The Entropy of Solution of Alkanes Measured by Gas-Liquid Chromatography and Interpreted by Means of Scaled Particle Theory†

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The entropy of solution was measured by gas-liquid chromatography for the alkanes from pentane to decane in dibutyl phthalate solution. The results are discussed in relation to the Wertz-type equation, which correlates the entropy of solution with the thermodynamic third-law entropy of the solute, and to the scaled particle theory. A scaled particle treatment assuming non-spheres(spherocylinders) is shown to give improved results and to be promising in reproducing the experimental values of the entropy of solution, whereas the same treatment of spheres failed to explain the trend in the experimental values.

The entropy of reaction in gas phase can be predicted in principle by a molecular statistical theory for thermodynamic functions, since it is equal to the standard entropy of the products minus that of the reactants.[1] However, it is usually not easy to estimate the entropy of a reaction in solution, because each component is solvated more or less in solution and its entropy is considerably affected by the state of solvation. In this sense, the entropy of solution, which represents the difference in entropy between the two phases of gas and solution, becomes important for the understanding of the entropy of reaction in solution.

The authors have previously reported the entropy of reaction in solution in the case of a metal complex formation of organotin compounds[2] and of an inclusion complex formation of α-cyclodextrin with alcohols,[3] where an equation proposed by Wertz[4,5] was utilized to estimate the entropy of solution. In the Wertz-type equaion, molecules are assumed to lose a definite part of their gas phase entropy when transferred from the gas phase to solution. Hence the entropy of solution is expressed as a function of the thermodynamic third-law entropy in the gas phase. In an alternative more theoretical approach, scaled particle theory can give an estimate for the entropy of solution.[6,7] This approach is reported to give reasonable results for nonpolar solutes dissolved in water but not for those dissolved in nonaqueous solvents.[8]

In the present study, the entropy of solution of alkanes in an organic solvent is measured by means of gas-liquid chromatography, and the data are discussed in terms of the scaled particle theory, taking into account the effect of the molecular shape of solute and solvent. As an organic solvent, dibutyl phthalate is chosen. The solutes used are the normal alkanes from pentane to decane.

Experimental

Dibutyl phthalate for the chromatographic stationary phase (solvent) was distilled under reduced pressure, and coated on 60/80 mesh Chromosorb W AW-DMCS (25 wt%). The alkanes from commercial sources were used without further purification. The retention data were measured on a Yanagimoto G1880 gas chromatograph with a TCD cell using a carrier of He gas. The column temperature was measured with a copper-constantan thermocouple. The temperature range studied was from 58 °C to 103 °C. The retention time was measured 5 times at each temperature and averaged. The amount of solute injected was 2 μl. A correction for the vanishing amount of sample injected was not made because it was negligibly small in a preliminary experiment.

Calculations of the above retention data and the entropy of solution described below were all done by using programs written in Basic mode and compiled on personal computers of the NEC 9800 series.

Results

Determination of the Entropy of Solution by Means of Gas-Liquid Chromatography. The partition coefficient (k) is related to the specific retention volume V_g as in Eq. 1 when k, which is defined as the ratio of the concentrations in the gas and liquid phases, is represented as atm (in gas phase)/mol fraction (in liquid).[9] In Eq. 1, M_1 means the molar

$$k=\{M_1/(273.15R)\}V_g \tag{1}$$

weight of solvent and R is the gas constant. The temperature dependence of k affords the enthalpy (ΔH_s^0) and entropy (ΔS_s^0) of solution (Eq. 2).

$$\ln k=-\Delta H_s^0/(RT)+\Delta S_s^0/R \tag{2}$$

The measurement of retention times of solutes (t_s) and air (t_a) on the chromatograph provides the value of the specific retention volume:[10]

$$V_g=\{(t_s-t_a)jF/W\}(273.15/T) \tag{3}$$

where j, F, and W are the correction factor for the pressure, the flow rate of carrier gas, and the weight of solvent in the column, respectively.

A typical plot of ln k vs. $1/T$ in Eq. 2 is shown in Fig. 1. The values of ΔH_s^0 and ΔS_s^0 thus determined are summaried in Table 1. Errors in these values were

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† The Solvation Effect on the Reactions in Solution. III.

Table 1. Enthalpies and Entropies of Solution for Alkanes in Dibutyl Phthalate Determined from Gas-Liquid Chromatography[a]

Solute	ΔH_s^0/kJ mol^{-1}	ΔS_s^0/JK^{-1} mol^{-1}
Pentane	−22.3±3.0	−80.6±8.6
	(−20.2±3.0)	(−36.0±8.6)
Hexane	−28.2±0.8	−90.2±2.4
	(−26.1±0.9)	(−45.6±2.5)
Heptane	−32.1±0.9	−94.0±2.5
	(−30.1±0.9)	(−49.4±2.5)
Octane	−34.8±0.9	−94.7±2.5
	(−32.7±0.9)	(−50.2±2.6)
Nonane	−38.3±0.8	−97.9±2.2
	(−36.2±0.8)	(−53.4±2.3)
Decane	−41.9±12.7	−101.8±37.0
	(−39.8±12.8)	(−57.3±37.4)

[a] The values are given for the standard states of 1 atm in gas phase and 1 mole fraction in liquid phase. Also listed in parentheses are the values for the standard state of 1 mol dm^{-3} in these two phases.

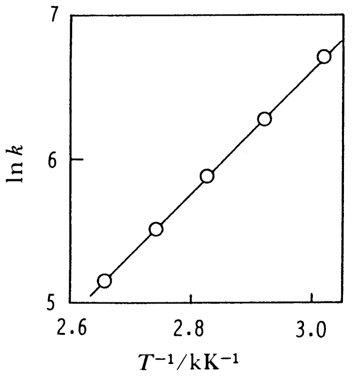

Fig. 1. The Plot of ln *k* measured by gas-liquid chromatography vs. 1/*T* for nonane in dibutyl phthalate.

estimated as equal to the 95% confidence range in the plot of ln *k* vs. 1/*T*. The values thus determined corresponds to a reference state of 1 atm in the gas phase and 1 mole fraction in the liquid phase. These values are discussed below in terms of the scaled particle theory. Also the values of ΔH_s^0 and ΔS_s^0 can be defined for a reference state of 1 mol dm^{-3} for both the gas and liquid phases. In this case, the partition coefficient (*K*) is expressed as the ratio of the molar concentration in the gas and liquid phases, and Eq. 1 is replaced by Eq. 4,[9]

$$K=(T\,\rho_1/273.15)\,V_g \tag{4}$$

where ρ_1 is the density of solvent. The plot of ln *K* vs. 1/*T* affords the ΔH_s^0 and ΔS_s^0 under a reference state of 1 mol dm^{-3} for both gas and liquid phases. The values thus determined are also listed in Table 1 in parentheses,[11] where the density of the dibutyl phthalate (ρ_1) was approximated by an equation,

$$\rho_1=-0.000805T+1.0615 \tag{5}$$

from the data between 79.4 and 142.2 °C.[12]

Discussion

The Wertz-type equation is derived as in Eq. 6 from the values of ΔS_s^0 given under the reference state of 1 mol dm^{-3} and from those of S_{298}^0 (g).[13]

$$\underset{(0.043)}{\Delta S_s^0=-0.095}\,S_{298}^0\,(g)\underset{(19.3)}{-6.0} \qquad r=0.952 \tag{6}$$

In this equation *r* is the correlation coefficient between the observed and the recalculated values of ΔS_s^0. The standard errors are listed in parentheses. This equation resembles that given for alkylbenzenes dissolved in dimethyl or dioctyl phthalate.[2] Although the Wertz-type equation can be predicted from the physical constants of the solvent, this was not possible in the present case because of the lack of S_{298}^0 of DBP in the gas and liquid phases. It is reported,[5] and also observed by the present authors, that the coefficients of the Wertz-type equation vary depending on the series of compounds treated. Therefore, an alternative theoretical approach is attempted below on the basis of a scaled particle theory.

Calculation of the Entropy of Solution under a Sphere Model. According to the scaled particle theory, the entropy of solution is given as in Eq. 7 for the spherical molecules of solute as well as for the solvent, where the terms for cavity formation and for a correction for the different reference states in the gas and liquid phases are included.[5]

$$\Delta S_s^0=S_{\mathrm{cav}}+\alpha_p RT-R-R\ln\,(V_g/V_l) \tag{7}$$

In this equation, α_p is the thermal expansion coefficient of the solvent, and V_g/V_l is equal to RT/V_1 under an ideal-gas assumption, V_1 being the molar volume of solvent. S_{cav} in Eq. 7 is calculated as in Eq. 8 according to the definition of $S=-(\partial G/\partial T)_P$ and to the equation for *G* given in Refs. 6 and 7:

$$\begin{aligned}S_{\mathrm{cav}}=R\,[&\{\ln(1-y)-3y/(1-y)\cdot(\sigma_2/\sigma_1)\\ &-(3y/2)(2+y)/(1-y)^2\cdot(\sigma_2/\sigma_1)^2\}\\ &+\alpha_p yT/(1-y)^3\cdot\{(1-y)^2+3(1-y)(\sigma_2/\sigma_1)\\ &+3(1+2y)(\sigma_2/\sigma_1)^2\}]\end{aligned} \tag{8}$$

where σ_1 and σ_2 are the diameter of solvent and solute, respectively, and where *y* is called a "reduced number density"[7] or a "compactness factor"[14] of the solvent which is equal to $\pi\rho_1\sigma_1^3/6$, ρ_1 being the number density of solvent (N_A/V_1). The value of σ_2 is usually estimated by the Stearn-Eyring equation:[8] $(\sigma_2)^3=V/N_A$ where *V* is the molar volume and N_A the Avogadro number. The best method of obtaining σ_1 is to utilize the Henry's law constants of rare gases in the relevant solvent. However, these constants are lacking, within the knowledge of the authors, and so σ_1 is also taken from the Stearn-Eyring equation. The values of ΔS_s^0 thus estimated lie between −55.1 J (K·mol)$^{-1}$ for pentane and −56.5 J (K·mol)$^{-1}$ for decane (Table 2): they only amount to around 60% of the experimental values, and the dependency on the carbon number of the solute is small compared to the experimental results. These estimated values are not improved even if σ_1 is varied near the initial values of 7.74 Å (Fig. 2). Therefore, it is clear that the sphere model fails to explain the experimental values measured in dibutyl phthalate. Similar results are reported[8] for other nonaqueous solvents. In the present study an alternative model which assumes spherocylinderical shapes for the solute and solvent molecules is attempted below.

Calculation of the Entropy of Solution under a Spherocylinder Model. For nonspherical molecules of solute and solvent, a scaled particle treatment has been developed for the spherocylinders in isotropic as well as anisotropic solutions.[15] In this case S_{cav} turns out to be a function of a, l, α, λ, V_1, α_p, and T as in Eq. 9,

$$\begin{aligned} S_{cav}=R[&\ln X+(\alpha_p T/X)(1-X)\\ &+(\alpha_p T/X-1)\{\pi a(l+2a)\rho_1/X\}(2\alpha+\lambda/2)\\ &+(\alpha_p T/X-1)\{\pi(l+4a)\rho_1/X\}(\alpha\lambda/2+\alpha^2)\\ &+(2\alpha_p T/X-1)\{\pi a(l+2a)\rho_1/X\}^2(\alpha\lambda+2\alpha^2)] \end{aligned} \tag{9}$$

Table 2. The Entropy of Solution Calculated for the Sphere Model[a)]

Solute	$\Delta S^0_{s,\,\mathrm{exptl}}$[b)]	σ_2[c)]	$\Delta S^0_{s,\,\mathrm{calcd}}$
Pentane	−80.6	5.78	−55.1
Hexane	−90.2	6.02	−55.3
Heptane	−94.0	6.26	−55.6
Octane	−94.7	6.48	−55.8
Nonane	−97.9	6.83	−56.2
Decane	−101.8	7.08	−56.5

a) Given in a unit of $\mathrm{J\,(K\cdot mol)^{-1}}$. The molar volume and the thermal expansion coefficient are 279.19 $\mathrm{ml\,mol^{-1}}$ and 0.840/1000 K, respectively, for the solvent. b) Experimental values. c) The diameter of the solute in Å.

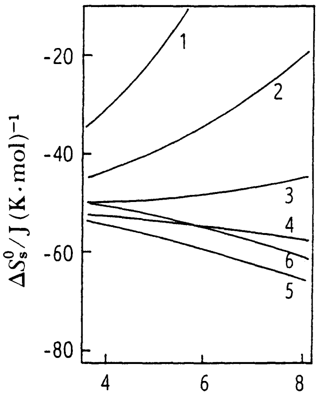

Fig. 2. The dependence of the calculated ΔS^0_s on the values of σ_1 and σ_2. Calculated under the sphere model by the use of Eq. 7. The values of σ_1 are 8.34, 8.14, 7.94, 7.74, 7.34, and 5.74 Å for curves 1 to 6, respectively. Note that the curve shifts upward in the figure on decreasing the values of σ_1 from 7.34 Å, whereas the experimental values ranges from −80 to −101 $\mathrm{J\,(K\cdot mol)^{-1}}$. The value of σ_1 estimated from the Stearn-Eyring equation is 7.74 Å.

where $X=1-\pi a^2 l\rho_1-4\pi a^2\rho_1/3$, and where α and λ are the radius and length of the solute molecule, respectively, and a and l those of the solvent, respectively (Fig. 3). Equation 9 is derived from Eq. 51 in Ref. 14, assuming that $\ln P_0$ in this reference is equal to $-G_{cav}/RT$ and $S_{cav}=-(\partial G_{cav}/\partial T)_P$. This model is equivalent to the above sphere model when l and λ are both taken as zero.

For the sake of model calculations, the size of the solute and solvent is estimated from the dimension of a single molecule. For solute molecules, a zigzag conformation is assumed and α is taken as the distance from the longer axis of symmetry to the CH_2 protons plus the van der Waals radius of hydrogen, λ being taken as a distance between the two end carbons (Fig. 4). The size of the solvent is not derived straightforwardly, a is set equal to 2.63 Å, a radius of the sphere for benzene derived from the Stearn-Eyring equation, and l is set equal to 7.77 Å to make the reduced number density equivalent to the sphere of radius 3.87 Å derived from the Stearn-Eyring equation for DBP. These values of a and l give the calculated values of $\Delta S^0_s/\mathrm{J\,(K\cdot mol)^{-1}}$ amounting from −55.0 for pentane to −59.1 for decane. When the values of a and l are estimated from a molecular model, where the two butyl ester groups extend to the same direction in the same manner, a=2.70 Å and l=4.53 Å are obtained. These values give much improved results as is shown by "spherocylinders" in Fig. 5, i.e., $\Delta S^0_s/\mathrm{J\,(K\cdot mol)^{-1}}$= −66.5 for heptane and −76.4 for decane. For these values of a and l, the reduced number density is equal to 0.41 and is well within a reasonable range. Therefore, a proper estimation of the size of the solvent

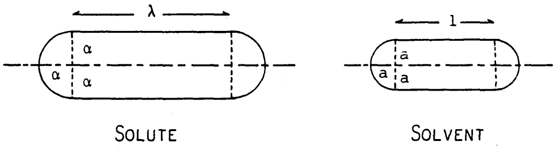

Fig. 3. The spherocylinder model of solute and solvent. –·–·–: the axis of rotation of the rotamer. α and a: the radius of semisphere. λ and l: the length of the part of cylinder.

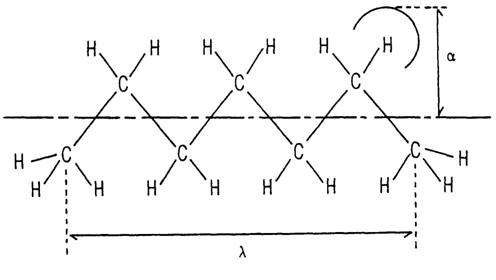

Fig. 4. The size of solute, α and λ, depicted typically for heptane. α is equal to 2.58 Å when the van der Waals radius of 1.2 Å is added. –·–·–: The longer axis of rotation.

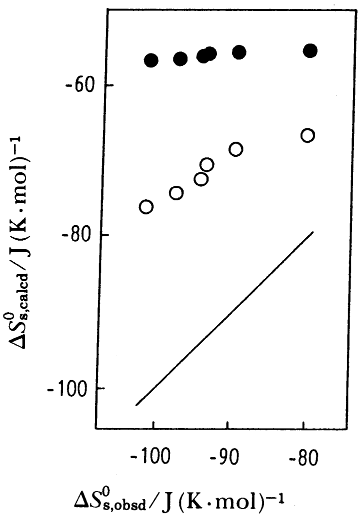

Fig. 5. The plot of ΔS^0_{s} calculated under the sphere and the spherocylinder models vs. $\Delta S^0_{\mathrm{s,obsd}}$. ●: Calculated by means of the sphere model. ○: Calculated by means of the spherocylinder model. ——: The ideal interrelation of $\Delta S^0_{\mathrm{s,calcd}}=\Delta S^0_{\mathrm{s,obsd}}$.

molecule is expected to give much improved calculations of the entropy of solution. However, more elaborate calculations are not attempted here, because the solvent used in the present study is rather complicated in structure including polar groups. More elaborate calculations are now underway for a few solvents better approximated by simple rotamers such as disks, cylinders, and spherocylinders.

It has been reported,[8] and also confirmed by the authors that the entropy of solution of alkanes in water is well reproduced by calculations based on a sphere model. Contrary to this, the entropy of solution in an organic solvent treated here is better reproduced by a non-sphere model which assumes spherocylinders. Such a contrast may be interpreted as due to the difference in the shape of the solvent and also to the shape of the solute in each solvent. That is, the alkanes are considered to take on a rather spherical form in water as a result of the intramolecular hydrophobic interaction within a single molecule whereas they are considered to acquire a stretched form in organic solvents depending on the solute-solvent interactions in solution.

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