Designation: ~~D4056 – 16~~ D4056 – 21

Standard Test Method for
Estimation of Solubility of Water in Hydrocarbon and Aliphatic Ester Lubricants[1]

This standard is issued under the fixed designation D4056; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers a procedure for estimating the equilibrium solubility of water and its vapor in hydrocarbon and aliphatic ester lubricants, at temperatures between 277 K and 373 K. The test method is limited to liquids of low to moderate polarity and hydrogen bonding, with predicted solubilities not over 1000 ppm by weight in hydrocarbons, or 30 000 ppm by weight in oxygenated compounds, at 298 K.

1.2 Specifically excluded are olefins, nitriles, nitro compounds, and alcohols.

1.3 This test method is recommended only for liquids not containing widely different chemical species. This excludes blends of esters with hydrocarbons, and lubricants containing detergents, dispersants, rust preventives, or load carrying additives.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate ~~safety~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D94 Test Methods for Saponification Number of Petroleum Products
D1218 Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids
D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
D2502 Test Method for Estimation of Mean Relative Molecular Mass of Petroleum Oils from Viscosity Measurements
D3238 Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.L0.07 on Engineering Sciences of High Performance Fluids and Solids (Formally D02.1100).
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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard.

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.1.2 *charge transfer ~~parameter~~—parameter, n—*the portion of the solubility parameter not attributed to London or Keesom forces.
3.1.2.1 *Discussion—*
It includes hydrogen bonds, induced dipoles, and other quasichemical forces.
3.1.2.2 *Discussion—*
The square of the solubility parameter equals the sum of the squares of the three partial parameters.

3.1.3 *dispersion ~~parameter~~—parameter, n—*the portion of the solubility parameter attributed to London forces.

3.1.4 *polar ~~parameter~~—parameter, n—*the portion of the solubility parameter attributed to Keesom (permanent dipole) forces.

3.1.5 *solubility ~~parameter~~—parameter, n—*the square root of the cohesive energy density (heat of vaporization minus work of vaporization, per unit volume of liquid), at 298 K.

3.2 *Symbols:*

C_A = percentage of aromatic carbons,
C_N = percentage of naphthenic carbons,
d = density of lubricant at 298 K, g/mL,
G = solubility by weight, mg/kg (ppm),
M = molecular weight of lubricant, g/mol,
n_D = refractive index of lubricant at 298 K,
RH = relative humidity, %,
S = saponification number, mg of KOH/g of lubricant,
T = system temperature, K,
V = molar volume of lubricant, mL/mol,
x = mole fraction of water in equilibrium mixture,
y = Lorentz-Lorenz refractivity function,
δ_d = dispersion parameter, $(MPa)^{0.5}$,
P = polar parameter, $(MPa)^{0.5}$,
H = charge transfer parameter, $(MPa)^{0.5}$,
φ_1 = volume fraction of lubricant in equilibrium mixture, and
φ_2 = volume fraction of water in equilibrium mixture.

4. Summary of Test Method

4.1 Data required are the density, refractive index, and molecular weight of a hydrocarbon. The saponification number is also required for an ester. From these are calculated the carbon distribution for a hydrocarbon, and then the partial solubility parameters. These in turn are used to calculate the volume fraction of water dissolved at 298 K at saturation. This is converted to mole fraction, and adjusted to system temperature. The mole fraction is then converted to solubility by weight. If the system atmosphere is not saturated, the solubility is multiplied by the relative humidity.

5. Significance and Use

5.1 Knowledge of the water content is important in lubrication, as large amounts of water can cause corrosion fatigue in steel bearings, and the complete absence of water can cause metal scuffing.

5.2 High water content has an accelerating effect on oxidation of lubricants, and can also contribute to foaming, especially at high altitude or temperature, or both.

6. Procedure

6.1 Calculate the molar volume of the lubricant as follows:

6.1.1 Determine the density at 298 K by Test Method D1298 or equivalent. If the density at 293 K is known (as required for Test Method D3238) multiply it by 0.996 to obtain d with sufficient accuracy.

6.1.2 Determine the molecular weight by Test Method D2502.

6.1.3 Calculate the molar volume as follows:

$$V = M/d \qquad (1)$$

6.2 Calculate the dispersion parameter by these steps:

6.2.1 Determine the refractive index at 298 K by Test Method D1218.
   If a value at 293 K is known (as required for Test Method D3238) multiply it by 0.998 to obtain n_D with sufficient accuracy.

6.2.2 Calculate the refractivity function as follows:

$$y = (n_D^2 - 1)/(n_D^2 + 2) \qquad (2)$$

6.2.3 Calculate the parameter as follows:

$$\delta_d = 45\,y^3 - 119\,y^2 + 108\,y - 4.58 \qquad (3)$$

6.3 For hydrocarbons, calculate δ_d and P as follows:

6.3.1 Determine C_A and C_N by Test Method D3238.

6.3.2 Calculate the parameters as follows:

$$P = 0.0143C_A \text{ and} \qquad (4)$$

$$H = 0.0286C_A + 0.0143C_N \qquad (5)$$

6.4 For esters, calculate P and H as follows:

6.4.1 Determine the saponification number by Test Methods D94.

6.4.2 Calculate the parameter as follows:

$$P = 0.00815\,Sd \text{ and} \qquad (6)$$

$$H = 0.00173\,SM/V^{0.5} \qquad (7)$$

6.5 Calculate the volume fraction of water at 298 K and saturation as follows:

$$1/\varphi_2 = \exp[0.00726\ \varphi_1^2\ ((18.00 - \delta_d)^2 + 2.39\ (15.55$$
$$-P)^2 + 2.39\ (16.27 - H)^2) + (1 - 18/V)\varphi_1] \qquad (8)$$

NOTE 1—For hydrocarbons, it may be safely assumed that $\varphi_1 = 1.00$. However, that can introduce a significant error for some esters, so calculate φ_2 stepwise. Start with $\varphi_1 = 1.00$, next step $\varphi_1 = 1 - \varphi_2$ from the first step, and so on until no further significant change is noted.

6.5.1 Rarely are more than three steps needed to obtain constancy to three significant figures. A small programmable calculator, which is strongly recommended for the whole procedure, can readily be set into the interative cycle described.

6.6 Calculate the mole fraction at 298 K as follows:

$$x = V\phi_2/18 \qquad (9)$$

6.7 Calculate the solubility by weight at 298 K, using Eq 10:

$$G = 18 \times 10^6 X/M(1 - X) \qquad (10)$$