Diffusion in the Liquid System Chloroform + Methyl Acetate

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We present and discuss the results of measurements of the diffusion coefficient D and the activity coefficients as functions of the mole fraction x of one of the components in the liquid system chloroform + methyl acetate at 10 °C, 30 °C, and 50 °C. The function $D(x)$ exhibits a pronounced maximum at each temperature, while the kinematic diffusion coefficient D^*, considered as function of x, shows a flat minimum, its composition dependence being nearer to a linear relation than that of $D(x)$.

Continuing our work on diffusion in binary liquid systems [1–5], we investigated [6] the nonideal liquid system chloroform + methyl acetate. The measurements cover the entire range of compositions at 10 °C, 30 °C, and 50 °C. The diffusion coefficients are derived from interferometric experiments. The limits of reproducibility lie within ±3%.

As shown by the isothermal vapour-liquid-equilibrium data [6], the system exhibits negative azeotropy (minimum of vapour pressure at all temperatures). The values of the thermodynamic factor (f_i: activity coefficient, x_i: mole fraction of component i, T: temperature, P: pressure)

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

are given in Table 1. We also present the values of the diffusion coefficient D, of the kinematic diffusion coefficient $D^* = D/\beta$ and of the quantities D_0^* and E_D defined by the relation [7]

$$D^* = D_0^* \exp(-E_D/RT).$$

The quantities D_0^* and E_D ("activation energy") depend on the composition only, which we describe by the mole fraction x of methyl acetate.

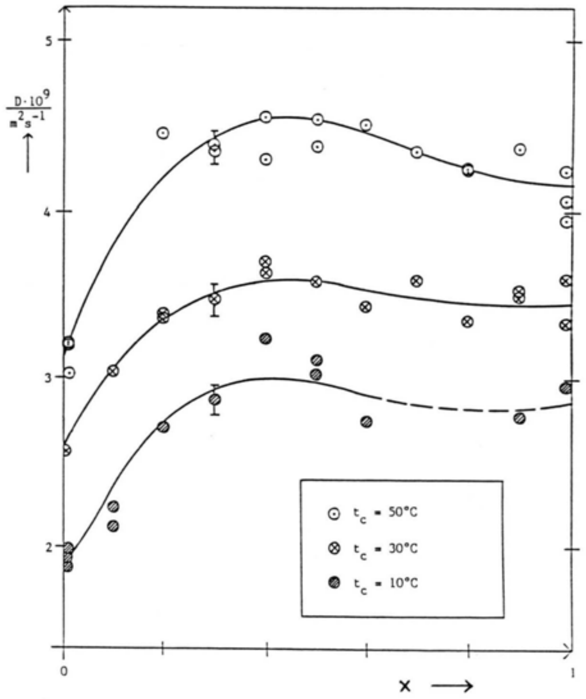

Fig. 1. Liquid system chloroform + methyl acetate: Diffusion coefficient D as function of the mole fraction x of methyl acetate and of the temperature t_c (see Table 1).

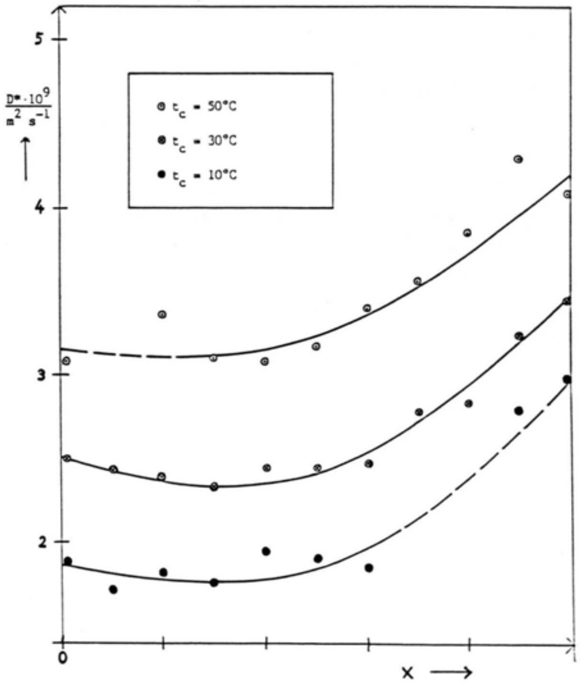

Fig. 2. Liquid system chloroform + methyl acetate: Kinematic diffusion coefficient D^* as function of the mole fraction x of methyl acetate and of the temperature t_c (see Table 1).

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Table 1. Liquid system chloroform + methyl acetate at 10 °C, 30 °C, and 50 °C. Thermodynamic factor β, diffusion coefficient D, kinematic diffusion coefficient D^* (both in units $10^{-9}\,\mathrm{m^2\,s^{-1}}$) as functions of the mole fraction x of methyl acetate.

$t_c/°\mathrm{C}$	10			30			50		
x	β	D	D^*	β	D	D^*	β	D	D^*
0.01	1.029	1.88 1.93 1.99	1.88	1.030	2.56	2.49	1.020	3.02 3.20 3.21	3.08
0.10	1.273	2.12 2.23	1.71	1.255	3.04	2.42	1.184	–	–
0.20	1.492	2.70	1.81	1.414	3.36 3.38	2.28	1.326	4.45	3.36
0.30	1.629	2.87	1.76	1.492	3.47	2.33	1.412	4.35 4.39	3.10
0.40	1.670	3.24	1.94	1.504	3.63 3.70	2.44	1.438	4.30 4.55	3.08
0.50	1.616	3.11 3.02	1.90	1.465	3.58	2.44	1.407	4.38 4.54	3.17
0.60	1.484	2.74	1.85	1.389	3.43	2.47	1.327	4.51	3.40
0.70	1.303	–	–	1.290	3.59	2.78	1.218	4.34	3.56
0.80	1.120	–	–	1.183	3.35	2.83	1.103	4.25 4.24	3.85
0.90	0.994	2.77	2.79	1.082	3.49 3.53	3.24	1.017	4.36	4.29
0.99	0.991	2.95	2.98	1.007	3.60 3.33	3.45	0.997	3.94 4.06 4.23	4.09

Table 2. Liquid system chloroform + methyl acetate. The quantities D_0^* and E_D (independent of temperature) as functions of the mole fraction x of methyl acetate.

x	$10^6\,D_0^*/(\mathrm{m^2\,s^{-1}})$	$E_D/(\mathrm{kJ\,mol^{-1}})$
0.01	0.132	10.0
0.20	0.166	10.6
0.40	0.180	10.9
0.60	0.148	10.2
0.80	0.090	8.6
0.99	0.049	6.7

Figures 1 and 2 show the plots of the functions $D(x)$ and $D^*(x)$ according to our measurements [6].

We see that the graph $D(x)$ exhibits a pronounced maximum, as to be expected for a system with negative deviations from Raoult's Law [5], while the graph $D^*(x)$ shows a flat minimum and is nearer to the straight line than the plot of the function $D(x)$. The numerical values of the activation energy E_D are considerably smaller than in other binary nonelectrolyte solutions [3–5].

For ideal systems ($f_i = 1$, $\beta = 1$, $D = D^*$), such as chlorobenzene + bromobenzene, we have: $E_D =$ const, while D_0^* is a linear function of x [2–4]. In nonideal liquid mixtures there is obviously no general rule with respect to the composition dependence of D^*, D_0^* and E_D.

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[7] We previously used the symbols B, D^0 and E^* for β, D_0^* and E_D, respectively.