Diffusion Coefficients of Aromatic Compounds at Infinite Dilution in Binary Mixtures at 298.15 K

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Infinite dilution diffusion coefficients of aromatic compounds (benzene, toluene, chlorobenzene, ethylbenzene, *p*-chlorotoluene, naphthalene, pyrene, and perylene) in mixtures of hexane + heptane and of benzene in polar mixtures (hexane + ethanol and acetone + ethanol) were measured at 298.15 K by the Taylor dispersion technique. Experimental data were correlated by means of literature models depending in most cases on the diffusion coefficient D_{1p}^{∞} of the solute at infinite dilution in the pure solvent. It is shown that the use of experimental values for D_{1p}^{∞} should always be preferred to the Wilke−Chang predictions, especially in the case of nonideal mixed solvents. All models provide equivalent predictions except the Maxwell−Stefan and Dullien−Asfour equations, which lead to less stable results.

Introduction

Experimental values of diffusion coefficients of organic compounds in liquid solvents are of importance, not only in chemical engineering design but also in the theory of transport properties. Hence, a good knowledge of transport properties of solutes in both pure solvents and in multicomponent mixtures is necessary.

In this paper, diffusion coefficients of several aromatic compounds (benzene, chlorobenzene, ethylbenzene, toluene, naphthalene, *p*-chlorotoluene, naphthalene, pyrene, and perylene) were measured at infinite dilution in binary solvents of hexane + heptane at 298.15 K. In order to check the influence of the solvent properties, diffusivity data of benzene in polar mixtures of hexane + ethanol and acetone + ethanol were also measured at this temperature. The Taylor dispersion technique[1] was used since it is well-known that it provides fast and accurate results and is easy to handle.[2−4]

Diffusion coefficients of a pure compound in a liquid, at a given temperature, are strongly dependent on its molar volume and on the density and viscosity of the solvent. For this purpose, viscosity values for the solvents considered in this work were taken from previous determinations.[5−8]

Several equations have been proposed to predict the infinite dilution diffusion coefficient D_{1m}^{∞} of a solute (1) in a binary mixture (*m*) from the diffusion coefficients D_{1p}^{∞} of the solute in the pure solvents. In this work, different equations were considered. In each case, results obtained from the Wilke and Chang[9] equation for the estimation of D_{1p}^{∞} were compared with the experimental determinations.

Experimental Section

The Taylor dispersion technique[1] was used to determine diffusion coefficients at infinite dilution. In a typical experiment, a small amount of sample solution is injected into a laminar flow of solvent through a capillary tube. According to Taylor's analysis for dispersion in liquids, the concentration profile at the far end of the tube is of Gaussian type. According to Levenspiel and Smith[10] and Ouano,[11,12] the diffusion coefficient D_{AB} of a solute (A) in a solvent (B) is

$$D_{AB}/\mathrm{cm^2{\cdot}s^{-1}} = 0.231 r^2 u \frac{t_R^2}{L W_{1/2}^2} \tag{1}$$

where *r* and *L* are respectively the radius and the length of the tube (in cm), *u* is the solvent velocity (in cm·s^{-1}), t_R is the retention time of the solute in the tube (in s), and $W_{1/2}$ is the peak width at half of its height (in s).

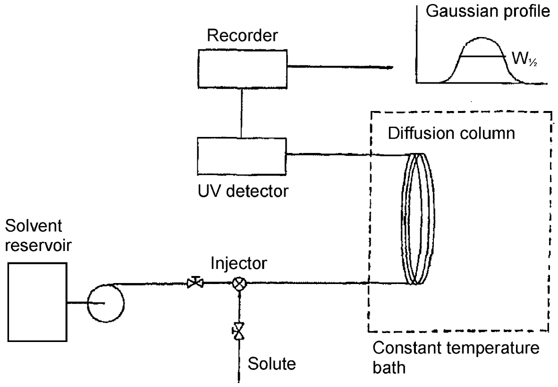

Figure 1. Experimental setup for the measurement of diffusion coefficients with the Taylor technique.

Table 1. Comparison between Experimental Measurements and Literature Values of Infinite Dilution Diffusion Coefficients D_{1p}^{∞}

		$10^5 D_{1p}^{\infty}/\mathrm{cm^2{\cdot}s^{-1}}$	
solute	solvent	this work	literature
benzene	hexane	4.70	4.79,[19] 4.76,[13] 4.75[22]
benzene	heptane	3.75	3.40,[14] 3.87,[22] 3.53,[23] [a] 3.91[24]
toluene	hexane	4.12	4.62,[15] 4.06,[23] [a] 4.21[25]
toluene	heptane	3.42	3.24,[23] [a] 3.72[25]
benzene	cyclohexane	1.93	1.90,[13] 1.86,[23] [a] 1.90,[24] 1.95[19]
toluene	cyclohexane	1.66	1.65,[13] 1.63,[23] [a] 1.57[24]
benzene	acetone	4.25	4.28[19]

[a] Measurements performed at 297 K.

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Table 2. Infinite Dilution Diffusion Coefficients of Aromatics (1) in Hexane (2) + Heptane (3) Mixtures[a]

	η_m	$10^5\,D^\infty_{1m}/\text{cm}^2\cdot\text{s}^{-1}$							
x_2	mPa·s	benzene	chlorobenzene	ethylbenzene	toluene	*p*-chlorotoluene	naphthalene	pyrene	perylene
0.0000	0.3874	3.75	3.42	3.15	3.42	3.11	2.81	2.16	1.89
0.1330	0.3744	3.85	3.50	3.22	3.50	3.18	2.89	2.21	1.93
0.2015	0.3678	3.91	3.54	3.25	3.54	3.21	2.93	2.23	1.96
0.3004	0.3583	3.99	3.60	3.30	3.60	3.27	2.99	2.26	1.99
0.4004	0.3488	4.08	3.67	3.35	3.66	3.33	3.07	2.30	2.03
0.4990	0.3395	4.17	3.74	3.41	3.73	3.38	3.14	2.34	2.07
0.5965	0.3304	4.26	3.82	3.46	3.80	3.45	3.21	2.40	2.11
0.6995	0.3213	4.39	3.90	3.53	3.88	3.52	3.29	2.43	2.15
0.8002	0.3121	4.49	3.98	3.59	3.95	3.59	3.38	2.48	2.20
0.9001	0.3033	4.59	4.07	3.66	4.04	3.66	3.46	2.53	2.25
1.0000	0.2920	4.70	4.16	3.73	4.12	3.74	3.55	2.58	2.30

[a] x_2 is the mole fraction of component (2) in the mixed solvent. η_m is the solvent viscosity.

Table 3. Infinite Dilution Diffusion Coefficients of Benzene in Polar Mixtures[a]

hexane (2) + ethanol (3)			acetone (2) + ethanol (3)		
	η_m	$10^5\,D^\infty_{1m}$		η_m	$10^5\,D^\infty_{1m}$
x_2	mPa·s	$\text{cm}^2\cdot\text{s}^{-1}$	x_2	mPa·s	$\text{cm}^2\cdot\text{s}^{-1}$
0.0000	1.0812	1.88	0.0000	1.0812	1.88
0.2024	0.8487	2.13	0.1163	0.8307	2.26
0.2864	0.7701	2.25	0.2030	0.7044	2.54
0.3942	0.6728	2.45	0.3396	0.5583	2.93
0.4739	0.6049	2.65	0.4016	0.5132	3.12
0.6082	0.5025	3.05	0.5058	0.4485	3.41
0.7083	0.4285	3.43	0.5437	0.4300	3.50
0.7796	0.3813	3.82	0.7084	0.3625	3.90
0.8913	0.3212	4.35	0.8097	0.3355	4.16
1.0000	0.2920	4.70	1.0000	0.3025	4.25

[a] x_2 is the mole fraction of component (2) in the mixed solvent. η_m is the solvent viscosity.

A schematic diagram of the experimental setup is shown in Figure 1. The measurement system has a conventional design, very similar to that published by Huss et al.[13] It is equipped with a packed liquid chromatography column (125 × 4 mm i.d. of 5 μm silica); the UV detector is a Merck UV/vis filter photometer operating at 254 nm.

The main source of error in the calculation of the diffusion coefficients are the measurement of the retention time t_R (0.5 %) and the determination of the width of the peak $W_{1/2}$ (1 %). Taking into account these uncertainties, the resulting error on the diffusion coefficients is about 3 %.

To determine the reliability of the technique, reference systems widely studied in literature were measured. In Table 1, our measurements of diffusion coefficients at infinite dilution are compared with those from the literature. For all systems, the dispersion of literature values was about 1 % to 20 %, and all our measurements were consistent with these reference data.

The experimental diffusion coefficients measured in this work at 298.15 K are reported in Tables 2 and 3. Results obtained for the infinite dilution of the aromatic hydrocarbons in binary mixtures of hexane + heptane are given in Table 2; those obtained with benzene in hexane + ethanol and in acetone + ethanol mixed solvents are reported in Table 3. For all these systems, the viscosities η_m of the mixtures were measured previously.[5,8] These values are reported in Tables 2 and 3.

Results and Discussion

Various equations that have been proposed in the literature for the prediction of diffusion coefficients of solutes at infinite dilution in mixtures were used for the modeling of our experimental results. A special attention was paid to the prediction of diffusion coefficients in mixed solvents from those in pure components.

Table 4. Pure Component Parameters Required for the Use of the Wilke and Chang Model[a]

solute		solvent			
	V			M	η
component	$\text{cm}^3\cdot\text{mol}^{-1}$	component	ϕ	$\text{g}\cdot\text{mol}^{-1}$	mPa·s
benzene	96.0	hexane	1.0	86.177	0.2920
chlorobenzene	117.0	heptane	1.0	100.204	0.3874
ethylbenzene	140.4	acetone	1.0	58.080	0.3025
toluene	118.2	ethanol	1.5	46.069	1.0812
p-chlorotoluene	139.1				
naphthalene	162.6				
pyrene	258.8				
perylene	325.4				

[a] Molar volume v of the solute at its normal boiling point, association factor ϕ, molar mass M, and viscosity η of the solvent.

Literature Models for Multicomponent Mixtures. Perkins and Geankopolis[14] extended to mixed solvents the Wilke and Chang equation[9] originally proposed for the diffusion coefficient D^∞_{1p} of a solute (1) at infinite dilution in a pure component (p):

$$D^\infty_{1p}/\text{cm}^2\cdot\text{s}^{-1} = 7.4\cdot10^{-8}\frac{\sqrt{\phi_p M_p}}{\eta_p {V_1}^{0.6}}T \qquad (2)$$

where T is the temperature (in K); ϕ_p and M_p (in $\text{g}\cdot\text{mol}^{-1}$) and η_p (in mPa·s) are respectively the association factor, the molar mass, and the viscosity of the pure solvent. V_1 is the molar volume (in $\text{cm}^3\cdot\text{mol}^{-1}$) of the solute at its normal boiling temperature. The values of these parameters are given in Table 4 for all the solutes and solvents studied in this work. From eq 2, Perkins and Geankopolis[14] proposed the following expression:

$$D^\infty_{1m}/\text{cm}^2\cdot\text{s}^{-1} = 7.4\cdot10^{-8}\frac{\sqrt{\phi_m \text{M}_\text{m}}}{\eta_m V_1^{0.6}}T \qquad (3)$$

in which subscript m for the mixed solvent replaces subscript p for the pure solvent in eq 2, and for binary mixed solvents:

$$\phi_m M_m = x_2\phi_2 M_2 + x_3\phi_3 M_3, \quad x_3 = 1 - x_2 \qquad (4)$$

where x_2 is the mole fraction of component (2) in the solvent.

Numerous correlations have been proposed in literature for representing the diffusion coefficients D_{1m} of solutes in mixed solvents. The analysis of the various formulas allows defining three classes of models at infinite dilution of solute:

Table 5. Percent Deviations ΔD_{1m}^{∞} between Experimental and Predicted Infinite Dilution Diffusion Coefficients of Benzene (1) in Hexane (2) + Heptane (3) Mixtures Using Wilke−Chang Prediction of D_{1p}^{∞} in Pure Solvents[a]

x_2	Perkins−Geankopolis	Holmes et al.	Tang−Himmelbau	Leffler−Cullinan	Eyring	Dullien−Asfour	Maxwell−Stefan
0.0000	(1.70)						
0.1330	1.85	1.88	1.72	1.92	1.75	1.23	1.81
0.2015	2.11	2.15	1.91	2.19	1.95	1.20	2.03
0.3004	2.23	2.29	1.97	2.35	2.01	1.00	2.11
0.4004	2.50	2.57	2.18	2.64	2.23	1.02	2.33
0.4990	2.71	2.78	2.36	2.85	2.41	1.07	2.49
0.5965	2.87	2.93	2.49	3.00	2.54	1.14	2.59
0.6995	3.84	3.90	3.40	3.96	3.44	1.89	3.38
0.8002	3.97	4.01	3.54	4.06	3.57	2.10	3.43
0.9001	4.10	4.13	3.67	4.15	3.68	2.27	3.41
1.0000	(3.50)						
AAD	2.91	2.96	2.58	3.01	2.62	1.44	2.62

[a] x_2 is defined as the mole fraction of component (2) in the mixed solvent. The values in parentheses were not considered in calculation of AAD.

Table 6. Average Absolute Percent Deviations AAD for the Prediction of Diffusion Coefficients of Aromatics at Infinite Dilution in Hexane + Heptane Mixtures Using Wilke−Chang Prediction of D_{1p}^{∞} in Pure Solvents

solutes	Perkins−Geankopolis	Holmes et al.	Tang−Himmelbau	Leffler−Cullinan	Eyring	Dullien−Asfour	Maxwell−Stefan
benzene	2.91	2.96	2.58	3.01	2.62	1.44	2.62
chlorobenzene	3.86	3.91	3.53	3.96	3.57	2.39	3.56
ethylbenzene	5.31	5.36	4.98	5.41	5.02	3.86	5.02
toluene	4.11	4.17	3.79	4.22	3.83	2.65	3.82
p-chlorotoluene	4.20	4.25	3.87	4.30	3.91	2.74	3.91
naphthalene	5.84	5.89	5.52	5.94	5.56	4.41	5.55
pyrene	4.67	4.72	4.35	4.77	4.39	3.22	4.38
perylene	5.82	5.87	5.50	5.92	5.54	4.39	5.54
mean value	4.59	4.64	4.27	4.69	4.30	3.14	4.30

(a) Linear Dependence of Diffusion Coefficients with Respect to the Mole Fraction of the Mixed Solvent:

$$D_{1m}^{\infty}\eta_m^{\alpha} = \sum_{i=2}^{m} x_i D_{1i}^{\infty}\eta_i^{\alpha} \tag{5}$$

According to the value of exponent α, we obtain either the expression of Holmes et al.,[15] which was originally introduced by Hartley and Crank[16] and later by Carman and Stein,[17] or the relation proposed by Tang and Himmelblau.[18] For binary mixed solvents, we get

$$\alpha = 1 \quad (\text{Holmes et al.}^{15}) \quad D_{1m}^{\infty}\eta_m = x_2 D_{12}^{\infty}\eta_2 + x_3 D_{13}^{\infty}\eta_3 \tag{5.1}$$

$$\alpha = 1/2 \quad (\text{Tang and Himmelblau}^{18}) \quad D_{1m}^{\infty}\,\eta_m^{1/2} = x_2 D_{12}^{\infty}\,\eta_2^{1/2} + x_3 D_{13}^{\infty}\,\eta_3^{1/2} \tag{5.2}$$

(b) Linear Dependence of Logarithms of Diffusion Coefficients with Respect to the Mole Fraction of the Mixed Solvent:

$$D_{1m}^{\infty}\,\eta_{1m}^{\alpha} = \prod_{i=2}^{m} (D_{1i}^{\infty}\,\eta_i^{\alpha})^{x}i \tag{6}$$

As in the previous case, the values of exponent α allow obtaining the equation proposed by Leffler and Cullinan,[19] Eyring,[20] or Dullien and Asfour;[3] always for binary mixed solvents:

$$\alpha = 1 \quad (\text{Leffler and Cullinan}^{19}) \quad D_{1m}^{\infty}\eta_m = (D_{12}^{\infty}\eta_2)^{x_2}\cdot(D_{13}^{\infty}\eta_3)^{x_3} \tag{6.1}$$

$$\alpha = 1/2 \quad (\text{Eyring}^{20}) \quad D_{1m}^{\infty}\,\eta_m^{1/2} = (D_{12}^{\infty}\,\eta_2^{1/2})^{x_2}\cdot(D_{13}^{\infty}\,\eta_3^{1/2})^{x_3} \tag{6.2}$$

$$\alpha = -1 \quad (\text{Dullien and Asfour}^{3}) \quad \frac{D_{1m}^{\infty}}{\eta_m} = \left(\frac{D_{12}^{\infty}}{\eta_2}\right)^{x_2}\cdot\left(\frac{D_{13}^{\infty}}{\eta_3}\right)^{x_3} \tag{6.3}$$

(c) Maxwell−Stefan Gas Diffusion Equation:

$$D_{1m}^{\infty} = \frac{1}{\dfrac{x_2}{D_{12}^{\infty}} + \dfrac{x_3}{D_{13}^{\infty}}} \tag{7}$$

Even if this equation was developed for gas diffusion, it was shown by Bird et al.[21] that it can be used for liquids if the solvent mixture can be considered as stationary.

Prediction of Diffusion Coefficients in Binary Solvents. Diffusion coefficients at infinite dilution D_{1m}^{∞} of the various solutes (1) in the different mixed solvents were predicted by means of the models presented in the previous section. Most of these equations (eqs 5 to 7) depend on the values of diffusion coefficients D_{1p}^{∞} in pure solvents. These latter can be predicted using the Wilke−Chang equation (eq 2), which provides a full prediction of the D_{1m}^{∞} values for each model considered; this technique is investigated in the next section. If no satisfactory predictions are obtained in this way, coefficients D_{1p}^{∞} should be experimentally determined; this leads to the prediction of D_{1m}^{∞} from experimental data in pure solvents; this method was considered for benzene in polar mixed solvents.

(a) Full Prediction. Results obtained with the various models for benzene in the different mixed solvents are presented in Tables 5, 7, and 8 for the measured mole fractions x_2, while the average deviations obtained for all the aromatic solutes in hexane + heptane mixed solvents are given in Table 6 ΔD_{1m}^{∞}

Table 7. Percent Deviations ΔD^{∞}_{1m} between Experimental and Predicted Infinite Dilution Diffusion Coefficients of Benzene (1) in Hexane (2) + Ethanol (3) Mixtures Using Wilke−Chang Prediction of D^{∞}_{1p} in Pure Solvents[a]

x_2	Perkins−Geankopolis	Holmes et al.	Tang−Himmelbau	Leffler−Cullinan	Eyring	Dullien−Asfour	Maxwell−Stefan
0.0000	(41.70)						
0.2024	32.82	32.89	28.40	32.96	32.19	29.82	39.21
0.2864	29.21	29.31	23.26	29.40	28.13	24.18	37.77
0.3942	24.66	24.78	17.57	24.89	23.31	18.36	36.19
0.4739	21.83	21.95	14.56	22.08	20.52	15.65	35.44
0.6082	17.03	17.15	10.40	17.27	16.02	12.17	33.30
0.7083	12.55	12.66	7.88	12.77	12.69	12.47	30.96
0.7796	11.10	11.19	8.35	11.28	12.23	15.04	29.81
0.8913	6.25	6.30	6.37	6.35	8.53	14.75	22.26
1.0000	(3.50)						
AAD	19.43	19.53	14.60	19.62	19.20	17.81	33.12

[a] x_2 is defined as the mole fraction of component (2) in the mixed solvent. The values in parentheses were not considered in calculation of AAD.

Table 8. Percent Deviations ΔD^{∞}_{1m} between Experimental and Predicted Infinite Dilution Diffusion Coefficients of Benzene (1) in Acetone (2) + Ethanol (3) Mixtures Using Wilke−Chang Prediction of D^{∞}_{1p} in the Pure Solvents[a]

x_2	Perkins−Geankopolis	Holmes et al.	Tang−Himmelbau	Leffler−Cullinan	Eyring	Dullien−Asfour	Maxwell−Stefan
0.0000	(41.70)						
0.1163	37.46	37.48	39.95	37.51	41.01	50.39	47.24
0.2030	34.84	34.88	38.57	34.92	40.22	53.67	49.76
0.3396	29.53	29.59	34.96	29.65	37.24	55.44	51.04
0.4016	28.38	28.44	33.97	28.51	36.39	55.19	51.27
0.5058	25.68	25.75	31.55	25.82	34.06	53.70	50.43
0.5437	24.72	24.79	30.51	24.86	33.01	52.52	49.66
0.7084	21.02	21.08	26.21	21.14	28.30	46.12	44.64
0.8097	20.72	20.77	24.57	20.81	26.12	40.01	39.74
1.0000	(15.43)						
AAD	27.79	27.85	32.54	27.90	34.54	50.88	47.97

[a] x_2 is defined as the mole fraction of component (2) in the mixed solvent. The values in parentheses were not considered in calculation of AAD.

and AAD are respectively the percent relative deviations on the infinite dilution diffusion coefficients and the average absolute percent deviation:

$$\Delta D^{\infty}_{1m} = 100\frac{D^{\infty\ \mathrm{exp}}_{1m} - D^{\infty\ \mathrm{calc}}_{1m}}{D^{\infty\ \mathrm{exp}}_{1m}} \tag{8.1}$$

$$\mathrm{AAD} = \frac{1}{n}\sum|\Delta D^{\infty}_{1m}| \tag{8.2}$$

where n is the number of experimental points.

Tables 5, 7, and 8 compare the influence of the polarity of the solvent on the diffusion coefficients of benzene in mixed solvents. Larger deviations occur as soon as heptane (in Table 5) is replaced by ethanol in Table 7; mean values of AAD from (12 to 30) % are then observed instead of (1.5 to 3.0) %. These deviations still increase in the case of the acetone + ethanol solvent; as is shown in Table 8, deviations are rather in the range of (30 to 50) %. It can also be observed that all models lead to positive systematic deviations ΔD^{∞}_{1m}; this is due to the fact that the Wilke−Chang equation (eq 2) underestimates the diffusion coefficients at infinite dilution, as is evidenced by deviations given in parentheses in Tables 5, 7, and 8.

Concerning aromatic solutes in hexane + heptane solvents, it can be shown from Table 6 that the behavior of the various models is quite similar for all the aromatic solutes. Deviations are usually less than *5 %*, and the best results are obtained with the Dullien−Asfour model (eq 6.3). A good agreement is thus observed between experimental data and predicted diffusion coefficients, taking into account the Wilke−Chang values of D^{∞}_{1p} (eq 2) for the aromatics in hexane + heptane. In that case, no preliminary experimental determination of D^{∞}_{1p} is necessary.

Table 9. Percent Deviations ΔD^{∞}_{1m} between Experimental and Predicted Infinite Dilution Diffusion Coefficients of Benzene (1) in Hexane (2) + Ethanol (3) Mixtures Taking into Account Measured Values of D^{∞}_{1p} in Pure Solvents[a]

x_2	Holmes et al.	Tang−Himmelbau	Leffler−Cullinan	Eyring	Dullien−Asfour	Maxwell−Stefan
0.2024	−5.07	−5.63	0.47	−5.16	−8.90	−0.47
0.2864	−6.22	−7.55	−4.89-	−6.66	−12.44	−0.89
0.3942	−7.35	−8.57	−5.71	−7.76	−14.69	−0.41
0.4739	−7.17	−8.30	−5.28	−7.55	−13.96	0.76
0.6082	−6.39	−6.88	−4.59	−5.90	−10.82	2.95
0.7083	−6.40	−5.54	−4.66	−4.96	−4.96	4.66
0.7796	−4.19	−2.09	−2.98	−1.57	1.57	7.59
0.8913	−3.45	−0.46	−2.53	−0.23	6.67	7.13
AAD	5.78	5.63	3.89	4.97	9.25	3.11

[a] x_2 is defined as the mole fraction of component (2) in the mixed solvent.

This behavior is obviously due to the fact that the hexane + heptane mixture is quite ideal and that, as is shown in Table 5, the Wilke−Chang model provides quite satisfactory predictions of D^{∞}_{1p} respectively in pure heptane and hexane. As a consequence, only polar solvents require the use of experimental values of diffusion coefficients D^{∞}_{1p} for a more reliable prediction of diffusion coefficients D^{∞}_{1m} in mixtures.

(b) Prediction from Experimental Data in Pure Solvents. The results obtained for the infinite dilution coefficients of benzene in hexane + ethanol and acetone + ethanol are presented in Tables 9 and 10 and in Figure 2. In the case of eqs 5 to 7, the measured values of D^{∞}_{1p} are those given in Table 3 for the mole fractions $x_2 = 0$ and $x_2 = 1.0$. With respect to Tables 7 and 8, the improvement due to the use of experimental values of D^{0}_{1p} is quite significant. From these two examples, it seems that the equations of Holmes et al. (eq 5.1), Tang−

Table 10. Percent Deviations ΔD_{1m}^{∞} between Experimental and Predicted Infinite Dilution Diffusion Coefficients of Benzene (1) in Acetone (2) + Ethanol (3) Mixtures Taking into Account Measured Values of D_{1p}^{∞} in Pure Solvents[a]

x_2	Holmes et al.	Tang−Himmelbau	Leffler−Cullinan	Eyring	Dullien−Asfour	Maxwell−Stefan
0.1163	−3.54	3.10	−2.65	3.10	18.58	11.06
0.2030	−5.12	4.72	−3.54	4.72	26.38	16.53
0.3396	−8.87	4.78	−6.48	5.12	32.76	20.82
0.4016	−8.33	5.77	−5.77	6.09	33.65	22.43
0.5058	−8.21	5.86	−5.57	6.16	34.31	23.17
0.5437	−8.00	5.71	−5.43	6.00	33.43	22.86
0.7084	−6.41	5.13	−3.85	5.38	28.97	20.26
0.8097	−2.40	6.01	−0.48	6.25	23.80	17.55
AAD	6.36	5.14	4.22	5.25	28.99	19.34

[a] x_2 is defined as the mole fraction of component (2) in the mixed solvent.

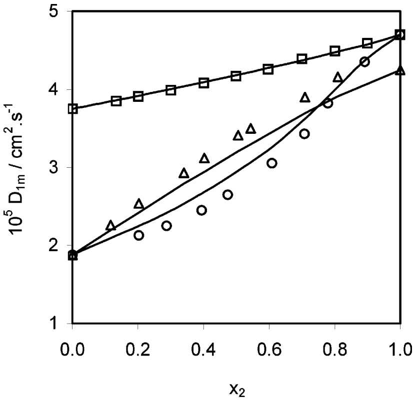

Figure 2. Correlation of diffusion coefficients D_{1m}^{∞} of benzene at infinite dilution in various mixed solvents with respect to the mole fraction of component (2) using the Tang and Himmelblau equation: □, hexane (2) + heptane; Δ, hexane (2) + ethanol; ○, acetone (2) + ethanol.

Himmelbau (eq 5.2), Leffler−Cullinan (eq 6.1), and Eyring (eq 6.2) provide the most reliable predictions, with deviations around (4 to 6) % for both systems. The Maxwell−Stefan relation (eq 7) is quite irregular, with deviations from (3 to 20) % in the case hexane + ethanol or acetone + ethanol solvents. For these systems, the Dullien−Asfour model (eq 6.3) provides the worst results. As a conclusion, for polar solvents, the use of experimental values for the infinite dilution diffusion coefficients D_{1p}^{∞} in pure solvents should always be preferred to the Wilke−Chang predictions (eq 2).

Conclusions

Diffusion coefficients of organic compounds in mixed solvents were experimentally determined in order to check the capabilities of literature models to predict diffusion coefficients in mixtures. The Taylor dispersion technique was used for measuring diffusion coefficients of aromatics in ideal and polar mixtures at 298.15 K.

Experimental determinations were correlated using literature equations, most of them depend on the values of diffusion coefficients D_{1p}^{∞} at infinite dilution in pure solvents. It is shown that the use of experimental values for the infinite dilution diffusion coefficients D_{1p}^{∞} in pure solvents should always be preferred to the Wilke and Chang predictions (eq 2), especially in the case of nonideal mixed solvents, which is the general case for natural multicomponent mixtures. It was also observed that, whatever the mixed solvent considered, all models provide equivalent predictions, except the Maxwell−Stefan and Dullien−Asfour equations, which lead to less stable results.

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