

Fig. 1.—Lupeol ($\times 60$).

Crystallographic Optical Properties

Lupeol.—In parallel polarized light (crossed nicols), the extinction is parallel; the elongation is negative. In convergent polarized light (crossed nicols) an optic normal interference figure is found on faces showing brightest white color. Refractive indices: $n_\alpha = 1.551$, found

lengthwise; $n_\beta = \text{indet.}$; $n_\gamma = 1.565$, found crosswise (both values ± 0.003) (see Fig. 1).

Lupeol Acetate.—In parallel polarized light (crossed nicols) many faces show practically no extinction, while a few show red and blue interference colors and parallel extinction. In convergent polarized light (crossed nicols) a biaxial, optic axis figure is common. The optic sign is negative. Refractive indices: $n_\alpha = 1.540$; $n_\beta = 1.567$ (both ± 0.003); $n_\gamma = \text{indet.}$

Lupeol Benzoate.—In parallel polarized light (crossed nicols) the extinction is parallel; the elongation is negative. Many of the rods show red, green and yellow interference colors. In convergent polarized light (crossed nicols) biaxial interference figures are common. The optic sign is positive. Refractive indices: $n_\alpha = 1.565$ found lengthwise on rods with red and blue interference colors; $n_\beta = 1.567$ found on fragments showing an optic axis interference figure; $n_\gamma = 1.634$ found crosswise, all ± 0.003 .

Summary

1. Lupeol has been isolated from the osage orange. Apparently it is a constituent of the latex.
2. Some crystallographic optical properties are presented for lupeol, lupeol acetate and lupeol benzoate.

LAFAYETTE, INDIANA

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Surface Tensions, Densities and Parachors of the Aliphatic Nitroparaffins

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Introduction

The synthesis and chemical properties of the aliphatic nitroparaffins previously have attracted considerable attention.¹⁻⁴ In view of the unusually high dipole moments shown ($\text{CH}_3\text{NO}_2 = 3.13$) by the molecules of these substances, it is of interest to determine the effect of this property upon the surface tension and the parachor. Since these liquids are extremely polar the possibility of two or more molecular species arises. Questions of this type sometimes may be settled by surface tension investigations.⁵

In the study reported, the variation of the surface tensions in the interval 25.0 to 60.0° of the first four members of the aliphatic nitroparaffins

and their secondary isomers have been measured. Additionally, the variation of density with temperature, the total surface energies at 25° , the parachors and the critical temperatures have been obtained.

Apparatus, Chemicals and Methods

Reports of measurements of the variation of the surface tension with temperature are far less numerous in the literature than is to be desired. The variety of methods suitable is limited by a number of practical considerations. In these researches the ring method³ was employed, and a clean liquid surface was insured by repeatedly overflowing the cup in which it was contained.

Although the question of technique and errors in the ring method has been discussed,^{3,6} our experience has convinced us of the necessity of stressing certain vital points again.

If accurate results are to be obtained, it is essential that the ring be entirely in one plane, and that the stirrup supporting the ring be such that this plane be horizontal to a high degree of trueness. The effect of ring tilt has

(1) C. L. Gabriel, *Ind. Eng. Chem.*, **32**, 887 (1940).

(2) W. D. Harkins, T. F. Young and L. A. Cheng, *Science*, **64**, 333 (1926).

(3) W. D. Harkins and H. F. Jordan, *THIS JOURNAL*, **52**, 1751 (1930).

(4) H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 439 (1936).

(5) E. L. Lind and T. F. Young, *J. Chem. Phys.*, **1**, 266 (1933).

(6) G. C. Nutting, F. A. Long and W. D. Harkins, *THIS JOURNAL*, **62**, 1496 (1940).

TABLE I
SURFACE TENSION, DENSITY, AND MOLECULAR SURFACE ENERGY OF THE ALIPHATIC NITROPARAFFINS FROM 25.0 TO 60.0°

Compound	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	
Nitromethane	39.25	0.1387	1.16576	0.001383	992.7	1.610
Nitroethane	34.03	.1090	1.06823	.001202	996.6	1.520
1-Nitropropane	31.74	.0985	1.02300	.001093	1056.2	1.578
2-Nitropropane	30.78	.1084	1.01208	.001119	1104.2	1.805
1-Nitrobutane	31.65	.0979	0.99170	.000960	1193.2	1.801
2-Nitrobutane	31.32	.1067	.98455	.000963	1251.2	2.026

been studied.³ However, warping of the plane of the ring is probably an error of a greater degree of seriousness. Although it is difficult to estimate quantitatively the error from this source, invariably low surface tension values are obtained unless precaution is taken.

It is desirable to carry out an analysis of errors in order that a precision measure of our results may be stated. The surface tension, γ , is given by the formula

$$\gamma = [Mg/4\pi R]F(R/r, R^3/V)$$

where M = maximum mass of the liquid column supported by the ring, g = gravitational constant, R = radius of ring (center of ring to center of wire), r = radius of wire. The maximum volume, V , of the liquid column elevated above the free surface of the liquid is given by

$$V = M/(D_L - D_v)$$

where D_L and D_v are, respectively, the densities of the liquid and of air saturated with the vapor of the liquid at the prevailing temperature and pressure. Evidently, the precision measure of the derived result (*i. e.*, the surface tension) is governed by the precision measure of components involving mass and length only.

Repeated experiments have shown that M can be determined to within ± 0.1 mg., and R to within ± 0.0005 cm. Harkins and Jordan³ state that the values of F are accurate to 0.3%, with a probable error of less than 0.2% for rings whose R/r ratios lie between 30 and 80. Using these data, a numerical computation of the actual error in the derived surface tension due to the actual error in each component in the case of nitromethane at 25° gave 35.78 = 0.12 dyne cm.⁻¹, or an accuracy of 0.33%.

The ring employed was made of platinum-iridium, and its mean radius was 0.6378 cm.; the value of R/r was 39.87. As a result of many observations, it was found that the precision of measurement was appreciably better than the 0.33% accuracy claimed. In the series of results being reported a reproducibility in a given surface tension value was observed to better than 0.20%.

Density determinations, performed simultaneously at the same temperatures as surface tension measurements, were carried out in conventional Ostwald pycnometers of approximately 18-ml. volume equipped with ground glass caps to check evaporation losses.

Temperatures were read to 0.05° on a totally immersed 0-50° thermometer graduated in tenths of a degree which had been compared with a calibrated Bureau of Standards thermometer.

Refractive indices were obtained with a Zeiss dipping refractometer maintained at 25.0° within 0.1°.

The compounds used throughout our researches were supplied through the generosity of the Commercial Sol-

vents Corp. by Messrs. F. K. Hoover and E. B. Hodge, and were of a high degree of purity. Their physical constants are given in Table III. The liquids were stored in the dark away from air, and, with the exception of nitromethane, no decomposition occurred over a period of three months.

Results

The results of the measurements of density and surface tension when plotted in a large graph against the temperature indicated that within the range 25 to 60° these quantities may be represented by linear equations. Thus the surface tension equation is

$$\gamma = a - bt \quad (1)$$

where a and b are constants independent of the temperature of the surface, t , in °C. Similar type equations for the density and molecular surface energy, $\gamma(Mv)^{2/3}$, can be written

$$\rho_i^3 = c - dt \quad (2)$$

and

$$\gamma(Mv)^{2/3} = e - fT \quad (3)$$

where M is the molecular weight, v , specific volume and T the absolute temperature. The values for the constants in the least squares equations summarize the experimental results (Table I).

The least squares equations fit the experimental surface tension data with a precision of better than 0.13%, and the densities better than 0.018%, with the exception of nitromethane where the precision is 0.06%.

An attempt to evaluate our surface tension and density data in terms of individual values existing in the literature met with small success. With the exception of the first two members of the series, no values were found. In the example of nitromethane a satisfactory comparison can be made. Table II lists values for the densities and surface tensions chronologically.

From the results of Table II, it would appear that the density of nitromethane at 25° must lie within the range: 1.1307 to 1.1313. The agreement between our value for the surface tension

TABLE II
A COMPARISON OF DENSITIES AND SURFACE TENSION
VALUES FOR THE ALIPHATIC NITROPARAFFINS AT 25°;
NITROMETHANE

ρ_{25}°	Year	Author ⁷
1.1297	1917	Jaeger
1.1325	1925	Williams
1.1319	1926	Mathews
1.1304	1929	I. C. T.
1.1312	1931	Wright, Murray-Rust and Hartley
1.1313	1932	Timmermans and Hennaut-Roland
1.1307	1933	Walden and Birr
1.1312	1940	Present work
γ_{25}		
34.99	1913	Morgan and Stone
34.9	1917	Jaeger
36.13	1929	I. C. T.
36.25	1932	Timmermans and Hennaut-Roland
35.78	1940	Present work

and that of the "International Critical Tables" (I. C. T.) is within 0.3 dyne cm.⁻¹.

No comparison of the densities for the other members of the homologous series can be made owing to the complete absence of reports of such measurements on pure compounds in the literature. In the case of nitroethane a comparison of the surface tension values can be made. The value of 31.6 dyne cm.⁻¹ at 25° interpolated from

Compound	ρ_{25}°	η_{25}°	T_b	γ_{25}	E_{25}	[P]	T_c	T_b/T_c
Nitromethane	1.13118	1.37872	375.0	35.78	77.11	132.7	622.7	0.60
Nitroethane	1.03819	1.39015	387.9	31.31	63.78	171.0	661.8	.59
1-Nitropropane	0.99569	1.39901	404.6	29.28	58.44	208.1	675.2	.60
2-Nitropropane	.98410	1.39206	393.1	28.07	60.38	208.3	617.9	.64
1-Nitrobutane	.96770	1.40851	426.7	29.20	58.39	247.6	668.5	.64
2-Nitrobutane	.96047	1.40222	413.1	28.65	60.46	248.3	623.7	.66

the "I. C. T." values is comparable with our value of 31.30 at the same temperature. It is believed that the general self-consistency of the parachor values (see Table III) and their increments offer additional evidence of the accuracy of the surface tension and density values found in this study.

Discussion

The data of Table I permit the calculation of three additional quantities of importance. The total surface energy, E_1 , at any one temperature may be obtained from the equation

$$E_1 = \gamma_1 - T \left(\frac{d\gamma_1}{dT} \right) \quad (4)$$

and some values are given in Table III.

(7) Jaeger, *Z. anorg. Chem.*, **101**, 1 (1917); Williams, *THIS JOURNAL*, **47**, 2648 (1925); Mathews, *ibid.*, **48**, 562 (1926); Wright, Murray-Rust and Hartley, *J. Chem. Soc.*, 199 (1931); Timmermans and Hennaut-Roland, *J. Chim. Phys.*, **29**, 529 (1932); Walden and Birr, *Z. physik. Chem.*, **168A**, 263 (1933); Morgan and Stone, *THIS JOURNAL*, **35**, 1505 (1913).

Parachors were computed from Sugden's⁸ formula

$$[P] = M\gamma^{1/4}/(D_l - D_v) \quad (5)$$

where M is the molecular weight; γ the surface tension; D_l the density of the liquid; and D_v the density of the saturated vapor at the desired temperature. This latter quantity was computed by means of the equation

$$\log (D_v/D_b) = 5(T/T_b - 1) \quad (6)$$

where D_b is the density of the vapor at the boiling point T_b , and was estimated, following Sugden, by the relation

$$D_b = 0.0122 M/T_b \quad (7)$$

The magnitude of the correction of the density of the saturated vapor to the liquid density, D_l , was less than 0.02%, and might have been neglected.

Molecular surface energies calculated in Table I are of use in the estimation of the critical temperatures, T_c , of these compounds. The equation of Ramsey and Shields

$$\gamma(Mv)^{2/3} = k(T_c - T - 6) \quad (8)$$

was used in conjunction with equation (3) in the calculations summarized in the eighth column of Table III.

It is apparent that the well-known rule that secondary compounds show a lower surface tension than corresponding primary members of a series is obeyed by the nitroparaffins.

The value listed by Sugden⁹ for the parachor of nitromethane is 132.0, in excellent agreement with Table III. The increment in the parachor per CH₂ group is 39 which compares favorably with the average of 38.3 from Table III. It is apparent also that the parachors of isomers are identical as is required by the principle of the additivity of atomic parachors.

The unusually high values for the critical temperatures of the nitroparaffins suggest that there may be considerable association in the liquid state. Thus, the compounds 1-nitrobutane, butyric acid, 1-amyl nitrile and butyl alcohol show values

(8) S. Sugden, *J. Chem. Soc.*, **127**, 1540 (1925).

(9) S. Sugden, "Parachor and Valency," p. 119.

of T_c equal to 669, 628, 602 and 560°K., respectively. However, allotropy of the liquid nitroparaffins, whether due to changes in molecular aggregation or to other causes, would probably affect surface tension. Within the temperature range here reported, such effects seem to be absent.

Summary

1. The surface tensions of the aliphatic nitroparaffins at 25.0° vary from 35.78 for nitromethane to 29.20 dyne cm.⁻¹ for 1-nitrobutane. The secondary isomers show characteristically lower free surface energies, with 2-nitrobutane giving 28.65 ergs cm.⁻².

2. The total surface energies of the nitroparaffins at 25.0° vary from 77.11 ergs cm.⁻² for nitromethane to 58.39 ergs cm.⁻² for 1-nitrobutane. The secondary isomers, however, exhibit a higher surface energy, with 2-nitrobutane giving 60.46 ergs cm.⁻².

3. The parachor values calculated from the measured surface tension and density are in good agreement with the predictions of Sugden.

4. Values of the critical temperatures calculated from the Ramsey-Shields equations are: nitromethane, 623°K.; nitroethane, 662°K.; 1-nitropropane, 675°K.; 2-nitropropane, 618°K.; 1-nitrobutane, 669°K.; and 2-nitrobutane, 624°K.

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The Composition and Structure of Molybdenum Blue

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The composition of molybdenum blue has been the subject of controversy ever since it was first discovered by Berzelius¹ in 1826. Even modern investigators are not yet in agreement as to its formula, the most recently reported values varying from Mo₅O₁₄ to Mo₈O₂₃.^{2,3,4} There is little doubt but that products of different composition are obtained when heteropoly acid formers such as phosphoric and arsenic acids are present, or when oxidizing agents such as nitric acid are used in acidifying solutions of molybdate. There is also the very good possibility that the common practice of "purifying" molybdenum blue by extraction from aqueous solution by means of organic solvents gives products which are different. For these reasons the authors undertook to develop methods of synthesis which would avoid these complicating factors.

Molybdenum blue has been prepared by a number of methods, carefully purified and analyzed. Samples were subjected to an X-ray examination and found to yield identical diffraction patterns. The colloidal nature of molybdenum blue was verified subsequently by a study of these products under the electron microscope.

(1) Berzelius, *Pogg. Ann.*, **6**, 380 (1826).

(2) Auger and Ivanoff, *Compt. rend.*, **204**, 1815 (1937).

(3) Auger, *ibid.*, **205**, 1070 (1937).

(4) Lautié, *Bull. soc. chim.*, [5] 1, 105 (1934).

Experimental

Preparation

(a) **Reduction of Molybdate with Trivalent Molybdenum.**—The recommended procedure, by which the majority of the samples were prepared, involves interaction of a solution of trivalent molybdenum, obtained by reduction of molybdate in a Jones reductor, with an acidified molybdate solution (pH 0.4). Specific directions follow: a receiver containing 500 ml. of 0.4 *M* sodium molybdate, Na₂MoO₄·2H₂O, and 200 ml. of 6 *N* hydrochloric acid is attached to the reductor. A solution containing 40 ml. of 0.4 *M* sodium molybdate, 60 ml. of 6 *N* hydrochloric acid and 100 ml. of water is passed slowly through the column and the resulting olive-green solution of trivalent molybdenum is allowed to drop directly into the solution of hexavalent molybdenum. The last of the solution in the reductor is washed into the receiver with dilute hydrochloric acid. The precipitate of molybdenum blue forms in the flask.

The precipitate and the solution are separated by centrifugation and the slightly colored supernatant liquid, containing an excess of trivalent molybdenum, is either discarded or treated as in method (c). The precipitate is washed by centrifuging three to five times with a solution of 5 ml. of 6 *N* hydrochloric acid in 100 ml. of distilled water. This is followed by similar treatment of the precipitate with successive portions of distilled water until both the supernatant liquid and the precipitate are chloride free. After each washing the suspension is centrifuged and the supernatant liquid decanted.

During the washing with dilute hydrochloric acid very little of the product is lost. As the electrolyte is subsequently removed by washing with distilled water considerable peptization takes place with the result that the