

Adsorption Isotherms and Equations of State of Insoluble Vapors at the Water-Gas Interface as Studied by Gas Chromatography

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In continuation of previous work on the study of water at interfaces by gas chromatography, the gas-liquid interfacial adsorption isotherms of six insoluble vapors (three *n*-alkanes and three branched alkanes) have been determined in the range of 4000–500 Å²/molecule. From these isotherms, isosteric heats of adsorption have been derived, and it has been shown that over the whole concentration range examined the isosteric heat of adsorption is equal to or less than the heat of liquefaction. This points to the fact that water is a low-energy surface for hydrocarbons. The free energy of adsorption and the entropy of adsorption at constant surface coverage have also been calculated. Equations of state have been determined, and it has been shown that nonideal behavior exists down to concentrations as low as 2500 Å²/molecule. In addition, non-ideality increases with chain length for the *n*-alkanes and decreases with branching. Finally, calculations of thicknesses of the surface films indicate that the hydrocarbons can be considered to lie flat on the water surface in most cases over the whole concentration range studied. Gas-liquid chromatography is thus shown to be a valid technique for the study of adsorption of vapors on liquids at finite surface coverages.

Introduction

In previous papers in this series,^{1–3} we have shown gas chromatography (gc) to be a valid method for the study of the adsorption at zero surface coverage of insoluble vapors on the gas-liquid interface of water and of the partition at infinite dilution of sparingly soluble vapors in thin layers of water coated on wide pore diameter silica. In this paper we wish to report on an expansion of this work to the study of adsorption of insoluble vapors at finite surface coverages by gc. In an earlier paper,² we presented some preliminary results on the determination of adsorption isotherms and showed that the water system is well suited for study by gc.

The thermodynamic functions of adsorption and equations of state have been examined for three normal and three branched-chain alkanes, namely heptane (*n*-C₇), octane (*n*-C₈), nonane (*n*-C₉), 2-methylheptane (2-MeC₇), 2,5-dimethylhexane (2,5-DMeC₆), and 2,2,4-trimethylpentane (2,2,4-TMeC₅). Analysis of the results in terms of van der Waals theory leads to an estimation of the film thickness. Since gc in the elution mode is most applicable to low concentrations, we have studied the adsorption process at surface coverages ranging from 4000 to 500 Å²/molecule. The latter figure is close to the lowest surface coverage region examined by earlier workers^{4–7} in the adsorption of insoluble vapors, including several of the above compounds, on water surfaces. Thus a comparison can be made between the dilute region in this study and the more concentrated region previously examined. In addition, Hauxwell and Ottewill^{8,9} have presented some results for the adsorption of hydrocarbons on

water surfaces at very low surface coverage which allow a critical comparison of the gc approach to static methods for the determination of the adsorption isotherm.

In our previous studies^{2,3} we have found water to be a low-energy surface when hydrocarbons are used as adsorbates. In addition, we reported standard heats and entropies of adsorption at zero surface coverage substantially less negative than the extrapolated values of static measurements.^{4,8} The further examination of this result is important, since a model of surface perturbation of water during the adsorption process has been postulated from the negative heats and entropies of adsorption.^{10,11}

Experimental Section

The general apparatus has been described previously.¹ The only change for this work was the in-

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corporation of a heated injection port in order to ensure rapid volatilization of the liquid samples. Solutes were injected using a 10- μ l Hamilton syringe. Density data, used to correct volumes to moles of sample, were obtained from Dreisbach.¹² All the solutes were reagent grade and were obtained from the following sources: *n*-C₇ and 2,2,4-TMeC₆, Fisher Scientific; 2-MeC₇ and 2,5-DMeC₆, J. T. Baker; *n*-C₈, K & K Laboratories; and *n*-C₉, Matheson Coleman and Bell. Chromatographic analysis at high sensitivity revealed no trace impurities.

The column packing consisted of 20% by weight water on 80–100 mesh Porasil D (Waters Associates, Framingham, Mass.), specific surface area ~ 29 m² g⁻¹. The weight per cent of water was determined both before and after column use by the weight difference of the coated and dried support. Good agreement was obtained in both cases.

All analyses were run in triplicate at each temperature. For the enthalpy determinations the temperature range was 8–16°, at intervals of roughly 2°. In addition, all studies were run close to the optimum gas velocity (highest column efficiency). Graphical integration was accomplished by the cut and weigh method. The flame ionization detector linearity was also checked and found to be obeyed over the concentration range of these experiments. An error analysis of this gc system for adsorption isotherm determination will be discussed in the Results section.

Theory

We have previously shown that at zero surface coverage the six hydrocarbon solutes in this study undergo negligible partition in their travel through the water-gas chromatographic column,^{1,2} the mechanism of retention being adsorption at the gas-liquid interface. From a consideration of the solubilities of these solutes in water¹³ and the fact that K_A increases with concentration in the gas phase, it is reasonable to assume that interfacial adsorption remains the only mechanism of retention over the concentration range in this work. Since a nonlinear isotherm results, the net retention volume per gram of packing, V_N^0 , can be written as¹⁴

$$V_N^0 = (1 - \phi j Y_o) \left(\frac{\partial a}{\partial c} \right)_T A_L^0 \quad (1)$$

where Y_o = mole fraction of the adsorbate in the gas phase at the column outlet, a = concentration of adsorbate at the gas-liquid interface in moles per square centimeter, c = concentration of adsorbate in the gas phase in moles per cubic centimeter, A_L^0 = surface area of the vapor-liquid interface per gram of packing, and where

$$j = J_3^2 \left[1 + \frac{Y_o^2 P_o B_{22}}{RT} (J_3^2 - 1) \right] \quad (2)$$

$$\phi = \frac{1 + k'(1 - Y_o J_2^1)}{1 + k'(1 - Y_o J_3^2)} \times \left[1 + \frac{2Y_o P_o B_{22}}{RT} (1 - Y_o J_2^1) \right] \quad (3)$$

where

$$J_n^m = \frac{n \left[(P_i/P_o)^m - 1 \right]}{m \left[(P_i/P_o)^n - 1 \right]}$$

B_{22} = second virial coefficient of pure solute (adsorbate), k' = capacity factor (mass ratio) of the solute, P_i = inlet pressure, and P_o = outlet pressure.

Equation 1 assumes that the contributions of the second virial coefficients of the carrier gas (helium plus *ca.* 0.02 mol fraction of (H₂O)) and the mixed second virial coefficient of the carrier gas with the solute are negligible compared to the overall virial coefficient of the gas phase. Hartkopf has calculated the virial coefficients:¹⁵ $B_{H_2O/He} = -10$ ml/mol and $B_{2/carrier\ gas} = +40$ ml/mol. The negligible contribution can be seen from the fact that the B values are small and of opposite sign. In addition, the mole fraction of solute in the gas phase typically never exceeds 10⁻² in this work, further reducing the influence of these coefficients.

The B_{22} coefficient can be approximated as -1000 ml/mol¹⁶ for the hydrocarbons in this study. If Y_o^2 is assumed to be no greater than 10⁻⁴, then calculations show that $j \approx J_3^2$ in eq 2, which is equivalent to the James and Martin compressibility correction factor.¹⁷ Consider next eq 3. Since the pressure drop is quite small ($P_i/P_o \approx 1.1$ – 1.2), $J_2^1 \approx 1$. If $Y_o = 10^{-2}$, then calculations show that the second term in the brackets of eq 3 is equal to -0.01 for $T = 285^\circ$ K. This term then provides a correction of only 1% at the highest concentration. Since most isotherm determinations are made at lower concentrations and the error of K_A is approximately 2%, we shall neglect this correction term. Examining the rest of eq 3, we can assume that J_3^2 , as well as J_2^1 , is equal to unity for the low pressure drops employed. From previous arguments, $\theta \approx 1$. Since the variation of flow due to sorption¹⁸ is incorporated into ϕ , we can assume that the sorption effect is negligible over the experimental concentration range in this study.

Equation 1 can now be simplified to

$$V_N^0 = \left(\frac{\partial a}{\partial c} \right)_T A_L^0 \quad (4)$$

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In the low concentration region, where the distribution becomes linear, the differential in eq 4 can be written as $\partial a/\partial c \cong a/c = K_A$, where K_A is the thermodynamic adsorption coefficient. For this work, Γ , the Gibbs surface excess, can be substituted for a in eq 4 on the assumption that the plane of adsorption is the Gibbs hypothetical dividing surface. In addition, c can be replaced by P_a/RT , where P_a , the partial pressure of adsorbate, in millimeters, is assumed equal to fugacity at the low pressures used in these experiments. Then

$$V_N^0 = RT \left(\frac{\partial \Gamma}{\partial P_a} \right)_T A_L^0 \quad (5)$$

The surface pressure, π , is defined as

$$\pi = RT \int_0^{P_a} \Gamma d(\ln P_a) \quad (6)$$

Adsorption isotherms were determined as described previously² by the elution by characteristic point method (ECP).¹⁹⁻²¹ In this method, the amount adsorbed, Γ , is given by

$$\Gamma = \frac{n}{wA'A_L^0} \int_0^h \lambda dh \quad (7)$$

where n = number of moles of solute, w = weight of packing in the column, A' = peak area, h = peak height, and

$$\lambda = X \frac{V_N^0 w}{F_c J_s^2} \quad (8)$$

The partial pressure, P_a , corresponding to peak height, h , can be computed from

$$P_a = \frac{nRT_m h}{J_s^2 A' F_m} \quad (9)$$

In eq 8 and 9, F_c = carrier gas flow rate within the column, X = recorder chart speed, T_m = flow meter temperature, and F_m = carrier gas flow rate at the end of the column. The integration was carried out graphically from the chromatogram by measuring the area from the inert peak to the peak maximum within the limits of 0 to h . The area was cut out and weighed. The correction for diffusion²² was found to be less than 2% and was neglected in this work.

In a previous paper² we have presented chromatograms of *n*-octane on water columns as a function of sample size. Similar diagrams are repeated in Figure 1 for *n*-C₈. The same behavior was found for the other five solutes. The excellent coincidence of the leading edges of the asymmetrical peaks is an indication that equilibrium on the column can be assumed at all concentration ranges.²³

Recently, Huber²⁴ has critically evaluated the various gas chromatographic methods for determining sorption isotherms. He finds experimentally that all methods give slightly different results from the one in which

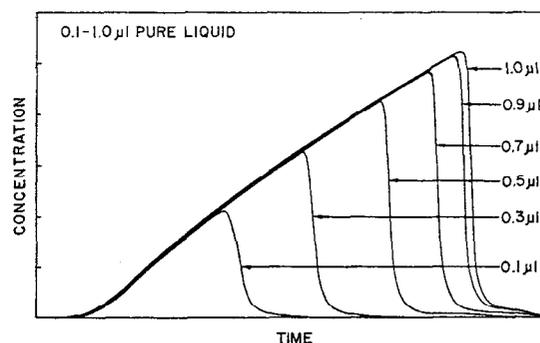


Figure 1. Chromatograms of octane on 20% H₂O-Porasil D (w/w) as a function of liquid volume sample sizes, $T = 12.1^\circ$.

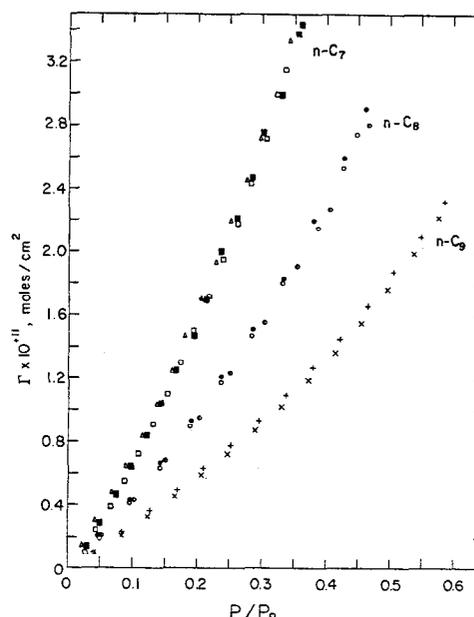


Figure 2. Adsorption isotherms for heptane, octane, and nonane on 20% H₂O (w/w) coated on Porasil D, $T = 12.1^\circ$. Different point types represent different experimental runs.

a true equilibrium is imposed throughout the whole column. However, the difference between the ECP approach and the true equilibrium method is slight when the isotherm does not deviate greatly from linearity. Typical isotherms in Figures 2 and 3 indicate that in the concentration region of this study, the ECP method can be used with validity. The problems in constructing an equilibrium apparatus, especially

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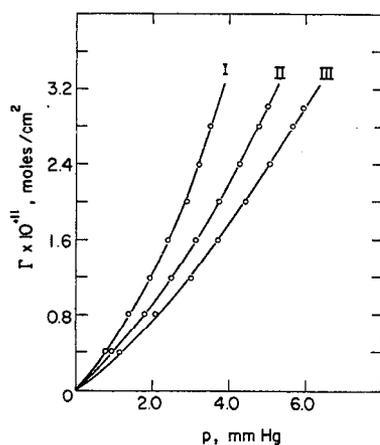


Figure 3. Adsorption isotherm for 2,5-dimethylhexane as a function of temperature: (I) 8.8°, (II) 14.0°, (III) 16.1°.

when using a volatile solvent as stationary phase, are great in comparison to the conventional chromatographic operation of the ECP approach. Thus, we chose the latter method and operated in concentration regions where it may be assumed to be equivalent to the true equilibrium method.

Once the isotherm has been determined, the thermodynamic adsorption coefficient near zero coverage region can be calculated from eq 4 and 5. As others,⁸ we have fitted the adsorption isotherm to a polynomial, using the least-squares method. We find the best fit with a four-term polynomial of the form

$$\Gamma = C_1 P_a + C_2 P_a^2 + C_3 P_a^3 + C_4 P_a^4 \quad (10)$$

where the C 's are constants. Note that the isotherm is assumed to pass through the origin, *i.e.*, at $P_a = 0$, $\Gamma = 0$ ($\pi = 0$ as well). In addition, combining eq 6 and 10 gives

$$\pi = RT \left(C_1 P_a + C_2 \frac{P_a^2}{2} + C_3 \frac{P_a^3}{3} + C_4 \frac{P_a^4}{4} \right) \quad (11)$$

The area per molecule, A , is related to the surface concentration by

$$A = 1/N\Gamma \quad (12)$$

where N is Avogadro's number.

Consider next the thermodynamic properties. The free energy of adsorption at constant surface coverage Γ , $(\Delta\bar{G}_A)_\Gamma$, can be expressed as

$$(\Delta\bar{G}_A)_\Gamma = RT \ln P_a/760 \quad (13)$$

for the process of transferring 1 mol of gas in its defined standard state (760 mm) to the adsorbed state, defined by the equilibrium pressure P_a (mm). The isosteric heat of adsorption, q_{st} , was calculated from the Clausius-Claperyon equation

$$q_{st} = -R \left(\frac{\partial \ln P_a}{\partial 1/T} \right)_\Gamma \quad (14)$$

Note that isosteric heat of adsorption is independent of the chosen standard state. The determination of P_a as a function of surface coverage can be made by use of eq 10. The entropy of adsorption at constant surface coverage was obtained by

$$T(\Delta S_A)_\Gamma = -q_{st} - (\Delta\bar{G}_A)_\Gamma \quad (15)$$

Finally, returning to eq 4, the gas-liquid interfacial area of the water surface per gram of packing, A_L^0 , was determined as previously,² by assuming that the adsorption coefficient of *n*-octane at zero surface coverage and 12.5° is 1.0×10^{-4} cm. This value was calculated by estimating that a 20% water coated Chromosorb P column had a surface area of 1 m²/g.

Results and Discussion

Adsorption Isotherms. Figure 2 shows adsorption isotherms for *n*-C₇, *n*-C₈, and *n*-C₉ at $T = 12.1^\circ$ on a column of 20% H₂O (w/w) coated on Porasil D. The experimental points are included in order to indicate the good reproducibility from run to run. An error analysis revealed that n , the number of moles of solute injected, varied at a maximum of 2% from the mean, while Γ varied at a maximum of 8% from its mean value. The larger error in Γ is a result of change in w and A_L^0 (see eq 7) due to the slow bleeding of water off the column (over 1-2 days).

In agreement with previous work,^{5-7,9,25,26} type III or "anti-Langmuir" isotherms are obtained. For the straight-chain series, adsorption at a given P/P_0 value is found to increase with decreasing carbon number. Although not shown, branched isomers also produced type III isotherms, with adsorption increasing with branching. Finally, Figure 3 shows a typical temperature dependence of the adsorption isotherm for 2,5-dimethylhexane, with decreasing adsorption as the temperature is increased.

Special note should be taken of the fact that the surface concentrations in the adsorption isotherms are a factor of 10 or more smaller than those of the original static measurements.^{5,26} This points to one of the big advantages of gc for adsorption studies, namely that the method works best at low concentrations. Recently, Hauxwell and Ottewill⁹ have studied similar adsorbates in the low-concentration region of this work. A comparison of data from Hauxwell's thesis²⁷ with that in Figure 2 reveals that the Γ values for a given partial pressure and temperature are a factor of approximately 2 larger in the present work. The discrepancy can arise from one of two sources or a combination of both. First, the surface area per gram of packing, A_L^0 , is an estimated quantity in the gas

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Table I: Thermodynamic Functions of Adsorption as a Function of Surface Coverage, $T = 12.1^\circ$

| Adsorbate | $\Gamma = 0.6 \times 10^{-11} \text{ mol/cm}^2$ | | $-(\Delta\bar{S}_A)\Delta^c$ | $\Gamma = 1.2 \times 10^{-11} \text{ mol/cm}^2$ | | $-(\Delta\bar{S}_A)\Gamma^c$ |
|--------------------------|---|------------|------------------------------|---|------------|------------------------------|
| | $-(\Delta\bar{G}_A)\Gamma^a$ | q_{st}^b | | $-(\Delta\bar{G}_A)\Gamma^a$ | q_{st}^b | |
| <i>n</i> -C ₇ | 3.35 | 7.7 | 15 | 3.02 | 7.7 | 15 |
| <i>n</i> -C ₈ | 3.85 | 8.7 | 17 | 3.51 | 9.2 | 20 |
| <i>n</i> -C ₉ | 4.33 | 9.6 | 19 | 4.00 | 9.7 | 20 |
| 2-MeC ₇ | 3.72 | 8.8 | 18 | 3.39 | 8.8 | 19 |
| 2,5-DMeC ₆ | 3.64 | 7.6 | 14 | 3.29 | 8.0 | 16 |
| 2,2,4-TMeC ₅ | 3.49 | 7.2 | 13 | 3.13 | 7.2 | 14 |
| | $\Gamma = 1.8 \times 10^{-11} \text{ mol/cm}^2$ | | | $\Gamma = 2.4 \times 10^{-11} \text{ mol/cm}^2$ | | |
| <i>n</i> -C ₇ | 2.83 | 7.9 | 18 | 2.71 | 8.1 | 19 |
| <i>n</i> -C ₈ | 3.32 | 9.6 | 22 | 3.21 | 10.2 | 24 |
| <i>n</i> -C ₉ | 3.83 | 10.1 | 22 | 3.73 | 9.7 | 21 |
| 2-MeC ₇ | 3.21 | 8.9 | 20 | 3.09 | 9.3 | 22 |
| 2,5-DMeC ₆ | 3.10 | 8.6 | 19 | 2.98 | 9.1 | 21 |
| 2,2,4-TMeC ₅ | 2.94 | 7.6 | 16 | 2.81 | 8.0 | 18 |

^a $(\Delta\bar{G}_A)_\Gamma$ = free energy of adsorption at constant surface coverage, kcal/mol. ^b q_{st} = isosteric heat of adsorption, kcal/mol. ^c $(\Delta\bar{S}_A)_\Gamma$ = entropy of adsorption at constant surface coverage, cal/(°K mol).

chromatographic studies, whereas in the static measurements the surface pressure π is determined independently from the interfacial surface area. Second, helium has been used as the major gas component in this work, whereas nitrogen has been used in the previous static measurements. The solubility of nitrogen is much higher than that of helium in water,²⁸ and as we have previously shown,³ at very low concentrations the retention volumes of solutes could be as much as 7% different for these two carrier gases. Cruickshank, *et al.*,²⁹ have pointed out that the influence of the "inert" gas on interfacial adsorption may be even more important than that due to the solubility effect. In fact, Vorozhbitova, *et al.*,³⁰ have noted significant changes in retention in gas-solid chromatography using carbon black as adsorbent when the carrier gas is changed from helium to nitrogen.

Of the two possibilities, it seems likely that the estimated surface area plays the larger role in the discrepancy of the results. However, more experimentation is needed using nitrogen as carrier gas before a definitive answer can be given. As a result, we will present our experimental data without correction. It is to be noted that q_{st} is independent of the value of the surface area of the water interface. In addition, since A , the area per molecule, and π , the surface pressure are calculated directly from Γ , no discrepancy would be expected between the static and dynamic measurements as far as the functional relation between π and A are concerned. The argument is strengthened by the fact that π - A data of the present work agree well with independent static data.²⁷ This agreement will be shown in the section on equations of state.

Table I presents the thermodynamic functions of adsorption for the six solutes at four different surface coverages. The free energies have a standard deviation of $\pm 1\%$. The trend in $(\Delta\bar{G}_A)_\Gamma$ with surface cov-

erage is to less negative values. As we will see, this is mainly due to the more negative change in $(\Delta\bar{S}_A)_\Gamma$ with surface coverage. The trend in $(\Delta\bar{G}_A)_\Gamma$ with solute structure follows the expected direction, namely more negative with increased carbon number in the straight-chain alkanes and less negative with increased branching. The free energy change per methylene group for the linear homologous series is constant at 0.50 kcal/mol, indicating correspondence to Traube's rule. This value compares well with the value of 0.42 kcal/mol determined by Aveyard and Haydon³¹ for liquid hydrocarbon adsorption on water.

As a check on the self-consistency of the data in this work with those previously determined by gas chromatography in the Henry's law region² as well as available static data,⁵ we have computed the differential free energy of adsorption, ΔG_A^0 , as $\Gamma \rightarrow 0$ by the equation

$$\Delta G_A^0 = -RT \ln B \left(\frac{\partial \Gamma}{\partial P_a} \right)_T \quad (16)$$

where B is the constant for the Kemball-Rideal standard state.²⁵ When P_a is expressed in mm, B is equal to $1.034 \times 10^{12} T$. The results of the two methods are shown in Table II along with the data of Jones and Ottewill.⁵ While there is complete agreement between the two chromatographic methods, the values reported by Jones and Ottewill⁵ are roughly 0.3 kcal/mol less negative. This discrepancy may be due to the estima-

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Table II: Comparison of Differential Free Energies and Isosteric Heats of Adsorption at Zero Surface Coverage

| Adsorbate | $-(\Delta G_A^0)^a$ | $-(\Delta G_A^0)^b$ | $-(\Delta G_A^0)^c$ | q_{st}^a | q_{st}^b | q_{st}^c |
|--------------------------|---------------------|---------------------|---------------------|------------|------------|------------|
| <i>n</i> -C ₇ | 3.76 ± 0.04 | 3.7 ± 0.05 | 3.42 | 7.3 ± 0.5 | 6.9 ± 0.2 | 7.2 |
| <i>n</i> -C ₈ | 4.27 ± 0.05 | 4.2 ± 0.05 | 3.91 | 7.6 ± 1.1 | 7.9 ± 0.2 | 7.9 |
| <i>n</i> -C ₉ | 4.75 ± 0.05 | 4.7 ± 0.05 | | 10.0 ± 0.7 | 8.9 ± 0.2 | |
| 2-MeC ₇ | 4.12 ± 0.05 | 4.2 ± 0.05 | | 8.4 ± 1.2 | 7.7 ± 0.2 | |
| 2,5-DMeC ₆ | 4.09 ± 0.05 | | | 7.1 ± 1.8 | | |
| 2,2,4-TMeC ₅ | 3.93 ± 0.04 | 3.9 ± 0.05 | 3.66 | 7.4 ± 0.5 | 7.1 ± 0.2 | 6.8 |

^a This work; 12.1°, kcal/mol. ^b Previous chromatographic measurements;^{1,2} 12.5°, kcal/mol. ^c Jones and Ottewill;⁵ 15°, kcal/mol.

tion of the surface area of the gas-water interface and/or the carrier gas effect, as mentioned earlier.

The isosteric heats of adsorption, q_{st} , shown in Table I were determined by eq 14. Figure 4 shows plots of $\ln P_a$ vs. $1/T$ at constant Γ for *n*-heptane. The calculated standard deviation for q_{st} at finite coverages was $\pm 5\%$, but at times was as high as $\pm 10\%$. The error is amplified by the small temperature interval employed in this work.

Table II also compares q_{st} at zero coverage with those of our previous papers.^{1,2} It should be noted that the q_{st} data in column 6 were obtained³² by adding RT (~ 0.6 kcal/mol) to our previously reported differential heat data. Some data computed by Jones and Ottewill⁵ are also included. When the stated errors in q_{st} in this paper are used, the two heats of adsorption are in close agreement; however, this comparison is not as critical a test of the present method as was the comparison of (ΔG_A^0) values in which the precision was much higher. It is also interesting to note that the chromatographically determined values of q_{st} compare well with the static data of Jones and Ottewill.⁵

The relatively parallel nature of the isosteres for *n*-C₇ in Figure 4 indicates that q_{st} does not vary greatly with coverage. This trend is observed for *n*-heptane in Table I. The changes in q_{st} for *n*-C₉ and 2-MeC₇ are also small over the surface coverage region studied. For other adsorbates, q_{st} changes with coverage by as much as 1.5 kcal/mol. It is difficult to assess how much of this change is real and how much due to error; however, a small increase in q_{st} with coverage is expected. It would appear that the anomalous results for *n*-C₈ at $\Gamma = 2.4 \times 10^{-11}$ mol/cm² are due to error. (Recall that $(\Delta \bar{G}_A)_\Gamma$ is determined with the least error and that this function increases with carbon number.)

Figure 5 shows the isosteric heat of adsorption as a function of surface coverage for *n*-heptane. Over the whole concentration range, q_{st} is less negative than the heat of liquefaction, ΔH_L^0 . Similar behavior was found for the other five solutes. No dramatic increase in q_{st} as $\Gamma \rightarrow 0$, as previously reported by Ottewill for hexane⁴ and toluene⁸ and used by Adamson in his model for the mechanism of adsorption of the vapors on the water surface,¹⁰ was found. The results in Fig-

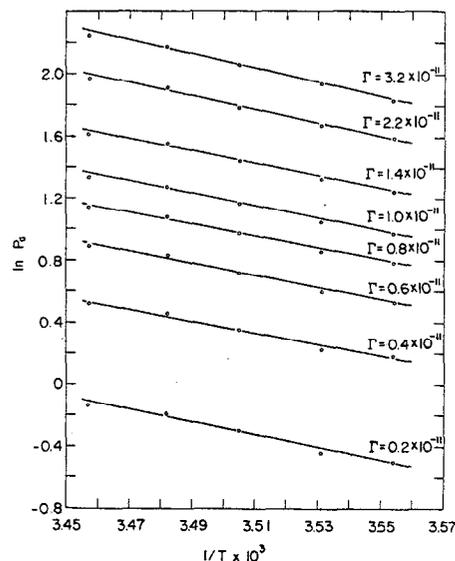


Figure 4. $\ln P_a$ vs. $1/T$ plots for *n*-heptane at constant surface coverages; Γ is expressed in units of moles per square centimeter.

ure 5 support our previous conclusion¹⁻³ that water is a low-energy surface when nonpolar adsorbates are employed. One might expect q_{st} to be less than ΔH_L^0 given the type III isotherms one obtains for these adsorbates. Beebe^{33,34} has raised the same point in reference to results obtained on ice.¹⁰

Returning to Table I, the entropies of adsorption at constant surface coverage are also reported. The standard deviation in $(\Delta \bar{S}_A)_\Gamma$ is $\pm 10\%$ in most cases, but it can be as high as $\pm 15\%$; consequently, caution must be exercised in interpreting the results. The trends in $(\Delta \bar{S}_A)_\Gamma$ follow those reported already for q_{st} , i.e., a more negative entropy of adsorption with increase in carbon number in the straight-chain series and with decrease in branching. The anomalous entropy results in Table I at $\Gamma = 2.4 \times 10^{-11}$ mol/cm² for *n*-C₈ has the same source as the presumed error in q_{st} .

(32) J. H. de Boer, "The Dynamical Character of Adsorption," Clarendon Press, Oxford, 1953, p 49.

(33) R. A. Beebe, *J. Colloid Interface Sci.*, **31**, 436 (1969).

(34) M. W. Orem, *ibid.*, **31**, 437 (1969).

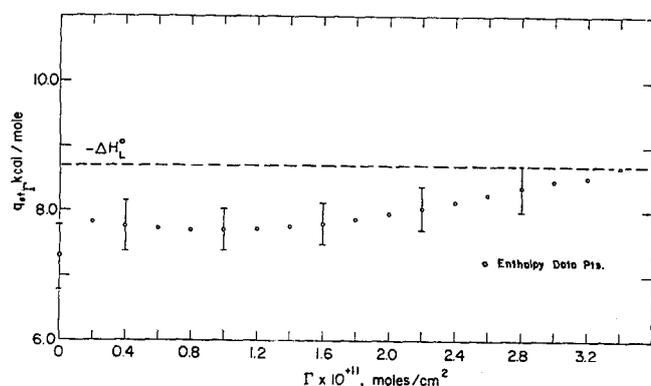


Figure 5. Isosteric heat of adsorption, q_{st} , as a function of surface coverage for n -heptane on water at $T = 12.1^\circ$.

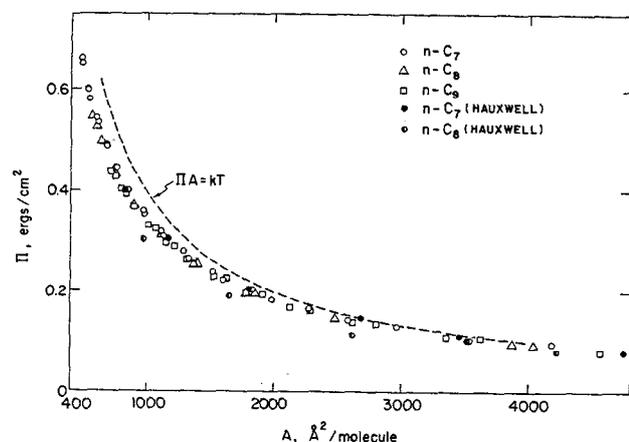


Figure 6. Surface pressure vs. area per molecule isotherms for the n -alkanes adsorbed on water at $T = 12.1^\circ$. Hauxwell²⁷ data obtained at 15.0° .

Ottewill has previously calculated the theoretical entropy change that results from the loss of one degree of translational freedom when the molecule adsorbs on a two-dimensional surface,^{5,6} *i.e.*, as a two-dimensional ideal gas. Using an identical procedure, we compute ΔS_i at 12.5° to be approximately -9 eu for the n -alkanes, which is less negative compared to the experimental values. The errors in $(\Delta \bar{S}_A)_T$ do not allow further interpretation. More information, however, can be derived from a consideration of the equations of state for the adsorbed species, which is presented in the next section.

Equations of State. To examine more fully the adsorbate-adsorbent system, it is useful to describe the two-dimensional equation of state over the whole concentration range studied. The surface pressure, π , can be calculated from eq 11 with known partial pressure values P_a . From the standard deviations of the regressions, the error in π was found to be between ± 2 and $\pm 7\%$ from concentrations of $2000 \text{ \AA}^2/\text{molecule}$ and lower, and between ± 0.5 and $\pm 3\%$ for concentrations higher than $2000 \text{ \AA}^2/\text{molecule}$.

Typical π - A isotherms for the normal alkanes at 12.1° are shown in Figure 6. The dotted curve represents the ideal equation of state, *i.e.*, $\pi A = kT$. The experimental data are found to lie below the ideal curve for concentrations as low as $2500 \text{ \AA}^2/\text{molecule}$. This nonideality might first appear striking; however, it is quite consistent with the adsorption isotherms shown previously. Similar behavior was found for the branched-chain alkanes studied from nonideal gaseous films at the vapor-water interface, even at very low surface coverage.

Similar observations have been made in the past^{5,8,26} for the adsorption of n -alkanes (C_5 to C_8) and isooctane at the vapor-water interface. Except for the recent work of Hauxwell and Ottewill,^{8,9} no extensive data are available in the very dilute region of Figure 6. Several values of π at different A values for n - C_7 and n - C_8 , obtained by Hauxwell²⁷ using a static procedure, are also included in Figure 6. A comparison of the static data with those of the present study reveals a maximum difference of only 2% over the entire range of surface concentration. This agreement shows that the π vs. A plots for both static and dynamic conditions follow the same functional dependence.

In order to have a more quantitative picture of the nonideal state, $(\pi A/kT)$ has been plotted as a function of π for the n -alkanes at $T = 12.1^\circ$ in Figure 7. Similar behavior was observed for the branched hydrocarbons. Below $\pi = 0.2 \text{ erg/cm}^2$, the errors in π and the small differences from adsorbate to adsorbate do not permit any discernible trends, other than that the πA products for all adsorbates approach the ideal line at low π values. Nevertheless, the data in all cases fall below the ideal line. As found previously in a higher concentration region,²⁶ the πA product decreases almost linearly with increase of π , obeying a modified Schofield-Rideal equation³⁵

$$\pi A = (1 - X)kT \quad (17)$$

This equation describes the nonideality of the equation of state in terms of an empirical correction term which in the case of neutral films should be proportional to the extent of van der Waals interaction between the adsorbates. From Figure 7, it can be seen that X for any solute increases linearly with surface pressure from 0 to a maximum value of roughly 0.2.

At any constant π and T , in the region $\pi > 0.2 \text{ erg/cm}^2$, X follows the sequence n - $C_9 > n$ - $C_8 > n$ - C_7 and 2 - $\text{MeC}_7 > 2,5$ - $\text{DMeC}_6 > 2,2,4$ - TMeC_5 . The results are in the expected order for van der Waals interactions of adsorbates. Thus, for the branched-chain alkanes, increased branching results in a reduced interaction, because of the lower hydrocarbon surface for such interaction. The trends in nonideality are in

(35) R. K. Schofield and E. K. Rideal, *Proc. Roy. Soc., Ser. A*, **109**, 57 (1925).

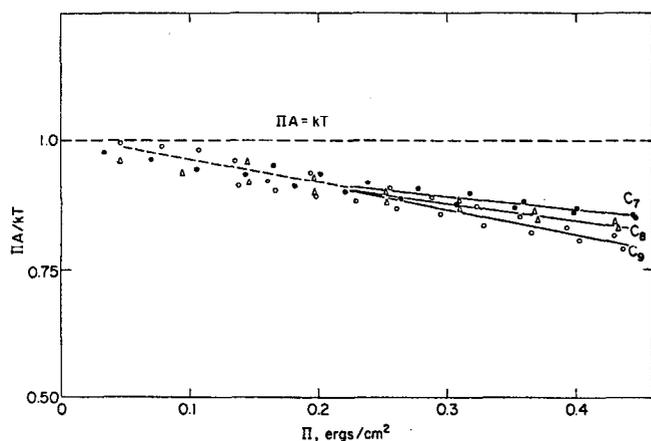


Figure 7. πA vs. π plots for the n -alkanes adsorbed on water at $T = 12.1^\circ$.

agreement with the entropy results in Table I. In addition, similar behavior has already been observed in the case of n -alkanes²⁶ and straight-chain fatty acids.³⁶

The two-dimensional equation of state for a nonideal gas at the vapor-liquid interface can be expressed as follows^{5,37,38}

$$(\pi + \pi_s)(A - A_0) = kT \quad (18)$$

where A_0 is the co-area of the adsorbed molecules, π_s is the cohesive surface pressure, and k is the Boltzmann constant. On the basis of the van der Waals gas equation, π_s can be written as^{36,39}

$$\pi_s = a_s/A^2 \quad (19)$$

where a_s is the two-dimensional analog of the van der Waals constant. The co-area A_0 , which can be assumed to be around 20–30 $\text{\AA}^2/\text{molecule}$, is negligibly small in comparison to the experimental values of A ranging from 500 to 4000 $\text{\AA}^2/\text{molecule}$. Combination of eq 18 and 19 gives

$$\left(\pi + \frac{a_s}{A^2}\right)A = kT \quad (20)$$

Finally, comparison of eq 17 and 20 reveals that

$$XkT = a_s/A \quad (21)$$

Figure 8 shows plots of XkT vs. $1/A$ for the three n -alkanes. For reasons stated earlier, only points at higher concentration are used. Within experimental error the plots are linear, passing through the origin. Again, similar behavior was found for the branched-chain alkanes. The results clearly indicate that all six hydrocarbons obey the van der Waals theory of intermolecular attraction in two dimensions (eq 19).

The slopes of the straight lines give the two-dimensional van der Waals constant, a_s . Table III presents the a_s values for the hydrocarbons. Also shown in this table are the three-dimensional van der Waals con-

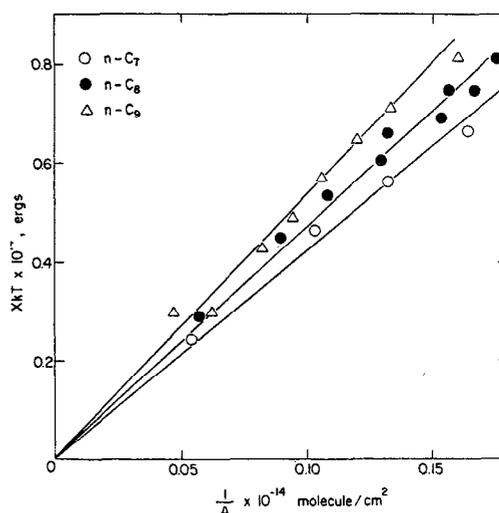


Figure 8. XkT vs. $(\text{area}/\text{molecule})^{-1}$ for the n -alkanes adsorbed on water at $T = 12.1^\circ$.

stants of attraction in the vapor state, a . These values are obtained from critical data of each hydrocarbon.⁴⁰ On comparison, both a_s and a are found to change in the same manner. Each increases in magnitude with the chain length of the hydrocarbon and for a given number of carbons decreases with branching.

Table III: Two-Dimensional van der Waals Constants and Film Thicknesses of Saturated Hydrocarbons at the Vapor-Water Interface, $T = 12.1^\circ$

| Solute | $a_s \times 10^{28}$, (ergs cm ²)/ molecule ² | $a \times 10^{24}$, (ergs cm ²)/ molecule ² | τ (at 50 \AA^2 / molecule), \AA | $\Delta_V \tau$, \AA |
|-------------------------|---|---|---|-----------------------------------|
| n -C ₇ | 4.1 | 0.86 | 3.6 | |
| n -C ₈ | 4.7 | 1.04 | 4.3 | 4.3 |
| n -C ₉ | 5.4 | 1.25 | 5.0 | |
| 2,2,4-TMeC ₅ | 3.7 | 0.92 | 4.0 | |
| 2,5-DMeC ₆ | 4.1 | 0.97 | 4.1 | 4.1 |
| 2-MeC ₇ | 4.4 | 1.01 | 4.2 | |

The thickness of the films, τ , can be obtained from eq 22^{36,39,41}

$$\tau = a/(a_s + kTA) \quad (22)$$

The τ values are presented in Table II at a surface con-

(36) A. K. Chatterjee and D. K. Chatteraj, *Kolloid-Z. Z. Polym.*, **234**, 1053 (1969).

(37) A. W. Adamson, "Physical Chemistry of Surfaces," Interscience, New York, N. Y., 1967, p 98.

(38) J. H. de Boer in ref 37, p 132.

(39) D. K. Chatteraj and A. K. Chatterjee, *J. Colloid Interface Sci.*, **21**, 159 (1966).

(40) F. D. Rossini, et al., Ed., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

(41) N. L. Gershfeld, *J. Colloid Interface Sci.*, **28**, 240 (1968).

centration of $500 \text{ \AA}^2/\text{molecule}$ and at $T = 12.1^\circ$. At this highest concentration studied in this work, the thicknesses, on the average, are found to be 4.3 and 4.1 \AA for the normal and branched-chain alkanes, respectively. The crystallographic cross-section area of the hydrocarbon chain is $12 \text{ \AA}^2/\text{molecule}$.⁴² On this basis, the thickness of the $-\text{CH}_2-$ chain is $\sim 4 \text{ \AA}$, which agrees remarkably well with the calculated average thickness of both series of films at $500 \text{ \AA}^2/\text{molecule}$. This means that the molecules of the hydrocarbon films lie mainly flat on the interface, even at the highest surface concentrations studied.

In work not presented in Table II, τ values calculated at coverages less than $500 \text{ \AA}^2/\text{molecule}$ were found to be somewhat smaller than 4 \AA . This result may be due to the entropy approximation made in deriving eq 22, namely that the surface molecules are fully extended and that only translational energy is lost on compression. This assumption may not hold for the present hydrocarbon films in the more dilute regions. Finally, a comparison of our results for *n*-heptane with those of octanoic acid,³⁸ which has the same effective number of CH_2 groups (both adsorbing on the water surface), shows that a_s for the acid is less than that of the hydrocarbon. This means that the presence of a polar group in the chain reduces the van der Waals attraction.⁴³

Conclusion

Gas-liquid chromatography has been shown to be a valid method for the measurement of the adsorption of insoluble vapors in liquid surfaces at finite surface coverage. The method provides a link between the zero surface coverage measurements made by linear elution chromatography¹⁻³ and the static measurements at higher surface coverages. Using a frontal development method of gas chromatography, it may be possible to extend the isotherm determinations into surface concentrations approaching monolayer coverage and above.

The water interface has been shown to be a low-energy surface for hydrocarbon adsorption. The non-ideality of the gaseous films at coverages as low as $2500 \text{ \AA}^2/\text{molecule}$ is probably a reflection of the greater attraction of adsorbate molecules to themselves, rather than to the water surface.

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(42) J. J. Jasper and R. D. van Dell, *J. Phys. Chem.*, **69**, 481 (1965).

(43) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, N. Y., 1961, pp 159, 230.