Density and Viscosity of Phenylphosphorus Dichloride and *Dichlorophenyl Phosphine Sulfide

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The density of phenylphosphorus dichloride over a temperature range from 30.90 °C to 66.00 °C and viscosity over a temperature range from 23.00 °C to 57.20 °C as well as the density and viscosity of dichlorophenyl phosphine sulfide over a temperature range from 20.00 °C to 55.00 °C were measured. The measured density data were fitted to a second-order polynomial. The absolute averaged deviation (AAD%) of density for phenylphosphorus dichloride and dichlorophenyl phosphine sulfide are (2.5×10^{-2})% and 7.08%, respectively. The measured viscosity data were fitted to the Andrade equation. The absolute averaged deviation (AAD%) of viscosity for phenylphosphorus dichloride and dichlorophenyl phosphine sulfide are 2.31% and 4.04%, respectively. Abnormal behavior (similar to that of pure water) of dichlorophenyl phosphine sulfide was found. Its density increases with temperature increase below a ≈33 °C with a maximum of 1.1230 $kg \cdot dm^{-3}$ at this temperature. Above this temperature, density decreases with increases in temperature.

1. Introduction

Phenylphosphorus dichloride and dichlorophenyl phosphine sulfide are two intermediates for the production of bis(4-carboxyphenyl)phenyl phosphine oxide, a halogen-free flame-retarding monomer that can be chemically incorporated into various macromolecules to produce flame-retarding polymers.[1] Phenylphosphorus dichloride is a slightly yellow transparent liquid and dichlorophenyl phosphine sulfide is a colorless liquid at ambient temperature. The density and viscosity in a range of operating temperatures are necessary for the design of an industrial process.

2. Experimental Section

2.1. Sample Preparation and Measurement of Densities. The phenylphosphorus dichloride was prepared from benzene and phosphorus via Friedel−Krafts reaction following the procedure given by Wan et al.,[2] and the dichlorophenyl phosphine sulfide was prepared from phenylphosphorus dichloride and sulfur following the procedure described by Wang et al.[1] A 50-cm^3 pyknometer calibrated with distilled water was used for all measurements. The mass was weighed on an electronic balance with precision of ±0.1 mg. The filled pyknometer was then immersed in a thermostated bath with temperature control precision of ±0.01 °C. A stirrer was applied to the bath to speed up the temperature equilibrium stablishment. The densities of phenylphosphorus dichloride and dichlorophenyl phosphine sulfide are listed in Table 1. The densities of pure water are literature values.[3]

2.2. Measurement of Viscosity. An Ubbelohde capillary viscometer was used for these measurements. The capillary was calibrated for kinetic energy correction with water and 1-propanol at the experimental temperature range,

$$\nu = k_1 t - k_2/t \qquad (1)$$

where t is flow time(s). The kinematic viscosity ν ($m^2 \cdot s^{-1} \times 10^{-3}$) for calibration was obtained from literature absolute viscosity and density values.[3] The capillary was 0.05 mm in diameter and 40 mm in length; therefore, the end correction could be neglected. The same viscometer was used for all measurements.

The temperature control set-up used was identical to that used for density measurements described earlier. The flow time t was recorded with a stop watch of precision 0.01 s. Each measurement was repeated three times and averaged as the final result. The measurement uncertainty was within 0.1 s. The density values used to convert kinematic viscosity to absolute values were calculated from fitted equations (see next section). The viscosities of phenylphosphorus dichloride and dichlorophenyl phosphine sulfide over a range of temperature are listed in Table 2.

Table 1. Densities of Phenylphosphorus Dichloride and Dichlorophenyl Phosphine Sulfide

phenylphosphorus dichloride		dichlorophenyl phosphine sulfide	
t	ρ	t	ρ
°C	$g \cdot cm^{-3}$	°C	$g \cdot cm^{-3}$
30.90	1.3567	20.00	1.1199
40.30	1.3421	25.10	1.1216
50.24	1.3308	34.90	1.1227
59.90	1.3240	46.08	1.1126
66.00	1.3199	55.00	1.1040

Table 2. Viscosity of Phenylphosphorus Dichloride and Dichlorophenyl Phosphine Sulfide

phenylphosphorus dichloride		dichlorophenyl phosphine sulfide	
t	η	t	η
°C	$mPa \cdot s$	°C	$mPa \cdot s$
23.00	3.68	20.00	2.78
29.45	2.99	25.10	2.49
40.60	2.53	34.90	1.64
50.24	2.17	46.08	1.30
57.20	1.98	55.00	1.10

3. Data Correlation

The measured data were fitted to equations.

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Density change versus temperature for phenylphosphorus dichloride:

$$\rho/\text{g}\cdot\text{cm}^{-3} = 1.4260 - 0.0280t/°\text{C} + 1.8370 \times 10^{-5}(t/°\text{C})^2 \quad (2)$$

Viscosity change versus temperature for phenylphosphorus dichloride:

$$\ln(\eta/\text{mPa}\cdot\text{s}) = -4.50 + 1705.71/(t/\text{K}) \quad (3)$$

Density change versus temperature for dichlorophenyl phosphine sulfide:

$$\rho/\text{g}\cdot\text{cm}^{-3} = 1.0987 + 0.0016t/°\text{C} - 2.8068 \times 10^{-5}(t/°\text{C})^2 \quad (4)$$

Viscosity change versus temperature for dichlorophenyl phosphine sulfide:

$$\ln(\eta/\text{mPa}\cdot\text{s}) = -8.01 + 2645.40/(t/\text{K}) \quad (5)$$

The absolute averaged deviation (AAD%) of the measured data to the fitted data is defined as follows,

$$\text{AAD\%}(\rho) = \frac{1}{N}\sum|\rho_i - \rho_i^{\text{cal}}|/\rho_i \times 100 \quad (6)$$

$$\text{AAD\%}(\eta) = \frac{1}{N}\sum|\eta_i - \eta_i^{\text{cal}}|/\eta_i \times 100 \quad (7)$$

where the superscript "cal" stands for the values calculated from eqs 2−5.

phenylphosphorus dichloride:

$$\text{AAD\%}(\rho) = (2.5 \times 10^{-2})\%, \quad \text{AAD\%}(\eta) = 2.31\%$$

dichlorophenyl phosphine sulfide:

$$\text{AAD\%}(\rho) = (7.08 \times 10^{-2})\%, \quad \text{AAD\%}(\eta) = 4.04\%$$

4. Discussion

Within the temperature range of the measurements, the variation of density and viscosity with temperature showed a normal decrease trend and the trend slowed at higher temperatures for phenylphosphorus dichloride, which is similar to general organic compounds. While the variation of viscosity with temperature for dichlorophenyl phosphine sulfide shared the same trend as that for phenylphosphorus dichloride, the density of dichlorophenyl phosphine sulfide showed abnormal behavior somewhat like that of pure water. Its density increased with temperature below ≈33 °C and reached a maximum of 1.1230 g·cm^{-3} at this temperature. With a further increase of temperature, its density began to decrease.

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