



Fig. 1.—Wettability by various liquids of cast films: upper (a) of polymer A; lower (b) of polymer S.

been described previously,^{5,6} as has the method of measuring contact angles.⁷ A series of Dow Corning silicone fluids, DC 200,⁸ of various viscosities and surface tensions ranging from 15.9 to 19.2 dynes/cm. at 25° also were included in this study in order to observe the wetting behavior with liquids having surface tensions below 20 dynes/cm. All measurements were made at $25 \pm 1^\circ$ and $50 \pm 2\%$ relative humidity.

Experimental Results and Discussion

The wettability curves for the polymer films are independent of the substrates. These curves are shown in Fig. 1a and 1b for polymer A and polymer S, respectively. Values of γ_c obtained by the homologous series of *n*-alkanes are 10.6 dynes/cm. for polymer A and 11.1 dynes/cm. for polymer S. The DC 200 liquids produced the same value of γ_c as the *n*-alkanes for polymer A and varied only 0.1 dyne/cm. for polymer S. Graphical points for the other families of liquids used each fitted linear curves, but their extrapolated intercepts do not coincide with the value defined by the *n*-alkanes. Similar effects had been observed and discussed in

previous investigations.^{5-7,9} It also can be seen that deviations from a straight line resulted with the hydrogen-bonding liquids, such as formamide and ethylene glycol. Such deviations for liquids having a surface tension above 45 dynes/cm. are in agreement with the results of Ellison and Zisman on halogenated organic solid surfaces.⁹

The critical surface tensions of 10.6 and 11.1 dynes/cm. of these two polymers are by far the lowest ever reported on any bulk solid organic surface. They compare with the γ_c values of 8.6 and 7.9 dynes/cm. characteristic for monolayers of perfluorohexanoic acid and perfluorooctanoic acid,³ and the γ_c values of 8.0 and 11.4 dynes/cm. determined for perfluoroheptyl- and perfluoropentylheptadecanoic acids, respectively.⁴ Since the γ_c values of the free surface of these polymeric coatings approach those of the vertically oriented and closely packed monolayers, one must conclude that the orientation and packing of the perfluoro side chains also closely approach those of the acid monolayers. The high contact angles of the cast polymer films thus are due to the adlineation of the long fluorinated side chains. The resulting surface is characterized by a closer packing of the terminal $-\text{CF}_3$ groups than is possible in a linear polymer such as poly-HFP, whose side chains consist of $-\text{CF}_3$ groups only, and whose surface is theoretically constituted of alternating $-\text{CF}_2-$ and $-\text{CF}_3$ groups.

It can be seen in Fig. 1 that the polymer with the $-\text{C}_8\text{F}_{17}$ side chain has a slightly higher γ_c value than the polymer having a $-\text{C}_7\text{F}_{15}$ side chain. From previous studies one would expect the compound with the longer perfluoro chain to exhibit a lower γ_c value than that with the shorter chain. This seeming irregularity can be explained on inspection of Stuart-Briegleb molecular ball models. The $-\text{C}_8\text{F}_{17}$ chains of the polymers pack less closely than the $-\text{C}_7\text{F}_{15}$ chains of polymer A because they are connected to the polymer backbone by much longer and bulkier groups which occupy larger spaces. Thus, the fluorinated chains do not necessarily adlineate since they are allowed a certain amount of freedom in spatial arrangement. On the other hand, the shorter and more compact side chains of polymer A force their perfluoro groups to orient vertically in the closest packing possible. Spatially, then, it is not the length of the perfluoro chain, but the total molecular side group that is determinant in the orientation and packing, and since closer packing can be achieved by the polymer A perfluoro chains it is this polymer that exhibits the lower γ_c value.

(9) A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **57**, 622 (1953).

DETERMINATION OF THE STABILITY CONSTANTS OF COMPLEXES BY GAS CHROMATOGRAPHY

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As gas chromatography permits convenient measurement of the partition coefficient between a gas and a liquid phase, it seemed likely that the

(5) H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, **5**, 514 (1950).
 (6) H. W. Fox and W. A. Zisman, *ibid.*, **7**, 428 (1952).
 (7) E. G. Shafrin and W. A. Zisman, *ibid.*, **7**, 166 (1952).
 (8) Dow Corning, Silicone Notes 3-106 b (1960).

method also could be used for the determination of stability constants.¹⁻³ The feasibility of this approach has been demonstrated in an investigation of olefin-silver ion complexes in ethylene glycol solutions.

Making the plausible assumption that the ratio of olefin (B) to silver ion is 1:1,⁴ the relationship between the stability constant $K = [\text{BAg}^+]/[\text{B}][\text{Ag}^+]$ and the partition coefficient (amount of solute per unit volume of stationary phase/amount of solute per unit volume of gas phase) is expressed by

$$K = (k - k_0)/k_0[\text{Ag}^+]$$

where k is the partition coefficient of the olefin between the silver nitrate-glycol and the gas phase, k_0 is the partition coefficient of the olefin between ethylene glycol containing sodium nitrate and the gas phase, and $[\text{Ag}^+]$ is the silver ion concentration (mole/l.).

k and k_0 were calculated from the specific retention volume V_g^s of the olefin on ethylene glycol containing 1.77 mole/l. of AgNO_3 and NaNO_3 , respectively. The stationary phase was coated in the ratio 1:3 on acid treated firebrick of 50-80 mesh, packed into glass tubes of 1 m. length and 4.2 mm. diameter. The temperature was 30° and the flow of helium 80-100 ml./min.

Since the activity coefficient (γ) of a solute can be determined easily by gas chromatography,⁶ it is further possible to calculate from the experimental data the value of $K'_0 = K/\gamma_B$, which is proportional to the thermodynamic equilibrium constant $K_0 = K\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+}\gamma_B$. At first approximation the ratio $\gamma_{\text{BAg}^+}/\gamma_{\text{Ag}^+}$ can be considered to be constant for a given ionic strength, and to change relatively little with the nature of the olefin in the series studied.⁷

Olefins coordinate practically instantaneously with silver ion,⁴ and therefore equilibrium conditions were expected to prevail at every point of the column. In order to test this assumption, the stability constants (K) for cyclohexene and octene-1 also were determined in the conventional way^{4,8} by distribution between two liquids (ethylene glycol, containing 1.77 mole/l. silver nitrate, and cyclohexane). The two methods were in good agreement (octene 3.2 and cyclohexene 7.2, as compared with 3.3 and 7.7, respectively, by gas-liquid phase chromatography). In both procedures the largest error is due to the relatively small solubility (corresponding to a small V_g) of the olefins in the solvent containing NaNO_3 . In the experimental conditions, the measurement of K is estimated to be accurate within $\pm 5\%$ and compares favorably with the conventional method.^{4,8}

(1) E. Gil-Av, J. Herling, and J. Shabtai, *J. Chromatog.*, **1**, 508 (1958); **2**, 406 (1959).

(2) R. O. C. Norman, *Proc. Chem. Soc.*, 151 (1958).

(3) G. P. Cartoni, R. S. Lowrie, C. S. G. Phillips, and L. M. Venanzi in "Gas Chromatography, 1960," R. P. W. Scott, ed., Butterworths, London, England, 1960, p. 273.

(4) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

(5) A. B. Littlewood, C. S. G. Phillips, and D. T. Price, *J. Chem. Soc.*, 1480 (1955).

(6) A. I. M. Keulemans, "Gas Chromatography," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1959, p. 182.

(7) F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 1333 (1952).

(8) J. G. Traynham and J. K. Olechowsky, *ibid.*, **81**, 571 (1959).

Except for the obvious interest of readily permitting measurements of complex-stability in organic solvents, the procedure further has the advantage of requiring only a few mg. of substance, which need not be purified previously.

Results are given in Table I. Comparing the data for the 1-alkyl cycloolefins (I and VIII) with the corresponding 3- and 4-alkyl isomers (II, III, IX, and X), it is seen that a methyl substituent at the double bond markedly reduces the stability of the complex, and the same effect is evident from the lower constant of VI as compared with IV. The observed influence of the methyl group is in accord with reported data for metal-olefin complexes, and has been ascribed essentially to steric effects in the case of silver coordination compounds.⁹ As the bulk of the substituent is increased, the stability is further decreased (compare I, V, and VII).

TABLE I
STABILITY CONSTANTS OF OLEFIN-SILVER ION COMPLEXES
AT 30° IN ETHYLENE GLYCOL SOLUTION
(1.77 N AgNO_3)

Compound	k_0	k	K	γ_B	$K'_0 \times$
					10^4
I 1-Methylcyclohexene	27.9	90	1.25	290	43
II 3-Methylcyclohexene	23.0	250	5.5	265	210
III 4-Methylcyclohexene	23.0	230	5.1	265	190
IV Methylene-cyclohexane	24.3	440	9.6	270	350
V 1-Ethylcyclohexene	55.8	185	1.3	405	32
VI Ethylidene-cyclohexane	55.8	355	3.0	450	67
VII 1-Isopropylcyclohexene	69.5	200	1.05	845	12.5
VIII 1-Methylcyclopentene	13.0	80	2.9	165	175
IX 3-Methylcyclopentene	10.0	225	12.0	145	810
X 4-Methylcyclopentene	10.6	115	5.5	140	400
XI Methylene-cyclopentane	13.4	155	6.0	160	370
XII 1-Ethylcyclopentene	24.3	180	3.6	285	125
XIII 3-Ethylcyclopentene	19.2	420	11.8	285	415
XIV 4-Ethylcyclopentene	19.2	260	7.1	285	290
XV 1-Methylcyclobutene	6.3	12.3	0.54	140	38
XVI Methylene-cyclobutane	7.2	110	8.1	140	585

On the other hand, electronic factors would appear to be responsible for the higher tendency for complex formation of the 3-alkylcyclopentenes (IX and XIII), as compared with the 4-alkyl isomers (X and XIV). The same trend is observed in the cyclohexene series.

In parallel with data found in aqueous solutions,⁸ cyclopentenes show a higher affinity for silver ion than corresponding cyclohexenes, and, similarly, the stability of complexes in the methylenecyclohexane series increases in the order cyclohexane \leq cyclopentane $<$ cyclobutane.

1-Methylcyclobutene (XV), for which no data are available in the literature so far, has, however, a lower stability constant than 1-methylcyclopentene, contrary to what could have been expected from its higher ring strain.

(9) J. Chatt, in "Cationic Polymerisation and Related Complexes," P. H. Plesch, ed., W. Heffer & Sons Ltd., Cambridge, England, 1953, p. 46.

THE HEAT OF FORMATION OF $\text{BF}_2(\text{g})$

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Appearance potential studies on $\text{BF}_3^{1,2}$ and on various organo-boron difluorides, including CH_3-