Self-Diffusion in Liquids Predicted by a Theory of Flow through Granular Media

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A new semiempirical model for prediction of self-diffusion phenomena in liquids is proposed. Assuming analogy between the concept of a free volume in liquids and a porosity of a granular medium, a capillary model of the granular bed and the Kozeny-Carman theory was applied to determine self-diffusion coefficients in liquids. The dimensionless free volume in liquids was evaluated using a combination of the proposed dependence and an appropriate formula available in the literature. The new model was tested for 89 sets of data concerning self-diffusion of different chemical substances at several values of a temperature. The average error of a prediction was between ± 1% and about 3% for some data points.

Introduction

Diffusion coefficients are the thermophysical properties necessary to evaluate mass-transfer phenomena and to design equipment for mass-transfer operations. Contrary to the diffusion in gases, the phenomenon of the diffusion in liquids still needs theoretical and experimental investigations because of the lack of general theory of liquids.

A determination of diffusion coefficients in liquids has been a subject of numerous reported scientific investigations. The so-called hydrodynamical theory of diffusion is probably the oldest approach to the problem (Dullien, 1972). This theory originates from the Nernst-Einstein equation (Bird et al., 1960), which allows to express the diffusivity D_{AB} of a component A through a medium B in the following form

$$D_{AB} = kT\frac{u_A}{F_A} \tag{1}$$

where u_A is the velocity of a molecule under an action of the force F_A, T is the temperature, and k is the Boltzmann's constant.

If one assumes that the molecules are like rigid spheres immersed in a liquid and that they are moving in a creeping flow regime, then the force F_A acting on the single sphere can be calculated using the following formula of the classical hydrodynamics (Lamb, 1953)

$$F_A = 6\pi\mu_B u_A R_A\left(\frac{2\mu_B + R_A\beta_{AB}}{3\mu_B + R_A\beta_{AB}}\right) \tag{2}$$

in which μ_B is the viscosity of a solvent, R_A is the radius of the diffusing particle, and β_{AB} is the coefficient of the sliding friction.

Two limiting values of the β_{AB} coefficient are usually considered. If there is no slip on the surface of particles, then β_{AB} is equal to infinity and Eq. 2 becomes the well-known Stoke's law

$$F_A = 6\pi\mu_B u_A R_A \tag{3}$$

which substituted into Eq. 1 gives after rearrangements the so-called Stokes-Einstein equation

$$\frac{D_{AB}\mu_B}{kT} = \frac{1}{6\pi R_A} \tag{4}$$

Equation 4 usually fits experimental data when the size of diffusing particles is large compared to the size of the solvent molecules. However, deviations up to 20% can be also expected (Bird et al., 1960; Cussler, 1976; Pollack et al., 1990).

If one makes an assumption that there is no friction on the surface of molecules ($\beta_{AB} = 0$), Eq. 2 becomes

$$F_A = 4\pi\mu_B u_A R_A \tag{5}$$

and Eq. 1 after the substitution of Eq. 5 can be written as

$$\frac{D_{AB}\mu_B}{kT} = \frac{1}{4\pi R_A} \tag{6}$$

It is usually assumed further that in a case of self-diffusion when all molecules are the same, they can form a cubic lattice with particles just touching. The diameter of the molecule can then be defined

$$2R_A = \left(\frac{V_{MA}}{N}\right)^{1/3} \tag{7}$$

where V_{MA} is a molecular volume, and N is an Avogadro number.

After the substitution of Eq. 7 into Eq. 6, one can write for a self-diffusion process

$$\frac{D_{AA}\mu_A}{kT} = \frac{1}{2\pi}\left(\frac{N}{V_{MA}}\right)^{1/3} \tag{8}$$

It was proved that using Eq. 8 it is possible to predict self-diffusion phenomena, however, sometimes with very limited accuracy (Li and Chang, 1955; Bird et al., 1960; Lamb et al., 1981).

The described theory is a rough tool. It allows in principle to predict only changes of the diffusivity with temperature and viscosity, and to estimate the order of magnitude of the diffusion coefficient in liquids. However, it is still widely used because of its simplicity (Cussler, 1976). An empirical modification of this theory is commonly known as the Wilke-Chang formula (Reid et al., 1988) generally used for the prediction of the diffusion coefficients in liquids for small concentrations of the diffusing component.

The force F_A in Eq. 1 is calculated using the hydrodynamical formula given by Eq. 2. In the present study an attempt was made to determine this force using another dependence predicting the interactions between viscous liquid and solid obstacles. For this purpose, the semiempirical Kozeny-Carman capillary model concerning the flow through granular media was chosen. Such an approach like the described classical hydrodynamical theory does not give too much insight into the physics of the diffusion phenomenon. However, because it deals with an array of particles it seems more realistic. As a result of this approach, an empirical correlation will be provided for a prediction of the self-diffusion coefficients in liquids. The final formula does not contain any system specific parameters.

Adaptation of Capillary Model

The semiempirical capillary model of a granular bed and the related theory were described in detail in several papers and monographs, e.g., Kembłowski et al. (1987). These considerations will be presented here from the point of view of the performed work.

The basic assumption of the capillary model is that the array of particles should be considered as a bundle of tortuous capillary tubes with a Newtonian liquid flowing along. The other assumptions are as follows:

- The flow of the liquid is laminar.
- The cross section of the bed perpendicular to the main direction of the flow is constant.
- The structure of the bed is uniform, so that there are no privileged directions of flow.
- The dimensions of particles are small in comparison with bed dimensions.
- The particles are of an arbitrary shape, not necessarily spherical.

The force F resisting the flow of the liquid through a bundle of capillaries can be calculated as a product of an average wall shear stress τ_w and a wetted surface of tubes S_w

$$F = \tau_w S_w \tag{9}$$

According to the theory of the capillary model, the average wall shear stress can be calculated as a function of a pressure drop Δp and the bed geometry

$$\tau_w = \frac{1}{6} d_p \frac{\epsilon}{1-\epsilon} \frac{\Delta p}{K_1 L} \tag{10}$$

where d_p is the effective diameter of a particle, ϵ is the porosity of the bed, L is the length of the bed along the main direction of the flow, and K_1 is the tortuosity factor of capillaries.

The effective diameter d_p of a particle is usually defined using a concept of its specific surface a_p

$$a_p = \frac{S_p}{V_p} \tag{11}$$

where S_p is the wetted surface of an individual particle and V_p is its volume.

In the case of spherical particles one has

$$a_p = \frac{\pi d_p^2}{\frac{\pi d_p^3}{6}} = \frac{6}{d_p} \tag{12}$$

which allows us to write generally

$$d_p = \frac{6}{a_p} \tag{13}$$

The porosity ϵ in Eq. 10 defines the free space in the bed as a ratio of the void volume V_o to the volume occupied by the bed V

$$\epsilon = \frac{V_o}{V} \tag{14}$$

The pressure drop Δp in the capillary medium can be expressed by the following equation

$$\Delta p = f_{BK} \frac{L}{d_p} \frac{1-\epsilon}{\epsilon^3} v_o^2 \rho \tag{15}$$

in which ρ is the liquid density, f_{BK} is the modified friction factor, and v_o is the superficial velocity, i.e., the mean linear velocity related to the overall cross section of the bed.

The modified friction factor f_{BK} can be calculated using the Blake-Kozeny-Carman formula

$$f_{BK} = \frac{C_{BK}}{Re_{BK}} \tag{16}$$

where C_{BK} is the proportionality parameter and Re_{BK} is the modified Reynolds number given by

$$Re_{BK} = \frac{v_o d_p \rho}{\mu(1-\epsilon)} \tag{17}$$

The substitution of Eqs. 16 and 17 into Eq. 15 allows us to predict the pressure drop across the bed in the form

$$\Delta p = C_{BK} \frac{(1-\epsilon)^2}{\epsilon^3} \frac{L}{d_p^2} v_o \mu \tag{18}$$

and the subsequent substitution of Eq. 18 into Eq. 10 gives the formula for the average wall shear stress

$$\tau_w = \frac{C_{BK}}{6K_1} \frac{(1-\epsilon)}{\epsilon^2} \frac{1}{d_p} v_o \mu \tag{19}$$

The wetted surface can be evaluated starting with a definition of a specific surface of the bed a_b defined as the ratio of S_w and the bed volume V

$$a_b = \frac{S_w}{V} \tag{20}$$

If all the particles in the bed are wetted, then Eq. 11 can be also presented as a dependence

$$a_p = \frac{S_p N_{pb}}{V_p N_{pb}} = \frac{S_w}{V_{pb}} \tag{21}$$

in which N_{pb} is the number of particles in the bed, and V_{pb} is the total volume of particles.

Equations 20 and 21 can be combined as a ratio of a_b and a_p to give

$$\frac{a_b}{a_p} = \frac{S_w}{V} \frac{V_{pb}}{S_w} = \frac{V_{pb}}{V} = \frac{V - V_o}{V} \tag{22}$$

or

$$a_b = a_p(1-\epsilon) \tag{23}$$

Taking advantage of Eqs. 12 and 20, and by using the dependence of Eq. 23, the wetted surface can be calculated

$$S_w = V \frac{6}{d_p}(1-\epsilon) \tag{24}$$

Substituting now Eqs. 19 and 24 into Eq. 9 one can get

$$F = \frac{C_{BK}}{K_1} V \frac{(1-\epsilon)^2}{\epsilon^2} \frac{v_o}{d_p^2} \mu \tag{25}$$

The evaluated formula (Eq. 25) determines the force resulting from the resistance to flow of the considered granular medium as a function of its geometry and the flow parameters. It can be modified further along the following path.

The superficial velocity v_o can be replaced by the velocity in capillary tubes v_c using the dependence

$$v_o = \frac{\epsilon v_c}{K_1} \tag{26}$$

The diameter of the particles can be also substituted using the definition of the porosity in the following form

$$\epsilon = 1 - \frac{\pi d_p^3 N_{pb}}{6V} \tag{27}$$

which gives after rearrangement

$$d_p = \sqrt[3]{\frac{6V(1-\epsilon)}{N_{pb}\pi}} \tag{28}$$

The parameter C_{BK} is usually presented in the form

$$C_{BK} = 36 K_o K_1^2 \tag{29}$$

where K_o is the parameter dependent on the shape of the cross section of capillaries.

Equation 29 for the purpose of this work can be written as

$$C_{BK} = C_K K_1^2 \tag{30}$$

By substituting Eqs. 26, 28 and 30 we can modify the formula of Eq. 25 as follows

$$F = C_K \left(\frac{\pi}{6}\right)^{2/3} \frac{(1-\epsilon)^{4/3}}{\epsilon} V^{1/3} N_{pb}^{2/3} v_c \mu \tag{31}$$

If the force acting on only the one particle is considered, Eq. 31 after a division of the both sides by N_{pb} may be presented as

$$F_N = C_K \left(\frac{\pi}{6}\right)^{2/3} \frac{(1-\epsilon)^{4/3}}{\epsilon} \left(\frac{V}{N_{pb}}\right)^{1/3} v_c \mu \tag{32}$$

Adapting now the theory presented to the self-diffusion process, one can make the following assumptions:

- The force F_N and the velocity v_c correspond to the force F_A and the velocity u_A in Eq. 1.

- The volume of the bed V is the same as the molecular volume of the liquid V_{MA}.
- The number of particles N_{pb} in that volume is equal to the Avogadro number N.
- The diameter d_p is regarded in the case of the diffusion as an effective diameter of the molecule.

Also, the term porosity should be replaced. The porosity of the granular bed ϵ characterizes a real free space between solid particles. From the viewpoint of molecular theories, the concept of the free volume in a liquid is also known as a modeling one (Hirschfelder et al., 1966). To distinguish between these two cases, the term dimensionless free volume ϵ defined as a ratio of the free volume in the liquid to the molecular volume will be used instead of porosity in this work.

Using the above assumptions, Eq. 32 can be presented now as follows

$$F_A = C_K \left(\frac{\pi}{6}\right)^{2/3} \frac{(1-\epsilon)^{4/3}}{\epsilon} \left(\frac{V_{MA}}{N}\right)^{1/3} u_A \mu \tag{33}$$

Substituting Eq. 33 into Eq. 1, one gets the formula which predicts the diffusivity in liquids using the principles of the flow through granular media. For a self-diffusion process, it can be written, after dropping the A subscript, in the following form

$$\frac{D\mu}{kT} = \frac{1}{C_K}\left(\frac{6}{\pi}\right)^{2/3} \frac{\epsilon}{(1-\epsilon)^{4/3}} \left(\frac{N}{V_M}\right)^{1/3} \tag{34}$$

or

$$\frac{D\mu}{kT} = C_K^* \frac{\epsilon}{(1-\epsilon)^{4/3}} \left(\frac{N}{V_M}\right)^{1/3} \tag{35}$$

where

$$C_K^* = \frac{1}{C_K}\left(\frac{6}{\pi}\right)^{2/3} \tag{36}$$

Also Eq. 27 can be presented now in the form

$$\epsilon = 1 - \frac{\pi d_p^3 N}{6 V_M} \tag{37}$$

Evaluation of C_K^* Parameter

Determination of the value of the C_{BK} parameter in the Blake-Kozeny-Carman formula (see Eq. 16) is a subject of scientific research and discussions for years presented in several papers concerning the flow through granular media. Many authors assume that the C_{BK} parameter should be regarded as a constant. Several, but sometimes very different, experimental values were reported (Kemblowski et al., 1987; MacDonald et al., 1991). According to another approach, the value of the C_{BK} is dependent on the parameters characterizing the geometry of the granular bed (Kemblowski et al., 1987; Wyllie and Gregory, 1955; Kyan et al., 1970).

The parameter C_{BK} is a function of K_o and K_1 parameters (see Eq. 29). One can presume that if the granular medium consists of the closely packed particles then the porosity, the tortuosity, and the shape of the capillaries will change in a narrow range as a function of the particles size and shape. In such a situation, K_o and K_1 will also change marginally and the C_{BK} parameter can be regarded as a constant.

For the medium in which the particles can be very close and quite apart like molecules in fluids at different values of temperature, the porosity can change widely, affecting the values of K_o and K_1. In such a situation, the C_{BK} coefficient should be a function of the bed porosity or the dimensionless free volume in a liquid.

During the modeling work, the K_1 coefficient was eliminated from the final formula. However, the C_K^* parameter is still a function of the bed geometry and it is difficult to determine analytically, particularly on the molecular level. The C_K^* should be therefore evaluated from experimental data.

To determine the dimensionless free volume ϵ in a liquid using Eq. 37, one must know the diameter of diffusing molecules. Several formulas were developed for this purpose (Lamb et al., 1981; Greiner-Schmid et al., 1991). For this work, the following equation proposed by Dullien (1972) was chosen

$$d_p = 2.2\sqrt{\frac{\mu D V_M}{RT}} \tag{38}$$

in which R is the universal gas constant.

Equation 38 was obtained as a result of considerations concerning momentum transfer during diffusion. It has an advantage that it defines an effective diameter of the molecules only as the function of experimental, macroscopic parameters characterizing the considered liquid and the diffusion process, as in Eq. 35. It seems also that such a definition all takes into account the phenomena of association, dissociation, and hydrogen bonding between molecules which have an influence on the rate of diffusion and the calculated values of d_p.

Substituting Eq. 38 into Eq. 37 one can get

$$\epsilon = 1 - \frac{\pi}{6}\frac{N}{V_M}\left(2.2\sqrt{\frac{\mu D V_M}{RT}}\right)^3 \tag{39}$$

The Dullien's model becomes physically meaningless in the vicinity of the critical point. For this region, the author (Dullien, 1972) has proposed another formula for a calculation of the effective diameter

$$d_p = \left(\frac{2}{3}\frac{V_{MC}}{0.63\sqrt{2}\,\pi N}\right)^{1/3} \tag{40}$$

where V_{MC} is a molecular volume in a critical state.

One finds that the dimensionless free volume ϵ calculated using Eq. 40 is liquid independent and equal to 0.875.

The data for an evaluation of the C_K^* parameter are presented in Table 1. This table contains necessary values for

Table 1. Data for Evaluation of C_K^* Parameter

Liquid	T K	$\mu \times 10^3$ Pa·s	$V_M \times 10^2$ m^3/kmol	$D_e \times 10^9$ m^2/s	$d \times 10^{10}$ m	ϵ	$D_p \times 10^9$ m^2/s	Err %
Argon	84.2	0.28	2.85	2.07	3.38	0.573	2.04	−1.45
Mercury	296.2	1.536	1.48	1.67	2.73	0.566	1.64	−1.80
Methane	90.7	0.205	3.52	2.6	3.47	0.625	2.61	0.38
Methane	95.2	0.176	3.57	3.05	3.43	0.645	3.09	1.31
Methane	100	0.153	3.63	3.7	3.46	0.641	3.74	1.08
Methane	106.1	0.132	3.71	4.45	3.46	0.649	4.51	1.35
Methane	110.5	0.121	3.77	5.45	3.62	0.604	5.43	−0.37
Methane	111.1	0.119	3.77	5	3.43	0.663	5.10	2.00
Carbontetrachloride	293.2	0.975	9.65	1.18	4.70	0.662	1.20	1.69
Carbontetrachloride	298.2	0.902	9.71	1.32	4.75	0.652	1.34	1.52
Carbontetrachloride	313.2	0.739	9.89	1.82	4.97	0.608	1.82	0.00
Carbontetrachloride	323.2	0.651	10.01	2	4.85	0.642	2.02	1.00
Carbontetrachloride	333.2	0.585	10.14	2.44	5.03	0.605	2.43	−0.41
Chloroform	200	2.2	7.18	0.5	4.80	0.516	0.49	−2.00
Chloroform	298.2	0.542	8.07	2.58	4.69	0.596	2.56	−0.78
n-Pentane	194.7	0.755	10.08	1.38	5.60	0.449	1.35	−2.17
n-Pentane	250.3	0.355	10.83	2.97	5.15	0.601	2.96	−0.34
n-Pentane	273.2	0.277	11.18	4.14	5.23	0.597	4.11	−0.72
n-Pentane	298.2	0.215	11.62	5.535	5.20	0.619	5.54	0.09
n-Pentane	308.7	0.195	11.82	6.29	5.23	0.619	6.30	0.16
n-Hexane	298.2	0.2937	13.16	4.21	5.64	0.571	4.15	−1.43
n-Heptane	194.7	2.51	13.11	0.415	6.39	0.372	0.42	1.20
n-Heptane	250.3	0.702	13.93	1.52	5.88	0.540	1.49	−1.97
n-Heptane	273.2	0.525	14.31	2.08	5.77	0.577	2.05	−1.44
n-Heptane	298.2	0.386	14.75	3.12	5.89	0.563	3.07	−1.60
n-Heptane	305.7	0.36	14.89	3.22	5.73	0.601	3.20	−0.62
n-Heptane	329.7	0.282	15.38	4.21	5.68	0.625	4.23	0.48
n-Heptane	353.4	0.229	15.88	5.76	5.87	0.597	5.72	−0.69
n-Heptane	369	0.202	16.25	6.56	5.83	0.616	6.56	0.00
n-Octane	298.2	0.5082	16.44	2.25	6.06	0.574	2.22	−1.33
n-Nonane	298.2	0.6621	17.98	1.7	6.29	0.564	1.67	−1.76
n-Decane	298.2	0.8527	19.59	1.31	6.54	0.551	1.28	−2.29
n-Octadecane	323.2	2.34	33.49	0.46	8.06	0.507	0.45	−2.17
2-Methylbutane	298.2	0.219	11.73	5.3	5.16	0.632	5.33	0.57
Neopentane	298.2	0.228	12.33	4.86	5.17	0.648	4.92	1.23
3-Methylpentane	298.2	0.307	13.06	3.61	5.32	0.637	3.64	0.83
2,3-Dimethylbutane	298.2	0.361	13.12	3.5	5.69	0.558	3.44	−1.71
2,2-Dimethylbutane	298.2	0.351	13.37	3.41	5.59	0.588	3.38	−0.88
2-Methylpentane	298.2	0.295	13.26	3.98	5.51	0.602	3.96	−0.50
Bromoethane	303.2	0.348	7.57	3.96	4.47	0.627	3.98	0.51
Iodoethane	292.5	0.582	8.07	2.212	4.55	0.633	2.23	0.81
Iodobutane	292.5	0.876	11.39	1.347	5.17	0.617	1.35	0.22
Benzene	288.2	0.696	8.83	1.87	4.82	0.600	1.86	−0.53
Benzene	298.2	0.599	8.94	2.22	4.82	0.606	2.21	−0.45
Benzene	308.2	0.52	9.05	2.59	4.80	0.615	2.59	0.00
Benzene	318.2	0.465	9.17	3.04	4.87	0.603	3.03	−0.33
Benzene	328.2	0.415	9.29	3.5	4.89	0.603	3.48	−0.57
Benzene	338.2	0.375	9.41	4.03	4.95	0.594	4.00	−0.74
Benzene	373.2	0.261	9.85	6.15	4.97	0.608	6.13	−0.33
Benzene	423.2	0.171	10.70	10	5.02	0.628	10.05	0.50
Benzene	473.2	0.121	11.89	15	5.15	0.637	15.13	0.87
Benzene	523.2	0.082	14.74	23.9	5.67	0.610	23.86	−0.17
Benzene	561.7	0.056	25.65	32.7	6.98	0.582	32.33	−1.13
Cyclohexane	298.2	0.903	10.88	1.39	5.16	0.601	1.38	−0.72
Bromobenzene	298.2	1.124	10.50	1.12	5.08	0.606	1.12	0.00
Nitromethane	293.2	0.67	5.38	2.72	4.41	0.497	2.65	−2.57
Acetone	298.2	0.3075	7.40	4.835	4.63	0.576	4.77	−1.34
p-Dioxan	307.2	1	8.64	1.49	4.94	0.560	1.46	−2.01
Water	273.2	1.7921	1.80	1.1	2.75	0.636	1.11	0.91
Water	293.2	1.005	1.81	2.2	2.82	0.610	2.20	0.00
Water	298.2	0.8937	1.81	2.51	2.81	0.611	2.51	0.00
Water	313.2	0.656	1.82	3.5	2.78	0.625	3.51	0.29
Water	333.2	0.4688	1.83	5.3	2.82	0.614	5.30	0.00
Water	353.2	0.3565	1.85	7.5	2.86	0.603	7.47	−0.40

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Table 1. Continued

Liquid	T K	$\mu \times 10^3$ Pa·s	$V_M \times 10^2$ m^3/kmol	$D_e \times 10^9$ m^2/s	$d \times 10^{10}$ m	ϵ	$D_p \times 10^9$ m^2/s	Err %
Water	373.2	0.2838	1.88	9.7	2.84	0.615	9.70	0.00
Water	473.2	0.133	2.08	23	2.80	0.668	23.48	2.09
Water	573.2	0.0896	2.53	44	3.18	0.598	43.73	−0.61
Water	623.2	0.0728	3.12	61	3.60	0.529	59.60	−2.30
Water	648.2	0.047	5.72	76	4.28	0.567	74.81	−1.57
Ammonia	213	0.39	2.38	3.8	3.10	0.604	3.78	−0.53
Ammonia	287	0.15	2.76	12	3.17	0.635	12.09	0.75
Methanol	268.2	0.894	3.58	1.26	2.96	0.772	1.27	0.79
Methanol	278.2	0.747	4.29	1.55	3.22	0.754	1.59	2.58
Methanol	288.2	0.623	4.03	1.91	3.11	0.764	1.94	1.57
Methanol	298.2	0.547	4.07	2.32	3.18	0.752	2.38	2.59
Methanol	308.2	0.482	4.12	2.71	3.19	0.752	2.78	2.58
Methanol	313.2	0.456	4.14	2.89	3.19	0.754	2.96	2.42
Methanol	318.2	0.428	4.16	3.37	3.31	0.724	3.48	3.26
Methanol	328.2	0.378	4.22	3.88	3.31	0.728	4.01	3.35
Ethanol	280	1.56	5.73	0.618	3.39	0.786	0.61	−1.29
Ethanol	288.2	1.303	5.80	0.77	3.43	0.781	0.76	−1.30
Ethanol	298.2	1.078	5.87	1.01	3.53	0.763	1.03	1.98
Ethanol	308.2	0.895	5.93	1.3	3.61	0.750	1.33	2.31
Ethanol	318.2	0.751	6.00	1.66	3.70	0.734	1.71	3.01
Ethanol	328.2	0.637	6.07	2.06	3.76	0.724	2.13	3.40
Ethanol	338.2	0.545	6.15	2.61	3.88	0.700	2.69	3.07
n-Propanol	288.2	2.522	7.44	0.504	4.37	0.646	0.51	1.19
i-Propanol	288.2	2.859	7.62	0.474	4.57	0.606	0.47	−0.84
t-Butanol	308.2	2.575	9.61	0.497	4.82	0.632	0.50	0.60

many one-component systems and was built using figures provided by Dullien (1972). All cited positions were checked against sources and errors were corrected. The diameter d_p was calculated for reference purposes using Eq. 38 and the dimensionless free volume ϵ using Eq. 39.

The data presented in Table 1 allowed the evaluation of the values of the C_K^* parameter on the basis of Eq. 35. The relation between this quantity and dimensionless free volume ϵ is presented in Figure 1 for all systems. One can see that for tested liquids the parameter ϵ changes in the range from 0.372 until 0.786 and the C_K^* from 0.336 until 0.0186, respectively. The concept of the constant value of C_K^* is therefore not valid here.

The data points could be approximated by the following function plotted in Figure 1 as a continuous line

$$C_K^* = \frac{a}{\epsilon^b} - c \tag{41}$$

where a, b, and c are constants equal to, respectively, 0.05405, 2.062, and 0.07060.

Equation 40 with the evaluated values of the constants approaches zero when ϵ equals 0.878. Nearly the same value was obtained using Eq. 40. It means that the proposed dependence predicted changes of the C_K^* parameter up to the critical point, however, with the exclusion of that one. If $C_K^* = 0$, Eq. 35 stops to describe properly the physical situation.

Verification of Formula

The substitution of Eq. 41 into Eq. 35 and an assignment of the numerical values to the constants a, b, c, N, and k gives the following formula after simple rearrangements

$$D = 10^{-16}\left(\frac{6.307}{\epsilon^{2.062}} - 8.231\right)\frac{\epsilon}{(1-\epsilon)^{4/3}}\,\frac{T}{\mu V_M^{1/3}} \tag{42}$$

Similar procedure applied to Eq. 40 gives

$$\epsilon = 1 - 4.43 \cdot 10^{21}\left(\frac{\mu D}{T}\right)^{3/2} V_M^{1/2} \tag{43}$$

Equations 42 and 43 with two unknowns D and ϵ form a tool which allows to predict the self-diffusion coefficients in liquids. Further substitution of Eq. 43 into Eq. 42 is, of course,

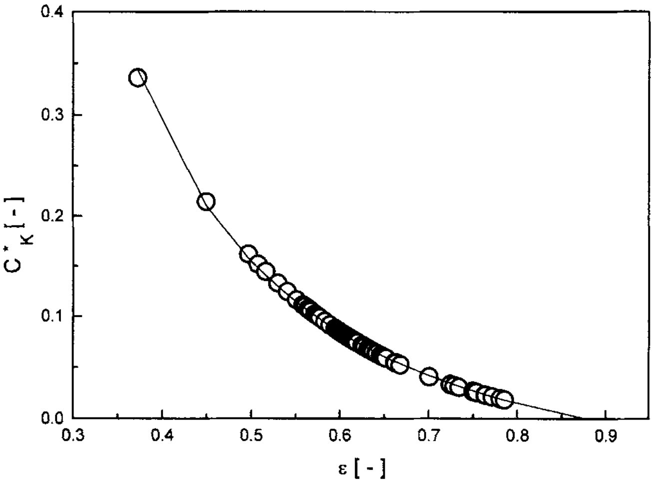

Figure 1. Dependence of the C_K^* parameter on the dimensionless free volume ϵ.

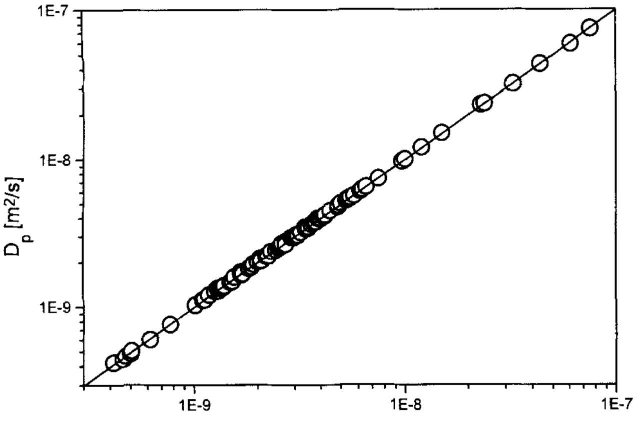

Figure 2. Predicted values of diffusion coefficients D_p calculated using the proposed model vs. those obtained experimentally D_e.

possible but it leads to the algebraically complicated dependence. Numerical solution of that set of equations seems to be more practical.

The values of the self-diffusion coefficients calculated using the proposed model are presented in Table 1 as D_p. The overall comparison between experimental values of the diffusion coefficients D_e and the predicted D_p for all substances is shown in Figure 2. The slope of the fitting straight line also plotted in Figure 2 was found to be equal to 0.99 with a standard error less than ±1%. The relative differences $(D_e - D_p)/D_e$ for individual data sets are placed in Table 1 also as an Err. One finds that only in few cases the Err values are maximally about 3% and generally within limits of the estimation of the presented experimental data.

For comparison, these individual differences (Err) are plotted in Figure 3 together with errors calculated when Eq. 8 is used for the prediction of the self-diffusion coefficients. One can find that this Eq. 8 is hardly usable and that in almost all cases the very significant improvement of an accuracy, even for lower alcohols (Dullien, 1972), can be noticed when the new model is applied.

The results of the prediction of self-diffusion coefficients using the Wilke-Chang correlation are presented separately in Figure 4 as the individual differences Err for 64 positions from Table 1. One can see that in this case also the new correlation compares very favorably.

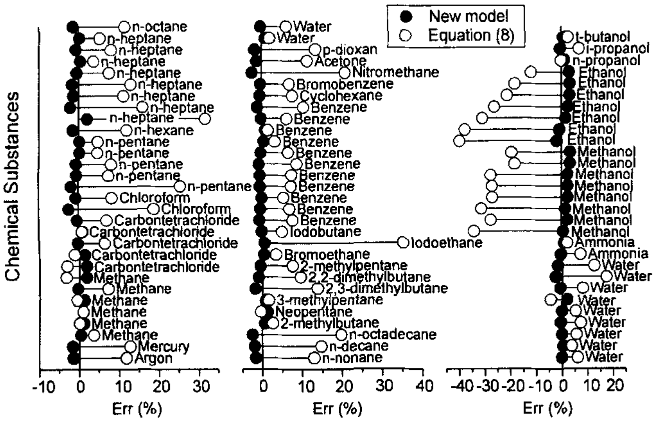

Figure 3. Relative differences Err $[(D_e-D_p)/D_e]$ calculated using proposed new model and Eq. 8.

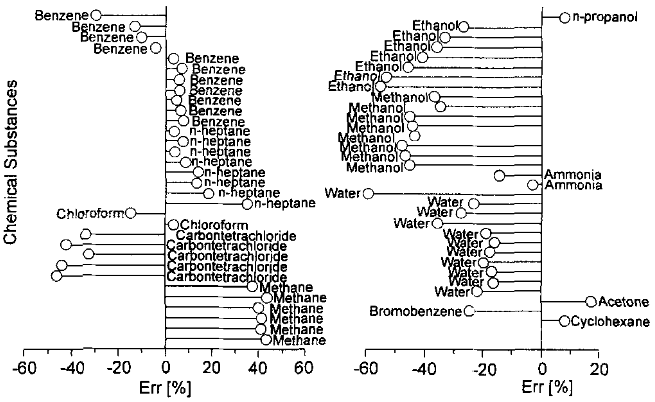

Figure 4. Relative differences Err $[(D_e-D_p)/D_e]$ calculated using the Wilke-Chang model.

The application of the Kozeny-Carman theory allowed to propose the accurate semiempirical correlation for the prediction of self-diffusion coefficients in liquids. The idea of a coupling of this model with a formula given by Eq. 38 proved to be the right approach from the point of view of the performed work. Moreover, to use this model one has to know only macroscopic parameters determining the diffusion process like temperature, viscosity, and molecular volume. This is very useful from an engineering point of view.

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