Diffusion in Non-ideal Liquid Mixtures

R. Haase and W. Engels

Institut für Physikalische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

An equation proposed recently (Haase and Jansen, 1980) relates to the dependence on composition and temperature of the diffusion coefficient D and of the kinematic diffusion coefficient D^* in a binary nonelectrolyte solution. This equation is now applied to our own measurements of the activity coefficients and of the diffusion coefficient in the non-ideal liquid system carbon tetrachloride + acetone at 20 °C and 40 °C over the entire range of compositions. (For 0 °C only values of D are available.) It turns out that the function $D(x)$, where x denotes the mole fraction of one of the components, exhibits a minimum at each temperature, while $D^*(x)$ nearly represents a straight line. We establish a correlation between the deviations from Raoult's Law and the sign of the difference $D - D^*$.

In a previous paper [1] we proposed the following expression for the diffusion coefficient (interdiffusion coefficient) D of a binary nonelectrolyte solution:

$$D = B\,D^* \qquad (1)$$

with

$$B = 1 + (\partial \ln f_i / \partial \ln x_i)_{T,\,P} \qquad (2)$$

and

$$D^* = D^\circ \exp(-E^*/RT)\,, \qquad (3)$$

B denoting the thermodynamic factor, D^* the kinematic (kinetic) diffusion coefficient, x_i the mole fraction, f_i the activity coefficient (on the mole-fraction scale) of component i ($i = 1, 2$), T the thermodynamic temperature, P the pressure, and R the gas constant. The quantities D° and E^* are supposed to be independent of the temperature.

To describe the composition of the liquid mixture (carbon tetrachloride + acetone, for example) we use the mole fraction $x\,(= x_2 = 1 - x_1)$ of the second component (acetone in our example). Then D, B and D^* are functions of T and x, while D° and E^* only depend on x, if we neglect the pressure dependence of all these quantities.

Except for the special case $f_i = 1$ ($B = 1$, $D = D^*$), that is for an ideal mixture (a system obeying Raoult's Law for all compositions), we were unable to derive the functions $D^\circ(x)$ and $E^*(x)$ from published data since these were incomplete or inconsistent [1, 2, 3].

We are now in the position to evaluate the data for the non-ideal liquid system carbon tetrachloride + acetone over the entire range of compositions from our own measurements [4, 5] of the activity coefficients (at 20 °C, 25 °C, 30 °C, 35 °C, and 40 °C) and of the diffusion coefficient (at 0 °C, 20 °C, and 40 °C).

We present all the results for 20 °C and 40 °C in Table 1, the data for 0 °C (D only) in Table 2. The diffusion coefficients measured by Czworniak, Andersen, and Pecora [6] at 20 °C agree with ours within the limits of error. Those determined by Anderson, Hall, and Babb [7] at 25 °C are consistent with the values interpolated from our data.

Figures 1 and 2 show the functions $D(x)$ and $D^*(x)$ at 20 °C and 40 °C, respectively. Obviously

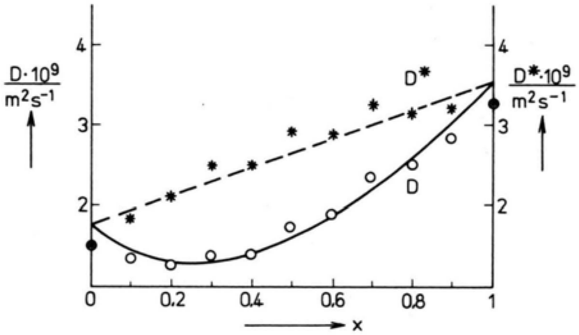

Fig. 1. Liquid system carbon tetrachloride + acetone at 20 °C: Diffusion coefficient D and kinematic diffusion coefficient D^* as functions of the mole fraction x of acetone (see Table 1).

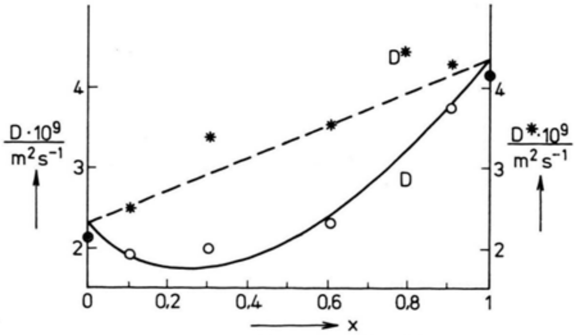

Fig. 2. Liquid system carbon tetrachloride + acetone at 40 °C: Diffusion coefficient D and kinematic diffusion coefficient D^* as functions of the mole fraction x of acetone (see Table 1).

Reprint requests to R. Haase, Institut für Physikal. Chemie der RWTH Aachen, Templergraben 59, 5100 Aachen.

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Table 1. Liquid system carbon tetrachloride + acetone at 20 °C and 40 °C [5]: Thermodynamic factor B, diffusion coefficient D (interpolated values), kinematic diffusion coefficient D^*, and the quantities $D°$ and E^* (independent of temperature) as functions of the mole fraction x of acetone.

	20 °C	20 °C	20 °C	40 °C	40 °C	40 °C		
x	B	$D \cdot 10^9$ / $\mathrm{m^2\,s^{-1}}$	$D^* \cdot 10^9$ / $\mathrm{m^2\,s^{-1}}$	B	$D \cdot 10^9$ / $\mathrm{m^2\,s^{-1}}$	$D^* \cdot 10^9$ / $\mathrm{m^2\,s^{-1}}$	$D° \cdot 10^7$ / $\mathrm{m^2\,s^{-1}}$	E^* / $\mathrm{kJ\,mol^{-1}}$
0	1	1.51	1.51	1	2.11	2.11	2.04	11.97
0.1	0.738	1.34	1.82	0.768	1.91	2.49	2.99	12.39
0.2	0.599	1.26[a]	2.10	0.635				
0.3	0.547	1.36	2.49	0.579	1.96	3.39	1.44	9.73
0.4	0.554	1.39	2.51	0.575				
0.5	0.596	1.74	2.92	0.606				
0.6	0.658	1.91	2.90	0.658	2.31	3.51	1.09	8.90
0.7	0.728	2.38	3.27	0.720				
0.8	0.805	2.54	3.16	0.791				
0.9	0.892	2.89	3.24	0.879	3.73	4.24	1.93	9.98
1	1	3.31	3.31	1	4.16	4.16	1.28	8.89

[a] This value is taken from the literature [6].

Table 2. Liquid system carbon tetrachloride + acetone at 0 °C [5]: Diffusion coefficient D (interpolated values) as function of the mole fraction x of acetone.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
$D \cdot 10^9$ / $\mathrm{m^2\,s^{-1}}$	1.08	0.66	0.56	0.76	0.80	0.91	1.34	1.66	1.84	2.17	2.28

$D(x)$ has a minimum (also at 0° C, see Table 2), while $D^*(x)$ nearly represents a straight line.

The functions $D°(x)$ and $E^*(x)$, which are independent of temperature, exhibit a somewhat irregular behaviour (see Table 1). In ideal mixtures $D°$ is a linear function of x, while E^* is constant [1, 3].

We notice that in the system at hand [4] with positive deviations from Raoult's Law ($f_i > 1$ for all compositions except the pure component i) we have $D/D^* < 1$ or $D < D^*$ (see Figs. 1 and 2), while in the system chloroform + acetone [1] which deviates negatively from Raoult's Law ($f_i < 1$) the statement $D/D^* > 1$ or $D > D^*$ holds. This rule is valid for all binary nonelectrolyte solutions, as far as the authors are aware. We will now prove that these correlations are not fortuitous.

We stipulate that the function $f_i(x_i)$ is monotonous. Experience shows that this is true for nearly all binary nonelectrolyte solutions. Then the inequality $f_i > 1$ ($f_i < 1$) implies the inequality

$$\partial \ln f_i / \partial x_i < 0 \quad (\partial \ln f_i / \partial x_i > 0) \,.$$

This follows in general from the fact that $f_i = 1$ for $x_i = 1$ and in particular from the first approximation for the activity coefficients f_1 and f_2 and the consequent expression for the thermodynamic factor B

$$\ln f_1 = b\, x_2^2, \quad \ln f_2 = b\, x_1^2, \quad B = 1 - 2\, b\, x_1\, x_2,$$

where b is constant for fixed temperature (and pressure). We thus derive from (1) and (2) for $f_i > 1$ ($f_i < 1$): $B < 1$ ($B > 1$), $D < D^*$ ($D > D^*$). Hence, the difference $D - D^*$ has the opposite sign of the difference $f_i - 1$.

If the function $D^*(x)$ is nearly linear (as in our system), the rule coincides with the statement [7] that positive (negative) deviations from Raoult's Law lead to negative (positive) deviations from the straight line in the $D(x)$-plot. This statement again holds for all published data we could trace (see also [8], [9]), though the additivity of D^* is by no means universal.

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[1] R. Haase and H.-J. Jansen, Z. Naturforsch. **35a,** 1116 (1980).
[2] R. Haase, R. Kottmann, and K.-H. Dücker, Z. Naturforsch. **30a,** 1084 (1975).
[3] R. Haase, Z. Naturforsch. **31a,** 1025 (1976).
[4] R. Haase and B. Bruch, Z. Naturforsch. **36a,** 915 (1981).
[5] W. Engels, Diplomarbeit, T. H. Aachen 1982.
[6] K. J. Czworniak, H. C. Andersen, and R. Pecora, Chem. Phys. **11,** 451 (1975).
[7] D. K. Anderson, J. R. Hall, and A. L. Babb, J. Phys. Chem. **62,** 404 (1958).
[8] P. A. Johnson and A. L. Babb, Chem. Revs. **56,** 387 (1956).
[9] H. J. V. Tyrrell, Diffusion and Heat Flow in Liquids, Butterworths, London 1961.

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