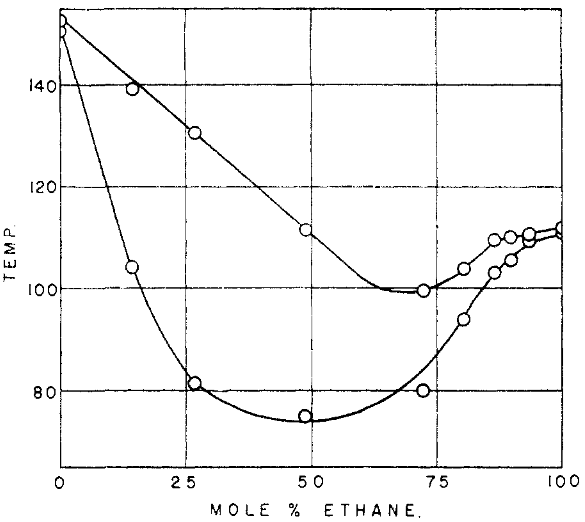

Fig. 3.—Phase diagram for 1,2-di-(γ-pyridyl)-ethane and -ethylene.

cc. of carbon tetrachloride was refluxed for 2 hours with 1.8 g. of N-bromosuccinimide and 0.1 g. of benzoyl peroxide. The filtered hot solution, from which crystals separated spontaneously upon cooling, was brought to dryness. The residue, recrystallized from *s*-butanol, formed silky needles of m.p. 265° (dec.). It was the monohydrobromide of 1,2-di-(γ-pyridyl)-ethylene.

Anal. Calcd. for $C_{12}H_{11}N_2Br$: Br, 30.4. Found: Br, 30.2 (potentiometric titration).

The hydrobromide was triturated at room temperature with an excess of aqueous ammonia and the insoluble product filtered and recrystallized from water. M.p. and mixed m.p. with an authentic sample of 1,2-di-(γ-pyridyl)-ethylene, 155°.

1,2-Di-(γ-pyridyl)-ethane and Chloranil.—A solution was prepared of 0.56 g. (2.46 mmoles) of chloranil in 18 g. of hot benzene and 0.42 g. (2.46 mmoles) of the ethane in 7 g. of hot benzene was added. Immediately, a brown-violet precipitate separated. After 2 hr. at room temperature, it was filtered, washed with benzene and dried; yield 1.0 g. The substance has no defined melting point; it decomposes gradually above 250°. The product peptizes in water; that the solution was colloidal was shown by the fact that addition of sodium or silver nitrate caused coagulation. This precipitate redispersed on washing to remove electrolyte. A water dispersion of the product was filtered and the filtrate was extracted with ether. The filtrate gave glistening black crystals on evaporation under the aspirator at 50°. Parr bomb analysis gave 30.0% chlorine, *vs.* 32.97% calculated for $C_{18}H_{12}O_2N_2Cl_4$, the molecular addition compound. On rewashing the product with ether, the chlorine fell to 28.6%. A second preparation was made as above, but with omission of the ether wash; black crystals, yield 100%. These were dried over calcium chloride and analyzed.

Anal. Calcd. for $C_{18}H_{12}O_2N_2Cl_4$: Cl, 32.97. Found: Cl, 32.1, 32.2.

Melting Point Diagram.—A sample of the pure ethylene obtained by the bromosuccinimide reaction was used as the standard for analysis of mixtures of ethane and ethylene by the absorption at 299 mμ of solutions in 95% ethanol. Beer's law was found to be valid. Assuming zero absorption at 299 mμ for the ethane, our best sample analyzed to 93.5%. Mixtures of this material with the pure ethylene were made, and melted. Both first liquefaction and final melting points were recorded. The samples were then cooled and remelted; the difference between initial and final values narrowed somewhat, due to the more intimate mixing in the melt. The remelt data are shown in Fig. 3; no eutectic point appears, and the two bases obviously form a continuous series of solid solutions. The point at 100% ethane is Thayer and Corson's value for their ethane prepared by catalytic hydrogenation of the ethylene.

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The Sorption of Vapors by Monolayers. V. The Differential Heats of Adsorption of *n*-Hexane on Stearic Acid Monolayers[1]

By Robert B. Dean[2] and Kenneth E. Hayes

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Adsorption of *n*-hexane on stearic acid monolayers has been calculated from measurements of surface pressure at 20°. Differential heats of sorption at 25° have been calculated from these data and data previously reported at 30°. On close packed monolayers the heat of sorption rises with increasing amounts of hexane sorbed reaching the heat of vaporization of hexane when the mole ratio of hexane to stearic acid is 0.5. On dilute stearic acid monolayers the initial heat of sorption is high but falls rapidly and, after passing through a minimum rises to approach the heat of vaporization when the surface is covered by a monolayer of hexane. On a clean water surface the heat of sorption is not significantly different from the heat of vaporization of *n*-hexane.

Very few measurements of adsorption have been made on plane surfaces where the area is known exactly and there are even fewer calculations of the heats of adsorption. Direct measurement of the quantity adsorbed is difficult because adsorption rarely exceeds 10 gibbs (10 × 10^{-10} mole/cm.^{2},[3]). The amount of a solute or vapor adsorbed on a liquid surface can be calculated from the changes in surface tension with concentration by means of the Gibbs equation. The calculation is straightforward for two component systems and Koenig[4] has recently shown how to calculate adsorption from surface tension data in multicomponent systems.

We have recently[5] calculated the adsorption of *n*-hexane on monolayers of stearic acid at 30°. This paper presents data on the same system at 20° together with heats of adsorption at 25° derived from the amounts adsorbed at 20 and 30°.

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(2) Chemical Division, The Borden Co., Bainbridge, N. Y.

(3) R. B. Dean, *J. Phys. Colloid Chem.*, **55**, 611 (1951).

(4) F. O. Koenig, "Calculation of Surface Concentrations from Surface Tension Data," Academic Press, Inc., New York, N. Y., in press.

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Experimental

The apparatus, technique and materials used in this work are identical with those used previously.[5,6] It was not possible to determine equilibrium spreading pressures by spreading from crystals of stearic acid at 20° since the rate of spreading is extremely low at this temperature. At 30° we found that the equilibrium spreading pressure of stearic acid at any vapor pressure of *n*-hexane lay on the intersection of the π–Γ_2 curve with the π–Γ_2 curve obtained in the absence of a vapor. (π is the surface pressure and Γ_2 the surface concentration of stearic acid.) The spreading pressure in the absence of hexane vapor is known at 20° by extrapolation of the data of Carey and Rideal.[7]

When the calculated equilibrium surface concentration of stearic acid was left in contact with a crystal of stearic acid under hexane vapor at 20° the calculated equilibrium surface pressure was observed unchanged for a period of two hours. We have therefore assumed that the equilibrium spreading pressure of stearic acid under *n*-hexane follows the same law at 20° as at 30°.

The calculation of the amount of hexane adsorbed, according to Koenig[4] involves evaluating the two terms inside the brackets of equation 1.

$$\Gamma_1 = \frac{P}{RT}\left[\left(\frac{\partial \pi}{\partial P}\right)_{\Gamma_2} - \Gamma_2\left(\frac{\partial \mu_2}{\partial P}\right)_{\Gamma_2}\right] \qquad (1)$$

Γ^1 is the surface excess of hexane, P is the partial pressure of hexane, and the other terms have their usual thermodynamic significance. The first term is readily available from the experimental data. To evaluate the second term we determine $\mu_2{}^\circ - \mu_2$ at various partial pressures taking the equilibrium spreading concentration as the standard state for $\mu_2{}^\circ$. From a plot of μ_2 *vs.* P it is then possible to get $(\partial\mu_2/\partial p)_{\Gamma_2}$.[5]

The second term is of course zero at Γ_2 0 where we have the simple case of sorption on a clean water surface. At $\Gamma_2 = 8$ gibbs the monolayer of stearic acid is so close to its standard state (the equilibrium spreading concentration) that $(\partial\mu_2/\partial P)_{\Gamma_2}$ is sensibly zero. On dilute monolayers of stearic acid we find that the second term adds about 20% to the calculated value of Γ_1.

Table I gives values of Γ_1 at Γ_2 0, 1, 1.5 and 8 gibbs at both 20 and 30°. The isotherms are similar in shape at both temperatures.

TABLE I

ISOTHERMS OF *n*-HEXANE Γ_1 IN GIBBS ON STEARIC ACID AT VARIOUS VALUES OF Γ_2 SURFACE CONCENTRATION OF STEARIC ACID

	$\Gamma_2 = 0$		$\Gamma_2 = 1$		$\Gamma_2 = 1.5$		$\Gamma_2 = 8$	
P	20°	30°	20°	30°	20°	30°	20°	30°
0.0	0	0	0	0	0	0	0	0
.1	.05	.07	.34	.13	.40	.21	.24	.36
.2	.15	.18	.72	.48	.84	.62	.63	.73
.3	.34	.38	1.17	.93	1.34	1.30	1.16	1.32
.4	.66	.70	1.74	1.58	1.96	2.16	2.06	2.11
.5	1.16	1.22	2.47	2.54	2.72	3.21	3.21	3.00
.6	1.88	1.95	3.38	2.66	3.67	4.42	4.70	4.23
.7	2.87	2.94	4.52	5.19	4.66	5.79	6.69	6.12
.8	4.18	4.24	5.94	6.69	6.25	7.29	7.43	7.88
.9	5.85	5.90	7.66	8.07	7.95	8.78	(7.20)	8.06

On water and on dilute films of stearic acid *n*-hexane is adsorbed along a type III isotherm to values in excess of a monolayer. Similar results have been obtained at lower temperatures by Jones.[8] On close packed stearic acid monolayers the isotherm is type V and stops sharply at a surface concentration corresponding to a tilted monolayer at 20°. We have not been able to calculate Γ_1 in transition regions where $(\partial\pi/\partial\Gamma_2)_P$ is zero over a range of values of Γ_2. It is probable that Γ_1 is very nearly a linear function of Γ_2 in the transition region. If so Γ_1 could be obtained by interpolation between known values at the ends of this region. However, when $(\partial\pi/\partial\Gamma_2)_P$ is small, as it is at values of Γ_2 immediately above the transition region, the error in the calculation of Γ_1 becomes large.

The differential heat of adsorption, q, of a vapor on a surface can be calculated from the well known equation

$$q = (\ln P_1/P_2)(RT_1T_2/T_2 - T_1)$$

from values of P_1 and P_2, the absolute pressures of hexane at corresponding states of the surface. Corresponding states must be at the same values of Γ_1, and Γ_2 but it is also necessary that they be in the same surface phase. Figure 1 shows that several surface phases exist between $\Gamma_2 = 1.5$ and $\Gamma_2 = 8$ gibbs and it is not obvious without data at intermediate temperatures that points at corresponding values of Γ_1 and Γ_2 are in the same surface phase. Since the sorption data themselves are subject to greater error in and near the transition region we have not attempted to calculate heats of sorption in this range. Figure 2 presents values for the heat of sorption of *n*-hexane on stearic acid monolayers at Γ_2 0, 1.0, 1.5 and 8.0 gibbs as a function of the amount of hexane adsorbed.

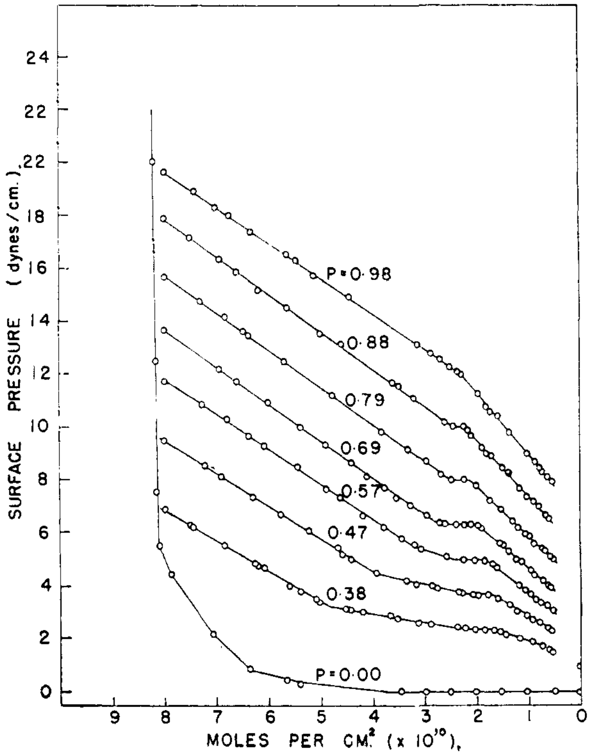

Fig. 1.—Surface pressure–surface concentration relationship for stearic acid monolayers under *n*-hexane vapor at 20°.

The horizontal dashed line represents the heat of vaporization of *n*-hexane at 25°. The error in the heat data has been calculated by assuming maximal errors of Γ_1 from the known precision in Γ_1 and P in such a direction as to produce the maximum change in q. At all except the two lowest values of Γ_2 the errors in q are less than 0.8 kcal. per mole. We are confident that reported values of q which fall outside the range 6.5 to 8.5 kcal. per mole represents heats of sorption which are significantly different from the heat of vaporization.

Discussion

On clean water surfaces the heat of sorption is not significantly different from the heat of vaporization over the whole range of sorption. This is somewhat unexpected since water might be expected to exert stronger van der Waals forces on hexane than hexane molecules exert on each other. However, the shape of the isotherm on clean water indicates clearly that the sorption is a coöperative phenom-

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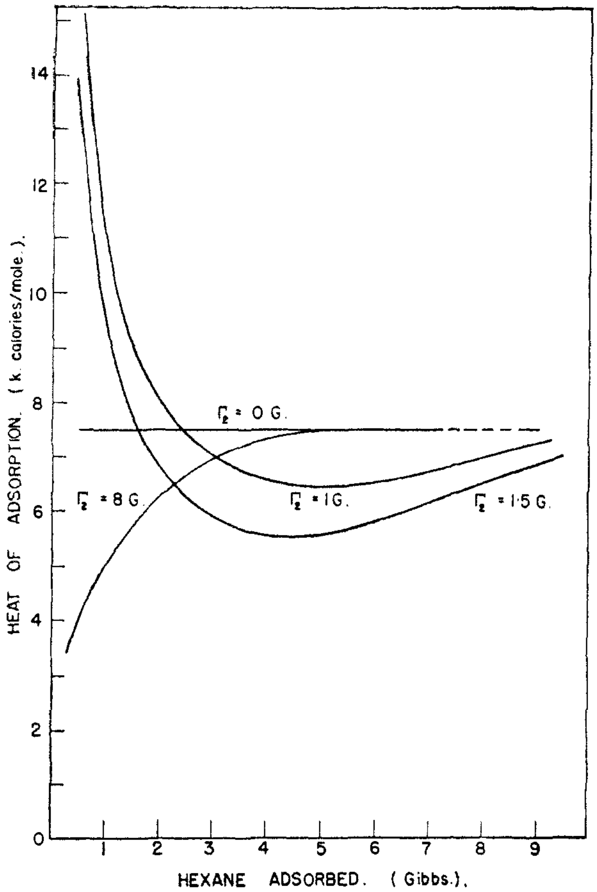

Fig. 2.—The heats of adsorption of *n*-hexane on monolayers of stearic acid at various values of the surface concentration of stearic acid, Γ_2.

enon and when there is as much as 0.5 gibbs of hexane on the surface these molecules have associated together into clusters which present an environment not significantly different from the surface of pure hexane.

There is a large heat effect when small quantities of hexane are adsorbed by expanded films of stearic acid. At 1.0 gibbs the stearic acid molecules are associated in crystal-like clusters or micelles which occupy about one-eighth of the total surface in equilibrium with a very dilute vapor. Adsorbed hexane dissolves these clusters until they interact with each other and form a duplex film. The heat of sorption should therefore start at a value close to that of the heat of solution of stearic acid in hexane plus the heat of vaporization of hexane. Values for the heat of solution of stearic acid in *n*-hexane are not available but should not differ greatly from the heat of fusion of stearic acid, 13.5 cal. per mole.[9] The minimum in the heat of sorption on stearic acid at 1.0 and at 1.5 gibbs is significant if our evaluation of the second term in equation 1 is correct. We have no explanation for this minimum at present.

The type V isotherms obtained on monolayers of stearic acid free from macroscopic pores together with heats of sorption greater than the heat of vaporization on dilute monolayers are inconsistent with the basic hypothesis of the B.E.T. theory.[10] We have not been able to fit our data to isotherms predicted by this theory.

On condensed films of stearic acid the hexane molecules are adsorbed on top of a surface of close packed methyl groups. The heat of sorption is less than the heat of vaporization. As hexane builds up a liquid layer on the surface the heat of sorption approaches the heat of vaporization of hexane. Sorption is coöperative but is limited sharply at a value which corresponds to a monolayer of *n*-hexane molecules standing nearly vertical. This is in partial agreement with the prediction of Halsey[11] that coöperative sorption on a uniform surface will produce stepped isotherms as successive layers are filled. Data to be presented on the isomeric hexanes[12] give additional support to this hypothesis.

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(9) "International Critical Tables," Vol. 5, p. 134.

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