CORRELATION BETWEEN THE EQUATIONS OF TRANSFER COEFFICIENTS AND THE EQUATION OF STATE FOR LIQUIDS

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On the basis of test data on p, v, T, thermal conductivity, and dynamic viscosity of toluene and water, it is shown that the equations of transfer coefficients can be represented in a form analogous to the equation of state.

Several articles have been published recently [1, 2] where an attempt is made to formally correlate the equations of transfer coefficients with the equation of state for substances.

In this study the authors have found not only a formal correlation between the respective equations for the liquid phase but also a simple relation between their parameters. The analysis, the results of which are given here, has been applied to toluene and water as typical examples.

The equation

$$\frac{pv}{RT} = 1 + B\rho + H\rho^7 \qquad (1)\dagger$$

describes, within test accuracy [3,4], the properties of liquid toluene over the range of temperatures from 25 to 400°C and of saturation pressures p_s up to 500 bars.

If, according to [5], the relation

$$p + p_{\text{attract}} = p_{\text{therm}} + p_{\text{repulse}}$$

is represented on the basis of (1) as

$$p + B^*\rho^2 = RT\rho + H^*\rho^8,$$

then $B^*\rho^2$ and $H^*\rho^8$ will characterize respectively the forces of attraction and repulsion between molecules.

TABLE 1. Values of the Parameters B, cm^3/g and H $(cm^3/g)^7$ in Eqs. (2)-(4)

t, °C	Data for z			Data for η			Data for λ		
	$-B$	H	$-\frac{B}{H}\rho_s^6$	$-B$	H	$-\frac{B}{H}\rho_s^6$	$-B$	H	$-\frac{B}{H}\rho_s^6$
25	55414,12	134035,28	0,41343	1,8628	4,4993	0,41402	0,5827	1,4086	0,41367
50	14588,76	41757,50	0,34937	1,5658	4,4664	0,35057	0,5705	1,6295	0,35011
100	1700,27	6977,00	0,24370	1,3235	5,0000	0,24470	0,5136	2,1174	0,24256
150	308,57	1929,19	0,15995	1,0025	6,2561	0,16024	0,4562	2,8303	0,16118
200	69,026	718,77	0,09603	0,8044	8,3947	0,09582	0,3450	3,5784	0,09641
250	15,2396	315,9586	0,04823	0,5156	12,3580	0,04172	0,2112	4,6377	0,04554
275	6,0166	208,0024	0,02893	0,4141	15,6021	0,02654	—	—	—

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† Equation (1) resembles the special case of the equation of state for real gases in the virial form, including the second and the eighth virial coefficient.

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Further analysis has shown that the groups

$$K_{p,v,T}=\frac{\frac{pv}{RT}-1}{\rho}\ ;\quad K_z=\frac{\frac{z}{z_s'}-1}{\rho}\ ;\quad K_\lambda=\frac{\frac{\lambda}{\lambda_s'}-1}{\rho}\ \text{ and } K_\eta=\frac{\eta/\eta_s'-1}{\rho}$$

are linear functions of ρ^6 for every isotherm within a certain range of values of the state variables.

Accordingly, the following equations are valid for liquid toluene within the range of values of the state variables:

$$\frac{z}{z_s'}=1+B_z\rho+H_z\rho^7; \tag{2}$$

$$\frac{\lambda}{\lambda_s'}=1+B_\lambda\rho+H_\lambda\rho^7; \tag{3}$$

$$\frac{\eta}{\eta_s'}=1+B_\eta\rho+H_\eta\rho^7. \tag{4}$$

Parameters (B and H), (B_z and H_z), (B_λ and H_λ), and (B_η and H_η) in the equation of state, the compressibility, the thermal conductivity, and the dynamic viscosity have been determined for each isotherm from test data [3, 6, 7] and on the basis of the linearity between ρ^6 and $K_{p,v,T}$, K_z, K_λ, K_η:

$$K=B+H\rho^6 \tag{5}$$

by the method of least squares.

The thus determined numerical values of these parameters are shown in Table 1 for various temperatures.

It is to be noted that the equality

$$B\rho_s+H\rho_s^7=0,$$

must be satisifed according to (2), (3), (4) when $z = z_s'$, $\lambda = \lambda_s'$, and $\eta = \eta_s'$, i.e.,

$$-\left(\frac{B}{H}\right)_z=-\left(\frac{B}{H}\right)_\lambda=-\left(\frac{B}{H}\right)_\eta=\rho_s^6. \tag{6}$$

Therefore, the B/H ratios in the equations of compressibility, thermal conductivity, and dynamic viscosity for every isothermal are the same and equal to the density of saturated liquid raised to the sixth power (Table 1).

According to Table 1, the equality $(B/H)_z = (B/H)_\lambda = (B/H)_\eta$ is not satisfied exactly, probably on account of the 1-2% error in the test values for λ and η.

The values of B/H can be calculated most exactly from the highly accurate p, v, T test data [3].

In order to determine the ratio B/H with the aid of the equation of state (1), it is necessary to start with the condition

$$B\rho_0+H\rho_0^7=0, \tag{7}$$

TABLE 2. Values of the Parameters B and H in the Equation of State (1) and of Density p_0 for Toluene

t, °C	$-B$, cm^3/g	H, (cm^3/g)^7	$-\frac{B}{H}=\rho_0^6$	ρ_0, g/cm^3	$p=\rho_0 RT$, bar
25	10,3588	22,2557	0,46544	0,88033	236,86
50	8,6937	21,4730	0,40487	0,86011	250,82
75	7,3400	20,8358	0,35228	0,84039	264,03
100	6,2087	20,2720	0,30627	0,82102	276,47
125	5,3058	20,0269	0,26493	0,80141	287,95
150	4,5263	19,9311	0,22710	0,78109	298,27
175	3,8942	19,9365	0,19533	0,76172	308,05
200	3,3825	20,3101	0,16654	0,74174	316,71
225	2,9257	20,5955	0,14206	0,72235	324,73
250	2,5009	21,1886	0,11803	0,70038	330,65
275	2,2296	21,9993	0,10135	0,68282	337,77
300	1,9376	22,7788	0,08506	0,66316	343,00

TABLE 3. Values of Parameter $H_{p,v,T}$ $(cm^3/g)^7$ for Toluene at t = 25°C, Calculated According to Eq. (8)

p, bar	$K_{p,v,T}=\frac{\frac{pv}{RT}-1}{\rho}$	$\rho^6-\rho_0^6$	$H_{p,v,T}=\frac{K_{p,v,T}}{\rho^6-\rho_0^6}$	$\frac{H^*-H_{p,v,T}}{H^*}100$ %
8,700	—1,114389	—0,05014	22,2255	0,14
59,878	—0,856835	—0,03841	22,3076	0,23
106,12	—0,628184	—0,02821	22,2681	0,06
208,76	—0,132889	—0,00595	22,3343	0,35
298,45	0,287582	0,01288	22,3278	0,32
398,74	0,745606	0,03355	22,2237	0,14
496,51	1,181350	0,05306	22,2644	0,04

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* H = 22.2557 from Table 2.

obtained when pv/RT = 1:

$$-\left(\frac{B}{H}\right)_{p,v,T}=\rho_0^6, \tag{8}$$

where ρ_0 denotes the density of liquid toluene along every pv/RT = 1 isotherm.

The values of ρ_0 can be found either from compressibility as a function of density ($z_T = f(\rho)$) or from relation (8), if B and H are known from the p, v, T test data evaluated by the method of least squares. Values of ρ_0 based on formula (8) are given in Table 2.

Parameters B and H can also be calculated from the appropriate K groups according to (5), with (6) and (8) taken into consideration, namely

$$\left(\frac{K}{H}\right)_z=\left(\frac{K}{H}\right)_\lambda=\left(\frac{K}{H}\right)_\eta=\rho^6-\rho_s^6 \tag{9}$$

and

$$\left(\frac{K}{H}\right)_{p,v,T}=\rho^6-\rho_0^6. \tag{10}$$

Results of calculations according to formula (10) are shown in Table 3. Calculatings according to formula (9) will result in large errors, because the accuracy of λ, η measurements is worse than the accuracy of p, v, T measurements.

A simultaneous solution of (9) and (10) will yield the K/H ratio for the various thermophysical coefficients in terms of the most accurately determinable ratio $(K/H)_{p,v,T}$:

$$\left(\frac{K}{H}\right)_z=\left(\frac{K}{H}\right)_\lambda=\left(\frac{K}{H}\right)_\eta=\left(\frac{K}{H}\right)_{p,v,T}+(\rho_0^6-\rho_s^6). \tag{11}$$

The closeness of the agreement between K/H values obtained in various ways can be evaluated on the basis of data for toluene (at t = 50°C and p = 300 bars) (see Table 3).

The validity of the relations in the case of toluene has also been confirmed in the case of water. For water we use the values of λ and η from International Critical Tables [8] and our proposed equation of state [4]:

$$\frac{pv}{RT}=1+B\rho+E\rho^4, \tag{12}$$

valid within the range of temperatures from 0 to 350°C and of pressures p_s up to 1000 bars.

The density ρ_0 appears here to be a very important parameter, and knowing its value is useful also for relating the forces of attraction and repulsion between molecules.

TABLE 3

$(K/H)_z$	$(K/H)_\lambda$	$(K/H)_\eta$	$(K/H)_{p,v,T}$	$(\rho_0^6-\rho_s^6)$	$\left(\frac{K}{H}\right)_{p,v,T}+(\rho_0^6-\rho_s^6)$
0,06584	0,06553	0,06504	0,01044	0,05550	0,06594

Following a modification of (8), these relations for liquid toluene are

$$-\left(\frac{H^*\rho^8}{B^*\rho^2}\right)_{p,v,T} = (\rho/\rho_0)^6. \tag{13}$$

According to (13) we have these special cases:

$$\rho < \rho_0;\ (B^*\rho^2)_{p,v,T} > (H^*\rho^8),$$
$$\rho = \rho_0;\ (B^*\rho^2)_{p,v,T} = (H^*\rho^8)_{p,v,T}\ ,$$
$$\rho > \rho_0;\ (B^*\rho^2)_{p,v,T} < (H^*\rho^8)_{p,v,T}\ ,$$

i.e., during isothermal compression of liquid toluene the attraction force exceeds the repulsion force at densities below ρ_0, both forces are equal at density ρ_0, and the repulsion force exceeds the attraction force at densities above ρ_0.

It is interesting to note that the ratio between these two forces varies proportionally to the sixth power of the density ratio (ρ/ρ_0) in the case of toluene and proportionally to the third power of the density ratio according to the equation of state (12) for water:

$$-\left(\frac{E^*\rho^5}{B^*\rho^2}\right)_{p,v,T} = \left(\frac{\rho}{\rho_0}\right)^3. \tag{14}$$

Our studies have established [4] that the equation of state (1) is the same for five aromatic hydrogen carbons (benzene, toluene, o-xylene, m-xylene, and p-xylene).

On the basis of relation (13), therefore, one may conclude that the ratio of attraction force to repulsion force between molecules is the same for all these liquids at any given temperature and the same density ratio ρ/ρ_0, namely:

$$\left(\frac{B^*\rho^2}{H^*\rho^8}\right)^{\text{benzene}}_{p,v,T} = \left(\frac{B^*\rho^2}{H^*\rho^8}\right)^{\text{toluene}}_{p,v,T} = \left(\frac{B^*\rho^2}{H^*\rho^8}\right)^{\text{o-, m-, p-xylene}}_{p,v,T}.$$

As a consequence of this homomorphism of the equations of state for the liquid phase of normal water and heavy water [4], the following equality will be valid under the stipulated conditions:

$$\left(\frac{B^*\rho^2}{E^*\rho^5}\right)^{H_2O}_{p,v,T} = \left(\frac{B^*\rho^2}{E^*\rho^5}\right)^{D_2O}_{p,v,T}.$$

Thus, the equations of transfer coefficients (λ and η) for liquid toluene can be represented in a form analogous to the equation of state, with a simple relation existing between the parameters of both.

There is reason to believe that the laws established here for liquid toluene and water as typical examples will be valid for other liquids as well, but this must still be experimentally verified.

NOTATION

p	is the external pressure;
p_{attract}	is the attraction pressure;
p_{therm}	is the thermal pressure;
p_{repulse}	is the repulsion pressure;
v	is the specific volume;
ρ	is the density;
ρ_S	is the saturation density of a liquid;
ρ_0	is the density of a liquid when $pv/RT = 1$;
R	is the gas constant;
T	is the absolute temperature;
B, E, H	are the parameters of the temperature function;
z_S	is the compressibility;
λ	is the thermal conductivity;
η	is the dynamic viscosity;
z'_S, λ'_S, η'_S	are the compressibility, thermal conductivity, and dynamic viscosity at saturation.

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