Semiempirical Relations in Molecular Liquids. I. Molecular Structure, Melting Temperature, and Effective Hard Core Diameter of Molecules[1)]

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A simple method for the estimation of the effective hard core diameter of a molecule (at melting point), which is the only parameter in the application of the scaled particle theory to molecular liquids, is proposed. For a nearly spherical molecule, the effective hard core diameter a in Å can be given by

$$a = 1.072\, P^{2/5} T_{\mathrm{m}}^{-1/10},$$

where P is the parachor of the molecule in cgs unit and T_{m} is the melting temperature in K. The factor 1.072 is equal to that predicted by the scaled particle theory.

The statistical mechanics of simple liquids has recently been developed and equilibrium properties can be calculated fairly accurately.[2)] On the other hand, statistical mechanical theories for molecular liquids remain undeveloped. Insight into the relationship between molecular structure and physical properties of molecular liquid is desirable.

The significant structure theory[3)] can predict physical properties of molecular liquids semiempirically, but its theoretical basis seems to be obscure. Another semiempirical theory so far developed is the scaled particle theory (SPT),[4)] which has a sound physical basis for a nearly spherical molecule. The SPT was originally developed[5)] to treat systems of hard spheres. However, it has been shown[6)] that, if the effective hard core diameters of the molecules are properly chosen, molecular liquids can be described by the SPT fairly well. So far, surface tension,[6,7)] isothermal compressibility,[7,8)] thermal expansivity,[8)] Henry's constant,[6)] heat capacity,[8)] and heat of vaporization[9)] have been calculated or correlated with each other by the SPT. The only parameter used in the SPT is the effective hard core diameter a of the molecule. If we know a and the density of the liquid, then we can calculate surface tension, isothermal compressibility, *etc.* The value of a can be estimated from density with the aid of information on the molecular structure.[4)] However, measurement of density at temperatures other than room temperature is not very easy.

In this paper we propose a method for estimating the effective hard core diameter of molecules at melting point from the knowledge of the molecular structure and the approximate value of the melting temperature which can be easily measured. This paper gives a simple method for estimation of $\mathrm{d}a/\mathrm{d}T$, where T is temperature.

Theory

Outline of the Scaled Particle Theory. The semiphenomenological version of the SPT[4,6)] can be summarized as follows. The chance p_0 that the spherical cell of radius r is devoid of molecular centers satisfies the relation

$$\mathrm{d}\ln p_0(r)/\mathrm{d}r = -4\pi r^2 \rho G(r), \tag{1}$$

where ρ is the number density. $G(r)$ is so defined that $\rho G(r)$ measures the concentration of molecular centers just outside the spherical cell. According to fluctuation theory, we have

$$p_0(r) \propto \exp\left[-W(r)/kT\right], \tag{2}$$

where W is the reversible work required to produce a spherical hole of radius r. By thermodynamic consideration we have

$$\mathrm{d}W = p\mathrm{d}V + \sigma \mathrm{d}A, \tag{3}$$

where p is the pressure, σ the surface tension which has the form $\sigma=\sigma_0(1—2\delta/r)$, V the volume of the hole, and A the surface area of the hole. Using Eqs. (1), (2) and (3), we obtain

$$G(r) = \frac{p}{\rho kT} + \frac{\sigma}{\rho kT}\frac{\mathrm{d}A}{\mathrm{d}V}. \tag{4}$$

On the other hand, we know $G(r)$ exactly for $r \leq a/2$:[4)]

$$G(r) = 1/(1-4\pi\rho r^3/3) \tag{5}$$

Equating G, $\mathrm{d}G/\mathrm{d}r$, and $G'' \equiv \mathrm{d}^2G/\mathrm{d}r^2$ calculated from both Eqs. (4) and (5) at $r=a/2$, we get p, σ_0, and δ as functions of $y=\pi\rho a^3/6$.

Some Remarks on the Application of the SPT to Molecular Liquids. Since it is known that G'' is not continuous at $r=a/2$, it is desirable not to use G'' in order to obtain p, σ_0 and δ. If G'' is not used, then not all the three quantities, p, σ_0, and δ, can be obtained. However, we can obtain σ_0 and δ as functions of y and p. For σ_0 we have

$$2\pi\sigma_0 a^2/3kT = 2y(1-y) + 3y^2/(1-y^2) - 2py. \tag{6}$$

Equation (1) is exact even if the particle has no hard core. The hard core assumption is used in Eq. (5), but the equation also holds in the case of the particle exerting attractive forces besides hard core repulsion. This implies that we can choose the so-called augmented van der Waals equation of state[10)] for the pressure p in Eq. (6), *i.e.*, attractive forces affect σ_0 and δ only through p.

If the molecule has a sufficiently hard core, then Eq. (5) is a good approximation, so that the SPT can be used for the case of molecular liquids with nearly spherical repulsion core. We can therefore use the observed pressure in Eq. (6). Then the last term on the right-hand side of Eq. (6) is negligible at higher densities. Consequently, surface tension scarcely depends on the details of van der Waals attractive forces at higher densities.

Basic Relation. With observed data on σ_0, ρ, and T, the quantity y can be determined from Eq. (6) with py discarded, *i.e.*,

$$\sigma_0 T^{-1}\rho^{-2/3} = 4.28 \times 10^{-17} y^{1/3}(2+y)/(1-y)^2, \tag{7}$$

Table 1. Table of the function $s(y)$ defined by Eq. (9)

y	$s(y)$
0.30	0.985
0.40	1.037
0.50	1.065
0.52	1.068
0.54	1.070
0.56	1.071
0.58	1.072
0.60	1.071
0.62	1.070

where σ_0 is in dyn/cm, T in K, and ρ in cm^{-3}. The effective hard core diameter obtained from Eq. (7) is a slightly decreasing function of temperature. Dependence of a on temperature has been estimated by Mayer.[11] However, since the data on gas viscosity are needed, his method is not useful.

Surface tension can be calculated semiempirically from the parachor P and the density by

$$P = \pi N_A \sigma_0^{1/4} a^3/6y, \tag{8}$$

where N_A is the Avogadro number. Eliminating σ_0 from Eqs. (7) and (8), we obtain

$$s(y) \equiv aP^{-2/5}T^{1/10} = 1.65y^{1/3}[(1-y)^2/y^{1/3}(2+y)]^{1/10}, \tag{9}$$

where P is in cgs unit and a in Å.

As can be seen from Table 1, $s(y)$ depends on y slightly. The function $s(y)$ is nearly constant when y is about 0.55. It can be shown that for many organic compounds the values of y at the melting point fall in the range 0.5—0.6. Thus we expect that the equation

$$aP^{-2/5}T^{1/10} = C, \tag{10}$$

where C is a constant, holds fairly accurately at melting point.

Validity of the Relation (10)

Validity of the relation (10) is demonstrated in Figs. 1—4. The effective hard core diameter a is calculated from surface tension data by means of Eq. (7) and extrapolated linearly to the melting point. Data are taken from Refs. 12—14, in which the values of calculated parachor are also cited. The linear relation between a and T is assumed to a first approximation. The lines in Figs. 1—4 denote Eq. (10) with C=1.072, the value being consistent with that in Table 1. It can be concluded from Figs. 1—4 that Eq. (10) holds fairly accurately when molecules are nearly spherical.

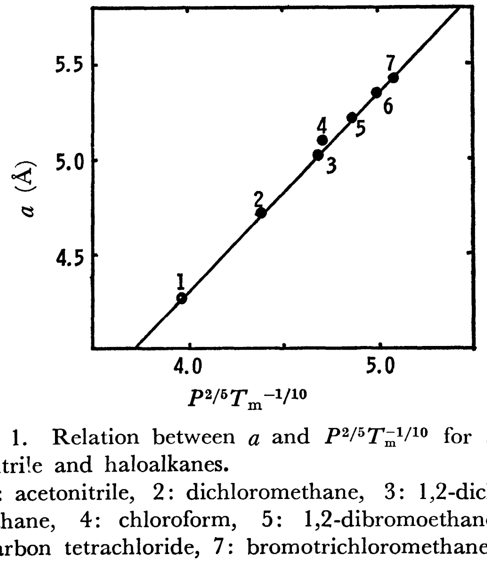

Fig. 1. Relation between a and $P^{2/5}T_m^{-1/10}$ for acetonitrile and haloalkanes.
1: acetonitrile, 2: dichloromethane, 3: 1,2-dichloroethane, 4: chloroform, 5: 1,2-dibromoethane, 6: carbon tetrachloride, 7: bromotrichloromethane.

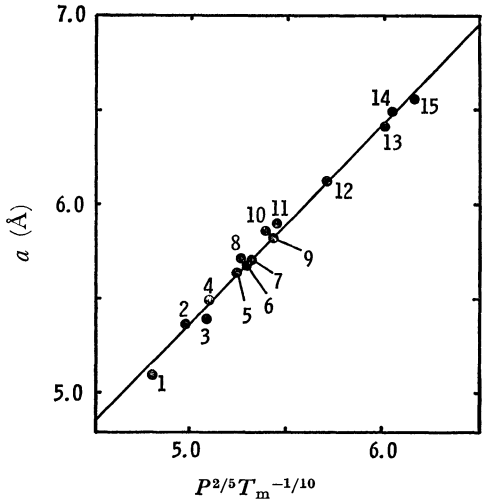

Fig. 2. Relation between a and $P^{2/5}T_m^{-1/10}$ for benzene, cyclohexane, and monosubstituted benzenes.
1: benzene, 2: fluorobenzene, 3: cyclohexane, 4: aniline, 5: chlorobenzene, 6: thiophenol, 7: bromobenzene, 8: nitrobenzene, 9: trifluoromethylbenzene, 10: toluene, 11: stylene, 12: ethylbenzene, 13: *n*-propylbenzene, 14: isopropylbenzene, 15: *t*-butylbenzene.

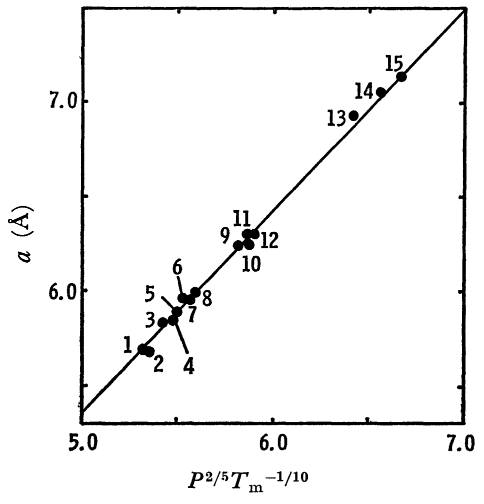

Fig. 3. Relation between a and $P^{2/5}T_m^{-1/10}$ for di- and tri- substituted benzenes.
1: *o*-chlorobenzaldehyde, 2: *p*-dichlorobenzene, 3: *p*-xylene, 4: *o*-dichlorobenzene, 5: *m*-dichlorobenzene, 6: *o*-xylene, 7: *p*-chloroacetophenone, 8: *m*-xylene, 9: 1,2,3-trimethylbenzene, 10: 1,3,5-trimethylbenzene, 11: 1,2,4-trimethylbenzene, 12: *o*-ethylnitrobenzene, 13: *p*-*t*-butylmethylbenzene, 14: *p*-diisopropylbenzene, 15: *o*-diisopropylbenzene.

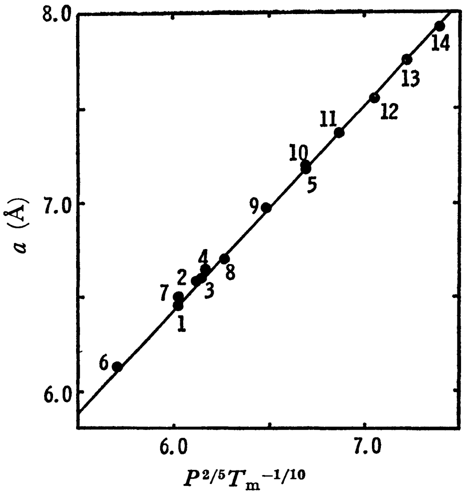

Fig. 4. Relation between a and $P^{2/5}T_m^{-1/10}$ for *n*-alkylbenzenes, naphthalenes, *etc.*
1: 1-methylnaphthalene, 2: *trans*-decalin, 3: 5-methyl-1,2,3,4-tetrahydronaphthalene, 4: *cis*-decalin, 5: 2-butylnaphthalene, 6: ethylbenzene, 7: *n*-propylbenzene, 8: *n*-butylbenzene, 9: *n*-pentylbenzene, 10: *n*-hexylbenzene, 11: *n*-heptylbenzene, 12: *n*-octylbenzene, 13: *n*-nonylbenzene, 14: *n*-decylbenzene.

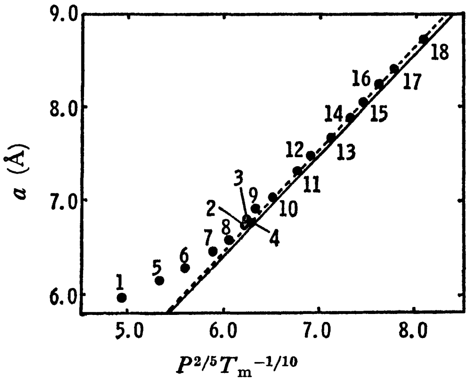

Fig. 5. Relation between a and $P^{2/5}T_m^{-1/10}$ for ethyl ether and alkanes.
1: ethyl ether, 2: 2-methylheptane, 3: 2,2,4-trimethylheptane, 4: 2-methyl-3-ethylpentane, 5: *n*-pentane, 6: *n*-hexane, 7: *n*-heptane, 8: *n*-octane, 9: *n*-nonane, 10: *n*-decane, 11: *n*-undecane, 12: *n*-dodecane, 13: *n*-tridecane, 14: *n*-tetradecane, 15: *n*-pentadecane, 16: *n*-hexadecane, 17: *n*-heptadecane, 18: *n*-nonadecane.

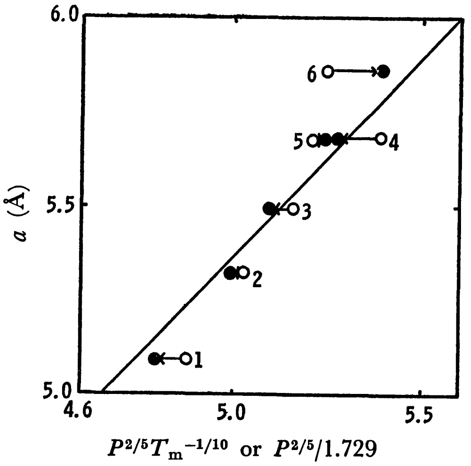

Fig. 6. Effect of $T_m^{-1/10}$ on the linear relation (10).
●: $P^{2/5}T_m^{-1/10}$, ○: $P^{2/5}/1.729$
1: benzene, 2: carbon tetrachloride, 3: aniline, 4: nitrobenzene, 5: chlorobenzene, 6: toluene.

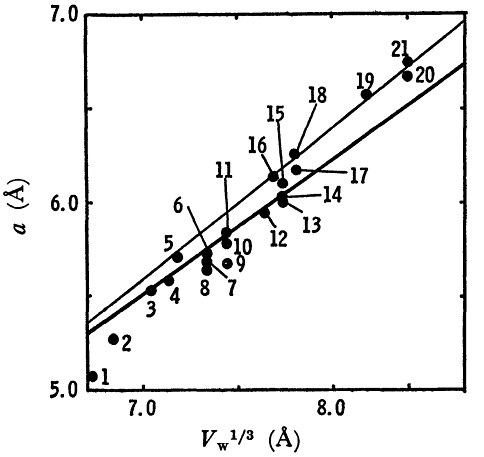

Fig. 7. Linear relation between a and $V_w^{-1/3}$.
——: $a=0.80\,V_w^{-1/3}$, ——: $a=0.79\,V_w^{-1/3}$
1: benzene, 2: fluorobenzene, 3: chlorobenzene, 4: bromobenzene, 5: toluene, 6: *m*-dichlorobenzene, 7: *o*-dichlorobenzene, 8: *p*-dichlorobenzene, 9: *p*-xylene, 10: *o*-xylene, 11: *m*-xylene, 12: 1,2-dichloro-4-methylbenzene, 13: 1,2,3-trimethylbenzene, 14: 1,3,5-trimethylbenzene, 16: isopropylbenzene, 17: 1-methylnaphthalene, 18: *t*-butylbenzene, 19: *p*-*t*-butylmethylbenzene, 20: *p*-diisopropylbenzene, 21: *o*-diisopropylbenzene.

Figure 5 shows that the relation (10) holds also for the case of non-spherical molecules. Normal alkanes asymptotically satisfy Eq. (10) with $C=1.080$, but this value cannot be explained in terms of the SPT (Table 1).

Discussion

For many organic liquids the factor $T^{-1/10}$ at melting point is *ca.* 0.6. Hence the main factor in Eq. (10) is $P^{2/5}$. Although $a \propto P^{2/5}$ holds approximately, the factor $T^{-1/10}$ markedly improves the approximate relation as shown in Fig. 6. Thus the factor $T^{-1/10}$ is indispensable for making C in Eq. (10) constant.

In the application of the SPT to molecular liquids the parameter a is considered to be the effective hard core diameter of the molecule. Thus if the physical picture of the SPT is correct, then a should be correlated with the actual dimension of a molecule. In the case of simple liquids, a and the distance where the repulsive potential is zero is almost the same.[5] In the case of molecular liquids, it is difficult to define or determine the dimension of complex molecules. For the sake of convenience, we choose, as a measure of actual dimension of a molecule, the cubic root of the van der Waals volume V_w estimated and tabulated by Bondi.[15] A roughly linear relation between a at melting point and $V^{1/3}$ is shown in Fig. 7. The physical picture of the

SPT is correct at least in the case of liquids consisting of nearly spherical molecules.

The value of a at room temperature can be calculated from the density at room temperature which can be measured very easily. The value of a at melting point can be estimated if the melting point is known. A rough measurement of the melting point is also very easy and $\mathrm{d}a/\mathrm{d}T$ can thus be estimated. We can therefore estimate a at desired temperature from density at room temperature, molecular structure and melting point. The $\mathrm{d}a/\mathrm{d}T$ estimated by the method mentioned above is rather large.[16] Hence the quantity should not be considered to represent the softness of the intermolecular repulsive force quantitatively but should be treated as a mere parameter for better applications of the SPT to molecular liquids.

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References

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