

COMPARISON OF MEASURED AND CALCULATED HEATS OF ADSORPTION FOR n-HEXANE ON ACTIVE CARBON

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Adsorption isotherms for n-hexane on active carbon "Supersorbon" were measured at 20 and 28°C and the integral heats of adsorption were determined with the use of an isothermal diphenyl ether calorimeter. The characteristic curve is given by the normal Gauss distribution equation (i.e. with vertical shift by a section μ) enabling to express the dependence of the adsorbed amount on pressure in a wider range of pore radii of the porous adsorbent than the equation proposed by Dubinin and Raduškevič. From the former equation, equations are derived for calculation of the isosteric and equilibrium heats which are compared with the measured integral molar heat.

In studying the thermodynamics of adsorption, the knowledge of adsorption heats, which can be measured directly or calculated from other measured adsorption data, is of great importance. Of a number of isothermal heats of adsorption defined by Hill^{1,2} and Everett³, those used most often in practice are the isosteric (q_{st}) and equilibrium (q_{Φ}) heats given by

$$q_{st} = RT^2(\partial \ln P/\partial T)_{n_s, A}, \quad (1)$$

$$q_{\Phi} = RT^2(\partial \ln P/\partial T)_{\Phi}, \quad (2)$$

where T denotes temperature, P equilibrium pressure in gaseous phase, n_s adsorbed amount per mass unit of adsorbent, A surface area of adsorbent and Φ spreading pressure. Neither of these heats is accessible to direct calorimetric measurement, but can be calculated from Eqs (1) and (2) on the basis of measured equilibrium isothermal data. The correctness of the adsorption heats thus calculated can be checked by mutual relations among heats defined in different ways, either calculated or measured directly. The relation between the molar integral heat U_S (directly measurable at constant temperature, volumes of gaseous and adsorbed phases* and at constant surface area of adsorbent) and the isosteric heat is

$$U_S = (1/n_s) \int_0^{n_s} q_{st} dn_s - RT. \quad (3)$$

* This condition is not fulfilled in practice, but the difference between the heat thus defined and the one measured is negligible.

The relation between the equilibrium and integral molar heats is

$$q_{\Phi} = U_S + RT - \Phi/\Gamma, \quad (4)$$

where Γ denotes surface concentration defined as n_S/A . A relation between the isosteric and equilibrium heats can be obtained by combination of Eqs (3) and (4). The spreading pressure (called "second pressure" by Everett) can be calculated from the Gibbs definition equation:

$$\Phi = RT \int_{-\infty}^P \Gamma d \ln P. \quad (5)$$

Another important quantity for the thermodynamic evaluation of adsorption is the change of entropy accompanying the transfer of molecules from the gaseous to the adsorbed phase. According to the heat from which it is calculated it is called either differential (\tilde{S}_S) or molar (S_S) entropy. If the calculated entropies are referred to a reference state, namely a liquid in equilibrium with its saturated vapour at pressure P^0 and temperature T , we obtain

$$S_{L,ref} - \tilde{S}_S = (q_{st} - q_L)/T + R \ln (P/P^0), \quad (6)$$

$$S_{L,ref} - S_S = (q_{\Phi} - q_L)/T + R \ln (P/P^0), \quad (7)$$

where q_L denotes heat of condensation of adsorbate.

The aim of this work was to calculate the mentioned differential heats and entropies from the measured adsorption isotherms and to compare them with the integral heat of adsorption measured directly.

THEORETICAL

For adsorbents with a prevailing portion of micropores, Dubinin and Raduškovič⁴ described mathematically the characteristic curve constructed on the basis of the Polányi potential theory⁵. Their assumption that the characteristic curve is similar to one half of the Gauss distribution curve in the normed form proved very well. The

$$W = W_0 \exp(-k\varepsilon^2) \quad (8)$$

equation applies for all adsorbents with a microporous structure ("first structural type"). For those with a large portion of wide pores ("second structural type"), Dubinin and coworkers⁶ derived an analogous equation of the characteristic curve:

$$W = W'_0 \exp(-m\varepsilon). \quad (9)$$

In both equations W_0 and W'_0 are limiting volumes of the adsorption space, k and m constants, ε adsorption potential and W filled volume of the adsorption space, which can be expressed at sufficiently lower temperatures than the critical as

$$W = n_S v^0, \quad (10)$$

where v^0 denotes molar volume of liquid adsorbate at the temperature of measurement. The adsorption potential is given by

$$\varepsilon = RT \ln (P^0/P), \quad (11)$$

where P denotes equilibrium pressure in gaseous phase and P^0 saturated vapour tension above liquid adsorbate at temperature T . With adsorbent containing besides micropores also transition pores, the characteristic curve is similar to that for adsorbents of the first structural type except for the region of higher filling where it resembles the Gauss curve in the normal form (rather than in the normed form (8)), *i.e.* with vertical shift by a section μ (Fig. 1):

$$W = W_0'' \exp [-k'(\varepsilon - \mu)^2]. \quad (12)$$

Here W_0'' denotes limiting filling of adsorption space for $\varepsilon = \mu$, whereas in Eqs (8) and (9) the W_0 and W_0' values are attained at zero adsorption potential. Eq. (12)

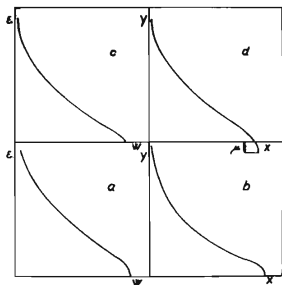


FIG. 1

Comparison of the Gauss Curve with Characteristic Curves

a Characteristic curve for purely microporous adsorbents, *b* Gauss curve in the normed form, *c* characteristic curve for microporous adsorbents with a fraction of transition pores, *d* Gauss curve in the normal form shifted vertically by a section μ . Adsorption potential denoted as ε , filling of the adsorption space as W .

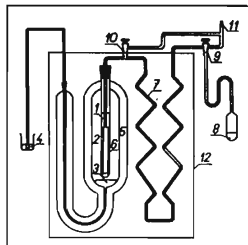


FIG. 2

Diphenyl Ether Calorimeter with Adsorption Apparatus

1 inner tube, 2 diphenyl ether, 3 mercury, 4 reservoir with mercury, 5 evacuated mantle, 6 brass calorimetric vessel with adsorbent, 7 tempering coil, 8 reservoir of adsorbate, 9 vacuum stopcock, 10 ground glass joint to high vacuum pump, 12 water thermostat.

gives for $\varepsilon = 0$: $W = W_0'' \exp(-k'\mu^2)$, but since k' is very small (of the order of 10^{-9}) and μ is not too large we can set $W_0 = W_0''$ within the limits of experimental error. The advantage of Eq. (12) as compared to (8) is that it enables description of the characteristic curve for a microporous adsorbent with transition pores including the region of higher filling of the adsorption space (Fig. 1). This is evidenced by our quantitative results as well as by the detailed analysis of the characteristic curve in the region of higher filling.

From the mentioned analytical expression of the characteristic curve the isosteric heat can be calculated by a method analogous to that of Bering and Serpinskij^{7,8} based on a single measured adsorption isotherm. On introducing rearranged Eqs (10)–(12) into (1) and integrating we obtain

$$q_{st} = \left\{ R \ln \frac{P_2^0}{P_1^0} - \frac{1}{T_2} \left[\left(\frac{1}{k'} \ln \frac{W_0''}{n_S v_2^0} \right)^{1/2} + \mu \right] + \frac{1}{T_1} \left[\left(\frac{1}{k'} \ln \frac{W_0''}{n_S v_1^0} \right)^{1/2} + \mu \right] \right\} / \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (13)$$

where the isosteric heat is assumed to be independent of temperature, indexes 1 and 2 refer to chosen limiting temperatures T_1 and T_2 and the symbols have the same meaning as before. Thus, q_{st} values can be calculated for adsorbed amount n_S ranging from zero to $W_0'' \exp(-k'\mu^2)/v_2^0$ and tabulated as $q_{st} = f(n_S)$. From the condition $(\partial q_{st}/\partial n_S)_T = 0$ and from the second derivative it follows the existence of a single extreme, namely minimum, for

$$n_S = (W_0''/v^0) \exp(-\alpha T/2v^0), \quad (14)$$

where α denotes the coefficient of thermal expansion of liquid adsorbate. The same extreme was derived by Bering, Dubinin and Serpinskij⁸ who started from Eq. (8).

The following method can be proposed for calculation of the equilibrium heat of adsorption q_Φ based on the validity of Eq. (12): First it is necessary to calculate the spreading pressure from Eq. (5). Since we need not know its absolute value, we substitute the adsorbed amount n_S for surface concentration Γ assuming an inert adsorbent (and similarly in Eq. (4)). Introducing Eqs (10)–(12) into (5) we get

$$\Phi = (RT W_0''/v^0) \int_{-\infty}^{\ln P} \exp[-k'(RT \ln(P^0/P) - \mu)^2] d \ln P. \quad (15)$$

By introducing $x = \sqrt{k'}(RT \ln(P^0/P) - \mu)$ we obtain

$$\Phi = (W_0'' \sqrt{k'}/v^0) \int_x^\infty \exp(-x^2) dx, \quad (16)$$

where the Laplace-Gauss integral can be rearranged to obtain the final expression:

$$\Phi = (W_0'' \sqrt{(k')/t^0}) \left[\int_0^\infty \exp(-x^2) dx - \int_0^{x_1} \exp(-x^2) dx \right]. \quad (17)$$

The first integral is equal to $\frac{1}{2} \sqrt{\pi}$ and the second can be calculated if its upper limit x is known. The condition $\Phi_1 = \Phi_2$ (spreading pressures corresponding to temperatures T_1 and T_2), which follows on integrating Eq. (2) within the limits for calculation of the heat q_Φ , leads after rearrangement to the equation

$$\int_0^{x_2} \exp(-x^2) dx = \frac{1}{2} \sqrt{\pi} - (v_2^0/v_1^0) \left[\frac{1}{2} \sqrt{\pi} - \int_0^{x_1} \exp(-x^2) dx \right], \quad (18)$$

where $x_i = \sqrt{(k')(RT_i \ln(P_i^0/P_i) - \mu)}$, $i = 1, 2$. Since the integrals in Eq. (18) cannot be expressed analytically it is necessary to calculate the integral on the right side for selected P_1 values at predetermined limiting temperatures and at corresponding P_1^0 , v_1^0 , P_2^0 and v_2^0 values; afterwards the upper limit x_2 of the integral on the left side is found (e.g. with the use of tables of error function), and from this the pressure P_2 is calculated. The pressure values thus found are introduced into the integrated form of Eq. (2):

$$q_\Phi = R[(\ln P_2 - \ln P_1)/(1/T_1 - 1/T_2)]_\Phi. \quad (19)$$

EXPERIMENTAL

Chemicals and Equipment

The adsorbent was a type Supersorbon active carbon (Hrušov, SŠHR, Czechoslovakia) of particle size 0.4–0.6 mm, from which traces of zinc chloride (activation agent used in its manufacture) were removed by extraction for 4×10 hours with acetic acid.

n-Hexane used as adsorptive was prepared from propyl iodide by reaction with sodium. The distilled and rectified product was of 99.95% purity (determined chromatographically). During filling the apparatus, *n*-hexane was degasified and recondensed through molecular sieve A 3 into the reservoir of adsorbate. It was further condensed several times from the reservoir into the adsorption tube (without adsorbent) and back, always after freezing out with liquid nitrogen and subsequent evacuation.

Adsorption measurements were performed on a gravimetric adsorption apparatus with a quartz spiral balance. Low pressures were measured with a mercury McLeod manometer, and pressures higher than 1.3 Torr with a U-shaped mercury manometer and a cathetometer the reading of which was precise to within ± 0.02 mm.

Integral isothermal heats of adsorption were measured in a diphenyl ether (DPE) isothermal calorimeter. A detailed description of its construction, filling, calibration and handling during measurement of adsorption heats, together with purification of diphenyl ether and comparison with similar devices were published earlier⁹. The adsorption apparatus with the DPE calorimeter are depicted schematically in Fig. 2. The latter consists of an inner tube 1 surrounded with pure

diphenyl ether 2 and evacuated mantle 5. Diphenyl ether is stopped by mercury 3 led through a capillary into vessel 4 in which the volume changes occurring during melting of diphenyl ether are determined by weighing. The adsorption apparatus consists of calorimetric vessel 6 made of brass, filled with adsorbent placed on ten perforated brass discs and allowing a uniform distribution of gaseous adsorbate into all compartments. This vessel is dipped during measurement in paraffin oil within the inner tube of the DPE calorimeter and joined through tempering coil 7 and vacuum stopcock 9 with reservoir 8 of liquid adsorbate. Stopcock 10 and ground glass joint 11 serve for joining the vessel to high vacuum pump. The calorimeter with tempering coil 7 are dipped in water thermostat 12 maintaining the temperature of the melting point of diphenyl ether with a precision to within $\pm 0.001^\circ\text{C}$. The working temperature of the DPE calorimeter is 26.89°C and its heat sensitivity 79.61 J/g of mercury.

Method of Measurement

The adsorbent in both apparatuses was evacuated prior to every measurement at least for four days at 360°C until the final pressure of 10^{-5} Torr was reached. Afterwards the isotherms were measured on the balance apparatus alternatively at 20 and 28°C , always two and two. Portions of the isotherms corresponding to low pressures were measured for several times. In the isothermal DPE calorimeter, the pressure was increased from a very low tension of n-hexane (reservoir 8 was cooled with solid carbon dioxide-ethyl alcohol mixture) after opening stopcock 9 up to a final value given by temperature of the bath surrounding the reservoir of adsorbate 8. The tension was calculated from the Antoine equation for which the constants¹¹ $A = 6.86775$, $B = 1165.74$, $C = 223.64$ were calculated by correlating the data for n-hexane¹⁰. The corresponding adsorbed amount was then read from the adsorption isotherm measured at the melting point of diphenyl ether, *i.e.* at 26.89°C .

RESULTS

All four measured adsorption isotherms are shown in Fig. 3. As typical for adsorbents containing large amount of micropores and adsorbates with a high coefficient of affinity for adsorption¹², β (for n-hexane $\beta = 1.295$ after ref.¹³), the initial portions of the isotherms at low pressures are very steep so that they cannot be measured by any of the sorption methods currently used. For example, for the isotherm at 28°C reproducibility of the initial portion was attained only at pressures higher than 0.01 Torr at which nearly 30% of the limiting amount of adsorbate is already adsorbed. The uncertainty in the measurement of the initial portion of the adsorption isotherm may be due, for example, to low accuracy of the McLeod mercury manometer in the low-pressure range, possible decomposition of n-hexane on the active carbon surface at low pressures, or competitive adsorption of n-hexane and some fluid trace impurities that remained on the adsorbent surface or in the apparatus, *etc.* (Simons¹⁴ derived after analysis of all possible errors of measurement with the McLeod manometer the dependence of the total maximum error on the measured pressure. Thus, for 10^{-3} Torr the expected error is up to 7% with a normal device, and 3% after correction for the change of capillary depression with the position of mercury in the capillary. This error increases strongly with decreasing pressure.)

In spite of various orientation measurements, it could not be decided which of the mentioned causes prevails¹⁵. Therefore it is not possible to calculate from two isotherms by the classical method the isosteric or the equilibrium heats of adsorption. For this reason the characteristic curve calculated from the measured points of all four isotherms in the reproducible region (Fig. 4a) was extrapolated into the region of lower filling of the adsorption space. The validity of this extrapolation can be checked by the relations (3) and (4) between the integral heat directly measured and the heats calculated with the use of the constants of the characteristic curve (12) for the whole interval of the adsorbed amount. The mentioned constants, W_0'' , k' and μ , were calculated by the least squares method; possible instability of the solution due to an ill-conditioned system of equations was suppressed by using an orthogonalization process¹⁶. This and all other calculations were performed on an NE

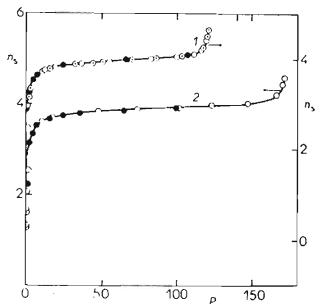


FIG. 3

Adsorption Isotherms of n-Hexane on Active Carbon Supersorbon SSHR

1 20°C, 2 28°C; n_s adsorbed amount in mmol/g, P equilibrium pressure in Torr; ○ first measurement, ● second measurement, ⊕ points calculated from the 28°C isotherm with the use of the potential theory.

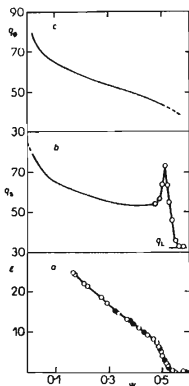


FIG. 4

Dependence of Calculated Thermodynamic Quantities on Volume Filling

a Characteristic curve; ϵ adsorption potential in J/mmol, W volume filling in cm^3/g ; ○ calculated from the 28°C isotherm, ● calculated from the 20°C isotherm. b Dependence of isosteric heat on volume filling; q_s denotes isosteric heat in J/mmol. c Dependence of equilibrium heat on volume filling; q_0 denotes equilibrium heat in J/mmol.

803 B type digital computer. For calculations of isosteric and equilibrium heats and of both entropies according to Eqs (6) and (7) a program in Algol was elaborated enabling their calculation in dependence on the adsorbed amount at arbitrarily chosen temperatures T_1 and T_2 . The Laplace-Gauss integral in Eq. (18) was calculated by the ERF method¹⁷ and the iteration was performed by halving the interval. Differential and molar entropies of adsorbed layer in dependence on adsorbed

amount are shown in Fig. 5 and are referred to pure liquid adsorbate at 24°C as reference state (*i.e.* the average temperature of the chosen interval T_1 293.15 K and T_2 301.15 K).

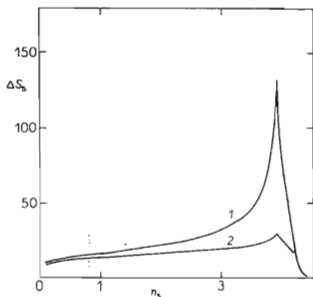


FIG. 5

Dependence of Entropies of Adsorbed Layer on Adsorbed Amount

1 Differential entropy ($S_{L,ref} - \tilde{S}_S$), 2 molar entropy ($S_{L,ref} - S_S$). ΔS_S denotes entropy change in $\text{J mol}^{-1} \text{K}^{-1}$, n_S adsorbed amount in mmol/g .

DISCUSSION

The type SSHR active carbon used in this work belongs after Dubinin classification to the first structural type with prevailing amount of micropores, but contains also transition pores and a small portion of macropores. The limiting volume of the adsorption space calculated from the Dubinin equation for the region below critical temperature¹⁸ $W_0 = 0.518 \text{ cm}^3/\text{g}$. The constants calculated from Eq. (12) for the same system are: $W_0'' = 0.526 \text{ cm}^3/\text{g}$, $k' = 1.733 \cdot 10^{-9} \text{ mol}^2/\text{J}^2$ and $\mu = -1050 \text{ J/mol}$. The difference between W_0 and W_0'' values is, as mentioned above, indeed negligible within the limits of experimental errors in the adsorption measurement. Eq. (12) describes the characteristic curve (Fig. 4a) for ε values up to about 0.8 J/mmol. The last four points lying closely above the W axis are not obtained from Eq. (12) since in this case capillary condensation in the transition pores takes place. That the form of Eq. (12) for the characteristic curve is more suitable than Eq. (8) is obvious from the standard deviation between the measured and calculated adsorbed amount. With the use of Eq. (8) proposed by Dubinin and Raduškovič the mean deviation is 0.66% for 11 points of the 20°C isotherm and 1.01% for 23 points of the 28°C isotherm, whereas with Eq. (12) the corresponding values are 0.60 and 0.92%. The differences are small since they occur only with last points at high filling; other calculated points are practically the same with both equations.

The calculated dependence of the isosteric heat on the degree of filling is plotted in Fig. 4b. The curve was calculated up to $n_s = W_0'' \exp(-k'\mu^2/v_2^0)$ (n_s value for $\varepsilon = 0$) corresponding to the point of sharp maximum. Our method is practically equivalent to that of Bering and coworkers⁸ regarding the amount of labour and the results, but enables calculation of q_{st} up to higher values of filling (where the characteristic curve is still known). Further points in Fig. 4b up to the heat of condensation of n-hexane q_L , as well as the points before the maximum were calculated by the classical method with the use of the integrated Eq. (1) from two measured isotherms (in the respective region the reproducibility of measurement is very good). For the mutual interrelation of heats by Eq. (3), the value of the integral on its right side was determined by graphical integration; an extrapolation was used between the first point of the curve for $n_s = 0.05$ mmol/g and the value $n_s = 0$ (cf. broken line in Fig. 4b). The equilibrium heat q_Φ calculated as indicated in Theoretical is plotted in Fig. 4c. Since it can be calculated also only to the maximum n_s value corresponding to $\varepsilon = 0$, its further course was extrapolated (broken line). The validity of this extrapolation was checked by the known method of calculation of q_Φ from the integrated Eq. (2) after plotting the spreading pressures and graphically evaluating the condition $\Phi_1 = \Phi_2$.

All values of the measured isothermal integral heat for two adsorbed amounts are summarized in Table I. The accord between the results of the individual measurements is an evidence for dependable functioning of our DPE calorimeter. Table II shows all data necessary for mutual comparison of the integral heat directly measured and isosteric and equilibrium heats calculated with the use of Eqs (3) and (4). The percentual deviations referred to experimental data indicate a good agreement, an evidence for the suitability of the potential theory used in the thermodynamic treatment of the system under study. The extrapolation of the characteristic curve towards low filling seems to be also justified in view of the mentioned results. This is evidenced also by the similar course of the calculated isosteric heat (Fig. 4b) and of differential heats measured on analogous systems¹⁹⁻²¹.

Kiselev and coworkers²¹ measured the differential adsorption heats of n-hexane on microporous active carbon with the use of a calorimeter with constant heat exchange. The adsorbed amount was determined on a volume apparatus with a capillary microburette allowing a relatively exact measurement even of small adsorbed amounts. The measured dependences of heats on filling are in good agreement with our results in the whole range of adsorbed amounts. A detailed verification of our method on their published data is not possible since only small diagrams of adsorption isotherms are shown²¹.

Juliš and coworkers¹⁵ measured the heats of wetting for n-hexane on an active carbon of the same type. The results correspond well to the integral molar heat of adsorption measured in the present work. (The heat of wetting of the pure active carbon surface is 28.3 J/mmol + heat of condensation of n-hexane¹⁰ 31.57 J/mmol =

= 59.80 J/mmol representing the total heat at 20°C and at maximum adsorption 4.52 mmol/g.) In a further work, we shall compare the achieved results with direct measurements of the differential heats of adsorption of the mentioned system in a new calorimeter.

CONCLUSIONS

Four adsorption isotherms, two at 20°C and two at 28°C, and the isothermal integral heat of adsorption were measured for n-hexane on active carbon "Supersorbon" in a diphenyl ether calorimeter. The characteristic curve for this system is described by Eq. (12) differing from that used by Dubinin and Raduškevič by a vertical shift μ .

TABLE I
Summary of Measured Integral Isothermal Heats of Adsorption

n_S mmol/g	$(U_S)_t^a$ J	U_S^b J	U_S J/mmol	\bar{U}_S J/mmol	δ_{\max}^c %
3.98	621.45	225.98	56.78	56.97	0.33
	625.72	227.48	57.16		
4.03	625.01	227.23	56.38	56.50	0.21
	625.97	227.61	56.48		
	627.35	228.10	56.60		

^a Total heat measured in calorimeter; ^b total heat referred to 1 g of adsorbent; ^c $\delta_{\max} = |U_S - \bar{U}_S| \times 100/\bar{U}_S$.

TABLE II
Comparison of Calculated and Measured Heats of Adsorption

n_S mmol/g	y^a J mmol ⁻¹	U_S Eq. (3) J mmol ⁻¹	U_S exp J mmol ⁻¹	δU_S^b %	Φ^c J g ⁻¹	q_Φ Eq. (19) J mmol ⁻¹	q_Φ Eq. (4) J mmol ⁻¹	δq_Φ^d %
3.98	60.28	57.78	56.97	1.42	74.15	41.55	40.84	1.74
4.03	60.25	57.75	56.50	2.21	76.50	40.95	40.02	2.32

^a $y = (1/n_S) \int_0^{n_S} q_{st} dn_S$ determined by graphical integration; ^b error in percent of experimental value; ^c read from plot of Φ against n_S ; ^d deviation between calculated q_Φ values.

This equation can be used with advantage for description of a system with a microporous adsorbent containing also a portion of transition pores. From Eq. (12) was derived Eq. (13) for calculation of the isosteric heat, and a method of calculation of the spreading pressure, Eq. (17), and equilibrium heat, Eqs (18) and (19), to which purpose a single measured isotherm is sufficient. Both heats as well as the differential and molar entropies can be rapidly calculated on a computer and compared on the basis of Eqs (3) and (4) with the integral heat measured directly. The agreement shown in Table II is very good.

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