2 mL/min constantly to zero. Diffusion is then allowed to occur between the two solutions of different composition. The changes of the concentration gradient by diffusion can be observed in real time by the laser holographic technique and can be recorded by a CCD- or a 35-mm camera. The characteristic interferential fringe patterns of such a diffusion experiment are represented in Figure 2.

The vertical fringes mark areas of homogeneous composition. The horizontally inclined fringes represent a concentration gradient. The distance between two neighboring inclined fringes corresponds to a constant difference of concentration. The number of the inclined interferential fringes is proportional to the whole difference of concentration between the two test solutions. At the beginning of a diffusion experi-

Table 1. Theoretical and Empirical Correlations for the Interdiffusion Coefficient

Ref.	Systems	Equations	Basis
Schreiner (1922)	Electrolytes in water HCl/water NaCl/water KCl/water	$D_{12} = D_0 * \left(\frac{d \ln a_1}{d \ln x_1}\right)$	Thermodynamic correction factor, Bjerrum's theory
Gordon (1937)	Electrolytes in water KCl/water NaCl/water KNO_3	$D_{12} = D_0 * \left(\frac{d \ln a_1}{d \ln x_1}\right) * \left(\frac{\eta_0}{\eta}\right)$	Thermodynamic and viscosity correction
Powell et al. (1941); Wilke (1949)	Chloroform/ether Chloroform/acetone water/*n*-propylalcohol	$D_{12} = \left(\frac{T}{\eta}\right) * \left[\left(\frac{D_{12}^{\infty} * \eta_1}{T} - \frac{D_{12}^{0} * \eta_2}{T}\right) * x_1 + \left(\frac{D_{12}^{0} * \eta_2}{T}\right)\right] * \left(\frac{d \ln a_1}{d \ln x_1}\right)$	Thermodynamic and viscosity correction absolute rate theory
Darken (1948)	Binary metallic systems: silver/gold	$D_{12} = (x_1 * D_2^* + x_2 * D_1^*) * \left(\frac{d \ln a_1}{d \ln x_1}\right)$	Thermodynamic correction factor (tracer diffusion)
Hartley and Crank (1949)	No data published in the original article	$D_{12} = (\phi_1 * D_2^* + \phi_2 * D_1^*) * \left(\frac{d \ln a_1}{d \ln x_1}\right); \ \phi_i = V_i * c_i$	Thermodynamic correction factor (tracer diffusion)
Carman and Stein (1956)	Ethyl/*n*-butyliodides	$D_{12} = \frac{1}{\eta} * (x_1 * \eta_1 * D_{12}^{\infty} + x_2 * \eta_2 * D_{12}^{0}) * \left(\frac{d \ln a_1}{d \ln x_1}\right)$	Thermodynamic correction factor
Caldwell and Babb (1956)	Benzene/CCl_4 chloro-/bromobenzene toluene/chlorobenzene	$D_{12} = \left(\frac{T}{\eta}\right) * \left[x_1 * \frac{D_{12}^{\infty} * \eta_1}{T} + x_2 * \frac{D_{12}^{0} * \eta_2}{T}\right]$	Ideal systems
Geet and Adamson (1964)	*n*-alkane mixtures	$D_{12} = (x_1 * D_{12}^{\infty} + x_2 * D_{12}^{0})$	Ideal systems
Vignes (1966)	16 ideal systems 14 nonideal systems (6 associating systems, with limited validity)	$D_{12} = (D_{12}^{\infty})^{x_1} * (D_{12}^{0})^{x_2} * \left(\frac{d \ln a_1}{d \ln x_1}\right)$	Thermodynamic correction factor
Rathbun and Babb (1966)	Alcohol/CCl_4 acetone/CCl_4 ketone/CCl_4 alcohol/benzene ketone/$CHCl_3$	$D_{12} = (x_1 * D_{12}^{\infty} + x_2 * D_{12}^{0}) * \left(\frac{d \ln a_1}{d \ln x_1}\right)^s$ $s = 0.6$; one non- and one associating component in the system $s = 0.3$; systems with negative deviations from Raoult's law	Modified thermodynamic correction factor
Leffler and Cullinan (1970)	7 ideal systems 4 nonideal systems (comparison with Vignes, 1966)	$D_{12} = \frac{1}{\eta} * (D_{12}^{\infty} * \eta_1)^{x_1} * (D_{12}^{0} * \eta_2)^{x_2} * \left(\frac{d \ln a_1}{d \ln x_1}\right)$	Thermodynamic correction factor absolute rate theory
Gainer (1970)	Ethanol/water ethanol/benzene cyclohexane/CCl_4	$D_{12} = \frac{1}{\eta} * D_{12}^{0} * \eta_2^{x_2} * \eta_1^{x_1} * K^{x_1} * \left(\frac{d \ln a_1}{d \ln x_1}\right)$ with $K = \left(\frac{\eta_2}{\eta_1}\right)^{0.5} * \left(\frac{M_2}{M_1}\right)^{0.25} * \left(\frac{\Delta H_{\text{vap}\,1} - RT}{\Delta H_{\text{vap}\,2} - RT}\right)^{0.5}$	Thermodynamic correction factor modified rate theory
Cussler (1980)	Alcohol/benzene; CCl_4 triethylamine/H_2O *n*-hexane/nitrobenzene analine/cyclohexane isobutyric acid/water	$D_{12} = D_0 \left[1 + \frac{C}{x_1 x_2}\left(\frac{d \ln x_1}{d \ln a_1} - 1\right)\right]^{-\frac{1}{2}}; \ C = \text{fit parameter}$	Cluster diffusion

Continued

Table 1. Theoretical and Empirical Correlations for the Interdiffusion Coefficient (Continued)

Ref.	Systems	Equations	Basis
Guerkan (1987)	Alcohol/benzene; CCl_4 nitromethane/CCl_4 acetone/water ethanol/water	$D_{12} = D_0 \left\{ 1 + C * \left[\frac{1}{x_1 x_2} \left(\frac{d \ln x_1}{d \ln a_1} - 1 \right) \right]^m \right\}^{-\frac{1}{2}}; \quad m \cong 1.23, \; C \cong 0.17$	Cluster diffusion new fit of Cussler's equation
McKeigue and Gulari (1984, 1989)	Alcohol/benzene alcohol/CS_2	$D_{12} = \left\{ \left[(1-x_1)(1-K\Phi_1)^2 \sum_{n=1}^{\infty} (n^{3/2}(K\Phi_1)^{n-1}) \right] (D_{12}^0 \eta_2) + x_1 (D_{12}^{\infty} \eta_1) \right\} \times \left(\frac{1}{\eta} \right) \left(\frac{d \ln a_1}{d \ln x_1} \right)$	Cluster diffusion
Cullinan (1985) Rollins and Knaebel (1991)	Acetone/benzene acetone/H_2O CCl_4/ethanol bromobenzene/benzene triethylamine/H_2O	$D_{12} = \frac{kT}{2\pi\eta V^{1/3}} \left[1 + \frac{1}{2\pi x_1 x_2} \left(\frac{d \ln x_1}{d \ln a_1} - 1 \right) \right]^{-\frac{1}{2}}$	Cluster diffusion
Clark and Rowley (1986) Wu et al. (1988)	n-hexane/methanol n-hexane/nitrobenzene	$D_{12} = D_0 \left(\frac{T - T_c}{T_c} \right)^{\alpha}; \quad \alpha = 0.685 \text{ (Clark)}, \; \alpha = 0.640 \text{ (Wu)}$	Critical phenomena consolute points
Matos Lopes et al. (1992)	n-hexane/nitrobenzene	$D_{12} = D_0 \left(\frac{T - T_c}{T_c} \right)^{\alpha} + \frac{RkT}{6\pi\eta\zeta_0} \left(\frac{T - T_c}{T_c} \right)^{\beta}$	Critical phenomena

ment, there is a steep concentration gradient which is visible by the small distances between the interference fringes. The concentration gradient is flattened by molecular diffusion and the fringe patterns are spread symmetrically during the experimental time t. The information about the concentration gradient as a function of time and position allows the calculation of the diffusion coefficient D_{12}. The methods proposed by Miller (1981, 1988), have been developed for one-dimensional free diffusion and also work for multicomponent systems. The analysis of the fringe patterns is carried out by a picture processing system, the structure of which is shown in Figure 3.

The picture processing system consists of a personal computer with an overlay frame grabber board from ITI, an additional graphic screen and the analysis software Optimas. The recorded fringe patterns can be scanned into the picture memory of the frame grabber by a video recorder or by the negatives with a CCD-camera which is fixed above a light desk. Experiments with a high number of fringes (> 60) as well as runs with very low distances between the fringes make the analysis of the video image difficult. In both cases the resolution of the fringe pattern on the video is not high enough to analyze the distances between the fringes.

To automate the analysis as far as possible, corresponding

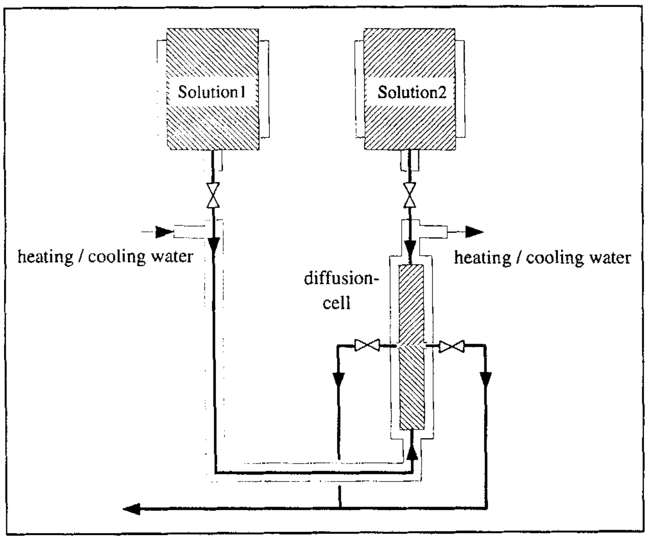

Figure 1. Principal sketch of the diffusion cell (interior volume of the cell according to height * width * depth = 60 × 4 × 30 mm^3).

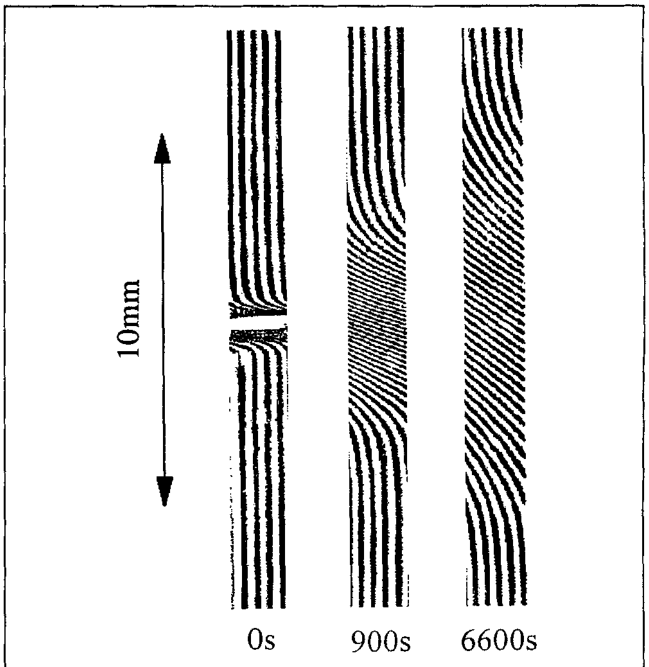

Figure 2. Fringe patterns of a diffusion experiment at different times.

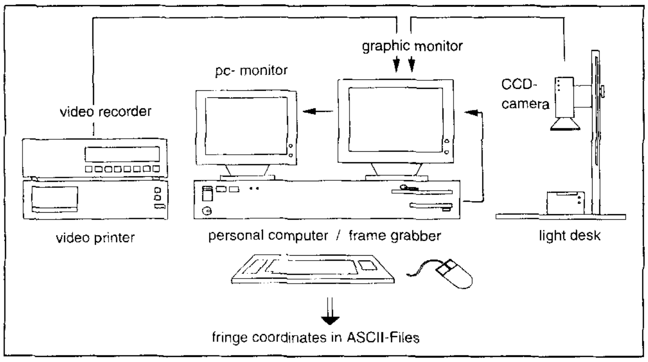

Figure 3. Picture processing system.

macros for the three different input alternatives—camera, video recorder, PC memory—were developed based upon Optimas-system language. The user's control was simplified by dialogue windows, which accelerated the fringe patterns analysis and increased reliability.

Figure 4 shows a comparison between different measurements of diffusion coefficients in the system water/*n*-butanol. Lyons and Sandquist (1953) used Gouy-Interferometry and Rutten (1992) used the Taylor-Method and our own measurements with holographic interferometry.

Good agreement between the techniques is found at infinite dilution. At higher concentrations, the maximum deviations of about 4% were obtained. The reason for this comparison is to assess the reproducibility and precision of the measurements of the diffusion coefficient. Normally in the holographic interferometry, a measuring error below ±1% is expected. The first results obtained in the water/*n*-butanol and acetone/glycerol systems showed a measuring error of more than ±6%, although analytical grade chemicals were used as supplied and doubly distilled water was used in all experiments.

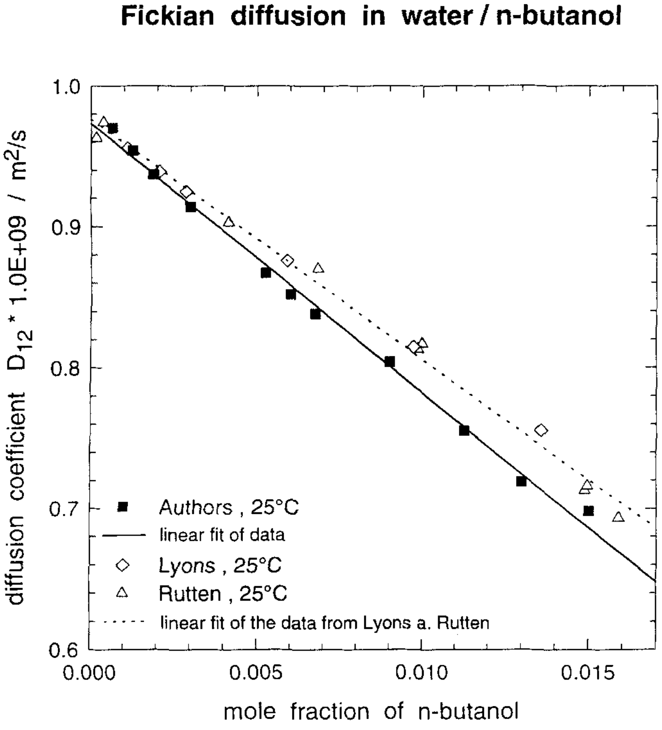

Figure 4. Comparison of diffusion coefficients in the system water/*n*-butanol.

A systematic error analysis led us to an improved experimental procedure. Instead of sucking the liquid off the measuring cell with the help of a variable speed gear-pump, the hydrostatic pressure gradient between the storage vessels and the measuring cell is now used to create a sharp concentration gradient, as described above in Figure 1. Moreover, the volume of the stream used during the rinsing of the cell with the two solutions is measured and held constant and as low as possible for every experiment. Hence, it was possible to get a reproducible sharp concentration gradient at the beginning of an experiment. The influence of any initial mixing at the boundary is corrected by adding a time interval Δt to the experimental time t as described by Albright and Sherill (1979). The initial time correction Δt was found to be 65 s for the water/butanol and around 20 s for the acetone/glycerol system. These small time corrections indicate that with the slit technique described, a very sharp concentration gradient is produced.

A calibration slit to give a known distance on the recorded image was placed at an arbitrary point in the parallel light flux of the laser beam. This was found to introduce a slight error and is now placed as close as possible to the measuring cell. This produced a sharper image, the influence of high-order diffraction effects on the measurement of the calibration length was decreased, and the error during the calibration was reduced to about 0.1%.

Accurate scanning of the negative of the light desk into the picture processing system is very important. Covering the film strip with a sheet of glass led to the result that the film was completely within the focusing plane of the CCD-camera and that the relative error declined a further 2%.

After an initial period, the diffusion coefficient which is obtained over eight to ten measurements is constant. With the above improvements the average relative error for water/*n*-butanol was reduced to ±0.6% and for acetone/glycerol to ±0.9%.

Results and Discussion

In order to predict the change of the diffusivity in highly nonideal associating liquid systems, a comparison with experimental data, obtained from this investigation and from the literature, is presented to test the applicability of the various approaches from Table 1. These approaches can be divided into six main groups as follows

- Ideal systems (Caldwell and Babb, 1956; Geet and Adamson, 1964)
- Tracer diffusion theories (Darken, 1948; Hartley and Crank, 1949)
- Theories with thermodynamic corrections only (Schreiner, 1922; Vignes, 1966; Rathbun and Babb, 1966)
- Theories with thermodynamic and viscosity corrections (Gordon, 1937; Powell et al., 1941; Carman and Stein, 1956; Leffler and Cullinan, 1970; Gainer, 1970)
- Cluster theories (Cussler, 1980; Cullinan, 1985; Gürkan, 1987; McKeigue and Gulari, 1984, 1989; Rollins and Knaebel, 1991)

Table 2. Diffusion Coefficients and Thermodynamic Factors

Water/*n*-Butanol (25°C): Lyons and Sandquist (1953)

mol % *n*-Butanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
0.1098	0.956	0.969
0.2066	0.939	0.942
0.2868	0.925	0.920
0.5904	0.876	0.840
0.9733	0.815	0.745
1.3572	0.756	0.656

Water/*n*-Butanol (25°C): Rutten (1992)

mol % *n*-Butanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
0.015	0.963	0.996
0.036	0.974	0.990
0.414	0.903	0.886
0.683	0.870	0.816
0.987	0.813	0.742
1.000	0.817	0.739
1.488	0.713	0.627
1.496	0.716	0.626
1.685	0.693	0.585

Water/*n*-Butanol (25°C): This Work

mol % *n*-Butanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
0.063	0.970	0.982
0.125	0.954	0.965
0.188	0.937	0.947
0.300	0.914	0.917
0.525	0.867	0.857
0.600	0.852	0.838
0.675	0.838	0.818
0.900	0.804	0.763
1.100	0.755	0.715
1.300	0.719	0.669
1.500	0.698	0.625

Water/*n*-Butanol (25°C): Emanuel and Olander (1963)

mol % *n*-Butanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
50.00	0.239	0.428
53.00	0.263	0.487
57.00	0.288	0.559
62.00	0.314	0.640
66.00	0.343	0.697
71.00	0.376	0.762
77.00	0.415	0.828
84.00	0.466	0.893
91.00	0.518	0.946
99.00	0.555	0.995

Water/MIPK (20°C): Thiel et al. (1990)

mol % *n*-Butanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
0.090	0.953	0.980
0.290	0.939	0.938
0.550	0.876	0.884
0.900	0.829	0.815

Water/MIPK (25°C): Thiel et al. (1990)

mol % *n*-Butanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
90.30	1.969	0.596
95.80	2.661	0.809
97.20	2.868	0.870
98.00	2.986	0.906

Water/TEA (20°C): Vitagliano et al. (1980)

mol % TEA	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
0.40	0.576	0.858
0.79	0.523	0.733
1.00	0.492	0.671
1.20	0.424	0.614
1.60	0.332	0.511

Water/TEA (20°C): Vitagliano et al. (1980)

mol % TEA	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
30.600	0.091	0.440
31.000	0.088	0.451
32.900	0.093	0.500
35.000	0.111	0.551
36.900	0.123	0.593
38.800	0.139	0.633
42.300	0.162	0.699
80.400	0.822	0.989
90.200	1.472	0.997
95.100	2.016	1.001

Glycerol/Acetone (25°C): This Work

mol % Acetone	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
96.100	1.320	0.603
96.300	1.350	0.620
97.000	1.400	0.685
98.000	1.620	0.782
98.500	1.700	0.834
99.500	2.190	0.943
99.800	2.350	0.977

n-Hexan/Methanol (30°C): Clark and Rowley (1986)

mol % Methanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
7.00	2.246	0.650
13.00	1.523	0.431
22.00	0.738	0.205

n-Hexan/Methanol (30°C): Clark and Rowley (1986)

mol % Methanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
76.00	0.334	0.126
77.00	0.341	0.144
83.00	0.745	0.275
91.00	1.475	0.536
98.00	2.441	0.876

CS_2/Methanol (20°C): McKeigue and Gulari (1984)

mol % Methanol	$D_{12}*1.E+0.9$ (m^2/s)	$d\ln a/d\ln x$
1.00	1.558	0.825
2.50	0.807	0.616
5.00	0.577	0.366
6.00	0.481	0.293
8.00	0.385	0.178

- Critical phenomena theories (Clark and Rowley, 1986; Wu et al., 1988; Matos Lopes et al., 1992).

The systems used, water/*n*-butanol, water/methyl-isopropyl-ketone (MIPK), water/triethylamine (TEA), *n*-hexane/methanol, carbondisulfide (CS_2)/methanol and glycerol/acetone all form two liquid phases at the investigated temperatures. The diffusion coefficients for these systems and the thermodynamic factors are presented in Table 2. Also included are the densities and the viscosities which were determined for the systems investigated, together with the UNIQUAC parameter (Sørensen and Arlt, 1979) used and the infinite dilution data (Table 3).

All previous investigations indicate that changes in the activity coefficient influence the diffusion coefficient, the ideal systems will no longer be considered. Because we are interested in the variation of the mutual diffusion coefficient with concentration away from the critical or consulate point, the tracer diffusion theories and the critical point theories, which consider the temperature dependence, will not be considered. All of the theories in the remaining three groups have

Table 3. Physical Properties

Density ρ, kg/m^3 $\rho = A_0 + A_1^* X_2 + A_2^* X_2^2 + A_3^* X_2^3$

(Comp. 1/Comp. 2)	T/°C	A0	A1	A2	A3	Correlation	Range
Water/n-butanol	25	996.828	−568.601	0.000	0.000	0.998	X2 < 0.0192
Water/n-butanol	25	904.757	−149.832	50.536	0.000	0.999	X2 > 0.4880
Water/MIPK	20	998.266	−749.700	19,525.116	0.000	0.998	X2 < 0.0139
Water/MIPK	25	853.507	−52.895	0.000	0.000	0.994	X2 > 0.8880
Water/TEA (Vitagliano	20	998.100	−853.400	1,265.700	0.000	1.000	X2 < 0.0249
Water/TEA et al., 1980)	20	1,093.100	−803.900	616.600	−178.800	1.000	X2 > 0.2480
n-Hexane/methanol	30	650.938	32.687	11.825	0.000	0.989	X2 < 0.2690
n-Hexane/methanol	30	1,064.582	−1,032.106	749.818	0.000	1.000	X2 > 0.7580
Carbon disulfide/methanol	20	1,262.143	−308.065	0.000	0.000	0.999	X2 < 0.1000
Glycerol/acetone	25	1,344.916	−561.029	0.000	0.000	0.994	X2 > 0.9599

Viscosity η, Pa·s $\eta = A_0 + A_1^* X_2 + A_2^* X_2^2 + A_3^* X_2^3$

(Comp. 1/Comp. 2)	T/°C	A0	A1	A2	A3	Correlation	Range
Water/n-butanol	25	9.174E-04	1.520E-02	0.000E+00	0.000E+00	0.994	X2 < 0.0192
Water/n-butanol	25	4.017E-03	−3.120E-03	1.693E-03	0.000E+00	0.998	X2 > 0.4880
Water/MIPK	20	1.002E-03	1.768E-02	0.000E+00	0.000E+00	0.995	X2 < 0.0139
Water/MIPK	25	1.740E-03	−2.299E-03	1.028E-03	0.000E+00	1.000	X2 > 0.8880
Water/TEA (Vitagliano	20	1.007E-03	2.880E-02	8.480E-01	2.490E+01	1.000	X2 < 0.0249
Water/TEA et al. 1980)	20	1.206E-02	−3.009E-02	2.613E-02	−7.750E-03	1.000	X2 > 0.2480
n-Hexane/methanol	30	2.847E-04	9.490E-06	2.943E-04	0.000E+00	1.000	X2 < 0.2690
n-Hexane/methanol	30	8.743E-04	−1.280E-03	9.159E-04	0.000E+00	1.000	X2 > 0.7580
Carbon disulfide/methanol	20	3.678E-04	3.319E-04	−1.963E-03	0.000E+00	0.999	X2 < 0.1000
Glycerol/acetone	25	7.002E-03	−1.213E-02	5.432E-03	0.000E+00	1.000	X2 > 0.9599

Uniquac parameter

(Comp. 1/Comp. 2)	T/°C	R1	Q1	R2	Q2	A12	A12
Water/n-butanol	25	0.9200	1.4000	3.4543	3.0520	267.1000	−9.7194
Water/MIPK (water-rich)	20	0.9200	1.4000	3.9215	3.4120	21.4190	506.9000
Water/MIPK	25	0.9200	1.4000	3.9215	3.4120	31.0410	419.3300
Water/TEA (Aspen)	20	0.9200	1.4000	5.0118	4.2560	189.4988	−61.3304
n-Hexane/methanol	30	4.4998	3.8560	1.4311	1.4320	592.3600	−7.3883
Carbon disulfide/methanol	20	2.0570	1.6500	1.4311	1.4320	628.5500	83.4660
Glycerol/acetone (Aspen)	25	3.5857	3.0600	2.5735	2.3360	140.4318	229.8944

Infinite dilution

(Comp. 1/Comp. 2)	T (°C)	D_{12}^{∞} (m^2/s)	D_{12}^{0} (m^2/s)	η_1 (Pa·s)	η_2 (Pa·s)	$\Delta H_{\text{vap }1}$ (kJ/kg)	$\Delta H_{\text{vap }2}$ (kJ/kg)
Water/n-butanol	25	9.74E-10	5.62E-10	9.174E-04	2.530E-03	2257.30	590.00
Water/MIPK (water-rich)	20	9.72E-10	2.57E-10	1.002E-03	4.955E-04	2257.30	392.32
Water/MIPK	25	1.17E-09	3.29E-09	8.901E-04	4.693E-04	2257.30	392.32
Water/TEA	20	6.79E-10	2.25E-09	1.007E-03	3.516E-04	2257.30	389.00
n-Hexane/methanol	30	3.29E-09	2.75E-09	2.848E-04	5.106E-04	317.00	1,100.00
Carbon disulfide/methanol	20	1.86E-09	2.37E-09	3.678E-04	5.840E-04	351.00	1,100.00
Glycerol/acetone	25	1.40E-12	2.53E-09	1.426E+00	3.055E-04	852.00	523.00

tested. The change of diffusivity has been calculated with a thermodynamic correction factor only, from the equations in Schreiner (1922), Vignes (1966) and Rathbun and Babb (1966), also with an additional viscosity correction term, according to the equations developed by Gordon (1937), Powell (1941), Carman and Stein (1956) and Leffler and Cullinan (1970). For the cluster theories we have used the Cullinan equation (Eq. 9).

Figures 5 to 10 show a comparison between experimentally determined Fickian diffusion coefficients and various approaches for the systems examined on both sides of the two phase region, except for the systems CS$_2$/methanol and glycerol/acetone where diffusion data are available only for one side of the miscibility gap.

In all cases, except for the triethylamine-rich side of the system water/TEA, the predictions from Eq. 5 (the Schreiner equation) were within 5% of the measurement values. The large deviation from Eq. 5 in the system water/TEA may be due to inaccuracies in the equilibrium data, as different solubility data are given in the literature at 20°C by various authors (Kohler and Rice, 1957). The Vignes relation, as shown in Figures 5 to Figure 7, shows no significant improvement over the simpler Schreiner equation; also, the Rathbun equation tends to underpredict the diffusion coefficient.

A better fit was obtained without the viscosity terms in almost all cases. As a result of strong viscosity variations with small changes in the concentration, the predictions of those theories which take into consideration the viscosity correction are very close together. As a representative of the theories that include viscosity corrections, the Gordon equation is shown in Figures 5 to 10.

The Cullinan theory describes the change of the diffusion coefficient quite well in systems with water on the water-rich side. It fails in all other cases except in water/TEA, where at least a qualitatively correct description is possible, but with doubtful equilibrium data (Kohler and Rice, 1957).

To further test the ability of the Schreiner equation (Eq. 5) to predict the variation of diffusion coefficient with chemical

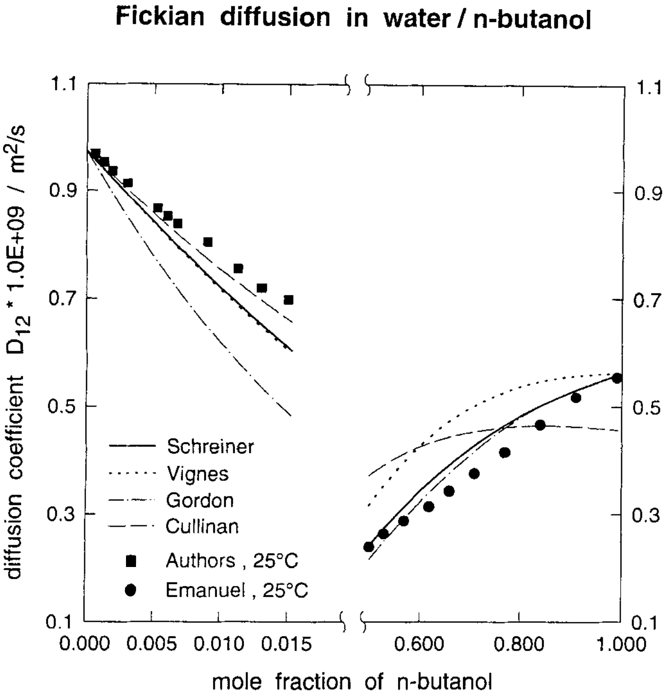

Figure 5. Dependence of the Fickian diffusion coefficient on concentration in the system water/ *n*-butanol at 25°C.

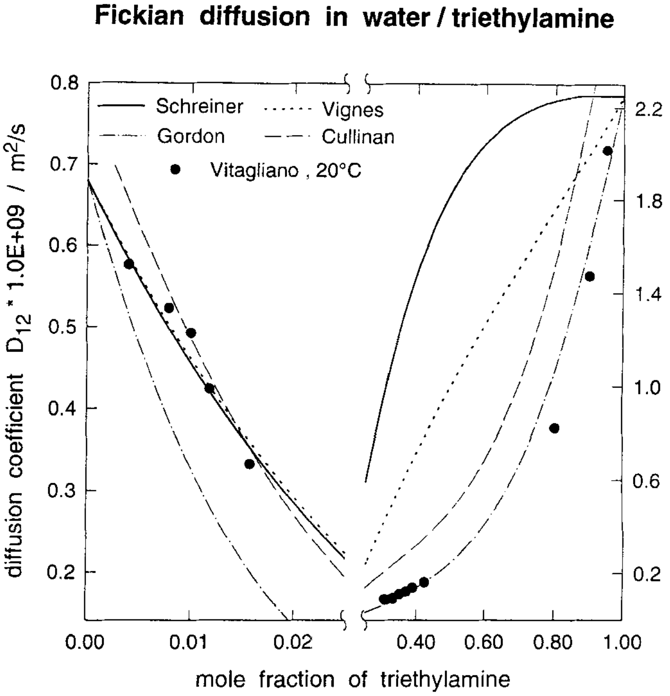

Figure 7. Dependence of the Fickian diffusion coefficient on concentration in the system water/ TEA at 20°C.

potential the data were fitted to this equation, where D_0 was estimated with the Levenberg-Marquart nonlinear regression algorithm. In all cases, the D_0 estimated corresponded to the value obtained by extrapolation to infinite dilution. As can be seen from Figures 5 to 10, Eq. 5 fits the data better than the cluster theories, indicating that the change in chemical potential predicted from UNIQUAC equation of state ade-

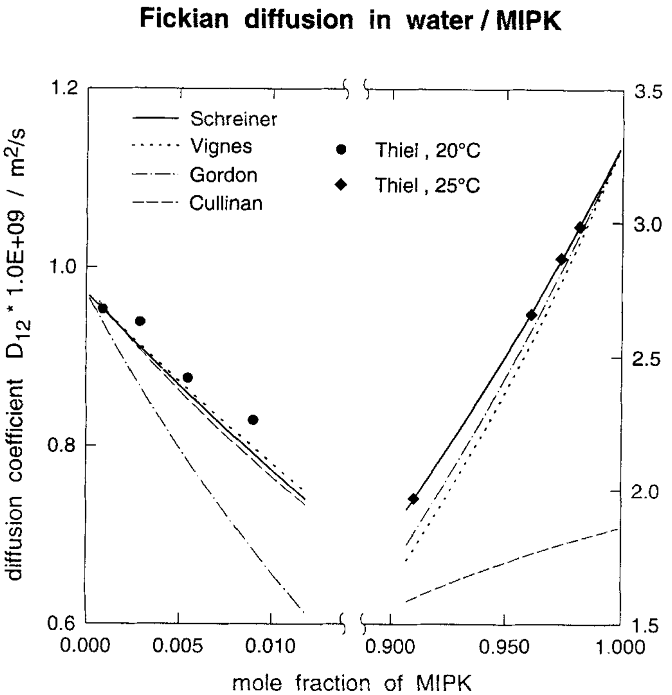

Figure 6. Dependence of the Fickian diffusion coefficient on concentration in the system water/ MIPK at 20°C and at 25°C on the MIPK-rich side.

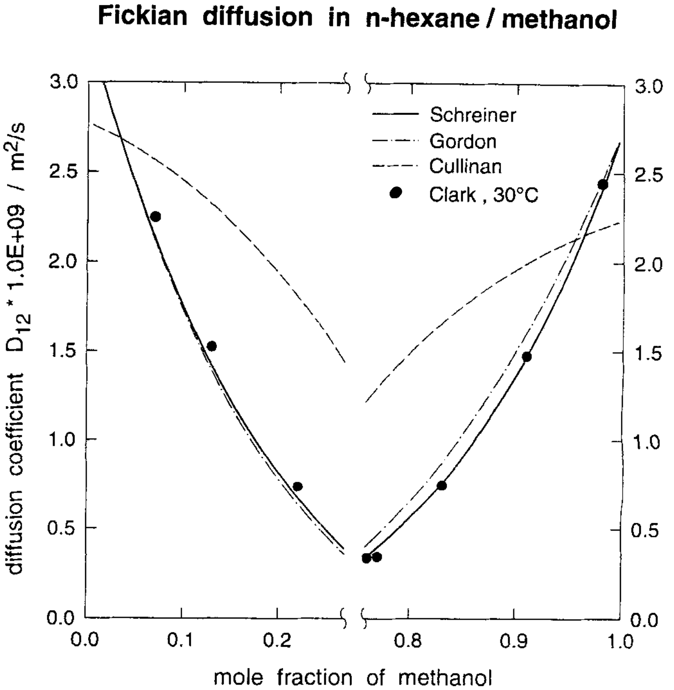

Figure 8. Dependence of the Fickian diffusion coefficient on concentration in the system *n*-hexane/methanol at 30°C.

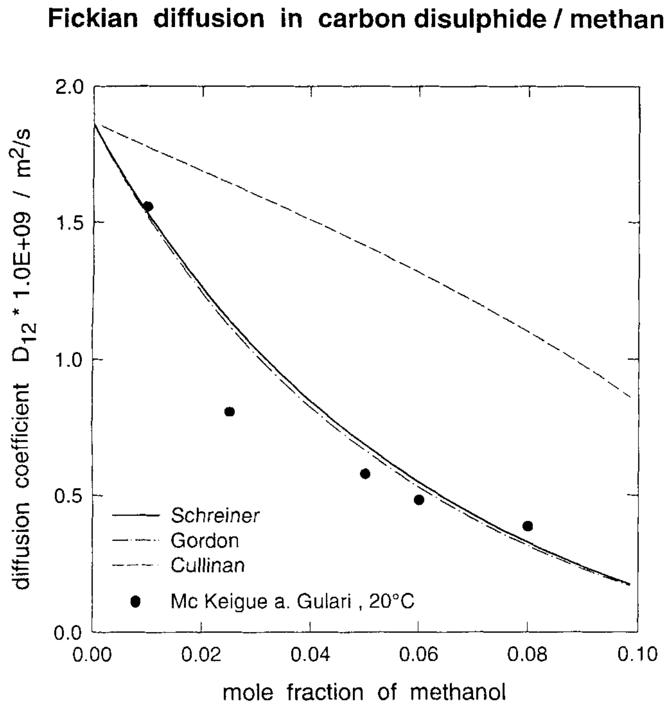

Figure 9. Dependence of the Fickian diffusion coefficient on concentration in the system CS_2/ methanol at 20°C.

quately describes the change in structure of the fluid and so the correlation length.

This is surprising, so to test the cluster theory further, the Cussler equation (Eq. 8) was fitted to the data for the binary systems with both parameters D_0 and C allowed to vary. A significant correlation was noticed between the parameters, but no significant improvement in the fit was obtained when compared with Cullinan's Eq. 9.

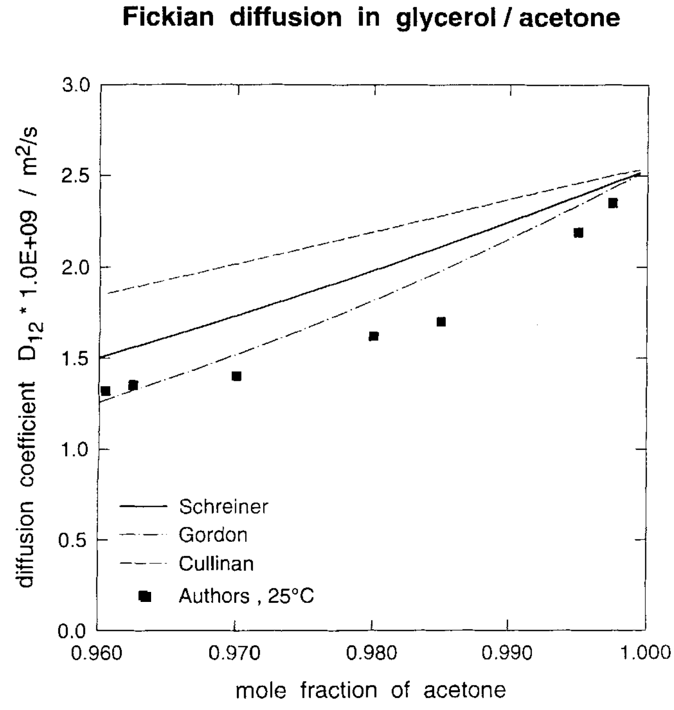

Figure 10. Dependence of the Fickian diffusion coefficient on concentration in the system glycerol/acetone at 25°C.

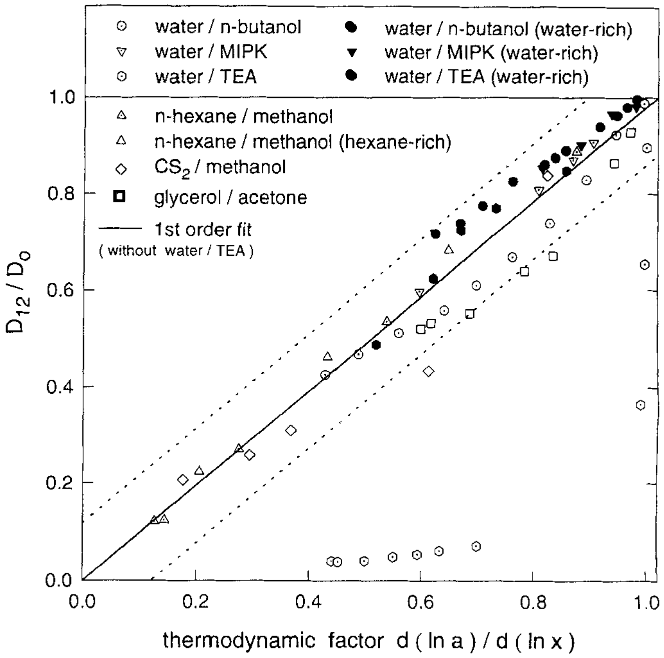

Figure 11. Variation of the diffusion coefficient versus the thermodynamic factor.

Figure 11 contains data for all the systems investigated and clearly shows that the diffusion coefficient D_{12} varies linearly with the thermodynamic factor up to the saturated state, indicating that the thermodynamic approach of Schreiner (1922) is more appropriate than the cluster models of Cussler (1980), Cullinan (1985) or McKeigue and Gulari (1984, 1989), which predict that the diffusion coefficient varies with the thermodynamic factor to the power of 0.5 to 0.62.

Figure 11 also indicates that the reference diffusion coefficient D_0 is independent of composition. This is probably only true for the systems investigated as they all have a small solubility gap. Although there is a large change in the thermodynamic factor as the solubility limit is approached, there is only a small change in the concentration indicating that these systems are ideal for investigating the effects of changes in the activity coefficient on the diffusion coefficient. For cases where there is a wide change in concentration, it is reasonable to expect that D_0 will vary with concentration and so the slope of the line in Figure 11 may not be one. This may be interpreted in terms of correlation length. By combining Eqs. 5 and 7 the correlation length ξ may be expressed as

$$\xi = \frac{k * T}{2 * \pi * \eta * D_0 * \left(\dfrac{d \ln a_1}{d \ln x_1}\right)} \qquad (10)$$

which indicates that the correlation length is inversely proportional to the thermodynamic factor and also to the reference diffusion coefficient D_0. As the two extreme cases of infinite dilution have different D_0s where the thermodynamic factor is equal to one, D_0 must vary in some way with concentration. Sufficient data are not available at this stage to determine quantitatively the nature of this variation. However, for the investigated systems in the unsaturated region this effect seems small and the decrease of the diffusivity D_{12} seems to be based on a continuous increase in the correlation length up to the saturated state. In cases where the solubility limit has been exceeded Myerson and coworkers (Kim and Myerson, 1994; Myerson and Lo, 1991; Ginde and Myerson, 1987) have shown that the diffusion coefficient declines rapidly, and depends on the age of the solution. Hence, indirect evidence for the existence of molecular clusters at supersaturated solutions was provided. Such evidence is unavailable for the postulated increase of the molecular agglomerates up to the saturated states.

Conclusions

The Fickian diffusion coefficient D_{12} has been shown to vary linearly with the thermodynamic factor in nonideal binary mixtures as they approach a saturated state (two-phase boundary). This indicates that the change in activity coefficient adequately reflects the change in the structure of the fluid and in the correlation length up to the point of saturation for these systems. The variation in the diffusion coefficient has been shown to be able to be predicted for the systems investigated by the Schreiner (1922) equation.

Thus, from a knowledge of the infinite dilution diffusion coefficients, the variation in the diffusion coefficient can be predicted through the whole concentration range, which can be up to an order of magnitude. It is important that this variation be included in developing models for the prediction of mass transfer in liquid-liquid systems, which commonly operate in saturated conditions. Further work is required to examine if a similar relation holds as the consolute point is reached or if the critical point or cluster theories become more accurate. Also in ternary systems the situation is still unclear.

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Financial support for equipment and personnel for this project is provided by the Deutsche Forschungsgemeinschaft (DFG) since 1990 and additionally support was received by the Deutschen Akademischen Austauschdienst (DAAD) which enabled the stay of Prof. Stevens at the Technical University of Munich in Autumn 1993. The authors are very grateful for this support.

Notation

a = activity
c = concentration, mol/m^3
D = diffusion coefficient, m^2/s
H_{vap} = heat of evaporation, kJ/kg
j = flux of component, mol/(m^2·s)
k = Boltzmann constant, 1.380662×10^{-23} J/K
M = molecular weight, kg/mol
N_A = Avogadro's number, 6.0221367×10^{23} 1/mol
R = gas constant, 8.31441 J/(K × mol)
T = temperature, K
T_c = critical temperature, K
V = molar volume, m^3/mol
x = mole fraction
z = distance, m

Greek letters

γ = activity coefficient
η = viscosity, Pa·s
μ = molar chemical potential, J/mol
μ^0 = molar chemical potential at standard state, J/mol
ξ = correlation length, m
ρ = mass density, kg/m^3
ϕ = volume fraction

Subscripts

0 = reference value, of diffusion coefficient or correlation length
1, 2 = component 1 or 2 in solution
i = component i

Superscripts

$0, \infty$ = infinite dilution

Literature Cited

Albright, J. G., and B. C. Sherill, "Methods for the Analysis of Ternary Free-Diffusion Processes by the Rayleigh Optical Interferometric Method," *J. Solut. Chem.*, **8**, 201 (1979).

Bjerrum, N., "Zur Thermodynamik des Aktivitätskoeffizienten und des osmotischen Koeffizienten," *Zeitschr. f. Phys. Chem.*, **2**, 406 (1923); Translated from *Fysisk Tidsskrift, Kopenhagen*, **15**, 66 (1918).

Caldwell, C. S., and A. L. Babb, "Diffusion in Ideal Binary Liquid Mixtures," *J. Phys. Chem.*, **60**, 51 (1956).

Carman, P. C., and L. H. Stein, "Self-Diffusion in Mixtures: I," *Trans. Farad. Soc.*, **52**, 619 (1956).

Clark, W. M., and R. L. Rowley, "The Mutual Diffusion Coefficient of Methanol—*n*-Hexane Near the Consolute Point," *AIChE J.*, **32**(7), 1125 (1986).

Cullinan, H. T., Jr., "An Explicit Formulation of the Theory of Cluster Diffusion," *AIChE J.*, **31**(10), 1740 (1985).

Cussler, E. L., *Multicomponent Diffusion*, Elsevier Science, Amsterdam (1976).

Cussler, E. L., "Cluster Diffusion in Liquids," *AIChE J.*, **26**(1), 43 (1980).

Darken, L. S., "Diffusion, Mobility and Their Interrelation through Free Energy in Binary Metallic Systems," *Amer. Inst. Min. Metall. Pet. Eng.*, **175**, 184 (1948).

Emanuel, A., and D. G. Olander, "Diffusion Coefficients of Copper Sulfate in Water and Water in *n*-Butyl Alcohol," *Chem. Eng. Data*, **8**, 31 (1963).

Ertl, H., R. K. Ghai, and F. A. L. Dullien, "Liquid Diffusion of Nonelectrolytes: II," *AIChE J.*, **20**(1), 1 (1974).

Gainer, J. L., "Concentration and Temperature Dependence of Liquid Diffusion Coefficients," *Ind. Eng. Chem. Fund.*, **9**(3), 381 (1970).

Geet, A. L. van, and A. W. Adamson, "Prediction of Diffusion Coefficients for Liquid *n*-Alkane Mixtures," *Ind. Eng. Chem.*, **57**(7), 62 (1965).

Ghai, R. K., H. Ertl, and F. A. L. Dullien, "Liquid Diffusion of Nonelectrolytes: I," *AIChE J.*, **19**(5), 881 (1973).

Ginde, R. M., and A. S. Myerson, *Viscosity and Diffusivity in Metastable Solutions*, AIChE Symp. Ser., **87**(284), 124 (1987).

Gordon, A. R., "The Diffusion Constant of an Electrolyte, and its Relation to Concentration," *J. Chem. Phys.*, **5**, 522 (1937).

Gürkan, T., "Note to the Editor," *AIChE J.*, **33**(1), 175 (1987).

Hampe, M. J., W. Schermuly, and E. Blaß, "Decrease of Diffusion Coefficients near Binodal States of Liquid-liquid Systems," *Chem. Eng. Technol.*, **14**, 219 (1991).

Hartley, G. S., and J. Crank, "Some Fundamental Definitions and Concepts in Diffusion Processes," *Trans. Farad. Soc.*, **45**, 801 (1949).

Jany, P., "Thermophysical Property Measurements Near the Critical Point," *Exp. Thermal and Fluid Sci.*, **3**, 124 (1990).

Kim, Y.-C., and A. S. Meyerson, "Diffusivity of Lysozyme in Undersaturated, Saturated and Supersaturated Solutions," *J. of Cryst. Growth*, **143**, 79 (1994).

Kirkwood, J. G., and F. P. Buff, "The Statistical Mechanical Theory of Solutions: I," *J. Chem. Phys.*, **19**(6), 774 (1951).

McKeigue, K., and E. Gulari, "Light-Scattering Measurements of Diffusion in Binary Solutions Containing an Associating Component," *J. Phys. Chem.*, **88**, 3472 (1984).

McKeigue, K., and E. Gulari, "Effect of Molecular Association on Diffusion in Binary Liquid Mixtures," *AIChE J.*, **35**(2), 300 (1989).

Kohler, F., and O. K. Rice, "Coexistence Curve of the Triethylamine-Water System," *J. Chem. Phys.*, **26**(6), 1614 (1957).

Leffler, J., and H. T. Cullinan, Jr., "Variation of Liquid Diffusion Coefficients with Composition," *I&EC Fund.*, **9**(1), 84 (1970).

Lyons, P. A., and L. C. Sandquist, "A Study of the Diffusion of *n*-Butyl Alcohol in Water Using the Gouy Interference Method," *J. Amer. Chem. Soc.*, **75**, 3896 (1953).

Matos Lopes, M. L. S., C. A. Nieto de Castro, and J. V. Sengers, "Mutual Diffusivity of a Mixture of *n*-Hexane and Nitrobenzene Near its Consolute Point," *Int. J. Thermophys.*, **13**(2), 283 (1992).

Miller, D. G., "Series Expansion Methods for Extracting Ternary Diffusion Coefficients from Rayleigh Interferometric Data," *J. Solution Chem.*, **10**, 831 (1981).

Miller, D. G., "A Method for Obtaining Multicomponent Diffusion Coefficients Directly from Rayleigh and Gouy Fringe Position Data," *J. Phys. Chem.*, **92**, 4222 (1988).

Myerson, A. S., and P. Y. Lo, "Cluster Formation and Diffusion in Supersaturated Binary and Ternary Amino Acid Solutions," *J. of Cryst. Growth*, **110**, 26 (1991).

Nath, A., and E. Bender, "On the Thermodynamics of Associated Solutions: I and II," *Fluid Phase Equilib.*, **7**, 275 (1981).

Nernst, W., "Zur Kinetik der in Lösung befindlichen Körper," *Zeitschr. f. Phys. Chem.*, **2**, 613 (1888).

Onsager, L., "Reciprocal Relations in Irreversible Processes," *Phys. Rev.*, **37**, 405 (1931).

Onsager, L., "Reciprocal Relations in Irreversible Processes," *Phys. Rev.*, **38**, 2265 (1931).

Onsager, L, "Theories and Problems of Liquid Diffusion," *Ann. New York Acad. Sci.*, **46**, 241 (1945).

Powell, R. E., W. E. Roseveare, and H. Eyring, "Diffusion, Thermal Conductivity and Viscous Flow of Liquids," *Ind. Eng. Chem.*, **33**(4), 430 (1941).

Rathbun, R. E., and A. L. Babb, "Empirical Method for Prediction of the Concentration Dependence of Mutual Diffusivities in Binary Mixture of Associated and Nonpolar Liquids," *I&EC Proc. Des. Dev.*, **5**(3), 273 (1966).

Rollins, D. K., and K. S. Knaebel, "Applicability of Cullinan's Equation for Liquid Binary Diffusivities," *AIChE J.*, **37**(3), 470 (1991).

Rutten, Ph. W. M., "Diffusion in Liquids," PhD Thesis, Technical Univ. Delft, Delft, The Netherlands (1992).

Schreiner, E., "Om Anvendelsen Av Bjerrums Elektrolytiske Teori Paa Elektrolytdiffusjonen Og Diffusjonspotensialet," *Tidsskrift for Kemi og Bergvaesen*, **2**(10), 151 (1922).

Sengers, J. V., "Transport Properties of Fluids Near Critical Points," *Int. J. of Thermophy.*, **6**(3), 203 (1985).

Skelland, A. H. P., *Diffusional Mass Transfer*, Wiley, New York (1974).

Sørensen, J. M., and W. Arlt, *Liquid-Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Ser., Vol. V, Part 1, Binary Systems, Frankfurt (1979).

Thiel, P., A. Paschke, and J. Winkelmann, "Diffusion Coefficients, Viscosities and Densities in the Binary Subsystems of Methyl-Isopropyl-Ketone/*n*-Butyl-Acetate/Water," *Ber. Bunsenges. Phys. Chem.*, **97**, 1119 (1993).

Taylor, R., and R. Krishna, *Multicomponent Mass Transfer*, Wiley, New York (1993).

Tyrell, H. J. V., and K. R. Harris, *Diffusion in Liquids*, Butterworths, London (1984).

Vignes, A., "Diffusion in Binary Solutions," *I&EC Fund.*, **5**(2), 189 (1966).

Vitagliano, V., R. Sartorio, E. Chiaravalle, and O. Ortona, "Diffusion and Viscosity in Water-Triethylamine Mixtures at 19 and 20°C," *J. Chem. Eng. Data*, **25**, 121 (1980).

Wilke, C. R., "Estimation of Liquid Diffusion Coefficients," *Chem. Eng. Prog.*, **45**(3), 218 (1949).

Wu, G., M. Fiebig, and A. Leipertz, "Messung des binären Diffusionskoeffizienten in einem Entmischungssystem mit Hilfe der Photonen-Korrelationsspektroskopie," *Wärm. Stoffüb.*, **22**, 365 (1988).

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