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Scaled Particle Theory of Non-Spherical Molecules Extended for the Elucidation of the Entropy of Solution[1)]

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Scaled particle theory is extended to non-spherical molecules such as spherocylinders and disks in order to interpret the entropies of solution. Application of this treatment to *normal* alkanes from pentane to decane dissolved in 9-heptadecanone and in 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one has shown that the entropies measured can be interpreted almost fully by assigning realistic sizes for the solutes as well as for the solvents, supporting an important role of the cavity formation in the process of dissolution when viewed from the standpoint of entropies.

The entropy of solution, which reflects a change in standard entropy accompanying dissolution of a solute from gas to solution, is important for the understanding of solubility[2)] as well as of the partition coefficient between two liquid phases. Hitherto, the entropy of solution has been discussed in relation to the thermodynamic third-law entropy of solute in gas phase[3,4)] and especially to scaled particle theory in more detail.[5,6)] The scaled particle theory is reported to reproduce well the entropy of solution in water, but it fails in doing so when non-aqueous solvents are involved.[4)] Furthermore, more extensive study seems to have been prevented by the limited number of available experimental data. The authors have recently reported that the entropy of solution in non-aqueous solvents can be better reproduced by the scaled particle theory when non-spherical shape is taken into account.[7)]

To investigate further the validity of the scaled particle theory of non-spherical molecules, the entropy of solution is discussed in such model solvents of spherocylinder and disk molecules as 9-heptadecanone(HPDN) and 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one(DDCO). The solutes used are *normal* alkanes from pentane to decane.

The entropy of solution was measured by gas-liquid chromatography. This method is well reviewed and documented[8)] to afford reliable data comparable to a calorimetric method. The chromatographic experiment was done in the same manner as in the previous report[7)] at several temperatures between 50 °C and 90 °C. 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 HPDN.

The loss of solvent during the measurement of retention times was also included in the data processing. The entropies of solution obtained are listed in Table 1 together with the standard deviations on repeated runs.

Equations of the entropy of solution were derived in the previous report[7] for spherocylinders of both solute and solvent, where a few equations derived by Cotter et al.[9] based on the scaled particle theory are utilized. Similar equations have been derived in the present study for a spherocylinder solute in a disk solvent:

$$\Delta S_s^0 = S_{cav} - R\{\ln(RT/V) - \alpha_p T + 1\} \quad (1)$$

$$S_{cav}/R = \ln(1-y) + y\alpha_p T/(1-y) + \pi\rho\{\alpha_p T/(1-y)-1\}\{(2a^2+\pi a l+l^2)(2\alpha+\lambda/2) + (\pi a+2l)(2\alpha^2+\alpha\lambda)\}/2(1-y) + \{\pi\rho/2(1-y)\}^2\{2\alpha_p T/(1-y)-1\}(2a^2+\pi a l+l^2)^2(2\alpha^2+\alpha\lambda) \quad (2)$$

where $y = \pi(a^2 l + \pi a l^2/4 + l^3/6)\rho$, ρ being the number density, α_p is the thermal expansion coefficient, and a, l, α, and λ are sizes of the solute and solvent (Fig. 1). This equation is reached by deriving first the equations of S(surface area), M(measure), and V(volume) for a disk, i.e., $S = 4\pi\alpha^2 + 2\pi^2\alpha\lambda + 2\pi\lambda^2$, $M = \pi^2\lambda + 4\pi\alpha$, and $V = (4/3)\pi\alpha^3 + \pi^2\alpha^2\lambda + 2\pi\alpha\lambda^2$ for a solute depicted in Fig. 1C. These equations for S, M, and V are consistent with those given by Kihara[10] for an oblate spherocylinders. In Eq. 1 the entropy term originating from solute-solvent interactions, S_{int}, is omitted as usually done.[5]

Calculations on the non-sphere model were made for various sizes of the solute and solvent. The solvent HPDN and solute alkanes were approximated by a spherocylinder and the solvent DDCO by a disk(Fig. 1). As for the size of HPDN, l was set equal to 20.30 Å which corresponds to the distance between the two terminal carbons for a stretched zig-zag conformation, and a was varied around 1.38 Å which is equal to the distance between the CH_2 protons and the longer axis of the carbon-carbon chain(Fig. 1A). The size of DDCO was estimated according to the structure reported in a crystal.[11] This molecule is folded in the center ring; the distance between the two most remote protons along the x axis is 9.89 Å and

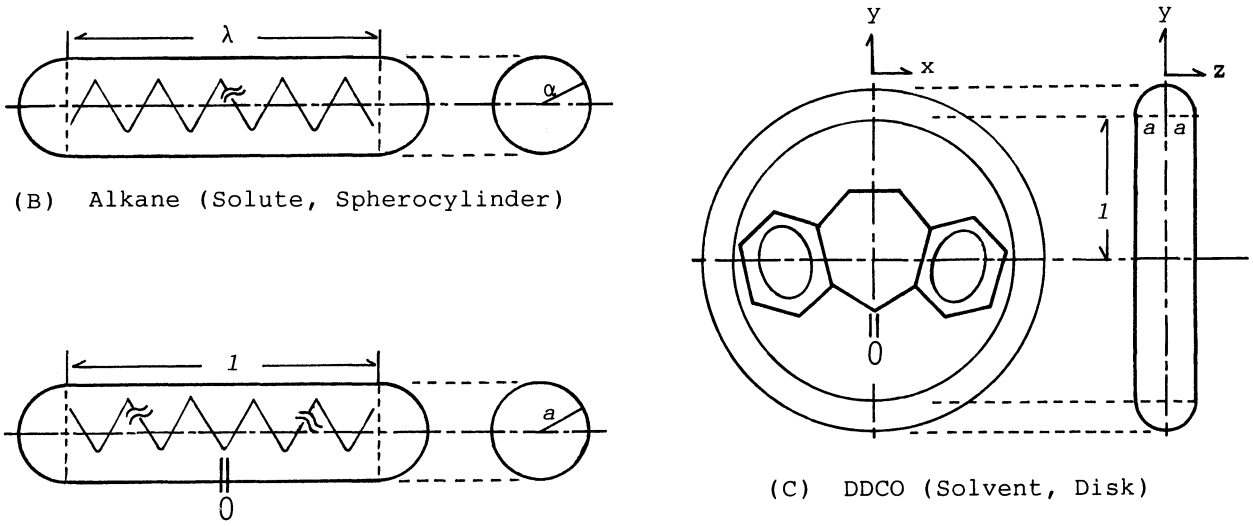

Fig. 1. Models of the solute and solvent used in the scaled particle treatment.

that along the z axis is 3.37 Å(Fig. 1C). The values of *a* and *l* were changed so that the disk shape resembles such a molecular size. The size of solute alkanes was estimated in a similar manner to HPDN, i.e., $\alpha = a$ (for HPDN) and $\lambda = 1.26(n-1)$, n being the carbon number of alkanes, were assumed(Fig. 1B). In case of alkanes dissolved in HPDN, the standard deviation (S.D.) between the experimental and recalculated entropies of solution for alkanes from pentane to decane was tested by varying the radius of alkyl chain that were assumed to be the same for both solute and solvent ($\alpha = a$).[12] The radius of 1.88 Å has been reached for a minimum of the S.D. value. This radius does not change considerably depending on the length *l* of solvent; the value changes to 1.98 Å when *l* is decreased by an amount of 2 Å. The radius of 1.88 Å corresponds to the distance from the longer axis of the carbon-carbon chain to CH_2 protons, 1.38 Å, plus around a half of the van der Waals radius for proton, 1.2 Å. For such a size of solvent, the compactness factor y given in Eq. 2 is calculated as 0.44, which lies within a reasonalbe range reported for other compounds.[13] The recalculated values of the entropies can explain around 80% of the experimental entropies(Table 1).

Table 1. The Entropies of solution measured and calculated for the alkanes dissolved in DDCO and HPDN

Solute	α/Å	λ/Å	HPDN[a] Experimental values[c]	HPDN[a] Calculated values[c]	DDCO[b] Experimental values[c]	DDCO[b] Calculated values[c]
Pentane	1.88	5.04	-80.7 1.1	-68.3	-97.3 4.7	-92.4
Hexane	1.88	6.30	-89.1 1.8	-71.0	-101.1 1.9	-97.3
Heptane	1.88	7.56	-91.7 1.6	-73.7	-104.1 2.5	-102.1
Octane	1.88	8.82	-96.7 0.9	-76.5	-105.2 1.5	-107.0
Nonane	1.88	10.08	-101.4 2.3	-79.2	-108.6 1.4	-111.8
Decane	1.88	11.34	-108.1 0.5	-81.9	-112.0 0.7	-116.6
			S.D.= 21.9		S.D.= 3.9	

a) $a = 1.88$ and $l = 20.30$ Å. b) $a = 2.96$ and $l = 3.07$ Å. c) In units of J/(K mol).

As for the system of alkanes dissolved in DDCO, the size of alkanes were taken as the same as those in above case. The S.D. value was tested thoroughly by varying the size of solvent. This value was found to change rather monotonously depending on the radius and length of the solvent, and the minimum of S.D. appeared at the size of solvent smaller than the maximum distances above mentioned($l = 3.37$ and $a = 3.26$ Å). When the same value is subtracted from both *l* and *a* considering the effective size of the solvent, $l = 3.07$ and $a = 2.96$ Å afford the S.D. value of 3.9 J/(K mol). For this size of solvent, the compactness factor y amounts to 0.55. When the size is taken as $l = 2.97$ and $a = 2.86$ Å, for which the compactness factor is 0.50, the S.D. value is increased slightly and equal to 4.5 J/(K mol). In this way, the entropies of solution of alkanes dissolved in DDCO are interpreted satisfactorily by the scaled particle treatment for non-spherical molecules.

The standard deviation is relatively large for the HPDN system, whereas it is satisfactorily small for the DDCO system(Table 1). The entropy term of solute-solvent interactions omitted in Eq. 1 is thought not to affect this deviation seriously, since the calculation is carried out quite successfully in the DDCO system. In contrast to DDCO, HPDN is composed of a long alkyl chain which is flexible and can take coiled forms other than the stretched one assumed. This effect is responsible to the relatively large deviation in the HPDN system.

Calculations based on a spherical model are also available for spherocylinder and disk molecules by setting the length of l and λ in spherocylinders and the radii r and α in disks equal to zero. When the radii of alkanes are cited from the standard values,[6] the S.D. value becomes very large for both of the solvents studied here, amounting to near 40 J/(K mol), in a range of a realistic values of the compactness factor y of the solvent from 0.4 to 0.6. Therefore, the spherical model is not satisfactory in interpreting the entropies of solution treated here.

In conclusion, the entropies of solution measured above can be interpreted for the most part by the scaled particle theory when non-spherical shape of molecules is taken into account. Hence, the cavity formation in solvent is supported to play an important role in the process of dissolution when viewed from the standpoint of entropies.

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