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Infinite Dilution Diffusion Coefficients of Several Aromatic Hydrocarbons in Octane and 2,2,4-Trimethylpentane

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The diffusion coefficients of benzene, toluene, *p*-xylene, *o*-xylene, ethylbenzene, and mesitylene at infinite dilution in octane and in 2,2,4-trimethylpentane in the temperature range 303.2−333.2 K were determined by the Taylor dispersion technique. A correlation based on a free-volume-type expression represented the results to within experimental uncertainty.

Introduction

Diffusion coefficient measurements are required in a number of engineering applications and also in testing transport property theories. For the determination of infinite dilution diffusion coefficients of liquid/liquid systems, several well-established methods have been discussed by Cussler (1984). The Taylor dispersion technique is one of the most useful methods for dilute solutions because it can give accurate results rapidly and can be operated easily. The application of this technique to determination of infinite dilution diffusion coefficients has been demonstrated in a number of recent papers (Matthews and Akgerman, 1987a,b; Rodden et al., 1988; Wong and Hayduk, 1990; Gustafson and Dickhut, 1994). In this paper, a new apparatus was constructed to determine diffusion coefficients of several aromatic hydrocarbons at infinite dilution in octane and in 2,2,4-trimethylpentane in the temperature range 303.2−333.2 K. The diffusion coefficient is highly dependent on molecular structures. A free-volume-type expression was used to correlate the results.

Experimental Section

Chemicals. The chemicals used in this work had the following purities as reported by the supplier (Shanghai Chemical Agent Supply Station): benzene (99.5% mass), toluene (99.5%), ethylbenzene (98%), *p*-xylene (98%), *o*-xylene (98%), mesitylene (1,3,5-trimethylbenzene) (99.9%), heptane (99%), octane (99%), 2,2,4-trimethylpentane (98.5%). The 2,2,4-trimethylpentane was further purified with silica gel adsorption in order to remove the impurities which may interfere with its UV absorbance.

Diffusion Apparatus. Diffusion coefficients were measured using the Taylor dispersion apparatus (Taylor, 1953). In a typical experiment, a small amount of sample solution is injected as a pulse into a solvent which undergoes steady laminar flow in a capillary tube. The combination of molecular diffusion and convection causes the pulse of solute to disperse axially. According to Taylor's analysis for dispersion in liquids (Taylor, 1953), the concentration profile at the far end of the tube is Gaussian. According to Levenspiel and Smith (1957) and Ouano (1972, 1975)

$$D_{AB} = 0.2310 r^2 u t_R^{\,2}/(L W_{1/2}^{\,2}) \qquad (1)$$

where L is the tube length, $W_{1/2}$ is the peak width at half its height, r is the radius of the tube, u is the solvent velocity, and t_R is the retention time of the solute in the tube.

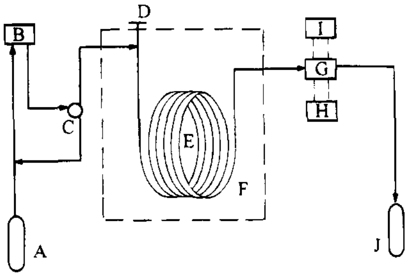

Figure 1. Schematic diagram of the experimental apparatus: (A) solvent reservoir, (B) solvent pump, (C) split-flow controller, (D) injector, (E) diffusion tube, (F) heated enclosure, (G) detector, (H) recorder, (I) computer, (J) waste vessel.

Table 1. Diffusion Coefficients of Benzene at Infinite Dilution in Heptane

$10^5 D_{AB}/(\mathrm{cm^2{\cdot}s^{-1}})$				
303.2 K	313.2 K	323.2 K	333.2 K	reference
3.88	4.41	4.91	5.33	this work
	4.45	5.05	5.51	Grushka and Kikta (1976)
3.64	4.14	4.78	5.61	Calus and Tyn (1973)
4.19	4.74	5.32	5.89	extrapolated from Sanni (1973)

Table 2. Diffusion Coefficients at Infinite Dilution in Octane

	$10^5 D_{AB}/(\mathrm{cm^2{\cdot}s^{-1}})$			
solute	303.2 K	313.2 K	323.2 K	333.2 K
benzene	3.39 ± 0.05	3.82 ± 0.12	4.23 ± 0.10	4.71 ± 0.04
toluene	3.05 ± 0.03	3.33 ± 0.06	3.69 ± 0.08	4.23 ± 0.06
p-xylene	2.82 ± 0.03	3.17 ± 0.04	3.71 ± 0.06	4.17 ± 0.01
o-xylene	2.65 ± 0.04	2.99 ± 0.02	3.44 ± 0.03	3.94 ± 0.03
ethyl benzene	2.56 ± 0.03	2.83 ± 0.09	3.09 ± 0.11	3.59 ± 0.05
1,3,5-trimethylbenzene	2.21 ± 0.02	2.51 ± 0.04	2.87 ± 0.07	3.23 ± 0.02

Shown in Figure 1 is the schematic diagram of the apparatus used. The solvent is delivered at a low and steady flow rate (0.1 $\mathrm{cm^3{\cdot}min^{-1}}$) with a high-performance liquid chromatography pump (Shimadzu Model LC-3A). The solute peak is detected with a Shimadzu UV detector (254 nm wavelength; model UVD-2). The capillary tube is made of 6825 cm long, 0.0203 cm i.d. coiled quartz glass capillary tube (coil diameter is 30 cm). The tube radius was determined gravimetrically by weighing the mass of water contained in the whole tube and further confirmed by measuring the retention time of a sample at a known volumetric flow rate. The apparatus was enclosed in a thermostat controlled to ±0.1 K. Secondary flow occurs

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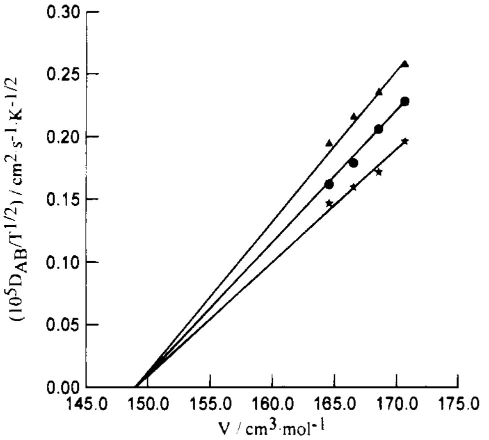

Figure 2. $D_{AB}/T^{1/2}$ against the molar volume of octane: ▲, benzene; ●, *p*-xylene; ★, ethylbenzene; —, calculated from eq 2.

Table 3. Diffusion Coefficients at Infinite Dilution in 2,2,4-Trimethylpentane

	$10^5D_{AB}/(cm^2 \cdot s^{-1})$			
solute	303.2 K	313.2 K	323.2 K	333.2 K
benzene	3.46 ± 0.05	3.94 ± 0.05	4.62 ± 0.04	4.93 ± 0.02
toluene	3.15 ± 0.03	3.67 ± 0.05	4.17 ± 0.06	4.50 ± 0.05
p-xylene	3.03 ± 0.03	3.60 ± 0.07	3.83 ± 0.08	4.18 ± 0.08
o-xylene	2.62 ± 0.04	3.16 ± 0.02	3.63 ± 0.03	3.93 ± 0.03
ethyl benzene	2.63 ± 0.03	3.07 ± 0.06	3.41 ± 0.01	3.73 ± 0.03
1,3,5-trimethylbenzene	2.26 ± 0.05	2.62 ± 0.03	3.13 ± 0.04	3.56 ± 0.02

Table 4. V_D and β for Solute in Octane and in 2,2,4-Trimethylpentane

	$\beta/(mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-0.5})$	
solute	octane $V_D = 148.97\ cm^3 \cdot mol^{-1}$	2,2,4-trimethylpentane $V_D = 150.80\ cm^3 \cdot mol^{-1}$
benzene	0.012 02	0.012 22
toluene	0.010 68	0.011 17
p-xylene	0.010 53	0.010 46
o-xylene	0.009 78	0.009 48
ethylbenzene	0.009 07	0.009 31
mesitylene	0.008 16	0.008 55

when fluid passes through a coiled tube. Alizadeh et al. (1980) recommended that if $De^2Sc < 20$, the effect of secondary flow is negligible. *De* is the Dean number $[Re/(Rc/R)^{1/2}]$ and *Sc* is the Schmidt number $[\mu/\varrho D_{AB}]$. In order to obtain accurate diffusion coefficients, the flow rate in the capillary tube must be less than 2 cm·s⁻¹. A split-flow controller was applied to ensure the value of De^2Sc was less than 2 in this work. The mole fraction of the injected sample was no higher than 0.01, and the volume of the solution injected was from 0.2 to 0.6 μL. The injector was a Shimadzu LC injector, model SIL-1A. We believe the result to be accurate to ±5%.

Results and Discussion

In order to test our apparatus, the diffusion coefficients of benzene in heptane were measured and compared with literature values in Table 1. The differences are less than 5%. The diffusion coefficients of benzene, toluene, *p*-xylene, *o*-xylene, ethylbenzene, and mesitylene in octane and in 2,2,4-trimethylpentane are given in Tables 2 and 3. Each reported value in these tables is the mean of three to four measurements.

Chen et al. (1982) developed a free-volume-type expression for diffusion in the form

$$D_{12}/T^{1/2} = \beta(V - V_D) \qquad (2)$$

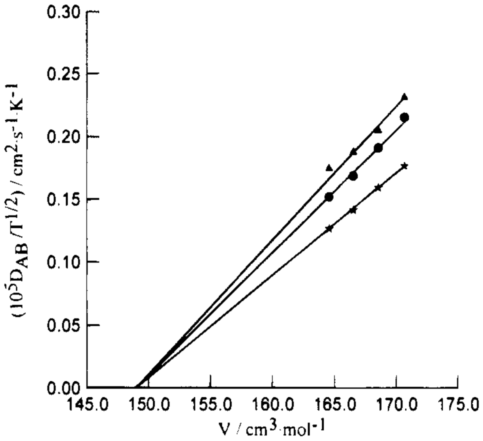

Figure 3. $D_{AB}/T^{1/2}$ against the molar volume of octane: ▲, toluene; ●, *o*-xylene; ★, mesitylene; —, calculated from eq 2.

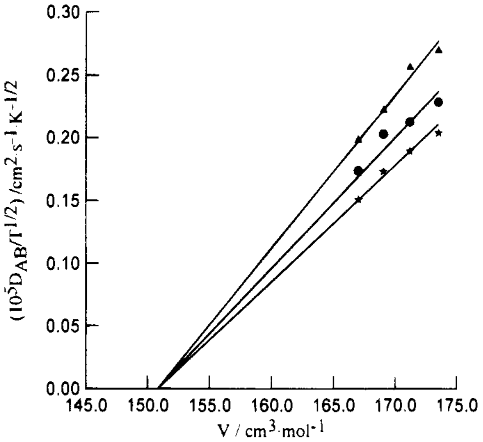

Figure 4. $D_{AB}/T^{1/2}$ against the molar volume of 2,2,4-trimethylpentane: ▲, benzene; ●, *p*-xylene; ★, ethylbenzene; —, calculated from eq 2.

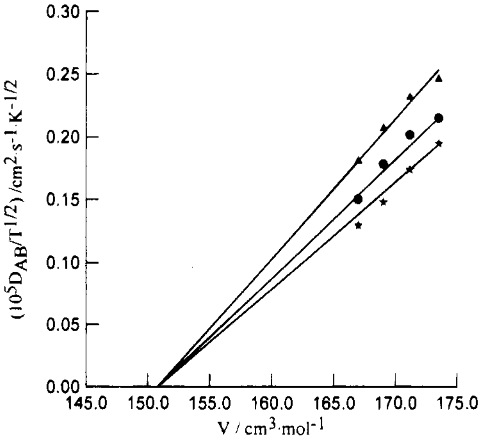

Figure 5. $D_{AB}/T^{1/2}$ against the molar volume of 2,2,4-trimethylpentane: ▲, toluene; ●, *o*-xylene; ★, mesitylene; —, calculated from eq 2.

where β is a function of the solute and solvent interaction, V_D is the theoretical molar volume at which the diffusion coefficient goes to zero. We treated V_D as a function only of the solvent just as a number of papers did (Wong and Hayduk, 1990; Matthews and Akgerman, 1987a), though V_D is also a weak function of solute size (Matthews and Akgerman, 1987b). Solvent densities were obtained from Vargaftik (1975). Figures 2 and 3 show the plot of $D_{AB}/T^{1/2}$ for each solute in octane, and Figures 4 and 5 show those in 2,2,4-trimethylpentane. Values of β and V_D are obtained using linear least squares and are shown in Table

4. The linear relationship was observed for all systems studied. The free-volume-type expression correlates the experimental results well. For the 48 diffusion values measured, the average absolute deviation is 1.8%.

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