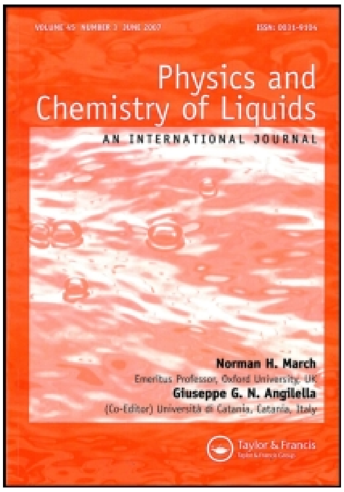

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Physical adsorption of some hydrocarbons - the two dimensional liquid state

Un Sik Kim[a]; Yong Kiel Sung[b]; Mu Shik Jhon[c]; Henry Eyring[d]
[a] Department of Chemistry, Pusan National University, Pusan, Korea [b] Department of Material Science, University of Utah, Salt Lake City, Utah, U.S.A. [c] Department of Chemistry and Chemical Engineering, Korea Advanced Institute of Science, Seoul, Korea [d] Department of Chemistry, University of Utah, Salt Lake City, Utah, U.S.A.

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Physical Adsorption of Some Hydrocarbons —The Two Dimensional Liquid State

UN SIK KIM†, YONG KIEL SUNG‡, MU SHIK JHON§, and HENRY EYRING||

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The significant structure theory of hydrocarbons such as methane, ethane, propane, i-butane, and n-butane has been applied to the physical adsorption on the homogeneous surface, occurring in the submonolayer region. The partition function for the two dimensional fluid adsorbed on the surface has been derived by considering the hindered rotation in the adsorbed phase.

The properties of the isotherm, isosteric heat, and hindered rotational entropy changes upon adsorption show good agreement with the available data from the literature.

INTRODUCTION

Recently, the significant structure theory of liquids[1,2] was applied to describe the physical adsorption of gases occuring in the submonolayer region.

McAlpin and Pierotti[3,4] applied the significant structure theory to the physical adsorption of inert gases, Wang, Ree, and Eyring[5] studied the physical adsorption of chloroform and tetrachloromethane.

Kim, Schmidt, Jhon, and Eyring[6] treated the physical adsorption of quantum gases such as hydrogen, deuterium, and helium.

In this paper, we extend the significant structure theory of liquids to the

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† Department of Chemistry, Pusan National University, Pusan, Korea.

‡Department of Material Science, University of Utah, Salt Lake City, Utah, U.S.A.

§ Department of Chemistry and Chemical Engineering, Korea Advanced Institute of Science, Seoul, Korea.

|| Department of Chemistry, University of Utah, Salt Lake City, Utah, U.S.A.

physical adsorption of hydrocarbons such as methane, ethane, propane, i-butane, and n-butane, which exhibit hindered rotational effects.

To derive the partition function, the Einstein model for a two dimensional solid is introduced into the solid-like partition function, while the hindered rotation is considered in the gas-like partition function. With the use of the derived partition function for the adsorbed phase, the calculated results for the adsorption isotherm, isosteric heat, and entropy change due to hindered rotation are compared with the experimental values.

THEORY

1 Formulation of the partition function

The partition function of the two-dimensional adsorbed fluid is written using the significant structure theory as follows:

$$f_{ads} = \{f_{2s}(1 + n_h \exp(-Ea/RT))\}^{NAs/A} \{f_{2g}\}^{N(A-As)/A} \tag{1}$$

where f_{ads} is the partition function for the adsorbed phase, f_{2s} and f_{2g} are the partition functions for the two-dimensional solid-like structure and for the two-dimensional gas-like structure, respectively. A_s is the molar area of the solid adsorbate; A is the molar area of the adsorbed phase at a given surface coverage θ; and N is the total number of molecules in the adsorbed phase. Eq. (1) can be written in a more convenient form that is measurable as follows:

$$f_{ads} = \{f_{2s}[1 + n_h \exp(-Ea/RT)]\}^{\theta^2 N_m} \{f_{2g}\}^{\theta(1-\theta)N_m} \tag{2}$$

where $\theta = N/N_m = A^{o}_{m}/A$, $A^{o}_{m} = A_m L/N_m$.
N_m is the number of molecules on the surface at $\theta = 1$, L is Avogadro's number, and A_m is the area of the surface.

We also choose the complete monolayer as an ideal two-dimensional solid, so that $A_s = A^{o}_{m}$. f_{2s} and f_{2g} in Eq. (2) can be written as a product of the partition functions as follows:

$$f_{2s} = f_{2E} \cdot f' \cdot f_{HR} \cdot f_{int} \cdot \exp[(u_0 + w)/RT] \tag{3}$$

$$f_{2g} = f_t \cdot f' \cdot f_{3p} \cdot f_{int} \cdot \exp u_0/RT \tag{4}$$

In Eq. (3), f_{2E} is the partition function of the two-dimensional Einstein crystal and is given by

$$\left[\frac{\exp \frac{\theta E}{2T}}{1 - \exp \frac{-\theta E}{T}}\right]^2$$

where θ_E is the Einstein characteristic temperature. f′ is the partition function for the vibration normal to the surface and is $\exp(-h\nu_l/2kT)/[1 - \exp(h\nu_l/kT)]$, where h is Planck's constant and ν_l indicates the vibrational frequency normal to the surface. f_{HR} is the hindered rotational partition function of the adsorbed hydrocarbon molecules on the surface. Then,

$$f_{HR} = [1 - \exp(-V/RT)]\cdot f_{3E} + \exp(-V/RT)\cdot f_{3R} \tag{5}$$

where V is the molar rotational energy barrier and is given by $V = B_0V_{so}/(V - V_{so})$ (1). Here B_0 is the parameter corresponding to the molar rotational energy barrier, V_{so} is the solid molar volume at the melting point at which molecular rotation starts, and V is the liquid molar volume. f_{3E} is the partition function of a three-dimensional Einstein crystal. f_{3r} is the free rotational partition function of the hydrocarbon and is given by

$$f_{3R} = \frac{8\pi^2(8\pi^3 I_A I_B I_C)^{1/2}(kT)^{3/2}}{\sigma h^3} \tag{6}$$

where I_A, I_B, and I_C are the three principal moments of inertia, σ is the symmetry number, and k is the Boltzmann constant. f_{int} is the internal partition function and has the same value in Eq. (3) and Eq. (4). U_0 is the molar adsorbate-adsorbent interaction energy and W is the molar two-dimensional lattice energy of the adsorbate.

In Eq. (4), f_t is the two-dimensional translational partition function of the adsorbed hydrocarbon and is given by

$$f_t = \frac{2\pi mkT}{h^2}\,\frac{eA_m^o}{L}\,\frac{1}{\theta} \tag{7}$$

Combining Eqs. (2)–(4), f_{ads} is given as follows:

$$\begin{aligned} f_{ads} = {} & \{f_{2E}[1 + n_n(1 - \theta)/\theta]\cdot f'\cdot f_{HR}\cdot f_{int}\cdot \exp[(u_o + w)/RT]\}^{\theta^2 Nm} \\ & \cdot \{f_t\cdot f'\cdot f_{3r}\cdot f_{int}\cdot \exp[U_o/RT]\}^{\theta(1+\theta)Nm} \end{aligned} \tag{8}$$

Then, the chemical potential of the adsorbed phase μ_{ads} is defined as

$$\mu_{ads} = \left(\frac{\partial A_{ads}}{\partial N}\right)_{A_m, T} \tag{9}$$

$$A_{ads} = -kT\ln f_{ads} \tag{10}$$

where A_{ads} is the Helmholtz free energy of the adsorbed phase and N is the total number of molecules of the adsorbed phase.

Using the Eqs. 9–10 μ_{ads} can be written as

$$\frac{-\mu_{ads}}{kT} = 2\theta \ln \left\{ \frac{f_{2E}[1 + n(1 - \theta)/\theta]\theta \cdot f_{HR} \cdot \exp[W/RT]}{C \cdot f_{3r}} \right\} + \frac{\theta[\theta + n - n\theta - 1] - n}{\theta + n - n\theta} + \ln \frac{C \cdot f' \cdot f_{3r} \cdot f_{int} \exp[U_o/RT]}{\theta} \tag{11}$$

where

$$C = \frac{2\pi mkT}{h^2} \cdot \frac{eA_m^o}{L} \tag{12}$$

2 The adsorption isotherm

For the equilibrium state, the chemical potential for the adsorbed phase and for the gas phase must be equal.

$$\mu_{ads} = \mu_{gas} \tag{13}$$

Then,

$$-\frac{\mu_{ads}}{kT} = -\left(\frac{\mu_{gas}^o}{kT}\right) - \ln p \tag{14}$$

where

$$\mu_{gas}^o = -kT \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} kT, f_{3r} \cdot f_{int} \tag{15}$$

With Eq. (13), the adsorption isotherm is given as follows:

$$\ln p = \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} - 2\theta \{ l_n f_{2E} \cdot \exp[W/RT] + \ln \frac{f_{Hp}}{c \cdot f_{3p}} + \ln(\theta + n - n\theta) \} - \frac{\theta[\theta + n - n\theta - 1] - n}{\theta + n - n\theta} - \ln f' \exp[U_c/RT] -- \ln \frac{\theta}{c} \tag{16}$$

3 The isosteric heat

The isosteric heat of adsorption q_{st} is given by

$$q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_\theta \tag{17}$$

Hence

$$q_{st} = \{2W + 5RT - 2R\theta_E - 4R\theta_E \left[\frac{\exp(-\theta_{E/T})}{1 - \exp(-\theta_{E/T})}\right] - 2H_R\}\theta + U_o + \left\{ \left(\frac{h\nu_l}{2\,kT}\right) \left(\frac{1 + \exp(-h\nu_{l/RT})}{1 - \exp(-h\nu_{l/RT})}\right) + \frac{3}{2} \right\} RT \tag{18}$$

TABLE I

Molecular parameters for hydrocarbons on P-33 (graphite)

		Methane	Ethane	Propane	i-Butane	n-Butane
θ	(°K)	52.81(75.33)[a]	68.87(131)[b]	67.3(128)[b]	55.37(106)[b]	53.1(101)[b]
ν_1	$(\mathrm{sec}^{-1}) \times 10^{-12}$	2.48[c]	1.9[c]	1.8	1.6	1.5[d]
A^o_m/L	$(\mathrm{cm}^2) \times 10^{16}$	15.1	18.0	21.9	24.9	25.5
$I_A \cdot I_B \cdot I_C$	$(g^3 \cdot \mathrm{cm}^6) \times 10^{117}$	0.164[b]	17.37[b,f]	320.32[b,f]	1965.0[f]	1540.0
σ		12[b]	6[f]	2[b,f]	3[b,f]	2[f]
W	(Cal/mol)	798 (897.6) [g,a]	3566	5124	5367	5418
U_o	(Cal/mol)	2770 (2754)[c]	4012	5143	5954	6260
B_o	(Cal/mol)	0	191.0	264.2	283.9	302.0
V	(Cal/mol)	0	2634 (2750)[h] (2800)[f]	3376 (3300)[f]	3549 (3600)[f]	3778

[a] Ref[7]. [b] Ref[9]. [c] Ref[10]. [d] Ref[11]. [e] Ref[12]. [f] Ref[13]. [g] Ref[5]. [h] Ref[15].

where H_R is the term contributed by hindered rotation and is given by

$$H_R = V + \frac{1}{f_{HR}} \left\{ \frac{3}{2} R\theta_E \cdot f_{3E} \left[1 - \exp(-V/RT)\right] \left[\frac{1 + \exp(-\theta_{E/T})}{1 - \exp(-\theta_{E/T})}\right] + \frac{3}{2} RTf_{3r} \cdot \exp(-V/RT) - V \cdot f_{3E} \right\} \quad (19)$$

4 Hindred rotational entropy changes upon adsorption

Using statistical thermodynamical relations, the hindered rotational entropy changes upon adsorption, ΔS_{rot}, is given by

$$\Delta S_{rot} = \overline{S}_{HR} - \overline{S}_{FR} = R\left[\ln f_{HR} - \ln f_{3r} + \frac{H_R}{RT} - \frac{3}{2}\right] \quad (20)$$

In Eq. (20), $\overline{S}_{HR}$ is the molar hindered rotational entropy of hydrocarbon on the adsorbed phase and $\overline{S}_{FR}$ is the molar free rotational entropy of hydrocarbon in the gas phase.

RESULTS AND DISCUSSION

The physical constants and parametric values used in this calculation are listed in Table I. The Einstein characteristic temperature θ_E is taken from experimental data for methane[7] and is chosen as the Debye characteristic temperature, θ_D, times 0.75[8] in ethane[9], propane[9], i-butane[9], and n-butane[9]. For the two-dimensional solid, the values of θ_E times 0.701[6] were used.

The vibrational frequencies, ν_1, normal to the surface are chosen from the experimental data[10,11], and the values for A_m^o/L are taken from liquid densities[7,12]. The moments of inertia are taken from the literature[9,13]. The

TABLE II

Pressure vs. coverage for hydrocarbons on P-33 (graphite) (at 297.89°K)

	Methane		Ethane		Propane		i-Butane		b-Butane	
P	P CmHg		P CmHg		P CmHg		P CmHg		P CmHg	
θ	Expt.[a,b]	Calc.	Expt.[a]	Calc.	Expt.[a]	Calc.	Expt.[a]	Calc.	Expt.[a]	Calc.
0.1	281.7	304.1	30.9	31.0	4.7	4.24	0.9	0.91	0.5	0.5
0.2	626.6	645.9	62.3	62.3	9.2	8.39	1.7	1.71	1.0	0.96
0.3	1108.0	1107.4	99.4	101.3	14.2	13.37	2.6	2.58	1.5	1.47
0.4	1877.0	1850.3	151.3	160.5	21.0	20.78	3.7	3.78	2.2	2.19
0.5					33.1	34.15	5.7	5.88	3.4	3.45
0.6					61.7	62.83	10.2	10.23	6.2	6.11

[a] Ref[14]. [b] Ref[16].

values for W and U_0 giving the best fit are used. The values used are compared with the literature[7,10] and are in agreement within 10% in the case of methane.

Using the physical constants and parameters in Table I, an example of the calculated isotherm at 297.89 °K is shown in Table II.

The other calculated results for the adsorption isotherms are shown in Figures 1–5. The results for the isosteric heat and differential heat are listed

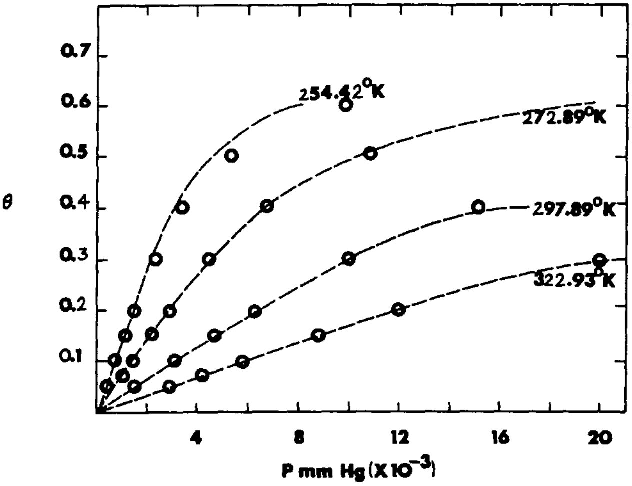

FIGURE 1 Methane-Graphite isotherms. –; Theoretical 0; Experimental [Ref. 14, 16].

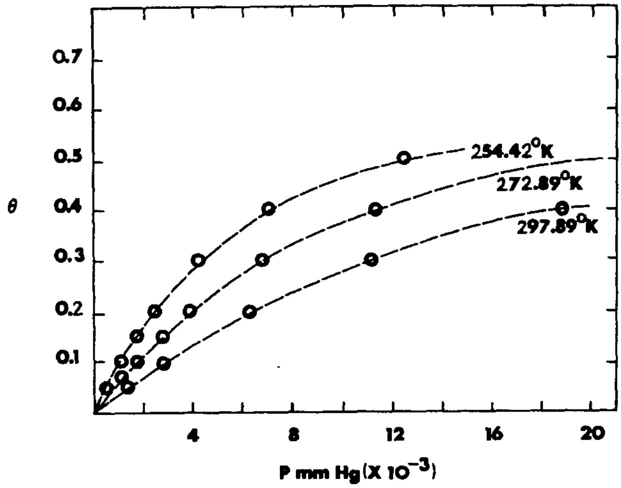

FIGURE 2 Ethane-Graphite isotherms. –; Theoretical 0; Experimental [Ref. 14].

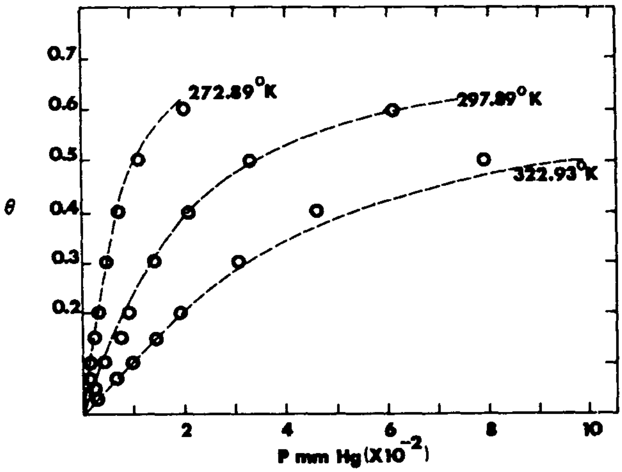

FIGURE 3 Propane-Graphite isotherms. –; Theoretical 0; Experimental [Ref. 14].

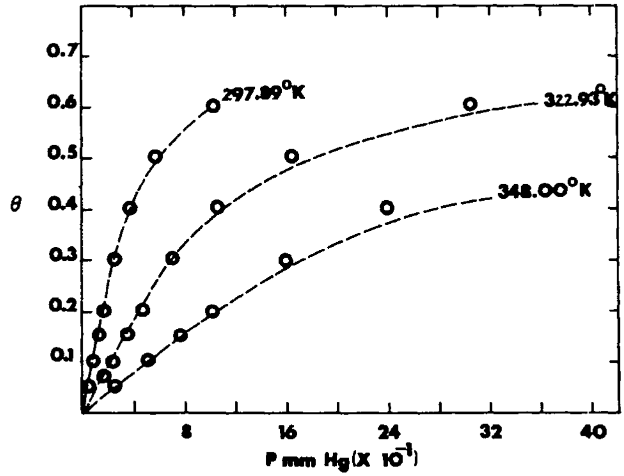

FIGURE 4 i-Butane-Graphite isotherms. –; Theoretical 0; Experimental [Ref. 14].

in Table III. In Table III, θ_s is the surface coverage at the standard spreading pressure π_s and is equal to

$$\theta_s = \frac{A^{\circ}_{m}}{L} \cdot \frac{\pi_s}{kT} \quad (14).$$

The fraction of free rotation and hindered rotational entropy changes upon adsorption at 297.89°K are shown in Table IV.

The agreement between theory and experiment is quite satisfactory.

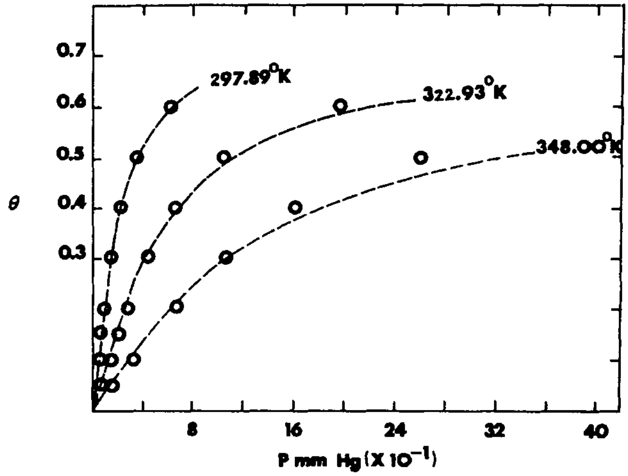

FIGURE 5 n-Butane-Graphite isotherms. –; Theoretical. 0; Experimental [Ref. 14].

TABLE III

The isosteric heats of hydrocarbons at 297.89 °K in Cal/mol.

	Methane	Ethane	Propane	i-Butane	n-Butane
lim $\theta \to 0$ q_{st} (Expt)	3020^{a,b}	4600^{a}	5870^{a}	6910^{a}	7450^{a}
q_{st} ($\theta = \theta_s$)(Calc)	3063	4370	5548	6406	6731
q^{diff} ($\theta = 0.5$)(Expt)	...	...	6800^{c}	...	8500^{c}
q^{diff} ($\theta = 0.5$)(Calc)	2668	5391	7151	8356	8786

[a]Ref[14]. [b]Ref[16]. [c]Ref[17].

TABLE IV

The fraction of free rotation and hindered rotational entropy changes upon adsorption at 297.89 °K

		Methane	Ethane	Propane	i-Butane	n-Butane
exp(−v/RT)		1	0.01668	0.003335	0.002492	0.001692
ΔS_r	Expt.	−0.06^{a}	−1.68^{a}	−2.64^{a}	−3.35^{a}	−4.07^{a}
Cal/mol deg	Calc.	0	−1.681	−2.64	−3.349	−4.07

[a]Ref[14].

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