

369. *The Surface Tension of Mercury and the Adsorption of Water Vapour and some Saturated Hydrocarbons on Mercury.*

By N. K. ROBERTS.

The surface tension of mercury has been found, by use of the sessile-drop method, to be (within 0.2%)

$$485.4 \text{ dynes cm.}^{-1} \text{ at } 25^\circ \text{ and } 487.3 \text{ dynes cm.}^{-1} \text{ at } 16.5^\circ.$$

The anomalous results obtained in the past for the adsorption of water vapour on mercury are examined.

The saturated aliphatic hydrocarbons n-pentane, n-hexane, n-heptane, n-octane, 2,2,4-trimethylpentane, and neopentane have been adsorbed on mercury. Adsorption isotherms have been determined at 16.5 and 25° and the results analysed on the basis of the Volmer and virial surface equations of state. From these two viewpoints, the hydrocarbon molecules appear to be curled up on the surface with their electron envelopes greatly distorted. For the symmetrical, incompressible hydrocarbon neopentane, the Volmer co-area is identical with the geometrical cross-section of the adsorbate molecule.

A comparison with the adsorption of some of these hydrocarbons on water reveals that the initial thickness of the surface layer on both media is almost the same.

SURFACE-TENSION measurements are frequently used to follow the course of adsorption on liquid surfaces, and a considerable amount of work has been reported on the adsorption of vapours on mercury, but only in very few instances has mercury of the correct surface tension been used. It was thought worthwhile to redetermine the surface tension of mercury and to study the adsorption of the saturated hydrocarbons, for comparison with the results obtained by Jones and Ottewill¹ for adsorption on a water surface.

EXPERIMENTAL

Apparatus.—The apparatus used was similar to Kemball's² modification of Burdon's³ apparatus. The measuring vessel was constructed from the central sections of factory lengths of glass tubing. It was found that the usual recommended "cleaning methods" did not alter the surface tension obtained in the "uncleaned" vessel. Therefore, it would appear that the elaborate cleaning procedures adopted previously are unnecessary.

Both the equator and vertex of the sessile drop were located by the method of Kemball² and Burdon.³

Materials.—Mercury was purified by the method of Kemball² and was cyclically distilled in the measuring vessel until the surface tension reached a steady value.

n-Hexane, n-heptane, and 2,2,4-trimethylpentane were supplied by the Industrial Chemistry Division, C.S.I.R.O., Victoria; the purity was stated to be not less than 99.8 mole per cent. n-Pentane was a Phillips product of purity 99 mole per cent. Synthetic n-octane (B.D.H.) was purified according to the method of Jones and Ottewill;¹ it then had $n_D^{20} = 1.3974$ [n_D^{20} (N.B.S.) = 1.39743]. Neopentane was a National Chemical Laboratory product of purity 99.8 mole per cent.

Vapour Pressures.—The vapour pressures of the hydrocarbons pentane, hexane, heptane, and octane were calculated from the temperature of the vapour source, using data given in the International Critical Tables. The results of Stull⁴ were used to calculate the vapour pressure of iso-octane. The vapour pressure of neopentane was measured directly with a manometer.

¹ Jones and Ottewill, *J.*, 1955, 4076.

² Kemball, *Trans. Faraday Soc.*, 1946, **42**, 526.

³ Burdon, *Trans. Faraday Soc.*, 1932, **28**, 866.

⁴ Stull, *Ind. Eng. Chem.*, 1947, **39**, 517.

RESULTS AND DISCUSSION

Surface Tension.—The surface tension of mercury was calculated from Ziesing's⁵ corrected version of Worthington's⁶ equation, using the value of 980.45 cm. sec.⁻² for the gravitational constant (determined by the staff of the Geology Department of this University). Measurements extended over a period of 12 months and the mean values were 487.3 ± 1.0 and 485.4 ± 1.2 dynes cm.⁻¹ at 16.5 and 25.0°, respectively. The deviations of 1.0 and 1.2 dynes cm.⁻¹ include the mean deviation of the measurements and the uncertainties involved in the radius of the pool, the level over which the cathotometer was moved, and the setting of the lamp used to define the equator of the pool.

Table 1 summarises the most recent determinations; the results of Kemball have been corrected for the error in the Worthington equation.

TABLE I.

Recent values for the surface tension of mercury at 25°.

Ref.	Method	Nature of apparatus	Surface tension at 25° (dynes cm. ⁻¹)
2	Sessile drop	Borosilicate glass	485.1 ± 1.5
5	Sessile drop	Silica	484.9 ± 1.8
7	Maximum pressure in a drop	Glass, type not stated	484.4 ± 0.8
			485.8 ± 0.8
Present work	Sessile drop	Borosilicate glass	485.4 ± 1.2

Adsorption of Water Vapour.—The adsorption of water vapour on mercury has been studied by three groups of workers who used mercury of the correct surface tension. The

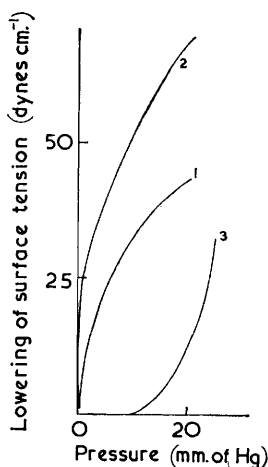


FIG. 1. Adsorption of water vapour on mercury.

1, Kemball.⁸⁻¹¹ 2, Karpartchev *et al.*¹²
3, Bering and Ioileva.¹³

adsorption isotherms obtained by Kemball,⁸⁻¹¹ Karpartchev, Smirnov, and Vorlchenkova,¹² and Bering and Ioileva¹³ are shown in Fig. 1. Both Kemball and Karpartchev *et al.* used the "sessile drop" method, and Bering and Ioileva used the "maximum pressure in a drop" method. Bering and Ioileva claimed that only their results corresponded to

⁵ Ziesing, *Austral. J. Phys.*, 1953, **6**, 86.

⁶ Worthington, *Phil. Mag.*, 1885, **20**, 51.

⁷ Bering and Ioileva, *Proc. Acad. Sci. (U.S.S.R.)*, 1953, **93**, 85.

⁸ Kemball and Rideal, *Proc. Roy. Soc.*, 1946, *A*, **187**, 53.

⁹ Kemball, *Proc. Roy. Soc.*, 1946, *A*, **187**, 73.

¹⁰ Kemball, *Proc. Roy. Soc.*, 1947, *A*, **190**, 117.

¹¹ Kemball, *Proc. Roy. Soc.*, 1950, *A*, **201**, 377.

¹² Karpartchev, Smirnov, and Vorlchenkova, *Russ. J. Phys. Chem.*, 1953, **27**, 1228.

¹³ Bering and Ioileva, *Bull. Acad. Sci. (U.S.S.R.)*, 1955, **9**.

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TABLE 3.

The lowering of surface tension of mercury at various relative pressures of hydrocarbon at $16.5 \pm 0.2^\circ$ ($\gamma_0 = 487.3 \pm 1.0$ dynes cm.⁻¹).

n-Pentane ($p = 366.5$ mm. Hg)			n-Hexane ($p = 102.6$ mm. Hg)			n-Heptane ($p = 31.05$ mm. Hg)			n-Octane ($p = 8.43$ mm. Hg)			2,2,4-Trimethylpentane ($p = 32.5$ mm. Hg)					
Temp. (°K)	$10^2(p'/p)$	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)	Temp. (°K)	$10(p'/p)$	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)	Temp. (°K)	$10^2(p'/p)$	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)	Temp. (°K)	$10^2(p'/p)$	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)	Temp. (°K)	$10^2(p'/p)$	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)	Temp. (°K)	$10^2(p'/p)$	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)
203.2	0.753	14.1	238.5	8.43	36.3	266.7	36.7	52.0	215.3	1.88	21.6	244.2	11.6	38.5	272.7	48.4	58.3
225.0	3.68	28.5	251.8	17.6	43.0	230.8	5.29	31.7	228.5	1.46	31.1	253.8	10.8	49.7	289.6	100.0	81.2
230.8	5.29	31.7	258.8	25.3	48.1	223.5	1.46	29.5	226.4	0.662	23.9	258.7	11.9	47.2	287.9	90.0	72.9
199.8	0.157	12.1	245.5	7.92	45.0	208.6	0.238	17.0	218.5	0.634	24.6	253.3	10.7	47.8	282.8	72.9	73.0
217.0	0.839	23.6	255.6	15.5	50.7	210.6	0.287	17.7	218.5	0.634	24.6	253.3	10.7	47.8	289.6	100.0	80.9
223.5	1.46	29.5	264.1	26.3	56.0	210.6	0.287	17.7	218.5	0.634	24.6	253.3	10.7	47.8	289.6	100.0	80.9
236.5	4.11	37.5	276.5	53.6	66.4	210.6	0.287	17.7	218.5	0.634	24.6	253.3	10.7	47.8	289.6	100.0	80.9
194.7	0.0522	7.5	235.9	2.92	36.6	208.6	0.238	17.0	218.5	0.634	24.6	253.3	10.7	47.8	289.6	100.0	80.9
208.6	0.238	17.0	238.7	3.32	37.9	210.6	0.287	17.7	218.5	0.634	24.6	253.3	10.7	47.8	289.6	100.0	80.9
210.6	0.287	17.7	245.0	5.93	43.7	210.6	0.287	17.7	218.5	0.634	24.6	253.3	10.7	47.8	289.6	100.0	80.9
218.5	0.634	24.6	253.3	10.7	47.8	218.5	0.634	24.6	218.5	0.634	24.6	253.3	10.7	47.8	289.6	100.0	80.9
228.5	1.46	31.1	253.8	10.8	49.7	228.5	1.46	31.1	228.5	1.46	31.1	253.8	10.8	49.7	289.6	100.0	81.2
195.6	0.0209	4.9	232.9	1.27	29.1	205.5	0.0622	9.5	214.7	0.186	15.0	250.4	6.09	43.0	269.5	26.5	55.4
205.5	0.0622	9.5	242.8	3.14	35.9	214.7	0.186	15.0	226.4	0.662	23.9	258.7	11.9	47.2	281.7	60.4	66.1
214.7	0.186	15.0	250.4	6.09	43.0	226.4	0.662	23.9	226.4	0.662	23.9	258.7	11.9	47.2	287.9	90.0	72.9
226.4	0.662	23.9	258.7	11.9	47.2	197.6	0.0621	9.3	206.1	0.174	14.1	252.1	9.87	48.2	278.5	54.2	67.9
197.6	0.0621	9.3	244.9	5.88	42.8	206.1	0.174	14.1	213.6	0.378	20.1	258.8	15.8	52.3	280.9	61.8	68.5
206.1	0.174	14.1	252.1	9.87	48.2	213.6	0.378	20.1	225.5	1.17	30.1	266.6	26.5	58.8	284.4	75.7	74.8
213.6	0.378	20.1	258.8	15.8	52.3	225.5	1.17	30.1	231.6	2.01	33.8	273.1	39.3	61.7	289.6	100.0	80.1
225.5	1.17	30.1	266.6	26.5	58.8	231.6	2.01	33.8	233.3	2.34	35.2	275.7	46.2	63.8	289.6	100.0	80.1
231.6	2.01	33.8	273.1	39.3	61.7	233.3	2.34	35.2									
233.3	2.34	35.2	275.7	46.2	63.8												

TABLE 4.

The lowering of surface tension of mercury at various pressures of neopentane at $20 \pm 0.2^\circ$ ($\gamma_0 = 484.8 \pm 1.1$ dynes cm.⁻¹).

p' cms. Hg	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)	p' cms. Hg	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)	p' cms. Hg	$\gamma_0 - \gamma$ (dynes cm. ⁻¹)
5.0	26.6	12.0	34.5	25.5	42.8
9.4	32.5	19.1	37.9	27.7	44.8

was found that, at 16.5° and at vapour pressures ≤ 2 mm. of mercury, the surface pressures were identical with those measured by Karpartchev *et al.*

The reason for the different results obtained by Kemball and by Bering and Ioileva is not obvious; however it appears that the explanations advanced by the latter workers are untenable.

Adsorption of some Saturated Hydrocarbons.—The lowering of surface tension (the surface pressure) at various relative pressures (p'/p) of the hydrocarbons (except neopentane) at 25 and 16.5° , is shown in Tables 2 and 3, respectively. Table 4 shows the results for neopentane at 20° . ($p =$ saturation vapour pressure. $\gamma_0 =$ initial surface tension. $\gamma =$ surface tension at pressure p' . $\Pi = \gamma_0 - \gamma =$ surface pressure.)

All adsorption isotherms were reversible, and the surface tension was restored to its initial value by the application of liquid nitrogen to the vapour-source.

All the hydrocarbons give rise to almost identical surface pressures at the same relative pressure. Pentane is the only hydrocarbon to show a significant variation but, at high relative pressures, its behaviour approaches that of the other hydrocarbons. Cutting and

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Jones¹⁴ and Jones and Ottewill¹ studied the adsorption of the same hydrocarbons on water, and found that as the hydrocarbon series is ascended, the decrease in vapour pressure is not matched by an equivalent increase in the intensity of adsorption, as it is on mercury, and consequently, at the same relative pressure, the order of intensity of adsorption is pentane > hexane > iso-octane > heptane > octane.

The isotherm for heptane may be compared with those obtained by Kemball⁸ and by Bering and Ioileva.¹⁵ The surface pressures obtained in the present investigation are almost exactly 4 dynes cm.⁻¹ higher at comparable vapour pressures. However, as mentioned previously, Kemball's value for the surface tension of mercury should be increased by 1.1 dynes cm.⁻¹ owing to the error in the Worthington equation. Also, it is not clear why Bering and Ioileva¹⁵ chose the lower of the two values for the surface tension of mercury which they reported two years previously in an account of their experimental procedure.⁷ However, the results obtained for n-heptane in this work fit in naturally with those for the other hydrocarbons.

The Adsorbed Layer as a Real Two-dimensional Gas.—All the adsorption isotherms are convex to the surface-pressure axis, indicating a predominance of repulsive forces between the adsorbed molecules,¹⁶ and the Volmer equation¹⁷ fits the experimental results:

$$\Pi (A - b) = \kappa T,$$

where A is the area occupied by a molecule, b is a constant, termed the co-area, and κ is the Boltzmann constant. A combination of the Volmer equation and the Gibbs adsorption isotherm yields the co-area for the various hydrocarbons. The co-area in the Volmer equation can be identified with the geometrical cross-section of the adsorbed molecule, by considering the adsorption of the symmetrical, rigid neopentane molecule. Its density¹⁸ at 20° is 0.5904 g./cm.³, which corresponds to a molecular volume of 202.8 Å³ or a cross-section of (202.8)^{2/3} Å², *i.e.*, 34.5 Å². This value agrees remarkably well with the corresponding co-area, 34.7 Å² (Table 5).

TABLE 5.

Standard thermodynamic quantities for the adsorption of some hydrocarbons on mercury and on water, and co-areas for their adsorption on mercury.

	Temp.	$-\Delta F$	$-\Delta H$		$-\Delta S$		Co-area (Å ²)	$-\Delta H$
		(cal. mole ⁻¹)	Mercury	Water	(cal. mole ⁻¹ deg. ⁻¹)	Mercury		(kcal. mole ⁻¹) Condensation
n-Pentane	16.5°	6946	10.3	5.1	11.8	8.7	28.8	6.46
	25.0	6844					29.1	
n-Hexane	16.5	8344	12.1	6.0	13.2	10.2	31.7	7.69
	25.0	8232					32.2	
n-Heptane	16.5	9257	13.0	6.6	13.1	11.0	33.7	8.90
	25.0	9139					34.2	
n-Octane	16.5	10,080	13.6	7.3	12.2	9.5	35.7	10.07
	25.0	9963					35.9	
2,2,4-Trimethyl- pentane	16.5	9226	13.0	6.2	13.1	8.7	34.6	8.53
	25.0	9113					35.1	
Neopentane	20.0	—	—	—	—	—	34.7	—

The thickness of the surface layers on mercury can now be determined by dividing the molecular volume by the co-area. These values may be compared with those obtained by Ward¹⁹ for a water surface, on the basis of energy considerations (Table 6).

¹⁴ Cutting and Jones, *J.*, 1955, 4067.

¹⁵ Bering and Ioileva, *Bull. Acad. Sci. (U.S.S.R.)*, 1955, 193.

¹⁶ Adam, "The Physics and Chemistry of Surfaces," 3rd edn., Oxford University Press, London, 1941.

¹⁷ Volmer, *Z. phys. Chem.*, 1925, **115**, 253.

¹⁸ Ross, "Physical Constants of the Principal Hydrocarbons," 4th edn., Texas Company, New York City, 1943.

¹⁹ Ward, *Trans. Faraday Soc.*, 1946, **42**, 399.

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TABLE 6.

Comparison of the thickness of the surface layers of some hydrocarbons on mercury with those on water.

	Molecular volume at 20° (Å ³)	Thickness of surface layers (Å)			Molecular volume at 20° (Å ³)	Thickness of surface layers (Å)	
		Mercury *	Water ¹⁹			Mercury *	Water ¹⁹
n-Pentane	193	6.7	7.0	n-Octane	268	7.5	7.7
n-Hexane	219	6.9	7.4	2,2,4-Trimethyl- pentane	272	7.8	—
n-Heptane ...	246	7.3	7.6	Neopentane	203	5.9	—

* Present study.

There is quite close agreement between the thickness of the surface layers on the two media. Also, it is clear from the areas that they occupy that adsorbed molecules are curled up on the mercury surface. Thus, the area occupied by a CH₂ group is approximately 7 Å², which, in the case of n-octane, leads to a value of 56 Å² for the area occupied by the fully extended form; however, the co-area is only 36.3 Å² at 25°.

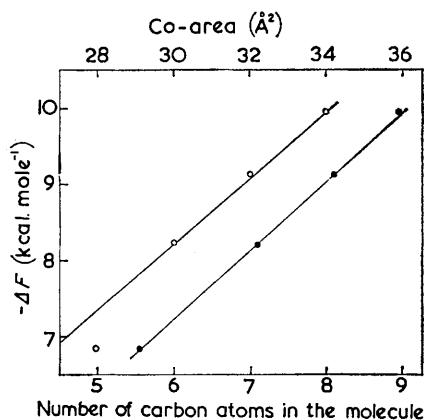


FIG. 2. Variation of the free energy of adsorption with the co-area and the number of carbon atoms per molecule.

● Molecular co-area. ○ Number of carbon atoms in the molecule.

The standard thermodynamic quantities for the adsorption process, together with the co-areas, are shown in Table 5. Kemball's approach was used to calculate the thermodynamic quantities for adsorption on mercury but, instead of assuming, as he did, a standard arbitrary surface-layer thickness of 6 Å, the actual thickness of the surface layer was used. The free-energy changes are reliable to within 10 cal. mole⁻¹, total energies to within 0.5 kcal. mole⁻¹, entropies to within 1.5 cal. mole⁻¹ deg.⁻¹, and the co-areas to within 0.3 Å².

It is interesting to note that there is a linear relationship between the co-area and the standard free energy of adsorption, whereas a plot of free energy against the number of carbon atoms is not strictly linear (Fig. 2). The mean increase in ΔF per carbon atom is 1 kcal. mole⁻¹, the corresponding increase for a water surface being ca. 420 cal. mole⁻¹. The variation of the standard free energy of adsorption on a water surface with the number of carbon atoms in a molecule of a homologous series is summarised in Traube's rule.²⁰ Langmuir²¹ interpreted Traube's rule to mean that initially each CH₂ group occupies a similar position on the surface, or, in other words, the hydrocarbon molecule is lying stretched out on the surface. Ward¹⁹ has pointed out that Langmuir's interpretation is unreasonable because it involves the implicit assumption that the molecules are stretched out in the bulk phase, which is unlikely for the following reason. The shape of the hydrocarbon molecule is determined by two factors, entropy and surface energy. When surface energies are without influence, as for a hydrocarbon surrounded

²⁰ Traube, *Annalen*, 1891, **265**, 27.

²¹ Langmuir, *J. Amer. Chem. Soc.*, 1917, **39**, 1883.

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by like molecules, the shape is determined solely by configurational probability. Treloar²² has calculated that the "most probable" shape is an approximate spheroid, intermediate between the extreme shapes of "fully stretched-out" and "rolled up into a sphere," with the minimum surface energy. Ward¹⁹ has deduced, from energy considerations, that a hydrocarbon molecule adsorbed on a water surface assumes the shape of a spheroid. Hence, that the free energy of adsorption of the saturated aliphatic hydrocarbons on a water surface varies linearly with the number of carbon atoms, is due to the fortuitous manner in which the molecular volumes cause the areas of the corresponding spheroids to vary in arithmetical progression. Results on the adsorption of the hydrocarbons on mercury indicate that this explanation is sound, as the co-area (*i.e.*, the area occupied by the molecules on the surface), and not the number of carbon atoms, varies linearly with the free energy of adsorption.

The standard entropy change on adsorption is also consistent with the picture of the molecules being curled up on the surface. It can be shown, using Kemball's⁹ analysis, that the entropy change may be considered to be due to a loss of one degree of translational freedom and to the conversion from random linkage in the gas phase to a spherical shape of minimum surface area, and hence minimum surface energy, in the surface phase.

In Table 7 the experimental entropy change, ΔS , is compared with the entropy change due to a loss of one translational degree of freedom, $\Delta S'$, and with that due to the conversion from random linkage in the gas phase to a spherical shape in the surface phase, $\Delta S''$. The sum of $\Delta S'$ and $\Delta S''$ compares favourably with the experimental entropy change. However, it should be recalled that ΔS is accurate to only 1.5 cal. mole⁻¹ deg.⁻¹.

TABLE 7.

	$-\Delta S$	$-\Delta S'$	$-\Delta S''$	$-(\Delta S' + \Delta S'')$		$-\Delta S$	$-\Delta S'$	$-\Delta S''$	$-(\Delta S' + \Delta S'')$
n-Pentane ...	11.8	8.7	3.6	12.3	n-Octane	12.2	9.2	4.1	13.3
n-Hexane ...	13.2	8.9	3.8	12.7	2,2,4-Trimethyl- pentane	13.1	9.2	4.1	13.3
n-Heptane...	13.1	9.1	3.9	13.0					

The total energies and entropies of adsorption are compared with those for water and with the heats of condensation in Table 5.

If the heat of condensation is considered as a heat of self adsorption, it appears that the hydrocarbon molecules are more firmly held in the liquid hydrocarbon than on a water surface and less firmly held than on the surface of mercury. In other words, the hydrocarbon-hydrocarbon attraction is greater than the hydrocarbon-water attraction and this results in an adsorption isotherm concave to the surface pressure axis, whereas the hydrocarbon-hydrocarbon attraction is less than the hydrocarbon-mercury attraction which gives rise to an adsorption isotherm convex to the surface pressure axis. The entropy changes are less on a water surface and correspond closely to a loss of one translational degree of freedom.

Region in which the Volmer Equation is Not Obeyed.—At high surface pressures, the plot of $\log_e p'/\Pi$ against Π [which results from a combination of the Volmer equation and the Gibbs adsorption isotherm in the form in which vapour pressure replaces fugacity (activity)] is not linear. This could be due to either or both of two factors: (*a*) the failure of the Volmer equation to express the state of the adsorbed molecules; and/or (*b*) the breakdown of the approximate form of the Gibbs adsorption isotherm. Newton²³ has shown that the ratio of the fugacity to the pressure, the "activity coefficient," is a function only of the reduced temperature and pressure for a large number of gases and vapours (including the saturated aliphatic hydrocarbons). No appreciable error is involved in assuming a coefficient of unity at room temperatures, but at high temperatures for the lower members of the series the error becomes significant, *e.g.*, saturated n-pentane

²² Treloar, *Proc. Phys. Soc.*, 1943, **55**, 345.

²³ Newton, *Ind. Eng. Chem.*, 1944, **36**, 1018.

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vapour at 50° has an activity coefficient of 0.93. Hence at the temperatures used in this investigation, the non-linear part of the $\log_e p'/\Pi$ versus Π plot must be due to the breakdown of the Volmer equation.

An inspection of the graphs of surface pressure versus relative pressure shows that near saturation all the hydrocarbons give almost equal surface pressures, and calculation from the Gibbs equation indicates that the molecular area on the surface approaches 20 Å² at saturation, which is the cross-sectional area of the hydrocarbon chain. It appears, therefore, that the hydrocarbon molecules unroll as the surface pressure increases and at saturation are adsorbed end-on to the surface, forming a close-packed monolayer.

The Adsorbed Layer as a Network of Nonlocalised Similarly-oriented Dipoles.—Since all the adsorption isotherms indicate a predominance of repulsive forces between the adsorbed molecules, it is feasible to consider these forces as being due to the repulsion between similarly oriented dipoles, the dipolar character of the molecule arising from the distortion of its electron envelope in the field of force of the mercury surface. It may appear to be an

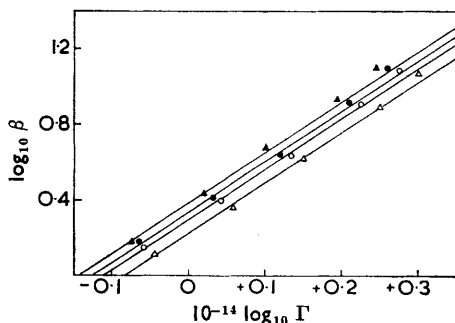


FIG. 3. Test of the virial equation for adsorbed layers. ▲ n-Octane. ● n-Heptane. ○ n-Hexane. △ n-Pentane.

oversimplification to consider a moderately large molecule as a single dipole; however, on the surface it is rolled into a sphere and the assumption is thus justifiable as a first approximation.

Bering and Serpinsky²⁴ derived, from the virial equation, the following equation for a two-dimensional network of similarly-oriented dipoles:

$$\Pi = T k \Gamma + 4.5 \mu_e^2 \Gamma^{5/2}, \quad (1)$$

where Γ is the surface concentration, and μ_e the effective dipole moment of the molecule oriented normal to the surface. On rearranging equation 1, and taking logarithms:

$$\log_e \beta = \log_e (\Pi - kT) = \log_e 4.5 \mu_e^2 + 5/2 \log_e \Gamma, \quad (2)$$

where β represents the departure of the actual isotherm from the ideal isotherm (which would be given by an ideal two-dimensional gas). μ_e may be determined from a plot of $\log_{10} \beta$ against $\log_{10} \Gamma$ (Fig. 3); 2,2,4-Trimethylpentane and neopentane are not shown. Table 8 lists the value of μ_e .

TABLE 8.

Values of μ_e for some hydrocarbons, determined by use of equation (2).

Hydrocarbon	μ_e (D) at 25°	Hydrocarbon	μ_e (D) at 25°	Hydrocarbon	μ_e (D) at 25°
n-Pentane	1.9	n-Heptane	2.2	2,2,4-Trimethyl-	
n-Hexane	2.1	n-Octane	2.3	pentane	2.2
				Neopentane	2.2

The induced dipole moments are of the same order as the permanent dipole moments of polar molecules, indicating that the electron envelopes of the adsorbed hydrocarbon molecules are greatly deformed in the field of the mercury surface. It is relevant that

²⁴ Bering and Serpinsky, *Reports Acad. Sci. (U.S.S.R.)*, 1951, **79**, 273.

Mignolet's surface-potential measurements on methane, acetylene, ethylene, and ethane on a mercury surface ranged from 0.16 to 0.27 v, from which he concluded that these molecules are strongly polarised on the surface.²⁵ Bering and Ioileva¹³ have shown that, for toluene, diethyl ether, and acetone, the induced dipole moment is proportional to the mean polarisability of the molecule. Using their data, it is possible to estimate the electric-field intensity at a mercury surface and hence to deduce the freedom of movement of the molecules on the surface. Thus:

$$\mu_e = \alpha F,$$

where μ_e is the induced dipole moment, F is the electric-field intensity, and α is the polarisability. The average value of the field intensity is 2×10^5 e.s.u. cm.⁻¹ (6×10^7 v cm.⁻¹), at 25°. The maximum energy of a dipole, μ (e.s.u.), in a field of intensity F (e.s.u. cm.⁻¹), is μF ergs. Hence, a molecule with an induced dipole moment of 2×10^{-18} e.s.u. has an associated energy of 4×10^{-13} ergs per molecule. If the adsorbed molecules are considered as a real two-dimensional gas, the thermal energy, as a first approximation, may be taken as kT per molecule which at 25° is 4.1×10^{-14} ergs per molecule. Since the energy of the dipole is ten times that of thermal agitation, the adsorbed molecules are quite firmly attached to the mercury surface.

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²⁵ Mignolet, *J. Chem. Phys.*, 1953, **21**, 1298.
