



Thermophysical and absorption properties of brominated vegetable oil



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ABSTRACT

Brominated vegetable oil (BVO) is a dense, bio-derived food additive used to emulsify citrus flavors in a variety of manufactured beverages. Although its high density is well known, accurate values for density and other properties, such as melting point, viscosity, refractive index and liquid phase heat capacity are not available in the literature. In this work, these properties are measured and correlated as a function of temperature from ~273 K to ~353 K. The volume expansivity, derived from the density, is also calculated. The density, viscosity and heat capacity are then compared with corresponding literature values for natural, unmodified oils. While the density and viscosity are markedly higher than the natural oils, the heat capacity is not significantly different. Through comparison with the viscosities of halogenated internal alkenes, it is shown that the increase in viscosity is likely due to enhanced dispersion forces, rather than enhanced polarity upon bromination. Additionally, the solubility of N₂O and CO₂ in brominated vegetable oil is measured at 310 K from 0.01 MPa to 2 MPa and, like unmodified olive oil, brominated vegetable oil exhibits higher N₂O solubility than CO₂ solubility. Such property trends are expected to be predictive of trends encountered when recently described lipidic ionic liquids are compared with their brominated analogs.

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1. Introduction

Brominated vegetable oil (BVO), synthesized by reacting Br₂ with soybean oil, has been used as an additive in the beverage industry since the early 1930s [1]. The addition of bromine across the double bond has two known significant effects on the physical properties of the oil. First, like hydrogenation, the addition of the bromine atoms results in a saturated triacylglycerol which is much less prone to oxidative degradation than the unsaturated oil; however, unlike hydrogenation, the resulting saturated oil remains a liquid. Second, the addition of the massive bromine atoms significantly increases the density of the oil, from ~0.9 g/cm³ to ~1.3 g/cm³. It is the latter property, enhanced density, which has been exploited by the beverage industry.

By adding small amounts (~8 ppm of total solution) of BVO to citrus flavor compounds, which are sparingly soluble in water, the density of the non-polar phase can be increased to approximate that of water, or more often, water containing sugars that make up the bulk of the beverage. The resulting emulsion is kinetically stable and remains so for the practical shelf life of the product. The safety of BVO as a food additive has been questioned for several decades [1,2], though its use has continued. Although still approved for use in the U.S. and Canada, recent

consumer led efforts [3] have resulted in decisions to remove BVO from popular beverages in the near future in favor of substitutes such as glycerol ester of wood rosin and sucrose acetate isobutyrate [4]. In addition to its use as a beverage additive, BVO has been examined as a potential flame retardant additive for consumer products [5].

Our interest in BVO stems from our work developing lipidic ionic liquids, or ionic liquids with considerable non-polar content. Lipidic ionic liquids are designed to have higher solubilities for non-polar species than do traditional ionic liquids, which are polar to moderately polar in nature. The first generation of lipidic ionic liquids we described were 1-methyl-3-*n*-alkylimidazolium bistriflimide salts where the alkyl chain contained 16–20 carbons with one or more double bonds [6]. Long alkyl chains were added to the imidazolium cation to increase its nonpolar character; however, it is known that adding saturated alkyl chains longer than 9 carbons results in melting point increasing with chain length [7–11]. Inspired by natural lipids, and using starting materials derived from them, we included unsaturations in the alkyl side chain and, as with unsaturated lipids compared with saturated lipids, we observed a significant decrease in melting point: a ΔT_m of ~75 °C when a *cis*-9,10 double bond is introduced into a C₁₈ alkyl side chain of the cation [6]. The melting point depression was observed for both *cis* and *trans* double bonds, but the effect was more pronounced for *cis* unsaturations, presumably due to a greater decrease in packing efficiency when the “kinked” *cis* bond was present. Additional structural moieties, such as cyclopropyl rings added mid-chain [12], were also observed to lower melting points relative to saturated *n*-alkyl chains and commercially available cationic lipids used for liposome formation and gene delivery were observed to collapse into ionic liquids when

Abbreviations: BVO, Brominated vegetable oil.

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hydrophilic anions (Cl^- , Br^-) were replaced with bistriflimide [13]. Recently, we have shown that the inclusion of a sulfur atom, rather than an unsaturation, in the side chain (resulting in 1-thiaalkyl-3-methylimidazolium bistriflimide salts) produces similar melting point depression without the possibility of oxidative cleavage of double bonds [14]. Notably, the position of the sulfur in the chain has a strong effect on the melting point depression in a fashion similar to that of molecular thioethers.

Bromination of the double bond in a lipidic ionic liquid side chain, in a manner similar to the synthesis of BVO, may also yield ionic liquids with large non-polar domains, low melting points and even greater thermal stability. Before endeavoring to synthesize such species, we wished to compare the thermophysical properties of BVO to those of vegetable oil to gain an understanding of how bromination may affect the properties of the lipidic ionic liquids. However, little information about the thermophysical properties of BVO is available in the literature, prompting this study. We have measured the mixture melting point, density, viscosity, refractive index and liquid phase heat capacity of a sample of commercially available BVO and compare several of these properties to those of natural, unmodified oils.

Additionally, unmodified natural oils, such as olive oil, are known to have higher N_2O solubility than CO_2 solubility, a property that is linked to the ability of N_2O to act as an anesthetic, while CO_2 has negligible anesthetic properties under the same conditions, as the biological activity of such anesthetics is tied to their ability to dissolve in a lipid bilayer. Recently, the authors have demonstrated that a significant differential solubility between these gases exists in lipid ionic liquids [15], even though the solubilities of the two gases are almost identical in shorter chain, conventional ionic liquids [16]. Here we have investigated the solubility of these gases in BVO to determine if this differential solubility persists in the brominated versions of natural oils.

2. Experimental

2.1. Materials

Brominated vegetable oil (Table 1) was donated by American Chemical Service, Inc. (ACS). The supplied material was 99% brominated soybean oil with 1% being epoxidized soybean oil. The nominal molar mass reported by the manufacturer was 1090 g/mol. The free fatty acid percent (as % oleic) was reported as 0.11 using AOCS Ca 5a-40 and iodine value was 3.09 as measured by AOCS Cd 1–25.

2.2. Melting point

The melting point of the BVO sample, which is a mixture of brominated triacylglycerols of differing chain lengths and degrees of unsaturation, was measured using a TA Instruments Q2000 Differential Scanning Calorimeter with samples of 5–25 mg. Samples were run in open pans under nitrogen and pretreated at 100 °C for at least 10 min to remove volatile contaminants. Additional thermal pretreatments to promote more uniform transition to the isotropic liquid phase are described below.

2.3. Density

Density measurements were made using an Anton Paar DSA 5000 vibrating tube densitometer. The densities of the BVO were measured in the temperature range from 273.15 K to 343.14 K (± 0.01 K). The densitometer was calibrated with millipore quality water prior to and during measurements, with no detectable drift in accuracy. The reported values are the average of three trials with the standard uncertainty calculated as the standard deviation of the mean.

2.4. Dynamic viscosity

Dynamic viscosity measurements were made using an Anton Paar AMVn microviscometer equipped with 1.6, 1.8, 3.0 and 4.0 mm glass capillary tubes, for varying viscosity ranges, using the rolling ball method. The steel ball and sample were loaded into the capillary tubes using the filling caps provided by the instrument manufacturer, ensuring no air bubbles were present in the tubes. The capillaries were then inserted into the temperature controlled rotor arm of the AMVn and allowed to come to thermal equilibrium. After the trials were completed, the temperature was changed and the process repeated. For each temperature at least 40 trials (rolls of the ball) were recorded. The viscosity of BVO was measured in the temperature range from 305.65 K to 363.15 K (± 0.01 K). The viscosity was calculated using Eq. (1), where k_c is the capillary tube constant, t_r is the roll time, ρ_{ball} is the ball density and ρ_{fluid} is the fluid density.

$$\eta(\text{mPa} \cdot \text{s}) = k_c t_r (\rho_{\text{ball}} - \rho_{\text{fluid}}). \quad (1)$$

The reported values are the average of the 40 trials with the reported standard uncertainty calculated as the standard deviation of the mean.

2.5. Refractive index

Indices of refraction were measured on a ThermoFisher Scientific Abbe Refractometer in the temperature range 273.15 K to 353.15 K (± 0.1 K). At each temperature the instrument was calibrated using standards from Cargille Laboratories ($n_D = 1.4600, 1.5000, 1.5200$) and measurements were reproducible to within ± 0.0005 . The reported values are the average of three trials with the standard uncertainty calculated as the standard deviation of the mean.

2.6. Heat capacity: differential scanning calorimeter

Liquid phase heat capacities were measured from 278.15 to 408.15 K using a TA Instruments Q2000 Differential Scanning Calorimeter with samples of 5–15 mg. Samples were run in open pans under nitrogen and pretreated at 100 °C for at least 10 min to remove volatile contaminants. Data was exported for analysis at 10 K intervals and the data reported is the average of three trials with the standard uncertainty calculated as the standard deviation of the mean.

2.7. Solubility of CO_2 and N_2O in BVO

Solubility measurements were made using a Hiden Isochema Intelligent Gravimetric Analyzer (IGA). The IGA utilizes a microbalance housed in a temperature and pressure controlled environment to expose a sample of solid or nonvolatile liquid to a gas or vapor stream while monitoring uptake of gas/vapor gravimetrically. The temperature is controlled accurately to within ± 0.1 K and the pressure to within ± 0.8 kPa. For these measurements, the IGA was used in static mode with intermittent gas flow to maintain a constant partial pressure of CO_2 or N_2O . Measurements were taken at 310 K (37 °C, body temperature) from 0.1 MPA to about 2 MPA. The IGA employs buoyancy correction, calculating the density of the gas phase using the Peng-Robinson EOS, to compensate for effects which can be appreciable at higher gas pressures. The buoyancy corrected absorption is recorded as mass percent increase relative to the original mass of the sample, which can then be converted to mole fraction of gas absorbed. 30–100 mg of BVO was used in the measurements described below. For this calculation, the nominally reported molar mass for BVO (1090 g/mol) was used; however, the effect of molar mass uncertainty by ± 2 bromine atoms (159.8 g/mol) is examined in the Supplementary Information. The authors note that although this uncertainty affects the absolute solubility and the Henry's constants, the comparison of the relative

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