## 424. *Contact Angles of Water against Saturated Hydrocarbons.*

By N. K. Adam and G. E. P. Elliott.

The contact angle between water and some pure saturated aliphatic hydrocarbons has been measured. The largest angle and therefore the smallest adhesion to water is found when only methyl groups are exposed. When only methylene groups are exposed, the angle is about 10° lower, indicating greater adhesion to water; and a still lower angle is found when some $-\overset{|}{C}H-$ groups are at the surface.

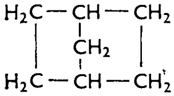
The contact angle for paraffin wax against water is variously given as 105° [1] to 112°,[2] higher angles being obtained with more carefully purified specimens. The contact angle of polyethylene is recorded as 94°,[3] decidedly lower. It was thought that this difference, which we confirm in this paper, might be due to exposure of mainly methyl groups by the more crystalline wax, with shorter hydrocarbon chains, while the polyethylene with longer chains would be likely to expose mainly methylene groups.

We have therefore examined a series of pure compounds to test whether such a variation in the saturated groups exposed can account for this difference between paraffin wax and polyethylene.

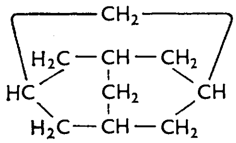
Hexamethylethane (2,2′,3,3′-tetramethylbutane), $(CH_3)_3C{\cdot}C(CH_3)_3$, can expose only methyl groups. It gave $115° \pm 3°$, the mean of the advancing and the receding angle: two specimens, one from Professor F. D. Rossini, then at the Carnegie Institute of Technology, Pittsburgh, the other from Mr. D. H. Desty, of the British Petroleum Company's Research Department, gave identical results. Three cycloparaffins, with severally 15, 16, and 17 $-CH_2-$ groups, each gave $104\frac{1}{2}° \pm 1°$. These, which can expose only methylene groups, were kindly given by Professor J. Coops of Amsterdam.

[1] Adam and Jessop, *J.*, 1925, **127**, 1866; Ablett, *Phil. Mag.*, 1923, **46**, 244.
[2] Ray and Bartell, *J. Colloid Sci.*, 1953, **8**, 214.
[3] Fox and Zisman, *J. Colloid Sci.*, 1952, **7**, 431; Bernett and Zisman, *J. Phys. Chem.*, 1959, **63**, 1241.

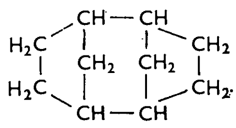
Norcamphane (I), which contains five $-CH_2-$ and two $-\overset{|}{C}H-$ groups, gave 102° ± 2°. Adamantane (II) and tricyclo[4,2,1,1$^{2,5}$]decane (III), with six $-CH_2-$ and four $-\overset{|}{C}H-$ groups, each gave 98° ± 2°; the last three compounds were from Mr. D. H. Desty.



(I)



(II)



(III)

A specimen of very pure paraffin wax, purified by boiling the wax with aqueous sodium hydroxide, rinsing it with hydrochloric acid and water, recrystallising it from hexane, and passing this material in hexane through alumina, gave 114° ± 2°, indicating a surface composed almost entirely of methyl groups.

There is clearly a decrease in contact angle of 10—12° on passing from a surface exposing only methyl groups to one exposing only methylene; and a further decrease when there is a probability that $-\overset{|}{C}H-$ groups are exposed. None of the pure compounds tried, however, shows as low an angle as polyethylene. The polyethylene used by Bernett and Zisman [3] had only one methyl to 200 methylene groups, the proportion of branched chains being very low. We have found an angle of 93° ± 2° on specimens of polythene from the Research Department of Imperial Chemical Industries Limited, Plastics Division; this had been made by the high-pressure process and was stated to have 21·3 methyl groups and 0·73 total unsaturation per 1000 carbon atoms. No plasticiser had been added and the use of mould lubricants was avoided by moulding between sheets of Melinex poly(ethylene terephthalate) film. The angles were measured on the glossy moulded surface after stripping off the very loosely adhering Melinex film. The low angles found for both Zisman's and our polyethylene cannot be explained if the surface consisted solely of saturated methylene groups: the most probable explanation is that there are traces of polar material in the surface. Boiling with alcoholic potassium hydroxide for 10 min. did not, however, alter the contact angle.

A higher contact angle indicates a lower adhesion to water, and *vice versa*, by Young's equation [4] $W_{SL} = \gamma_L(1 + \cos\theta)$, which relates the work of adhesion $W_{SL}$ to the liquid surface tension $\gamma_L$ and the equilibrium contact angle $\theta$. Therefore methylene groups have a 30% higher attraction for water than methyl, and $-\overset{|}{C}H-$ groups a still higher attraction. Both Zisman's and our polyethylene have about 60% higher attraction for water than hexamethylethane and the very pure paraffin wax.

Some hysteresis was found with all specimens. We have used the mean of the advancing and the receding angle as a measure of the equilibrium angle and the adhesion to water. This is customary and finds some justification because the mean angles are much more consistent than either the advancing or the receding angle and are generally in good agreement with the results of those workers who record only a single angle. Until the precise causes of hysteresis are known in each case, however, taking the mean angle is not wholly satisfactory. In this work it appears that roughness increases [5] but does not entirely account for hysteresis. Penetration of water into the surface layers is certainly another cause of hysteresis. Our specimen of polythene had a smooth, glossy surface but showed about 20° difference between advancing and receding angles. Immersion of polythene in water for several hours lowered both angles, but the receding angle much more than the

[4] For the use of Young's name for this equation see Adam, *Nature*, 1957, **182**, 809.
[5] Cf. Shuttleworth and Bailey, *Discuss. Faraday Soc.*, 1948, **3**, 16.

| Compound | Tilting plate $\theta_A$ | Tilting plate $\theta_R$ | Tilting plate Mean | Drop profile $\theta_A$ | Drop profile $\theta_R$ | Drop profile Mean |
|---|---|---|---|---|---|---|
| Hexamethylethane (Rossini) | 130° | 106° | 118° | 126° | 100° | 113° |
| | 124 | 106 | 115 | | | |
| | 126 | 106 | 116 | | | |
| Hexamethylethane (Desty) | 132 | 100 | 116 | 118 | 106 | 112 |
| | 137 | 95 | 116 | | | |
| | 130 | 100 | 115 | | | |
| Cyclopentadecane (Coops) | 111 | 97 | 104 | 109 | 101 | 105 |
| | 109 | 100 | 104½ | | | |
| Cyclohexadecane ,, | 110 | 97 | 103½ | 112 | 96 | 104 |
| | 110 | 100 | 105 | | | |
| Cycloheptadecane ,, | 110½ | 100½ | 105½ | 110½ | 99½ | 105 |
| | 109 | 100 | 104½ | | | |
| Norcamphane (I) (Desty) | 120 | 80 | 100 | 116 | 90 | 103 |
| | 115 | 91 | 103 | | | |
| | 115 | 85 | 100 | | | |
| Adamantane (II) ,, | 121 | 77 | 99 | 119 | 77 | 98 |
| | 116 | 77 | 96½ | | | |
| | 119 | 75 | 97 | | | |
| Tricyclodecane (III) ,, | 109 | 91 | 100 | 106 | 86 | 96 |
| | 108 | 93 | 100½ | | | |
| | 103 | 95 | 99 | | | |
| Purified paraffin wax (Eley & Miller) | 135 | 98 | 116½ | 131 | 95 | 113 |
| | 126 | 97 | 112 | | | |
| | 125 | 103 | 114 | | | |
| Polythene (I.C.I.) | 105 | 85 | 95 | 101 | 82 | 91½ |
| | 102 | 84 | 93 | | | |
| ,, ,, boiled 10 min. in alc. KOH | 105 | 81 | 93 | | | |
| | 105 | 82 | 93½ | | | |
| ,, ,, soaked in water 6½ hr. | 96 | 54 | 75 | | | |
| ,, ,, ,, ,, 17½ hr. | 95 | 38 | 66½ | | | |
| Polytetrafluoroethylene (I.C.I.) rough surface | 131 | 87 | 109 | | | |
| Polytetrafluoroethylene (I.C.I.) rough surface soaked 6½ hr. | 131 | 73 | 102 | | | |
| Polytetrafluoroethylene (I.C.I.) rough surface soaked 17½ hr. | 130 | 73 | 101½ | | | |
| Polytetrafluoroethylene (I.C.I.) planed surface | 128 | 102 | 115 | | | |
| ,, ,, ,, | 128 | 98 | 113 | | | |

advancing angle. Soaking in water produced some lowering of angle with polytetrafluoroethylene but much less than with polythene.

## EXPERIMENTAL

Two methods were used: the tilting plate method described by Adam and Jessop,[6] and photographing the magnified profile of a drop on a plate inclined so that the drop was just about to slide.[7] The tilting-plate method incorporates means of raising and lowering the plate, and gives the advancing and receding angles $\theta_A$ and $\theta_R$ just after motion has ceased; the drop-profile method gives the moving angles at very low speeds. The results by both methods agreed as closely as the variations in angle in different parts of the surface, shown up well by the tilting-plate method, permitted.

The plates were prepared by pressing the powdered substances between small aluminium plates, in a press capable of giving many tons pressure. The plates were then separated by insertion of a razor blade; after one or more trials a smooth area of 1 sq. cm., sufficient for measurement of contact angle, remained on one of the plates. Hexamethylethane was so volatile at room temperature that measurements had to be completed within about 15 min., before the layer had evaporated: fairly rapid working was necessary also with tricyclodecane (III).

Measurements were made at room temperature, 20—24°. We have verified on several of the hydrocarbons that temperature has a very slight, if any, effect on contact angle between 20° and 35°.

The annexed Table shows the results. Each value for $\theta_A$ and $\theta_R$ with the tilting-plate method is the mean of two or more measurements agreeing usually to 3° or better.

[6] Adam and Jessop, *J.*, 1925, 1866; Adam, " The Physics and Chemistry of Surfaces," Clarendon Press, Oxford, 1941, p. 182; Adam and Morrell, *J. Soc. Chem. Ind.*, 1934, **53**, 257T.

[7] Cf. Macdougall and Ockrent, *Proc. Roy. Soc.*, 1942, *A*, **180**, 151.

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