Diffusion Coefficients of Substituted Benzenes and Alcohols at High Dilution in Octan-1-ol

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Interdiffusion coefficients D_{ao} in octan-1-ol of benzene, toluene, chlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, bromobenzene, 1,2-dibromobenzene, and 1,4-dibromobenzene have been measured at 25 °C at average solute mole fractions from 0.001 to 0.000 05 using the Taylor dispersion technique. The D_{ao} values range from 0.5×10^{-9} m^2/s to 0.3×10^{-9} m^2/s with standard deviations below 4% in all but the highest dilutions and show only minor (and statistically insignificant) variations with solute concentration. In addition, corresponding interdiffusion coefficients of methanol, ethanol, propan-1-ol, butan-1-ol, 2-methylpropan-2-ol and phenol were determined at average mole fractions around 0.0004. For both groups of compounds, distinct but separate dependencies of D_{ao} on molecular size were observed. The results are discussed from the viewpoint of the Stokes−Einstein equation, and in comparison with literature data for the corresponding diffusion in water. The analysis reveals different dependencies of the interdiffusion coefficients on solvent viscosity for the two classes of compounds. Current chemical engineering correlations to predict D_{ao} at high dilution (D_{ao}^{∞}) yield only moderate agreement for the benzenes and perform particularly poorly for the alcohols, suggesting that additional experimental work is needed to better understand molecular diffusion in more viscous media.

Introduction

The transfer of chemical contaminants between environmental compartments is often driven by passive diffusion processes. This holds also for the uptake of organic compounds from ambient water in aquatic organisms, which can be described with a physicochemical model based on first-order kinetics and passive diffusion through aqueous and lipid layers (Gobas et al., 1986). For these and other applications, diffusion coefficients are needed to quantify the mass transfer within and across fluid phases.

Besides experimental techniques to determine diffusion coefficients, there are also available estimation methods with varying complexity (Reid et al., 1987). However, most of the theoretical methods have not been tested thoroughly for their applicability to hydrophobic compounds in water. For a group of mono- and disubstituted benzenes, an investigation of interdiffusion coefficients at high dilution in water revealed that prominent chemical engineering correlations give rather poor results when compared with recent experimental values (Gabler et al., 1996). This is illustrated with a particularly simple equation for the diffusion coefficient in water, D_{aw}, at 25 °C, which is based only on molecular weight (Schwarzenbach et al., 1993). Its application for benzene, and 1,4-dichloro- and 1,4-dibromobenzene gives calculation errors of 8%, −19%, and −33%, respectively, which suggests increasingly large deviations for increasingly hydrophobic solutes. With regard to diffusion of these and other hydrophobic aromatic compounds through more viscous media, there are only few experimental data available, and there is almost no experience with the respective prediction performance of chemical engineering correlations.

From the environmental viewpoint, hydrophobic compounds such as the halogenated aromatics are of particular concern owing to their generally high persistence and their potential for bioconcentration in aquatic media through passive uptake into organisms (Schüürmann and Markert, 1998). As noted above, quantification of bioconcentration kinetics would need diffusion coefficients of the compounds in water and in lipid. According to the Stokes−Einstein equation, the latter would be related to the former through the inverse ratio of the solvent viscosities. However, there is sufficient evidence that differences in solvent viscosity, in general, do not translate quantitatively into corresponding differences in the diffusion coefficients (e.g., Tyrrell and Harris, 1984; Reid et al., 1987). For the class of hydrophobic compounds, it is thus unclear whether and how diffusion coefficients in lipids or other more viscous media could be extrapolated from results in water.

In the present investigation, we use the Taylor dispersion technique to determine interdiffusion coefficients of eight benzenes at high dilution in octan-1-ol, whose viscosity is approximately eight times greater than that of water ($\eta_o = 7.288 \times 10^{-3}$ Pa s and $\eta_w = 0.890 \times 10^{-3}$ Pa s at T = 298.15 K) (Lide, 1992). The Taylor dispersion technique had been applied earlier to carrier liquids such as octan-1-ol and solvents having similar viscosities (Evans et al., 1979; Chen et al., 1983), and we have used the same method in our previous study of the corresponding diffusion in water (Gabler et al., 1996). With this class of compounds, there are only few experimental diffusion coefficients in octan-1-ol available (Ramprasad et al., 1990, 1991a,b), which, however, have been determined with large initial concentration gradients using a diaphragma apparatus and cannot be transformed to differential values at high dilution.

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In addition to benzene and the seven hydrophobic benzene derivatives, the interdiffusion coefficients in octan-1-ol of phenol and five aliphatic alcohols were also determined. With these alcohols, comparison of the measurement results was possible with literature data for both octan-1-ol (Miller, 1991) and water (Hao and Leaist, 1996) as solvents. Furthermore, the solute−solvent interactions are stronger for alcohols than for hydrophobic benzenes in both solvents, which offers an interesting starting point for a comparative analysis of the results with these two compound classes.

Experiment and Procedure

Our Taylor dispersion apparatus and the procedure for numerical data analysis have been described earlier (Gabler et al., 1996). Although the flow regime with octan-1-ol as carrier liquid differs from the case with water, the apparatus meets the requirements (Alizadeh et al., 1980; Baldauf and Knapp, 1983) to fulfill the boundary conditions for the use of Taylor's solution of the dispersion equation (Taylor, 1953). The working regime of our apparatus can be characterized by the following dimensionless parameters: Reynolds number $Re = 0.3$; squared length-to-radius ratio of the capillary $L^2/R^2 = 2.04 \times 10^9$; Peclet number $1.2 \times 10^8 \leq Pe \leq 4.8 \times 10^8$.

The test compounds were purchased with quality "p.a." or "pure" (with a purity greater than 99%) from Merck, Darmstadt, Germany, and were used without further purification. The dispersion measurements were carried out at constant temperature (298.15 ± 0.1 K) with pure octan-1-ol as the carrier liquid, and the potential dependence of the measurement values on the solute concentration was studied explicitely by analyzing for each compound series of solutions with different solute mole fractions. All solutions were prepared gravimetrically, and the solute mole fractions of the test samples (x_a^{sample}) ranged from 0.001 to 0.02 (the uncertaity in mole fraction is below 0.0001). For each solution (concentration level), the measurement (i.e. three or more injections) was repeated two or more times on different days. Statistical tests at the 95% confidence level confirmed the correctness of overall averaging of corresponding experimental data.

The measured interdiffusion coefficients refer to average solute mole fractions x_a in the region between the injected sample and the carrier solution, which are calculated by means of eq 1 (Baldauf, 1981), taking into account that the solute concentration in the carrier solution is zero:

$$x_a \approx x_a^{\mathrm{sample}} \cdot \frac{h}{2} \left(\frac{\pi u R^2 L}{48 D_{ao}} \right)^{-1/2} \tag{1}$$

The relevant experimental parameters of our apparatus are as follows: pulse length $h = 10.2$ cm, linear velocity $u = 33.6$ cm/min, capillary radius $R = 0.252$ mm, capillary length $L = 11.30$ m.

To enable a comparison of the experimental values with predictions from the Stokes−Einstein model, molecular van der Waals radii of the compounds in solution, r_a, were required for an application of the corresponding equation that yields the interdiffusion coefficient D_{ab}^{∞} of solute a in solvent b at infinite dilution as a function of r_a and the dynamic viscosity of the solvent, η_b:

$$D_{ab}^{\infty} = \frac{k_B T}{n_{SE} \cdot \pi \cdot \eta_b \cdot r_a} \tag{2}$$

Table 1. Measured Interdiffusion Coefficients D_{ao} and Their Standard Deviations at the Mole Fraction x_a (Calculated According to Eq 1) in Octan-1-ol at 25 °C and the Respective Number n of Individual Measurements and Calculated Molecular van der Waals Radii r_a

substance	x_a	n	$D_{ao} \times 10^9$/ $\mathrm{m^2 \cdot s^{-1}}$	$r_a \times 10^{10}$/ m
methanol	0.000 46	10	0.215 ± 0.003	1.91
ethanol	0.000 43	9	0.189 ± 0.003	2.17
propan-1-ol	0.000 41	10	0.172 ± 0.005	2.39
butan-1-ol	0.000 40	11	0.160 ± 0.007	2.57
2-methlypropan-2-ol	0.000 37	9	0.143 ± 0.004	2.57
phenol	0.000 36	9	0.132 ± 0.002	2.63
benzene	0.000 07	15	0.470 ± 0.025	2.55
	0.000 14	28	0.501 ± 0.022	
	0.000 34	20	0.484 ± 0.016	
	0.000 71	15	0.507 ± 0.007	
toluene	0.000 07	20	0.436 ± 0.031	2.71
	0.000 13	18	0.442 ± 0.017	
	0.000 34	15	0.459 ± 0.010	
	0.000 67	9	0.461 ± 0.008	
chlorobenzene	0.000 06	13	0.422 ± 0.031	2.69
	0.000 13	17	0.428 ± 0.017	
	0.000 33	13	0.449 ± 0.010	
	0.000 66	8	0.444 ± 0.008	
	0.001 32	8	0.445 ± 0.003	
1,2-dichlorobenzene	0.000 06	18	0.316 ± 0.015	2.82
	0.000 11	12	0.335 ± 0.005	
	0.000 29	12	0.344 ± 0.004	
	0.000 59	8	0.349 ± 0.002	
	0.001 18	4	0.354 ± 0.002	
1,4-dichlorobenzene	0.000 06	10	0.387 ± 0.010	2.82
	0.000 64	9	0.411 ± 0.004	
bromobenzene	0.000 06	9	0.401 ± 0.010	2.75
	0.000 63	12	0.407 ± 0.006	
1,2-dibromobenzene	0.000 05	8	0.295 ± 0.022	2.92
	0.000 54	8	0.302 ± 0.003	
1,4-dibromobenzene	0.000 06	8	0.355 ± 0.011	2.93
	0.000 59	9	0.354 ± 0.003	

Here, k_B denotes the Boltzmann constant, T the absolute temperature (298.15 K for our measurements), and n_{SE} another model parameter (Stokes−Einstein number) that is typically between 4 (slip limit) and 6 (stick limit). The van der Waals radii r_a were derived from molecular volumes V_M of the compounds according to

$$r_a = \left(\frac{3}{4\pi} \cdot V_M \right)^{1/3} \tag{3}$$

where the V_M values were calculated with MOLSV (Smith, 1985) from three-dimensional geometries of the compounds optimized at the semiempirical AM1-COSMO level (Klamt and Schüürmann, 1993) using standard parameters for aqueous solution as in our previous study (Gabler et al., 1996). For a nonspherical molecule, r_a requires careful attention and in our case is defined by the radius of the sphere with the same volume as the compound, which is consistent with applying eq 3 on both spherical and nonspherical molecules. It should be noted that from a more general viewpoint, both r_a and n_{SE} could be regarded as parameters of the Stokes−Einstein model (cf. Skipp and Tyrell, 1975).

Results and Discussion

The experimentally determined interdiffusion coefficients D_{ao} in octanol of six alcohols, benzene, and seven benzene derivatives are listed in Table 1 together with the calculated molecular van der Waals radii r_a. The alcohols were analyzed at sample mole fractions x_a^{sample} of 0.01 corresponding to average solute mole fractions x_a of around 0.0004 (cf. eq 1), yielding D_{ao} values from 0.132×10^{-9} $\mathrm{m^2\ s^{-1}}$ (phenol) to 0.215×10^{-9} $\mathrm{m^2\ s^{-1}}$ (methanol), with relative standard errors around or below 4% as usually described for this technique. Interestingly, the present results are smaller by (0.019 to 0.046) × 10^{-9} m^2 s^{-1} as compared to literature values (Miller, 1991). At this stage, a more thorough evaluation is not possible because the literature data were reported without specifying the experimental errors and the actual concentration levels used for the measurements with the capillary method. In any case, both data sets show a clear decrease of D_{ao} with increasing molecular size of the alcohols as expected from the Stokes–Einstein model.

For the more hydrophobic subset of benzene, toluene, and the mono- and dihalogenated benzenes, D_{ao} was studied at different sample mole fractions in the range of 0.02 to 0.001 corresponding to x_a values from 0.001 to 0.000 05, and the results are listed in Table 1. As expected, the experimental uncertainty as expressed in terms of standard deviations (sd) increases with decreasing concentration, and the greatest sd value of 0.031 × 10^{-9} m^2 s^{-1} was observed for toluene and chlorobenzene at 0.000 07 and 0.000 06 mole fractions, respectively. At lower solute concentrations, realiable measurements were not possible. With all other measurements summarized in Table 1, the relative standard errors are again around or below 4%. A similar situation is found for differences between the individual D_{ao} values of a compound taken at different mole fractions. It follows that in the concentration range tested, the interdiffusion coefficients can be regarded as essentially constant. Owing to the acceptable precision of the measurements at x_a^{average} values around 0.000 05, the respective values are taken as the interdiffusion coefficients at infinite dilution.

The interdiffusion coefficients in octan-1-ol of the benzene derivatives range from 0.47 × 10^{-9} to 0.30 × 10^{-9} m^2 s^{-1} and are thus 2–3 times smaller than corresponding values in water as reported recently (Gabler et al., 1996). Interestingly, with water, measurements can be made at much lower average solute mole fractions (around 10^{-5} to 10^{-7}) corresponding to factors up to 100 below the current lower limit in octanol, using the same Taylor dispersion apparatus with a differential refractometer as for the present study. This may be due to a combination of two unfavorable effects: First, the slower diffusion in octan-1-ol causes broader dispersion profiles with more noise. Second, the detector sensitivity is smaller owing to the smaller differences in the refractive indexes of solvent and solute.

In Figure 1, the diffusion coefficients in octan-1-ol and water are compared for all 14 compounds and plotted against the molecular van der Waals radius. For the eight benzenes, the experimental data in water were available from our previous study (Gabler et al., 1996), and the respective values for the six alcohols were taken from Hao and Leaist (1996). As can be seen from the figure, significant correlations can be found between D_{ao} and the (calculated) molecular van der Waals radius for both solvents and groups of chemicals. In addition, the figure shows the range of theoretical diffusion coefficients for both octanol (bottom) and water (top) predicted through the Stokes–Einstein equation (eq 2). The respective four curves are derived from the upper and lower boundaries of the Stokes–Einstein number: $n_{SE} = 6$ corresponds to the stick limit representing a complete solute–solvent contact (solid lines in Figure 1), and $n_{SE} = 4$ (broken lines in Figure 1) characterizes the slip limit with no direct solute–solvent contact (cf. Bird et al., 1960).

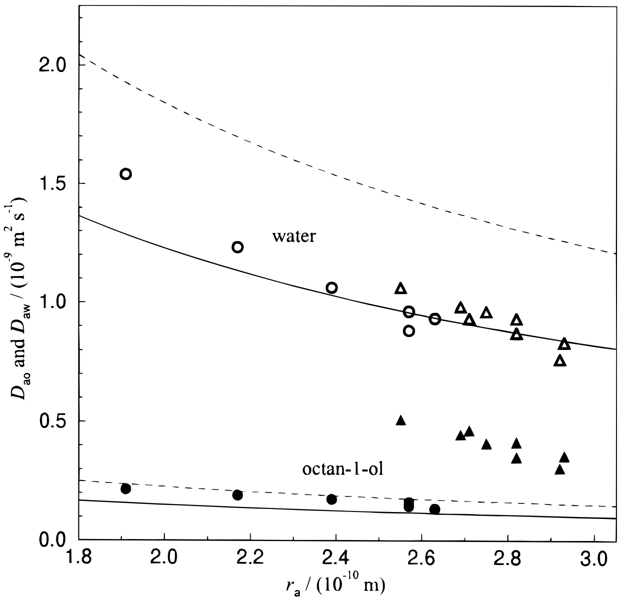

Figure 1. Experimental interdiffusion coefficients D_{ao} and D_{aw} at 25 °C in octan-1-ol and in water vs molecular van der Waals radius r_a of solutes a: ● alcohols in octan-1-ol (this work), ○ alcohols in water (Hao and Leaist, 1996), ▲ benzene derivatives in octan-1-ol (this work), △ benzene derivatives in water (Gabler et al., 1996). The solid lines represent the stick limit and the dashed lines the slip limit of the Stokes–Einstein equation for both solvents.

In the top part of Figure 1, the experimental diffusion coefficients in water (w), D_{aw} (determined at low solute concentrations), show a significant correlation with the molecular van der Waals radius for the combined set of benzene, seven benzene derivatives, and six alcohols. For larger molecules (right-hand side of the figure), the experimental values are close to the stick limit, and decreasing molecular size apparently leads to a decrease in the solute–water contact from the viewpoint of the Stokes–Einstein hydrodynamic model. A possible explanation might be that smaller solutes offer less space to build up solute-specific solvation shells. From this viewpoint it would follow that interdiffusion coefficients in water of particularly small solutes should approach the slip limit of $n_{SE} = 4$.

For the presently determined interdiffusion coefficients in octan-1-ol, D_{ao}, Figure 1 reveals substantial differences in the dependence on molecular size between the subsets of eight aromatic compounds and six alcohols. The latter show a good agreement with D_{ao}^{∞} according to the slip limit of the Stokes–Einstein model, with minor deviations for phenol and *tert*-butyl alcohol. Diffusion close to the stick limit in water thus contrasts with diffusion closer to the slip limit in octanol, reflecting the smaller solvation capacity of octanol. It should be noted, however, that increasing solvent viscosity decreases the difference between the stick and slip limits, and that in the case of octanol the predicted values for $n_{SE} = 4$ and $n_{SE} = 6$ are already quite close as shown by the respective curves in the figure.

With the eight hydrophobic aromatic compounds, Figure 1 shows that the D_{ao} values are much greater than expected from the slip limit and thus far outside the range predicted through eq 2. Again, there is a significant correlation of D_{ao} with the molecular van der Waals radius, but intercept and slope differ substantially from those of the alcohol subset, which contrasts with the situation in water.

Following the Stokes–Einstein model of diffusion (and assuming ideal behavior with identical n_{SE} in both solvents), the ratio of the diffusion coefficients in water and octan-1-ol (D_{aw}/D_{ao}) should equal the inverse ratio of the viscosities of the solvents ($\eta_o/\eta_w \approx 8$ at $T = 298.15$ K). This is approximately fulfilled for the investigated alcohols (D_{aw}/D_{ao} = 6.0−7.2). In contrast, the corresponding ratio is only 2.0−2.5 for the substituted benzenes. It indicates an apparent octan-1-ol viscosity of only (2.4−3.5) × 10^{-3} Pa s for these substances (calculated from eq 4 with $n_{SE} = 4$). Conversely, the above-mentioned ratio between the diffusion coefficients in water and octan-1-ol would correspond to n_{SE} values of 1.3 to 1.9 for the hydrophobic benzenes. Correspondingly increased interdiffusion coefficients in more viscous media of relatively planar compounds as compared to (almost) spherical molecules in more viscous media were already observed some time ago and were tentatively explained by smaller effective cross sections for diffusion owing to a reduced ability for free rotation (Skipp and Tyrell, 1975).

In any case it is well-known that, over a wider range of viscosity, a simple relationship between diffusion coefficient and viscosity does not hold true (Reid at al., 1987). From this viewpoint, the most interesting aspect of the present findings is the observed systematic difference between the corresponding relationships for the two groups of chemicals. A closer look into solute−solvent interactions is possible through application of near-infrared spectroscopy, which has already been used to study hydrogen bonding in fluid mixtures of varying composition (Weyer, 1985). A corresponding investigation with some alcohols and benzenes is currently on the way.

A final note is given to the applicability of chemical engineering relationships to predict diffusion coefficients in fluid solutions (Reid et al., 1987; Siddiqui and Lucas, 1987). For the case of substituted benzenes in octanol, the best results are obtained with the Nakanishi correlation (Nakanishi, 1978), yielding a mean deviation of 12.9%. In contrast, no satisfactory results are found with any of the well-known relationships for the diffusion coefficients of alcohols in octan-1-ol. It shows that more experimental investigations are needed to better understand the diffusion of chemical compounds in more viscous media.

Conclusions

The comparative analysis of the diffusion at 25 °C of benzene, hydrophobic benzene derivatives, and alcohols in octan-1-ol and water has revealed significant differences in the effect of solvent viscosity on the interdiffusion coefficients, D_{ao} and D_{aw}. Separate dependencies of D_{ao} on molecular size for both compound classes contrast with a combined relationship for D_{aw}, suggesting that in octan-1-ol differences in solute−solvent interactions will affect molecular diffusion much more than in water. On one hand, these findings confirm the more frequently made observation that a general relationship between solvent viscosity and diffusion coefficient according to the Stokes−Einstein equation does not hold true. On the other hand, the distinct intragroup dependences of diffusion coefficient on solvent viscosity suggest that corresponding separate relationships (which do not obey the Stokes−Einstein equation in the quantitative sense) may be more generally expected for chemically similar groups of compounds.

Finally, the results confirm the applicability of the Taylor dispersion technique to determine interdiffusion coefficients in more viscous media with acceptable error margins. It is likely that the currently observed detection limit in octan-1-ol of 0.000 05 average solute mole fractions can be improved by replacement of the differential refractometer by a more sensitive concentration monitor.

Literature Cited

Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. The Theory of the Taylor Dispersion Technique for Liquid Diffusivity Measurements. *Int. J. Thermophys.* **1980**, *1*, 243−284.

Baldauf, W. Experimental Determination of Binary Diffusion Coefficients in Some Recommended Systems for Liquid−Liquid Extraction. Ph.D. Thesis, Technische Universität, Berlin, 1981.

Baldauf, W.; Knapp, H. Measurements of Diffusivities in Liquids by the Dispersion Method. *Chem. Eng. Sci.* **1983**, *38*, 1031−1037.

Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; Wiley: New York, 1960.

Chen, S. H.; Evans, D. F.; Davis, H. T. Tracer Diffusion in Methanol, 1-Butanol and 1-Octanol from 298 to 433 K. *AIChE J.* **1983**, *29*, 640−645.

Davis, H. T.; Tominaga, T.; Evans, D. F. Correlation Between Tracer Diffusivity, Solvent Viscosity, and Solute Sizes. *AIChE J.* **1980**, *26*, 313−314.

Evans, D. F.; Tominaga, T.; Chan, C. Diffusion of Symmetrical and Spherical Solutes in Protic, Aprotic and Hydrocarbon Sovents. *J. Solution Chem.* **1979**, *8*, 461−478.

Gabler, T.; Paschke, A.; Schüürmann, G. Diffusions Coefficients of Substituted Benzenes at High Dilution in Water. *J. Chem. Eng. Data* **1996**, *41*, 33−36.

Gobas, F. A. P. C.; Opperhuizen, A.; Hutzinger, O. Bioconcentration of Hydrophobic Chemicals in Fish: Relationship with Membrane Permeation. *Environ. Toxicol. Chem.* **1986**, *5*, 637−646.

Hao, L.; Leaist, D. G. Binary Mutual Diffusion Coefficients of Aqueous Alcohols. Methanol to 1-Heptanol. *J. Chem. Eng. Data* **1996**, *41*, 210−213.

Klamt, A.; Schüürmann, G. COSMO: A New Approach to Dielectric Screening in Solvents with Explicit Expressions for the Screening Energy and its Gradient. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799−805.

Lide, D. R. *CRC Handbook of Chemistry and Physics*, 73rd ed.; CRC Press: Boca Raton, FL, 1992.

Miller, D. M. Evidence that Interfacial Transport is Rate-Limiting during Passive Cell Membrane Permeation. *Biochim. Biophys. Acta* **1991**, *1065*, 75−81.

Nakanishi, K. Prediction of Diffusion Coefficient of Nonelectrolytes in Dilute Solution Based on Generalized Hammond-Stokes Plot. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 253−256.

Ramprasad, G.; Das, T. R.; Mukherjee, A. K. Mutual Diffusion Coefficients of Some Binary Liquid Systems: Xylene−*n*-Alkyl Alcohol. *J. Chem. Eng. Jpn.* **1990**, *23*, 444−446.

Ramprasad, G.; Mukherjee, A. K.; Das, T. R. Mutual Diffusion Coefficients of Some Binary Liquid Systems: Benzene−*n*-Alkyl Alcohol. *J. Chem. Eng. Data* **1991a**, *36*, 124−126.

Ramprasad, G.; Das, T. R.; Mukherjee, A. K. Mutual Diffusion Coefficients of Some Binary Liquid Systems: Toluene−*n*-Alkyl Alcohol. *J. Chem. Eng. Jpn.* **1991b**, *24*, 389−391.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

Schüürmann, G.; Markert, B., Eds.; *Ecotoxicology*; John Wiley and Spektrum Akademischer Verlag: New York, 1998.

Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993; p 196.

Siddiqi, M. A.; Lucas, K. Correlations for Prediction of Diffusion in Liquids. *Can. J. Chem. Eng.* **1986**, *64*, 839−843.

Skipp, C. J.; Tyrrell, H. J. V. Diffusion in Viscous Solvents, Part 2. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1744−1753.

Smith, G. M. *MOLSV*, QCPE program 509, 1985.

Taylor, G. Dispersion of Soluble Matter in Solvent Flowing Slowly through a Tube. *Proc. R. Soc. London* **1953**, *A219*, 186−203.

Tyrrell, H. J. V.; Harris, K. R. *Diffusion in Liquids*; Butterworth: London, 1984.

Weyer, L. G. Near-Infrared Spectroscopy of Organic Substances. *Appl. Spectrosc. Rev.* **1985**, *21*, 1−43.

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