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

II. INTERACTION ENERGIES OF CONTACT PAIRS OF METHYL AND METHYLENE SEGMENTS

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SUMMARY

The intermolecular energies of *n*-alkane solute molecules in *n*-alkane solvents at infinite dilution have been determined by gas-liquid chromatography. According to the quasi-lattice model, the intermolecular energies of solute molecules can be expressed as the sum of interaction energies of each pair of a segment of the molecules with segments of neighbouring molecules. The interaction energies of contact pairs of CH₃-CH₃, CH₃-CH₂ and CH₂-CH₂ have been estimated by an equation derived from a theory of solute-solvent interactions. A consistent set of the values was found for all of the solute-solvent systems studied without the need to adjust the model parameters.

INTRODUCTION

Gas-liquid partition chromatography (GLC) is a rapid and reliable method for studying the thermodynamic properties of infinitely dilute solutions of volatile solutes. Attempts have been made to compare the thermodynamic properties at infinite dilution with statistical mechanical theories. A successful method of interpreting the thermodynamic properties of solutions is to consider molecules as consisting of various groups or segments and to determine a single set of parameters that characterize the molecular structure and group interactions.

In Part I¹, the intermolecular energy (the negative of the cohesive energy) of solute molecules at infinite dilution was determined from GLC retention volumes. In the case of long-chain molecules, each molecule is divided into a certain number of elements (segments), each of which occupies one site on the quasi-crystalline lattice². As the intermolecular energy can be expressed as the sum of interaction energies of each pair of segments adjacent to each other on lattice sites, the interaction energies between segments can be taken from the molecular structures of the solute and solvent. This treatment, although not very exact, has a sound theoretical basis and is more flexible than the more sophisticated solution theories

concerning the cohesive energy of molecules in solutions. It has been employed with some success to predict the thermodynamic properties of a range of *n*-alkane mixtures. The parameters in this model, which are given as energies of attraction for contact pairs of segments, have adequate physical significance.

THEORETICAL

We can use the quasi-crystalline model of a lattice in liquid mixtures, each site of which is considered to be occupied by one segment. This concept of liquid mixtures has been developed mainly by Guggenheim².

It will be assumed that the intermolecular energy can be expressed as the sum of interaction energies of each pair, depending on the nature of both segments on the nearest neighbouring lattice sites forming the pair. At first we shall consider a simple binary liquid mixture, each of components containing only one segment. Later, this treatment will be extended to more complicated systems, each with components containing several segments or several different kinds of segments.

In a binary liquid mixture of components A and B, each of the components contains only one segment. Considering a certain molecule of component B, the molecule is surrounded by molecules of both components A and B. The total interaction energy with respect to the molecule is $z(1-x_B)w_{AB} + zx_Bw_{BB}$ with a completely random arrangement of molecules in the mixture, where z is the number of pairs of neighbouring sites, w_{AB} and w_{BB} are the interaction energies of A-B and B-B contact pairs, respectively, and x_B is the mole fraction of component B in the mixture. Next, if a molecule of B is removed from the liquid mixture out of the system, all surrounding molecule segments that formed a contact pair with one of the segments of the molecule that has been removed, form new contact pairs with each other. Therefore, the total interaction energy with respect to newly formed contact pairs of segments in molecules that formerly surrounded the molecule that has been removed, is $1/2 z(1-x_B)^2w_{AA} + zx_B(1-x_B)w_{AB} + 1/2 z x_B^2w_{BB}$, where w_{AA} is the interaction energy of an A-A contact pair.

The molar intermolecular energy, ΔE_{im} , of component B can be estimated by the lattice model, and is given by

$$\Delta E_{im} = Lz \left[(1-x_B)w_{AB} + x_Bw_{BB} - \frac{1}{2}(1-x_B)^2w_{AA} - x_B(1-x_B)w_{AB} - \frac{1}{2}x_B^2w_{BB} \right] \quad (1)$$

where L is the Avogadro constant. At infinite dilution of component B, $x_B \ll 1$ and eqn. 1 can be rewritten as

$$\Delta E_{im}^\infty = Lz \left(w_{AB} - \frac{1}{2}w_{AA} \right) \quad (2)$$

If we continue to consider that each molecule of both components of a binary mixture is divided into segments, each segment occupying one site on the lattice, the number of pairs of neighbouring sites of each molecule, which consists of r segments, is denoted by zq and the kinds of segments are denoted by i (or j). Of the zq_x contact pairs of each molecule X, $zq_x f_i^x$ contact pairs come from segment i of the molecule X,

that is, f_i^x is the fraction of the number of pairs associated with segment i in a molecule. In a binary mixture of molecules A and B, the molar intermolecular energy, ΔE_{im}^∞ , of component B at infinite dilution under a completely random arrangement of the molecules is given by

$$\Delta E_{im}^\infty = L \left(\sum_{i,j} z q_B f_i^A f_j^B w_{ij} - \frac{1}{2} \cdot \frac{z q_B}{z q_A} \cdot \sum_{i,j} z q_A f_i^A f_j^A w_{ij} \right) \quad (3)$$

where w_{ij} is the interaction energy of the i - j contact pair of segments i and j . The potential energy of a segment i in an imaginary sea of segment j is given by $z w_{ij}$, which is denoted by u_{ij} .

In the case where each molecule of the components of a binary mixture consists of only one kind of segment but are different from each other, eqn. 3 now reduces to

$$\Delta E_{im}^\infty = L z q_B \left(w_{AB} - \frac{1}{2} w_{AA} \right) \quad (4)$$

In particular, if $r_B = 1$ (naturally, $q_B = 1$), then eqn. 2 is obtained again.

In the case of a pure substance ($x_B = 1$), the molar intermolecular energy of substance B is given by

$$\Delta E_{im}^0 = \frac{1}{2} L z q_B \sum_{i,j} f_i^B f_j^B w_{ij} \quad (5)$$

DISCUSSION

Interaction energy of contact pairs

The intermolecular energy of solute molecules at infinite dilution has been determined previously by GLC¹. For n -alkane solutes in n -alkane solvents, there are only methyl and methylene groups as segments. If $z \gg 1$, f_i in the above equations can be adequately approximated by the fraction of segment i in a molecule. Analysis of the results in Table VI in ref. 1 using eqn. 3 gives the interaction energies of contact pairs, which are listed in Table I. The value of $u_{\text{CH}_3-\text{CH}_3}$ is less accurate than the other two in view of the rather small fraction of methyl group involved. Using the interaction energies in Table I, the differences between the intermolecular energies obtained by using eqn. 3 and the actual values are less than 0.2 kJ mole⁻¹.

For about 60% of the solute-solvent systems studied, the values are within 0.05 kJ mole⁻¹ of the actual values.

The temperature dependence of the interaction energies of segment contact pairs may not be ascertained exactly from the above discussion. Roughly, the interaction energies decrease slightly with an increase in temperature.

Application to other systems

Although a very narrow range of samples was examined, the findings may be applied to the other n -alkane- n -alkane systems.

The solute-solvent interaction mainly determines the solubility of a solute molecule in a solvent. From the intermolecular energy of a solute, the solubility of the solute can be determined, *e.g.*, the Henry's law constant. The Henry's law constant

TABLE I

SEGMENT-SEGMENT INTERACTION ENERGIES OF CONTACT PAIRS OF METHYL AND METHYLENE SEGMENTS ($zw_{ij} = u_{ij}$)

Temperature (°K)	$-u_{\text{CH}_3-\text{CH}_3}/kT$	$-u_{\text{CH}_3-\text{CH}_2}/kT$	$-u_{\text{CH}_2-\text{CH}_2}/kT$
351.2	6.494 ± 0.972	3.191 ± 0.067	3.112 ± 0.016
357.2	6.671 ± 0.952	3.077 ± 0.066	3.036 ± 0.015
363.2	6.705 ± 0.953	2.972 ± 0.066	2.962 ± 0.016
369.2	6.693 ± 0.968	2.925 ± 0.067	2.940 ± 0.016
375.2	6.307 ± 0.962	2.796 ± 0.067	2.824 ± 0.016

is predicted from the intermolecular energy through eqns. 10 and 12 in ref 1. The intermolecular energy of a solute molecule can be estimated from the interaction energies in Table I by using eqn. 3. We tried to apply this to *n*-alkane-*n*-tetracosane systems, and the predicted Henry's law constants are given in Table II. The differences between the calculated and experimental Henry's law constants, which were determined from the specific retention volumes in ref. 3, are also given in Table II. For all systems but one, the K_p values obtained were within 10% of the actual values. This difference arises from the approximate treatment of the solution theory in this study.

TABLE II

COMPARISON OF EXPERIMENTAL HENRY'S LAW CONSTANTS (atm) WITH THOSE PREDICTED IN *n*-C₂₄H₅₀ SOLVENT AT 84.0 °C

Solute	K_p (theoretical)	K_p (experimental)*	Difference (%)
<i>n</i> -Hexane	1.017	1.171	-13.2
<i>n</i> -Heptane	0.498	0.511	-2.5
<i>n</i> -Octane	0.206	0.221	-6.8
<i>n</i> -Nonane	0.0903	0.0975	-7.4

* Values calculated using eqn. 3 in ref. 1 from specific retention volumes in ref. 3, which should be corrected from N.T.P. to the column temperature.

This theory can be applied to pure liquid substances. We used pure *n*-heptane, for which the molar heat capacity in the gas and liquid phases have been determined^{4,5}, and the molar heat of vaporization of which can therefore readily be calculated precisely, to predict its molar enthalpy of vaporization by this theory of solutions. The molar enthalpy of vaporization was predicted from the segment-segment interaction energies through eqn. 5 in this paper and eqn. 12 in ref. 1. The calculated enthalpies are given in Table III, and agree very closely with the actual values.

CONCLUSION

According to this simple treatment of the theory of solutions, the determination of thermodynamic properties by GLC is found to afford much effective and valuable information on the interactions of molecules. Thus, the use of this treatment of the

TABLE III
MOLAR ENTHALPIES OF VAPORIZATION OF *n*-HEPTANE (kJ mole⁻¹)

Temperature (°K)	$\Delta H_{\text{vap.}}$ (theoretical)*	$\Delta H_{\text{vap.}}$ (experimental)**	Difference (%)
351.2	33.49	32.78	2.17
357.2	33.33	32.46	2.68
363.2	33.06	32.14	2.86
369.2	33.27	31.82	4.56
375.2	32.25	31.50	2.38

* Values calculated using the interaction energies in Table I.

** Values calculated by Kirchoff's law using molar heat capacities of *n*-heptane vapour⁴ and liquid⁵.

theory of solutions permits the prediction of the intermolecular energy (the negative of the cohesive energy) and the solubility of simple hydrocarbons in other simple hydrocarbons at infinite dilution, or of pure liquid substances. Moreover, this method could lead to a better knowledge of the relative contributions of the segment-segment interaction energies due to several different segments.

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