# Viscosity, Solubility, Density of Isopropenyl Stearate and Isopropenyl Acetate

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**The viscosity (40–70° C) and density (40–70° C) of isopropenyl stearate and isopropenyl acetate are presented. The solubility of isopropenyl stearate in isopropenyl acetate and in petroleum ether is reported along with the solubility of stearic acid and stearic anhydride in isopropenyl stearate.**

In 1949, Phillips reported the synthesis of enol esters from isopropenyl acetate (IPA) and carboxylic acids (*3*). In 1962, Rothman reported that IPA would react with stearic acid (HST) to produce isopropenyl stearate (IPS) (*6*). The development of a process for this reaction requires the determination of physical data to at least the accuracy required for engineering calculations.

The assumption has been made that IPS synthesized from triple-pressed stearic acid, which presumably will be used in the process, has essentially the same chemistry as IPS made from pure stearic acid (95% stearic). However, the physical property data for IPS made from triple pressed stearic acid are more essential to the process than data for the pure compound. Physical property data for IPS made from stearic acid (95% stearic) are included.

## EXPERIMENTAL

**Viscosity.** Viscosity was determined with an Ostwald viscometer. Tube constants were determined using distilled degassed water at seven temperatures (30-80° C) and fitted to an equation (*7*) of the form

$$\ln k = A + B(1/T^\circ \mathrm{K}) \qquad (1)$$

A least-squares fit of the data to this equation was highly significant ($p < 0.001$). Tube constants were calculated from this equation for subsequent viscosity determinations. The estimated error in the viscosity determinations is ±0.03 cS.

**Solubility.** The solubility apparatus consisted of two test tubes, one inside the other, with a rubber O-ring to keep them separated, partially submerged in a Forma-Temp controlled temperature bath. The outer tube was 32 mm o.d. by 200 mm. The inner tube was 25 mm o.d. by 200 mm.

The air-filled annular space between the two test tubes provided an efficient thermal lag that minimized temperature gradients in the solution. A 16-mm Teflon-coated magnetic stirring bar was placed in the solution.

To determine solubilities, a weighed amount of solute was dissolved in a weighed amount of solvent. The set of test tubes was placed in the controlled temperature bath which was set about 5° above the anticipated crystallization temperature. When the solution equilibrated, the temperature of the controlled temperature bath was manually adjusted lower in discrete steps until crystallization was visually observed. These slow-cooling rates should have greatly reduced any supercooling. The average cooling rate was less than 0.05° C/min. Supercooling still was excessive in some solutions, necessitating keeping the temperature constant for up to 3 hr.

The overall error in determining the temperature of crystallization can be estimated by comparing experimental data to literature values for the solubility of stearic acid in acetone from Bailey et al. (*1*) who used highly purified stearic acid. Although HST (I) contained 95.6% stearic acid, it also contained 0.8% unsaturated fatty acids. As Ralston and Hoerr have pointed out (*4*, *5*), the presence of one fatty acid in another tends to increase the solubility. It appears justified to expect the solubility temperature of solutions of HST (I) to be lowered appreciably. The average difference between the literature and experimental data is 3.6°. The error in these solubility determinations is estimated as less than 1° C.

**Density.** Density determinations were made using a nominal 10-ml pycnometer calibrated with distilled degassed water. The estimated error in these determinations is ±0.001 g/ml.

All temperature determinations were observed with a calibrated precision, NBS specification, total immersion thermometer graduated from −10–101° C with an accuracy of ±0.1° C.

## REAGENTS

Isopropenyl acetate was purchased from Matheson, Coleman, and Bell and purified by distillation. Stearic acid (I), recrystallized once from acetone, was purchased from Humko Products. Stearic acid (II) was USP triple-pressed powder from Merck and Co., Inc., and used without purification. Petroleum ether and acetone were Baker-analyzed reagents purchased from J. T. Baker Chemical Co.

Isopropenyl stearate (I) was synthesized by reaction of stearic acid (I) with isopropenyl acetate and purified by florisil column chromatography (*6*). Stearic anhydride (I) was obtained as a by-product of this reaction and purified by crystallization from petroleum ether. Isopropenyl stearate (II) and stearic anhydride (II) were similarly prepared from HST (II). Gas-liquid chromatography (GLC) analyses of stearic acid and isopropenyl stearate are presented in Table I.

## RESULTS

**Viscosity.** The kinematic viscosity of isopropenyl acetate was determined from 40–70° C, and the data fit the equation

$$\ln \eta = -3.867 + 985.0\ (1/T^\circ\mathrm{K}) \qquad p < 0.001 \tag{2}$$

The viscosities of IPS (I and II) were determined over a similar range. The data for IPS (I) fit the equation

$$\ln \eta = -5.247 + 2209.9\ (1/T^\circ\mathrm{K}) \qquad p < 0.001 \tag{3}$$

The equation for IPS (II) is

$$\ln \eta = -5.301 + 2187.1\ (1/T^\circ\mathrm{K}) \qquad p < 0.001 \tag{4}$$

The experimental viscosity data are available (*2a*).

**Solubility.** For ideal solutions (activity coefficients $\doteq$ 1), or over small temperature intervals solubility follows the correlation (*2*).

$$\ln m = -(\Delta H/R)(1/T^\circ\mathrm{K}) + C \tag{5}$$

where $\Delta H$ equals the differential heat of solution. The systems studied follow this equation over the range of the experimental data. The systems studied, constants, and corresponding temperature ranges over which the data were determined are listed in Table II. In all cases, the fit of the data to the equation was highly significant ($p <$ 0.001).

IPS is more soluble in isopropenyl acetate than in petroleum ether. Also, IPS made from triple-pressed acid is more soluble than the ester made from acids such as stearic acid (I). Stearic acid is more soluble than stearic anhydride in IPS.

The average molecular weight of 297 was used for IPS (II), 518 for SA (II), and 267 for HST (II). The average molecular weight of 323 was used for IPS (I), 550 for SA (I), and 284 for HST (I).

**Density.** The densities of IPS (I and II) and IPA were determined over the range 40–70° C and fitted to linear correlations. Over the temperature range studied, the densities of IPS (I) and IPS (II) were not significantly different. The equations are as follows:

$$\rho_{\mathrm{IPA}} = 0.9473 - 0.001191\ (T, {}^\circ\mathrm{C}) \qquad p < 0.001 \tag{6}$$

$$\rho_{\mathrm{IPS}} = 0.8811 - 0.000736\ (T, {}^\circ\mathrm{C}) \qquad p < 0.001 \tag{7}$$

Table I. Percent Composition by Gas-Liquid Chromatography

| No. C atoms : no. double bonds | HST (I) | IPS (I) | HST (II) | IPS (II) |
|---|---|---|---|---|
| 14:0 | 0.17 | | 2.97 | |
| 15:0 | | | 0.88 | |
| 16:0 | 1.56 | 3.01 | 50.46 | 51.7 |
| 17:0 | 0.42 | 0.73 | 2.39 | |
| 18:0 | 95.64 | 95.4 | 39.73 | 44.5 |
| 19:0 | | 0.20 | | |
| 20:0 | 1.45 | 0.64 | | |
| 15:1 | | | 0.16 | |
| 16:1 | | | 0.89 | |
| 18:1 | 0.48 | | 2.55 | |
| 22:1 | 0.30 | | | |

Table II. Constants for Solubility Equations

| Solution | | | | |
|---|---|---|---|---|
| Solute | Solvent | $\Delta H/R$ | C | Temperature range, ° C |
| IPS (I) | IPA | 14744 | 52.74 | −5 to +10 |
| IPS (II) | IPA | 16623 | 61.36 | −7 to −1 |
| IPS (I) | Pet. ether | 9664 | 35.17 | −2 to 12 |
| IPS (II) | Pet. ether | 9274 | 35.35 | −7 to 0 |
| HST (I) | IPS (I) | 12730 | 39.16 | 38 to 51 |
| SA (I) | IPS (I) | 14908 | 44.79 | 43 to 54 |
| HST (II) | IPS (II) | 11900 | 38.41 | 17 to 35 |
| SA (II) | IPS (II) | 15979 | 49.895 | 25 to 41 |

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## NOMENCLATURE

$A, B, C$ = empirical constants
cS = centistokes, 0.01 cm$^2$/sec
$k$ = viscometer tube constant, cS/sec
$m$ = molality, g mol/kg
$p$ = probability
$R$ = gas constant, 1.987 cal/g mol, ° K
$T$ = temperature, ° C or ° K
$\eta$ = kinematic viscosity, cS
$\rho$ = density, g/ml
$\Delta H$ = differential heat of solution, cal/g mol

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RECEIVED for review September 3, 1970. Accepted January 17, 1971. Use of a company or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be available. Experimental viscosity data for IPS (I), IPS (II), and IPA will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 16th St., N.W., Washington, D.C. 20036. Refer to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.