

referred to other calculations<sup>17</sup> which suggest that membranes with effective thicknesses in this range cannot be prepared from asymmetric films.

**Acknowledgment.** We are grateful to our colleague, Robert Ullman, for constructive criticism in the course of this work.

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## Effect of Pressure on the Surface Tension of Water. Adsorption of Low Molecular Weight Gases on Water at 25°<sup>1</sup>

R. Massoudi and A. D. King, Jr.

Department of Chemistry, University of Georgia, Athens, Georgia 30602 (Received March 14, 1974)

Publication costs assisted by the National Science Foundation

The variation of interfacial tension with hydrostatic pressure has been determined for a number of gas-water systems at 25° using the capillary-rise method. Measurements are reported for water with He, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Ar, CO, CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and *n*-C<sub>4</sub>H<sub>10</sub>. Adsorption isotherms are derived from polynomial fits to the data through the Gibbs equation. Depending upon the gas, adsorption isotherms of types I and III are found<sup>2</sup> with low molecular weight gases exhibiting type I behavior and the more polarizable gases yielding type III isotherms. In general, the degree of adsorption increases monotonically with polarizability of the gas. At low surface coverages however, it is found that adsorption coefficients for CO<sub>2</sub>, N<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub> are abnormally large. This is interpreted as indicating that in addition to van der Waals forces, weak interactions, either electrostatic or chemical in nature, exist between molecules of these gases and the aqueous surface. It is also found that in the zero-coverage limit, the free energy of adsorption for the *n*-alkanes is a linear function of the number of methylene groups indicating correspondence with Traube's rule. Values extrapolated to higher members of this series agree well with those determined experimentally using gas chromatographic methods.<sup>3</sup>

### Introduction

In recent years there has been a resurgence in interest concerning bulk and surface properties of water.<sup>4</sup> One area of research that has received comparatively little attention concerns the effect of pressure on the surface tension of water. This is somewhat surprising since such experiments are capable of providing a great deal of information concerning adsorption of low molecular weight species at aqueous surfaces. To these authors' knowledge, refs 5-11 constitute a complete bibliography on this subject.

This paper reports results obtained in measuring interfa-

cial tension as a function of pressure for a wide variety of gas-water systems at 25°. The data for the hydrocarbon gases represent an extension to lower carbon numbers of earlier work by Cutting and Jones.<sup>12</sup> The isotherms derived from these data also complement recent studies by Karger, *et al.*,<sup>3</sup> in which net retention volumes of various hydrocarbons chromatographed on columns having water as the stationary liquid phase are used to determine isotherms directly at low surface coverages.

The systems involving water with carbon dioxide and nitrous oxide were of particular interest since it is known that on one hand these gases are more soluble than expected in

bulk water<sup>13</sup> while on the other hand water is abnormally soluble in compressed CO<sub>2</sub> and N<sub>2</sub>O<sup>14</sup> leading to the question of whether a corresponding anomaly is to be found with respect to adsorption at the interface of water with these two gases.

### Experimental Section

The changes in surface tension of water under dense gas atmospheres were determined using the capillary-rise technique. The experiments were carried out in a thermostated cylindrical brass bomb having an internal diameter of 1.75 in. and a length of 8 in. A single capillary (0.3-mm i.d.) was suspended from a polished 0.125-in. diameter stainless steel rod which passes through an "O" ring in the top closure. This rod was connected to a micrometer drive mounted on the outside of the closure thus allowing the suspended capillary to be raised or lowered while the system is under pressure. This permitted a series of capillary-rise determinations to be made using the same section of capillary bore at all pressures. A thin-walled glass liner was used to contain the liquid at the bottom of the bomb. The bomb was equipped with a 0.5 in. diameter Plexiglas window providing a 0.75 × 3.5 in. viewing area along one side. Capillary rise was measured to 0.03 mm with a cathetometer, and pressures were measured with Bourdon gauges which were periodically calibrated against a dead-weight tester. The system was designed with a safety factor of 2 at the upper limit in pressure of 1000 psi. The temperature of the bomb was controlled to within ±0.2°, and all measurements reported here were made at 25° as determined by a thermocouple located in the central cavity of the bomb.

Surface tensions were calculated using the relation<sup>15</sup>

$$\gamma = \frac{1}{2}rg(h \pm r/3)(\rho_l - \rho_g) \quad (1)$$

where  $\gamma$  is the surface tension,  $g$  the acceleration of gravity, and  $h$  the capillary rise, with  $\rho_l$  and  $\rho_g$  being the densities of the bulk liquid and gas phases, respectively. The radius  $r$  of the section of capillary used in a given series of measurements was determined from eq 1 using a value of  $h$  extrapolated to zero pressure and a value of  $\gamma_0 = 71.98$  dyn/cm,<sup>16</sup> for the surface tension of water in equilibrium with its pure vapor at 25°.

Gas densities were calculated from PVT data found in ref 17-28 while that for water was assumed constant over the pressures of this work. All gases used in these experiments were CP grade or the equivalent having quoted purities of 99.0% or higher for the hydrocarbon gases and 99.5% or higher for the others. Laboratory-distilled water was used without further purification.

### Results and Discussion

A representative sample of the experimental data is shown in Figure 1 where the relative surface tension,  $\gamma/\gamma_0$ , of water is shown plotted against total pressure. The experimental surface tension data for each H<sub>2</sub>O-gas system were fit to a polynomial expansion in pressure and the results are shown in Table I. The curves generated by the polynomials in Table I are capable of reproducing the experimental results within an average deviation of ±0.2 dyn/cm for CO<sub>2</sub> and N<sub>2</sub>O and ±0.06 dyn/cm for all other gases. The decreased precision of the CO<sub>2</sub> and N<sub>2</sub>O data reflects the increased experimental error associated with systems for which gas solubility in the liquid phase is significant. Polynomial expansions of degree 2 or less provided a satisfactory fit to all data except those involving CO<sub>2</sub> and N<sub>2</sub>O. The

TABLE I: Interfacial Tension as Function of Pressure for Pure Water with Various Gases at 25°

Gas	$\gamma = \gamma_0 + BP + CP^2 + DP^3$		
	B, dyn/cm atm	C, dyn/cm atm <sup>2</sup>	D, dyn/cm atm <sup>3</sup>
He	0.0000		
H <sub>2</sub>	-0.0250		
O <sub>2</sub>	-0.0779	+0.000104	
N <sub>2</sub>	-0.0835	+0.000194	
Ar	-0.0840	+0.000194	
CO	-0.1041	+0.000239	
CH <sub>4</sub>	-0.1547	+0.000456	
C <sub>2</sub> H <sub>6</sub>	-0.6353	+0.00316	
C <sub>3</sub> H <sub>8</sub>	-0.4376	-0.00157	
C <sub>4</sub> H <sub>10</sub>	-0.9681	-0.0589	
N <sub>2</sub> O	-0.6231	+0.00287	-0.000040
CO <sub>2</sub>	-0.7789	+0.00543	-0.000042
n-C <sub>4</sub> H <sub>10</sub>	-2.335	-0.591	

\* All coefficients are quoted to one extra significant figure in order to minimize effects of round-off error in generating values for  $\gamma$ .

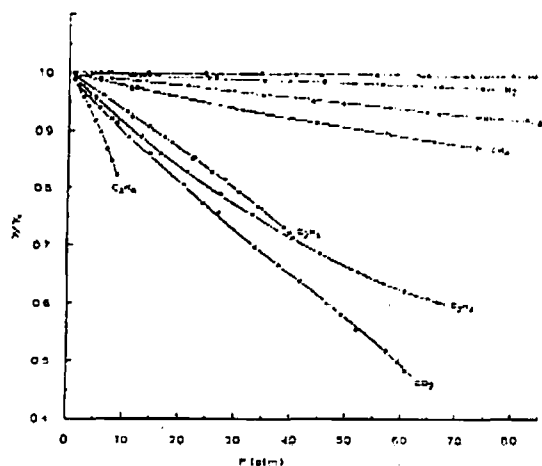


Figure 1. Relative surface tension as a function of pressure for various gas-water systems at 25°.

$\gamma$ - $P$  curves for the latter two gases exhibited a point of inflection at about 30 atm necessitating the cubic terms found in Table I. Similar measurements involving water with He, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> at room temperature, approximately 25°, have been reported in graphical form by Slowinski, *et al.*<sup>7</sup> More precise measurements were subsequently carried out for the systems water-N<sub>2</sub> and water-Ar, at 30°, by Masterton, Bianchi, and Slowinski.<sup>8</sup> Hough and coworkers<sup>10</sup> have used the pendent-drop method to determine the surface tension of water in the presence of compressed CO<sub>2</sub> at temperatures of 100°F and greater. The data obtained here for water with He, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> at 25° agree well with those shown in ref 7. A comparison of the N<sub>2</sub>, Ar, and CO<sub>2</sub> data with those taken at higher temperature<sup>8,10</sup> indicates that the drop in surface tension with pressure is somewhat larger at the lower temperature of this work as would be expected where positive adsorption of gas occurs at the aqueous interface. No minimum is found in the surface tension data for water with CO<sub>2</sub> at 25° over the range of pressures encountered here.

TABLE II: Surface Excess ( $\Gamma_2^{(1)}$ ) for Various Gases on Water at 25° (molecules/cm<sup>2</sup> × 10<sup>-14</sup>)

$P$ , atm	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	CO
10	0.06	0.18	0.19	0.20	0.25
20	0.12	0.36	0.37	0.37	0.46
30	0.18	0.53	0.53	0.54	0.66
40	0.23	0.69	0.66	0.68	0.83
50	0.29	0.84	0.78	0.80	0.98
60	0.35	0.99	0.88	0.91	1.1
70	0.40	1.1	0.96	1.0	1.2
80			1.0	1.1	1.2
$\Delta G_A = 0.5$ kcal/mol $\Delta G_A = -0.2$ kcal/mol $\Delta G_A = -0.2$ kcal/mol $\Delta G_A = -0.2$ kcal/mol $\Delta G_A = -0.3$ kcal/mol					
$P$ , atm	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	N <sub>2</sub> O	C <sub>2</sub> H <sub>4</sub>
10	0.36	1.5	1.8	1.5	1.2
20	0.69	2.8	3.4	3.1	3.0
30	0.98	4.0	5.0	5.0	5.5
40	1.2	5.2	7.1	7.8	10
50	1.4	6.3	10	12	
60	1.6	7.8	15		
70	1.7				
$\Delta G_A = -0.8$ kcal/mol $\Delta G_A = -1.4$ kcal/mol $\Delta G_A = -1.5$ kcal/mol $\Delta G_A = -1.4$ kcal/mol $\Delta G_A = -1.2$ kcal/mol					
$P$ , atm	C <sub>2</sub> H <sub>2</sub>	$P$ , atm	C <sub>2</sub> H <sub>6</sub>		
2	0.60	0.5	0.36		
4	1.5	1.0	0.88		
6	2.7	1.5	1.6		
8	4.4				
$\Delta G_A = -1.7$ kcal/mol		$\Delta G_A = -2.2$ kcal/mol			

Such minima have been reported in data taken at higher pressures and temperature.<sup>10</sup>

Surface excesses for the various gases,  $\Gamma_2^{(1)}$ , have been calculated according to the common convention which places the Gibbs plane such that the surface excess of water equals zero using the equation

$$\left(\frac{\partial \gamma}{\partial P}\right)_T = -\Gamma_2^{(1)} \left(\frac{ZkT}{P}\right) \quad (2)$$

Here  $Z$  represents the compressibility factor of the pure gas at pressure  $P$  and temperature  $T$  while  $k$  designates the Boltzmann constant. The surface excesses listed in Table II were calculated using eq 2 with values of  $(\partial \gamma / \partial P)_T$  derived from the appropriate polynomial expansion from Table I. Values of  $Z$  were taken from ref 17-28.

Figure 2 shows the surface excess  $\Gamma_2^{(1)}$  as a function of gas concentration for a representative sample of gases. While not shown, the isotherm for nitrous oxide parallels that of the CO<sub>2</sub> while  $\Gamma_2^{(1)}$  for CO, N<sub>2</sub>, and O<sub>2</sub> nearly coincide with the data for argon. Since the molecular areas of the gases are typically of the order of 20 Å<sup>2</sup> per molecule, a coverage of 5 × 10<sup>14</sup> molecules/cm<sup>2</sup> approximates complete monolayer coverage for these gases. Thus it is seen that the adsorption behavior of the gases fall into two general categories. The gases having critical temperatures well below 25° all exhibit type I isotherms and appear to approach saturation coverages corresponding to 50% or less of monolayer coverage. On the other hand, the higher molecular weight hydrocarbon gases having critical temperatures above 25° exhibit type III behavior with isotherms that are concave upward and pass smoothly through the monolayer region. The isotherms do not, however, become asymptotic to their saturated vapor concentration in agreement with earlier investigations concerning the adsorption of higher molecular weight alkanes on water by Cutting and Jones.<sup>12</sup>

Ethylene appears to occupy a position intermediate to the other gases in that its isotherm is concave to the concentration axis and yet passes smoothly to values exceeding those expected for monolayer coverage.

Both CO<sub>2</sub> and N<sub>2</sub>O are unique among the gases studied here in that their isotherms exhibit points of inflection which occur in the vicinity of  $\Gamma_2^{(1)} = 5 \times 10^{14}$  cm<sup>-2</sup>, that is, at conditions of approximately 100% monolayer coverage. This suggests that the overall mechanism for adsorption at low coverages differs from that responsible for multilayer adsorption for these two gases. At the right of this point of inflection in the multilayer adsorption region the surface excesses at a given gas concentration arrange themselves in an ascending order with increasing gas polarizability ( $\alpha$ ) as might be expected if London dispersion forces were the dominant mode of attraction while to the left at low coverages the order relative to ethane ( $\alpha = 4.5$  Å<sup>2</sup>) is reversed in the case of CO<sub>2</sub> ( $\alpha = 2.7$  Å<sup>2</sup>), N<sub>2</sub>O ( $\alpha = 3.0$  Å<sup>2</sup>), and even C<sub>2</sub>H<sub>4</sub> ( $\alpha = 4.3$  Å<sup>2</sup>). The anomalous behavior of these gases is revealed quite clearly in Figure 3 which shows the adsorption coefficient at zero coverage

$$K_A = \lim_{C_2 \rightarrow 0} \left( \frac{\partial \Gamma_2^{(1)}}{\partial C_2} \right)$$

plotted against gas polarizability for each gas. It is apparent that in the zero-coverage limit the adsorption isotherms of these three gases differ significantly from the rest.

The absence of information regarding enthalpies and entropies of adsorption of these gases precludes any detailed discussion concerning likely causes for the anomalous adsorption of CO<sub>2</sub> and N<sub>2</sub>O. Nevertheless, a qualitative picture emerges in which at monolayer coverages or less, CO<sub>2</sub> and N<sub>2</sub>O are adsorbed at the aqueous interface to a greater extent than would be expected if van der Waals forces were the sole cause of attraction between water and these gases.

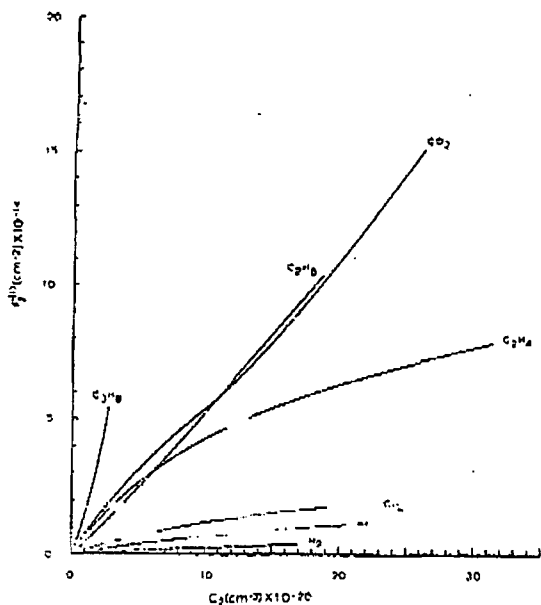


Figure 2. Surface excess as a function of gas concentration for various gas-water systems at 25°. Estimated error in  $\Gamma_2^{(1)}$ :  $\pm 3\%$ .

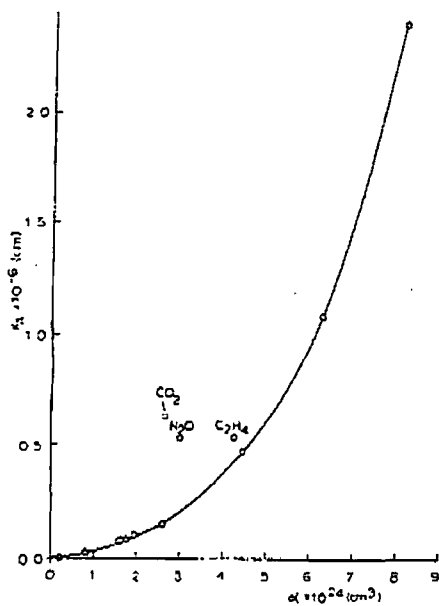


Figure 3. Adsorption coefficient at zero coverage vs. average polarizability of gaseous component.

In this sense the enhanced adsorption of these gases at low coverages parallels earlier observations that mutual solubilities of these gases with water are unusually large both in the liquid phase<sup>13</sup> and the gas phase.<sup>14</sup> On the other hand, multilayer adsorption of these three gases appears to involve a mechanism more in common with the other gases.

There is considerable evidence suggesting that a high degree of order exists at the surface of hydrogen-bonded liquids.<sup>29</sup> In the case of water it is thought that a preponderance of the molecules near the surface are oriented with their hydrogen atoms directed toward the gas phase.<sup>30,31</sup> This suggests that the anomalous adsorption of these gases at low coverages may be the result of hydrogen bonding with the highly oriented water molecules acting as proton donors to the carbonyl-like functions of  $\text{CO}_2$  and  $\text{N}_2\text{O}$ . Such a mechanism also explains the enhanced adsorption of ethylene at low coverages since olefins are known to serve as proton acceptors in hydrogen bonds.<sup>32</sup> Karger and coworkers have invoked a similar argument to explain the enhanced adsorption of di-*n*-propyl ether on water at low coverages.<sup>33</sup> Such a model is consistent with the observed rearrangement in the order of  $\Gamma_2^{(1)}$  for  $\text{CO}_2$  and  $\text{N}_2\text{O}$  relative to the other gases shown in Figure 3 since beyond a monolayer coverage only physical interactions of a van der Waals type can be effective in determining the degree of adsorption for these gases. It should be pointed out that other factors such as dipole-quadrupole interactions or the known acidity of  $\text{CO}_2$  may also play a significant role in determining the adsorption behavior of these gases.<sup>34</sup>

The idea that at low coverage specific interactions exist between water and certain gases in addition to dispersion forces is supported in the case of  $\text{CO}_2$  by other data of Slowinski, *et al.*,<sup>7</sup> which show that, in contrast to the data of Figure 1, the surface tensions of *n*-hexane with  $\text{CO}_2$  lie intermediate to those of *n*-hexane with methane and ethane at all pressures as would be expected if London dispersion forces alone were effective.

Standard free energies of adsorption at zero coverage,  $\Delta G_A$ , have been calculated for the various gases using 1 atm and the Kemball-Rideal<sup>35</sup> convention as standard states. The results are listed in Table II. It is seen that beginning with ethane,  $\Delta G_A$  increases by a constant increment of  $-0.5$  kcal/mol per methylene group indicating a correspondence with Traube's rule. The free energy increment calculated here is in exact agreement with those obtained by Posner, *et al.*<sup>36</sup> In addition, extrapolation to the next higher member this series, *n*-pentane, yields  $\Delta G_A = -2.7$  kcal/mol, which when corrected to 12.5° using the Gibbs-Helmholtz equation and a value of  $\Delta H_A = -5.7$  kcal/mol<sup>3</sup> becomes  $\Delta G_A = -2.8$  kcal/mol, agreeing with the value obtained by Karger, *et al.*, using gas chromatographic techniques.<sup>3</sup> The excellent correlation between the free energies obtained in this work and those derived from the direct determination of surface excesses at low coverages by Karger, *et al.*, is very encouraging and supports the validity of the extrapolations to zero surface coverage used here.

**Acknowledgment.** The authors are grateful for support provided by the National Science Foundation (NSF Grant No. GP-38386) and the National Institutes of Health Biomedical Sciences Support Grant (5 505 RR07025).

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## Surface Drag Viscosity of Bovine Serum Albumin Monolayers

Henri L. Rosano,\* Shu Hsien Chen, and James H. Whittam

The City College of the City University of New York, New York, New York 10031 (Received January 11, 1974;  
Revised Manuscript Received May 28, 1974)

It has been observed that compression or decompression of bovine serum albumin monolayers spread on an aqueous substrate near the isoelectric point will produce surface pressures that are dependent on the distance between the measuring device and the compression barrier. As the pH of the substrate is varied, either above or below the isoelectric point, the effect diminishes. Similar results have been observed with  $\beta$  casein. This phenomenon fails to appear for small molecules (myristic acid, eicosyl sodium sulfate) even when the substrate contains substituted alkanol amines. A theory is provided which suggests that the major effect is due to a surface drag viscosity.

### Introduction

Proteins are often used in emulsion and foam formulations because of their stabilizing properties. A useful method to correlate the effects of proteins on the above systems is to study the properties of protein monolayers on liquid substrates. As can be expected, the surface behavior of these macromolecules are quite different from ordinary low molecular weight compounds.

This paper is concerned with an interesting series of effects observed with bovine serum albumin (BSA) when spread on a clean liquid surface.

### Experimental Section

The experimental apparatus for measuring surface pressures has previously been described by Christodoulou and

Rosano.<sup>1</sup> The compression and expansion rates were varied between 0.009 and 0.03 cm/sec. Isotherms were determined by compressing (and expanding) for short durations of time and then allowing the system to reach equilibrium.

The surface pressures were determined from surface tension measurements which were made by suspending a wettable sand-blasted platinum blade from a microforce transducer-amplifier system (Model 311 A, The Sanborn Co., Waltham, Mass.). The transducer output was recorded continuously on an x-y recorder (Model 370, Keithley Instruments, Inc., Cleveland, Ohio). The surface tensions were reproducible within  $\pm 0.1$  dyn.

An aqueous protein solution containing 0.5% of 1-pentanol was deposited onto the aqueous substrate with an Agla micrometer syringe (Burroughs Wellcome Co., Tuckahoe, N.Y.). The substrate and film were retained in an edge paraffin coated silica trough (65 X 14 X 2 cm).