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Intermolecular Forces between the *n*-Alkanes Methane to Butane Adsorbed at the Water/Vapor Interface

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Experimental data on the dependence of the surface tension of water on the adsorption of *n*-alkanes (methane to butane) from the vapor phase over a range of temperatures are re-interpreted to obtain improved estimates of the two-dimensional second virial coefficients for comparison with calculations based on the Lennard–Jones (L–J) formalism in two dimensions. The analysis includes the fugacity corrections for the alkane gases and takes the L–J parameters as known for the three-dimensional gases. The new L–J calculations use a closed-form analytical solution of the basic equation for the two-dimensional second virial coefficient. These older published computations are correct and, as expected, are in complete agreement with the results by numerical integration with modern computer software. Together with estimates of the standard entropies of adsorption, the results indicate that no significant structuring of the surface water molecules occurs upon adsorption of the alkanes. The two-dimensional second virial coefficients are in fair accord with the L–J predictions, except for butane. The reduction of the attractive component of the potentials of mean force between physisorbed molecules arising from the frequency-dependent interaction with their electrostatic images in the bulk aqueous phase, as described by McLachlan (*Mol. Phys.* **1964**, *7*, 381), or from the polarization of the adsorbates by a surface electric field (surface field polarization) is minor for methane, ethane, and propane. For butane, these effects may be significant but possible changes in conformation upon adsorption may weaken the validity of the gas-phase L–J parameters in estimating the two-dimensional virial coefficients for this alkane.

Introduction

The understanding of lateral intermolecular forces between adsorbed molecules underlies the interpretation of many surface properties and processes. Two-dimensional second virial coefficients [$B_2(T)$] for molecules spread or adsorbed at the air or gas/water interface have been estimated for lipids,[1,2] alkanes,[3] cyclic amides,[4] and proprionic acid[2] and have been used to quantify the intermolecular potentials of mean force [$\Phi(r)$] between pairs of identical molecules at the surface. Intermolecular potentials between the molecules of adsorbed gases such as methane have also been estimated from second virial coefficients at gas/metal interfaces.[5,6] Intermolecular potentials for physisorbed molecules will differ in principle from those acting in the gas phase through the effect of the adsorbent–adsorbate interaction, as described notably by the McLachlan[7] inclusion of the frequency-dependent electrical images of the adsorbed molecules in the analysis.

These effects have been shown to be relevant to gases adsorbed on metal crystals[5,6] but have been little considered for aqueous and other liquid interfaces. Estimates of $B_2(T)$ for the insoluble monolayers of phospholipids in the heptane/water interface (at which screening of the lipid chains by the paraffin solvent greatly reduces the van der Waals force component of the lipid pair potentials) are also available and have been interpreted largely in terms of the zero frequency electrostatic images of the zwitterion headgroups[8] but not the dispersion terms included in the McLachlan treatment. Another aspect of the adsorbent–adsorbate interaction potentially contributing to repulsion in the adsorbent pair potentials is polarization of the adsorbed molecules in the electric field due to the adsorbent dipoles at the phase boundary (surface field polarization, SFP). A lattice model for the adsorption of the alkanes pentane to heptane and benzene[9] on water indicates that SFP contributes significantly to the heat of adsorption. This is confirmed for benzene adsorption by a molecular dynamics study.[10]

Earlier estimates[1] of $B_2(T)$ for uncharged lipid molecules at the air/water interface were based on experiments on insoluble spread air/water monolayers of long-chain compounds such as fatty acids giving the surface pressure (Π) as a function of the surface density (Γ) or surface area/molecule (A). The results were interpreted in terms of the Lennard–Jones (L–J) vacuum pair potentials for extended chains lying flat in the interface, the probable configuration in dilute long-chain lipid air/water mono-

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(1) Pethica, B. A.; Glasser, M. L.; Mingins, J. *J. Colloid Interface Sci.* **1981**, *81*, 41.
(2) Hasmonay, D.; Billoudet, F.; Badiali, J. P.; Dupeyrat, M. *J. Colloid Interface Sci.* **1994**, *165*, 480.
(3) Pethica, B. A. *Langmuir* **1996**, *12*, 5851.
(4) Lou, A.; Pethica, B. A.; Somasundaran, P. *Langmuir* **1996**, *12*, 5845. Pethica, B. A.; Senak, L.; Zhu, Z.; Lou, A. *Colloids Surf., A* **2001**, *186*, 113.
(5) Kevan, S. D.; Skelton, D. C.; Wei, D.-H. *Crit. Rev. Surf. Chem.* **1994**, *3*, 77. Elliot, G. S.; Wei, D.-H.; Wu, K. J.; Kevan, S. D. *J. Chem. Phys.* **1990**, *93*, 4152. Elliot, G. S.; Wu, K. J.; Kevan, S. D. *Phys. Rev. Lett.* **1991**, *66*, 433.
(6) Rauber, S.; Cole, M. W.; Bruch, L. W. *Surf. Sci.* **1982**, *123*, 173. Bruch, L. W. *Surf. Sci.* **1993**, *125*, 194. Bruch, L. W.; Cole, M. W.; Zaremba, E. *Physical Adsorption: Forces and Phenomena*; Clarendon Press: Oxford, 1997.
(7) McLachlan, A. D. *Mol. Phys.* **1964**, *7*, 381.

(8) Taylor, J. A. G.; Mingins, J.; Pethica, B. A. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2694. Mingins, J.; Stigter, D.; Dill, K. A. *Biophys. J.* **1992**, *61*, 1603. Stigter, D.; Mingins, J.; Dill, K. A. *Biophys. J.* **1992**, *61*, 1616.
(9) Vidal-Madjar, C.; Gulochon, G.; Karger, B. L. *J. Phys. Chem.* **1976**, *80*, 394.
(10) Dang, L. X.; Feller, D. *J. Phys. Chem. B* **2000**, *104*, 4403.

layers. $B_2(T)$ for extended long chains in the surface plane is dominated by the large van der Waals forces when the chains are close and parallel. Summation of the pair potentials for long chains of CH_2 groups obeying the L−J 12−6 dependence on separation gives a 12−5 form for the whole molecules, as shown by Salem.[11] The 12−5 relationship gave a reasonable account of the chain length dependence of the two-dimensional $B_2(T)$ values, as estimated from the then-available lipid monolayer data.[1] Graphical representations of the calculated $B_2(T)$ on a scale of σ^2 as a function of ϵ/k were given for both the 12−5 and 12−6 cases,[1] where σ, ϵ, r and k have their customary significance in the L−J relationship $\Phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ and its 5th power analogue.

The available experimental data for short-chain gaseous normal alkanes (methane to butane) adsorbed at the water/gas interface were analyzed to obtain estimates for the hydrocarbon chain interactions at the water/vapor surface,[3] in part to assist the interpretation of the interaction potentials for the polar headgroups of the spread lipid monolayers. In particular, the experimental estimates of $B_2(T)$ for adsorbed methane at several temperatures were compared with values for a two-dimensional L−J gas, using the bulk gas phase 12−6 parameters for methane and the computations given earlier[1] for $B_2(T)$ as a function of σ and ϵ/k. The agreement was fair, implying that the interaction of pairs of methane molecules adsorbed on water is not materially influenced by the adjacent water phase.

A reanalysis of the data for the alkanes on water became desirable for two reasons. First, the recently developed general analytical closed-form solutions of the basic equations for the virial coefficients of a L−J gas for a range of dimensions[12] were used to calculate $B_2(T)$ for two-dimensional gases. The results showed small but significant discrepancies with the results given earlier by numerical integration.[1,3]

These new calculations from the analytical solution are in complete agreement, as expected, with numerical integrations using a modern computer and software. The early tabulations for $B_2(T)$ given by Morrison and Ross[13] give results very close to the new computations and remain useful. We note that the earlier results[1] for second virial coefficients in two dimensions based on the 12−5 form of the L−J potentials, as given by Salem[11] for long paraffin chains, are confirmed upon recomputation. Second, the earlier estimates of the virial coefficients from the experimental data for the alkanes on water were made using the vapor pressures without fugacity corrections, applying graphical methods to estimate the slopes and curvatures of the gas pressure−surface pressure curves at the low-pressure limit. The customary neglect of fugacity coefficients in analyzing gas adsorption data has recently been shown to be unsatisfactory[14] for alkane adsorption on carbon, and a reanalysis of the data for adsorption on water was clearly required. The amended estimates of $B_2(T)$ for the alkanes methane to butane are compared for all four alkanes with values calculated from the two-dimensional L−J relation using the available σ and ϵ/k values for the three-dimensional gases assuming spherical symmetry[15−17] substituted into the basic relation for a two-dimensional gas of spherical molecules:

$$B_2(T) = \pi \int \{1 - \exp[-\Phi(r)/kT]\} r \, dr \qquad (1)$$

Data and Methods

Of the early published data on the surface tension of water in contact with alkane vapors, only the work of King and colleagues[18,19] using the capillary rise method was judged reliable for analysis for second virial coefficients at several temperatures.[3] These papers give extensive data on the adsorption of several hydrocarbons from the gas phase on water, including the normal alkanes from methane to butane. Methane was studied up to pressures of ~65 atm. These results for methane were later confirmed by the experiments of Sachs and Meyn at 25 °C using the drop-shape method[20] and extended to ~450 atm. The sets of data for Π as a function of the alkane vapor pressure (p) were previously analyzed for estimates of $B_2(T)$ neglecting gas nonideality on the grounds that extrapolations to low pressure were required by the method proposed.[3]

The surface virial expansion in the surface density (Γ) is

$$\Pi/kT\Gamma = 1 + B_2(T)\Gamma + B_3(T)\Gamma^2 + \dots \qquad (2)$$

When the surface density is taken from the Gibbs adsorption isotherm for an ideal vapor, the virial expansion can be written[3] as

$$\Pi/p = kT\sum_n B_n(T)p^{n-1}(1/kT \, d\Pi/dp)^n \qquad (3)$$

where $B_n(T)$ is the nth virial coefficient, with $B_1(T) = 1$. $B_2(T)$ will be given by

$$B_2(T)/kT = -\beta/\alpha^2 \qquad (4)$$

where $\alpha = \lim(d\Pi/dp)$ and $\beta = \lim[d(\Pi/p)/dp]$ as p and Π go to 0.

The corrections to the Gibbs adsorption isotherm arising from the effect of pressure on the surface excess volume of formation of the surface per unit area[21,22] may be neglected, at least up to 80 atm, because the data on the effect of helium on the surface tension of water indicate a near-zero effect up to that pressure.[23]

If the assumption that the alkane vapors can be treated to a good approximation as ideal gases is dropped, the equations above can be retained with substitution of the gas fugacity (p^*) in place of the pressure, and α^* and β^* in place of α and β. Because the trend lines for Π as a function of both p and p^* must pass through the origin, estimates of α and α^* can be estimated graphically within a close range. Strictly, α and α^* should be identical, and in fact the estimates of α^* are identical or close to the values of α given previously.[3] However, it was found that the extrapolation procedure used previously for β is unsatisfactory because in the low-pressure range the experimental error in Π/p^* becomes proportionately larger as Π approaches the experimental error of ~0.1 mN m^{-1}

(11) Salem, L. *J. Chem. Phys.* **1962**, *37*, 2100; *Nature* **1962**, *193*, 476.

(12) Glasser, M. L. *Phys. Lett. A* **2002**, *300*, 381.

(13) Morrison, I. D.; Ross, R. *Surf. Sci.* **1973**, *39,* 21.

(14) Pan, H.; Ritter, J. A.; Balbuena, P. B. *Langmuir* **1998**, *14*, 6323.

(15) Gupta, D.; Eubank, P. T. *J. Chem. Eng. Data* **1997**, *42*, 961.

(16) Hirschfelder, J. O.; Curtis, C. F.; Byron Bird, R. *Molecular Theory of Gases and Liquids*; John Wiley and Sons: New York, 1964.

(17) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Liquids and Gases*; McGraw-Hill: New York, 1987.

(18) Jho, C.; Nealon, D.; Shogbola, S.; King, A. D. *J. Colloid Interface Sci.* **1978**, *65*, 141.

(19) Massoudi, R.; King, A. D. *Colloid Interface Sci.* **1976**, *3*, 331.

(20) Sachs, W.; Meyn, V. *Colloids Surf., A* **1995**, *94*, 291.

(21) Guggenheim, E. A. *Thermodynamics. An Advanced Treatment for Chemists and Physicists*, 2nd ed.; N. Holland Publishing Co.: Amsterdam, 1950; p 99.

(22) Turkevich, L. A.; Mann, J. A. *Langmuir* **1990**, *6*, 445.

(23) Massoudi, R.; King, A. D. *J. Phys. Chem.* **1974**, *78*, 2262.

for the bulk of the data[18,19] and the extrapolation becomes overly dependent on the higher pressure data and, hence, the fugacity coefficients. The estimates of $B_2(T)$ given here do not use the previous extrapolation method via estimates of β and differ increasingly from the values given earlier[3] as the curvature of the $\Pi-p^*$ plots increases and the fugacity coefficients decrease.

With the introduction of the alkane gas fugacities, a preferable overall approach to the analysis of the data is to use the virial expansion in the surface pressure and then correlate the surface pressure and surface fugacity to obtain the surface virial coefficients. This correlation can be made over the entire experimental range for all the data of Jho et al.[18] and Massoudi et al.[19] For the data of Sachs and Meyn[20] for methane at 25 °C, the analysis was not carried beyond 100 atm in the first instance, corresponding to an estimated surface area of ~0.5 nm²/ molecule from the Gibbs adsorption isotherm. This area is well above the anticipated close-packed area of approximately 20 nm²/molecule and compares with $3\pi\sigma^2/2$ for methane (0.69 nm²/molecule), the critical area as given by the two-dimensional van der Waals equation, which usually substantially underestimates the critical density in three dimensions. Analysis beyond 100 atm is correspondingly speculative. Gas fugacities are readily obtained from the vapor-phase virial coefficients and were obtained by this method for ethane and propane.[24,25] The fugacity coefficients for methane and ethane are tabulated by Din.[26] The fugacities for ethane from the second virial coefficients and those from Din's tables are close, supporting the use of the virial coefficients for propane. For methane, fugacity values obtained from the later compilation of methane compressibility factors given by Douslin et al.[27] were essentially identical to the values in Din's tables. New estimates of the compression factors, the second and third virial coefficients, and L−J parameters for butane vapor have been obtained recently from critical experiments allowing for adsorption corrections in the experimental system[15] and are adopted in this study.

In a pseudo-one-component Gibbs surface, the surface compression factor can be expressed by the two-dimensional virial expansion as a power series in Π:

$$\Pi A/kT = 1 + (B\Pi + C\Pi^2 + ...)/kT \quad (5)$$

where B, C, and so forth are second, third, and so forth temperature-dependent virial coefficients. B and C are related to the second and third virial coefficients in the density expansion by[21] $B = B_2(T)$ and $B_3(T) = [B_2(T)]^2 + kTC$.

The surface fugacity (Π^*) can be expressed via the gas fugacity (p^*) as[21]

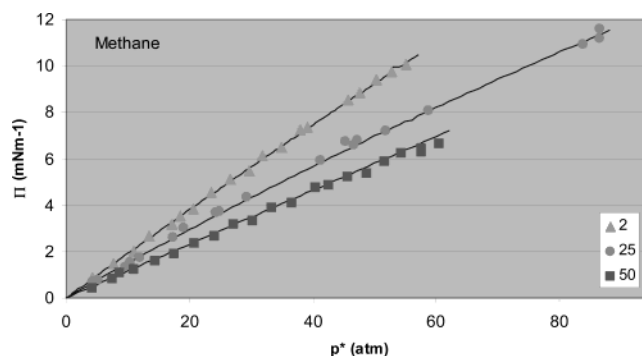$$\Pi^* = \alpha^* p^* = \Pi \exp(B\Pi + C\Pi^2/2 + ...)/kT \quad (6)$$

where α^* is accessible from measurements of Π at low p^*. Estimates of α^* were first made from the $\Pi-p^*$ plots, using graphical methods and polynomials. The α^* values are readily defined in a narrow range. The conventional procedure for analyzing the experimental data sets for B for each alkane and temperature by regression of $\ln(p^*/\Pi)$ as a polynomial in Π, corresponding with the exponent

Figure 1. Methane adsorption on water. Dependence of the surface pressure (Π) on the methane fugacity (p^*) and temperature. The lines are drawn from eq 6 with the values of α^* and $B_2(T)$ from Table 1, neglecting the higher virial coefficients. The data from Jho et al.[18] and Sachs and Meyn[20] at 25 °C merged.

in eq 5, was first applied to the complete data sets[18,19] for ethane, propane, and butane and to methane at 2 and 50 °C. For methane at 25 °C, the data from Jho et al.[18] were merged at this stage of the analysis with the Sachs and Meyn[20] data to ~100 atm. The polynomials were restricted to the linear and quadratic in Π, assuming that all virial coefficients in the pressure expansion beyond either the second or the third are 0. The derived values of α^* from these plots fell within the range admissible from the $\Pi-p^*$ plots, and the corresponding values of B were noted. No physically realistic values of C could be identified because the apparent values for a given alkane change sign with a change in the temperature. However, the objections to the use of logarithmic functions for the experimental data in a conventional regression analysis have been well described,[28] and alternative statistical procedures were examined.
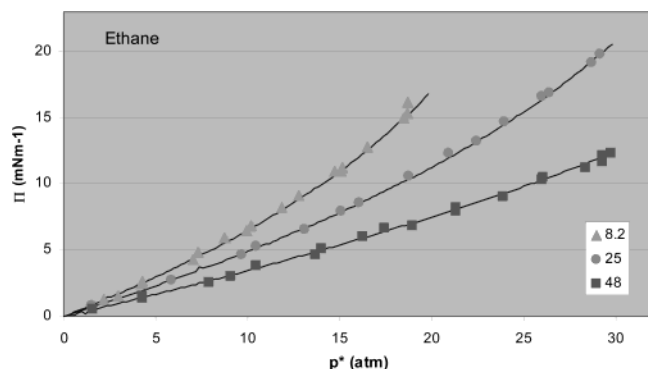
Further analysis was made by a nonlinear least-squares method using eq 6 directly on the assumption that C and the higher coefficients are 0. As the dependent variable, Π was calculated from p^* at each data point from $\alpha^*p^* = \Pi \exp(B\Pi/kT)$ for a spread of α^* values near to and enclosing the realistic range for α^* observed for each data set from analysis of the data at low surface pressures, together with a spread of B values spanning the values from the log plots. Values of R^2 from the least-squares correlations with the experimental sets were displayed as a "landscape" over the chosen ranges of α^* and B. The landscape showed a clear steep-sided "ridge" of high R^2 values with the realistic α^* range on the broad summit. The best values for α^* were chosen from the highest R^2 in the defined α^* range by inspection of the R^2 landscape, and the corresponding B value was read off. The estimated error ranges for B were also made from the R^2 landscapes by noting the variation of B across the realistic α^* ranges. The analysis procedure for the possible identification of C from the high-pressure region of the methane data at 25°C is described in the discussion section.

Results

The tabulated experimental data together with the relevant gas fugacities are given in the online supplement (see Supporting Information) to the printed version of this paper. Plots of the experimental surface pressures as a function of the vapor fugacities for all four alkanes are shown in Figures 1−4. The units are milliNewtons per meter for Π and atmospheres for the pressure and gas fugacity, corresponding with the units used in the bulk

(24) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures. A Critical Compilation*; Clarendon Press: Oxford, 1980.

(25) Dymond, J. H.; Cholinsky, J. A.; Szafranski, A.; Wyrzykowska-Stankiewicz, D. *Fluid Phase Equilib.* **1986**, *27*, 1.

(26) Din, F., Ed. *Thermodynamic Functions of Gases*; Butterworths: London, 1961.

(27) Douslin, D. R.; Harrison, R. H.; Moore, R. T.; McCullogh, J. *J. Chem Eng. Data* **1964**, *9*, 358.

(28) Johnson, M. L. *Anal. Biochem.* **1992**, *206*, 215.

Figure 2. Ethane adsorption on water. Dependence of the surface pressure (Π) on the ethane fugacity (p^*) and temperature. The lines are drawn from eq 3 with the values of α^* and $B_2(T)$ from Table 1, neglecting the higher virial coefficients.
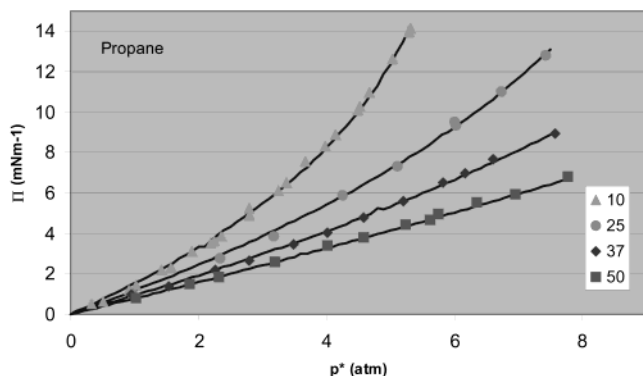
Figure 3. Propane adsorption on water. Dependence of the surface pressure (Π) on the propane fugacity (p^*) and temperature. The lines are drawn from eq 6 with the values of α^* and $B_2(T)$ from Table 1, neglecting the higher virial coefficients.
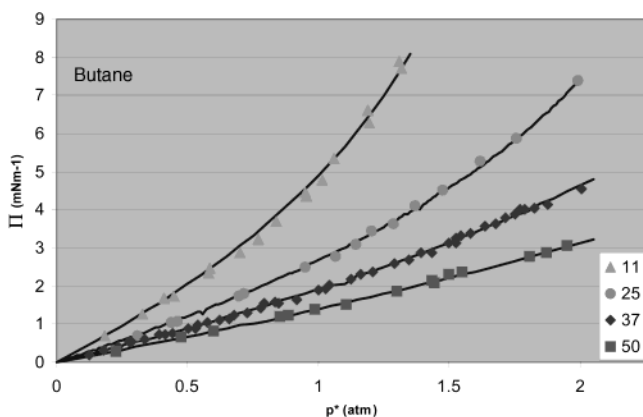

Figure 4. Butane adsorption on water. Dependence of the surface pressure (Π) on the butane fugacity (p^*) and temperature. The lines are drawn from eq 6 with the values of α^* and $B_2(T)$ from Table 1, neglecting the higher virial coefficients.

of the experiments. The lines shown on these charts are calculated from the values of α^* and B [=$B_2(T)$] given in Table 1.

The estimates of α^* and $B_2(T)$ (with related R^2 values) for the four alkanes given in Table 1 show consistent overall trends with the temperature and homologous sequence, with the exception of the result for $B_2(T)$ for methane at 50 °C, which appears definitely anomalous. A possible factor for this anomalous result at 50 °C is that the data do not go to such high surface pressures as do those for the other temperatures, making the estimation of $B_2(T)$ more difficult. The variation of α^* with the

reciprocal temperature is linear and gives standard integral heats of adsorption of the four alkanes (-7.6, -10.0, -10.7, and -19.1 kJ mol^{-1} for methane to butane, respectively), within the experimental error, identical to those published previously.[18] The value for butane is also close to the result expected from the extrapolation of the linear variation of the standard differential (isosteric) heats of adsorption in the series heptane to pentane obtained by a chromatographic method.[29] The extrapolated differential heat is equivalent to a standard integral heat of adsorption for butane of 17.5 kJ/mol. The values of α^* and $B_2(T)$ for the four alkanes shown in Table 1 supersede those published previously, the differences being more marked as the homologous series is ascended.

Also shown in Table 1 are the calculations for $B_2(T)$ from the L$-$J 12$-$6 relationship in two dimensions, using published values of σ and ϵ.[15-17] For ethane and propane, values of $B_2(T)$ were calculated with three sets of L$-$J parameters from the sources quoted.[16,17] The parameters for butane cited by Reid et al.[17] from the tabulation given by Svelha[30] were not applied because they are grossly out of line with the other linear alkanes tabulated and with the recent new experimental *PVT* data.[15] The L$-$J coefficients for the vapors other than methane effectively bundle the orientational (and for butane the conformational) components of the potentials of mean force by adopting the spherical symmetry basic to the L$-$J formalism. This bundling may alter upon adsorption if the orientations or conformations are modified, particularly with the higher homologues to which gauche$-$trans conformations may be ascribed, starting with butane, as discussed in the following.

Analysis of the methane data above 100 atm is problematical. The surface density may reach the unknown critical density, and neglect of the excess volume of formation of the interface may become significant. At 250 atm and higher, the surface tension reaches a constant value of 52 mN m^{-1}. This is comparable with the interfacial tension for water/liquid alkanes and can be taken as the interfacial tension for water and supercritical methane. Plainly, analysis for virial coefficients at such densities is unrealistic. Extending the analysis to 150 atm by fitting for a second virial coefficient only gave unrealistic α^* values and a lower R^2 value than those for the lower pressure range. A good statistical fit was obtained by retaining the α^* and $B_2(T)$ values from Table 1 and including a third virial coefficient $C = 0.37 \times 10^{-2}$ nm^2/(molecule mN m^{-1}). An alternative insight into the relevance of the third virial coefficient for methane at the higher pressures comes from comparison of the methane surface areas calculated from eq 5, using only the second coefficient, with areas obtained from the application of the Gibbs adsorption isotherm. For example, up to about 80 atm ($\Pi = 10.5$ mN m^{-1}) at 25 °C, the areas are in reasonable accord, definitely diverging at higher pressures and indicating that higher virial coefficients are required. The Gibbs area at 150 atm ($\Pi = 16$ mN m^{-1}) is 0.48 ± 0.02 nm^{-2}/molecule. Solving eq 5 with the tabulated $B_2(T)$ and including the third virial coefficient gives C as 1.0×10^{-2} nm^2/molecule, too large for a fit at 80 atm, indicating that the higher virial coefficients cannot be neglected at 150 atm and above. The analysis at this point is at the limit for the data, and we may conclude that C is positive, with a value of $\sim 0.4 \times 10^{-2}$ nm^{-2} as an approximate estimate for methane.

(29) Hartkopf, A.; Karger, B. L. *Acc. Chem. Res.* **1973**, *6*, 209.
(30) Svelha, R. A. NASA Technical Report R-132, NASA: Springfield, VA, 1962.

Table 1. Second Virial Coefficients for Adsorbed Alkanes at the Vapor/Water Surface[a]

Methane				
temperature (°C)	2.0	25.0	50.0	
α^{*b} (m Nm^{-1} atm^{-1})	0.194	0.153	0.116	
$B_2(T)^b$ (Å^2 molecule^{-1})	2.0 ± 1.0	5.9 ± 1.0	0 (see text)	
L–J $B_2(T)^{c,d}$	3.755	5.201	6.495	
Ethane				
temperature (°C)	8.2	25	48.0	
α^{*b} (m Nm^{-1} atm^{-1})	0.55	0.44	0.323	
$B_2(T)^b$ (Å^2 molecule^{-1})	-10.0 ± 1.0	-9.0 ± 1.0	-8.8 ± 0.5	
L–J $B_2(T)^{c,e}$ i	-9.92;	-7.61;	-4.96;	
ii	-9.65	-7.01	-3.97	
iii	-6.82	-4.41	-1.61	
Propane				
temperature (°C)	10.0	25.0	37.0	50.0
α^{*b} (m Nm^{-1} atm^{-1})	1.43	1.05	0.91	0.78
$B_2(T)^b$ (Å^2 molecule^{-1})	-17.0 ± 0.5	-16.0 ± 2.0	-12.8 ± 0.5	-6.7 ± 1.0
L–J $B_2(T)^{c,f}$ i	-19.28	-15.16	-12.23	-9.37
ii	-18.91	-15.32	-12.78	-10.29
iii	-14.51	-11.23	-8.89	-6.60
Butane				
temperature (°C)	11.0	25.0	37.0	50.0
α^{*b} (m Nm^{-1} atm^{-1})	3.60 ± 0.04	2.22 ± 0.02	1.68 ± 0.02	1.28 ± 0.02
$B_2(T)^b$ (Å^2 molecule^{-1})	-24.7 ± 1.0	-28.5 ± 1.5	-30.0 ± 1.0	-28.5 ± 3.0
L–J $B_2(T)^{c,g}$	-49.29	-43.01	-38.24	-32.24

[a] The results in Table 1 are derived from the adsorption data sets of refs 18–20. These sets and the related gas fugacities are tabulated in the Supporting Information. [b] The best fit α^* and $B_2(T)$ values show $R^2 \geq 0.997$, except for butane at 11.0 °C ($R^2 = 0.996$). For the error estimates shown for $B_2(T)$ and for α^* ($\pm 1-2\%$), see text. [c] L–J $B_2(T)$ from eq 1 using the values of ϵ/k and σ listed in footnotes $d-g$ were taken from the references indicated. [d] ϵ/k (K), σ (Å): 148.2, 3.817, from *PVT* data (ref 16). The average of the values from the viscosities (refs 16 and 17) is close to these. [e] ϵ/k (K), σ (Å): (i) 243, 3.954, from *PVT* data (ref 16); (ii) 230, 4.418, from viscosities (ref 16); (iii) 215.7, 4.443, from viscosities (ref 16). [f] ϵ/k (K), σ (Å): (i) 242, 5.637, from *PVT* data (ref 16); (ii) 254, 5.061, from viscosities (ref 16); (iii) 237.1, 5.118, from viscosities (ref 17). [g] ϵ/k (K), σ (Å): 317, 5.77, from *PVT* data (ref 15).

Discussion

When the $B_2(T)$ value for methane at 50 °C is left aside, the agreement between the surface second virial coefficients from experiment and from the L–J calculations is remarkably close for methane, ethane, and propane, with the least agreement at the highest temperatures. This broad agreement shows that the proximity of these three alkanes to the bulk water phase has little effect on the alkane pair potentials. Correspondingly, induction of surface water structures such as the formation of local surface cages is ruled out. This also follows from the standard entropies of adsorption on water at 25 °C for these three alkanes, which are equivalent to the loss of less than one degree of translational freedom, indicating a weak vibrational mode normal to the surface, little rotational restriction, and negligible water structuring.[3,18] The effect of the adjacent water phase on the alkane pair potentials is expected to fall off rapidly with the distance of the adsorbed species from the surface of the bulk phase.[7,10] The weak vibrational mode of adsorption can be regarded as corresponding to adsorption at an average distance from the surface larger than that at close contact, with consequent reduction of the SFP and McLachlan effects. The apparent absence of the SFP effects for these lower alkanes is in accord with recent simulation modeling[31] of the adsorption of methane and ethane on water, which gave excellent agreement between the calculated and experimental heats of adsorption without invoking SFP of the adsorbed molecules. By contrast, earlier modeling for adsorption of pentane to heptane gave good agreement with the inclusion of SFP.[9] The simulation study also showed that the rotational orientation of ethane is weakly damped upon adsorption to water, again in accord with the above analysis of the entropy of adsorption.

The results for butane are more complex. When it is noted that the result at 11 °C is less reliable (as discussed previously), the $B_2(T)$ values for butane from experiment are more positive than the L–J values, approaching equality at the higher temperatures. Correspondingly, the change in the butane experimental $B_2(T)$ with temperature is much less than that for the L–J values. The more positive values from experiment are in the direction anticipated from the effect of the bulk water phase on the potentials of the mean force between two adsorbed molecules, as indicated by McLachlan or from SFP, but the decreasing difference between the experimental and L–J values for $B_2(T)$ as the temperature increases suggests alternative or additional effects. Jho et al.[18] reviewed the data for the standard entropies of adsorption to water for higher alkanes at 25 °C and concluded that they are more negative than the entropy loss associated with one degree of translational freedom. The entropy loss increases as the homologous series is ascended, indicating that chain-length-dependent conformation changes occur upon adsorption. The standard entropy loss upon adsorption for butane is borderline, close to one degree of translational freedom. A rising temperature would be associated with larger displacements in a weak vibrational mode for the adsorbed molecules, with a consequent qualitative attenuation of any SFP or McLachlan effect. In addition, possible temperature-dependent conformation differences between gaseous and adsorbed butane should be taken into account. Butane is the smallest *n*-alkane to show gauche–trans stereoisomerism. If the extended configuration for butane is more preferred on the surface than in the gas phase, the corresponding $B_2(T)$ values will be more negative than those for an unchanged configuration,[1] and the experimental results would be stronger evidence for corrections of the SFP or McLachlan type. If butane were stretched out on the surface, an approximation for the consequent $B_2(T)$ can be obtained from the Salem 5–12

(31) Ashbaugh, H. S.; Pethica, B. A. *Langmuir*, in press.

potential function for long chains, giving a value of -0.55 nm^2/molecule at 25 °C. This value is overly negative because the long-chain assumption is weak for butane, but the result does reinforce interest in the possible role of SFP and McLachlan corrections. Comparison of the molecular areas for butane from the Gibbs adsorption isotherm and from eq 5 using the tabulated $B_2(T)$ value gives good agreement at the higher pressures studied (e.g., at 25 °C for $\Pi = 5.5$ mN m^{-1} and $A = 0.45 \pm 0.02$ and 0.46 nm^2/molecule from the Gibbs and virial methods, respectively), confirming that the third virial coefficient is not significant over the experimental range. This area can accommodate either "L−J spheres" or butane extended flat on the surface.

These considerations lead back to the validity of the L−J parameters for the alkane gases for calculating the two-dimensional virials and, hence, to judging the difference between the calculated and the experimental virial coefficients for evidence of a polarization or McLachlan effect. Possible differences in the conformations of the gaseous and adsorbed states become significant for butane and higher homologues and will modify the bundling of the conformational modes into the single ϵ and σ format of the L−J relation. A more detailed analysis explicitly including the conformations will be required for further progress. It is concluded that the SFP and McLachlan corrections to the potentials of mean force for alkane molecules adsorbed on water are small for methane, ethane, and propane and, of present, have a probable but uncertain significance for butane and higher homologues. SFP and McLachlan corrections are not absent, but are attenuated for the weakly adsorbed lower alkanes on water.

The $B_2(T)$ results for methane on water contrast markedly with the substantial shift in $B_2(T)$ found for methane adsorbed on silver,[5] as compared to that calculated from the gas-phase L−J parameters. The experimental values in this case are said to be in fair agreement with the corrected L−J values using McLachlan's theory[7] for the effect of the metal adsorbent, showing a marked reduction of the attractive component of the pair interaction potential. So far as we know, no computations of the McLachlan potential corrections for molecules adsorbed on water have yet been made. Estimates to be published of the two-dimensional second virial coefficients for other hydrocarbons adsorbed on mercury and water, using published experimental data[32−34] on the surface tension as a function of the hydrocarbon pressure, show more positive values on mercury than those for the same molecules on water. For example, the attractive component in the pair potential for hexane on the mercury surface is virtually abolished, giving a positive second virial coefficient comparable to the molecular co-area, in contrast to the large negative value ($\sim$1 nm^2/molecule) at the water surface from recent experiments.[33] These differences in the effect of the adsorbent phase on the pair potentials from the analysis of a wider range of hydrocarbons at these and other surfaces will be the subject of a further communication.

For methane dissolved in water, the corrections required for the potentials of mean force between methane molecules (as compared to the pair potentials in the gas phase) are plainly larger than the corrections at the water/vapor interface. The difficult experimental measurements of the second virial coefficients for methane dissolved in water have given diverse results of opposite sign.[35,36] The computation of the potentials of mean force for methane in water have shown that the distance dependence is complex.[37] For example, Smith, Zhang, and Haymet[38] find that the potential of mean force undulates on approach, largely as a result of the different packing volumes of the methane and water molecules in the dense liquid phase, with the potential energy minimum nearest to the close approach of two methane molecules in water about twice the depth of the L−J minimum for methane in the gas phase. In contrast, methane at the water surface appears to translate above the upper water molecules in a loosely bound state with little perturbation of the liquid surface or to the pair potentials of the adsorbed molecules. The McLachlan corrections are sensitive to the mean distance of the adsorbed molecules from the adsorbent surface, and the weak vibration mode of adsorption would correspondingly imply lower corrections to the attractive term in the potentials of mean force in the adsorbed layer as compared to a tightly bound adsorbate. Hydrophobic effects begin upon immersion.

Conclusions

Application of a closed-form solution for the two-dimensional second virial coefficient of a L−J gas and reanalysis with gas fugacity corrections of the data for the adsorption of the *n*-alkanes from methane to propane on water shows that the surface second virial coefficients from experiment are in fair agreement with those calculated from the L−J equation using the parameters derived from the three-dimensional gas state. The experimental second virials for butane are significantly less negative than the calculated values, possibly because of the interaction of the adsorbed butane with the electrostatic self-images in the water phase (McLachlan effect) or because of SFP in a closer binding state than that for the lower alkanes. This conclusion is tentative until the possible changes in the conformation of butane upon adsorption at the surface are quantitatively taken into account. The SFP and McLachlan corrections to the potentials of mean force between alkane molecules adsorbed on water are minor for methane, ethane, and propane, probably reflecting the entropy evidence that these molecules are adsorbed at the surface in a weak vibrational mode. There is no evidence from the virial coefficients or the entropies of adsorption of the adsorbate-induced water structure at the surface with these alkanes.

Supporting Information Available: Tabulated experimental data together with the relevant gas fugacities for methane to butane. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Roberts, N. K. *J. Chem. Soc.* **1964**, 1907. Kemball, C.; Rideal, E. K. *Proc. R. Soc. London, Ser. A* **1946**, *187*, 53. Kemball, C. *Proc. R. Soc. London, Ser. A* **1946**, *187*, 117.
(33) Lou, A.; Pethica, B. A. *Langmuir* **1996**, *13*, 4933.
(34) Bruant, R. G., Jr.; Conklin, M. H. *J. Phys. Chem. B* **2002**, *106*, 2232.

(35) Kennan, R. P.; Pollack, G. L. *J. Chem. Phys.* **1990**, *93*, 2724.
(36) Culberson, O. L.; McKetta, J. J. *Trans. Am. Inst. Min. Metall. Pet. Eng.* **1951**, *192*, 223.
(37) Watanabe, K.; Anderson, H. C. *J. Phys. Chem.* **1986**, *90*, 795.
(38) Smith, D. E.; Zhang, L.; Haymet, A. D. *J. Am. Chem. Soc.* **1992**, *114*, 5875.