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LETTER

Aqueous ammonium thiocyanate solutions as refractive index-matching fluids with low density and viscosity

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Abstract We show that aqueous solutions of ammonium thiocyanate (NH_4SCN) can be used to match the index of refraction of several transparent materials commonly used in experiments, while maintaining low viscosity and density compared to other common refractive index-matching liquids. We present empirical models for estimating the index of refraction, density, and kinematic viscosity of these solutions as a function of temperature and concentration. Finally, we summarize the chemical compatibility of ammonium thiocyanate with materials commonly used in apparatus.

1 Introduction

In recent decades, particle image velocimetry (PIV), laser Doppler anemometry (LDA), and laser-induced fluorescence (LIF) have become standard tools in the experimentalist's toolbox. A common problem that arises when using these techniques is that as light passes through the various interfaces of the experimental apparatus, it refracts, leading to distorted images that are difficult to analyze. For measurements in liquids, a common solution to this problem is to use refractive index-matching fluids to minimize these effects (Budwig 1994).

Typical refractive index-matching fluids include mixtures of halogenated hydrocarbons with organic solvents or aqueous solutions of heavy ionic salts (Donnelly 1981). Most of these fluids have viscosities greater than that of water, making it difficult to achieve high Reynolds numbers in experiments. They can also have relatively high specific gravities, which makes it challenging to find density-matched tracers for particle-based measurements. As we will show, ammonium thiocyanate (NH_4SCN) solutions have indices of refraction that match those of transparent materials frequently used in the construction of apparatus, while having physical properties much closer to those of water. This makes them useful when employing optical techniques to study high Reynolds number flows in complicated geometries.

Aqueous ammonium thiocyanate solutions have previously been used as refractive index-matching media by several authors, including Budwig and his collaborators, who used them to aid flow visualization within aortic aneurysm models (Budwig et al. 1993; Egelhoff et al. 1999). More recently, NH_4SCN solutions have been used in PIV studies of flow through randomly packed porous beds (Patil and Liburdy 2013) and in tomographic PIV studies of turbulent structures in Taylor–Couette flow (Borrero-Echeverry 2014). However, data on the optical, physical, and chemical properties of NH_4SCN solutions are not well documented in the literature. We aim to fill this gap and provide a useful guide for researchers to develop NH_4SCN-based refractive index-matching fluids.

Our discussion will be limited to pure solutions of NH_4SCN, which result in index-matching fluids with the low viscosities and densities that are of interest to us. However, NH_4SCN solutions can also be used as a starting point in formulating refractive index-matching fluids with other design criteria. A good example of this is provided by Bailey and Yoda (2003), who document a procedure for developing refractive index- and density-matched solutions for

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use with PMMA particles using ternary mixtures of water, NH_4SCN, and glycerin. Their approach mimics earlier work (Jan et al. 1989; Budwig et al. 1997) where glycerin was used to tune the viscosity of the working fluid, while maintaining its useful refractive index-matching properties.

The remainder of this letter is organized as follows: Section 2 discusses the optical properties of NH_4SCN solutions. Section 3 discusses the dependence of their viscosities and densities on temperature and NH_4SCN concentration. Section 4 discusses the chemical compatibility of NH_4SCN with materials commonly used to build experimental apparatus, as well as toxicity and handling information. Finally, Sect. 5 provides a summary of our results.

2 Optical properties of NH_4SCN solutions

We began our experiments by preparing solutions with concentrations of 49.8, 55.1, and 62.6 % NH_4SCN by weight as determined using an analytical scale. These concentrations were chosen because preliminary experiments showed that at room temperature their refractive indices match those of fused quartz, borosilicate glass, and acrylic, respectively. The solutions were prepared with 99+ % pure ammonium thiocyanate (available for ~US$100 per kg from Acros Organics) and deionized water. Because the solvation of NH_4SCN is endothermic, the solution was gently heated as NH_4SCN was added to help it dissolve more quickly. Despite the purity of the NH_4SCN used, some insoluble impurities remained, which made the solutions slightly cloudy. These impurities were removed using filter paper.

The index of refraction n of NH_4SCN solutions at 589.3 nm was measured as a function of temperature using a Bausch and Lomb Abbe-3L refractometer. A recirculating heat bath allowed us to adjust the temperature of the refractometer and solution to within 0.01 °C. Measurements of the index of refraction of each solution were taken at 1 °C intervals from 15 to 30 °C with five runs taken at each concentration. It was determined that, as with sodium iodide-based index-matching fluids (Narrow et al. 2000), the index of refraction of NH_4SCN solutions decreases approximately linearly with increasing temperature (at fixed concentration) for the range of parameters studied. The data at each temperature and concentration were averaged, and the aggregate data were fit to linear regression models, as shown in Fig. 1. The fit parameters for the three data sets are summarized in Table 1.

Five additional data runs were taken for solutions with concentrations of 52.6, 57.6, and 60.1 % NH_4SCN by weight at temperatures of 17, 23, and 29 °C only. These were combined with the original data set to study the dependence of index of refraction on NH_4SCN concentration. It was found that the index of refraction increases approximately linearly with concentration at fixed temperature, as shown in Fig. 2. The fit parameters for linear regression models of these data are summarized in Table 2.

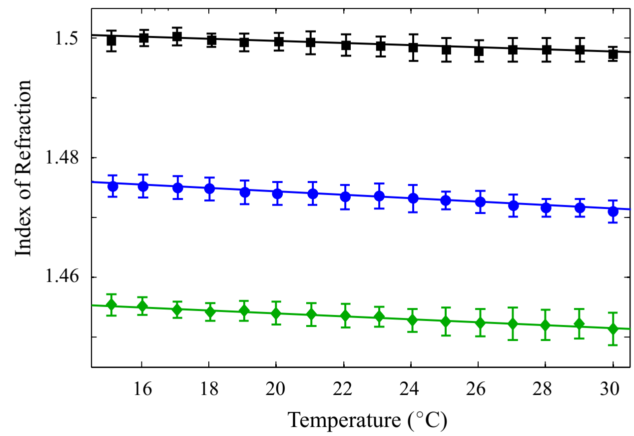

Fig. 1 The index of refraction of NH_4SCN solutions decreases approximately linearly with temperature for fixed concentrations of 49.8 % (*green diamonds*), 55.1 % (*blue circles*), and 62.6 % (*black squares*) NH_4SCN by weight. *Error bars* indicate the sample standard deviation of the index of refraction at a given temperature and concentration

Table 1 Fit parameters for index of refraction versus temperature T models at fixed concentration, $n(T) = n_0 + n_1 T$

Concentration (% by weight)	n_0	n_1 (°C^{-1})	r^2
62.6	1.503	-1.764×10^{-4}	0.910
55.1	1.480	-2.832×10^{-4}	0.979
49.8	1.459	-2.506×10^{-4}	0.976

r^2 is the coefficient of determination

Because the fits presented in Tables 1 and 2 are approximately parallel, the dependence of the index of refraction of ammonium thiocyanate solutions on temperature and concentration should be well captured by a bivariate linear fit. Our data are well represented by

$$n(c, T) = 1.2845 + 0.003513\, c - 0.0002474\, T, \qquad (1)$$

with 95 % of our refractive index data falling within 0.004 of the fit. Here, T is the temperature in °C and c is the concentration of NH_4SCN in percent by weight. This behavior agrees qualitatively with that reported by Narrow et al. (2000) for sodium iodide solutions.

3 Physical properties of NH_4SCN solutions

Unlike many other index-matching fluids, NH_4SCN solutions have physical properties that are relatively close to

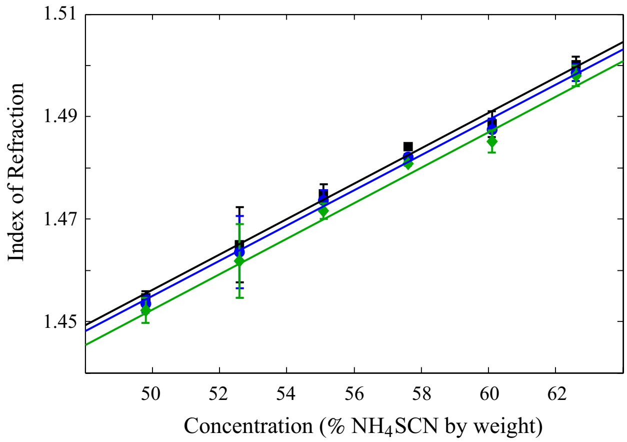

Fig. 2 The index of refraction of NH_4SCN solutions increases approximately linearly with concentration (% NH_4SCN by weight) at fixed temperatures of 17 °C (*black squares*), 23 °C (*blue circles*), and 29 °C (*green diamonds*). *Error bars* indicate the sample standard deviation of the index of refraction at a given concentration and temperature

Table 2 Fit parameters for index of refraction versus concentration c models at fixed temperature, $n(c) = n_2 + n_3\, c$

Temperature (°C)	n_2	n_3 (% by weight^{-1})	r^2
17	1.283	3.463×10^{-3}	0.991
23	1.283	3.440×10^{-3}	0.993
29	1.279	3.466×10^{-3}	0.991

r^2 is the coefficient of determination

those of water. For example, whereas sodium iodide (NaI) solutions used to index-match borosilicate glass have a specific gravity of ~1.7 and a kinematic viscosity of ~2.5 cSt (Narrow 1998), the equivalent NH_4SCN solution has a specific gravity of ~1.1 and a kinematic viscosity of ~1.4 cSt.

The density ρ of NH_4SCN solutions was measured as a function of concentration using an ERTCO No. 2540 hydrometer. It was determined that their density increases approximately linearly with increasing NH_4SCN concentration. Our measurements agree well with historical measurements at lower concentrations compiled by Washburn (2003). Figure 3 shows both data sets along with a linear fit to the combined data, such that

$$\rho(c) = \rho_0 + \rho_1 c, \tag{2}$$

with $\rho_0 = 0.9824$ g/cc and $\rho_1 = 0.002583$ g/cc/%. This fit falls within 0.002 g/cc of all the data with a coefficient of determination of $r^2 = 0.996$.

The kinematic viscosities ν of NH_4SCN solutions having concentrations of 49.8, 55.1, and 62.6 % NH_4SCN by weight were measured using a No. 75 Cannon–Fenske Routine viscometer. The temperature was controlled to within ±0.01 °C by immersing the viscometer in a temperature-controlled bath. As shown in Fig. 4, the temperature dependence of the viscosity of these solutions is well captured by linear fits for the range of temperatures studied. Table 3 summarizes the fit parameters for all the solutions tested.

We also measured the dependence of kinematic viscosity on NH_4SCN concentration at fixed temperature (23 °C). Because the density of NH_4SCN solutions depends only

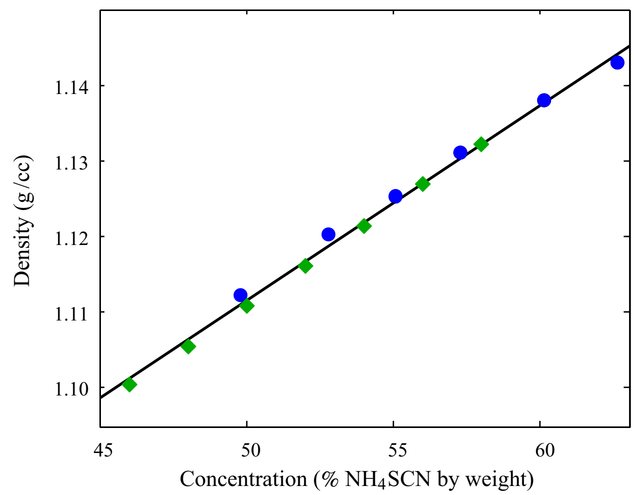

Fig. 3 Density as a function of NH_4SCN concentration at ~23.5 °C. Our data (*blue circles*) agree well with the historical data summarized by Washburn (2003) (*green diamonds*). The combined data set shows an approximately linear increase in density with increasing NH_4SCN concentration, i.e., $\rho(c) = \rho_0 + \rho_1 c$

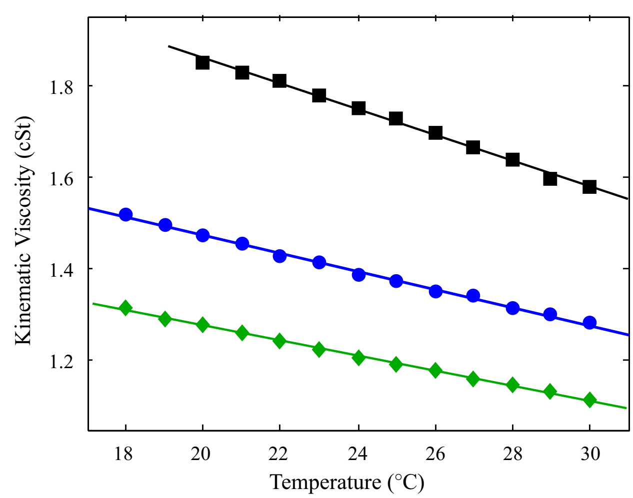

Fig. 4 The kinematic viscosity of NH_4SCN solutions with 49.8 % (*green diamonds*), 55.1 % (*blue circles*), and 62.6 % (*black squares*) NH_4SCN by weight decreases linearly [i.e., $\nu(T) = \nu_3 + \nu_4\, T$] with temperature at fixed concentration

Table 3 Fit parameters for linear viscosity versus temperature models at fixed concentration, $\nu(T) = \nu_3 + \nu_4 T$

Concentration (% by weight)	ν_3 (cSt)	ν_4 (cSt/°C)	r^2
62.6	2.417	−0.02795	0.996
55.1	1.867	−0.01967	0.996
49.8	1.604	−0.01633	0.997

r^2 is the coefficient of determination

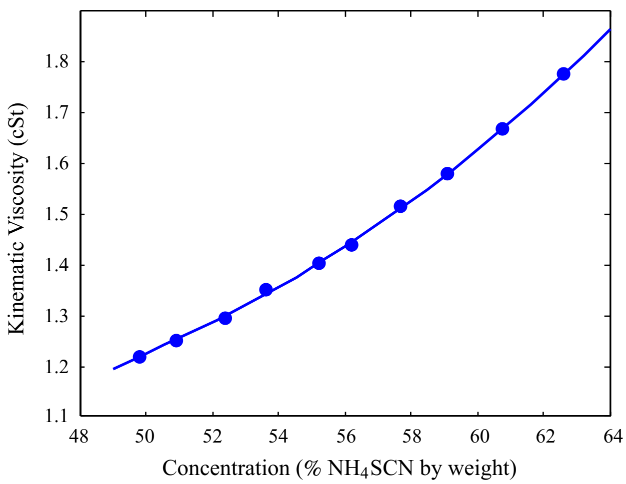

Fig. 5 Kinematic viscosity as a function of NH_4SCN concentration at 23 °C (*blue circles*). The data is well represented by a modified Jones–Dole model of the form $\nu(c) = \nu_0 + \nu_{1/2}\sqrt{c} + \nu_1 c + \nu_2 c^2$

weakly on concentration in the range of concentrations studied, their kinematic viscosity is well captured by a modified Jones Dole model of the form

$$\nu(c) = \nu_0 + \nu_{1/2}\sqrt{c} + \nu_1\, c + \nu_2\, c^2, \tag{3}$$

where $\nu_0 = -19.98$ cSt, $\nu_{1/2} = 8.20$ cSt/$\sqrt{\%}$, $\nu_1 = -0.92$ cSt/%, and $\nu_2 = 0.0037$ cSt/%^{2}, similar to that developed by Kaminsky for the dynamic viscosities of concentrated electrolyte solutions (Kaminsky 1957). The empirical fit presented in Fig. 5 represents the data to better than 0.01 cSt and has a coefficient of determination r^2 of 0.999.

4 Chemical properties of NH_4SCN solutions

The chemical compatibility of several materials with NH_4SCN solutions is tabulated in Washburn (2003). Standards governing these compatibility tests are a useful guide, but are designed for industrial applications, and we believe them to be too stringent for research applications (e.g., ASTM standards consider cosmetic changes to a material as grounds to recommend against using it). Therefore, we conducted a series of tests where samples of materials commonly used in apparatus were submerged in a solution with 55 % NH_4SCN by weight over 19 days and observed for degradation.

Our tests showed that NH_4SCN solutions are compatible with 6061 aluminum, anodized aluminum, and 316 stainless steel, as well as commonly used plastics and glass, but quickly corrode plain steel and 18-8 stainless steel. Brass and bronze become blackened, but the reaction seems to stop there and the mechanical properties and finish of the parts are not significantly affected. The results of these corrosion tests are corroborated by PIV experiments in Taylor–Couette flow (Borrero-Echeverry 2014) in which NH_4SCN solution was used over several years and no significant degradation of bronze and 316 stainless steel parts was observed.

Working with and handling NH_4SCN is similar to working with other refractive index-matching fluids based on heavy ionic salts such as sodium iodide. Handling of powdered ammonium thiocyanate should be done with care and appropriate protective equipment (gloves, dust mask, safety goggles), as it is toxic if inhaled or ingested (GHS category 4) and can be a skin irritant. Once in solution, however, it is easy to work with safely as long as it is contained within the experimental apparatus. Appropriate care should be taken when disposing NH_4SCN solutions, as they could be potentially harmful to aquatic life (GHS Category 3).

5 Summary

We have shown that NH_4SCN solutions provide an alternative to common refractive index-matching fluids and presented an empirical model for n as a function of temperature and NH_4SCN concentration. Our data show that these solutions can be used to match the index of refraction of fused quartz, borosilicate glass, and acrylic. They are also chemically compatible with other materials frequently used to build experimental apparatus. Most uniquely, their viscosities and densities are close to those of water, which make them useful working fluids for researchers carrying out optical measurements at high Reynolds numbers.

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