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Thermodynamic Properties of Solution of Nonspherical Molecules Determined from Gas-Liquid Chromatography and Calculated by the Scaled Particle Theory Using the Kihara Potential[1)]

Hideaki FUJIWARA,* Ikuji OHTAKU, Rieko MIYAGI, and Yoshio SASAKI
Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565
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The free energies, enthalpies, and entropies of solution have been determined for nonspherical molecules by gas-liquid chromatography and the data are discussed on the basis of a simple theory of solution, the scaled particle treatment. The solutes used are normal alkanes from pentane to decane and the solvents used are 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (DDCO), 9-heptadecanone (HPDN), and squalane. Some basic equations are derived for the nonspherical molecules by regarding the alkane solutes, HPDN and squalane as spherocylinders and DDCO as a disk and by incorporating the Kihara potential in estimating the nonspherical interactions. The enthalpies and entropies observed can be reproduced fairly well by assigning appropriate values of the sizes and potential constants for the solutes as well as for the solvents. However, these two properties tend to cancel each other in yielding the free energies, and the free energies are not reproduced so well as the enthalpies and entropies separately are. The presence of long alkyl chains in HPDN and squalane needs be allowed for better prediction of the entropies and, especially, the free energies. The present method of calculation is also applied to a spherical solute of tetramethyltin in the solvents of HPDN and DDCO with reasonable results. In this way, a relatively simple treatment of the scaled particle theory and the Kihara potential is shown to be fruitful in discussing the thermodynamic properties of solution for nonspherical molecules.

Thermodynamic properties of solution such as the changes in free energy, enthalpy, and entropy accompanying dissolution of a solute from gas phase to liquid phase are key parameters in the studies of partition coefficients and solubilities.[2)] In dealing with these properties, the scaled particle theory has disclosed an important role of cavity formation when transferring a solute from gas to liquid.[3)] Pierotti has shown successful calculations of the solubility properties of gases by applying the scaled particle theory to obtain the cavity term and by combining the Lennard-Jones potential to obtain the solute-solvent interaction terms.[3a)] A merit of the scaled particle treatment is its simplicity with moderate fitness to the experimental results. However, Abraham and Nasehzadeh[4)] reported that a version of the scaled particle treatment yields reasonable values of the free energy of solution ΔG_s^0 for nonpolar solutes in nonaqueous solvents but not for those in water, and that it yields also reasonable values of the entropy of solution ΔS_s^0 for nonpolar solutes in water but not for those in nonaqueous solvents. Hitherto, the scaled particle theory has been developed and applied almost always by assuming both solute and solvent as spheres. The effects of nonspherical shape have also been discussed and found nontrivial by several investigators with regard to the virial coefficients, the excess volumes, the Gibbs free energies and the equations of state.[5a-c)] The scaled particle treatment is also utilized in the perturbation study of solubilities of some simple gases.[5d)]

Recently, the authors have reported that the entropies of solution of several alkanes in nonaqueous solvents measured by the gas-liquid chromatography are interpreted by the scaled particle theory extended to nonspherical molecules.[6)] In the present study we further extend such a treatment to include the enthalpy of solution by using the Kihara potential in estimating the interaction term, and thermodynamic properties of solution are examined with regard to the free energies, enthalpies, and entropies.

Experimental

Gas-Liquid Chromatogaphic Experiments. The gas-liquid chromatographic measurements were made on a Yanagimoto G-1880 gas chromatograph with a TCD cell. A Pyrex glass column with i.d. 3.4 mm and length 2 m was used after a treatment with dichlorodimethylsilane. The solutes used were normal alkanes from pentane to decane. The stationary phases used were 10,11-dihydro-5*H*-dibenzo-[*a*,*d*]cyclohepten-5-one (DDCO), 9-heptadecanone (HPDN), and squalane (2,6,10,15,19,23-hexamethyltetracosane) which were coated on 60/80 mesh Chromosorb W DMCS to an amount of 25 wt%. The column temperature was set at five temperatures between 50 °C and 90 °C for the two solvents, DDCO and HPDN, and between 66 °C and 140 °C for squalane, and monitored with a copper-constantan thermocouple. The retention time was measured 5 times at each temperature and averaged. Such measurements were repeated 3 times for the solvent DDCO and 2 times for that HPDN. The solvent coated lost its quantity slightly during the measurement of retention time. This weight loss was less than 1% and was taken into account in the data treatment.

Materials. The solvents HPDN and DDCO from commercial sources were distilled under reduced pressure. The coating was achieved by using distilled dichloromethane as a diluent. The solutes, normal alkanes from pentane to decane, tetramethyltin, and squalane, all from commercial sources, were used without further purification.

Results

The enthalpies, entropies and free energies of solution were measured by gas-liquid chromatography, which is reported to produce reliable values[7] comparable to a calorimetric method.[8] The solvents DDCO, squalane and HPDN were selected as stationary phases suitable for the GLC measurements. The standard states are selected as 1 atm in gas phase and 1 mole fraction in liquid phase, and so the relationships used for the determination of the thermodynamic properties are:[7,9]

$$V_g^0 = [(t_r - t_a)jF/w](273.15/T) \quad (1)$$

$$K = (W_M/273.15R)V_g^0 \quad (2)$$

$$\ln K = -\Delta H_s^0/RT + \Delta S_s^0/R. \quad (3)$$

In these equations, the meanings of symbols are: V_g^0= specific retention volume, K=partition coefficient, t_r=retention time of sample, t_a=retention time of a reference (air), j=correction factor for the pressure, F=flow rate of the carrier gas (He), w=weight of solvent in the column, T=absolute temperature, W_M=molecular weight of solvent, and R=the gas constant. From the measurement of retention times, V_g^0 is obtained (Eq. 1), which is converted to K through Eq. 2. And then, the plots of ln K vs. $1/T$ afford the values of ΔH_s^0 and ΔS_s^0 (Eq. 3). The plots of ln K vs. $1/T$ are linear successfully as indicated by the correlation coefficients larger than 0.999. The observed thermodynamic properties of solution are listed

Table 1. Thermodynamic Properties of Solution for the Alkanes Dissolved in DDCO[a]

Solute	Experimental			Calculated			
	ΔG_s^0	$-\Delta H_s^0$	$-T\Delta S_s^0$	ΔG_s^0	$-\Delta H_s^0$	$-T\Delta S_s^0$	$G_{int}=H_{int}$
Pentane	4.5±3.3	24.5±1.9	29.0±1.4	0.3	27.2	27.5	−50.1
Hexane	1.6±1.5	28.5±0.9	30.1±0.6	−1.1	30.1	29.0	−56.3
Heptane	−1.4±1.8	32.4±1.1	31.0±0.7	−2.6	33.0	30.4	−62.5
Octane	−6.9±1.0	38.3±0.6	31.4±0.4	−3.8	35.7	31.9	−68.5
Nonane	−8.1±0.6	40.5±0.2	32.4±0.4	−5.3	38.6	33.3	−74.7
Decane	−8.9±0.4	42.3±0.2	33.4±0.2	−6.6	41.4	34.8	−80.9

a) All values are given in the unit of kJ mol^{-1} and at 298.15 K.

Table 2. Thermodynamic Properties of Solution for the Alkanes Dissolved in HPDN[a]

Solute	Experimental			Calculated			
	ΔG_s^0	$-\Delta H_s^0$	$-T\Delta S_s^0$	$\Delta G_s^{0b)}$	$-\Delta H_s^0$	$-T\Delta S_s^{0c)}$	$G_{int}=H_{int}$
Pentane	0.3±0.7	23.8±0.4	24.1±0.3	−7.3(−2.0)	27.7	20.4(25.7)	−42.0
Hexane	−2.8±0.9	29.4±0.4	26.6±0.5	−9.4(−3.9)	30.6	21.2(26.7)	−47.0
Heptane	−5.7±1.1	33.0±0.6	27.3±0.5	−11.5(−5.8)	33.5	22.0(27.7)	−52.0
Octane	−8.4±0.6	37.2±0.3	28.8±0.3	−13.3(−7.4)	36.1	22.8(28.7)	−56.7
Nonane	−11.2±1.5	41.4±0.8	30.2±0.7	−15.4(−9.3)	39.0	23.6(29.7)	−61.7
Decane	−14.0±0.4	46.2±0.2	32.2±0.2	−17.4(−11.1)	41.8	24.4(30.7)	−66.6

a) All values are given in the unit of kJ mol^{-1} and at 298.15 K. b) In parentheses listed are the free energies estimated according to an equation $\Delta G_s^0=\Delta H_s^0-T(1.26\Delta S_s^0)$ (see text). c) In parentheses listed are the entropies corrected (see text).

Table 3. Thermodynamic Properties of Solution of Alkanes Dissolved in Squalane[a]

Solute	Experimental			Calculated			
	ΔG_s^0	$-\Delta H_s^0$	$-T\Delta S_s^0$	$\Delta G_s^{0b)}$	$-\Delta H_s^0$	$-T\Delta S_s^{0c)}$	$G_{int}=H_{int}$
Pentane	−1.6±0.7	25.4±0.4	23.8±0.3	−11.5(−3.1)	28.6	17.1(25.5)	−38.5
Hexane	−4.7±0.7	31.5±0.4	26.8±0.3	−13.9(−5.3)	31.6	17.7(26.3)	−43.0
Heptane	−7.5±0.5	34.6±0.3	27.1±0.2	−16.4(−7.5)	34.6	18.2(27.1)	−47.5
Octane	−10.2±0.4	38.2±0.2	28.0±0.2	−18.5(−9.4)	37.3	18.8(27.9)	−51.8
Nonane	−12.8±0.5	41.8±0.3	29.0±0.2	−20.9(−11.4)	40.2	19.3(28.8)	−56.1
Decane	−15.5±0.7	45.7±0.4	30.2±0.3	−2.32(−13.5)	43.1	19.9(29.6)	−60.5

a) The units of ΔG_s^0, ΔH_s^0, and $T\Delta S_s^0$, are all in kJ mol^{-1}. ΔG_s^0 and $T\Delta S_s^0$ are calculated at 298.15 K. Molecular parameters of the solvent used are: a=1.88 Å, l=28.98 Å, and $U_{0,B}/k$=4285 K. When a and $U_{0,B}$ are changed as : a=2.08 Å and $U_{0,B}/k$=4744 K, the values of ΔH_s^0 change to −29.1, −31.9, −34.7, −37.2, −39.9, and −42.5 from pentane to decane, and those of $-T\Delta S_s^0$ change to 16.2, 16.7, 17.1, 17.5, 17.9, and 18.3 from pentane to decane, respectively. b) In parentheses listed are the values estimated from: $\Delta G_s^0=\Delta H_s^0-T(1.49\Delta S_s^0)$ (see text). c) In parentheses listed are the entropies corrected (see text).

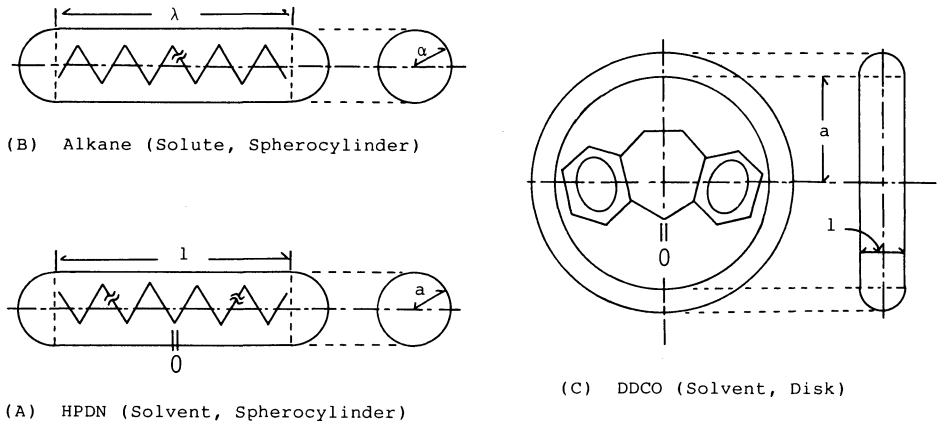


Fig. 1. The nonspherical models of the solute and solvent. The designation of a and l in DDCO needs be corrected as above in the Figure of Ref. 6a.

in Tables 1 to 3. All of these values change linearly with the number of carbons in the alkane solutes. Experimental values of ΔH_s^0 and $T\Delta S_s^0$ are both negative and their absolute values increases with the number of carbons in normal alkanes, and hence they are in a compensation relation. ΔG_s^0 decreases with the carbon number, indicating a relative importance of the enthalpy term.

Discussion

The entropy of solution ΔS_s^0 of nonspherical molecules can be better interpreted by a scaled particle treatment with reasonable molecular sizes when and only when nonspherical shapes are taken into account in the calculation, as already reported in the preliminary report.[6] However, when such a treatment is applied to obtain the cavity term of the enthalpy of solution, positive values are obtained, indicating a necessity of a solute–solvent interaction term to make the enthalpies negative. The authors adopted here the Kihara potential[10] to estimate the interaction term for nonspherical molecules, and derived equations of the thermodynamic properties of solution for spherocylinder and disk shaped molecules (see Appendix).

The solvents HPDN and squalane and the solutes alkanes are approximated as spherocylinders, and the solvent DDCO is approximated as a disk (Fig. 1). The entropy of solution is interpreted reasonably by such models of solute and solvent as discussed in the preliminary report.[6] To calculate the enthalpy of solution ΔH_s^0, the potential constants and the molecular sizes are needed for the normal alkanes as well as for the solvents. The molecular sizes have been determined so as to reproduce the entropy of solution ΔS_s^0 (Table 1 in Ref. 6a) with reasonable precision, and the potential constants are available for several normal alkanes[10a,11] from the data of virial coefficients. The potential constants for nonane and decane are currently unavailable but can be obtained by the extraporation of the data for other normal alkanes. The potential constants of the two solvents are determined by a trial and error method so that they minimize the square sum of the difference between the observed and calculated enthalpies of solution (Fig. 2). Standard deviations between the experimental and recalculated enthalpies are relatively small, supporting a usefulness of the simple model used here. Thermodynamic properties of solution obtained in the experiment and in the calculation are summarized in Tables 1 to 3 for the DDCO, HPDN, and squalane solvents, respective-

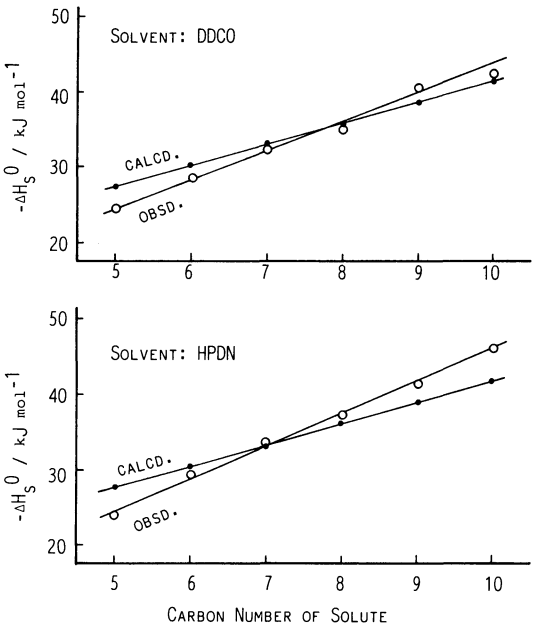


Fig. 2. Comparison of the enthalpies calculated and observed for the normal alkanes in HPDN (lower plots) and DDCO (upper plots). Potential constants of the solvents are $U_{0,B}/k$=3669 K (HPDN) and $U_{0,B}/k$=4080 K (DDCO).

Table 4. Thermodynamic Properties of Solution of Tetramethyltin Dissolved in the Solvents of DDCO and HPDN[a)]

Solvent	Experimental			Calculated				
	ΔG_s^0	$-\Delta H_s^0$	$-T\Delta S_s^0$	$\Delta G_s^{0b)}$	$-\Delta H_s^0$	$-T\Delta S_s^{0c)}$	α	$U_{0,B}/k$
DDCO	1.1±0.1	28.1±0.1	29.2±0.14	10.5	17.8	28.3	3.07 Å	400 K
				0.2	28.1	28.3	3.07 Å	495 K
				10.4	18.6	29.0	3.18 Å	400 K
				0.9	28.1	29.0	3.18 Å	482 K
HPDN	−3.9±0.1	30.8±0.1	26.9±0.1	0.02(5.4)	20.7	20.7(26.1)	3.07 Å	400 K
				−7.4(−2.0)	28.1	20.7(26.1)	3.07 Å	481 K
				0.5(5.0)	21.6	21.1(26.6)	3.18 Å	400 K
				−7.0(−1.5)	28.1	21.1(26.6)	3.18 Å	467 K

a) All values are given in the unit of kJ mol^{-1} and at 298.15 K. b, c) See footnotes b and c in Table 2. The same factor of 1.26 is used here.

ly. The enthalpies and entropies of solution calculated fit well with the experimental ones in DDCO (Table 1). However, these two parameters tend to cancel each other in yielding the free energy as already described in the Results section. The errors in estimating the free energies, therefore, become relatively large after such cancellation. Quite a similar trend is seen in the system of HPDN (Table 2). In this case deviations in the entropies are relatively large between the experiment and the calculation. This may be related to some extent to the presence of long alkyl chain. To investigate further an effect of long alkyl chain, squalane is tested as a stationary phase (Table 3). Squalane molecule is regarded to be in a stretched zigzag conformation and approximated by a spherocylinder, for which the length l is estimated to be 28.98 Å, i.e., 23×1.26 Å, and the radius a is set equal to 1.88 Å (the compactness factor y=0.38). This radius is tested with a little larger values, considering several methyl group branches from the normal alkane chain. A relatively good fit is obtained when a is smaller than 2.08 Å (Table 3). The calculated values of ΔS_s^0 become smaller by ca. 7% and larger by ca. 40% when a is changed from 2.08 Å (y=0.46) to 1.88 Å (y=0.38) and 2.28 Å (y=0.56), respectively. Therefore, the entropies of solution observed for the normal alkanes in squalane are said to be reproduced by the calculation to an extent of about 65—70%. This percentage certainly drops from the value of 80% observed in the HPDN solvent having a shorter length of chain. That is, the reproducibility of the entropy of solution decreases much more by the presence of longer alkyl chain in the solvent molecule. This is probably because the flexibility of the long alkyl chain is not taken into account in the present model. An improvement of the model by incorporating this molecular flexibility is not a simple task. But when the correction is assumed to be proportional to the entropies calculated by neglecting the flexibility, the correction factor is determinable so that the corrected entropies fit better with the experimental ones for all of the alkane solutes treated here. Such corrections are included in Tables 2 and 3 (see footnotes b and c). The enthalpies observed in squalane are best fitted by setting $U_{0,B}/k$=4744 K (S.D.=2.4 kJ mol^{-1}) and $U_{0,B}/k$=4285 K (S.D.=2.0 kJ mol^{-1}) when a is set to 2.08 Å and 1.88 Å, respectively. These values of U_0 are higher than that for octane (1150) reflecting the increased molar volume.

To investigate further the applicability of our model, tetramethyltin is tested as a sphere solute (Table 4). The GLC experiment was done once and the errors were estimated from the linear plot of ln K vs. $1/T$. The spherical molecule of tetramethyltin can be included in a spherocylindrical model with vanishing length (λ=0). Note that we have assumed a line with a definite length for the core of spherocylinder, and hence the Kihara function becomes equivalent to the Lennard-Jones one in case of spheres.[12)] The standard values of the molecular radius and the potential constant are known to be σ (diameter)=6.13 Å and ε/k=400 K.[4)] Several model calculations are compared with the experimental results in Table 4. In the DDCO system ΔH_s^0 and ΔS_s^0 are reproduced best by a calculation using the parameters for DDCO above obtained and the values of α=3.18 Å and $U_{0,B}/k$=482 K for tetramethyltin. The latter value is slightly larger than the average of reported values, 400 K.[4)] However, the potential constant reported is relatively large in nonpolar solvents,[13)] and hence the value reached in the present study may be accepted as reasonable. In the HPDN system about 80% of ΔS_s^0 is reproduced by the calculation (Table 4). This percentage is the same with that observed[6)] for the normal alkane solutes in the same solvent. ΔH_s^0 is seen to be reproduced well by the potential constant quite similar to the above DDCO system.

Conclusion

The main purpose of this study is to examine if thermodynamic properties of solution determined by the GLC method, which has been accepted to yield reliable values of these properties, are reproduced well

by relatively simple modifications of the scaled particle theory and the Kihara potential when nonspherical shapes of molecules are taken into account. The entropies of solution observed are explained almost fully by the cavity term derived from the scaled particle theory, indicating negligible contribution from the interaction term. In the HPDN solvent, however, a flexibility in its long alkyl chain seems to affect the entropies, and some correction factor is necessary for the improved reproducibility of the entropies and free energies of solution.

The enthalpies of solution observed are well reproduced by the calculation when reasonable values are assigned to the potential constants of the solvents. The calculation indicates that the interaction term is dominant for the enthalpies, whereas the cavity term contributes positively (unstably) to the total energy. For the precise estimation of the free energies of solution, much precise estimation of the enthalpy and entropy terms is needed since these two parameters tend to cancel each other in yielding the free energy.

In conclusion, the scaled particle theory is evidenced to be applicable in calculating the thermodynamic properties of solution for nonspherical molecules when nonspherical shapes are taken into account and nonspherical interactions are included through the Kihara potential in the calculation.

Appendix

Equations of the Thermodynamic Properties of Solution for Nonspherical Molecules Derived Basing on the Scaled Particle Theory Incorporated with the Kihara Potential. The free energy of solution ΔG_s^0 is divided into three terms of a cavity formation, solute-solvent interactions, and a correction for the standard states in gas and liquid phases:[3b]

$$\Delta G_s^0 = G_{cav} + G_{int} + RT\ln(RT/V_1) \quad (4)$$

where V_1 means the solvent molar volume and the gas constant R is expressed as 0.08206 atm·l(K·mol)$^{-1}$. Similarly, the enthalpy ΔH_s^0 and entropy ΔS_s^0 of solution are divided as follows:[3,4]

$$\Delta H_s^0 = H_{cav} + H_{int} + \alpha_p RT^2 - RT \quad (5)$$

$$\Delta S_s^0 = S_{cav} + S_{int} + \alpha_p RT - R - R\ln(RT/V_1) \quad (6)$$

G_{cav} in Eq. 4 includes terms of PV work and surface energy. The PV work is expressed as $W=P<V_{A+B}>$, where V_{A+B} is the volume excluded by the center of molecule B surrounding a solute A and $<>$ means a statistical average for the relative orientation of the two molecules. A following equation is reached for $<V_{A+B}>$,[10] where S is the surface area and M is

$$<V_{A+B}> = V_A + V_B + (S_A M_B + S_B M_A)/4\pi \quad (7)$$

the measure which is defined as the mean curvature integrated over the whole surface of the convex molecule.[10] The three fundamental values V, S, and M are derived for a few convex bodies and listed in Table 5. On the other hand, the surface energy is expressed by a differential equation $dW=\gamma dS$, where γ is the surface tension. Here the surface tension is considered to be dependent on the curvature of a surface,

$$\gamma/\gamma_0 = 1 - 2\delta_0 C = 1 - \delta_0(1/R_1 + 1/R_2) \quad (8)$$

where γ_0 is the surface tension for a flat plane and δ_0 the distance corresponding to the plane interface, and where C is the curvature which is equal to $1/R_1+1/R_2$, R_1, and R_2 being the principal radii of curvature.[14]

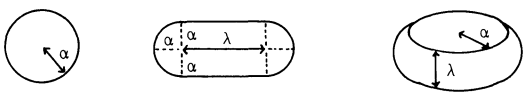
The free energy term of solute-solvent interactions is obtained as follows. To take into account nonspherical shape of molecules we adopted the Kihara potential[10] for intermolecular interactions.[15] The Kihara potential assumes a core in each molecule and energy of interaction is expressed as a function of the closest distance ρ between the cores of the two interacting molecules:

$$U(\sigma) = U_0[(\sigma_0/\sigma)^{12} - 2(\sigma_0/\sigma)^6] \quad (9)$$

Here, σ_0 and $-U_0$ are the closest core distance and energy, respectively, under the most stable interaction. In the present study we assume for simplicity that a core possesses a vanishing thickness and a molecule is made up of a surface located at a constant distance ρ_0 from the core (Fig. 3). Equation 9 is also adopted here for the potential, where $\sigma_0=\rho_{0,A}+\rho_{0,B}$, $\sigma=\sigma_0+\rho$, and $U_0=(U_{0,A}\cdot U_{0,B})^{1/2}$ are assumed between the interacting molecules of A and B. Therefore, the most stable interaction is reached when surfaces of the two molecules come into contact ($\rho=0$), ρ being the closest distance between the surfaces of the two molecules (Fig. 3). The interaction energy E_{int} is approximated to be equal to the free energy of interaction and is expressed as follows:

Table 5. The Three Fundamental Measures V, S, and M of Convex Bodies

	Sphere	Spherocylinder	Disk
V	$4\pi\alpha^3/3$	$\pi(4\alpha^3/3+\alpha^2\lambda)$	$\pi(\alpha^2\lambda+\alpha\lambda^2/4+\lambda^3/6)$
S	$4\pi\alpha^2$	$2\pi(2\alpha^2+\alpha\lambda)$	$\pi(2\alpha^2+\pi\alpha\lambda+\lambda^2)$
M	$4\pi\alpha$	$\pi(4\alpha+\lambda)$	$\pi(\pi\alpha+2\lambda)$



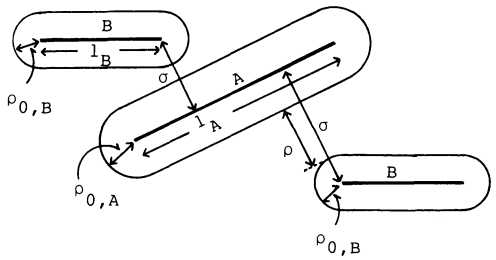


Fig. 3. A model for the Kihara potential of the interacting spherocylindrical molecules of solute (A) and solvent (B). —: Core of the molecule. See text for further details.

$$G_{int} \simeq E_{int} = <N\int_{vol} U(\sigma)\cdot dg\cdot d\tau> \quad (10)$$

where N means the Avogadro Number, dg is the number density d multiplied by the radial distribution function g, and $d\tau$ is the volume element equal to $S_{A+B+\rho}\cdot d\rho$, $S_{A+B+\rho}$ being the surface area when solute A is surrounded by solvent B separated by a distance of ρ. The symbol "vol" means the integration over the whole system, but the region with positive interaction energies is excluded in practice.[3b] When $g=1$ is assumed over the region of integration, Eq. 10 turns out to be Eq. 11 since ρ is independent of the mutual orientation of the two interacting molecules.

$$G_{int} \simeq E_{int} = Nd\int_{vol} U(\sigma)<S_{A+B+\rho}>d\rho \quad (11)$$

The statistically averaged surface area $<S_{A+B+\rho}>$ is substituted as follows by using Eq. 7 for $<V_{A+B+\rho}>$:

$$\begin{aligned}<S_{A+B+\rho}> &= d<V_{A+B+\rho}>/d\rho \\ &= S_A + S_B + M_A M_B/2\pi + 2(M_A+M_B)\rho + 4\pi\rho^2. \quad (12)\end{aligned}$$

When dg is independent of temperature, $G_{int}=H_{int}$ and $S_{int}=0$ hold, and hence,

$$\begin{aligned}G_{int}=H_{int} &= Nd\int_{2^{-1/6}-1}^{\infty} U_0[\{\sigma_0/(\sigma_0+\rho)\}^{12}-2\{\sigma_0/(\sigma_0+\rho)\}^6]\cdot \\ &\quad \{S_A+S_B+M_AM_B/2\pi+2(M_A+M_B)\rho+4\pi\rho^2\}d\rho \\ &= -NdU_0[17(\rho_{0,A}+\rho_{0,B})\{S_A+S_B+M_AM_B/2\pi\}/55 + \\ &\quad 2(\rho_{0,A}+\rho_{0,B})^2(M_A+M_B)/11 + 128\pi(\rho_{0,A}+\rho_{0,B})^3/495 \quad (13)\end{aligned}$$

As described above, ΔG_s^0, ΔH_s^0, and ΔS_s^0 are calculated when molecular shapes and sizes of solute (A) and solvent (B) are known as well as the potential constants $U_{0,A}$ and $U_{0,B}$ and the surface tension of solvent γ_0. Usually the surface tension appears only implicitly in the scaled particle treatment. That is, the form of G_{cav} is determined by considering its dependency on the size parameters of solute.[3a,5c] This process follows to that reported for a spherocylindrical solute in a spherocylindrical solvent.[5c] Equations of the thermodynamic properties related to the cavity formation are listed below which are reached in the present study for a few systems of nonspherical solute in nonspherical solvent. A more advanced theory of solutions, Percus-Yevick theory, predicts that a correction term is necessary in the intuitive Pierotti's expressions when intermolecular interactions are taken into account.[16-18] Such a correction term is now studied to apply to the nonspherical cases together with the terms of induced and dipolar interactions.

i) Spherocylindrical solute in spherocylindrical solvent:

$$\begin{aligned}G_{cav} &= RT\{-\ln(1-y)+\pi d(2a^2+al)(2\alpha+\lambda/2)/(1-y)+ \\ &\quad \pi d(4a+l)(\alpha^2+\alpha\lambda/2)/(1-y)+[\pi d(2a^2+al)/ \\ &\quad (1-y)]^2(2\alpha^2+\alpha\lambda)\}+NP\pi(\alpha^2\lambda+4\alpha^3/3)\end{aligned}$$

$$\begin{aligned}H_{cav} &= \{y+\pi d(2a^2+al)(2\alpha+\lambda/2)/(1-y)+\pi d(4a+l)\cdot \\ &\quad (\alpha^2+\alpha\lambda/2)/(1-y)+[\pi d(2a^2+al)/(1-y)]^2\cdot \\ &\quad (\alpha^2+\alpha\lambda/2)\}\alpha_p RT^2/(1-y)+NP\pi(\alpha^2\lambda+4\alpha^3/3)\end{aligned}$$

$$\begin{aligned}S_{cav} &= R\{\ln(1-y)+y\alpha_pT/(1-y)+\pi d(2a^2+al)(2\alpha+\lambda/2)\cdot \\ &\quad [\alpha_pT/(1-y)-1]/(1-y)+\pi d(4a+l)(\alpha^2+\alpha\lambda/2)\cdot \\ &\quad [\alpha_pT/(1-y)-1]/(1-y)+[\pi d(2a^2+al)/(1-y)]^2\cdot \\ &\quad (2\alpha^2+\alpha\lambda)[2\alpha_pT/(1-y)-1]\} \\ &\quad y=\pi a^2(4a/3+l)d\end{aligned}$$

ii) Spherocylindrical solute in disk-like solvent:

$$\begin{aligned}G_{cav} &= RT\{-\ln(1-y)+\pi d(2a^2+\pi al+l^2)(\alpha+\lambda/4)/(1-y) \\ &\quad +\pi d(\pi a+2l)(\alpha^2+\alpha\lambda/2)/(1-y)+[\pi d(2a^2+\pi al \\ &\quad +l^2)/(1-y)]^2(\alpha^2/2+\alpha\lambda/4)\}+NP\pi(\alpha^2\lambda+4\alpha^3/3)\end{aligned}$$

$$\begin{aligned}H_{cav} &= \{y+\pi d(2a^2+\pi al+l^2)(\alpha+\lambda/4)/(1-y)+\pi d(\pi a \\ &\quad +2l)(\alpha^2+\alpha\lambda/2)/(1-y)+[\pi d(2a^2+\pi al+l^2)/ \\ &\quad (1-y)]^2(\alpha^2+\alpha\lambda/2)\}\alpha_pRT^2/(1-y)+ \\ &\quad NP\pi(\alpha^2\lambda+4\alpha^3/3)\end{aligned}$$

$$\begin{aligned}S_{cav} &= R\{\ln(1-y)+y\alpha_pT/(1-y)+\pi d(2a^2+\pi al+l^2)\cdot \\ &\quad (\alpha+\lambda/4)[\alpha_pT/(1-y)-1]/(1-y)+\pi d(\pi a+2l)\cdot \\ &\quad (\alpha^2+\alpha\lambda/2)[\alpha_pT/(1-y)-1]/(1-y)+[\pi d(2a^2+ \\ &\quad \pi al+l^2)/(1-y)]^2(\alpha^2/2+\alpha\lambda/4)[2\alpha_pT/(1-y)-1]\} \\ &\quad y=\pi(a^2l+\pi al^2/4+l^3/6)d\end{aligned}$$

iii) Disk-like solute in disk-like solvent:

$$\begin{aligned}G_{cav} &= RT\{-\ln(1-y)+\pi d(2a^2+\pi al+l^2)(\pi\alpha/4+\lambda/2)/ \\ &\quad (1-y)+\pi d(\pi a+2l)(\alpha^2/2+\pi\alpha\lambda/4+\lambda^2/4)/(1-y) \\ &\quad +[\pi d(a^2+\pi al/2+l^2/2)/(1-y)]^2(\pi^2\alpha^2/8+\pi\alpha\lambda/2 \\ &\quad +\lambda^2/2)\}+NP\pi(\alpha^2\lambda+\alpha\lambda^2/4+\lambda^3/6)\end{aligned}$$

$$\begin{aligned}H_{cav} &= \{y+\pi d(2a^2+\pi al+l^2)(\pi\alpha/4+\lambda/2)/(1-y)+\pi d(\pi a \\ &\quad +2l)(\alpha^2/2+\pi\alpha\lambda/4+\lambda^2/4)/(1-y)+[\pi d(a^2+\pi al/2 \\ &\quad +l^2/2)/(1-y)]^2(\pi^2\alpha^2/4+\pi\alpha\lambda+\lambda^2)\}\alpha_pRT^2/(1-y) \\ &\quad +NP\pi(\alpha^2\lambda+\alpha\lambda^2/4+\lambda^3/6)\end{aligned}$$

$$\begin{aligned}S_{cav} &= R\{\ln(1-y)+y\alpha_pT/(1-y)+\pi d(a^2+\pi al/2+l^2/2)\cdot \\ &\quad (\pi\alpha/2+\lambda)[\alpha_pT/(1-y)-1]/(1-y)+\pi d(\pi a/2+l)\cdot \\ &\quad (\alpha^2+\pi\alpha\lambda/2+\lambda^2/2)[\alpha_pT/(1-y)-1]/(1-y)+ \\ &\quad [\pi d(a^2+\pi al/2+l^2/2)/(1-y)]^2(\pi^2\alpha^2/8+\pi\alpha\lambda/ \\ &\quad 2+\lambda^2/2)[2\alpha_pT/(1-y)-1]\} \\ &\quad y=\pi(a^2l+\pi al^2/4+l^3/6)d\end{aligned}$$

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