p, T-Dependence of Self Diffusion in Mixtures of Hexane/Ethanol and Hexane/Dimethylether

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Self-diffusion in ethanol/hexane and dimethylether/hexane mixtures of various compositions has been measured at 215–350 K and up to 200 MPa. Qualitative analysis of the results indicates that, as expected, hydrogen bonding retards the self-diffusion of ethanol in the mixture, especially at the low temperatures. Dimethylether shows a slight effect of dipole-dipole interactions on the self-diffusion, as seen by a higher $\Delta E^{\neq}$ value than for the alkane. However there is no significant difference in the pressure dependence for both mixtures. This is shown by considering the ratio of the two diffusion coefficients, which suggests that, contrary to what is observed for pure alcohols, pressure has little effect upon the hydrogen bonding of ethanol in the mixture. In additon, there is surprisingly little concentration dependence on the ratios for either mixture.

Key words: Binary mixtures, Self diffusion, High pressure.

Introduction

In the previous paper [1] the influence of polar groups and hydrogen bonding upon self-diffusion in monomolecular liquids is discussed. The data and conclusions derived there will be applied in this paper for a qualitative analysis of the p, T-dependence of the self-diffusion coefficients D in two binary mixtures: Dimethylether/Hexane (D/H) as a prototype of a mixture consisting of an unpolar and a slightly polar molecule, and Ethanol/Hexane (E/H) as an example of a mixture in which one component has the ability to form transient twodimensional hydrogen bonded aggregates. D in mixtures of two alkanes (Propane/Tetradecane) was studied in [2]. The comparison of the data obtained there with those obtained in the present work should allow a more detailed evaluation of the influence of the dipole moment of dimethylether upon D in the mixtures. Comparable studies on the p, T-dependence of the diffusion coefficients in binary mixtures are few in the literature [3, 4], contrary to those in pure liquids [5].

Molecular dynamics (MD) simulations of hard sphere (HS) liquid mixtures have been done for a limited range of mass and diameter ratios [6] and for the tracer diffusion of each component only [7]. The comparison with experimental results is still fairly limited, the most comprehensive one being a study by Easteal and Woolf [8] on some equimolar mixtures.

Another reason for studying the p, T-dependence of diffusion in alkane-alcohol mixtures is the interest in their use as fuel substitutes. Prototype engines and results from performance trials are available [9]. However the paucity of good thermophysical data and hence incomplete understanding of the high temperature and pressure behaviour of such mixtures have hampered the optimisation of new engine systems.

Experimental

Dimethylether (99.8%), hexane (pa), and ethylalcohol (pa) were purchased from E. Merck (Darmstadt, FRG). The dimethylether was purified as described in [1]. Ethanol was stored over activated molecular sieve (3 Å) in order to remove residual moisture. From all substances oxygen and nitrogen was removed by freeze-pump-thaw-cycles.

The ethanol/hexane (E/H) mixtures were prepared by weight and filled into standard 5 mm high pressure glass capillaries as described in [10, 11]. The experimental setup used for the preparation of the dimethylether/hexane (D/H) mixture has been published in detail in [2]. An adequate amount of degassed hexane was filled into the high pressure mixing chamber, which was filled up with dimethylether drawn from

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the high pressure apparatus used in [1] for pure ether. The mixture was kept for at least 24 h at room temperature under a pressure of approx. 100 MPa and the mixing chamber turned upside down several times in order to facilitate complete homogenisation of the contents. The composition of the mixtures in the glass cells was determined before each experiment by integrating the proton NMR spectra. The integrations were reproducible to ± 0.5%. The concentrations determined are judged reliable to ± 1%. In order to avoid partial demixing by the formation of a gas phase the pressure in the D/H mixtures was always kept above 50 MPa.

For the determination of the diffusion coefficients, the methods described in [1] were used. The measured values are judged reliable to ± 5%, and their reproducability was ± 2% to 4%, except for the very dilute solutions. Since in the systems studied here the diffusion coefficients have only a rather slight dependence on concentration, the uncertainties in the concentrations do not contribute significantly to the error. However, the lower signal to noise ratio of mixtures containing a large excess of one substance introduces additional uncertainties.

Results and discussion

Tables 1 to 3 give the experimental diffusion coefficients. Since these data can only be compared with those of pure liquids, and since there are no sets of pVT data for the systems studied nor any published molecular dynamics simulations for these or similar systems, one must be content with a qualitative analysis.

Table 1. Self diffusion coefficients $D\,(10^{-9}\ \mathrm{m^2/s})$ in ethanol (E)/hexane (H) mixtures.

p (MPa)	5		50		100		150		200	
T (K)	H	E	H	E	H	E	H	E	H	E
10 mole% E/90 mole% H										
400.0	10.86	13.02	7.10	7.93	5.06	5.67	4.12	4.75	3.33	3.87
347.0	6.20	6.00	4.44	4.21	3.31	3.08	2.61	2.32	2.16	1.88
321.5	5.01	3.70	3.35	2.50	2.64	2.08	2.10	1.69	1.70	1.21
294.5	3.57	2.33	2.65	1.70	1.96	1.29	1.52	0.92	1.20	0.75
274.5	2.86	1.60	2.02	1.21	1.46	0.92	1.16	0.61	0.91	0.48
252.0	2.01	1.02	1.44	0.70	1.33	0.65	0.77	0.37	0.58	0.26
230.5	1.39	0.57	0.97	0.28	0.67	–	0.47	0.17	0.39	0.15
223.5	1.20	0.51	0.84	0.36	0.58	0.24	0.40	–	0.30	–
212.5	0.96	0.41	0.63	0.25	0.41	0.17	0.30	0.10	0.20	–
20 mole% E/80 mole% H										
374.5	9.02	9.03	–	–	–	–	–	–	–	–
371.5	–	–	5.69	5.61	4.16	4.20	3.35	3.25	2.72	2.63
353.0	6.61	5.64	4.64	3.79	3.57	2.84	2.74	2.25	2.24	1.84
324.0	4.91	3.92	3.46	2.50	2.62	1.74	2.01	1.29	1.59	1.05
293.5	3.35	1.95	2.42	1.46	1.73	1.05	1.38	0.80	1.15	–
274.0	2.60	1.31	1.78	0.91	1.38	0.68	1.08	0.53	0.83	0.41
253.5	1.92	0.86	1.34	0.60	0.97	0.43	0.74	0.32	0.62	0.27
222.5	1.11	0.42	0.78	0.29	0.54	0.20	0.40	0.14	0.31	0.12
210.5	0.83	0.28	0.60	0.21	0.37	0.16	0.27	0.105	0.22	0.095
50 mole% E/50 mole% H										
396.5	9.27	9.06	6.37	6.19	4.73	4.45	3.68	3.54	3.18	3.04
353.5	6.21	4.28	4.28	3.46	3.18	2.53	2.50	2.03	2.16	1.67
321.0	4.54	2.97	3.15	2.02	2.31	1.50	1.83	1.19	1.48	0.96
294.0	3.08	1.71	2.28	1.17	1.72	0.92	1.31	0.72	1.04	0.57
274.0	2.38	1.05	1.76	0.78	1.30	0.60	0.99	0.47	0.93	0.42
254.5	1.86	0.78	1.31	0.55	0.95	0.39	0.72	0.30	0.66	0.27
239.5	1.44	0.53	1.03	0.37	0.70	0.25	0.55	0.18	0.43	0.16
221.0	1.03	0.347	0.74	0.245	0.52	0.170	0.37	0.123	0.33	0.110
193.5	0.49	0.120	0.36	0.099	0.23	0.068	0.16	0.042	0.14	0.028

Table 2. Self diffusion coefficients D (10^{-9} m^2/s) in ethanol (E)/hexane (H) mixtures. (The lower part contains data on hexane D (H) and ethanol D (E) diffusion in very dilute solutions. For technical reasons one of the two compounds was deuterated. Within the accuracy of the data no dynamic isotope effect was observable.)

p (MPa)	5		50		100		150		200	
T (K)	H	E	H	E	H	E	H	E	H	E
					70 mole% E/30 mole% H					
419.0	10.66	7.51	6.61	6.91	5.06	5.40	4.40	4.28	3.41	3.76
370.0	6.31	4.98	4.01	3.47	3.14	2.75	2.52	2.26	2.12	1.95
346.5	4.48	3.34	3.18	2.43	2.45	1.90	1.93	1.58	1.56	1.31
321.0	3.36	2.05	2.29	1.49	1.72	1.19	1.36	0.99	1.16	0.84
295.0	2.16	1.29	1.42	0.49	1.21	0.75	0.94	0.63	0.75	0.51
275.5	1.65	0.72	1.13	0.54	0.82	0.42	0.70	0.35	0.54	0.29
248.5	1.06	0.39	0.79	0.30	–	–	–	–	–	–
250.0	–	–	–	–	0.55	0.24	0.43	0.21	0.34	0.17
227.0	0.61	0.19	0.49	0.15	–	–	–	–	–	–
229.0	–	–	–	–	0.35	0.13	0.26	0.098	0.20	0.078
216.5	0.54	0.14	0.36	0.10	0.27	0.082	0.19	0.062	0.15	0.051
204.0	0.45	0.11	0.30	0.089	0.19	0.066	0.14	0.054	0.11	0.045

D(H), 98 mole% E–d_6/2 mole% H

p (MPa) T (K)	5	50	100	150	200
417.0	8.54	6.01	4.30	3.53	3.20
390.5	6.24	4.45	3.38	2.72	2.41
364.0	4.60	3.30	2.46	2.01	1.76
342.5	3.34	2.45	1.88	1.51	1.30
319.5	2.68	2.00	1.53	1.21	1.07
291.5	1.62	1.12	0.85	0.72	0.58
272.5	1.13	0.81	0.61	0.48	0.41
262.5	1.08	0.71	0.51	0.39	0.32
251.5	0.75	0.54	0.39	0.30	0.26
229.0	0.51	0.36	0.25	0.19	0.15
208.0	0.29	0.19	0.13	0.093	0.0076

D(E), 95 mole% E/5 mole% H–d_{14}

p (MPa) T (K)	5	50	100	150	200
426.5	10.23	7.13	5.45	4.66	4.04
385.5	5.58	4.21	3.38	2.84	2.38
351.5	3.23	2.55	2.08	1.74	1.49
320.5	1.83	1.47	1.20	1.01	0.87
294.5	1.04	0.84	0.69	0.58	0.50
272.5	0.61	0.49	0.41	0.34	0.30
244.0	0.28	0.22	0.18	0.15	0.13
222.5	0.14	0.12	0.092	0.076	0.065
198.5	0.052	0.039	0.029	0.022	0.017

For the slope of the various isobars in Arrhenius plots activation energies $\Delta E^{\neq}(p)$ at constant pressure may be calculated. In the study of the unpolar binary mixture propane/tetradecane [2] it was observed that both constituents of each mixture have, within experimental error, identical activation energies, while for the two pure substances the lighter and smaller propane has a significantly lower $\Delta E^{\neq}(p)$. Although the difference in $\Delta E^{\neq}(p)$ for the pure substances D and H is smaller than in the case studied in [2] ($\Delta E^{\neq}(p) = 6.5 \pm 0.5$ kJ/mole for D [1] and 9.2 ± 1 kJ/mole for H [12]), it appears that the dipolar compound shows a slightly larger temperature dependence of D, as apparent from the isobars given in Fig. 1 for the mixture with 69 mole% D and 31 mole% H. However, the slope in the lower temperature range of the isobars is the same within experimental error. The activation energy calculated, for instance, for all three D/H mixtures at 230 K is

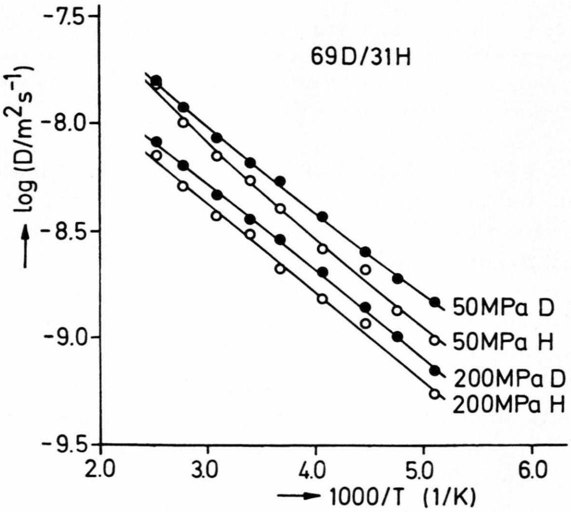

Fig. 1. Isobars of the self diffusion coefficients D in a mixture containing 69 mole% dimethylether (D) and 31 mole% hexane (H).

Table 3. Self diffusion coefficients D (10^{-9} m^2/s) in dimethylether (D)/hexane (H) mixtures.

p (MPa)	50		100		150		200	
T (K)	H	D	H	D	H	D	H	D
32 mole% D/68 mole% H								
428.0	9.89	14.62	7.42	10.76	5.53	8.20	4.88	7.19
391.5	6.78	10.98	5.12	8.09	4.43	6.78	4.02	6.01
365.5	5.03	9.28	4.09	6.84	3.27	5.38	2.81	4.72
323.0	3.78	6.19	2.75	4.67	2.26	3.82	1.94	3.28
292.0	2.69	4.40	2.01	3.38	1.61	2.70	1.41	2.43
274.0	2.08	3.521	1.61	2.764	1.29	2.272	1.12	2.00
251.0	1.62	2.61	1.23	1.97	0.94	1.55	0.80	1.35
222.0	0.98	1.55	0.70	1.18	0.53	0.89	0.47	0.80
198.0	0.56	0.91	0.40	0.66	0.29	0.48	0.24	0.42
41 mole% D/59 mole% H								
454.0	12.07	17.46	8.73	12.87	7.04	10.53	6.06	8.96
418.5	9.18	13.62	6.96	10.13	5.66	8.33	4.81	7.13
388.0	7.54	11.14	5.78	8.48	4.62	6.86	3.93	5.96
356.5	6.01	8.75	4.62	6.85	3.64	5.57	3.14	4.75
326.5	4.61	6.35	3.62	5.11	2.93	4.13	2.26	3.56
295.0	3.42	5.21	2.75	4.30	2.12	3.01	1.71	2.69
273.5	2.76	4.15	2.07	3.14	1.68	2.54	1.34	2.02
260.5	2.07	3.19	1.65	2.59	1.25	2.11	1.12	1.79
242.0	1.70	2.55	1.34	2.02	1.06	1.59	0.81	1.25
230.0	1.38	2.15	1.05	1.57	0.79	1.23	0.63	1.00
213.0	1.01	1.56	0.75	1.12	0.56	0.89	0.42	0.71
207.5	0.94	1.42	0.75	1.07	0.46	0.77	0.40	0.65
183.0	0.47	0.76	0.35	0.55	0.23	0.39	–	–
69 mole% D/31 mole% H								
395.5	15.25	15.86	10.52	11.60	8.23	9.49	7.04	8.22
360.0	10.09	11.84	7.72	9.10	5.93	7.27	5.12	6.38
324.5	7.04	8.57	5.75	6.69	4.43	5.51	3.69	4.63
295.0	5.41	6.51	4.17	5.18	3.47	4.20	3.03	3.59
272.5	3.98	5.33	3.08	4.14	2.68	3.27	2.08	2.85
246.0	2.60	3.64	2.14	2.82	1.83	2.28	1.52	2.00
224.0	2.07	2.51	1.57	1.91	1.36	1.51	1.16	1.36
210.0	1.32	1.86	1.09	1.47	0.89	1.16	–	1.00
195.5	0.97	1.44	0.74	1.10	0.66	0.86	0.54	0.70

7.8 ± 1 kJ/mole and identical for both compounds and independent of composition and pressure. For the E/H mixtures a significant difference in slope is seen for all concentrations studied (Figure 2). The hydrogen bonding between the alcohol molecules retards the self-diffusion of this compound with falling temperature much faster than that of the unpolar alkane. At lower temperatures one calculates for all E/H mixtures for the alcohol a concentration independent $\Delta E^{\neq}(p) = 13 \pm 1$ kJ/mole, while for the alkane $\Delta E^{\neq}(p) = 10 \pm 1$ kJ/mole is derived. For both components of the E/H mixtures the activation energies seem to increase slightly with pressure. However, this increase is well within experimental error.

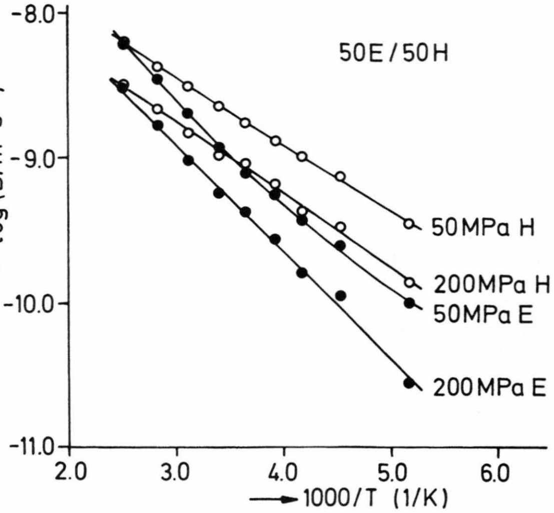

Fig. 2. Isobars of the self diffusion coefficients D in an equimolar mixture of ethanol (E) and hexane (H).

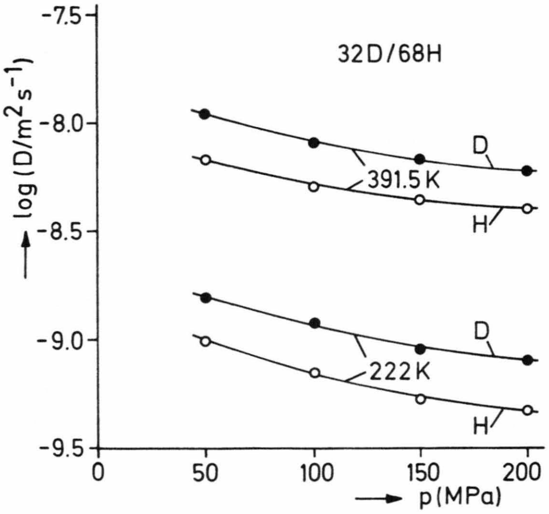

Fig. 3. Isotherms of the self diffusion coefficients D in a mixture containing 32 mole% dimethyleter (D) and 68 mole% ethanol (E).

In Fig. 3 two isotherms for the self diffusion of each component of the D/H mixture are given. Typically the diffusion coefficient decreases with pressure, with the slope becoming smaller with increasing pressure. For all temperatures and compositions studied here the isotherms for the diffusion coefficients of both compounds run parallel within experimental accuracy. This holds as well for all E/H mixtures as given

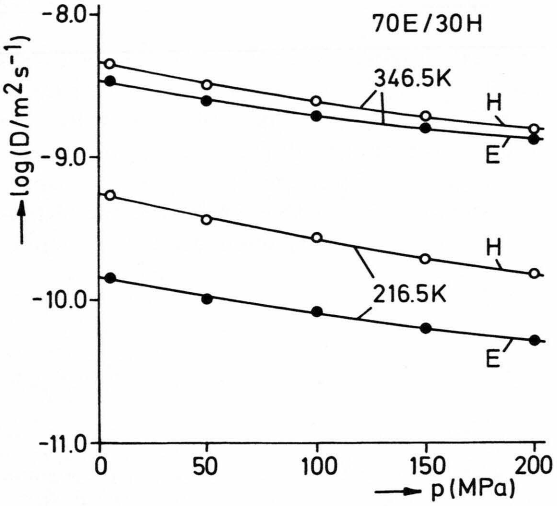

Fig. 4. Isotherms of the self diffusion coefficients D in a mixture containing 70 mole% ethanol (E) and 30 mole% hexane (H).

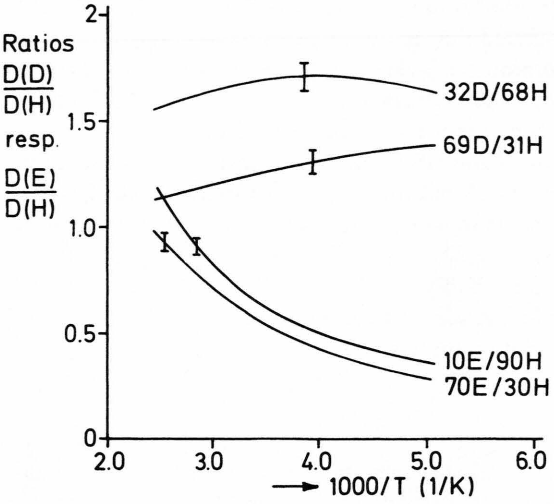

Fig. 5. Ratios of the self diffusion coefficients $D(\mathrm{D})/D(\mathrm{H})$ and $D(\mathrm{E})/D(\mathrm{H})$ for four binary mixtures. (The numbers given at the individual curves are the concentrations in mole%.) Error bars indicate standard deviations. Any pressure dependence of these ratios is well within these limits.

in Fig. 4 and Tables 1 to 3. The activation volume $\Delta V^{\neq}$, as defined in [1], is positive and becomes smaller with increasing pressure. Also there is a significant increase of $\Delta V^{\neq}$ with temperature, this effect being more pronounced for the D/H system. At 150 MPa $\Delta V^{\neq}$ typically increases from 8 $(10^{-6}\ \mathrm{m^3/mole})$ at 215 K to 15 $(10^{-6}\ \mathrm{m^3/mole})$ at 350 K. There is no significant difference in the pressure dependence between the two mixtures studied. This leads to the conclusion that hydrogen bonding in the E/H mixture is only marginally influenced by the applied pressures. This is contrary to the very pronounced effects observed upon lowering the temperature (Figs. 1 and 2). For simple monoalcohols and similar compounds, the reaction volume ΔV for the formation of a hydrogen bond is normally [13] between 2 and 6 $(10^{-6}\ \mathrm{m^3/mole})$. Pressure thus must slightly favor the aggregation of the alcohols in the mixture. However, the p-dependence of the self-diffusion is obviously not very sensitive to slight changes in the association equilibria.

In the absence of density data it appears impossible to compare the two systems more quantitatively, since diffusion is a rather sensitive function of density [14]. However, the p, T-dependence of the ratio of the two self diffusion coefficients in each mixture should reveal rather sensitively the general trends typical for these classes of binary systems. For all the data collected in the Tables 1 to 3 the isobars were fitted to second order polynomials, and from these polynomials the ratios of the two diffusion coefficients ($D(\mathrm{D})/D(\mathrm{H})$ and $D(\mathrm{E})/D(\mathrm{H})$) were calculated. These ratios are, within experimental error, independent of pressure, emphasizing the trend discussed for the isobars above. Thus in Fig. 5 the mean of the ratios of all isobars for 4 mixtures are compiled. The standard deviation being typically 3% to 4%. Qualitatively these ratios are similar for all concentrations in each of the binary systems studied. In the D/H system a slight increase is observed with falling temperature, indicating that the larger mass and volume of the unpolar hexane molecule leads to a slightly greater temperature dependence for diffusion and that the influence of the dipolar attraction upon the diffusion of the ether can be only small. In all alcohol containing mixtures the formation of more, larger and longer lived transient hydrogen bonded aggregates with falling temperature is obvious from the rapid decrease of these ratios. It appears remarkable and unexpected that the concentration dependence of these ratios is also rather weak in the hydrogen bonded system.

A more detailed analysis of these results will be possible if density data for the two systems become available. Also an extension of the hard-sphere liquid molecular dynamics studies will be essential for a better understanding of the quantitative aspects. It can be predicted that it will be possible to describe mixtures containing dipolar molecules, which experimentally show slight deviations from the behaviour of the systems consisting of unpolar molecules only, by extensions of the HS-model as for instance the interacting sphere [15] and the rough hard sphere model [16]. The mixtures in which one component participates in hydrogen bonding pose a more complex problem, and most probably should be studied in molecular dynamics simulations with explicit inclusion of the hydrogen bonding interaction.

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