

Surface Characterization of Poly(ethylene Terephthalate) Film by Inverse Gas Chromatography

JOHN ANHANG and DEREK G. GRAY, *Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Quebec H3A 2A7*

Synopsis

The gas-chromatographic retention of a series of *n*-alkanes at effectively zero coverage was measured on a poly(ethylene terephthalate) film surface, and the free energy of adsorption per $-\text{CH}_2-$ segment of *n*-alkane at zero surface coverage, $\Delta\bar{G}_{A(\text{CH}_2)}^0$, was calculated. This quantity is a direct measure of the London (nonpolar) interactions of the surface. A value of 40 mN/m for γ_s^L , the London component of the polyester surface free energy, may be estimated from the gas-chromatographic results, in good agreement with results from contact angle measurements. The complete adsorption isotherm and spreading pressure for *n*-decane were also measured by finite-concentration gas chromatography. The method is restricted to polar or crystalline polymers, where the *n*-alkane does not penetrate the bulk of the material during the measurements.

INTRODUCTION

The surface properties of polymeric materials are of critical importance in fiber and film utilization, surface coatings, and adhesion. Many methods are used for surface characterization, ranging from modern surface-specific spectroscopic methods for chemical analysis such as the various electron spectroscopies (Auger, ESCA) to simple empirical tests of wettability.¹ One often-quoted quantity relating to adhesion and wettability is the surface free energy of the material. For liquids, this is readily equated with the surface tension γ_L . However, for solids, the surface free energy is much less accessible both theoretically and experimentally.² The traditional route has been to measure the contact angle between nonwetting liquids and the surface.³ The results of the measurements are interpreted in terms of a "critical surface tension" γ_C ^{4,5} or the London (nonpolar) component of surface energy γ_s^L .⁶ Contact angle methods are very widely used to characterize polymer surfaces,¹ but surface roughness, heterogeneity, and sorption of the liquid into the bulk of the polymer often result in contact angle hysteresis (the advancing rather than the receding angle is normally measured). The thermodynamic significance of the results is often suspect. An alternative simple method to quantify the surface energy would be useful.

The adsorption of vapors has been a classical method for investigating surfaces. However, it has been little used in investigating polymeric surfaces, due mainly to their low surface area and relatively low affinity for the permanent gases normally adsorbed on inorganic surfaces. The development of gas-chromatographic methods for physical measurements⁷ has extended the possibilities of sorption measurements to a range of organic sorbates. The method has been widely used to measure interactions between bulk polymers and organic vapors,⁸ but it is also applicable to measurements of adsorption isotherms of nonswelling

vapors on glassy, crystalline, or other polymer surfaces,^{9,10} where bulk sorption is negligible in the time scale of the experiment. In particular, the surfaces of cellulose fibers and film, of great importance technologically, have been studied in the dry¹¹⁻¹⁴ and moist¹⁵⁻¹⁷ states by inverse gas chromatography.

When surface adsorption is the only retention mechanism, the surface concentration Γ of adsorbate is formally related to the GC retention volume $V_N(p)$ by

$$\Gamma = \frac{1}{ART} \int_0^p V_N(p) dp \quad (1)$$

where A is the total surface area of the stationary phase, R is the gas constant, T is the absolute temperature, and p is the vapor pressure of the adsorbate. (For clarity, the standard GC corrections are here omitted, and the adsorbate vapor is assumed to be ideal.) The spreading pressure π exerted by a vapor adsorbed on a surface measures the lowering of the surface free energy by adsorption, and this quantity may also be derived from the GC data by means of the integrated form of the Gibbs adsorption equation¹⁸ and eq. (1):

$$\pi = RT \int_0^p \Gamma d(\ln p) = \frac{1}{A} \int_0^p \int_0^p V_N(p) dp d(\ln p) \quad (2)$$

The measurement of accurate adsorption isotherms by the methods of finite concentration gas chromatography requires considerable care.⁷ It would be desirable from the point of view of simplicity of apparatus and measurement to utilize the concentration range where GC is normally employed, namely, the so-called "infinitely dilute" region, where very small amounts of vapor are injected. The resultant GC retention volume V_N is independent of the injection size⁷ and is related to the limiting slope at zero concentration of the adsorption isotherm. For simplicity, we again omit the standard GC corrections⁷ and note that at infinite dilution,

$$V_{N(c \rightarrow 0)} = A \left(\frac{d\Gamma}{dc} \right)_{c \rightarrow 0} = AK_s \quad (3)$$

where V_N is the corrected GC net retention volume at infinite dilution, A is the surface area of the polymer in the GC column, Γ is the amount of vapor adsorbed per unit area of polymer, c is the gas phase concentration of adsorbate, and K_s is a surface partition coefficient. The retention volume is thus proportional to an equilibrium constant for vapor partition between the surface and the vapor phase, and a corresponding free energy change can be associated with the adsorption process if suitable standard states are chosen.⁷

The essence of the method proposed here is to characterize polymer surfaces according to the differential free energy change associated with the adsorption from the vapor phase of a suitable "probe," namely, a $-\text{CH}_2-$ segment of the n -alkane chain, at effectively zero surface coverage. This quantity is readily related to measured quantities¹⁴ by

$$\Delta \bar{G}_{A(\text{CH}_2)}^0 = -RT \ln \frac{K_s^{n+1}}{K_s^n} \quad (4)$$

where $\Delta \bar{G}_{A(\text{CH}_2)}^0$ is the incremental standard free energy of adsorption per mole of $-\text{CH}_2-$ group at zero coverage ("infinite dilution"); R is the gas constant;

T is the absolute temperature; and K_s^{n+1} , K_s^n are the partition coefficients for n -alkanes with $n + 1$ and n carbon atoms, respectively. For measurements on a given column at constant temperature and carrier gas flow rate, assuming gas phase ideality,

$$\frac{K_s^{n+1}}{K_s^n} = \frac{V_R^{n+1}}{V_R^n} = \frac{t_R^{n+1}}{t_R^n} \quad (5)$$

where V_R^{n+1} , V_R^n are the net retention volumes for alkanes with $n + 1$ and n carbon atoms, respectively; and t_R^{n+1} , t_R^n are the corresponding peak retention times (measured from the elution time of a noninteracting vapor⁷). In principle, $\Delta\bar{G}_{A(\text{CH}_2)}^0$ can thus be measured directly from the ratio of the retention times for a homologous series of n -alkanes injected together as a mixture of vapors, without knowledge of the adsorbent surface area or carrier gas flow rate.

The use of the free energy per $-\text{CH}_2-$ increment avoids the necessity of choosing standard surface and gas-phase states for the process; it is sufficient to assume that the states are the same for each n -alkane. Obviously, only nonpolar forces can contribute to $\Delta\bar{G}_{A(\text{CH}_2)}^0$. It is thus analogous to the work of adhesion, W_A , between a nonpolar liquid and a surface, which Fowkes¹⁹ related to the surface tensions of the two components by

$$W_A = 2(\gamma_1\gamma_2^L)^{1/2} \quad (6)$$

where γ_1 is the surface tension of the nonpolar liquid and γ_2^L is the London component of the surface tension of the second component. It has recently been suggested¹⁴ that the work of adhesion, W_A , may be replaced by the free energy of desorption per unit area of methylene group probe, which gives

$$\frac{\Delta\bar{G}_{A(\text{CH}_2)}^0}{Na_{\text{CH}_2}} = 2(\gamma_{\text{CH}_2}\gamma_2^L)^{1/2} \quad (7)$$

where N is Avogadro's constant, a_{CH_2} is the area occupied by a methylene group on the surface, and γ_{CH_2} is the surface tension of a hypothetical $-\text{CH}_2-$ liquid. The London component of the surface free energy of the adsorbent, γ_2^L , can thus be estimated if γ_{CH_2} and a_{CH_2} are known.

In this report, finite-concentration GC is used to measure the adsorption isotherm and spreading pressure of n -decane on poly(ethylene terephthalate) film; the London component of the surface energy is then estimated by GC measurements of n -alkane retention at infinite dilution.

EXPERIMENTAL

The poly(ethylene terephthalate) film (du Pont Mylar) 1 mil ($\sim 25 \mu\text{m}$) thick was cut into narrow strips and passed through a cleaned paper tape punch. The perforated strips were discarded, and the discs ("holes") were collected, washed with methanol-water, extracted in a Soxhlet condenser with acetone for 3 hours, and air dried. The Mylar discs, 6.816 g, were packed into a carefully cleaned 1.8 m \times 4.0 mm diam. glass-chromatographic column. The n -alkanes were supplied by the Polyscience Corp. or Aldrich Chemical Co. Gas-chromatographic measurement procedures were conventional and have been described in detail previously.^{13,14} Typical experiments were carried out at nitrogen flow rates of 15 ml/min, with very low pressure drop in the column ($< 0.1 \text{ kN/m}^2$). The pressure

drop correction was negligible, but flow rates were corrected for the effect of water vapor in the soap-bubble flowmeter. Maximum injection size in the finite-concentration experiments was less than $10 \mu\text{mol}$ *n*-decane; in the "infinitely dilute region," injection sizes were about three orders of magnitude smaller. Care was taken to flush residual volatile materials from the column by heating to 105°C in a stream of nitrogen before making measurements.

RESULTS AND DISCUSSION

The variation in GC retention volume with concentration of vapor was calculated by the "elution of a characteristic point" method⁷; the locus of the peak maxima for a series of finite-concentration GC peaks was taken to define the retention curve. (Strictly speaking, this is only correct in the absence of kinetic effects and for isotherms with no point of inflection.⁷) The corresponding adsorption isotherm for *n*-decane on poly(ethylene terephthalate) film (curve 1 of Fig. 1) closely resembles those for *n*-alkanes on cellulose film.⁷ The isotherms for both systems are concave downward at low vapor pressures. This is more clearly seen in the GC retention curve, which is in effect the differential of the isotherm [see eq. (1)]. The increase in retention volume with decreasing sample size, also observed on cellulose surfaces,^{12,13,17} corresponds to an isotherm with downward curvature.

The Brunauer-Emmett-Teller (BET) equation for multilayer adsorption¹⁸ fits the data very well in the usual range of $0.05 < p/p_0 < 0.35$. The point of monolayer coverage according to the BET analysis occurs at 0.165×10^{-3} mol/kg decane on polyester film. The geometric surface area of the film in the column packing was estimated from the dimensions of the packing to be $65 \text{ m}^2/\text{kg}$. If this is taken to be the area available to the adsorbate molecules, then monolayer coverage requires 2.54×10^{-6} mol/ m^2 *n*-decane, corresponding to an area per molecule at monolayer coverage of 0.65 nm^2 . This seems physically reasonable;

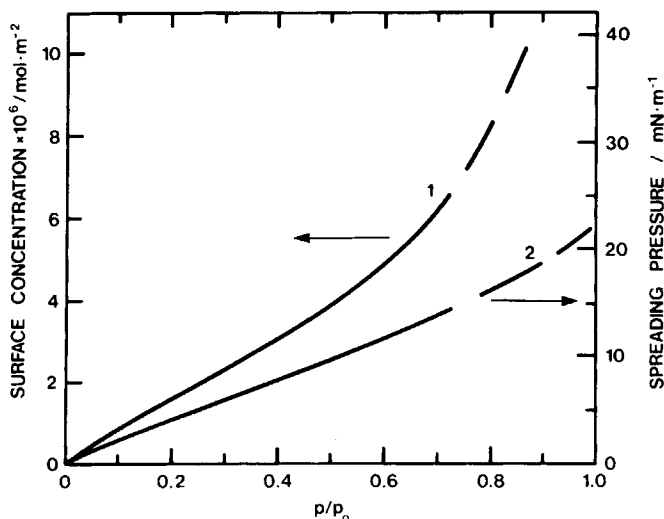


Fig. 1. Adsorption isotherm (curve 1) and spreading pressure (curve 2) for *n*-decane on poly(ethylene terephthalate) film at 25°C . The saturated vapor pressure for *n*-decane at 25°C is 0.173 kPa .²²

a "hard-sphere" model for *n*-decane¹² gives an area of 0.52 nm² per molecule, and *n*-alkanes appear to occupy an area at monolayer coverage rather greater than predicted by the hard-sphere model.^{13,17} The BET plot for *n*-decane on polyester film gives a value of 3.9 for *C*, a parameter related to the heat of adsorption.¹⁸ This low value indicates a weak adsorbate-adsorbent interaction but is slightly larger than values reported for hydrocarbons on regenerated cellulose film.

Integration of the adsorption isotherm gives the spreading pressure π of *n*-decane on the film (curve 2, Fig. 1). By extrapolating to $p = p_0$, the value of π_0 , the equilibrium pressure, was found to be 22 mN/m. This may be compared with the values of 17 and 24 mN/m for *n*-decane on cellulose film¹⁷ and paper,¹³ respectively. Some uncertainty in the π_0 values must arise from the extrapolation at high vapor pressures. Ellipsometry may be a useful technique for complementary measurements in this region.^{20,21}

According to the Girifalco-Good-Fowkes theory,^{5,6} the contact angle, spreading pressure, and dispersion component of the surface free energy are related by

$$\cos \theta = -1 + \frac{2(\gamma_1^L \gamma_2^L)^{1/2}}{\gamma_1} - \frac{\pi_0}{\gamma_1} \quad (8)$$

For *n*-decane at 25°C, $\gamma_1 = \gamma_1^L = 23.8$ mN/m, and *n*-decane spreads on the film, so that $\cos \theta = 1$. With $\pi_0 = 22$ mN/m, eq. (8) gives a value for γ_2^L of 51.5 mN/m. However, eq. (8) is based on a semiempirical model for nonwetting systems, and its applicability here is questionable. Furthermore, measurements of π_0 for different hydrocarbons on the same surface give a range of values for γ_2^L ,^{13,17} and so no great significance can be attached to this value for γ_2^L .

The maximum finite concentration peak area used to construct the isotherm resulted from the injection of 2 μ l of liquid *n*-decane. The "zero-coverage" retention volumes were measured to the maximum of peaks whose area was three orders of magnitude less. The peaks at infinite dilution were only slightly skewed, with virtually no dependence of retention volume on injection size. This indicated that the polyester surface was relatively uniform; specific sites with high affinity for the *n*-alkane vapors were absent under the chromatographic conditions. (Alternatively, it is possible that the N₂ carrier gas or other volatile material becomes irreversibly adsorbed on such sites, rendering the surface more uniform.) The retention data are thus thought to be characteristic of the polymer surface and not of surface heterogeneities.

Retention volumes at zero coverage for three temperatures are given in Figure 2. The logarithm of the retention volumes varied linearly with the number of carbon atoms in the *n*-alkane chain. The values for $\Delta \bar{G}_{A(\text{CH}_2)}^0$ at each temperature were calculated from the slopes of these lines according to eqs. (4) and (5). The results are given in Table I. The values are not sufficiently precise to indicate the temperature dependence; the average for $-\Delta \bar{G}_{A(\text{CH}_2)}^0$ is 2.7 ± 0.1 kJ/mol. In order to obtain γ_2^L , the London component of the polyester surface free energy from eq. (7), values for γ_{CH_2} and a_{CH_2} are required. The surface tension of the hypothetical $-\text{CH}_2-$ liquid may be estimated as 35.6 mN/m at 20°C, either by extrapolation of surface tension data for polyethylene melts²³ to room temperature, or by extrapolation of surface tension data for linear alkanes to infinite chain length.²⁴ The area a_{CH_2} of a methylene group on the surface may

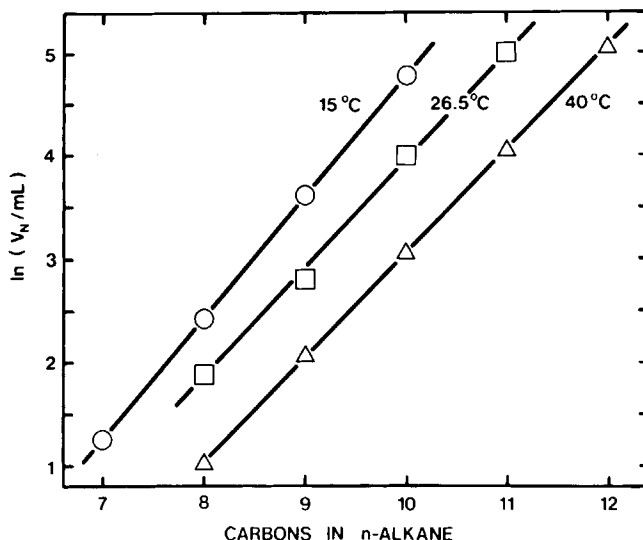


Fig. 2. Natural logarithm of retention volume (ml) for *n*-alkanes at zero coverage on polyester film, plotted against number of carbon atoms in *n*-alkane, at 15, 26.5, and 40°C.

be estimated in a variety of ways; a value of 0.06 nm^2 was used, as previously.¹⁴ Substitution of these values for $\Delta\bar{G}_{A(\text{CH}_2)}^0$, γ_{CH_2} , and a_{CH_2} in eq. (7) gives a value of $40 \pm 2 \text{ mN/m}$ for $\gamma_{\frac{1}{2}}$, the London component of the surface free energy of the polyester film. This value is in good agreement with literature values derived from contact angle measurements for the critical surface tension or the London component of the surface free energy of polyester films (Table II). However, it should be noted that spreading pressure was neglected in arriving at the literature values, because no absorption data were available. For *n*-decane on polyester film, we have shown that π^0 is substantial (22 mN/n at 25°C), and significant spreading pressures have been reported in some nonwetting systems.^{20,21} Inclusion of a spreading pressure term should lead to an increase in the literature values quoted in Table I.

The temperature dependence of the GC retention data may be used to estimate the enthalpy of adsorption of the *n*-alkanes at effectively zero coverage, by means of the relationship²⁹

$$\Delta\bar{H}_A^0 = -R \frac{d \ln V_N}{d(1/T)} \quad (9)$$

where $\Delta\bar{H}_A^0$ is the partial molar enthalpy of adsorption at zero coverage of the

TABLE I
Values for $\Delta\bar{G}_{A(\text{CH}_2)}^0$ and $\gamma_{\frac{1}{2}}$ Calculated from Eqs. (4) and (7)

Temperature, °C	$-\Delta\bar{G}_{A(\text{CH}_2)}^0$, kJ/mol	$\gamma_{(\text{CH}_2)}$, ^a mN/m	$\gamma_{\frac{1}{2}}$, mN/m
15	2.83	35.9	42.6
26.5	2.64	35.2	37.9
40	<u>2.62</u>	34.4	<u>38.0</u>
Average	2.69		39.5

^a Extrapolation of surface tension data for polyethylene melts.²³

TABLE II
Surface Energy Values for Poly(ethylene Terephthalate) Film

Quantity reported	Value, mN/m	Method	Reference
Critical surface tension	43.0	contact angle, water, and organic liquids	Ellison and Zisman ²⁵
Critical surface tension	43	contact angle, water, and organic liquids	Dann ²⁶
London (nonpolar) component of surface free energy	43.2, 37.8	contact angles for water and methylene iodide	Owens and Wendt ²⁷
London (nonpolar) component of surface free energy	43.2	calculated from Zisman's data ²³	Owens and Wendt ²⁷
London component of surface free energy	36.6	calculations based on contact angle measurements	Kaeble (28)
London component of surface free energy	40	empirical method based on <i>n</i> -alkane vapor adsorption	this work

hydrocarbon. Ideal gas behavior is assumed. The least-squares slopes of the $\ln V_N$ vs. $1/T$ lines for *n*-octane, *n*-nonane, and *n*-decane on the polyester gave values for $-\Delta H_A^0$ of 41.9, 46.4, and 51.6 ± 0.1 kJ/mol, respectively. These values are very close to the corresponding latent heats of vaporization of the *n*-alkanes, again indicating the absence of strong surface interactions.

The experimental method described here is only applicable to polymers which interact with hydrocarbons by surface adsorption alone. It cannot be employed if bulk sorption of vapor occurs. This excludes its direct application to the surfaces of semicrystalline polymers such as the polyolefins above their glass transition temperatures, where bulk sorption is the predominant retention mechanism. Even for polymers such as polystyrene which are glassy at room temperature, and for which finite concentration GC measurements are possible,⁹ slow bulk sorption causes spreading and distortion of GC measurements at zero coverage and thus renders this method unreliable.³⁰ In principle, if the bulk sorption is rapid, then GC measurements for a range of polymer layer thicknesses allow calculation of the surface excess of sorbate at the polymer surface, even in the presence of bulk sorption.⁸ In practice, the method is best restricted to highly crystalline or polar polymers which do not sorb hydrocarbons into the bulk polymer in the time scale of the GC experiment. We might add that many polymer-liquid systems examined by contact angle methods must also show sorption of the liquid and vapor into the polymer at and near to the liquid-polymer interface. The composition of the solid phase (pure polymer plus measuring liquid) must therefore be time dependent. This may well contribute to the contact angle hysteresis often observed even on very smooth polymeric surfaces. In contrast, the GC measurements require only brief exposure of the surface to the probe vapor and result in equilibrium measurements of the initial surface properties. Kinetic effects—adsorption hysteresis or bulk sorption—are readily detected from the peak elution behavior^{7,8}; these effects were negligible for *n*-alkanes on poly(ethylene terephthalate).

In conclusion, the results show that finite concentration GC allows adsorption measurements to be made directly on polymeric films. Monolayer capacities and spreading pressures may then be deduced for the adsorption isotherms. Perhaps more novel are GC adsorption measurements with very dilute vapor

concentrations. From the measured retention time of very small injections of a series of n -alkanes, the free energy of adsorption per $-\text{CH}_2-$ segment at zero coverage, $\Delta\bar{G}_{A(\text{CH}_2)}^0$, may be calculated. We emphasize that this readily accessible quantity is a direct measure of the London nonpolar interactions of the surface. A value of 40 mN/m for γ_2^L , the London component of the polyester surface free energy, may be derived from $\Delta\bar{G}_{A(\text{CH}_2)}^0$, in good agreement with values from contact angle measurements. However, both routes to γ_2^L have serious weaknesses; a more direct theory relating $\Delta\bar{G}_{A(\text{CH}_2)}^0$ to the surface free energy of the adsorbent is desirable.

The authors thank Dr. G. Dorris for helpful discussions. The Natural Sciences and Engineering Council of Canada supplied funds for a summer studentship (J.A.).

References

1. L.-H. Lee, Ed., *Characterization of Metal and Polymer Surfaces*, Vol. 2, Academic, New York, 1977; D. T. Clark and W. J. Feast, Eds., *Polymer Surfaces*, Wiley, New York, 1978.
2. J. J. Bikerman, *Topics Curr. Chem.* **77**, 1 (1978).
3. R. J. Good, in *Surface and Colloid Science*, R. J. Good and R. R. Stromberg, Eds., Vol. 11, Plenum, New York, 1979, p. 1.
4. H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, **5**, 520 (1950).
5. R. J. Good and L. A. Girifalco, *J. Phys. Chem.*, **64**, 561 (1960).
6. F. M. Fowkes, *J. Phys. Chem.*, **66**, 682 (1962).
7. J. R. Conder and C. L. Young, *Physicochemical Measurements by Gas Chromatography*, Wiley, New York, 1979; R. J. Lamb and R. L. Pecsok, *Physicochemical Applications of Gas Chromatography*, Wiley, New York, 1978.
8. J.-M. Braun and J. E. Guillet, *Adv. Polym. Sci.*, **21**, 108 (1976); D. G. Gray, in *Progress in Polymer Science*, Vol. 5, A. D. Jenkins, Ed., Pergamon, Oxford, 1977, pp. 1-60.
9. D. G. Gray and J. E. Guillet, *Macromolecules*, **5**, 316 (1972).
10. J.-P. Houriet, P. Ghiste, and F. Stoeckli, *Helv. Chim. Acta.*, **57**, 851 (1974); B. Chabert, J. Chauchard, and G. Edet, *CR Acad. Sci. Paris, Ser. C*, **271**, 38 (1970); G. Courval and D. G. Gray, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 689 (1976); M. A. Llorente, C. Meduñña, and A. Horta, *J. Macromol. Sci.-Phys.*, **B17**, 117 (1980).
11. U.-B. Mohlin and D. G. Gray, *J. Colloid Interface Sci.*, **47**, 747 (1974).
12. P. R. Tremaine and D. G. Gray, *J. Chem. Soc. Faraday Trans. 1*, **71**, 2170 (1975).
13. G. M. Dorris and D. G. Gray, *J. Colloid Interface Sci.*, **71**, 93 (1979).
14. G. M. Dorris and D. G. Gray, *J. Colloid Interface Sci.*, **77**, 353 (1980).
15. P. R. Tremaine, U.-B. Mohlin, and D. G. Gray, *J. Colloid Interface Sci.*, **60**, 548 (1977).
16. G. M. Dorris and D. G. Gray, *J. Chem. Soc. Faraday Trans. 1*, **77**, 725 (1981).
17. S. Katz, *J. Colloid Interface Sci.*, **82**, 326, 339 (1981).
18. A. W. Adamson, *Physical Chemistry of Surfaces*, 3rd ed., Wiley, New York, 1976.
19. F. M. Fowkes, *J. Colloid Interface Sci.*, **28**, 493 (1968).
20. P. Hu and A. W. Adamson, *J. Colloid Interface Sci.*, **59**, 605 (1977).
21. J. Tse and A. W. Adamson, *J. Colloid Interface Sci.*, **72**, 515 (1979).
22. *Selected Properties of Hydrocarbons and Other Related Compounds*, American Petroleum Institute Project 44, Thermodynamics Research Centre, College Station, Texas, June 1974.
23. G. L. Gaines, Jr., *Polym. Eng. Sci.*, **12**, 1 (1972).
24. R. Aveyard, *J. Colloid Interface Sci.*, **52**, 621 (1975).
25. A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **58**, 503 (1954).
26. J. R. Dann, *J. Colloid Interface Sci.*, **32**, 302 (1970).
27. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969).
28. D. H. Kaeble, *Physical Chemistry of Adhesion*, Wiley, New York, 1971, p. 164.
29. S. A. Greene and H. Pust, *J. Phys. Chem.*, **62**, 55 (1958); A. V. Kiselev and Y. I. Yashin, *Gas Adsorption Chromatography*, Plenum, New York, 1969.
30. J. Anhang and D. G. Gray, unpublished results.

Received March 10, 1981

Accepted July 6, 1981