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## ENTROPY OF SOLUTION AT INFINITE DILUTION OF 1-HALOGENOALKANES IN *n*-ALKANE SOLVENTS DETERMINED BY GAS-LIQUID CHROMATOGRAPHY

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### SUMMARY

Vapour-liquid equilibrium constants at infinite dilution of 1-chloroalkane, 1-bromoalkane and 1-iodoalkane solutes in *n*-octacosane, *n*-dotriacontane and *n*-hexatriacontane solvents were determined by gas-liquid chromatography at five temperatures, 78.0, 84.0, 90.0, 96.0 and 102.0°C. From these constants, the entropy of solution from the gas phase to infinitely dilute solution was evaluated. The entropy of solution is discussed on the basis of a linear relationship between the number of CH<sub>2</sub>, CH<sub>3</sub>, Cl, Br and I groups in the solute molecule and the nature of the solvent molecules. It could be related to the structures of the solute and solvent molecules.

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### INTRODUCTION

Gas-liquid chromatography (GLC) is an effective and advantageous method for determining thermodynamic properties of infinitely dilute solutions. The thermodynamic properties of solution at infinite dilution have been determined by GLC<sup>1-17</sup>. The interactions between the solute and solvent molecules were interpreted in terms of current theories of solutions. In this study the entropies of solution of 1-halogenoalkanes (1-chloro-, 1-bromo- and 1-iodoalkanes) from their vapours to infinitely dilute solutions in long chain *n*-alkanes are evaluated.

Specific retention volumes determined by GLC can provide vapour-liquid equilibrium constants at infinite dilution, which in turn yield the entropy of solution at infinite dilution. The entropy is analyzed by utilizing equations which describe the molecule-molecule interactions. These interactions can be estimated from a consistent set of values for all solute-solvent systems studied.

### EXPERIMENTAL

The gas chromatograph used (Shimadzu GC-6A) was equipped with a thermal conductivity detector. The column temperature could be maintained constant within 0.1°C. Hydrogen was used as a carrier gas. The carrier gas flow-rate was measured at room temperature with a soap-film flowmeter placed at the detector outlet. The

inlet and outlet pressures of the carrier gas were determined by mercury manometry.

The stationary liquids *n*-octacosane (*n*-C<sub>28</sub>H<sub>58</sub>), *n*-dotriacontane (*n*-C<sub>32</sub>H<sub>66</sub>) and *n*-hexatriacontane (*n*-C<sub>36</sub>H<sub>74</sub>) were obtained from Tokyo Chemical Industry Co. (Tokyo, Japan). They were purified by recrystallization from ethanol. The solutes 1-chloroalkanes, 1-bromoalkanes and 1-iodoalkanes were used without further purification.

The liquid stationary phase was coated on the solid support (hexamethyldisilazane-treated Celite 545, 80–100 mesh) in the usual manner. The amount of each liquid phase was varied from 8 to 15 wt. %. The coated support was packed into 1 m × 3 mm I.D. stainless-steel tubing. For a reference, support which was not coated with stationary liquid was packed into another tubing. Each column was conditioned at 110°C for about 24 with a gentle flow of a carrier gas. The minimum detectable sample sizes were used at all times so as to ensure operation in the Henry's law region of solute concentrations<sup>18,19</sup>. Samples were injected together with a detectable amount of air. The retention times the solutes were corrected for an air peak. The exact weight of stationary liquid was determined by Soxhlet extraction with *n*-hexane after each experiment.

The specific retention volumes of 1-chloroalkanes, 1-bromoalkanes and 1-iodoalkanes in the stationary liquids *n*-C<sub>28</sub>H<sub>58</sub>, *n*-C<sub>32</sub>H<sub>66</sub>, and *n*-C<sub>36</sub>H<sub>74</sub> were measured at five temperatures, 78.0, 84.0, 90.0, 96.0 and 102.0°C.

## RESULTS AND DISCUSSION

### *Specific retention volumes*

The specific retention volumes of C<sub>5</sub>–C<sub>8</sub> 1-chloroalkanes, C<sub>4</sub>–C<sub>7</sub> 1-bromoalkanes and C<sub>2</sub>–C<sub>5</sub> 1-iodoalkanes in three stationary liquids, *n*-C<sub>28</sub>H<sub>58</sub>, *n*-C<sub>32</sub>H<sub>66</sub> and *n*-C<sub>36</sub>H<sub>74</sub>, were determined by GLC. The standard deviation of the specific retention volumes under various experimental conditions, *e.g.*, weight of stationary liquid and carrier gas flow-rate, was estimated to be within 0.5% for all solute–solvent systems studied.

The effects of solute adsorption onto the surface of the support material and treatment of the active sites on the support with hexamethyldisilazane upon the retention volumes were also studied. A column packed with solid support, which was not coated with a stationary liquid was used for this purpose. In this case the GLC peaks of air and *n*-heptane could not be separated at column temperatures of 60.0 and 90.0°C. The above two effects were almost negligible.

Specific retention volumes of 1-halogenoalkanes are listed in Table I. Corresponding values for *n*-alkanes (C<sub>6</sub>–C<sub>10</sub>) were published previously<sup>20</sup>. Some of the specific retention volumes are compared with literature values<sup>9</sup> in Table II.

### *Vapour–liquid equilibrium constants*

The vapour–liquid equilibrium constant,  $K_p$ , *i.e.*, Henry's law constant, of a solute in solution is generally expressed as follows

$$K_p = p_2/x_2 \quad (1)$$

where  $p_2$  is the vapour pressure of solute in the vapour phase in equilibrium with the

TABLE I

SPECIFIC RETENTION VOLUMES,  $V_R$  ( $\text{cm}^3 \text{g}^{-1}$ )

Solutes: 1-Cl-C<sub>5</sub> = 1-chloropentane; 1-Cl-C<sub>6</sub> = 1-chlorohexane; 1-Cl-C<sub>7</sub> = 1-chloroheptane; 1-Cl-C<sub>8</sub> = 1-chlorooctane; 1-Br-C<sub>4</sub> = 1-bromobutane; 1-Br-C<sub>5</sub> = 1-bromopentane; 1-Br-C<sub>6</sub> = 1-bromohexane; 1-Br-C<sub>7</sub> = 1-bromoheptane; 1-I-C<sub>2</sub> = 1-iodoethane; 1-I-C<sub>3</sub> = 1-iodopropane; 1-I-C<sub>4</sub> = 1-iodobutane; 1-I-C<sub>5</sub> = 1-iodopentane.

Solute	Temperature ( $^{\circ}\text{C}$ )				
	78.0	84.0	90.0	96.0	102.0
<i>In n-C<sub>28</sub>H<sub>58</sub></i>					
1-Cl-C <sub>5</sub>	249.2	209.2	175.6	147.5	123.9
1-Cl-C <sub>6</sub>	582.9	475.2	388.1	317.6	260.4
1-Cl-C <sub>7</sub>	1354.7	1073.1	852.9	680.1	544.2
1-Cl-C <sub>8</sub>	3134	2413	1865	1449	1130
1-Br-C <sub>4</sub>	213.5	180.7	153.2	130.1	110.7
1-Br-C <sub>5</sub>	501.0	412.0	339.8	281.0	233.1
1-Br-C <sub>6</sub>	1161.8	929.3	745.9	600.9	485.7
1-Br-C <sub>7</sub>	2699	2094	1632	1280	1009
1-I-C <sub>2</sub>	88.82	78.21	68.67	60.10	52.45
1-I-C <sub>3</sub>	212.8	181.7	155.0	132.1	112.5
1-I-C <sub>4</sub>	495.7	411.8	341.9	283.7	235.3
1-I-C <sub>5</sub>	1134.5	918.2	742.8	600.9	485.9
<i>In n-C<sub>32</sub>H<sub>66</sub></i>					
1-Cl-C <sub>5</sub>	233.9	195.2	163.8	138.2	117.3
1-Cl-C <sub>6</sub>	546.4	443.8	362.6	297.9	246.1
1-Cl-C <sub>7</sub>	1269.2	1000.7	794.8	635.8	512.4
1-Cl-C <sub>8</sub>	2938	2246	1733	1350	1061
1-Br-C <sub>4</sub>	201.4	169.6	134.5	122.0	104.4
1-Br-C <sub>5</sub>	473.4	387.4	319.1	264.5	220.6
1-Br-C <sub>6</sub>	1099.0	874.0	700.1	564.9	459.1
1-Br-C <sub>7</sub>	2548	1968	1532	1203	952.2
1-I-C <sub>2</sub>	85.04	74.38	65.12	57.07	50.07
1-I-C <sub>3</sub>	203.9	172.5	146.7	125.5	108.0
1-I-C <sub>4</sub>	473.7	389.6	322.5	268.7	225.3
1-I-C <sub>5</sub>	1085.1	867.1	698.7	567.9	465.4
<i>In n-C<sub>36</sub>H<sub>74</sub></i>					
1-Cl-C <sub>5</sub>	221.2	183.6	153.4	129.0	109.1
1-Cl-C <sub>6</sub>	515.8	417.1	339.4	277.9	229.0
1-Cl-C <sub>7</sub>	1195.4	939.9	744.0	592.9	475.7
1-Cl-C <sub>8</sub>	2763	2110	1623	1258	982.7
1-Br-C <sub>4</sub>	191.2	159.6	134.5	114.5	98.35
1-Br-C <sub>5</sub>	449.2	365.2	299.5	247.8	206.9
1-Br-C <sub>6</sub>	1042.9	821.2	654.3	527.5	430.3
1-Br-C <sub>7</sub>	2418	1847	1430	1122	892.0
1-I-C <sub>2</sub>	82.79	71.71	62.36	54.44	47.72
1-I-C <sub>3</sub>	198.6	165.7	139.6	118.8	102.1
1-I-C <sub>4</sub>	461.1	373.2	305.7	253.5	212.8
1-I-C <sub>5</sub>	1052.1	833.8	666.9	538.4	438.6

TABLE II

COMPARISON OF EXPERIMENTAL SPECIFIC RETENTION VOLUMES,  $V_g$ Solvent (stationary phase):  $n\text{-C}_{36}\text{H}_{74}$ . Temperature: 84.0°C.

Solute	$V_g$ ( $\text{cm}^3 \text{g}^{-1}$ )	
	This work*	Ref. 9
1-Cl-C <sub>5</sub>	140.4	138.8
1-Cl-C <sub>6</sub>	319.0	316.4
1-Cl-C <sub>7</sub>	718.8	724.6

\* Values corrected to  $V_g$  through eqn. 4.

liquid mixture which contains a mole fraction,  $x_2$ , of the solute.

Strictly speaking, the pressure  $p_2$  should be expressed in the terms of the fugacity,  $f_2$ , of the solute. The relationship between  $p_2$  and  $f_2$  can be expressed as follows

$$f_2 = p_2 \exp[(2B_{23} - B_{33})p/RT] \quad (2)$$

where  $p$  is the total pressure of the gas phase,  $B_{23}$  the mixed second virial coefficient of the solute vapour and carrier gas and  $B_{33}$  the second virial coefficient of the carrier gas;  $R$  is the gas constant and  $T$  the absolute temperature of the GLC column.

According to several GLC theories, the specific retention volume can be related to the partition coefficient. From the relationship between the vapour-liquid equilibrium constant and the partition coefficient, the former is given by

$$K_p^\infty = \frac{RT}{M_r V_R} \cdot \exp[(2B_{23} - B_{33})p/RT] \quad (3)$$

where  $M_r$  is the molecular weight of the stationary liquid. The actual specific retention volume,  $V_R$ , represents the real volume of a carrier gas passing through the GLC column. It is related to the currently used specific retention volume,  $V_g$ , by:

$$V_R = \frac{T}{273.15} \cdot V_g \quad (4)$$

The pressure  $p$  is given by the mean pressure along the column.

#### Thermodynamics of solution

The chemical potential of the solute in the gas phase and that in solution are given by

$$\mu(\text{g}) = G_2^0(\text{g}) + RT \ln f_2 \quad (5)$$

$$\mu(\text{l}) = G_2^0(\text{l}) + RT \ln x_2 \gamma_2 \quad (6)$$

where  $f_2$  is the fugacity of the solute in the gas phase and  $x_2$  and  $\gamma_2$  are the mole

fraction and activity coefficient of the solute in the solution, respectively. The standard molar free energy of the solute,  $G_2^0(\text{g})$ , in the gas phase is given by the molar free energy at  $f_2 = 1$  atm. The standard molar free energy of the solute,  $G_2^0(\text{l})$ , in solution is given by the standard molar free energy at infinite dilution. This standard state in solution is applicable when  $\gamma_2 \rightarrow 1$  as  $x_2 \rightarrow 0$ <sup>15,19</sup>.

At equilibrium,  $\mu(\text{g})$  is equal to  $\mu(\text{l})$ . The standard molar free energy of solution,  $\Delta\bar{G}_{\text{soln}}$ , from the gas phase to solution is given by:

$$\begin{aligned}\Delta\bar{G}_{\text{soln}} &= G_2^0(\text{l}) - G_2^0(\text{g}) \\ &= RT \ln f_2 - RT \ln x_2\gamma_2\end{aligned}\quad (7)$$

For hydrogen as a carrier gas, both  $B_{23}$  and  $B_{33}$  are less than  $50 \text{ cm}^3$  for most solutes studied. Neglecting the exponential term in eqn. 3, we have a relative error of 0.3% in the value of the vapour-liquid equilibrium constant. Under the GLC conditions,  $x_2$  is always near to 0. Hence, the activity coefficient of the solute,  $\gamma_2$ , is unity in this study. The standard molar free energy of solution at infinite dilution is related to the vapour-liquid equilibrium constant,  $K_p^\infty$ , by the following equation:

$$\Delta\bar{G}_{\text{soln}}^\infty = RT \ln K_p^\infty \quad (8)$$

The standard molar free energies of solution could be calculated from the values of the specific retention volumes using eqns. 3 and 8.

#### Entropy of solution

The standard molar entropy of solution,  $\Delta\bar{S}_{\text{soln}}^\infty$ , from the vapour phase to an infinitely dilute solution could be determined from the temperature dependence of the standard molar free energy of solution:

$$\Delta\bar{S}_{\text{soln}}^\infty = - \left[ \frac{\partial(\Delta\bar{G}_{\text{soln}}^\infty)}{\partial T} \right]_p \quad (9)$$

The standard molar entropy of solution of *n*-alkanes, 1-chloroalkanes, 1-bromoalkanes and 1-iodoalkanes from the vapour phase to *n*-alkane solvents are given in Table III.

The difference between the values of the entropy of solution of a given solute in different solvents is found to be independent of the kind of solute. It can be estimated from the nature of the solvent molecules. The contribution of the entropy due to the solvent is denoted by  $\Delta S_{\text{solv}}$ .

The entropies have linear relationships with the number of carbon atoms of the solute molecule for each type of solutes. The increment of the entropy is constant for all types of solutes. The entropy of solution is given by

$$\begin{aligned}\Delta\bar{S}_{\text{soln}}^\infty &= n_{\text{CH}_2}\Delta S_{\text{CH}_2} + n_{\text{CH}_3}\Delta S_{\text{CH}_3} + n_{\text{Cl}}\Delta S_{\text{Cl}} \\ &+ n_{\text{Br}}\Delta S_{\text{Br}} + n_{\text{I}}\Delta S_{\text{I}} + \Delta S_{\text{solv}}\end{aligned}\quad (10)$$

TABLE III

PARTIAL MOLAR ENTROPIES OF SOLUTION AT INFINITE DILUTION,  $\Delta\bar{S}_{\text{soln}}^{\infty}$  ( $\text{J K}^{-1} \text{mol}^{-1}$ )Solutes:  $n\text{-C}_6 = n\text{-Hexane}$ ;  $n\text{-C}_7 = n\text{-heptane}$ ;  $n\text{-C}_8 = n\text{-octane}$ ;  $n\text{-C}_9 = n\text{-nonane}$ ;  $n\text{-C}_{10} = n\text{-decane}$ .

Solute	Solvent		
	$n\text{-C}_{28}\text{H}_{58}$	$n\text{-C}_{32}\text{H}_{66}$	$n\text{-C}_{36}\text{H}_{74}$
$n\text{-C}_6$	- 84.80 ± 0.60	- 83.90 ± 0.66	- 84.08 ± 0.23
$n\text{-C}_7$	- 90.80 ± 0.44	- 90.90 ± 0.36	- 90.09 ± 0.36
$n\text{-C}_8$	- 97.50 ± 0.43	- 97.89 ± 0.30	- 97.58 ± 0.34
$n\text{-C}_9$	-104.99 ± 0.29	-105.79 ± 0.04	-105.98 ± 0.50
$n\text{-C}_{10}$	-111.49 ± 0.23	-112.32 ± 0.03	-112.33 ± 0.65
1-Cl- $\text{C}_5$	- 89.16 ± 0.98	- 87.54 ± 0.11	- 89.11 ± 0.05
1-Cl- $\text{C}_6$	- 96.05 ± 0.87	- 94.44 ± 0.22	- 95.81 ± 0.11
1-Cl- $\text{C}_7$	-102.84 ± 0.77	-101.66 ± 0.09	-103.03 ± 0.20
1-Cl- $\text{C}_8$	-109.98 ± 0.75	-109.13 ± 0.10	-110.65 ± 0.23
1-Br- $\text{C}_4$	- 85.00 ± 0.66	- 84.51 ± 0.07	- 84.91 ± 0.65
1-Br- $\text{C}_5$	- 92.00 ± 0.63	- 91.21 ± 0.06	- 92.18 ± 0.38
1-Br- $\text{C}_6$	- 98.94 ± 0.68	- 98.41 ± 0.05	- 99.49 ± 0.72
1-Br- $\text{C}_7$	-106.54 ± 0.52	-105.87 ± 0.06	-107.04 ± 0.82
1-I- $\text{C}_2$	- 75.41 ± 1.31	- 75.06 ± 0.62	- 77.08 ± 0.15
1-I- $\text{C}_3$	- 82.57 ± 1.14	- 81.53 ± 0.06	- 84.65 ± 0.70
1-I- $\text{C}_4$	- 89.52 ± 1.20	- 88.51 ± 0.03	- 91.72 ± 0.94
1-I- $\text{C}_5$	- 95.98 ± 1.29	- 95.07 ± 0.21	- 98.04 ± 0.30

where  $\Delta S_{\text{soln}}$  is the value corresponding to the nature of the solvent; its value is dependent only on the solvent. The stationary liquid  $n\text{-C}_{36}\text{H}_{74}$  is taken as a standard solvent.

The other terms are independent of the solvent. The variation of  $\Delta\bar{S}_{\text{soln}}^{\infty}$  caused by a change in the number of  $\text{CH}_2$  groups in a solute molecule is indicated by  $\Delta S_{\text{CH}_2}$ ;  $n_{\text{CH}_2}$  denotes the number of  $\text{CH}_2$  groups in the alkyl chain of a solute molecule. The contribution of  $\text{CH}_3$  groups and functional groups Cl, Br and I to the value of the entropy of solution are represented by  $\Delta S_{\text{CH}_3}$ ,  $\Delta S_{\text{Cl}}$ ,  $\Delta S_{\text{Br}}$  and  $\Delta S_{\text{I}}$ , respectively.  $n_{\text{CH}_3}$ ,  $n_{\text{Cl}}$ ,  $n_{\text{Br}}$  and  $n_{\text{I}}$  are the numbers of methyl groups and chlorine, bromine and iodine atoms in the solute molecule.

By use of the method of least squares, the standard entropy terms for methylene, methyl, chlorine, bromine and iodine in eqn. 10 can be determined. They are given in Table IV.

The small magnitude of the standard deviation of these parameters suggests that the entropy of solution at infinite dilution has a linear relationship with the number of segments, such as the methylene and methyl groups and chlorine, bromine and iodine atoms, in a solute molecule. The partial entropy of each of the segments except methylene is linearly related with the volume of the segment. The trifling value of the parameter for  $\text{CH}_2$ ,  $\Delta S_{\text{CH}_2}$ , shows that the free movement of methylene groups, such as rotation and bending, is restricted by its rigidity because the degree of spatial freedom reflects on the entropy. This fact means less flexibility of methylene groups in solution.

TABLE IV

PARTIAL ENTROPIES OF SOLUTION AS A FUNCTION OF  
 $\Delta\bar{S}_{\text{soln}}^{\infty} = n_{\text{CH}_2} \Delta S_{\text{CH}_2} + n_{\text{CH}_3} \Delta S_{\text{CH}_3} + n_{\text{Cl}} \Delta S_{\text{Cl}} + n_{\text{Br}} \Delta S_{\text{Br}} + n_1 \Delta S_1 + \Delta S_{\text{solv}}$

Value for segment ( $J K^{-1} \text{ mol}^{-1}$ )	Value for solvent, $\Delta S_{\text{solv}}$ ( $J K^{-1} \text{ mol}^{-1}$ )
$\Delta S_{\text{CH}_2} = -7.06 \pm 0.08$	<i>n</i> -C <sub>28</sub> H <sub>58</sub> 1.17 $\pm$ 0.22
$\Delta S_{\text{CH}_3} = -28.14 \pm 0.25$	<i>n</i> -C <sub>32</sub> H <sub>66</sub> 0.60 $\pm$ 0.22
$\Delta S_{\text{Cl}} = -32.75 \pm 0.29$	<i>n</i> -C <sub>36</sub> H <sub>74</sub> 0 (standard)
$\Delta S_{\text{Br}} = -36.20 \pm 0.24$	
$\Delta S_1 = -41.07 \pm 0.22$	

The variation of the contribution of the entropy from the different solvents is no more than  $1.17 J K^{-1} \text{ mol}^{-1}$ , which is little in comparison to the other parameters. This result means that the freedom of movement of a solute molecule in solution in a long chain *n*-alkane is scarcely affected by the length of the solvent alkyl chain.

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