J. Chem. Eng. Data **2010,** *55,* 5449–5452

Diffusion Coefficients of Organic Compounds at Infinite Dilution in Ternary Mixtures: Experimental Determinations and Modeling[†]

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In this study, infinite dilution diffusion coefficients of aromatic compounds in ternary mixtures were measured at 298.15 K using the Taylor dispersion technique. The experimental data of benzene in mixtures of hexane + heptane + cyclohexane, hexane + decane + cyclohexane, and methanol + ethanol + acetone and benzaldehyde in methanol + ethanol + water systems are reported. Modeling of experimental data was performed with literature models commonly considered for binary systems. Special attention was paid to their extension to ternaries using mixture viscosity correlations.

Introduction

The solution to many engineering problems involving heat and mass transfer requires quantitative information on the mobility of molecular compounds in pure solvents or mixtures. From this point of view, diffusion coefficients are of great interest for chemical engineering applications involving mass-transfer processes. However, very few experimental data of liquid diffusion coefficients are available in the literature, especially for ternary solvents. This explains the need of experimental measurements and accurate correlations of infinite dilution diffusion coefficients.

In this work, the diffusion coefficients, D_{1m}^{∞}, at infinite dilution of benzene (1) in mixtures of hexane + heptane + cyclohexane, hexane + decane + cyclohexane, and methanol + ethanol + acetone and benzaldehyde (1) in methanol + ethanol + water systems were measured at 298.15 K using the Taylor dispersion technique.[1]

The modeling of experimental data was performed using literature models commonly considered for binary systems, and special attention was paid to their extension to ternaries using mixture viscosity correlations. A previous work[2] concerning the Maxwell−Stefan,[3] Leffler−Cullinan,[4] Eyring,[5] and Dullien-Asfour[6] models has shown that the use of the experimental values of diffusion coefficients, D_{1i}^{∞}, of the solute (1) in the pure solvents (i) clearly improves the description of diffusion coefficients, D_{1m}^{∞}, in mixed solvents, especially in the case of nonideal mixtures. It was also observed that the Leffler−Cullinan and Eyring models provide the best results, assuming experimental values of mixture viscosities, η_m. When these data are not available, the use of reliable predictive correlations is required. For this purpose, a comparison was performed[7,8] between the Grunberg−Nissan[9] and universal functional activity coefficient (UNIFAC-VISCO)[10,11] group contribution methods. Both models yielded satisfactory results for binary hydrocarbon solvents and turned out to be less accurate for polar and associating compounds.

The aim of this study is to check the extension of these methods to the correlation of infinite dilution diffusion coefficients in ternary solvents.

Experimental Section

The Taylor dispersion technique[1] was used to determine diffusion coefficients in ternary solvents. The experimental apparatus and procedures for the measurement of diffusion coefficients of solutes in binary solvents have been described in previous papers.[2,7,8,12] A model 655A liquid chromatographic pumping system (Merck-Hitachi) was used to provide constant laminar flow at 0.1 mL·min^{-1}. The diffusing tube (a stainless steel pipe) was 10 000 cm long with an inner diameter of $d_{\text{tube}} = 0.0476$ cm and coil diameter of $d_{\text{coil}} = 22$ cm. The whole tubing was immersed in a water bath at 298.15 K. The UV detector was a Merck UV−vis filter photometer operating at 254 nm.

In this mode, the reciprocal of the Peclet number ($r_c u/2D_{1,m}$) is less than 1, where r and u are the radius of the tube and the solvent velocity, respectively. The retention times are still acceptable (ca. 3 h). The effect of the secondary flow due to the diffusion column coiling was negligible because the criterion,[13] $\text{De}\cdot\text{Sc}^{1/2} < 8$, was fulfilled for all measurement conditions, where De is the Dean number $\text{De} = (u\cdot\rho\cdot d_{\text{tube}}/\eta)(d_{\text{tube}}/d_{\text{coil}})^{1/2}$, ρ and η are the density and viscosity of the mobile phase, and the Schmidt number $\text{Sc} = \eta/\rho\cdot D_{1m}$.

As previously reported,[7,8] the main sources of relative uncertainties in the calculation of diffusion coefficients are the measurement of the retention time (0.5 %) and the determination of the width of the peak (1 %). Taking account of these experimental errors, the resulting relative uncertainty on the diffusion coefficients was estimated to be about 3 %.

The infinite dilution diffusion coefficients of benzene and benzaldehyde in the ternary solvents measured at 298.15 K are reported in Tables 1 and 2.

Materials. All solutes (Merck) were of the highest purity research grade (99 %); the solvents (Merck) were of the highest purity Lichrosolv grade (99.9 %).

[†] Part of the “Workshop in Memory of Henry V. Kehiaian”.

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10.1021/je1005642

Table 1. Experimental Values of Diffusion Coefficients at Infinite Dilution of Benzene (1) in Ternary Hydrocarbon Mixtures[a] Together with Pure Solvent Viscosities

benzene (1) in hexane (2) + heptane (3) + cyclohexane (4)				benzene (1) in hexane (2) + decane (3) + cyclohexane (4)			
		$10^5 D_{1m}^\infty$	η			$10^5 D_{1m}^\infty$	η
x_2	x_3	$cm^2 \cdot s^{-1}$	mPa·s	x_2	x_3	$cm^2 \cdot s^{-1}$	mPa·s
1.0000	0.0000	4.70	0.2920	1.0000	0.0000	4.70	0.2920
0.0000	1.0000	3.75	0.3874	0.0000	1.0000	2.16	0.8434
0.0000	0.0000	1.92	0.8830	0.0000	0.0000	1.92	0.8830
0.2111	0.1463	2.82		0.2111	0.1463	2.56	
0.2957	0.3586	3.47		0.2957	0.3586	2.71	
0.2691	0.4941	3.67		0.2691	0.4941	2.66	
0.1850	0.2552	2.93		0.1850	0.2552	2.45	
0.1873	0.4706	3.40		0.1873	0.4706	2.44	
0.1557	0.7030	3.76		0.1557	0.7030	2.36	
0.0798	0.2586	2.73		0.0798	0.2586	2.21	
0.0757	0.4724	3.09		0.0757	0.4724	2.19	
0.0686	0.8205	3.68		0.0686	0.8205	2.17	
0.3605	0.3979	3.66		0.3605	0.3979	2.70	

[a] x_2 and x_3 are the mole fractions of component (2) and (3) in the mixed solvent; $x_4 = 1 - x_2 - x_3$.

Table 2. Experimental Values of Diffusion Coefficients D_{1m}^∞ at Infinite Dilution of Benzene (1) or Benzaldehyde (1) in Ternary Polar Mixtures[a] Together with Pure Solvent Viscosities

benzene (1) in methanol (2) + ethanol (3) + acetone (4)				benzaldehyde (1) in methanol (2) + ethanol (3) + water (4)			
		$10^5\ D_{1m}^\infty$	η			$10^5\ D_{1m}^\infty$	η
x_2	x_3	$cm^2 \cdot s^{-1}$	mPa·s	x_2	x_3	$cm^2 \cdot s^{-1}$	mPa·s
1.0000	0.0000	2.66	0.5526	1.0000	0.0000	1.84	0.5526
0.0000	1.0000	1.88	1.0812	0.0000	1.0000	1.02	1.0812
0.0000	0.0000	4.25	0.3025	0.0000	0.0000	0.86	0.8923
0.2111	0.1463	3.90		0.0903	0.4376	0.67	
0.2957	0.3586	3.20		0.2086	0.5100	0.85	
0.2691	0.4941	2.81		0.3959	0.3465	1.00	
0.1850	0.2552	3.45		0.4889	0.1113	0.96	
0.1873	0.4706	2.91		0.5523	0.1901	0.93	
0.1557	0.7030	2.41		0.7103	0.0608	1.12	
0.0798	0.2586	3.66		0.8499	0.0331	1.33	
0.0757	0.4724	3.07					
0.0686	0.8205	2.34					
0.3605	0.3979	2.91					

[a] x_2 and x_3 are the mole fractions of component (2) and (3) in the mixed solvent; $x_4 = 1 - x_2 - x_3$.

Diffusion Coefficient and Viscosity Correlations

The modeling of diffusion coefficients at infinite dilution of aromatics in the hydrocarbon and polar mixtures was performed using the following approach.

Diffusion Coefficients. Two kinds of equations were considered:

The Maxwell−Stefan[3] gas diffusion equation:

$$D_{1m}^\infty = \left(\sum_{i=2}^{m} \frac{x_i}{D_{1i}^\infty} \right)^{-1} \tag{1}$$

The linear dependence of the logarithms of diffusion coefficients with respect to the mole fraction of the mixed solvent, as represented by the following correlations:

$$\ln(D_{1m}^\infty) = \sum_{i=2}^{m} x_i \ln(D_{1i}^\infty) + \sum_{i=2}^{m} x_i \ln(\eta_i/\eta_m) \qquad \text{(Leffler−Cullinan)[4]} \tag{2}$$

$$\ln(D_{1m}^\infty) = \sum_{i=2}^{m} x_i \ln(D_{1i}^\infty) + \frac{1}{2}\sum_{i=2}^{m} x_i \ln(\eta_i/\eta_m) \qquad \text{(Eyring)[5]} \tag{3}$$

$$\ln(D_{1m}^\infty) = \sum_{i=2}^{m} x_i \ln(D_{1i}^\infty) - \sum_{i=2}^{m} x_i \ln(\eta_i/\eta_m) \qquad \text{(Dullien−Asfour)[6]} \tag{4}$$

where D_{1m}^∞ and D_{1i}^∞ are respectively the diffusion coefficients of the solute (1) in the mixture (m) and the pure solvent (i); η_m and η_i are respectively the viscosities of the mixture and the pure solvents. The experimental values of D_{1i}^∞ and η_i determined in this work are reported in Tables 1 and 2.

Liquid Mixture Viscosities. Except for the Maxwell−Stefan equation (eq 1), all other correlations (eqs 2 to 4) require the knowledge of the mixture viscosity η_m. In the absence of experimental values, this property is estimated using the general formalism:

$$\ln(\eta_m) = \sum_{i=2}^{m} x_i \ln(\eta_i) + \Delta_{\ln \eta} \tag{5}$$

Table 3. Influence of Diffusion Coefficient, D^∞_{1i}, Estimations and ARDs between Experimental and Calculated Diffusion Coefficients D^∞_{1m} Using the Maxwell−Stefan Relation (eq 1) and the Ideal Mixing Rule for Viscosities (eq 7)

	experimental		from Wilke−Chang[14]	
D^∞_{1i}	eq 1	eq 7	eq 1	eq 7
benzene (1) in				
hexane (2) + heptane (3) + cyclohexane (4)	12.87	7.61	25.37	17.45
hexane (2) + decane (3) + cyclohexane (4)	6.07	3.33	19.40	14.11
methanol (2) + ethanol (3) + acetone (4)	14.83	10.10	43.33	36.38
benzaldheyde (1) in				
methanol (2) + ethanol (3) + water (4)	27.46	33.70	33.94	38.61

Table 4. Influence of Mixture Viscosity, η_m, Estimations and ARDs between Experimental and Calculated Diffusion Coefficients D^∞_{1m} Using the Leffler−Cullinan (eq 2), Eyring (eq 3), and Dullien−Asfour (eq 4) Models and the Experimental Values of D^∞_{1i}

	from Grunberg−Nissan[7]			from UNIFAC-VISCO[8,9]		
η_m	eq 2	eq 3	eq 4	eq 2	eq 3	eq 4
benzene (1) in						
hexane (2) + heptane (3) + cyclohexane (4)	3.30	5.48	11.71	2.32	4.99	12.56
hexane (2) + decane (3) + cyclohexane (4)	2.67	2.97	4.04	4.65	3.31	2.62
methanol (2) + ethanol (3) + acetone (4)	8.40	2.40	24.96	13.27	2.22	28.27
benzaldheyde (1) in						
methanol (2) + ethanol (3) + water (4)	5.54[a]	4.94[b]	8.35[c]	–	–	–

[a] ARD using: $\Delta_{water} = -1.5104$. [b] ARD using: $\Delta_{water} = -2.7832$. [c] ARD using: $\Delta_{water} = 1.6823$.

In this work, we only focus on predictive expressions of the mixture viscosity. The following methods were considered:

–The ideal mixing rule for viscosity:

$$\Delta_{\ln \eta} = 0 \tag{6}$$

With this assumption, eqs 2 to 4 reduce to a single expression of the logarithm of diffusion coefficients independent of viscosities:

$$\ln(D^\infty_{1m}) = \sum_{i=2}^{m} x_i \ln(D^\infty_{1i}) \tag{7}$$

–The Grunberg−Nissan group correlation:[9]

$$\Delta_{\ln \eta} = \frac{1}{2}\sum_i \sum_j x_i x_j G_{ij} \tag{8}$$

Parameters G_{ij} are estimated from the group contributions developed by the authors. Since the original model does not cover aqueous mixtures, the water group contribution parameter was determined in this work.

–The UNIFAC-VISCO method:[10,11]

$$\Delta_{\ln \eta} = \sum_i x_i \ln\left(\frac{v_i}{v_m}\right) + \frac{\Delta^* G^E}{RT} \qquad v_m = \sum_i x_i v_i \tag{9}$$

where v_m and v_i are respectively the molar volumes of the mixture and pure components; $\Delta^* G^E$ is the excess molar Gibbs energy of activation, which is estimated according to the group contributions developed in the original works.

Results and Discussion

As was outlined in the introduction, the purpose of this work was to study the extension to ternary solvents of the methods previously considered[2,7,8] for the correlation of infinite dilution diffusion coefficients D^∞_{1m} in binary mixtures. First of all, we check the influence of the estimation of the diffusion coefficients D^∞_{1i} of the solute (1) in the pure solvent (i), by considering only the correlations independent of the viscosities (eqs 1 and 7); second, we compare the results obtained with the other models (eqs 2 to 4) according to the method used for estimating the mixture viscosities η_m.

Results obtained with the various modelings are presented in Tables 3 and 4. ARD is the average relative deviation:

$$\mathrm{ARD} = \frac{1}{n}\sum |(D^\infty_{1m} - D^{\infty\mathrm{calc}}_{1m})/D^\infty_{1m}| \tag{10}$$

where n is the number of experimental points.

Influence of Diffusion Coefficient, D^∞_{1i}, Estimation. For a given pure solvent (i), the infinite dilution diffusion coefficients D^∞_{1i} of the aromatics (1), benzene or benzaldehyde, were estimated, either from the experimental values determined in this work (Tables 1 and 2) or from the well-known Wilke−Chang[14] correlation:

$$D^\infty_{1i}/\mathrm{cm}^2\cdot\mathrm{s}^{-1} = 7.4\cdot 10^{-8}\frac{\sqrt{\phi_i M_i}}{\eta_i V_1^{0.6}}T \tag{11}$$

where T is the temperature in Kelvin; ϕ_i, M_i (in g·mol^{-1}), and η_i (in mPa·s) are respectively the association factor, the molar mass, and the viscosity of the pure solvent (i), while V_1 is the molar volume (in cm^3·mol^{-1}) of the solute at its normal boiling temperature.

The influence of these estimation methods was checked by correlating experimental data with the only two relations independent of mixture viscosities, η_m, which means eqs 1 and 7. Results obtained are presented in Table 3. The following can be observed:

–As for nonaqueous binary mixtures,[2] the Wilke−Chang correlation yields poor results, so that the use of experimental values of D^∞_{1i} is recommended for the modeling of mixture diffusion coefficients D^∞_{1m}. Table 3 also shows that, for these systems, quite similar descriptions of D^∞_{1m} are obtained from the Maxwell−Stefan correlation (eq 1) and the ideal mixing rule for viscosities (eq 7).

–In the case of aqueous mixtures, it appears that none of the models independent of mixture viscosities (eqs 1 and 5) is able to correlate the diffusion coefficients of aromatics in the mixed solvent, even using the experimental values of D_{1i}^{∞}.

Influence of Mixture Viscosity, η_m, Estimation. The same ternary mixtures were studied by means of the three other models, Leffler−Cullinan (eq 2), Eyring (eq 3), and Dullien−Asfour (eq 4), using the experimental D_{1i}^{∞} values. The nonaqueous systems were modeled with the two predictive Grunberg−Nissan[9] and UNIFAC-VISCO[10,11] models described previously (eqs 8 and 9) for the mixture liquid viscosities, η_m. Results obtained are presented in Table 4. The following conclusions can be drawn:

–Whatever the predictive method considered, Grunberg−Nissan or UNIFAC-VISCO, the Dullien−Asfour correlation of D_{1m}^{∞} leads to the worse results.

–The Leffler−Cullinan and Eyring equations provide rather similar results with, however, a better description of D_{1m}^{∞} using the Eyring model associated with the UNIFAC-VISCO group contributions.

The Grunberg−Nissan model[9] was extended to aqueous systems by fitting the group contribution of water to methanol + ethanol + acetone system (Table 2). According to the original model, the binary parameter G_{ij} in eq 8 is expressed as:

$$G_{ij} = \sum_i \Delta - \sum_j \Delta + W = G_{ji} \tag{12}$$

where $\sum\Delta_i$ and $\sum\Delta_j$ are the sums of the group increments related to components i and j and ΔW is a binary contribution characteristic of hydrocarbon mixtures. For aqueous solvents, eq 12 only depends on Δ_{water} and on the published group increments $\sum\Delta_j$. Two problems that were encountered in the estimation of the water group parameter can be drawn:

–On one hand, the choice of the “first” component i (in eq 12) is crucial, since G_{ij} should be equal to G_{ji}. Following the classification proposed by Grunberg and Nissan, we have assumed that “*water*” should be the first component “*i*”, so that components *i* and *j* are classified as follows: water, methanol, ethanol, acetone, and hydrocarbons.

–The Grunberg and Nissan method is devoted to the description of liquid mixture viscosities, η_m; however, in this work, according to eq 8, the estimation of Δ_{water} (eq 12) was performed by correlating diffusion coefficients D_{1m}^{∞}. Consequently, various sets of Δ_{water} values were obtained with the different models: Leffler−Cullinan, Eyring, and Dullien−Asfour (Table 4).

Results presented in Table 4 show that all models provide quite similar results, once the aqueous group parameter is fitted to the experimental diffusion coefficients D_{1m}^{∞}. However, as was already observed in Table 3, the Dullien−Asfour model presents a quite different behavior, with an estimated value of $\Delta_{\text{water}} = 1.6823$, instead of -1.5104 and -2.7832 for the Leffler−Cullinan and Eyring equations.

Conclusion

Diffusion coefficients at infinite dilution of aromatics in ternary solvents, involving aqueous mixtures, were measured at 298.15 K using the Taylor dispersion technique.

Experimental determinations were first correlated with the Maxwell−Stefan and the “ideal” mixing viscosity equations, to check the influence of diffusion coefficient, D_{1i}^{∞}, estimations. Results obtained show that, exactly as in the case of binary mixtures containing hydrocarbons or polar compounds, poor results were obtained with the Wilke−Chang D_{1i}^{∞} correlation. In the case of aqueous mixtures, it was also observed that none of the models independent of mixture viscosities is able to correlate the diffusion coefficients of aromatics in the mixed solvent, even using the experimental values of D_{1i}^{∞}.

Experimental data were also correlated with the Leffler−Cullinan, Eyring, and Dullien−Asfour models using mixture viscosities estimated from the Grunberg−Nissan and UNIFAC-VISCO group contributions. As for binary mixtures, the Dullien−Asfour correlation of D_{1m}^{∞} leads to the worse results, while the Leffler−Cullinan and Eyring equations provide rather similar results. The Grunberg−Nissan method was also extended to aqueous mixtures, and satisfactory results were thus obtained.

Acknowledgment

We are grateful to Prof. Jean-Louis Chevalier from the University of Méditerranée (Marseille, France), for the development of the Taylor dispersion setup and for his valuable comments on the interpretation of the experimental measurements.

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Received for review May 27, 2010. Accepted September 3, 2010.

JE1005642