Correlations for binary diffusion coefficients of solutes in supercritical fluids and liquids using hydrodynamic equation with molecular volume

Junichi Sakabe*, Toshitaka Funazukuri
Department of Applied Chemistry, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo, 112-8551, Japan
* sakabe@kc.chuo-u.ac.jp

Abstract

A simple model using a hydrodynamic equation is developed for predicting diffusion coefficient prediction in supercritical CO_2 and liquid organic solvents, considering the influence of solute molecular volume estimated from quantum calculation on D_{12}. The D_{12} values in m^2 s^{-1} for the fifty-three compounds in the literature were represented by the new prediction equation over a wide range of viscosity with average absolute relative deviation of 6% for 1678 data points.

Introduction

Transport coefficients are fundamental properties for simulation and design of multiphase reaction processes. In particular, the binary diffusion coefficient at infinite dilution of a solute in a solvent is one of the most important transport coefficients. Many researchers reported several equations to predict or correlate diffusion coefficients by different approaches [1-3]. Accurate modified hydrodynamic models for predicting of tracer diffusivities in supercritical carbon dioxide were reported [4,5]. Some of these models require a set of property data for each pair of molecules in the mixture, such as critical properties, molar volumes at normal boiling point, dipole moments, Lennard-Jones force constants. Furthermore, the data fitting is required for optimizing some parameters in the models. The reduction of the number of the fitting parameters in the diffusion coefficient calculations allows it to extend the application of the model to the system that few data set are available. Thus, the development of a simple and accurate prediction model for diffusion coefficients of solutes in solvents over wide ranges of temperature and pressure is required.

A simple and accurate correlation model, a modified hydrodynamic equation, was presented, in our previous work [6]. The model proved the necessity of consideration of solute molecular sizes for the correlation. In particular, for acac metal complex compounds, the diffusion coefficients were dependent on not solute molecular weight but the number of ligand in the complex molecules. In this work, a new prediction model for binary diffusion coefficients of solutes is proposed. It is appropriate for liquid and supercritical phases over wide ranges of temperature and pressure. Moreover, the model is applicable to systems consisting of polar and non-polar, small and large, light and heavy and metal complex molecules. The model is based on a hydrodynamic equation model, and contains only one parameter: the molecular volume of a solute. The molecular volumes of solutes were obtained by quantum calculation based on conductor-like screening model (COSMO) [7]. The binary diffusion coefficients of solutes in a wide range of viscosity were predicted by this model using the hydrodynamic equation. The calculation performance of the diffusion coefficient of solutes in liquid and supercritical phase was investigated.

Model development

The relationship between D_{12} and temperature (T) and solvent viscosity (η_1) based on the hydrodynamic theory can be assumed as follows [8]:

$$D_{12} \propto \frac{T}{\eta_1} \tag{1}$$

D_{12} values were almost the same values for the metal complexes having the same number of the acac ligand: the solute molecular sizes (V), irrespective of molecular weights [6].

$$D_{12} \propto \frac{1}{V} \tag{2}$$

The final D_{12} model is obtained from Eq. 1 and 2.

$$(D_{12}/T)V \propto 1/\eta_1 \tag{3}$$

This model requires temperature, viscosity of solvent and molecular volume. The viscosity is calculated from empirical equations. The molecular volume is obtained from quantum calculation using COSMO.

Results and discussions

Fig. 1 indicates the relationship between molecular volume estimated from quantum calculation and D_{12} in supercritical carbon dioxide at 313 K and 11 MPa for the literature data [9]. The data details are listed in Table 1. The data for polar and metal complex

compounds are represented by the straight line with a slope of -0.5 over a wide range of molecular volumes from 2.9 to 100×10^{-5} m^3 mol^{-1}.

Fig. 2 shows the correlation plots of $(D_{12}/T)V^{0.5}$ versus CO_2 viscosity for thirteen compounds (Benzoic acid, Methanol, Ethanol, 1-Propanol, 2-Propanol, $Pd(acac)_2$, $Co(acac)_3$, Oleic acid, Oleic acid ME, Oleic acid EE, Monoolein, Diolein and Triolein). All data are represented by the correlation in Eq.4.

$$(D_{12}/T)V^{0.5} = 4.1807 \times 10^{-14}\eta_1^{-0.824} \quad (4)$$

where D_{12} is the diffusion coefficient (m^2 s^{-1}), T is the absolute temperature (K), V is the solute molecular volume (m^3 mol^{-1}) and η_1 is the solvent viscosity (Pa s), respectively.

Tables 2 and 3 list the prediction results of the diffusion coefficients of the 54 compounds in supercritical carbon dioxide and liquid organic solvents using Eq. 4. The prediction performance of the model is evaluated by the average absolute relative deviation (*AARD*) with the experimental data.

$$AARD\ (\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|D_{12}^{\text{exp.}} - D_{12}^{\text{cal.}}\right|}{D_{12}^{\text{exp.}}} \quad (5)$$

where superscripts exp. and calc. are the experimental data and predicted results, respectively. N denotes the number of the data point of the D_{12}.

Fig. 3 shows the prediction results of the pressure dependence on the diffusion coefficients for metal complex compounds ($Co(acac)_3$ and Copper(II) trifluoroacetylacetonate) in Fig. 3a and large and small compounds (methanol and trinervonin) in Fig. 3b.

Table 1

The values of molecular weight, molecular volume and diffusion coefficient of various compounds.

Compound	M	V (10^{-5} m^3 mol^{-1})	D_{12} (10^{-8} m^2 s^{-1})
Methanol	32	2.917	2.55
Ethanol	46.1	4.220	2.147
Acetone	58.1	5.188	1.926
1-Propanol	60.1	5.545	1.874
2-Propanol	60.1	5.560	1.91
2-Butanone	72.1	6.457	1.74
Benzene	78.1	6.632	1.856
2-Pentanone	86.1	7.795	1.587
3-Pentanone	86.1	7.727	1.623

Phenol	94.1	7.276	1.561
Benzoic acid	122.1	8.883	1.367
Vitamin K_3	172.2	12.345	1.227
α-Linolenic acid	278.4	24.572	0.832
γ-Linolenic acid	278.4	24.279	0.805
Linoleic acid	280.4	25.723	0.803
Oleic acid	282.5	25.060	0.807
Elaidic acid	282.5	25.062	0.809
γ-Linolenic acid methyl ester	292.5	25.652	0.924
Linoleic acid methyl ester	294.5	26.829	0.848
Oleic acid methyl ester	296.5	26.450	0.864
Elaidic acid methyl ester	296.5	26.394	0.864
EPA	302.5	26.664	0.784
Arachidonic acid	304.5	26.985	0.776
α-Linolenic acid ethyl ester	306.5	27.437	0.828
γ-Linolenic acid ethyl ester	306.5	26.871	0.89
Linoleic acid ethyl ester	308.5	28.037	0.841
Oleic acid ethyl ester	310.5	27.712	0.856
Elaidic acid ethyl ester	310.5	27.710	0.849
DHA	328.5	28.811	0.831
DHA methyl ester	342.5	30.039	0.812
DHA ethyl ester	356.5	31.320	0.81
Monoolein	356.5	29.242	0.735
α-Tocopherol	430.7	36.880	0.765
β-Carotene	536.9	46.955	0.561
Dilinolein	617	53.191	0.602
Diolein	621	53.719	0.601
Ubiquinone CoQ10	863.4	75.230	0.516
Trilinolenin	873.4	75.853	0.512
Trilinolein	879.4	76.742	0.522
Triolein	885.4	77.595	0.53
Trielaidin	885.4	77.407	0.53
Triarachidonin	951.5	84.069	0.508
Trierucin	1053.8	93.650	0.457
Trinervonin	1137.9	100.984	0.433
Li(acac)	106.1	8.331	1.672

Ferrocene	186	11.675	1.376
1,1'-Dimethyl-ferrocene	214.1	14.095	1.209
$Pd(acac)_2$	304.6	16.255	0.971
$Al(acac)_3$	324.3	21.881	0.925
$Cr(acac)_3$	349.3	21.856	0.852
$Pt(acac)_2$	393.3	16.244	0.935
$Co(acac)_3$	356.3	24.806	0.877

Table 2

Prediction results for diffusion coefficient of 53 compounds in supercritical carbon dioxide.

Compound	*M*	*V* (10^{-5} m^3 mol^{-1})	*AARD* (%)
1,1'-Dimethylferrocene	214.1	14.095	8.13
1,2-Dichlorobenzene	147.0	9.270	6.63
1,3-Divinylbenzene	130.2	11.155	1.25
1-Hexadecene	224.4	21.686	8.78
1-Methylnaphthalene	142.2	11.331	17.39
1-Propanol	60.1	5.545	3.81
2,4-Dimethylphenol	122.2	9.902	11.86
2,6-Dimethylnaphthalene	156.2	12.697	2.24
2,7-Dimethylnaphthalene	156.2	12.725	4.34
2-Bromoanisole	187.0	10.418	12.21
2-Butanone	72.1	6.457	4.70
2-Ethyltoluene	120.2	10.477	2.84
2-Fluoroanisole	126.1	9.232	11.04
2-Pentanone	86.1	7.795	5.39
2-Propanol	60.1	5.560	3.75
2-Propanone	58.1	5.188	3.25
3-Ethyltoluene	120.2	10.441	3.10
3-Pentanone	86.1	7.727	5.76
4-Ethyltoluene	120.2	10.609	2.42
Acetone	58.1	5.188	4.93
Allylbenzene	118.2	10.309	3.59
α-Linolenic acid	278.5	24.572	2.27
Anisole	108.1	8.707	6.83
Arachidonic acid	304.5	26.985	4.38
Benzene	78.1	6.632	11.39

Benzoic acid	122.1	8.883	3.00
$Co(acac)_3$	356.3	24.806	3.07
Copper(II) trifluoroacetylacetonate	369.7	19.009	5.42
DHA	328.5	28.811	7.40
Diolein	622.0	53.719	5.27
EPA	302.5	26.664	4.57
Ethanol	46.1	4.220	2.80
Ferrocene	186.0	11.675	6.98
Linoleic acid	280.5	25.723	2.31
Methanol	32.0	2.917	3.28
Monoolein	356.6	29.242	5.84
Naphthalene	128.2	10.108	15.22
n-Butylbenzene	134.2	11.952	1.42
Oleic acid	282.5	25.060	4.33
Oleic acid ethyl ester	310.5	27.712	2.90
Oleic acid methyl ester	296.5	26.450	3.04
$Pd(acac)_2$	304.6	16.255	2.90
p-Dichlorobenzene	147.0	9.356	7.52
Phenol	94.1	7.276	1.23
tert-Butylbenzene	134.2	11.854	3.77
Triarachidonin	951.5	84.069	12.05
Trierucin	1053.8	93.650	5.60
Trinervonin	1137.9	100.984	6.25
Triolein	885.4	77.595	8.17
Ubiquinone (CoQ-10)	863.4	75.230	6.82
Vitamin K_3	172.2	12.345	1.64
α-Tocopherol	430.7	36.880	9.39
β-Carotene	536.9	46.955	8.43

Table 3

Prediction results for diffusion coefficients of metal complex compounds in ethanol and hexane.

Compound	*M*	*V* (10^{-5} m^3 mol^{-1})	In ethanol *AARD* (%)	In hexane *AARD* (%)
Ferrocene	186.04	11.675	8.83	6.44
1,1'-Dimethylferrocene	214.09	14.095	6.55	8.26
Ethylferrocene	214.08	14.331	7.89	8.07

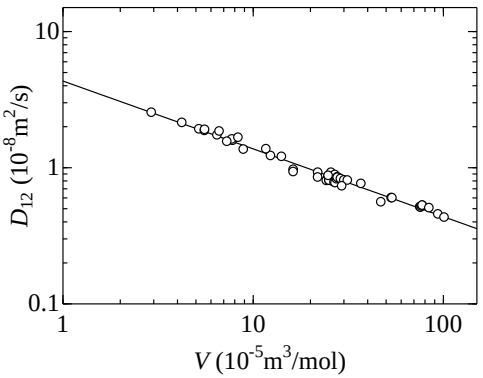

Fig. 1 Relationship between diffusion coefficient and molecular volume in supercritical carbon dioxide at 313 K and 11 MPa for various compounds listed in Table 1.

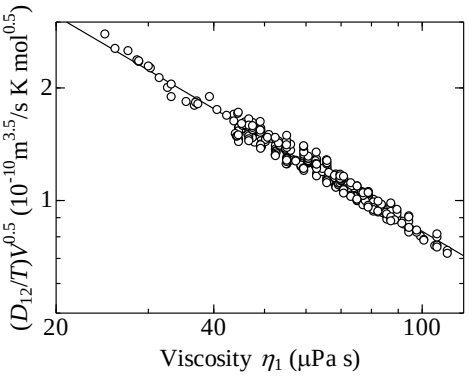

Fig. 2 $(D_{12}/T)V^{0.5}$ vs solvent viscosity for thirteen compounds.

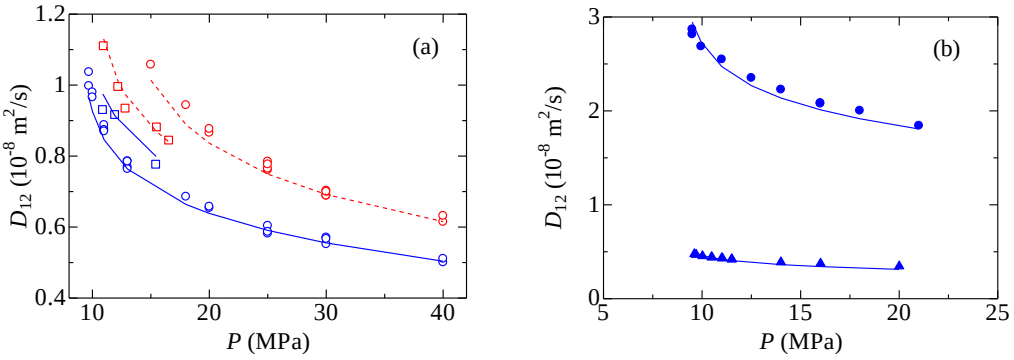

Fig. 3 Prediction results of D_{12} for metal complex compounds and large and small compounds. (a) $Co(acac)_3$: ○ and Copper(II) trifluoroacetylacetonate: □, (b) Methanol: ● and Trinervonin: ▲

Conclusion

In this work, a new simple model to predict diffusion coefficients in supercritical and liquid solvents is proposed. In this modeling, the prediction of the diffusion coefficient in supercritical carbon dioxide and liquids can be conducted using the only molecular volume in the equation. The simple prediction model proposed in the present study involves a single parameter, which is a solute molecular volume calculated from quantum calculation using COSMO, and is considered as a useful tool for diffusion coefficients of various compounds in supercritical carbon dioxide and liquid organic solvents.

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