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THERMODYNAMIC PROPERTIES OF SOLUTE MOLECULES AT INFINITE DILUTION DETERMINED BY GAS-LIQUID CHROMATOGRAPHY

I. INTERMOLECULAR ENERGIES OF *n*-ALKANE SOLUTES IN C₂₈-C₃₆ *n*-ALKANE SOLVENTS

TOSHIAKI SUGIYAMA, TSUGIO TAKEUCHI and YOSHIHITO SUZUKI

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya (Japan)

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SUMMARY

Gas-liquid partition chromatography has been used to obtain thermodynamic properties of solute molecules at infinite dilution for *n*-alkane solutes in three *n*-alkane solvents (*n*-C₂₈H₅₈, *n*-C₃₂H₆₆ and *n*-C₃₆H₇₄). Henry's law constants at infinite dilution of *n*-alkane solutes in *n*-alkane solvents have been determined from gas-liquid chromatographic retention volume data at five temperatures. From the Henry's law constants, intermolecular energies of *n*-alkane solute molecules in *n*-alkane solvents have been estimated by an equation derived from the quasi-lattice model of a liquid mixture of long-chain molecules. The intermolecular energy of solute molecules at infinite dilution varies not only greatly with the chain length of the solute molecules but also with that of the solvent molecules.

INTRODUCTION

The intermolecular energy (the negative of the cohesive energy) at infinite dilution is one of the basic properties that are used for the prediction of the properties of mixtures in general solution theories. It is usually calculated from experimental heat of vaporization or vapour pressure data. When such data do not exist, as in the case of infinite dilute solutions, another method is necessary.

Gas-liquid partition chromatography (GLC) is a rapid and advantageous method for determining the thermodynamic properties of infinite dilute solutions¹⁻¹⁴. The partial molar enthalpies determined by GLC have been compared with data obtained calorimetrically.

In this paper, Henry's law constants of *n*-alkane solutes in *n*-alkane solvents were determined at five temperatures by GLC. From the Henry's law constants, the intermolecular energies of solute molecules at infinite dilution were estimated by an equation derived from certain ideas underlying some refined versions of Guggenheim's lattice theory of liquid mixtures in the zeroth approximation¹⁵.

EXPERIMENTAL

Liquid phases

Three stationary liquid phases were used: *n*-octacosane ($n\text{-C}_{28}\text{H}_{58}$), *n*-dotriacontane ($n\text{-C}_{32}\text{H}_{66}$) and *n*-hexatriacontane ($n\text{-C}_{36}\text{H}_{74}$). Each of them was found to have a minimum purity of 99% by high-temperature gas chromatography. The solid support used was Celite 545, 80–100 mesh, hexamethyldisilazane treated. The liquid phase was coated on to the support material in the usual manner. The amount of each liquid phase on the support material was varied from 10 to 15 wt.-%. The coated support was packed into 1 m \times 3 mm I.D. stainless-steel tubing. Each column was conditioned at 110°C for about 24 h with a gentle flow of a carrier gas.

The exact weight of stationary liquid was determined by Soxhlet extraction with *n*-hexane after all experiments.

Apparatus and procedure

The gas chromatograph used was Hitachi K53 equipped with a thermal conductivity detector. The column temperature was 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 smallest detectable sample sizes were used at all times so as to ensure operation in the Henry's law region of solute concentrations.

RESULTS AND DISCUSSION

Specific retention volume

The specific retention volume, V_R , is calculated from the corrected peak retention time and the column operating conditions using the expression derived by Pease and Thorburn¹⁶. The specific retention volume is, however, corrected to the real volume of gas passing through the column. This volume is obtained by multiplying the specific retention volume at N.T.P. (V_R) by $T/273.15$, where T is the absolute temperature of the column oven. The volume V_R is more appropriate for application to a thermodynamic study in view of the plate theory than is the volume V_R . For each liquid phase, samples were run on several columns with different liquid weight percentages and with different flow-rates of the carrier gas. Each influence on the specific retention volume was found to vary by less than 1%. Average values are given in Tables I – III. Specific retention volumes obtained in this work are com-

TABLE I
SPECIFIC RETENTION VOLUMES (ml/g) ON $n\text{-C}_{28}\text{H}_{58}$ AS LIQUID PHASE

Solute	Temperature (°C)				
	78.0	84.0	90.0	96.0	102.0
<i>n</i> -Hexane	85.6	73.6	63.3	54.6	47.2
<i>n</i> -Heptane	199.5	166.8	139.9	117.7	99.4
<i>n</i> -Octane	463	377	308	252	208
<i>n</i> -Nonane	1078	850	674	538	432
<i>n</i> -Decane	2460	1887	1458	1135	890

TABLE II
SPECIFIC RETENTION VOLUMES (ml/g) ON $n\text{-C}_{32}\text{H}_{66}$ AS LIQUID PHASE

Solute	Temperature ($^{\circ}\text{C}$)				
	78.0	84.0	90.0	96.0	102.0
$n\text{-Hexane}$	79.0	68.0	58.6	50.6	43.7
$n\text{-Heptane}$	185.7	154.9	129.7	109.1	92.1
$n\text{-Octane}$	432	350	285	234	192.3
$n\text{-Nonane}$	1008	790	625	498	400
$n\text{-Decane}$	2298	1755	1351	1050	823

TABLE III
SPECIFIC RETENTION VOLUMES (ml/g) ON $n\text{-C}_{36}\text{H}_{74}$ AS LIQUID PHASE

Solute	Temperature ($^{\circ}\text{C}$)				
	78.0	84.0	90.0	96.0	102.0
$n\text{-Hexane}$	74.6	63.8	54.9	47.3	41.0
$n\text{-Heptane}$	173.8	144.2	120.6	101.7	86.4
$n\text{-Octane}$	403	325	264	217	179.5
$n\text{-Nonane}$	939	733	578	461	371
$n\text{-Decane}$	2135	1620	1244	968	762

pared with published values in Table IV. The values in this work were slightly higher than the values of Pease and Thorburn¹⁶ for lower hydrocarbons. It is thought that the difference in the specific retention volumes arises from the different air peak markers (methane in Pease and Thorburn's work and air in this work).

TABLE IV
COMPARISON OF SPECIFIC RETENTION VOLUMES WITH PUBLISHED VALUES (ml^3/g) AT 80.0°C

Stationary liquid	Solute	This work*	Published	
			Ref. 16	Ref. 9
$n\text{-C}_{28}\text{H}_{58}$	$n\text{-Hexane}$	63.0	60.67	
	$n\text{-Heptane}$	145.4	142.4	
	$n\text{-Octane}$	334	330.9	
$n\text{-C}_{32}\text{H}_{66}$	$n\text{-Hexane}$	58.2	56.89	
	$n\text{-Heptane}$	135.2	132.8	
	$n\text{-Octane}$	312	308.1	
$n\text{-C}_{36}\text{H}_{74}$	$n\text{-Hexane}$	54.8	53.13	52.57
	$n\text{-Heptane}$	126.2	124.6	124.7
	$n\text{-Octane}$	290	289.8	288.1
	$n\text{-Nonane}$	669		651.3

* Interpolated to 80.0°C and corrected to N.T.P.

Henry's law constant

Consider the procedure for the determination of Henry's law constant by means of GLC. The Henry's law constant, K_p , of solute component in solution is, in general, given as follows:

$$K_p = \frac{p_B}{N_B/(N_A + N_B)} \quad (1)$$

where p_B is the vapour pressure of solute B in equilibrium with a liquid mixture, which consists of N_A molecules of solvent A and N_B molecules of solute B.

According to several GLC theories, the specific retention volume, V_R , is related to the partition coefficient, K_C , by the equation

$$V_R = K_C V_A \quad (2)$$

where

$$K_C = \frac{\text{number of solute molecules in unit volume of liquid phase}}{\text{number of solute molecules in unit volume of gas phase}}$$

and V_A is the specific volume of the stationary liquid (solvent).

Neglecting the interactions between the solute vapour and carrier gas in the gas phase, the solute vapour behaves as an ideal gas because the partial pressure of the solute vapour is lower in the GLC column. If hydrogen is used as a carrier gas, the interaction is very small⁶.

Hence, the Henry's law constant at infinite dilution can be determined by GLC. Eqn. 1 can be rewritten as

$$K_p = \frac{RT}{M_r V_R} \quad (3)$$

where R is the gas constant, T the absolute temperature and M_r the molecular weight of the stationary liquid.

The Henry's law constants of five *n*-alkane solutes can be calculated from the specific retention volumes in Tables I, II and III. The results are given in Table V.

Thermodynamics of vaporization

Consider the molar entropy of vaporization at infinite dilution. For a binary liquid mixture of N_A molecules of component A each of molecules having r_A segments in a molecule and N_B molecules of component B each having r_B segments, the molar entropy of mixing is given by Guggenheim's eqn. 10.10.8 (ref. 15). The partial molar entropy of mixing for component B, therefore, can be rewritten as

$$\begin{aligned} \Delta S_{\text{mix}} &= \frac{\partial(\Delta S_{\text{mix}})}{\partial\left(\frac{N_B}{L}\right)} \\ &= -R \left[\ln\left(\frac{r_B N_B}{r_A N_A + r_B N_B}\right) + \frac{N_A(r_A - r_B)}{r_A N_A + r_B N_B} + \frac{1}{2} z q_B \ln\left(\frac{r_A N_A / r_B + N_B}{q_A N_A / q_B + N_B}\right) \right] \quad (4) \end{aligned}$$

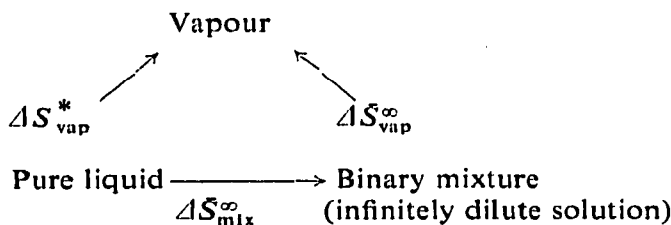
TABLE V
HENRY'S LAW CONSTANTS, K_p (atm), IN n -C₂₈H₅₈, n -C₃₂H₆₆ AND n -C₃₆H₇₄ SOLVENTS

Solute	Solvent	Temperature (°C)				
		78.0	84.0	90.0	96.0	102.0
n -Hexane	n -C ₂₈ H ₅₈	0.852	1.009	1.192	1.405	1.654
n -Heptane		0.366	0.445	0.540	0.652	0.784
n -Octane		0.1575	0.1971	0.245	0.304	0.375
n -Nonane		0.0677	0.0874	0.1120	0.1426	0.1804
n -Decane		0.0297	0.0393	0.0518	0.0676	0.0876
n -Hexane	n -C ₃₂ H ₆₆	0.809	0.956	1.128	1.329	1.563
n -Heptane		0.344	0.420	0.509	0.616	0.741
n -Octane		0.1480	0.1857	0.232	0.288	0.355
n -Nonane		0.0634	0.0822	0.1058	0.1349	0.1707
n -Decane		0.0278	0.0370	0.0489	0.0640	0.0830
n -Hexane	n -C ₃₆ H ₇₄	0.762	0.906	1.071	1.262	1.481
n -Heptane		0.327	0.401	0.488	0.588	0.703
n -Octane		0.1409	0.1778	0.222	0.276	0.338
n -Nonane		0.0605	0.0789	0.1017	0.1297	0.1636
n -Decane		0.0266	0.0357	0.0472	0.0617	0.0796

If z , the number of pairs of neighboring sites in the lattice model, is much greater than unity, then $q_A \approx r_A$ and $q_B \approx r_B$. At infinite dilution of component B, $N_A \gg N_B$, and the partial molar entropy of mixing of component B is given by

$$\Delta S_{\text{mix}}^{\infty} = -R \left[\ln \left(\frac{r_B N_B}{r_A N_A} \right) + \frac{r_A - r_B}{r_A} \right] \quad (5)$$

Hence, the partial molar entropy of vaporization for component B from an infinitely dilute solution is generally as follows:



where ΔS_{vap}^* is the molar entropy of vaporization of pure substance B at temperature T :

$$\begin{aligned} \Delta S_{\text{vap}}^{\infty} &= \Delta S_{\text{vap}}^* - \Delta S_{\text{mix}}^{\infty} \\ &= \Delta S_{\text{vap}}^* + R \left[\ln \left(\frac{r_B N_B}{r_A N_A} \right) + \frac{r_A - r_B}{r_A} \right] \end{aligned} \quad (6)$$

Next, the molar free energy of vaporization will be considered. The vapour

pressure of component B, p_B , is in equilibrium with the binary liquid mixture, consisting of N_A molecules of component A and N_B molecules of component B.

The partial molar free energy of vaporization of component B from the above binary mixture is

$$\Delta \bar{G}_{\text{vap}} = G_{\text{gas}}^0 - \bar{G}_{\text{soln}}^0 \quad (7)$$

$$= -RT \ln f_B \quad (8)$$

where G_{gas}^0 is the standard free energy of pure substance B in the gas phase under normal conditions ($T^\circ\text{K}$, 1 atm), \bar{G}_{soln}^0 the standard partial molar free energy of the substance B in the binary mixture, and f_B (atm) the fugacity of B in the above mixture, which becomes equal to partial pressure of B, p_B , reducing the pressure. The partial molar free energy of vaporization from infinitely dilute solution is denoted by $\Delta \bar{G}_{\text{vap}}^\infty$.

By combining eqn. 6 for the molar entropy of vaporization at infinite dilution with eqn. 8 for the molar free energy of vaporization at infinite dilution, the molar enthalpy of vaporization of component B at infinite dilution is obtained as follows:

$$\begin{aligned} \Delta \bar{H}_{\text{vap}}^\infty &= \Delta \bar{G}_{\text{vap}}^\infty + T \Delta S_{\text{vap}}^\infty \\ &= -RT \ln \left(\frac{p_B}{N_B/N_A} \right) + T \Delta S_{\text{vap}}^* \\ &\quad + RT \left[\ln \left(\frac{r_B}{r_A} \right) + \frac{r_A - r_B}{r_A} \right] \end{aligned} \quad (9)$$

$$= -RT \ln K_p + T \Delta S_{\text{vap}}^* - \delta RT \quad (10)$$

where δ is the parameter of the statistical contributions to the mixing at infinite dilution:

$$\delta = - \left(\ln \frac{r_B}{r_A} + \frac{r_A - r_B}{r_A} \right) \quad (11)$$

For the model of a liquid mixture in this study, it will be assumed that each of the components, solvent and solute, is divided into segments, each of which contains only one carbon atom. Each segment occupies one site on the quasi-crystalline lattice. Component A having r_A carbon atoms and component B having r_B carbon atoms in a molecule are both n -alkanes, and therefore consist of r_A and r_B segments, respectively. Then, the value of δ can be estimated by eqn. 11. Although the statistical effect related to the difference in size of the molecules was expressed in terms of the volume fraction of solvent and solute molecules rather than the number of segments, it was not established theoretically with any certainty.

From eqn. 10, the partial molar enthalpy of vaporization at infinite dilution can be estimated by GLC. The molar entropy of vaporization of a pure substance at a temperature $T^\circ\text{K}$, ΔS_{vap}^* , can be calculated by Kirchhoff's law. The required properties of pure substances are available in the literature¹⁷⁻²². The partial molar enthalpy of vaporization of solute molecules at infinite dilution, therefore, can be estimated from the values of K_p and ΔS_{vap}^* and δ from eqn. 10.

TABLE VI

INTERMOLECULAR ENERGIES OF *n*-ALKANE SOLUTES IN *n*-ALKANE SOLVENTS AT INFINITE DILUTION, ΔE_{im}^{∞} (kJ mole⁻¹)

Solute	Solvent	Temperature (°C)				
		78.0	84.0	90.0	96.0	102.0
<i>n</i> -Hexane	<i>n</i> -C ₂₈ H ₅₈	-28.80	-28.50	-28.18	-27.86	-27.52
<i>n</i> -Heptane		-33.63	-33.30	-32.96	-32.60	-32.24
<i>n</i> -Octane		-37.94	-37.58	-37.20	-36.81	-36.41
<i>n</i> -Nonane		-42.44	-42.04	-41.62	-41.19	-40.75
<i>n</i> -Decane		-46.94	-46.50	-46.06	-45.60	-45.13
<i>n</i> -Hexane	<i>n</i> -C ₃₂ H ₆₆	-28.64	-28.35	-28.03	-27.70	-27.36
<i>n</i> -Heptane		-33.51	-33.18	-32.83	-32.47	-32.10
<i>n</i> -Octane		-37.84	-37.47	-37.08	-36.68	-36.28
<i>n</i> -Nonane		-42.36	-41.94	-41.51	-41.08	-40.64
<i>n</i> -Decane		-46.87	-46.42	-45.96	-45.50	-45.02
<i>n</i> -Hexane	<i>n</i> -C ₃₆ H ₇₄	-28.53	-28.22	-27.89	-27.56	-27.23
<i>n</i> -Heptane		-33.39	-33.03	-32.68	-32.32	-31.97
<i>n</i> -Octane		-37.72	-37.33	-36.94	-36.54	-36.15
<i>n</i> -Nonane		-42.25	-41.81	-41.37	-40.93	-40.50
<i>n</i> -Decane		-46.75	-46.28	-45.81	-45.35	-44.89

Intermolecular energy

The intermolecular energy, ΔE_{im}^{∞} , of a certain molecule in an infinitely dilute solution can be determined from the enthalpy of vaporization at infinite dilution as follows²³:

$$\Delta E_{im}^{\infty} = -\Delta H_{vap}^{\infty} + P \Delta V - \frac{3}{2} R T \quad (12)$$

$P \Delta V$ could not be determined in this study, but it is approximately equal to $R T$ at lower pressures of the solute vapour. The intermolecular energies were estimated for five *n*-alkane solutes in three *n*-alkane solvents and are given in Table VI.

The intermolecular energy of solute molecules at infinite dilution varies not only greatly with the chain length of the solute molecules but also with that of solvent molecules. The environmental conditions may affect the behaviour of solute molecules energetically.

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