



cal and experimental study of the structure of water at liquid–solid interfaces.<sup>2</sup> Likewise, the properties of the gas–liquid interfaces of water and aqueous solutions of electrolytes are of growing importance in oceanography.<sup>3,4</sup>

The interfacial structure of water and the nature of water–solute interactions in thin films of water play an important role in living systems.<sup>5–7</sup> For example, the rate processes involved in plant nutrition are highly dependent on the structure of water in soil.<sup>8</sup> On a higher level, the presence of structured water layers at cell membranes is critical for the proper functioning of a cell,<sup>9,10</sup> and differences in the nmr spin–lattice and spin–spin relaxation times of structured water in rat and mouse tissue can be used to distinguish malignant tumors from normal tissues.<sup>11,12</sup> Moreover, the Pauling–Miller theory of the mechanism of gaseous anesthesia<sup>13,14</sup> postulates an interaction between interfacial water in brain cells and the anesthetic gas.

In spite of their importance, remarkably little is known about the nature of water (and ice) interfaces. Any interfacial layer must have a finite thickness of at least one molecule, and there has been general agreement<sup>15–20</sup> that water near interfaces is structured for the much greater distance of five to ten molecular layers into the bulk of the liquid.<sup>21</sup> It is clear that more experimental work is needed to examine the surface structure of liquids in general and of water in particular.<sup>16,24–26</sup>

### Experimental Study of the Interfacial Structure of Water

Investigation of the simultaneous adsorption on and solution in thin layers of water coated on a porous solid should provide information for several of the above-mentioned problems. Indeed, this is one of

the few available ways to characterize either gas–liquid or liquid–solid interfaces.<sup>27–31</sup> Furthermore, if measurements are made in the Henry's law region, the solute can act exclusively as a probe of water structure, since solute–solute interactions are essentially nonexistent in this region.

Such studies on water (and ice) interfaces have only rarely been carried out over the years because of the difficulties associated with the measurements. The volatility of the water, the relatively small extent of adsorption (and solution in certain cases), and the difficulties involved in preparation of clean surfaces all make such measurements complicated. Furthermore, the problems are increased at low solute concentrations, and extrapolation to this region from higher concentrations can result in large errors.

In general, studies of the adsorption of nonelectrolytes at the water–solid interface have been aimed at elucidating adsorbate–adsorbate interactions, with little being said about solute–water interactions near the surface. Much more work has been done on adsorption at the gas–liquid interface. Isotherms, equations of state, and thermodynamic parameters of adsorption have all indicated that the gas–liquid interface of water behaves as a low energy surface with the hydrogen atoms pointed in the net direction toward the vapor phase.<sup>32–40</sup> There is also good theoretical justification for this model.<sup>41</sup>

This qualitative description of the gas–liquid interface of water has recently been modified by Adamson. He studied the surface of ice through physical adsorption<sup>42–44</sup> and found that the isosteric heats of adsorption of compounds such as *n*-hexane at coverages corresponding to 0.1 monolayer or less were up to twice as large as the heat of vaporization. (The isosteric heat of adsorption,  $q_{st}$ , is formally the "heat of vaporization" of the adsorbed state<sup>29,31</sup> at a given surface coverage.) This value decreased to the heat of vaporization at coverages of roughly 0.5 monolayer. Unexpectedly large entropy losses,  $\Delta S_A$ , upon adsorption were also observed at low coverages. (In his thesis in 1951,<sup>40</sup> Ottewill had reported similar

- (2) L. C. Allen, *J. Colloid Interface Sci.*, **36**, 554 (1971).
- (3) R. A. Horne, "Marine Chemistry," Wiley-Interscience, New York, N. Y., 1969.
- (4) J. P. Riley and R. Chester, "Introduction to Marine Chemistry," Academic Press, New York, N. Y., 1971.
- (5) G. N. Ling, *Food Technol. (Chicago)*, **22**, 1254 (1968).
- (6) R. D. Schultz and S. K. Asunmaa, "Recent Progress in Surface Science," J. F. Danielli, A. C. Roddiford, and M. D. Rosenberg, Ed., Academic Press, New York, N. Y., 1970, p 291.
- (7) M. V. Tracey, *Proc. Roy. Soc., Ser. B*, **171**, 59 (1968).
- (8) P. F. Low, *Soil Sci.*, **93**, 6 (1965).
- (9) E. Roacker, Ed., "Membranes of Mitochondria and Chloroplasts," Van Nostrand-Reinhold, New York, N. Y., 1969.
- (10) L. I. Rothfield, Ed., "Structure and Function of Biological Membranes," Academic Press, New York, N. Y., 1971.
- (11) R. Damadian, *Science*, **171**, 1151 (1971).
- (12) N. Iijima and N. Fujii, *JEOL News*, **9a** (4), 5 (1972).
- (13) L. Pauling, *Science*, **134**, 14 (1961).
- (14) S. L. Miller, *Proc. Nat. Acad. Sci., U. S.*, **47**, 1515 (1961).
- (15) W. Drost-Hansen, *Ind. Eng. Chem.*, **57** (4), 18 (1965).
- (16) W. Drost-Hansen, *Ind. Eng. Chem.*, **61** (11), 10 (1969).
- (17) J. C. Henniker, *Rev. Mod. Phys.*, **21**, 322 (1949).
- (18) R. A. Horne, A. F. Day, R. P. Young, and N. T. Yu, *Electrochim. Acta*, **13**, 397 (1968).
- (19) P. F. Low, *Advan. Argon*, **13**, 269 (1961).
- (20) A. Szent-Gyorgi, "Bioenergetics," Academic Press, New York, N. Y., 1957.
- (21) According to Drost-Hansen,<sup>16</sup> a thicker disorganized region somewhat similar to bulk water may exist beyond these five to ten structured layers up to a thickness of 100 molecular diameters. In very narrow pores this may well be the case. There is evidence from nmr studies that a modified water structure exists in porous silica, for example.<sup>22,23</sup>
- (22) J. H. Pickett and L. B. Rogers, *Anal. Chem.*, **39**, 1892 (1967).
- (23) H. A. Resing, *Advan. Mol. Relaxation Processes*, **1**, 109 (1968).
- (24) F. Fowkes, *Ind. Eng. Chem.*, **56** (12), 40 (1964).
- (25) H. Pack, *J. Korean Chem. Soc.*, **12**, 18 (1968).
- (26) F. C. Tompkins, Ed., *Spec. Discuss. Faraday Soc.*, No. 1 (1971).
- (27) A. W. Adamson, *J. Chem. Educ.*, **44**, 710 (1967).
- (28) R. Aveyard and D. A. Haydon, *Trans. Faraday Soc.*, **61**, 2255 (1965).
- (29) J. H. deBoer, "The Dynamical Character of Adsorption," 2nd ed., Oxford University Press, London, 1968.
- (30) L. M. Dormant and A. W. Adamson, *J. Colloid Interface Sci.*, **28**, 459 (1968).
- (31) S. Ross and J. P. Oliver, "On Physical Adsorption," Interscience, New York, N. Y., 1964.
- (32) M. Blank and R. H. Ottewill, *J. Phys. Chem.*, **68**, 2206 (1964).
- (33) B. Case and R. Parsons, *Trans. Faraday Soc.*, **63**, 1224 (1967).
- (34) C. L. Cutting and D. C. Jones, *J. Chem. Soc.*, 4067 (1955).
- (35) R. B. Dean and K. E. Hayes, *J. Amer. Chem. Soc.*, **74**, 5982 (1952).
- (36) F. Hauxwell and R. H. Ottewill, *J. Colloid Interface Sci.*, **34**, 473 (1970).
- (37) K. E. Hayes and R. B. Dean, *J. Amer. Chem. Soc.*, **73**, 4483 (1951); *J. Phys. Chem.*, **57**, 80 (1953).
- (38) D. C. Jones and R. H. Ottewill, *J. Chem. Soc.*, 4076 (1955).
- (39) D. C. Jones, R. H. Ottewill, and A. P. J. Chater, *Proc. Intern. Congr. Surface Activity*, 2nd, London, **1**, 188 (1957).
- (40) R. H. Ottewill, Doctoral Thesis, University of London, 1951.
- (41) N. H. Fletcher, *Phil. Mag.*, **18**, 1287 (1968).
- (42) A. W. Adamson, L. M. Dormant, and M. Orem, *J. Colloid Interface Sci.*, **25**, 206 (1967).
- (43) M. W. Orem and A. W. Adamson, *J. Colloid Interface Sci.*, **31**, 278 (1969).
- (44) A. W. Adamson and B. R. Jones, *J. Colloid Interface Sci.*, **37**, 831 (1971).

trends for the adsorption of *n*-hexane on liquid water.)

Adamson explained these results in terms of a surface perturbation when the adsorbate came into contact with the water. He suggested that troughs or pockets of low entropy domains formed into which the adsorbate positioned itself. More recently, careful surface pressure measurements of adsorbed toluene on liquid water at low coverage between 5° and 25° added weight to this model.<sup>45</sup> The isosteric heat of adsorption of toluene (extrapolated to zero coverage) was found to be *ca.* 5 kcal/mol greater than the heat of vaporization, and the entropy loss on adsorption was found to be much greater than would be expected from a simple loss of one degree of translational freedom.

On ice, the trend in isosteric heat of adsorption seemed to persist down to about -35°. At lower temperatures, opposite trends occurred. Adamson interpreted these results as an indication that a liquid layer exists on ice until -35°, at which point solidification of this layer takes place.

The increases in  $q_{st}$  and  $-\Delta S_A$  at low coverage are crucial to the model proposed by Adamson. It is therefore essential to examine the region near zero surface coverage in detail, in order to test his explanation. However, from standard surface pressure measurements on liquid water it is very difficult to obtain accurate and reproducible thermodynamic functions of adsorption at low coverages, as discussed above. The results are limited in their accuracy even further due to the necessity of extrapolating to zero coverage, and then determining the temperature dependence of that extrapolation to obtain the heat of adsorption. Consequently, there is a need to develop other experimental approaches which can directly provide thermodynamic measurements at very low concentrations.

A technique which is well suited for such measurements is gas chromatography (gc), which has become a standard method for determining thermodynamic functions in the Henry's law region of gas-liquid solution and gas-solid adsorption<sup>46-49</sup> and for determining sorption isotherms.<sup>48,50,51</sup> Gas-liquid surface adsorption has also been studied, primarily as a complicating factor in gas-liquid solution studies.<sup>52-54</sup>

In general, several retention mechanisms can occur simultaneously in a gc column: adsorption on the liquid surface, partition in the bulk liquid, and adsorption on the solid support. With water as a liquid phase and nonpolar or weakly polar compounds as samples, adsorption effects on the solid surface are

negligible, since the water effectively deactivates the support. On the other hand, since the liquid phase is spread in a thin layer on the moderately high surface area porous support, the surface area to volume ratio of the liquid is several orders of magnitude greater than that for the liquid phase in a container. Thus even a small tendency toward surface adsorption is magnified in the gc column. In the extreme case, when saturated hydrocarbons are the solutes, interfacial adsorption is the only detectable mechanism of retention.<sup>55,56</sup> Under these conditions, adsorption isotherms and thermodynamic parameters of adsorption at both zero and finite surface coverages can be directly determined.

For a variety of other more soluble compounds, both partition and liquid surface adsorption can occur simultaneously in the column. By proper separation of the retention mechanisms, partition coefficients and heats of solution in water at effectively infinite dilution can be measured, in addition to thermodynamic parameters for adsorption at zero surface coverage. Thus, both the surface properties and the bulk properties of thin films of water (<100 Å) can be examined using this technique. Furthermore, since the water is coated on a solid, the influence of this surface of the solid on the structure of the water can be assessed by studying the partition and adsorption properties of the liquid as its film thickness is varied.

Water and other volatile solvents have been used as gc liquid phases in the past,<sup>56-68</sup> and studies of the solution of nonelectrolytes have been carried out.<sup>59,60</sup> Thus most of the experimental work involved for the research described below has been relatively straightforward. With flame ionization detection, extremely small sample sizes can be utilized. Also, the

(55) B. L. Karger and A. Hartkopf, *Anal. Chem.*, **41**, 215 (1969).

(56) B. L. Karger, A. Hartkopf, and H. N. Posmanter, *J. Chromatog. Sci.*, **7**, 315 (1970).

(57) O. Grubner and L. Duskova, *Collect. Czech. Chem. Commun.*, **26**, 3109 (1961).

(58) S. P. Wasik and W. Tsang, *Anal. Chem.*, **42**, 1648 (1970).

(59) R. E. Pecsar and J. J. Martin, *Anal. Chem.*, **38**, 1661 (1966).

(60) D. L. Shaffer and T. E. Daubert, *Anal. Chem.*, **41**, 1585 (1969).

(61) B. L. Karger, P. A. Sewell, R. C. Castells, and A. Hartkopf, *J. Colloid Interface Sci.*, **35**, 328 (1971).

(62) B. L. Karger, R. C. Castells, P. A. Sewell, and A. Hartkopf, *J. Phys. Chem.*, **75**, 3870 (1971).

(63) B. L. Karger, A. K. Chatterjee, and J. W. King, *J. Colloid Interface Sci.*, **41**, 71 (1972).

(64) J. W. King, A. K. Chatterjee, and B. L. Karger, *J. Phys. Chem.*, **76**, 2769 (1972).

(65) J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, **64**, 3100 (1968).

(66) In the low concentration region where Henry's law applies, the partial derivative terms in eq 1 and 3 reduce to simple ratios. Under these conditions  $K_A$  and  $K_L$  are constants independent of the magnitude of  $C_G$  and can be obtained from plots of  $V_N^0/V_L^0$  vs.  $A_L^0/V_L^0$ , or  $V_N^0/A_L^0$  vs.  $V_L^0/A_L^0$ . If the coefficients obtained from the two plots agree, then partition and liquid surface adsorption are the only retention mechanisms. See C. Eon, A. J. Chatterjee, and B. L. Karger, *Chromatographia*, **5**, 28 (1972).

(67) Surface area determinations by the BET method would require freezing the water in the column, and a danger exists that the surface area of the resulting ice would not be the same as that of the original water (e.g., cracking); however, in a recent paper by Sawyer the BET approach has been claimed to have been successfully applied (J. P. Okamura and D. T. Sawyer, *Anal. Chem.*, **45**, 80 (1973)). Alternatively, if reliable static measurements of  $K_A$  in the Henry's law region were available, then  $A_L^0$  could be obtained directly from eq 2 by selecting a compound of known  $K_A$  whose solubility in water is so low that the second term in the equation is negligible. Unfortunately, the zero coverage values in the literature are not known with any degree of confidence. We are currently carrying out our own static measurements.

(68) D. E. Martire, R. C. Pecsok, and J. H. Purnell, *Trans. Faraday Soc.*, **61**, 2496 (1965).

(45) F. Hauxwell and R. H. Ottewill, *J. Colloid Interface Sci.*, **28**, 514 (1968).

(46) J. R. Conder, "Progress in Gas Chromatography," J. H. Purnell, Ed., Interscience, New York, N. Y., 1968.

(47) A. J. B. Cruickshank, M. L. Windsor, and C. L. Young, *Proc. Roy. Soc., Ser. A*, **295**, 259 (1965).

(48) A. V. Kiselev and Y. I. Yashin, "Gas Adsorption Chromatography," J. E. S. Bradley, Trans., Plenum Press, New York, N. Y., 1969.

(49) C. L. Young, *Chromatogr. Rev.*, **10**, 129 (1968).

(50) E. Cremer and H. F. Huber, *Angew. Chem.*, **73**, 461 (1961).

(51) H. Knozinger and H. Spannheimer, *J. Chromatogr.*, **16**, 1 (1964).

(52) R. L. Martin, *Anal. Chem.*, **33**, 347 (1961).

(53) D. E. Martire, "Progress in Gas Chromatography," J. H. Purnell, Ed., Interscience, New York, N. Y., 1968.

(54) R. L. Pecsok, A. de Yllana, and A. Abdul-Karim, *Anal. Chem.*, **36**, 452 (1964).

detector does not respond to water, which means that there are no large background signals to cope with due to the finite partial pressure of the water in the carrier gas.

This Account summarizes our work to date<sup>61-64</sup> on extending gas chromatographic methods in the study of the interfacial properties of water through physical adsorption and solution and illustrates the types of information which one can obtain from such a study.

### Theory

**Retention.** The fundamental retention equation when both partition in and adsorption on the liquid phase occur simultaneously and independently can be written as<sup>65</sup>

$$V_N^0 = \left(\frac{\partial C_S}{\partial C_G}\right)_T A_L^0 + \left(\frac{\partial C_L}{\partial C_G}\right)_T V_L^0 \quad (1)$$

$$V_N^0 = K_A A_L^0 + K_L V_L^0 \quad (2)$$

where  $V_N^0$  is the net retention volume of the sample per gram of column packing,  $A_L^0$  and  $V_L^0$  are the surface area and volume of the liquid phase per gram of packing,  $K_A$  is the adsorption coefficient, and  $K_L$  is the partition coefficient.  $C_L$  and  $C_G$  are concentrations in the liquid and gas phases;  $C_S$  is the concentration in the surface phase in excess to that in the bulk liquid ( $=\Gamma$ , the Gibbs surface excess). Since  $C_G$  can be approximated by  $P/RT$ , the adsorption term in eq 1 can be written as<sup>66</sup>

$$V_N^0 = RT \left(\frac{\partial \Gamma}{\partial P}\right)_T A_L^0 \quad (3)$$

While  $V_L^0$  can be obtained directly from the weight of water in the column, there is no comparably direct way to obtain  $A_L^0$ .<sup>67</sup> For the work to date we therefore selected an indirect method to furnish an estimate for  $A_L^0$ . Martire, *et al.*,<sup>68</sup> have carefully measured  $K_A$  values for benzene and aniline adsorbing on the surface of  $\beta, \beta'$ -thiodipropionitrile (TDPN). They used these  $K_A$  values to calculate  $A_L^0$  for TDPN columns of various loadings on Chromosorb P. We have assumed that, for a given per cent loading,  $A_L^0$  is the same for TDPN and for water. (In reality, the water columns would be expected to have a somewhat higher  $A_L^0$  because the water would wet the support better. However, for a heavily loaded column the difference should not be too great.) A 20% w/w column was selected as standard with a surface area of  $1 \text{ m}^2/\text{g}$ .

A saturated hydrocarbon, *n*-octane, was then chosen as a reference compound. The mole fraction solubility of all alkanes above butane is very low (for *n*-octane, it is  $4 \times 10^{-6}$  at  $12.5^\circ$ ),<sup>69</sup> and as a result they can be assumed to undergo only gas-liquid interfacial adsorption on water columns. Other evidence also points to this single retention mechanism, such as the constancy of the heat of sorption of these compounds over wide ranges of liquid loading.<sup>61</sup> Using eq 2 (with  $K_L V_L^0 \approx 0$ ) the adsorption coefficient of *n*-octane on the 20% water column was calculated to be  $1.0 \times 10^{-4} \text{ cm}$ . The liquid surface areas of other

columns were then calculated using this value of  $K_A$  and the retention volume of *n*-octane at  $12.5^\circ$ . Recent results from our laboratory in a comparison of static and chromatographic measurements indicate that our estimate of  $A_L^0$  is quite reasonable.

It should be noted that the only values whose measurement error is directly proportional to the error in estimating  $A_L^0$  are  $K_A$  and  $\Gamma$ . The effect on the free energy,  $\Delta G_A$ , and entropy,  $\Delta S_A$ , of adsorption is small, due to the logarithmic relationship between  $\Delta G_A$  and  $K_A$ . For example, even if the error in  $A_L^0$  were as high as  $-50\%$ , the resulting errors in  $\Delta G_A$  and  $\Delta S_A$  would be  $+0.4 \text{ kcal/mol}$  and  $+1.0 \text{ cal/(deg mol)}$ , respectively. Of course, the heat of adsorption is unaffected by the choice of  $A_L^0$ .

Finally, it should be pointed out that, under the conditions of our experiments, the gas phase can be assumed to be ideal.<sup>61,62,70</sup> Thus, nonideality effects in the liquid and/or adsorbed phases can be assessed directly in both the Henry's law and finite concentration regions.

**Isotherm Determinations.** The adsorption isotherm of any compound whose retention mechanism is exclusively gas-liquid interfacial adsorption can be obtained directly from the chromatographic data, using the elution by characteristic point (ECP) method.<sup>50,51,71</sup> In this procedure,  $\Gamma$  is determined as a function of  $P$  by direct integration for varying sample sizes of adsorbate. The resulting isotherms can then be fitted to polynomials of the form

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

**Thermodynamics of Adsorption and Solution.** The integral molar free energy change for the transfer of 1 mol of solute from its gaseous standard state (760 Torr) to an infinitely dilute solution in the liquid phase is given by<sup>46,49,72</sup>

$$\Delta G_S = -RT \ln K_L \quad (5)$$

Similarly, the integral molar free energy change for the transfer of 1 mol of adsorbate from the same standard state to an adsorbed state defined by its equilibrium partial pressure  $P$  is<sup>29,31</sup>

$$\Delta G_A = -RT \ln 760/P \quad (6)$$

At zero surface coverage, a standard adsorbed state must be chosen and related to  $P$ . Previous results on liquid surfaces have generally used a standard layer thickness of  $6 \text{ \AA}$  and a derived standard surface pressure analogous to a standard three-dimensional pressure of 760 Torr.<sup>73</sup> With this standard state

$$\Delta G_A = -RT \ln [(1.67 \times 10^7)(K_A)] \quad (7)$$

Applying the Gibbs-Helmholz relation to eq 5 and 7 gives the differential molar enthalpy of solution or adsorption,  $\Delta H_L$  or  $\Delta H_A$ . At zero coverage or infi-

(70) A. Hartkopf, Ph.D. Thesis, Northeastern University, Boston, Mass., 1970.

(71) J. F. K. Huber in "Gas Chromatography 1962," M. van Swaay, Ed., Butterworths, London, 1962.

(72) B. L. Karger, *Anal. Chem.*, **39** (8), 24A (1967).

(73) Thus  $\pi_S = (1.013 \times 10^6 \text{ dyn/cm}^2) \times (6 \times 10^{-8} \text{ cm}) = 0.0608 \text{ dyn/cm}$ . In the zero surface coverage region, where the adsorption isotherm is linear,  $K_A = \pi/P = \pi_S/P_S$ . Substituting in the value for  $\pi_S$  and converting  $P_S$  (760 Torr) to the units of  $\text{dyn/cm}^2$  result in eq 7. See C. Kemball and E. K. Rideal, *Proc. Roy. Soc., Ser. A*, **187**, 53 (1946).

(69) R. L. Bohon and W. F. Claussen; *J. Amer. Chem. Soc.*, **73**, 157 (1951).

**Table I**  
**Thermodynamic Functions of Adsorption of Vapors at Zero Surface Coverage on the Surface of the Water at 12.5°**

Adsorbate	$K_A \times 10^4$ , cm <sup>a</sup>	$-\Delta H_A$ , kcal/mol <sup>b</sup>	$-\Delta G_A$ , kcal/mol <sup>b</sup>	$-\Delta S_A$ , cal/(deg mol) <sup>b</sup>	$-\Delta H_L$ , kcal/mol <sup>c</sup>
<i>n</i> -Pentane	0.1	5.7	2.8	9	6.4
<i>n</i> -Hexane	0.2	6.6	3.3	11	7.5
<i>n</i> -Heptane	0.4	7.5	3.7	13	8.7
<i>n</i> -Octane	1.0	8.5	4.2	15	9.9
<i>n</i> -Nonane	2.3	9.5	4.7	17	11.1
<i>n</i> -Decane	5.3	10.7	5.2	19	12.3
2-Methylheptane	0.9	8.3	4.2	15	9.5
2,4-Dimethylhexane	0.7	8.0	4.0	14	9.0
2,2,4-Trimethylpentane	0.6	7.7	3.9	13	8.4
Cycloheptane	0.5	7.5	3.8	13	9.2
Cyclooctane	1.1	8.5	4.3	15	10.4
<i>cis</i> -2-Octene	2.0	8.6	4.6	14	9.8 <sup>d</sup>
<i>trans</i> -2-Octene	2.0	8.6	4.6	14	9.8 <sup>d</sup>
Dichloromethane	0.4	5.6	3.7	7	6.8
Chloroform	0.7	6.4	4.0	8	7.3
Carbon tetrachloride	0.3	5.6	3.5	7	7.8
1,2-Dichloroethane	1.7	7.8	4.5	12	8.5
Benzene	0.9	7.5	4.2	12	8.1
Toluene	2.5	8.9	4.7	15	9.1
Ethylbenzene	5.8	9.9	5.2	16	10.1
Fluorobenzene	1.1	7.8	4.2	12	8.4
Chlorobenzene	2.6	8.4	4.7	13	9.6
<i>n</i> -Propyl ether	36.3	12.8	6.3	22	8.7
Methyl formate	4.7	7.8	5.1	9	6.2
Ethyl formate	0.9	6.9	4.2	9	7.8 <sup>e</sup>

<sup>a</sup> Standard deviation, 10%. <sup>b</sup> Standard deviations:  $\Delta H_A$ , 0.2 kcal/mol;  $\Delta G_A$ , 0.1 kcal/mol;  $\Delta S_A$ , 1 cal/(deg mol). <sup>c</sup> Except as noted, data from J. D. Cop and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970. <sup>d</sup> R. R. Driesbach, *Advan. Chem. Ser.*, No. 15 (1955). <sup>e</sup> J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N. Y., 1950.

nite dilution, these quantities are equal to the integral heats.<sup>31,74</sup> For compounds which only adsorb,  $\Delta H_A$  can be obtained directly from the retention data.<sup>63</sup> Finally, the integral molar entropy of either solution or adsorption at zero coverage or infinite dilution can then be obtained from the second law.

At finite surface coverage, the adsorption heat which is most useful for interpreting the experimental results is the isosteric heat of adsorption, which is given by<sup>29,31</sup>

$$q_{st} = -R \left( \frac{\partial \ln P}{\partial (1/T)} \right)_\Gamma \quad (8)$$

To calculate  $q_{st}$ , values of  $P$  corresponding to a constant  $\Gamma$  at various temperatures can be obtained from eq 4.

**Errors.** In addition to those discussed elsewhere in this Account, there are several potential sources of error in the measurements: lack of equilibrium in the gc process; surface curvature effects on the water in the solid-support pores; adsorption or solution of the carrier gas on or in the water; and pretreatment of the solid support (*e.g.*, acid washing *vs.* base washing). Each of these is considered in one or more of the original papers and its influence on the results assessed. In all cases the influence is negligible.

### Adsorption Measurements

**Adsorption Parameters at Zero Surface Coverage.** Table I presents thermodynamic functions of adsorption at zero surface coverage, determined as

(74) J. H. Purnell, "Gas Chromatography," 2nd ed, Wiley-Interscience, New York, N. Y., 1971.

described under Theory. Note first that the heats of adsorption of all but two of the adsorbates are less negative than the corresponding heats of liquefaction. This result suggests that the adsorbed films are gaseous or liquid-expanded, the adsorbate being held on the surface by relatively weak forces, and contradicts the previously noted static measurements extrapolated to the zero surface coverage region.<sup>36,40,45</sup> On the other hand, the free energies of adsorption in Table I are in reasonable agreement with previous results. (It should be noted that  $\Delta G_A$  is the function determined with the greatest precision and accuracy in the static measurements.) The free-energy increment for the *n*-alkanes in Table I is a constant  $-0.45$  kcal/mol, indicating correspondence with Traube's rule.<sup>75</sup> This value compares well with values of  $-0.42$  kcal/mol at 15° obtained by Jones and Ottewill,<sup>38</sup>  $-0.44$  kcal/mole at 20° calculated by Aveyard and Haydon<sup>28</sup> from interfacial tension measurements, and  $-0.5$  kcal/mol at 25° obtained by Posner, *et al.*<sup>76</sup>

The entropy loss associated with transformation of a three-dimensional ideal gas into a two-dimensional ideal gas has been calculated by Kembal,<sup>77</sup> and for the adsorbates in Table I it ranges between  $-9$  and  $-10$  cal/(deg mol). An additional entropy loss associated with clustering of long hydrocarbon chains has

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

(76) A. M. Posner, J. R. Anderson, and A. E. Alexander, *J. Colloid Sci.*, 7, 623 (1952).

(77) C. Kembal and E. K. Rideal, *Proc. Roy. Soc., Ser. A*, 187, 73 (1946).

been calculated by Huggins.<sup>78</sup> His model does not apply strictly to molecules as small as those discussed here, but it does allow an estimate of  $-4$  cal/(deg mol) for the effect of clustering. Examination of Table I reveals that the measured  $\Delta S_A$  of most of the adsorbates can be accounted for by some combination of these two types of entropy changes. (For the higher  $n$ -alkanes, the clustering effect apparently partially hinders vibrational and rotational freedom, as indicated by the greater entropy loss upon adsorption.)

Since no clustering is possible for the benzene derivatives, some other effect must be invoked to account for the fact that their  $\Delta S_A$  values are more negative than  $-10$  cal/(deg mol). At zero surface coverage, the benzene ring can be considered to lie flat on the water surface to allow maximum interaction between the phenyl group and the water dipoles on the surface. This orientation would be expected to hinder partially the rotational and vibrational freedom of the molecule, thus accounting for the additional entropy change of  $-2$  to  $-6$  cal/(deg mol). (A similar effect is probably occurring with the cycloalkanes, 1,2-dichloroethane, and the plane of the double bonds of *cis*- and *trans*-2-octene.) The magnitude of this interaction can be estimated by calculating the difference between the free energy of adsorption of benzene and that of cyclohexane (estimated from Table I to be  $-3.3$  kcal/mol). The resulting value of  $-0.9$  kcal/mol agrees reasonably well with the estimate of  $-1.2$  kcal/mol obtained by Pomerantz, Clinton, and Zisman<sup>79</sup> on the basis of interfacial tension measurements.

One exception to the general trends in the thermodynamic functions in Table I is  $n$ -propyl ether. Its heat and entropy of adsorption point to a strong interaction between the ether and the water surface, and it is reasonable to assume that this interaction involves a hydrogen bond between the lone-pair electrons on the ethereal oxygen and the hydrogens of the water molecule. This is the first experimental evidence for the existence of hydrogen bonding of adsorbates to water surfaces. The results agree with the theoretical model of Fletcher<sup>41</sup> and the surface potential measurements of others,<sup>32,80</sup> indicating that the hydrogen atoms of the water molecules on the surface are relatively directed more toward the gas phase. The adsorption behavior of chloroform also supports this model. The heat of adsorption of this compound, which has a proton capable of hydrogen bonding, is less negative than its heat of liquefaction, indicating that the lone pairs on the oxygen of the water molecule are not as accessible at the surface.

The other exception to the trend in  $\Delta H_A$  is methyl formate. Its heat of adsorption is slightly more negative than its heat of liquefaction. This may be due to some specific interaction between the ester linkage and a water molecule (either dipole-dipole or hydrogen bonding). On the other hand, the heat of adsorption of ethyl formate on the surface of water does not suggest any specific interaction. Similar results were

obtained by Martire,<sup>81</sup> who measured adsorption coefficients on the surface of TDPN and found that methanol adsorbed strongly on the liquid surface but ethanol did not adsorb at all.

Aside from  $n$ -propyl ether and methyl formate, it is clear that water has a low-energy surface for adsorption of nonpolar vapors at zero coverage. The type III adsorption isotherm shapes (see below) also agree with this conclusion. It must therefore be concluded that the perturbation model of Adamson<sup>42,43</sup> is unsupported. Not only are the heats of adsorption not sufficiently negative, but the entropy changes are too small to account for "domain" formation.

**Adsorption Isotherms and Equations of State.** The determination of sorption isotherms using gc offers two advantages over static measurements:<sup>71</sup> the method is applicable at low coverage; and surface concentrations are measured directly. Isotherms obtained in this way agree reasonably well with static measurements, especially at low partial pressures.<sup>82</sup> We have determined the adsorption isotherms of several normal and branched chain alkanes (those listed in Table II) at surface coverages ranging from 500 to 4000  $\text{\AA}^2/\text{molecule}$ . In agreement with previous work, type III or "anti-Langmuir" isotherms are obtained for all six adsorbates.

In order to describe more fully the adsorbate-adsorbent system at finite surface coverage, it is useful to examine how closely the adsorbates follow the ideal two-dimensional gas equation of state:<sup>29,31,75</sup>  $\pi A_M = kT$ , where  $\pi$  is the surface pressure of the adsorbate,  $A_M$  the area occupied per molecule on the surface ( $=1/6.02 \times 10^{23} \Gamma$ ), and  $k$  is Boltzmann's constant. The surface pressure of the adsorbate can be calculated by integrating eq 4 as described in ref 64 for various values of  $P$  and the area per molecule directly from eq 4 for the same values of  $P$ .

Plots of  $\pi$  vs.  $A_M$  for all six adsorbates fall on the same curve, which lies below the one expected for ideal behavior down to concentrations as low as 2500  $\text{\AA}^2/\text{molecule}$ . These plots were successfully fitted to the two-dimensional van der Waals equation of state. From the van der Waals constants it was possible to calculate the thickness of the hydrocarbon films. At the surface coverage of 500  $\text{\AA}^2/\text{molecule}$ , the thickness was found to be  $\sim 4$   $\text{\AA}$ , which indicated that the hydrocarbon chains lie mainly flat on the water interface.

The above results indicate that the molecules studied form nonideal gaseous films on water surfaces, even at very low coverages. This nonideality arises from adsorbate-adsorbate interaction as opposed to adsorbate-surface interactions.<sup>29,76</sup> Similar observations at much higher surface coverages have been made in the past.<sup>35,38,39,83</sup>

The only static low surface coverage measurements have been carried out by Hauxwell and Otte-will,<sup>36,45,84</sup> who studied adsorption of several of the same alkanes. A comparison with data from Hauxwell's thesis<sup>84</sup> reveals that our  $\Gamma$  values are

(78) M. L. Huggins, *J. Chem. Phys.*, **8**, 181 (1940).

(79) P. Pomerantz, W. C. Clinton, and W. A. Zisman, *J. Colloid Interface Sci.*, **24**, 16 (1967).

(80) B. Case and R. Parsons, *Trans. Faraday Soc.*, **63**, 1224 (1967).

(81) D. E. Martire, *Anal. Chem.*, **38**, 244 (1966).

(82) J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, **58**, 137 (1971).

(83) E. A. Guggenheim and N. K. Adam, *Proc. Roy. Soc., Ser. A*, **139**, 218 (1933).

(84) F. Hauxwell, Doctoral Thesis, University of Bristol, 1969.

**Table II**  
**Thermodynamic Functions (kcal/mol) of Adsorption as a**  
**Function of Surface Coverage at 12.1°**

	$-\Delta G_A)_\Gamma^a$		$q_{st}^b$	
	$\Gamma = 0.6 \times 10^{-11}$	$\Gamma = 1.2 \times 10^{-11}$	$\Gamma = 1.2 \times 10^{-11}$	$\Gamma = 2.4 \times 10^{-11}$
	moles/cm <sup>2</sup>		moles/cm <sup>2</sup>	
<i>n</i> -Heptane	3.35	7.7	3.02	7.7
<i>n</i> -Octane	3.85	8.7	3.51	9.2
<i>n</i> -Nonane	4.33	9.6	4.00	9.7
2-Methylheptane	3.72	8.8	3.39	8.8
2,5-Dimethylhexane	3.64	7.6	3.29	8.0
2,2,4-Trimethylpentane	3.49	7.2	3.13	7.2
	$\Gamma = 1.8 \times 10^{-11}$		$\Gamma = 2.4 \times 10^{-11}$	
	moles/cm <sup>2</sup>		moles/cm <sup>2</sup>	
<i>n</i> -Heptane	2.83	7.9	2.71	8.1
<i>n</i> -Octane	3.32	9.6	3.21	10.2
<i>n</i> -Nonane	3.83	10.1	3.73	9.7
2-Methylheptane	3.21	8.9	3.09	9.3
2,5-Dimethylhexane	3.10	8.6	2.98	9.1
2,2,4-Trimethylpentane	2.94	7.6	2.81	8.0

<sup>a</sup> Standard deviation, 1%. <sup>b</sup> Standard deviation, 10%.

consistently a factor of approximately two larger. This discrepancy may be due to the error in the estimated surface areas of the gc columns, as discussed under Theory. However, more work is needed to show that the problem is really a result of inaccurate  $A_L^0$  values or inaccuracies in Hauxwell's measurements. In any case, the differences in the free energies of adsorption derived from the isotherms are only 0.3 kcal/mol for all adsorbates. Furthermore, the  $\pi$  vs.  $A_M$  values in this work differ from those obtained by Hauxwell by a maximum of only 2% over the whole range of surface concentrations.

**Thermodynamic Parameters of Adsorption at Finite Surface Coverage.** Using equations presented in the theory section, thermodynamic functions of adsorption for the six adsorbates can be calculated from the isotherm data. The results are given in Table II. In all cases  $(\Delta G_A)_\Gamma$  becomes less negative as surface concentration increases. Most of this change can be attributed to entropy changes. As  $\Gamma$  increases the adsorbed state becomes more ordered, and hence the entropy loss on adsorption becomes greater.

The isosteric heats of adsorption are seen to be nearly constant within experimental error for a given adsorbate, and over the whole concentration range are less than the heats of vaporization listed in Table I. (More extensive calculations of  $q_{st}$  at concentrations ranging from 0.2 to  $3.2 \times 10^{-11}$  mol/cm<sup>2</sup> in intervals of  $0.2 \times 10^{-11}$  mol/cm<sup>2</sup> give the same results.<sup>64</sup> No dramatic increases in  $q_{st}$  are found; instead, the results support our earlier conclusion that water is a low-energy surface toward nonpolar adsorbates.

As a check on the consistency of the finite coverage measurements,  $\Delta G_A$  at zero surface coverage can be calculated from the isotherm data by combining eq 3, 4, and 7. Also,  $\Delta H_A$  at zero surface coverage can be obtained by adding  $RT$  to  $q_{st}$ .<sup>31</sup> In all cases, the functions agree within experimental error for the two measuring procedures.<sup>64</sup> This lends further support to the validity of gc as a tool to measure adsorp-

tion isotherms on liquid surfaces at low surface concentrations.

### Partition Measurements

**Influence of the Support.** It might be expected that the first few layers of water on the solid supports used in this work are structurally perturbed to some extent. The nature and extent of this perturbation are of interest in many areas of research (see introduction). One procedure for investigating the influence of the support is to carry out adsorption and partition measurements at different liquid coating thicknesses. If the support were modifying the structure of the water, the effect should diminish as the thickness of the water is increased, resulting in changes in  $K_A$  and  $K_L$ . In fact, however, on and in layer thicknesses ranging from 2000 down to  $\sim 30$  Å (calculated assuming approximately homogeneous coverage), the thermodynamic parameters for both adsorption and partition are constant within experimental error.

This is at first a surprising result; moreover, it may be argued that thermodynamic measurements, which represent gross macroscopic properties, cannot reflect any subtle structural changes which might take place in the water. Yet the types of structural changes which are postulated to occur at interfaces (see, for example, ref 16) ought to result in detectable changes with coating thickness, at least for the partition coefficients. The fact that no changes are observed indicates that the support is not significantly altering the structure of the water.

It may also be argued that water does not coat the supports uniformly so that domains of greater thickness occur in the column. If this were the case, regions of support covered with only a monolayer of water would be exposed. Again, the constancy of the thermodynamic parameters over a wide range of coverage suggests that this is not occurring, and that at thicknesses ranging from  $\sim 30$  to  $\sim 2000$  Å layers of water coated on the solid supports are thermodynamically equivalent.<sup>85</sup> Of course, it is another question whether the liquid is indeed bulk water. To answer this it is necessary to compare the thermodynamic measurements obtained by gc to static measurements.

**Solution Parameters.** Values for  $K_L$  and the enthalpy, free energy, and entropy of solution for all the water-soluble adsorbates in this study are listed in Table III, along with available literature data. The agreement with the literature is remarkable when one considers all the possible errors in the literature data and in our calculations. All the results are consistent with current theories of water-solute interactions<sup>86,87</sup> For example, the large enthalpy and entropy changes accompanying the solution of *n*-propyl ether result from hydrogen bonding between

(85) It must be kept in mind that the supports used in this work possess very wide pore diameters (for Spherosil, ca. 800 Å; for Chromosorb P, ca. 10<sup>4</sup> Å), while the measurements indicating the presence of modified water in porous solids have been carried out with pore sizes on the order of 10 to 100 Å.<sup>22,23</sup>

(86) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, New York, N. Y., 1969.

(87) R. A. Horne, *Survey Progr. Chem.*, 4, 1 (1968).

Table III  
Thermodynamic Functions of Partition of Vapors at Infinite Dilution in Water at 12.5°

	$K_L$		$-\Delta G_S$ , kcal/mol		$-\Delta H_S$ , kcal/mol		$-\Delta S_S$ , cal/(deg mol) <sup>a</sup>
	This work <sup>a</sup>	Lit. <sup>b</sup>	This work <sup>a</sup>	Lit. <sup>g</sup>	This work <sup>a</sup>	Lit. <sup>g</sup>	
Dichloromethane	19	17 <sup>c</sup>	1.7	1.6	8.1	7.8	22
Trichloromethane	14	12 <sup>c</sup>	1.5	1.4	9.6	9.7	28
Tetrachloromethane	1.9	1.6 <sup>c</sup>	0.4	0.3	9.8		33
1,2-Dichloromethane	36	36 <sup>c</sup>	2.0	2.0	8.2	7.8	22
Benzene	9.6	7.8 <sup>d</sup>	1.3	1.2	8.4	7.8	25
Toluene	9.7	8.3 <sup>d</sup>	1.3	1.2	9.1	8.9	27
Ethylbenzene	9.6	7.9 <sup>d</sup>	1.3	1.2	12.1	10.0	38
Fluorobenzene	6.8		1.1		8.1		25
	3.0 (30°) <sup>e</sup>	3.2 <sup>f</sup>	0.7 (30°)	0.7			
Chlorobenzene	13.5		1.5		9.2		27
	5.3 (30°) <sup>e</sup>	5.1 <sup>f</sup>	1.0 (30°)	1.0			
<i>n</i> -Propyl ether	20		1.7		17.6		56
Methyl formate	170		2.9		7.5		16
Ethyl formate	9.0		1.2		8.5		26

<sup>a</sup> Standard deviations as in Table I. <sup>b</sup> Calculated as in ref 77, with  $\gamma^0 = 1/x$ , where  $\gamma^0$  is the effectively infinite dilution activity coefficient of the solute in water and  $x$  is its mole fraction solubility (see J. A. V. Butler, "Chemical Thermodynamics," 4th Edition, Macmillan, 1946). Solubility data were taken from the references cited; vapor pressure data from R. R. Dreisbach, *Advan. Chem. Ser.*, No. 15 (1955). <sup>c</sup> A. Siedell, "Solubilities of Organic Compounds," Vol. II, 3rd ed, Van Nostrand, Princeton, N. J., 1941. <sup>d</sup> R. L. Bohon and W. F. Claussen, *J. Amer. Chem. Soc.*, 73, 157 (1951). <sup>e</sup> Extrapolated value. <sup>f</sup> Calculated from the solubility at 30° in footnote c. <sup>g</sup> Calculated from the literature  $K_L$  values.

water and the ethereal oxygen, combined secondarily with hydrophobic bonding around the propyl groups.

### Conclusions

Gas chromatography has been shown to be a valid method for characterizing the surface and bulk properties of thin layers of water. Our results suggest that at thicknesses greater than 5–10 layers ( $\sim 30$  Å) thin films of water coated on wide-pore silicas are similar to the bulk, at least in their partition and adsorption characteristics. The surface of water is of low energy for the adsorption of a variety of nonpolar or weakly polar molecules. Adsorbed films on the surface can be considered gaseous, with a measurable nonideality at surface coverages as low as 2500 Å<sup>2</sup>/molecule. It would seem that the current model of adsorption on liquid water<sup>42,43</sup> is untenable in view of our results.

Future work will be aimed at extending the application of the method. First, gas chromatography has recently been applied to the study of adsorption on and partition in thin films of electrolyte solutions.<sup>88</sup> Work has been completed on a detailed examination of NaCl solutions up to 5 M, and studies are now in progress on tetraalkylammonium bromide salt solutions. It should be noted that the structural effects which occur in bulk water containing electrolytes have been well-documented in the past;<sup>86,87</sup> structural effects at aqueous interfaces have not been so intensively studied. Horne<sup>3</sup> has commented that the future direction of chemical oceanography will be the investigation of phenomena occurring at the ocean's phase boundaries.

Second, adsorption isotherms for polar compounds will be determined in order to provide information

on surface hydrogen bonding and adsorbate orientation at higher coverage. Moreover, for both polar and nonpolar molecules it is possible to extend the isotherm determinations into the monolayer region and above by combining a frontal development gas chromatographic procedure<sup>89</sup> with computer control and data acquisition. At these high surface concentrations, the question of multilayer *vs.* lens formation<sup>36</sup> and other complex problems in wettability<sup>90–92</sup> can be investigated.

Third, the gas chromatographic approach will be applied to the study of single-component and mixed-lipid films.<sup>93,94</sup> Adsorption characteristics of hydrocarbons will be determined as a function of surface coverage for long-chain alcohols and acids which form either liquid-expanded or liquid-condensed films. The natural occurrence of such films (*e.g.*, cell membrane) make these studies of some interest in the biological sciences.

Finally, gas chromatography offers an alternate means to obtain adsorption measurements for hydrocarbons on the surface of ice. The presence or absence of a liquid layer on the surface of ice, for example,<sup>17,41,43,95</sup> can be studied by chromatographic experiments similar to those above at temperatures below 0°.

*This Account is based on work performed at Northeastern University and supported by the Office of Naval Research under Contract N00014-68-A-0207. Dr. Karger also thanks Gulf Research and Development Corporation for a research award.*

(89) P. Valentin, Doctoral Thesis, Ecole Polytechnique, Paris, 1971.

(90) E. G. Shafrin and W. A. Zisman, *J. Phys. Chem.*, 71, 1309 (1967).

(91) A. W. Adamson, *J. Colloid Interface Sci.*, 27, 180 (1968).

(92) A. Hartkopf, *J. Colloid Interface Sci.*, 40, 313 (1972).

(93) N. L. Gershfeld and R. E. Pagano, *J. Phys. Chem.*, 76, 1231 (1972).

(94) R. E. Pagano and N. L. Gershfeld, *J. Phys. Chem.*, 76, 1238 (1972).

(95) H. H. G. Jellinek, *J. Colloid Interface Sci.*, 25, 192 (1967).

(88) J. W. King and B. L. Karger, 164th National Meeting, American Chemical Society, New York, N. Y., Sept 1972.