Statistical Thermodynamic Study of Polar Organic Liquids

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A statistical thermodynamic study of polar organic liquids has been worked out on the basis of the liquid model as an assembly of particles immersed in a uniform background potential, which was proposed in the preceding paper (*Bull. Chem. Soc. Jpn.*, **63**, 307 (1990). The liquid model is regarded as a kind of mean field approximation. Calculations of thermodynamic functions of eight polar liquids (acetone, 2-butanone, dimethyl sulfoxide, chlorobenzene, bromobenzene, benzonitrile, nitrobenzene, and aniline) have been performed. The results show that the theory is effectively applicable to four polar liquids (acetone, 2-butanone, dimethyl sulfoxide, and nitrobenzene) as well as to nonpolar ones. However, for other four liquids (chlorobenzene, bromobenzene, benzonitrile, and aniline) some deviations of calculated values from experimental data have been found, which are supposed to occur from some restriction of free rotation of molecules in these liquids. Detailed considerations have been given on this subject.

Statistical thermodynamic calculations for nonpolar organic liquids have been reported recently,[1] and the liquid model which is described as an ensemble of hard spheres immersed in a uniform background potential resulting from attractive forces between molecules has turned out to be adequate and effective for nonpolar liquids. Therefore, we have undertaken here the computation of statistical thermodynamic functions for eight polar organic compounds (acetone, 2-butanone, dimethyl sulfoxide, chlorobenzene, bromobenzene, benzonitrile, nitrobenzene, and aniline) to elucidate the applicability of the liquid model further and to have new insight into polar organic liquids.

Theoretical

The Basic Liquid Model. As shown in the preceding paper,[1] a liquid is regarded as an assembly of particles immersed in the uniform background potential. The uniform background potential comes from the overall effect of the actions of the attractive forces between molecules. In the model, which is a kind of mean field approximation, a molecule in the liquid is regarded as a free rotor and, with respect to vibrational motions, intramolecular modes only are taken into consideration.

The Partition Function and Thermodynamic Functions. The total partition function Z for the model used is expressed as a product

$$Z = Q_{\text{trans.}}\, Q_{\text{rot.}}\, Q_{\text{vib.}}\, Q_{\text{BG}} \tag{1}$$

in terms of the translational, rotational, vibrational and background potential contribution, respectively. The theoretical scheme, and notations used, are quite identical to that in the preceding paper,[1] and only the equations required for the following calculations are given here. Its details are described in the previous papers.[1-4]

Concerning the translational partition function $Q_{\text{trans.}}$, following expressions[2-4] are given in the combined form with the background potential factor Q_{BG}.

$$Q_{\text{trans.}} \cdot Q_{\text{BG}} = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} efv\right]^N \exp(-\langle V_N\rangle_{\text{av.}}/kT), \tag{2}$$

where v is the volume for a molecule $(=V/N)$ and $-\langle V_N\rangle_{\text{av.}}$ is the uniform background potential. The effective free volume fraction f is derived from the volume fraction ξ of hard sphere molecules in the liquid.

$$f \equiv (1-\xi)\exp\left[-\left(\frac{3\,\xi(2-\xi)}{2(1-\xi)^2}\right)\right], \tag{3}$$

To calculate ξ, the following expression is used.

$$\frac{1+\xi+\xi^2}{(1-\xi)^3} = \frac{a_{\text{ii}}/V}{RT} \tag{4}$$

The term a_{ii}/V in Eq. 4 corresponds to the uniform background potential $-\langle V_N\rangle_{\text{av.}}$

The rotational partition function $Q_{\text{rot.}}$ and the vibrational partition function $Q_{\text{vib.}}$ are expressed as

$$Q_{\text{rot.}} = \left[\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}(I_A I_B I_C)^{1/2}\right]^N \tag{5}$$

$$Q_{\text{vib.}} = \left[\prod_{j=1}^{r}\left\{\frac{\exp(h\nu_j/2kT)}{1-\exp(-h\nu_j/kT)}\right\}\right]^N \tag{6}$$

where r is the number of intramolecular vibrational modes.

Numerical Computations

Procedure of Computations. As described in the preceding paper,[1] the energy parameter a_{ii} is determined through Eq. 7 from the heat of vaporization ΔH_{vap} and V.

$$a_{\text{ii}} = V(\Delta H_{\text{vap}} - RT), \tag{7}$$

Then, ξ is determined by Eq. 4 and a is

$$a = (6\xi N/\pi V)^{1/3}. \tag{8}$$

Fundamental parameters a_{ii} and a including calculated values of ξ at 25 °C are shown in Table 1 together with the dipole moment μ, the density d, ΔH_{vap} and V.

Table 1. Fundamental Energy Parameters ΔH_{vap}, V, Density d, a_{ii}, Calculated Values of ξ, a and Dipole Moment μ for Polar Compounds (25 °C)

	ΔH_{vap}	V	d	a_{ii}	ξ	a	μ
	kJ mol^{-1}	cm^3 mol^{-1}	g cm^{-3}	kJ cm^3 mol^{-2}		Å	Debye[a]
$(CH_3)_2CO$	30.96[b]	73.99	0.7849[c]	2107	0.4717	4.80	2.90[d]
$CH_3COC_2H_5$	34.75[e]	90.17	0.7997[f]	2910	0.4897	5.19	2.76[g]
$(CH_3)_2SO$	52.89[h]	71.32	1.096[i]	3595	0.5500	4.99	4.3[j]
C_6H_5Cl	40.96[k]	102.2	1.101[c]	3933	0.5143	5.50	1.782[d]
C_6H_5Br	44.43[l]	105.5	1.488[m]	4426	0.5259	5.60	1.73[d]
C_6H_5CN	55.47[g]	103.0	1.001[c]	5459	0.5564	5.66	4.14[d]
$C_6H_5NO_2$	55.00[n]	102.8	1.198[c,o]	5399	0.5553	5.66	4.21[d]
$C_6H_5NH_2$	55.75[p]	91.54	1.017[f]	4876	0.5571	5.45	1.53[d]

a) Debye=3.3356×10^{-30} C m. b) B. D. Smith and R. Srivastava, "Thermodynamic Data for Pure Compounds. Part A. Hydrocarbons and Ketones," Elsevier, Amsterdam (1986), p. 264. c) J. Timmermans, "Physico-chemical Constants of Pure Compounds," Elsevier, Amsterdam (1950). d) "Kagaku-Binran Kiso-Hen II," rev. 3rd ed, ed by Chem. Soc. Jpn., Maruzen, Tokyo (1984), pp. 720—722. e) J. K. Nickerson, K. A. Kobe, and J. J. Mcketta, *J. Phys. Chem.*,**65**, 1037 (1961). f) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," McGraw-Hill, New York (1926), Vol. III, p. 27 ff. R. W. Gallant, *Hydrocarbon Processing,* **47**(8), 127 (1968). g) J. A. Riddick and W. B. Bunger, "Organic Solvents: Physical Properties and Methods of Purification," 3rd ed, Wiley Interscience, New York (1970). h) L. Clever and E. F. Westrum, *J. Phys. Chem.*, **74**, 1309 (1970). i) J. F. Casteel and P. G. Sears, *J. Chem. Eng. Data,* **19**, 196 (1974). j) D. Martin, A. Weise and H. J. Niclas, *Angew. Chem. Int. Ed. Engl.* **6**, 318 (1967). k) W. J. Jones and S. T. Bowden, *Phyl. Mag.*, **37**, 480 (1946). l) D. R. Stull, E. F. Westrum Jr., and G. C. Sinke "The Chemical Thermodynamics of Organic Compounds," John Wiley and Sons, New York (1969). m) J. Meyer and B. Mylius, *Z. Phys. Chem.*, **95**, 349 (1920). n) K. M. Watson, *Ind. Eng. Chem.*, **23**, 360 (1931). o) G. Palmer, *Ind. Eng.* **40**, 89 (1948). p) W. E. Hatton, D. L. Hildebrand, G. C. Sinke, and D. R. Stull, *J. Chem. Eng. Data,* **7**(2), 229 (1962).

Table 2. Molecular Parameters I_{A}, I_{B}, I_{C}, σ

	I_{A}	I_{B}	I_{C}	σ
	10^{-40} g cm^2	10^{-40} g cm^2	10^{-40} g cm^2	
$(CH_3)_2CO$[a]	82.55	98.54	170.89	2
$CH_3COC_2H_5$[a]	$I_{\mathrm{A}}\cdot I_{\mathrm{B}}\cdot I_{\mathrm{C}}=5961.2\times10^{-37}$ g cm^2			1
$(CH_3)_2SO$[a]	$I_{\mathrm{A}}\cdot I_{\mathrm{B}}\cdot I_{\mathrm{C}}=2880.0\times10^{-37}$ g cm^2			1
C_6H_5Cl[a]	147.9	535.8	683.8	2
C_6H_5Br[a]	148.0	847.7	996.0	2
C_6H_5CN[a]	148.3	542.5	691.0	2
$C_6H_5NO_2$[a]	209.2	653.6	861.2	2
$C_6H_5NH_2$[b]	149.5	323.6	472.2	1

a) "Landolt-Börnstein Tabellen," Neue Serie, II Band, 4 Teil, SS. 22 ff., Springer-Verlag, Berlin (1961). b) Moment of inertia was calculated from molecular structural data ("Landolt-Börnstein Tabellen," Neue Serie, II Band, 7 Teil, S. 334, Springer-Verlag, Berlin (1961)).

Molecular parameters I_{A}, I_{B}, I_{C} and σ required to calculate thermodynamic functions are shown in Table 2. The intramolecular vibrational frequencies have been taken from various sources.[5—10]

Free energy F and entropy S are expressed as follows:

$$F_{\mathrm{trans.}}=-RT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}efv\right]-\langle V_{\mathrm{N}}\rangle_{\mathrm{av.}}, \tag{9}$$

$$F_{\mathrm{rot.}}=-RT\ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2kT}{h^2}\right)^{3/2}(I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}})^{1/2}\right] \tag{10}$$

$$F_{\mathrm{vib.}}=-RT\ln\left[\prod_{j=1}^{r}\left\{\frac{1}{1-\exp(-h\nu_j/kT)}\right\}\right], \tag{11}$$

$$S_{\mathrm{trans.}}=R\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}efv\right]+\frac{3}{2}R, \tag{12}$$

$$S_{\mathrm{rot.}}=R\ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2kT}{h^2}\right)^{3/2}(I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}})^{1/2}\right], \tag{13}$$

$$S_{\mathrm{vib.}}= R\sum_{j=1}^{r}\left[\frac{(h\nu_j/kT)\exp(-h\nu_j/kT)}{1-\exp(h\nu_j/kT)}-\ln\{1-\exp(-h\nu_j/kT)\}\right], \tag{14}$$

where zero-point vibrational energy is subtracted in Eq. 11.

Calculated Results. Computations of thermodynamic functions, F, U, and S have been carried out according to the quite identical procedure as described in the preceding paper[1] and the results are given through Fig. 1 to Fig. 8 and through Table 3 to Table 10.

Discussion

Liquid Structural Feature of Polar Compounds. According to the development of the liquid state theory in recent years,[11] ξ is well-known as the most important quantity which primarily governs the thermodynamic properties of fluids. For normal fluids treated in the preceding paper[1] its magnitudes are nearly 0.47—0.48, as shown formerly by the computer simulation studies by Hoover and Ree.[12]

As seen in Table 1, the magnitudes of ξ are larger than 0.51 except for the cases of acetone and 2-butanone. There is seen a pararellism between ΔH_{vap} or a_{ii}/V and ξ, which is considered to be natural.

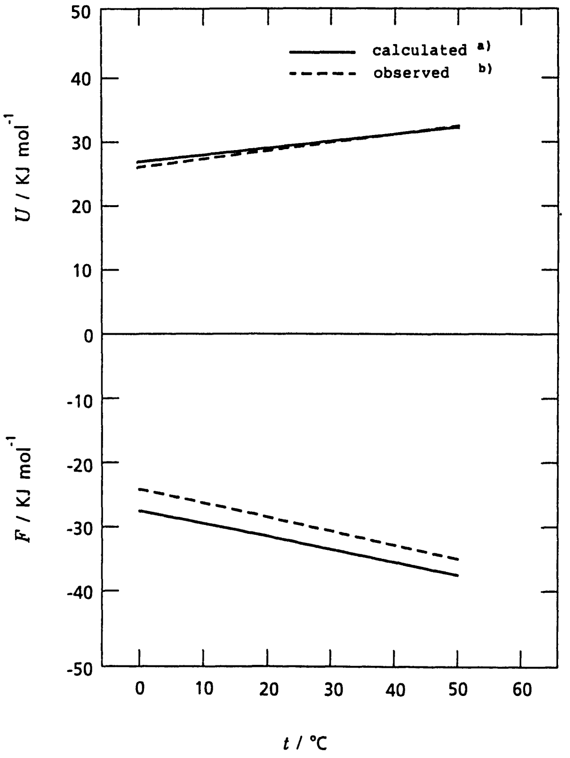

Fig. 1. Temperature dependence of U and F for liquid $(CH_3)_2CO$.
a) 44.39 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) R.C. Wilhoit, J. Chao, and K.R. Hall, *J. Phys. Chem. Ref. Data,* **14**, 1 (1985).

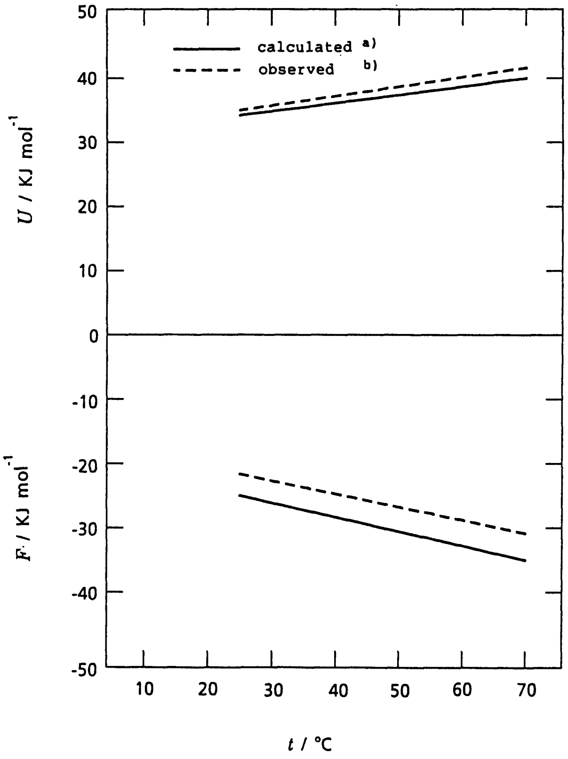

Fig. 3. Temperature dependence of U and F for liquid $(CH_3)_2SO$.
a) 70.12 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) H.L. Clever and E.F. Westrum, Jr., *J. Phys. Chem.,* **74**, 1309 (1970).

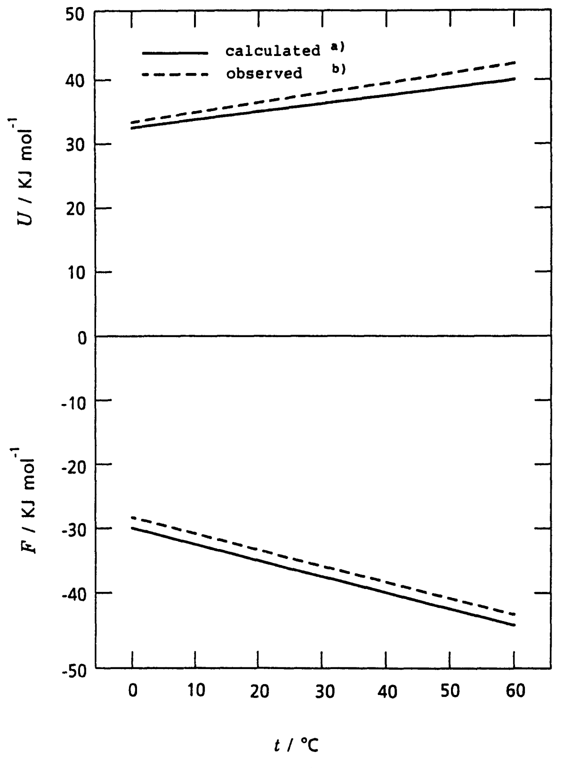

Fig. 2. Temperature dependence of U and F for liquid $CH_3COC_2H_5$.
a) 50.84 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) G.C. Sinke and F.L. Oetting, *J. Phys. Chem.,* **68**, 1354 (1964).

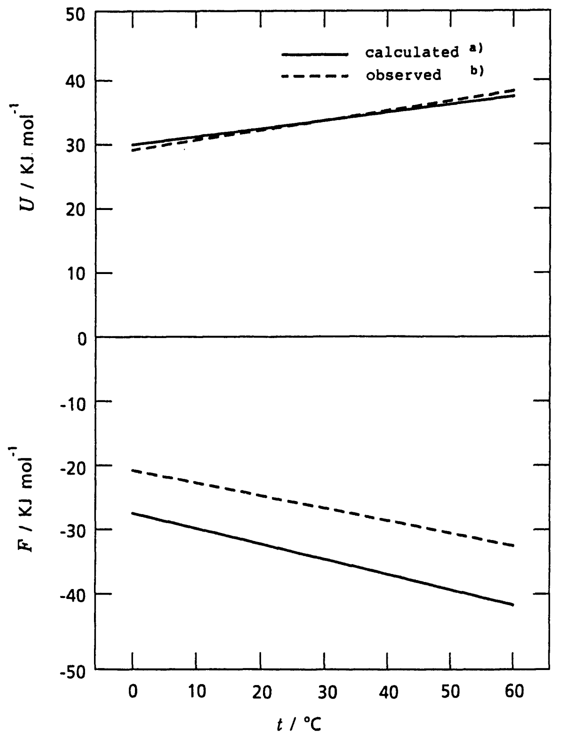

Fig. 4. Temperature dependence of U and F for liquid C_6H_5Cl.
a) 57.24 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) D.R. Stull, *J. Am. Chem. Soc.,* **59**, 2726 (1937). C.L. Yaws and J.L. Liang, *Chem. Eng.,* **82**, Oct. 27, 119 (1975).

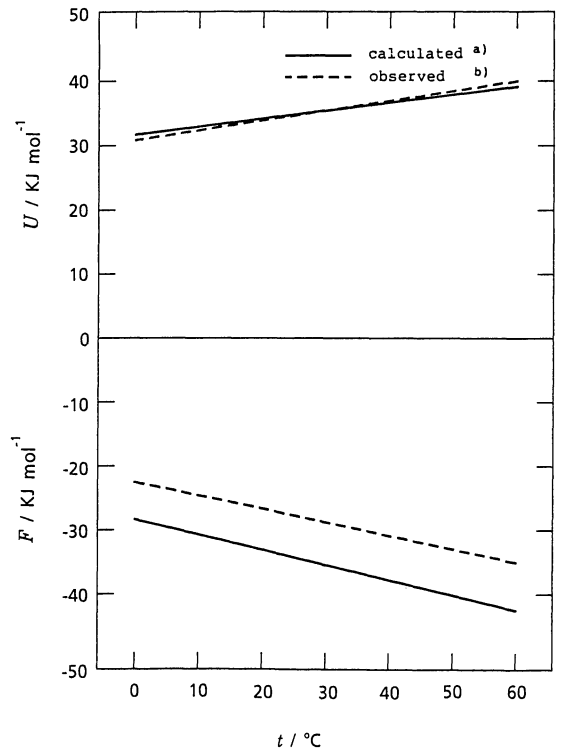

Fig. 5. Temperature dependence of U and F for liquid C_6H_5Br.
a) 61.38 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) See footnote b) of Fig. 4.

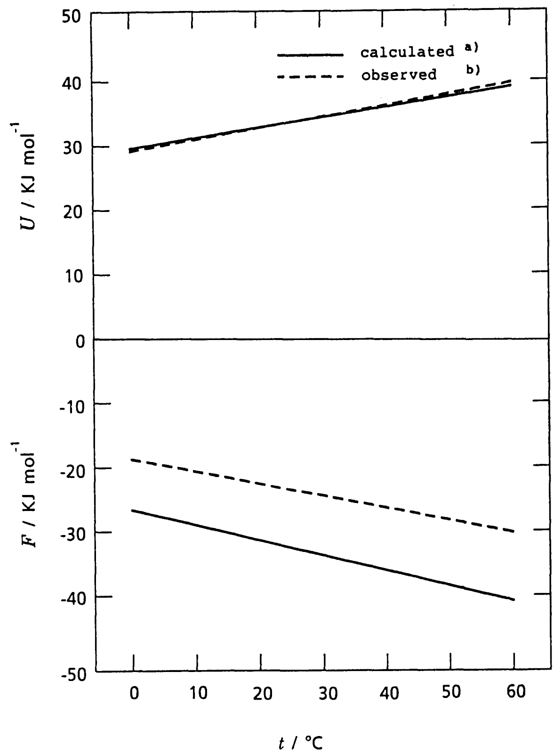

Fig. 6. Temperature dependence of U and F for liquid C_6H_5CN.
a) 70.12 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) Thermodynamic functions have been calculated from specific heat data of solid, heat of fusion (data from Design Institute for Physical Property Data, issued by American Institute of Chem. Engineers, New York (1989)) and specific heat data of liquid (A.A. Mir aliev, Sh. G. Shakhmuradov, and S.O. Guseinov, *Izv. Vyssh. Uchebn. Zaved., Neft Gaz,* **30**(4), 55 (1987)).

Especially for the cases of dimethyl sulfoxide, benzonitrile, nitrobenzene and aniline, where μ is larger than 4 Debye (Debye=3.3356×10^{-30} C m) with the exception of aniline, the magnitudes of ξ are seen to amount to 0.55. This gives a clear account of strong compactness of molecular packing in these strong polar liquids in general.

Behaviors of Thermodynamic Functions (Acetone, 2-Butanone, Dimethyl Sulfoxide and Nitrobenzene). From Figs. 1, 2, 3, and 7, Tables 3, 4, 5, and 9, it can be seen that calculated values of F, U and S are rather in good agreement for acetone, 2-butanone, dimethyl sulfoxide and nitrobenzene in spite of the strong polarities of these compounds. The deviations of S_{calc} from S_{obs} are under 6% for these polar liquids. Especially for dimethyl sulfoxide and nitrobenzene, the calculated values are fundamentally in good agreement with the observed ones in spite of their very strong polarity. This means that the liquid model of free rotor picture immersed in uniform background potential is applicable enough to such strong polar compounds.

Effectiveness of the Generalized van der Waals Picture for Liquids. As shown in the preceding paragraph the present liquid model has turned out to be useful to represent thermodynamic properties of strong polar fluids, dimethyl sulfoxide and nitrobenzene as well as to be so for nonpolar liquids.[1)] The present model is a kind of the mean field approximation and also a form of the generalized van der Waals picture. It is the idea that the harsh repulsive forces, the hard core interactions, dominate the liquid structure for dense fluids where the overall attractive interactions play as a uniform background potential to the motions of hard core molecules on the whole.[13,14)]

It has been shown by the authors group that the model is useful in describing the thermodynamic behaviors of liquid metals[15)].

Concerning the dynamical properties of fluids, Dymond and Alder[16)] proved the usefulness of the picture in the calculation of transport coefficient for rare gas fluids at densities greater than their critical regions, where the free-flight approximation as the movement of particles in straight lines between hard core collisions dominates the Brownian-motion approximation[17)] involving many soft collisions occurring from attractive part of the potentials (Rice-Alnatt theory[17)]). This situation is supposed to occur at high densities as stated by Weeks, Chandler, and Andersen,[18)] and the authors group and others have shown it in the MD simulation studies.[19,20)]

In addition to the overall views concerning the

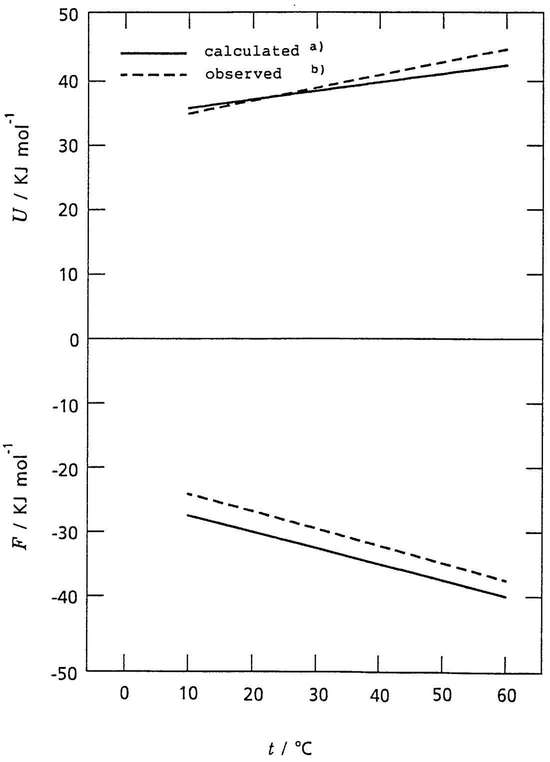

Fig. 7. Temperature dependence of U and F for liquid $C_6H_5NO_2$.
a) 73.78 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) Thermodynamic functions have been calculated from specific heat data of G.S. Parks, S.S. Todd, and W.A. Moore, *J. Am. Chem. Soc.*, **58**, 398 (1936) and N.B. Vargaftik, "Tables on the Thermophysical Properties of Liquids and Gases," 2nd ed., Halsted Press, New York (1975).

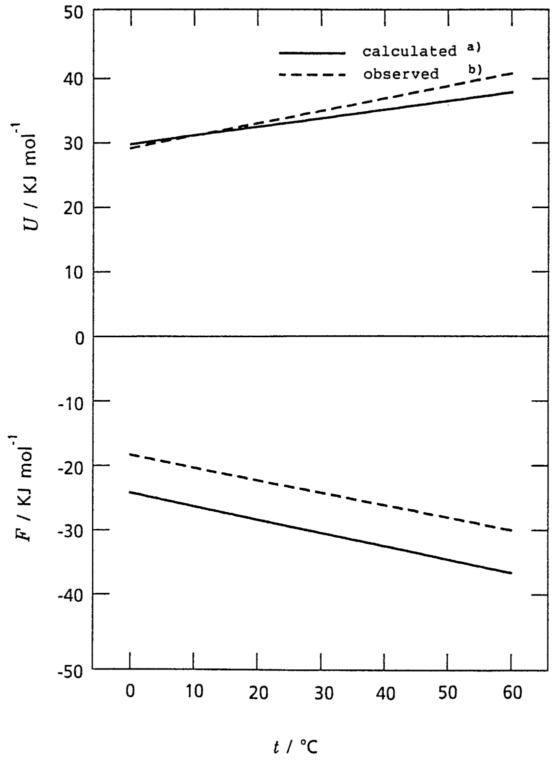

Fig. 8. Temperature dependence of U and F for liquid $C_6H_5NH_2$.
a) 71.63 kJ mol^{-1} (ΔH_{sub} at 0 K) has been added to U.
b) See footnote p) of Table 1.

generalized van der Waals picture described above, it has turned out in the present work including preceding paper[1)] that the liquid model is useful in representation of their thermodynamic behaviors when their effective hard sphere diameters are determined from the equation of state even if their molecular shapes are not spherical. This has proved to be true for strong polar fluids such as dimethyl sulfoxide when no specific or associative molecular interactions are present. The usefulness is supported by the constancy of the magnitude of the effective hard sphere diameter a with variation of temperature as shown in Table 1 of the preceding paper.[1)] Strong polarity has an effect in general to increase the packing fraction ξ (Table 1) and this strengthens the above-described dominance of hard core interactions as Weeks et al. emphasized.[18)]

The most important reason why the present liquid model is so successful in representing thermodynamic behaviors of non-associated liquids in spite of its simplicity is clearly ascribed to the usefulness of the equation of state as a kind of high temperature approximation as follows;

$$\frac{pV}{NkT}=\frac{1+\xi+\xi^2}{(1-\xi)^3}-\frac{a_{ii}}{NkTV}+O\left(\frac{1}{T^2}\right). \qquad (15)$$

We use Eq. 15, ignoring the term $O\ (1/T^2)$ in the present work. Equation 15 has a striking feature that the first and second terms in the high temperature expansion series are large in their magnitudes and have inverse sign, and the approximation in Eq. 4 is always effective.

Furthermore, in the present calculation we have used no adjustable parameters as usually made in these calculations. We used experimental values of ΔH_{vap} at 25 °C to determine a_{ii}, which has turned out to be practically kept constant in the range of temperatures for these liquid as shown in Table 1 in the preceding paper.[1)]

Behaviors of Entropy for Benzene Derivatives. In Tables 6, 7, and 8, it is seen that deviations of S_{calc} from S_{obs} amount to 10—15% for chlorobenzene, bromobenzene and benzonitrile. In these molecules, it is supposed that the rotation around the axis of the largest moment of inertia is restricted (Table 2). In these cases, vibro-rotational motion in intermolecular vibrational modes is expected instead. As for benzene and benzene derivatives in solid state, such intermolecular vibrational motions have been observed.

These intermolecular vibrational frequencies are reported as 40—50 cm^{-1}[21,22)] for solid benzene, and then it is expected that there exist nearly the same intermolecular vibrational frequencies near 40 cm^{-1}, a little smaller than those in solid state may be, for benzene derivatives in liquid state.

Table 3. Entropy of Liquid $(CH_3)_2CO$ ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
0	68.8	94.1	37.0	199.9	188.7
10	70.8	94.6	38.5	203.9	192.9
20	72.7	95.0	40.1	207.8	197.5
25	73.7	95.2	40.8	209.7	199.6
30	74.6	95.4	41.6	211.6	201.7
40	76.3	95.8	43.2	215.3	205.8
50	78.1	96.2	44.7	219.0	209.6

a) ν_j were adopted from Ref. 5, p. 123. b) See footnote b) of Fig. 1.

Table 4. Entropy of Liquid $CH_3COC_2H_5$ ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
0	69.5	106.0	53.7	229.2	225.1
10	71.6	106.4	55.9	233.9	230.7
20	73.5	106.8	58.2	238.5	236.1
25	74.5	107.1	59.3	240.9	238.8
30	75.4	107.3	60.4	243.1	241.5
40	77.2	107.7	62.6	247.5	246.6
50	79.0	108.1	64.9	252.0	251.8
60	80.7	108.4	67.1	256.2	256.8

a) ν_j were adopted from Ref. 5, p. 149. b) See footnote b) of Fig. 2.

Table 5. Entropy of Liquid $(CH_3)_2SO$ ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
25	58.8	104.0	37.7	200.5	188.8
30	59.8	104.2	38.6	202.6	190.8
40	61.8	104.6	40.4	206.8	195.8
50	63.8	105.0	42.2	211.0	200.8
70	67.6	105.8	45.9	219.3	210.5

a) ν_j were adopted from Ref. 6, p. b) See footnote b) of Fig. 3.

Table 6. Entropy of Liquid C_6H_5Cl ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
0	70.7	109.4	30.5	210.6	184.5
10	72.8	109.8	32.6	215.2	189.8
20	74.8	110.3	34.8	219.9	195.0
25	75.7	110.5	35.9	222.1	197.5
30	76.6	110.7	36.9	224.2	200.1
40	78.5	111.1	39.1	228.7	205.0
50	80.2	111.5	41.4	233.1	209.8
60	81.9	111.9	43.6	227.4	214.6

a) ν_j were adopted from Ref. 7. b) See footnote b) of Fig. 4.

Table 7. Entropy of Liquid C_6H_5Br ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
0	72.2	112.8	34.2	219.2	194.5
10	74.3	113.3	36.3	233.9	200.0
20	76.3	113.7	38.5	228.5	205.4
25	77.3	113.9	39.6	230.8	208.1
30	78.2	114.1	40.8	233.1	210.5
40	80.1	114.6	43.0	237.7	215.7
50	81.8	114.9	45.3	242.0	220.7
60	83.6	115.3	47.6	246.5	225.6

a) ν_j were adopted from Ref. 7. b) See footnote b) of Fig. 4.

Table 8. Entropy of Liquid C_6H_5CN ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
0	57.8	109.5	39.8	207.0	176.0
10	60.1	109.9	42.2	212.2	181.9
20	62.3	110.4	44.7	217.4	187.7
25	63.4	110.6	45.9	219.9	190.6
30	64.5	110.8	47.1	222.4	193.4
40	66.5	111.2	49.6	227.3	199.1
50	68.5	111.6	52.2	232.3	204.6
60	70.4	112.1	54.7	237.2	210.1

a) ν_j were adopted from Ref. 8. b) See footnote b) of Fig. 6.

Table 9. Entropy of Liquid $C_6H_5NO_2$ ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
10	62.7	118.8	41.6	223.1	214.9
20	64.9	119.2	44.2	228.3	221.2
25	65.9	119.5	45.5	230.9	224.4
30	67.0	119.7	46.9	233.6	227.4
40	68.9	120.1	49.6	238.6	234.9
50	70.9	120.5	52.3	243.7	239.7
60	72.7	120.8	55.0	248.5	245.6

a) ν_j were adopted from Ref. 9. b) See footnote b) of Fig. 7.

Table 10. Entropy of Liquid $C_6H_5NH_2$ ($J\,K^{-1}\,mol^{-1}$)

$t/°C$	S_{trans}	S_{rot}	$S_{\mathrm{vib}}^{\mathrm{a)}}$	S_{total}	$S_{\mathrm{obs}}^{\mathrm{b)}}$
0	55.4	111.5	29.0	195.9	174.8
10	57.7	112.0	31.3	201.0	181.5
20	59.9	112.4	33.6	205.9	188.0
25	61.0	112.6	34.8	208.4	191.3
30	62.0	112.8	36.0	210.9	194
40	64.0	113.2	38.5	215.7	200
50	66.0	113.6	40.9	220.5	206
60	67.8	114.0	43.4	225.2	213

a) ν_j were adopted from Ref. 10. b) See footnote b) of Fig. 1.

Table 11. Recalculated Thermodynamic Functions for C_6H_5Cl, C_6H_5Br, and C_6H_5CN (25 °C)

		F	U					S				
			kJ mol^{-1}					J K^{-1} mol^{-1}				
		kJ mol^{-1}	kin	vib	inter-mol	U_{BG}	Total	trans	rot	vib	inter-mol	Total
C_6H_5Cl	calc	−32.83	7.45	7.20	—	18.74	33.39	75.7	110.5	35.9	—	222.1
	recalc	−25.12	6.21	7.20	2.25	18.74	34.40	75.7	66.0	35.9	22.0	199.6
	obs	−25.49					33.39					197.5
C_6H_5Br	calc	−32.25	7.45	7.74	—	19.43	34.58	77.3	113.9	39.6	—	230.8
	recalc	−26.07	6.21	7.74	2.25	19.43	35.63	77.3	68.0	39.6	22.0	206.9
	obs	−27.45					34.60					208.1
C_6H_5CN	cals	−31.88	7.45	8.74	—	17.11	33.30	63.4	110.6	44.6	—	218.6
	recalc	−24.17	6.21	8.74	2.25	17.11	34.31	63.4	66.1	44.6	22.0	196.1
	obs	−23.27					33.56					190.6

Thus, a tentative consideration is made as in the following. That is, for chlorobenzene, bromobenzene and benzonitrile the thermodynamic functions are recalculated, deleting one mode of free rotation corresponding to the largest moment of inertia and counting in one intermolecular vibrational mode instead. The partition function for intermolecular vibro-rotational mode is expressed as Eq. 16.

$$Q_{\text{vibrot.}} = \prod_{j=1}^{r} ([\exp(-hf_j/2kT)][1-\exp(-hf_j/kT)]^{-1}), \qquad (16)$$

where f_j is the intermolecular vibrational frequencies and r is the number of degree of freedom (r=1 in the present case). The partition function for two free rotational mode is expressed as Eq. 17.

$$Q_{\text{rot.}} = [(1/\sigma)(8\pi^2 kT/h^2)(I_A I_B)^{1/2}]^N \qquad (17)$$

where I_A and I_B are the moments of inertia for free rotational axes. Thermodynamic functions are calculated from Eqs. 16 and 17. The recalculated values are given in Table 11.

In Table 11, the results show very good agreement of S_{calc} with S_{obs} than original calculated values. Thus, it can be said that for such compounds as chlorobenzene, bromobenzene and benzonitrile free rotation is forbidden about the largest moment of inertia and a rotational vibration appears instead, and to other two axes free rotation is allowed.

The situation is different for nitrobenzene and aniline. The reason why rather good agreement is seen between calculated and observed values for nitrobenzene in sharp contrast with the case of benzonitrile, which has quite similar properties with nitrobenzene (Table 1), is not clear. For aniline some deviations are observed. The reason is attributed to the presence of hydrogen bonds between molecules, probably.

Concluding Remarks

The statistical thermodynamic approach presented in the preceding paper was applied to estimate thermodynamic functions of eight polar liquids. Calculated values were rather in good agreement with observed ones on the whole for polar compounds such as acetone, 2-butanone, and dimethyl sulfoxide including nitrobenzene in spite of their strong polarities. For aromatic derivatives such as chlorobenzene, bromobenzene, and benzonitrile, however, fairly large deviations of calculated values from observed ones were found. The reason was elucidated by taking account of restricted rotation of the molecules and intermolecular vibrational mode in these liquids.

The liquid model presented here has, thus, proved to be effective and useful as well for polar liquids as for nonpolar ones if the method is applied deliberately.

References

1) S. Kawai and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **63**, 307 (1990).

2) K. Arakawa and K. Kojima, *Bull. Chem. Soc. Jpn.*, **48**, 26 (1975).

3) K. Tokiwano and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **50**, 2217 (1977).

4) K. Arakawa, K. Tokiwano, and K. Kojima, *Bull. Chem. Soc. Jpn.*, **50**, 65 (1977).

5) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," Consolidated Volume I, The Secrecy of Commerce on Behalf of the United States Government, Washington (1972), pp. 123, 149.

6) H. Lawrence Clever and Edgar F. Westrum, Jr., *J. Phys. Chem.*, **74**, 1309 (1970).

7) D. H. Whiffen, *J. Chem. Soc.*, **1956**, 1350.

8) J. Jacobsen, *Spectrochim. Acta*, **21**, 127 (1965).

9) J. H. S. Green, W. Kynaston, and A. S. Lindsay, *Spectrochim. Acta*, **17**, 486 (1961).

10) J. C. Evans, *Spectrochim. Acta*, **16**, 428 (1960).

11) K. Arakawa, Kagaku Sōsetsu, No. 11 "Ions and Solvents," Gakkai Shuppan Center, Tokyo (1976), Chap. 2.

12) W. G. Hoover and F. H. Ree, *J. Chem. Phys.*, **49**, 3609 (1968).

13) D. Chandler, *Ann. Rev. Phys. Chem.*, **29**, 441 (1978).

14) J. P. Hansen and J. R. McDonald, "Theory of Simple Liquids," Chap. 6., Acad. Press (1976).

15) N. Ohtomo and K. Arakawa, *J. Phys. Soc. Jpn.*, **51**,

1282 (1981); Y. Tanaka, N. Ohtomo, and K. Arakawa, *J. Phys. Soc. Jpn.*, **52**, 2093 (1982).

16) J. H. Dymond and B. J. Alder, *J. Chem. Phys.*, **45**, 2061 (1966).

17) A. R. Alnatt and S. A. Rice, *J. Chem. Phys.*, **34**, 2144 (1961); **34**, 2156 (1961); S. A. Rice and P. Gray, "The Statistical Mechanics of Simple Liquids," Wiley, New York (1965), Chap. 6.

18) J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, **54**, 5237 (1971).

19) K. Tokiwano and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **54**, 1031 (1981).

20) R. Vogelsang and C. Hoheisel, *Phys. Rev.*, **39**, 6391 (1989).

21) E. Burgos, H. Bonadeo, and E. D'Alessio, *J. Chem. Phys.*, **63**, 38 (1975).

22) H. Bondadeo, M. P. Marzocchi, E. Castellucci, and, S. Califano, *J. Chem. Phys.*, **37**, 4299 (1972).