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# Limiting Binary Diffusivities of Aniline, Styrene, and Mesitylene in Supercritical Carbon Dioxide

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Measurements of binary diffusion coefficients of aniline, styrene, and mesitylene have been carried out by means of the Taylor−Aris chromatographic method. The diffusivities of mesitylene are consistent with those of Suárez et al. (*Fluid Phase Equilib.* **1998**, *153*, 167−212) and Swaid and Schneider (*Ber. Bunsenges.* **1979**, *83*, 969−974) but do not agree with the data of Sassiat et al. (*Anal. Chem.* **1987**, *59*, 1164−1170) at low densities. The new data for styrene do not agree with those of Suárez et al. Of the many predictive equations tested, the only two that can predict the experimental data of the three substances reasonably well are the expressions of Sitaraman−Ibrahim−Kuloor (*J. Chem. Eng. Data* **1963**, *8*, 198−201) and Eaton−Akgerman (*Ind. Eng. Chem. Res.* **1997**, *36*, 923−931), although both predict that aniline diffuses faster than styrene, which does not appear to be the case.

## Introduction

Carbon dioxide is a benign substance that has a low critical temperature and a moderate critical pressure and so can be employed as a supercritical fluid in mass transfer operations, first in extraction because of its low viscosity, low surface tension, and high diffusivity. The solvent power and selectivity of separation can be manipulated by slight variations in operating conditions, such as temperature, pressure, or introducing a cosolvent, and the extracted substances can be recovered without solvent residue.

From a design perspective, binary diffusion coefficients are important because they are required as input information for calculating mass transfer coefficients. The limiting binary diffusivities of a solute A in a solvent B ($D_{\mathrm{AB}}$) are the diffusion coefficients when the concentration of the solute tends to zero, and in supercritical fluids, they can be easily measured by the Taylor−Aris dispersion method.[1,2]

In the present work, $D_{\mathrm{AB}}$ has been measured in carbon dioxide for benzenamine (aniline), ethenylbenzene (styrene), and 1,3,5-trimethylbenzene (mesitylene) from (313.16 to 333.16) K and at five pressures between (15 and 35) MPa by the Taylor−Aris technique. The first two substances have considerable industrial importance: aniline is employed to synthetize methylene diphenyl diisocyanate (which is used in the production of polyurethane), and styrene is the monomer of plastics such as polystyrene. Experimental data are compared with those of other researchers and with the results of 25 predictive equations.

## Theoretical Background

The Taylor−Aris dispersion technique (the so-called peak-broadening technique) is based on the "broadening" of a narrow pulse of solute A after injection in the capillary column of length $L$ and internal radius $r_0$, where a solvent B flows in laminar regime with a mean velocity $v_0$. The molecular binary diffusivity of solute A in solvent B will be the positive root of[3,4,8]

$$D_{\mathrm{AB}} = \frac{v_0}{4}\left[\frac{\mathrm{s}(x)^2}{L} \pm \sqrt{\left(\frac{\mathrm{s}(x)^2}{L}\right)^2 - \frac{r_0^{\,2}}{3}}\right] \qquad (1)$$

where the peak variance can be estimated from the curve-width at half-height, $w_{0.5}(x)$, as

$$\mathrm{s}(x) = \frac{w_{0.5}(x)}{2.354} \qquad (2)$$

If the experimental apparatus expresses the curve-width in units of time instead of in units of length, this has to be multiplied by the mean velocity $v_0$ to obtain the correct units.

## Experimental Section

The experimental apparatus is a commercial Hewlett-Packard C1205A supercritical fluid chromatograph. This and the procedure have been described in previous works.[4,5] An entirely empty coiled stainless steel tubing of $r_0 = 0.381$ mm and $L = 30.48$ m was used as a diffusion column. The coil radius was 0.13 m. Solutes were manually introduced into the carbon dioxide stream at room temperature. The total mass flow varies between (0.14 and 0.12) g·min$^{-1}$, and the retention time for all experimental conditions is (100 to 120) min.

Chemicals injected in the supercritical chromatograph were purchased from Merck. The minimum purity for aniline and styrene is 99 %, and for mesitylene it is 98 %. The carbon dioxide, supplied by Air Liquide, had a minimum purity of 99.998 %. Experiments were carried out at (313.16, 323.16, and 333.16) K and pressures of (15, 20, 25, 30, and 35) MPa. A multiple-wavelength UV detector was employed for monitoring the Gaussian concentration profile leaving the column, and the wavelengths at which it measured such a profile were (304, 306, and 308) nm for aniline, (283, 288, and 291) nm for styrene, and (254, 266, and 273) nm for mesitylene. A Philips PU 8720 spectrophotometer was employed to determine the absorption spectra of the three compounds.

To reduce the dead volume of the system, low dead volume connections and a low dead volume UV detection cell were utilized. A Rheodyne model 7520 injector of ultralow dispersion with a 0.2 $\mu$L loop was used.

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**Table 1. Experimental Values of $D_{AB}$ for the Three Substances Studied**

| $T$ | $P$ | $\rho$ | $10^6\ \eta$ | $D_{AB}/10^{-9}\ m^2 \cdot s^{-1}$ | | |
|---|---|---|---|---|---|---|
| K | MPa | $kg \cdot m^{-3}$ | Pa·s | aniline | styrene | mesitylene |
| 313.16 | 15 | 778.92 | 67.2 | 10.23 | 11.95 | 10.38 |
| | 20 | 822.17 | 77.2 | 9.75 | 10.75 | 9.15 |
| | 25 | 852.47 | 85.0 | 9.06 | 9.58 | 8.21 |
| | 30 | 876.03 | 93.1 | 8.43 | 8.74 | 7.78 |
| | 35 | 895.4 | 102.3 | 7.76 | 8.27 | 7.46 |
| 323.16 | 15 | 678.16 | 57.1 | 11.78 | 13.17 | 11.95 |
| | 20 | 745.26 | 68.8 | 10.81 | 11.18 | 11.06 |
| | 25 | 806.3 | 77.0 | 9.66 | 10.55 | 9.33 |
| | 30 | 846.2 | 85.1 | 9.1 | 9.2 | 9.23 |
| | 35 | 878.65 | 91.5 | 8.7 | 8.77 | 8.6 |
| 333.16 | 15 | 607.37 | 47.6 | 13.33 | 15.5 | 14.21 |
| | 20 | 700.86 | 59.8 | 11.89 | 14.09 | 12.28 |
| | 25 | 761.68 | 68.7 | 10.97 | 12.2 | 11.48 |
| | 30 | 807.12 | 73.8 | 10.17 | 10.9 | 10.44 |
| | 35 | 843.51 | 83.9 | 9.47 | 10.23 | 9.89 |

The adsorption of the solute by inner walls may determine an appreciable asymmetry of the peaks and discrepancies in the elution time of different solvents. Fortunately, no tailing was observed, and the peaks were symmetrical in all the runs. The dispersion curve for all experiments was Gaussian with a linear correlation coefficient of 0.9996−0.9998 between ln $\langle c \rangle$ and $\chi^2$ ($\langle c \rangle$ being the cross-sectional average concentration and $\chi$ being the distance from the peak apex). Peaks that have an asymmetric factor greater than 1.05 have been rejected for analysis.

## Results and Discussion

Table 1 lists the experimental $D_{AB}$ values for aniline, styrene, and mesitylene in supercritical carbon dioxide, together with the temperatures and pressures at which they were measured and with the densities and viscosities of the solvent. Each point is the average of 5 to 10 measurements, and the reproducibility of the experimental values is 3 % (absolute average deviation). Densities were calculated with the equation of state of Pitzer and Schreiber,[6] and viscosities were taken from Stephan and Lucas.[7] Table 2 compiles several properties of these benzene derivatives: as can be seen, mesitylene is larger than styrene and so diffuses more slowly. Nevertheless, aniline is the smallest and the lightest compound, and its diffusion coefficients are similar to those of mesitylene.

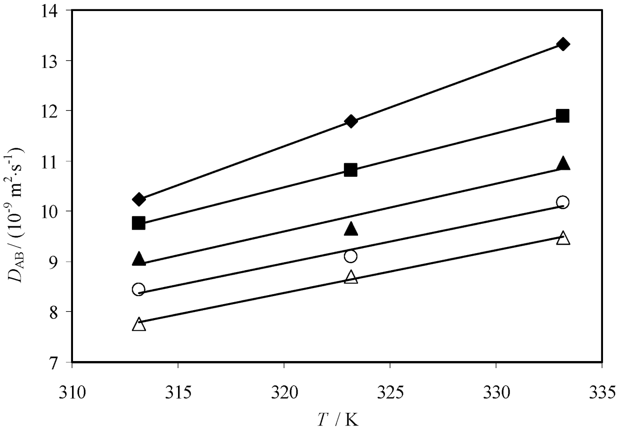

**Figure 1.** Binary diffusivities of aniline as a function of temperature: ◆, 15 MPa; ■, 20 MPa; ▲, 25 MPa; ○, 30 MPa; △, 35 MPa.

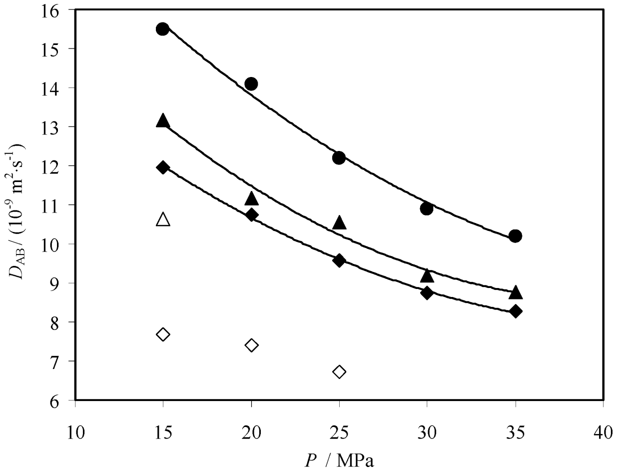

**Figure 2.** Binary diffusion coefficients of styrene in carbon dioxide as a function of pressure: ◆, ◇, 313.15 K; ▲, △, 323.15 K; ●, 333.15 K. Filled symbols are those of this work, and white symbols are those published by Suarez et al.[1]

The temperature and pressure dependence of all data is not unexpected. When the temperature goes up, the kinetic energy of the molecule increases but the density and viscosity of the fluid both decrease, which also contributes to greater diffusivity, as illustrated in Figure 1 for aniline by way of example. In the narrow range of temperatures in which our experiments were carried out, the increase is nearly linear. When the pressure rises isothermically, $D_{AB}$ decreases because the molecules are more densely packed and cannot move very well, but the dependence is more significant at low pressures. This tendency can be seen in Figure 2 for styrene, together with the values obtained by Suarez et al.[1] Our values are higher than those, but bearing in mind that most of the predictive equations cited in Table 3 give values closer to ours than to Suarez et al.,[1] the four values of these authors are probably erroneous.

**Table 2. Properties of the Substances Studied[a]**

| property | symbol/unities | aniline | styrene | mesitylene | CO$_2$ |
|---|---|---|---|---|---|
| critical temperature[15] | $T_c$/K | 699 | 636.06 | 637.36 | 304.10 |
| critical pressure[15] | $P_c$/MPa | 5.31 | 3.84 | 3.127 | 7.38 |
| normal boiling temperature[15] | $T_b$/K | 457.6 | 418.36 | 437.86 | 194.70 |
| critical volume[15] | $10^6 V_c/(m^3 \cdot mol^{-1})$ | 274 | 352 | 432.9 | 93.9 |
| critical compressibility[15] | $Z_c$ | 0.250 | 0.256 | 0.256 | 0.274 |
| molar mass[15] | $10^3 M/(kg \cdot mol^{-1})$ | 93.13 | 104.20 | 120.20 | 44.01 |
| acentric factor[15] | $\omega$ | 0.384 | 0.2971 | 0.399 | 0.239 |
| radius of gyration[15] | $10^{10} r_g$/m | 3.393 | 3.81 | 4.341 | 0.992 |
| dipolar moment[15] | $\mu_p$/Debyes | 1.6 | 0.1 | 0.1 | 0.0 |
| molar volume at normal boiling point[12] | $10^6 V_b/(m^3 \cdot mol^{-1})$ | 106.33 | 132.77 | 163.12 | 35.02 |
| parachor[15] | $P/(g^{0.25} \cdot cm^3 \cdot mol^{-1} \cdot s^{-0.5})$ | 232.1 | 273.2 | 338.1 | 49.0 |
| van der Waals volume parameter[15,45] | $R^{vdW}$ | 3.7165 | 4.3671 | 5.3928 | 1.3 |
| van der Waals surface parameter[15,45] | $Q^{vdW}$ | 2.816 | 3.296 | 4.104 | 1.12 |
| heat of vaporization at normal boiling point[45] | $\Delta_{vap}H(T_b)/(kJ \cdot mol^{-1})$ | 44.21 | 37.07 | 38.83 | 23.08 |

[a] Most of them are necessary for calculations of Table 3.

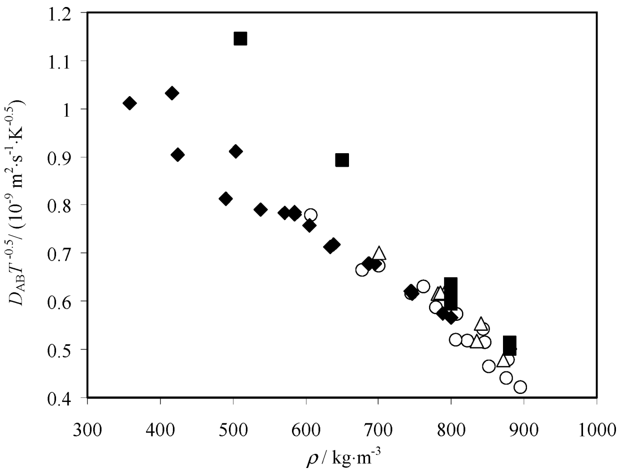

**Figure 3.** Values of $D_{AB}/T^{-0.5}$ as a function of density for mesitylene: ○, this work; △, Suarez et al.;[1] ◆, Swaid and Schneider;[10] ■, Sassiat et al.[11]

**Table 3. Average Absolute Deviations (AAD) for Several Predictive Equations**

| | 100 AAD | | |
|---|---|---|---|
| | aniline | styrene | mesitylene |
| Wilke−Chang[15] | 33.34 | 5.38 | 4.60 |
| Scheibel[15] | 51.85 | 17.74 | 12.09 |
| Reddy−Doraiswamy[16] | 92.33 | 62.04 | 64.26 |
| Lusis−Ratcliff[17] | 48.92 | 20.37 | 18.39 |
| Tyn−Calus[18] | 6.20 | 11.81 | 12.48 |
| Nakanishi[19] | 12.68 | 13.12 | 12.06 |
| Kooijman[20] | 60.75 | 36.44 | 36.07 |
| King−Hsue−Mao[21] | 15.24 | 11.52 | 14.73 |
| Sitaraman−Ibrahim−Kuloor[22] | 5.30 | 6.90 | 5.68 |
| Umesi−Danner[23] | 13.45 | 5.21 | 5.32 |
| Lai−Tan[24] | 33.65 | 14.72 | 17.83 |
| Liu−Ruckenstein[25] | 22.90 | 11.61 | 12.60 |
| Woerlee[26] | 6.85 | 20.03 | 24.11 |
| Hippler−Schubert−Troe[27] | 25.96 | 6.95 | 8.03 |
| Catchpole−King[28] | 16.08 | 5.76 | 5.89 |
| Eaton−Akgerman[29] | 6.37 | 9.97 | 8.35 |
| He of 1997[30] | 19.06 | 4.25 | 5.87 |
| He of 1998[31] | 24.42 | 8.54 | 9.67 |
| He−Yu of 1997[32] | 17.36 | 3.61 | 5.10 |
| He−Yu of 1998[33] | 16.62 | 3.32 | 4.54 |
| Funazukuri−Hachisu−Wakao[34] | 37.43 | 11.66 | 10.50 |
| Funazukuri−Kong−Kagei[35] | 24.82 | 6.27 | 5.25 |
| Liu−Silva−Macedo[36] | 4.10 | 11.40 | 11.76 |
| Zhu et al.[37] | 22.24 | 9.08 | 10.25 |
| Dariva−Coelho−Oliveira[38] | 10.90 | 10.32 | 11.78 |

In Figure 3, all available experimental data for mesitylene are plotted. The function $D_{AB}/T^{0.5}$ as a function of density was used for clarity because at high densities this function should only be density dependent.[8,9] The data of Swaid and Schneider[10] do not cover the high-density region. The diffusivities of Sassiat et al.[11] are in disagreement at low densities, but between (700 and 900) kg·m$^{-3}$ all values are in good agreement. On the other hand, the density dependence of the diffusion coefficients at isothermal conditions is due to the fact that the solvent molecules are more densely packed, thus holding the solute particles back from moving across (an effect similar to that provoked by the build of pressure).

Concerning the prediction of $D_{AB}$, Table 3 lists the average absolute deviations (AAD) of 25 equations. The first 14 are of type Stokes−Einstein, and the remaining 11 are based on the Rough−Hard−Sphere theory. Details of the input data and of calculations are given in the corresponding references. For the formula of Nakanishi, molar volumes at 298.16 K were taken from Perry and Green,[12] except for carbon dioxide, which was calculated from the molar volume at normal boiling point, $V_b$, according to this author. The interaction parameters of the Peng−Robinson equation of state, which are necessary for the Liu−Ruckenstein expression, were taken for styrene from Tan et al.[13] and for mesitylene from Occhiogrosso et al.[14] There are no vapor−liquid equilibrium data of the system $CO_2$ + aniline, so the interaction parameters that Liu and Ruckenstein recommend for that case were chosen. The Lennard-Jones parameters employed in the Hippler−Schubert−Troe equation were calculated with the empirical formulas of Chung.[15] The formulas of Chung were also employed for calculating the diameter ($\sigma$) of the excluded volume ($b$) in the Woerlee equation, $b = (2/3)\pi N_{av}\sigma^3$. Diffusivities at low pressure in the equation of Funazukuri−Hachisu−Wakao were calculated with the formula of Fuller et al.[15] Viscosities at low pressure are from Stephan and Lucas.[7]

Table 3 shows that only the equations of Sitaraman−Ibrahim−Kuloor[22] and Eaton−Akgerman[29] can predict the diffusivities of the three solutes with AAD < 10 %. Also, for each formula, the errors for styrene and mesitylene are similar but differ considerably from the AAD of the aniline (except for the equations of Nakanishi,[19] King−Hsue−Mao,[21] Sitaraman−Ibrahim−Kuloor,[22] and Dariva−Coelho−Oliveira[38]). Besides, the only equations that predict that aniline diffuses more slowly than styrene are those of Nakanishi and King−Hsue−Mao, denoted as eqs 3 and 4, respectively. According to the formula of Nakanishi, the diffusion coefficient is a function of temperature, solvent viscosity ($\eta_B$), solute and solvent molar volumes at 298 K and 0.1 MPa ($V_{298}$), and four empirical parameters which account for solute−solvent interactions ($j_A$, $q_A$, $s_B$, $a_B$). For the three solutes, $q_A$, $s_B$, and $a_B$ are equal to unity. $j_A$ takes into account the polarity of the solute and is equal to 1.5 for highly polar substances (iodine, pyridine, aniline, nitrobenzene, etc.) and equal to unity for nonpolar compounds. If this parameter was not considered, the overestimation of diffusivities of aniline would be 39 %.

$$D_{AB} = \frac{T}{\eta_B}\left[\frac{9.97\cdot10^{-17}}{(j_A q_A V_{298A})^{1/3}} + \frac{2.4\cdot10^{-15} a_B s_B V_{298B}}{j_A s_A q_A V_{298A}}\right] \qquad (3)$$

The diffusion coefficient in the formula of King−Hsue−Mao is a function of temperature, solvent viscosity, solute, and solvent molar volumes at normal boiling temperature ($V_b$) and enthalpy of vaporization ($\Delta_{vap}H$) at normal boiling point ($T_b$). The good performance of eq 4 is due to the fact that the enthalpy of vaporization of aniline is large, whereas the molar volume of aniline is low. As $\Delta_{vap}H(T_b)$ tries to take into account the diffusive effects that are not related with the molecular size, a compensation between both types of effect occurs. Nevertheless, the inclusion of $\Delta_{vap}H(T_b)$ cannot be considered a panacea because the equation of Sitaraman−Ibrahim−Kuloor also includes this term, and it is predicted that $D_{AB}$(styrene) < $D_{AB}$(aniline).

$$D_{AB} = 4.4\cdot10^{-15}\frac{T}{\eta_B}\left(\frac{V_{bB}}{V_{bA}}\right)^{1/6}\left(\frac{\Delta_{vap}H_B(T_{bB})}{\Delta_{vap}H_A(T_{bA})}\right)^{1/2} \qquad (4)$$

If a suitable multiplicative factor is introduced in eqs 3 and 4, the AAD values are now minimized, including that for aniline. The factors are 0.8904 for Nakanishi and 0.8822 for King−Hsue−Mao, and deviations are around 6 % for aniline and 4.5 % for the other two solutes (see Table 4).

According to the equation of Nakanishi, this abnormality could be attributed to the high polarity of this molecule (see Table 2). However, the works of Easteal and Woolf[39] and Chan[40]

**Table 4. Average Absolute Deviation (AAD) for Modified Equations 3 and 4**

| modification | 100 AAD | | |
|---|---|---|---|
| | aniline | styrene | mesitylene |
| 0.8904 × (Nakanishi) | 6.01 | 4.02 | 4.61 |
| 0.8822 × (King−Hsue−Mao) | 6.16 | 4.55 | 4.61 |

on diffusion in liquids at atmospheric pressure show that the dipole moment of the solute is not important when the solvent is nonpolar. Another explanation could be solute polymerization because aniline is a hydrogen-bonding substance. Nevertheless, for carboxylic acids (which are known to dimerize even in the vapor phase), polymerization in supercritical carbon dioxide is not observed,[41] although in liquid carbon tetrachloride this phenomenon exists.[42] Yamamoto et al.[43] measured the equilibrium constants of acetic acid and palmitic acid in supercritical $CO_2$ and found that they were smaller than those in organic liquid solvents, which indicates that the monomeric carboxylic acid is more stable in supercritical $CO_2$ than in the organic liquid solvents. Having in mind that the strength of hydrogen bonds in amines is expected to be lower than that in carboxylic acid,[44] the dimerization of aniline has to be disregarded.

## Conclusions

At infinite dilution, binary diffusion coefficients of aniline, styrene, and mesitylene were determined at temperatures from (313.15 to 333.15) K and pressures ranging from (15 to 35) MPa by the peak-broadening method. The experimental diffusion coefficients take values from $(7.46 \text{ to } 15.50)\cdot 10^{-9}\ \mathrm{m^2\cdot s^{-1}}$ over a considerable range of densities. Predictions of 25 semiempirical equations are contrasted with them.

Our data for styrene are in disagreement with some points reported in the literature, but for mesitylene the agreement is good. The influence of temperature and pressure does not show any anomaly, but the low values obtained in all the experimental conditions for aniline were unexpected.

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