A PAIR OF IMMISCIBLE TERNARY LIQUIDS WITH MATCHABLE REFRACTIVE INDEXES OVER A WIDE RANGE OF DENSITY AND VISCOSITY RATIOS

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THESIS

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ABSTRACT

Use of particle image velocimetry, laser-induced fluorescence, and a number of other modern optical diagnostic techniques in two-phase flows is severely limited by the difference in refractive index across a fluid/fluid interface, which leads to optical distortion and significantly complicates data interpretation. This problem can be avoided if a surrogate pair of fluids is available, for which the index of refraction can be matched. Beyond that, dynamic similarity also requires that the density ratio of the two surrogate fluids, as well as their ratio of viscosities, match the corresponding ratios in the original fluid pair of interest. Here, we show how that matching can be accomplished, using two ternary liquids, for which adjustment of four independent composition variables (two for each phase if each component of each phase is insoluble in the opposite phase) allows matching of the refractive index over a range of density ratios and a wide range of viscosity ratios. The approach is illustrated for two pairs of fluids. In each case, one fluid is an oil phase consisting of a solution of a light silicone oil, a heavy silicone oil, and 1-bromooctane, which at room temperature are fully miscible over the entire range of compositions. Two opposite phases are considered: a “polar phase” consisting of N-methyl-2-pyrolidone, ethanol, and water, and an “aqueous phase” consisting of 1,2-propanediol, CsBr, and water. For the oil phase, the index, density, and viscosity were measured at 120 binary and ternary compositions. For the polar phase and aqueous phase, binary and ternary data were available in the literature, along with the saturation curve for the aqueous phase, in which the diol and water are fully miscible, but the solubility of the CsBr in water and the diol are both limited. (For the polar phase, the three components are fully miscible over the entire range of compositions at room temperature.) For each fluid phase, polynomials in the composition variables were least-squares fitted to the index and density, and to the logarithm of the kinematic viscosity.
For both fluid pairs (polar and oil phases, and aqueous and oil phases), the range in overlap of index was determined, and the polynomial fits were used to determine the range of accessible density ratios that could be achieved for each index in the range of overlap. Both pairs of liquids are shown to provide compositions for which the density ratio and viscosity ratio of liquid CO$_2$-water systems at high pressure can be matched, while simultaneously matching the index of the two surrogate fluids. While simple solubility tests indicate that one component of the oil phase (namely 1-bromooctane) has significant solubility in the polar phase, there is good reason to believe that for the other fluid pair, no component of the oil phase is soluble in the aqueous phase, and no component of the aqueous phase is soluble in the polar phase. Finally, a second aqueous phase (1,2-propanediol, NaBr, and water) is identified that should have even better “matchability” characteristics than the 1,2-propanediol + CsBr + water phase, and will be attractive from economic and safety standpoints.
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The development of modern optical diagnostics, including particle image velocimetry\textsuperscript{1} and particle tracking velocimetry\textsuperscript{2,3}, laser-induced fluorescence\textsuperscript{4}, and other approaches\textsuperscript{5}, has had a major impact on our understanding of many phenomena in fluid dynamics. Optical diagnostics also play a significant role in understanding mass transfer\textsuperscript{6,7}, and in making spatially resolved measurements of temperature\textsuperscript{8,10,11,14,15,18,19}, sometimes simultaneously with velocity\textsuperscript{20,21,22,23}. Application of these techniques to two-phase flows, however, has been limited by the fact that the refractive index difference across a material interface significantly complicates (and sometimes effectively prevents) interpretation of data. In addition, there are two-phase systems in which experiments are made difficult by toxicity of one or both of the fluids, by opacity at the optical wavelength(s) of interest, or by the extreme temperatures or pressures at which phenomena of interest occur. (In what follows, the discussion is restricted to two fluids, as opposed to gas-particle flows, or flow of a single fluid through a porous medium.)

For these reasons, it is of interest to develop “surrogate” systems that allow experiments to be performed using a pair of liquids whose refractive indexes can be matched\textsuperscript{24}. (Since the index of a gas is typically close to unity and the index of a liquid is typically at least 1.3, the surrogate systems will necessarily be pairs of liquids.) To simplify the discussion, the fluids of original interest are denoted by 1 and 2, and the surrogate fluids by SA and SB. In addition to matching the indexes of SA and SB (\(n_{SA}\) and \(n_{SB}\)), it is desirable to perform experiments under conditions of dynamic similarity\textsuperscript{25}, so that the density ratio for fluids 1 and 2 (\(\rho_1/\rho_2\)) matches that for SA and SB (\(\rho_{SA}/\rho_{SB}\))
and the viscosity ratios are also equal \((\mu_{SA}/\mu_{SB} = \mu_1/\mu_2)^*\). Depending on the length scales, surface tension at the interface can be important, and one might also want to match an appropriate dimensionless material parameter involving surface tension for fluids 1 and 2 to the corresponding parameter for SA and SB. In that case, the correct choice is \(\sigma^3 \rho/(\mu^4 g)\), where \(\sigma\) and \(g\) are the surface tension and gravitational acceleration, respectively. Inclusion of \(g\) means that this parameter is not strictly a material property. However, it involves no extrinsic length scale, and so achieving \(\sigma^3_{SA-SB} \rho_1/(\mu^4 g) = \sigma^3_{1-2} \rho_1/(\mu^4 g)\) will allow for complete dynamic similitude in cases where surface tension effects are important†.

While it was long ago recognized that the index of a liquid could be matched to that of its container in order to facilitate optical measurements through a curved solid/liquid interface26, and that use of a binary (two-component) liquid allows either for the liquid index to be matched to that of the facility,27,28 or for its viscosity to be made equal to that of the fluid of interest,29 less work has been done to deal with the case of two fluids having different values of the index.

Smedley and Coles30 and Smedley31 took the approach of identifying two pure liquids with nearly identical index of refraction at a wavelength of 589 nm (e.g., 1,3-propanediol and 1-bromobutane, both with an index of 1.440 at 20°C). This approach, however, has three shortcomings. First, the index of refraction is a function of wavelength, so one should generally not expect that two pure liquids chosen because they have equal refractive indexes at 589 nm (the sodium D line) will also have equal indexes at the wavelength of interest. To the extent that the index mismatch at wavelength \(\lambda_\alpha\) is

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* Note that the Reynolds number in each phase \(Re_i = ULi/\mu_i\) (where \(i = 1, 2, \) or \(i = SA, SB\)) necessarily involves a length and a velocity, neither of which is a material property. Matching the density ratio for phases SA and SB to the density ratio for phases 1 and 2, and matching the corresponding viscosity ratios, allows for the Reynolds numbers to be matched, provided that geometric similitude is achieved, and that the length scale is appropriately chosen. Note that if the density and viscosity ratios are not matched, it is not possible to achieve dynamic similitude.

† We could equivalently match \(\sigma^3_{SA-SB} \rho_1/(\mu^4 g) = \sigma^3_{1-2} \rho_1/(\mu^4 g)\), since the density and viscosity ratios are also matched.
significant for a pair of pure liquids whose indexes match at \( \lambda_{\rho} \), there is little that can be done to improve the match, other than changing the temperature. Second, to the extent that the index depends on temperature, liquids whose indexes match at the temperature at which data are tabulated (typically 20°C or 25°C, but not both) will typically not have matched indexes at another temperature. Again, if this mismatch is significant, little can be done to address the situation. Third, while one can find a certain number of surrogate pairs of pure liquids whose indexes are close, it is unlikely that \( \rho_{SA}/\rho_{SB} \) will match the desired value of \( \rho_1/\rho_2 \), or that \( \mu_{SA}/\mu_{SB} = \mu_1/\mu_2 \), and again, there is no way to adjust either ratio.

A step beyond matching the index of refraction of two liquids was taken by Budwig\(^{32}\), who used two essentially immiscible binary solutions (sucrose in water and an unspecified isomer of trichlorotrifluoroethane in 1-octanol), for which the two degrees of freedom allowed for matching the indexes of the two liquids and also matching the densities \( \rho_{SA}/\rho_{SB} = 1 \). A related approach was developed by Koh et al.\(^{33}\), Krishnan et al.\(^{34}\), Lyon and Leal,\(^{35}\) and Bailey and Yoda,\(^{36}\) who each used a different ternary solution to match the index and density of small particles.

To the best of our knowledge, there has been no previous work to match the index of refraction of two liquids and achieve specified values of more than one additional physical property.

The problems identified above point to the importance of being able to continuously adjust the index of one or both of the two phases, in order to achieve a matching of the two indexes. Since the index depends only weakly on temperature and pressure, the approach we have chosen is a generalization of that demonstrated by Hendriks and Aviram\(^{27}\) and Budwig\(^{32}\) in which advantage was taken of the dependence of index on composition. But instead of the single degree of freedom afforded by the dependence of the index of an aqueous solution of zinc iodide on ZnI\(_2\) concentration\(^{27}\) or the two degrees of freedom provided by the compositions of two binary solutions\(^{32}\), here we seek to
develop systems with sufficient flexibility to allow matching the index and both the density and viscosity ratios. That will require at least three degrees of freedom, which can, in principle, be achieved using a ternary solution (with two independent composition variables) for one liquid phase, and a binary solution (with one independent composition variable) for the other\(^*\). To provide even greater flexibility, we focus on systems with four degrees of freedom, and in particular, on two ternary liquids. The additional degree of freedom, beyond the three required to the index and density and viscosity ratios, can be used to a) match an appropriate dimensionless parameter, e.g., involving the surface tension between the two phases; b) match the index at two wavelengths (e.g., the excitation and emission wavelengths for fluorescence); or match the index of an optically transparent material in the boundary of the flow facility.

The remainder of the thesis is organized as follows. In Chapter 2, the three components chosen for the oil phase are discussed, along with two possible ternary counter-phases for which index, density, and viscosity data are available in the literature. The criteria used to select these systems are also discussed, and guidance that might prove useful in selecting other systems is also provided. Chapter 3 provides a description of the experimental methods used to prepare the oil-phase solutions, and to measure index, density, and dynamic viscosity, along with the results of those measurements. Chapter 4 presents simple least-squares fits of our experimental data for the oil phase and the literature data for two counter-phases. Chapter 5 discusses how the accessible combinations of density and viscosity ratio are obtained when the two phases are index-matched, for the case where the counter-phase is completely miscible over the entire composition range, and when it is not, and presents results for both situations. In Chapter 6, the results are discussed in terms of the available temperatures and pressures of a water-CO\(_2\) system for which these pairs of ternary liquids could serve as a surrogate. In

\(^*\) This presumes that each component of each phase is insoluble in the other phase. If that is not the case, then the Gibbs Phase Rule\(^{37}\) shows that the number of degrees of freedom is only two.
Chapter 7, we present results of a simple experiment in which a particular composition of the oil phase was mixed with a particular composition of the polar phase, and it is argued that that pair of phases is not an ideal choice. In Chapter 8, we discuss more generally the effects of nonzero solubility of the components in the opposite phase, and of variation of index with wavelength and temperature. A discussion of other multicomponent liquid phases is offered in Chapter 9, followed by some conclusions in Chapter 10.
CHAPTER 2
SURROGATE SYSTEM SELECTION

2.1 DESIGN REQUIREMENT FOR THE TWO PHASES

The design considerations for the liquids were fairly straightforward: a) avoid toxicity and other safety issues; b) avoid pure components that react with air or with each other (including at the interface), are photochemically unstable (especially at the wavelength(s) of interest), or react with or otherwise degrade (e.g., by dissolution, swelling, or crazing) solid materials typically used in flow facilities; c) provide optical transparency, at least at the wavelength(s) of interest; d) avoid excessive cost, e) allow for matching of index over a range of index, f) provide a relatively wide range of combinations of the density ratio and viscosity ratio, under conditions where the index is matched, g) avoid components with high vapor pressure, to minimize evaporation during mixing, property measurements, and in fluid mechanics experiments; and h) to the extent possible, use components in each phase that are nearly insoluble in the other phase. While no two liquids are completely immiscible (e.g., benzene\textsuperscript{38} and mercury\textsuperscript{39} each has a small nonzero solubility in water), the advantage of an approach in which each component has essentially no solubility in the opposite phase is that the index, density, and the viscosity of each such ternary solution can be measured in isolation, and will be almost unchanged when equilibrated with the other phase. If this was not the case, then each measurement of index, density, and viscosity in each ternary solution would need to be made after it had been equilibrated with the other ternary solution. Given the relative slowness of diffusive mass transfer, that is not a welcome prospect. Moreover, in that case, the equilibrium concentrations would depend on the relative volumes of the two phases. More tellingly, as mentioned in Chapter 1, the Gibbs Phase Rule\textsuperscript{37} shows that if any of the components of either phase is soluble in the other phase, the number of
degrees of freedom is reduced by one. All of these problems would greatly reduce the utility of the approach.

2.2 CHOICE OF TERNARY SYSTEMS

There is a large number of ternary systems for which the index, density, and viscosity have been measured and tabulated\textsuperscript{39,40,66-73} by a single set of authors, and it was initially thought that two such systems that would meet our design requirements could be identified, without any experimental measurements being necessary. That, unfortunately, proved to not be the case, with most of the possible pairs failing the requirement for very low solubility of each component in the opposite phase. (In no case was data for the equilibrium concentrations of six plausible components in a two-phase system found, and so experimental data for the solubility of each candidate component of a ternary system in each component of the opposite “tabulated ternary” phase were sought. Absent such data, information about solubility of chemically similar pairs was used, and two chemists were consulted.) It thus became clear that we would need to “design” at least one of the phases.

A key parameter in liquid/liquid systems is the viscosity ratio. For example, in liquid CO\textsubscript{2}/water systems, the viscosity ratio can be as low as 0.1. So an important design consideration is the capability to achieve a significant viscosity ratio for the surrogate fluid pair. That might be done using, for example, a solution of silicone oils, or a solution of glycerol and water.

We decided on an “oil” phase including two silicone oils. It was initially thought that it would be desirable to use a standard polydimethylsiloxane (PDMS) oil and a fluorinated silicone oil, since changing their relative proportions would provide flexibility on index and density. (The densities and index values of PDMS oils are essentially independent of mean molecular weight, or viscosity.) But that approach was abandoned when it became clear that PDMS and fluorinated silicone oils are almost completely
insoluble in each other and that the only known cosolvent is methyl ethyl ketone (Dr. K. Koczo, private communication), which is soluble in water and also has a high vapor pressure. For simplicity, a “light” (5 cSt) silicone oil and a “heavy” (50 cSt) silicone oil (hereinafter referred to as LSO and HSO, respectively) were chosen, with the idea that varying their relative proportions would allow for the viscosity to be adjusted relatively independently of index and density, which are quite close for the two oils. In order to allow for adjustment of index and density in this phase, 1-bromooctane (referred to as 1-BO), a relatively benign, unreactive, and inexpensive liquid with reasonably high index and density, was chosen.

In an initial attempt to minimize the burden of experimental property measurements, we first identified a promising ternary system for which data are available, consisting of water, ethanol, and \( N\)-methyl-2-pyrrolidone (NMP). (The latter is a common industrial solvent, sold in tank-car quantities. It is relatively inexpensive and benign.) As discussed in Chapter 4, this ternary system (which we refer to as the “polar” phase), has the distinct advantages that a) the index of refraction has a considerable overlap with that of our oil phase, and b) the index, density, and viscosity each depend quite differently on composition, which suggests that a significant portion of the \( \rho_{SA}/\rho_{SB} \) - \( \mu_{SA}/\mu_{SB} \) plane might be accessible. This system was also attractive because the polar nature of its components suggested that each would be essentially insoluble in our oil phase, and that the components of the oil phase would be essentially insoluble in the polar phase.

These two phases (NMP + ethanol + water, and LSO + HSO + 1-bromooctane) provide a range of viscosity ratio from near unity up to about 50, with a significant range of overlap in refractive index. The density in the polar and oil phases can vary by about 50% and 22% respectively. (The range of combinations of \( \mu_{SA}/\mu_{SB} \) and \( \rho_{SA}/\rho_{SB} \) that can be achieved under conditions where the index values are matched is discussed in Chapter 5.)
After bringing together one composition of the oil phase and one composition of the NMP + water + ethanol polar phase in a preliminary solubility experiment discussed in Chapter 7, it became clear that 1-bromooctane has a measurable solubility in the polar phase. At that point, we identified a second potential counter-phase (1,2-propanediol + CsBr + water), for which index, density, and viscosity data\cite{40} had been published after the NMP + water + ethanol system was selected. For our oil phase and this counter-phase, a fairly extensive review of the literature failed to identify any issues related to solubility of any component in the opposite phase. In addition, there is a much wider range of viscosity variation available in this phase than in the NMP + water + ethanol phase. This system also provided a good testbed for development of approaches to deal with the case in which the components of one ternary phase are not fully miscible over the entire range of composition, which is the situation that obtains in a closely related and very promising counter-phase (1,2-propanediol + NaBr + water) whose advantages are discussed in Chapter 9.
CHAPTER 3
MATERIALS AND EXPERIMENTAL METHODS AND RESULTS

3.1 MATERIALS AND EXPERIMENTAL METHODS

Singly distilled water was obtained in one-gallon containers from a commercial source. USP grade ethanol was from Decon. The 5 cSt (light) and 50 cSt (heavy) silicone oils, 1-bromoctane (99%), and NMP (biotech. grade, ≥ 99%) were obtained from Sigma-Aldrich. All materials were used without further purification.

Solutions of the LSO, HSO, and 1-bromoctane were prepared gravimetrically, along six lines in and on the ternary composition triangle shown in Figure 1. Along three of these lines (AD, AE, and AF), the ratio of two components was held constant as the third component was varied. For the remaining three series, solutions were prepared along each binary edge of the triangle, in each case by adding one liquid to an initial mass of the other. In each case, the mass of added liquid was determined by difference between the masses of solution before and after addition, so that errors in mass readings are not additive.

Measurement of density, viscosity, and refractive index at a large number of compositions is desirable in order to “cover” the entire ternary triangle, and also to minimize the effects of measurement error on fitted polynomials. After a decision was made about the compositions at which measurements were to be made, an attempt was made to develop sequences in which to prepare the compositions so as to minimize the quantities of the components needed. The three properties were measured at roughly 20 compositions for each binary combination, and at about 60 points inside the ternary triangle. In total, measured properties were tabulated for 120 different points, roughly covering the entire composition space.

Refractive index measurements were made at the sodium D line (589.29 nm) using an Atago PAL-RI refractometer. Dynamic viscosity was measured with a Brookfield
model LVDV II +P viscometer. To facilitate viscosity measurements as low as 2 cP, an additional UL Adapter (from Brookfield) was employed. The other advantage of using the UL Adapter was that much less sample is needed to make each viscosity measurement. Density was measured using calibrated hydrometers. A Sartorius BL310 balance, with a readability of 10 mg and repeatability of 10 mg was used to prepare solutions in a glass beaker containing a magnetic stirring bar. Index was measured with a precision of four decimal digits. An index measurement was accepted when four consecutive readings were identical. The precision of the density measurement was three decimal digits. For very viscous fluids, in which settling time of the hydrometer was significant, after the hydrometer appeared to reach its equilibrium position and a density value was recorded, the hydrometer was gently pushed down several millimeters, and the density was again recorded after the hydrometer had risen to its equilibrium position. In each case that this was done, the readings were identical to within the instrumental precision. Viscosity measurements were accurate to three significant figures. The ambient temperature, measured by a digital thermometer (with precision of 1°C) was almost always 22°C or 23°C. The temperature measured by the refractometer was always between 21.0°C and 23.8 °C.

The hydrometers are long cylindrical glass tubes with narrow upper stems, and are calibrated so that when immersed in a particular liquid, the density is read from the vertical scale that intersects the surface of the liquid. Each hydrometer came fitted with a weight in its bottom to augment stability when floating and to reduce deviations of its axis from the vertical. Each hydrometer has a measurement range of 0.1 g/cm³, with 100 subdivisions, providing a precision of 0.001 g/cm³. For each solution, the approximate density (estimated from measurements of previous solutions) guided the choice of the hydrometer with the appropriate range. A vertical glass tube (with a flat base) was fabricated with an inner diameter approximately 2 mm larger than the outside diameter of
the hydrometer having the largest diameter, and length as long as the longest hydrometer. Making measurements in this tube significantly reduced the sample volume required.

The density measurements required the largest sample volumes. The minimum volume needed for making density measurements was 65 mL, but sometimes as much as 75 mL was required, depending on the density and the hydrometer required. Thus, each series of solution compositions began with a minimum volume of ~75 mL.

As liquid was added from one composition to the next, mass was measured at each stage using the balance. A detailed description of how different solution compositions were achieved and property measurements made is illustrated as follows.

Consider a binary traverse that begins at the pure LSO vertex in Figure 1. We begin by measuring the mass of a 250 mL Griffin beaker and a small magnetic stirring bar, recording the value, \( M_B \), and taring. Roughly 75 mL of LSO is then poured into the beaker and the added mass \( M_{1a} \) is recorded. Then LSO is poured from the beaker for density and viscosity measurements, and is withdrawn by pipette for index measurement. Almost all of the liquid (pure LSO in this case) is poured back into the beaker (with the stirring bar) and the mass is recorded, \( M_{1b} \). (This accounts for losses in the pipette and three instruments during measurement.) After taring, a small mass \( M_{2a} \) of 1-BO (determined as described below) was added to the beaker and recorded. In this way, mass fractions of components are determined accurately at each stage, accounting for mass losses during measurement and transfer. The solution is magnetically stirred for 10-15 minutes to provide good mixing and thermal equilibration*. Once the solution was mixed thoroughly and equilibrated, property measurements are made. After the measurements, liquid was poured back into the beaker and the mass recorded. A measured amount of 1-BO was added to the solution, and the entire process repeated.

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* The heat of solution of 1-bromooctane in (any) silicone oil is not known at any composition.
To cover the ternary triangle at minimum cost, the solutions were prepared and measurements were performed as follows. Consider the composition triangle in Figure 1. Let \((y_1, y_2, y_3)\) be the composition of the oil phase, where \(y_i\) denotes the mass fraction of component \(i\), and components 1, 2, and 3 are light silicone oil (LSO), heavy silicone oil (HSO), and 1-bromooctane, respectively. Points A, B, and C represent pure 1-BO, pure LSO, and pure HSO, respectively. Points on segments AB, BC, and AC correspond to binary solutions of LSO and 1-BO, LSO and HSO, and HSO and 1-BO, respectively. All points lying inside the triangle ABC correspond to ternary solutions of the three components.

We note that it is not possible to start with one pure liquid and reach another vertex by adding liquid. While one can, say, start at A and move towards B by adding LSO, one can never get to B by this process. (The closer one gets to B, the larger the solution volume, and the more LSO is needed.) This shows that each binary leg of the triangle must be broken into two series of solutions, each starting at a vertex. Similar considerations hold for the ternary compositions in the interior of the triangle.

Locations on the binary legs and in the interior of the triangle at which two series of compositions should "meet" can be identified as "break points" (denoted by P, Q, R, S, and T) and "turn points" (denoted by D, E, and F). These were determined in advance by a simple cost calculation, which estimates the amount of mass, and subsequently the cost, for each component needed while traversing from either direction for a given segment. The break points and turn points are determined to reduce the total cost of the components.

Figure 2 depicts the compositions at which measurements were made. The series of compositions was as follows.

**Series 1:** Starting at point B, with an initial 75 mL of pure LSO, a traverse was made along segment BP by adding 1-BO in small quantities.
**Series 2:** A second traverse started at point A (pure 1-BO), and progressed by small additions of LSO, stopping just short of point P.

**Series 3:** For the next series of measurements, we started at point C (pure HSO) and traversed to Q on the HSO-1-Bo binary.

**Series 4:** Segment CA was completed by a traverse from pure 1-BO to point Q.

**Series 5:** This series starts with 75 mL of LSO at point B, and adds HSO on the LSO-HSO binary until reaching turn point D, where the composition is nearly $y_1 = 0.75, y_2 = 0.25$. The series then proceeds into the interior of the triangle towards A by adding 1-BO, keeping the LSO/HSO ratio constant. The traverse is stopped at the break point R.

**Series 6:** This series starts with ~75 mL of HSO at point C, and adds LSO on the LSO-HSO binary until reaching turn point F, where the composition is nearly $y_1 = 0.25, y_2 = 0.75$. The series then proceeds into the interior of the triangle towards A by adding 1-BO along FT, keeping the LSO/HSO ratio constant. The series is stopped at the break point T.

**Series 7:** This series starts with ~75 mL of the LSO + HSO binary at point D, and adds HSO until reaching turn point E, where the composition is nearly $y_1 = 0.5, y_2 = 0.5$. The series then proceeds into the interior of the triangle towards A by adding 1-BO along ES, keeping the LSO/HSO ratio constant. The series is stopped at the break point S.

**Series 8:** This series starts with ~75 mL of LSO at point B, and adds HSO until reaching turn point D, where the composition is nearly $y_1 = 0.75, y_2 = 0.25$. The series then proceeds into the interior of the triangle towards A by adding 1-BO along DR, keeping the LSO/HSO ratio constant. The series is stopped at the break point R.

**Series 9:** This series starts with ~75 mL of the LSO + HSO binary at point F, where the composition is nearly $y_1 = 0.25, y_2 = 0.75$, and adds 1-BO until nearly reaching point E.
Series 10: This series starts with ~ 75 mL of pure 1-BO at A, and adds measured masses of the LSO and HSO (individually, i.e., not as binary solution) in a ratio close to one part of LSO to three parts of HSO, until break point T is nearly reached.

Series 11: This series starts with ~ 75 mL of pure 1-BO at A, and adds measured masses of the LSO and HSO (individually, i.e., not as binary solution) in a ratio close to equal parts of LSO and HSO, until break point S is nearly reached.

Series 12: This series starts with ~ 75 mL of pure 1-BO at A, and adds measured masses of the LSO and HSO (individually, i.e., not as binary solution) in a ratio close to three parts of LSO to one part of HSO, until break point R is nearly reached.

Table 1 presents the experimental data.

As discussed above, the balance had a readability and a repeatability of 0.01 g. Except for solutions in Series 10-12, no mass addition was less than 3 g of liquid. This corresponds to a maximum relative error in the mass fraction of the most dilute component of 0.3%. For the binary and ternary solutions closest to a vertex, the most dilute component has a mass fraction between 0.0087 and 0.08. The absolute error in mass fraction should therefore not exceed 0.0003. The solutions in Series 10-12 were prepared by separately adding LSO and HSO. The smallest mass addition was approximately 0.7 g, and close to vertex A, the relative error in mass fraction of the most dilute component could be as high as 1.4%. The largest relative uncertainties in mass fraction occur for the first ternary solution in each of these series. Based on the actual mass additions used to prepare these solutions and the corresponding actual mass fractions, the largest absolute uncertainty in mass fraction for Series 10-12 is less than $1.3 \times 10^{-4}$. 
3.2 EXPERIMENTAL PROTOCOL

Each solution was weighed before and after each trio of index, density, and viscosity measurements in order to accurately account for the loss of solution. The complete measurement protocol was as follows

1. Weigh an empty 250 mL Griffin beaker: \( M_0 \)
2. Weigh the empty beaker + magnetic stir bar: \( M_1 \)
3. Weigh the beaker + magnetic stirring bar + solution: \( M_2 \)
4. Stir the solution (on a magnetic stirrer) for 10-15 minutes to achieve a uniform, thermally equilibrated solution.
5. Perform the index, density, and viscosity measurements.
6. Return as much solution as possible to the beaker after measurements.
7. Weigh the beaker and record the total mass of the beaker + stirring bar + solution: \( M_3 \)
8. Ready to add additional liquid to obtain the next composition.

Thus, the mass of solution before measurements was \( M_2 - M_1 \), and the mass of solution after measurements was \( M_3 - M_1 \).

For each straight-line segment of each solution series, the difference in initial mass fraction and final mass fraction was divided into an equal number of parts and the required mass of the component(s) to be added was computed in order to achieve the targeted mass fraction. This allowed for approximately equal spacing between data points. These “target” values of the mass fractions of the components were set before the measurements, and converted to targeted values of the masses of components to be added to a measured amount of the initial component or solution. After each addition, the mass actually added was used to update the actual solution composition. The difference \( M_3 - M_2 \) (mass of solution lost during measurements) was used to update the remaining mass, which was then used to update the targeted masses and mass addition used to prepare the next solution.
We note that several solutions in Series 1 were prepared by adding uniform increments of mass, which, as shown on the segment BP in Figure 2, did not result in uniform increments of mass fraction. That caused no problem in developing the polynomial fits described in Chapter 4.
In each ternary phase, there are two independent composition variables, which we take as the mass fractions of LSO and HSO (denoted by $y_1$ and $y_2$, respectively) in the oil phase, as the mole fractions of NMP and water (denoted by $x_1$ and $x_2$, respectively) in the polar phase, and as the mass fractions of 1,2-propanediol and CsBr (denoted by $w_1$ and $w_2$, respectively) in the aqueous phase. We used mole fractions in the polar phase, and mass fractions in the aqueous phase because these are the composition variables used by Blanco et al.$^{39}$ and Li et al.$^{40}$ for the same systems. Mass fractions have been used in the oil phase because the light and heavy silicone oils are polydisperse, with each consisting of polymer molecules having a range of chain length and molecular weight. Hence, the LSO and HSO each has a range of molecular weights, with an unspecified molecular weight distribution, so that the number of moles of each chain length, or for all chain lengths, is not known.

**Oil Phase.** The measured oil-phase values of the index of refraction and density were least-squares fitted to bicubic equations of the form

$$n_{\text{oil}}(y_1, y_2) = n_0 + n_1 y_1 + n_2 y_2 + n_3 y_1^2 + n_4 y_1 y_2 + n_5 y_2^2 + n_6 y_1^3 + n_7 y_1^2 y_2 + n_8 y_1 y_2^2 + n_9 y_2^3$$

(1a)

$$\rho_{\text{oil}}(y_1, y_2) = \rho_0 + \rho_1 y_1 + \rho_2 y_2 + \rho_3 y_1^2 + \rho_4 y_1 y_2 + \rho_5 y_2^2 + \rho_6 y_1^3 + \rho_7 y_1^2 y_2 + \rho_8 y_1 y_2^2 + \rho_9 y_2^3$$

(1b)

wheras the dynamic viscosity was first divided by density and then logarithmically transformed and fitted, using a variant of the McAllister equation (cf. Eq. 3 of Blanco et al.$^{39}$)

$$\ln \frac{\nu_{\text{oil}}(y_1, y_2)}{\text{cm}^2\text{s}^{-1}} = a_0 + a_1 y_1 + a_2 y_2 + a_3 y_1^2 + a_4 y_1 y_2 + a_5 y_2^2 + a_6 y_1^3 + a_7 y_1^2 y_2 + a_8 y_1 y_2^2 + a_9 y_2^3$$

(1c)

The coefficients for these fits are shown in Table 2. For the index and density, the rms errors are $5.02 \times 10^{-4}$ and $1.12 \times 10^{-3}$ g/mL, respectively, and the maximum fractional
errors are $1.12 \times 10^{-3}$ and $2.84 \times 10^{-3}$ respectively. For the absolute viscosity, the rms error in $\mu$ is 0.248 and the maximum fractional error is $6.63 \times 10^{-2}$. Figures 3(a-c) show contours of the fitted functions in the oil-phase ternary triangle.

**Polar Phase.** For the polar phase, the tabulated experimental results for index, density, and dynamic viscosity at 293.15 K of Blanco et al.\textsuperscript{39} for 36 ternary compositions, and of Garcia-Abuin et al.\textsuperscript{74} for 11 compositions of each binary solution involving NMP, were used to construct least-squares fitted polynomials of the form

$$n_{polar}(x_1, x_2) = b_0 + b_1x_1 + b_2x_2 + b_3x_1^2 + b_4x_1x_2 + b_5x_2^2 + b_6x_1^3 + b_7x_1^2x_2 + b_8x_1x_2^2 + b_9x_2^3$$  \hspace{1cm} (2a)

$$\rho_{polar}(x_1, x_2) = c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + c_6x_1^3 + c_7x_1^2x_2 + c_8x_1x_2^2 + c_9x_2^3$$  \hspace{1cm} (2b)

The tabulated experimental results of those authors for the dynamic viscosity were used to least-squares fit the kinematic viscosity ($\nu_{polar} = \mu_{polar}/\rho_{polar}$) to the McAllister equation. The same coefficients obtained by Blanco et al. (their Table 7) were obtained by fitting only the ternary data reported by them, with the exception that values for two pairs of interaction coefficients in the McAllister equation are interchanged ($\nu_{13}$ and $\nu_{21}$ are interchanged, as are $\nu_{23}$ and $\nu_{31}$). Blanco et. al. fitted the kinematic viscosity to only their ternary data, whereas we have used both their ternary data and the binary data for NMP + water and NMP + ethanol from an earlier paper by the same group (Garcia-Abuin et al.\textsuperscript{74}) to develop our functional approximations. Hence, the coefficients obtained by us were different from, but consistent with, those of Blanco et. al. For the index and density, the rms discrepancies between our fits and Blanco et. al’s ternary data (at 293.15 K) are $1.88 \times 10^{-3}$ and $3.66 \times 10^{-3}$ g mL\(^{-1}\), respectively, and the maximum fractional discrepancies are $5.28 \times 10^{-3}$ and $1.77 \times 10^{-2}$, respectively. For the absolute viscosity, the
rms discrepancy in $\mu$ is 0.318 mPa s and the maximum fractional discrepancy is 0.219.\(^*\)

Contours of the fitted functions in the polar ternary composition triangle are shown in Figures 4(a-c). We note that our viscosity contours differ somewhat from those of Blanco et al. We believe that Blanco et al. obtained their contours by using plotting software to generate contours directly from their 36 ternary compositions, whereas we obtained our contours from polynomial functions least-squares fitted to 58 composition points, including 22 on two of the boundaries of the triangle. Substantial confirmation for that hypothesis comes from using OriginLab plotting software to produce viscosity contours in the ternary composition triangle using the 36 “interior” points of Blanco et al.\(^{39}\) The contours were nearly identical to those shown by those authors.

**Aqueous phase.** As discussed later in Chapter 7, the choice of the polar and the oil phase is complicated by significant solubility of 1-bromooctane in the polar phase. The second counter-phase was taken to be the ternary 1,2-propanediol + CsBr + water system, as discussed in Chapter 2. (In what follows, we refer to 1,2-propanediol as the “diol.”)

Index, density, and viscosity data for the ternary diol + CsBr + water system were recently reported by Li et al.,\(^{40}\) who also reported saturation data for the same ternary system. In addition, binary data for the diol + water binary\(^{78-83}\) and for the CsBr + water binary\(^{84-89}\) are also available. Bicubic polynomials were fitted to the data for index, density and viscosity (as discussed in Chapter 4), using all of the 298.15 K ternary data of Li et al.\(^{40}\) except for the anomalous viscosity measurement at $w_1 = 0.0791$, $w_2 = 0.2088$.\(^{†}\)

We included values of the CsBr + water density values of Beattie (see, Ref. 90) based on

\(^*\) There are 10 binary and ternary compositions at which the relative discrepancy between the dynamic viscosity reported by Blanco et. al.\(^{39}\) or García-Abuín\(^{74}\) differs from the value obtained from our fit by 10% or more. (When dynamic viscosity values computed from Blanco et. al.’s McAllister fit are compared to Blanco’s ternary data, there are four points at which the discrepancy exceeds 10%. That there are more points exceeding this threshold when we use values fitted from our McAllister equation is not surprising given that our fit to the McAllister equation and the resulting comparison include 22 binary compositions not considered by Blanco et. al.) These discrepancies are much larger than can be attributed to measurement error in their viscosity data, which are thought to be accurate to about one part in one thousand. While it is not clear whether these discrepancies are due to inadequacy of the ternary McAllister equation used to fit the data, or to errors in the composition of the solutions in Ref. 4 (see Chapter 7), the significant nonideality of the NMP + ethanol + water ternary\(^{39,74,75-77}\) lends considerable support to the former hypothesis.

\(^†\) Following a private communication with A. J. Pearlstein, the corresponding author of Ref. 40 (Mancheng Hu) stated that he had performed two new measurements at each of two compositions very near to the composition in question. The values he communicated are consistent with the anomalous value of the kinematic viscosity in Ref. 40.
his critical review of the older data\textsuperscript{86-89}, and the viscosity data for the same binary reported by Desnoyers and Perron\textsuperscript{84} (with their reported values of kinematic viscosity being converted to dynamic viscosity using a least-squares fit to the density values\textsuperscript{90} for the binary system. (The viscosity data of Patil et al.\textsuperscript{85} cover a much more limited range of composition than those of Desnoyers and Perron\textsuperscript{84}, and were not used.) We included the data for density of the diol + water binary reported by Zemánková et al.\textsuperscript{80} and Maximino\textsuperscript{78}, the index data of Verbeeck,\textsuperscript{82} and the viscosity data of Tanaka\textsuperscript{79} and Maximino,\textsuperscript{78} all for the same binary system. (We did not use the density data of Romero et al.\textsuperscript{81}, because it was less internally consistent than the other density data used, and also not consistent with the other density data.) Figures 5(a-c) show contour plots for index, density, and viscosity, respectively, for the aqueous phase, all on the side of the saturation curve in which the only phase is liquid.
CHAPTER 5
ACCESSIBLE RANGE OF DENSITY AND VISCOSITY RATIOS ACHIEVABLE
IN INDEX-MATCHED PHASES

The key question to be asked about any index-matched pair of phases is “for what values of the density ratio \( \gamma = \rho_{SA}/\rho_{SB} \) and viscosity ratio \( \phi = \mu_{SA}/\mu_{SB} \) can the system serve as a surrogate?” The answer to that question requires consideration of all the index values for which \( n_{SA} \) can be matched to \( n_{SB} \).

The approach taken in the present study is first discussed for the polar/oil pair. Modifications required by the limited solubility of CsBr in water and in the diol are discussed later in this chapter.

**Polar/oil pair.** The ranges of \( n_{oil} \) and \( n_{polar} \) are first determined from Figures 3a and 4a, respectively, as
\[
1.3946 = n_{LSO} \leq n_{oil} \leq n_{1-BO} = 1.4493 \quad \text{and} \quad 1.3330 = n_{1-H2O} \leq n_{polar} \leq n_{NMP} = 1.4706,
\]
respectively. To match the indexes, consideration is restricted to the intersection of those two ranges, i.e., the range of index \( [n_L, n_U] \) that can be achieved in both phases, where \( n_L = 1.3946 \) is the index at the pure-LSO vertex of the ternary triangle and \( n_U = 1.4493 \) is the index of the oil phase at the pure LSO vertex.

For \( n_{polar} = 1.3946 \), Figures 4a and 4b show that there is a range of compositions (and hence density and viscosity combinations) possible along a constant-\( n \) contour in the polar-phase ternary triangle. Thus, for \( n_L = 1.3946 \), the index of the oil phase is at the pure LSO vertex of the oil phase ternary triangle, and the accessible values of \( \gamma \) and \( \phi \) lie along a curve on which \( \gamma = \rho_{polar}/\rho_{LSO} \) and \( \phi = \mu_{polar}/\mu_{LSO} \), where \( \rho_{polar} \) and \( \mu_{polar} \) depend on the position of the \( n_{polar} = 1.3946 \) curve. Similarly, for \( n_U = 1.4493 \), the index of the oil phase is at the 1-BO vertex of the oil-phase ternary triangle, and the accessible values of \( \gamma \) and \( \phi \) lie along a curve on which \( \gamma = \rho_{polar}/\rho_{1-BO} \) and \( \phi = \mu_{polar}/\mu_{1-BO} \). The \( \phi - \gamma \) curves for these limiting values of \( n \) are shown in Figure 6.

For each intermediate value of \( n \), however, there is a region of accessible \( \gamma \) and \( \phi \).
In other words, for each index value in \([n_L, n_U]\), there is a curve in each ternary triangle on which the index has the value \(n\). (This differs from the case at the limiting values of index, in that for those \(n\), there is one phase in which the composition is a pure component.) For the ternary systems of interest, for each index value in the ternary triangle there is a single contour whose two endpoints lie on legs of the ternary triangle, or on one leg and the saturation curve inside the triangle. Figures 3a, 3b, and 3c show that the density and viscosity of the oil phase vary monotonically with arclength on each constant-\(n\) contour. Thus, for the oil-phase, the lowest and highest accessible values of \(\rho_{\text{oil}}\) and \(\mu_{\text{oil}}\) will be found on the edges of the ternary triangle. The contours shown in Figures 4a, 4b, and 4c show that the density and viscosity of the polar phase also vary monotonically with arclength on each constant-\(n\) contour, so that the lowest and highest accessible values of \(\rho_{\text{polar}}\) and \(\mu_{\text{polar}}\) will also be found on the edges of the triangle. The minimum and maximum densities thus found in the polar phase are denoted by \(\rho_{\text{polar}, \text{min}}(n)\) and \(\rho_{\text{polar}, \text{max}}(n)\), respectively. Similarly, (2a) and (2b) are used to determine the minimum and maximum densities that can be achieved in the oil phase, which are denoted by \(\rho_{\text{oil}, \text{min}}(n)\) and \(\rho_{\text{oil}, \text{max}}(n)\), respectively. For this value of \(n\), the smallest and largest accessible values of \(\rho_{\text{polar}}/\rho_{\text{oil}}\) are therefore \(\gamma_{\text{min}}(n) = \rho_{\text{polar}, \text{min}}(n)/\rho_{\text{oil}, \text{max}}(n)\) and \(\gamma_{\text{max}}(n) = \rho_{\text{polar}, \text{max}}(n)/\rho_{\text{oil}, \text{min}}(n)\), respectively.

A more general approach that properly deals with systems in which either the density or viscosity varies nonmonotonically along at least one constant-index contour in at least one phase is as follows. First the minimum and maximum achievable densities (and viscosities) for a given value of index between \([n_L, n_U]\) are determined for each phase. This is done as follows. For a given \(n\), the composition variable, \(x_1\), is discretized as 0, 0.001, 0.002, ..., 1. For each \(x_1\), we can then determine \(x_2\) from (2a), since \(n\) is specified. The density and viscosity are computed for the \((x_1, x_2)\) pair and stored. After the entire composition space has been scanned, \(\rho_{\text{polar}, \text{min}}(n)\), \(\rho_{\text{polar}, \text{max}}(n)\) and \(\mu_{\text{polar}, \text{min}}(n)\) and \(\mu_{\text{polar}, \text{max}}(n)\) are determined. By a completely analogous procedure, \(\rho_{\text{oil}, \text{min}}(n)\), \(\rho_{\text{oil}, \text{max}}(n)\) and \(\mu_{\text{oil}, \text{max}}(n)\) are determined.
\( \rho_{\text{oil}, \max}(n) \), \( \mu_{\text{oil}, \min}(n) \) and \( \mu_{\text{oil}, \max}(n) \) are determined. Such an approach takes into account cases in which the minima/maxima lie inside the triangle instead of only on a boundary (as for the monotonic variation of density and viscosity on the constant-\( n \) contours described in the previous paragraph for the oil and polar phases). To account for the fact that this approach typically “misses” the points at which the constant-\( n \) contours intersect the triangle boundaries, the approach adopted here is a combination of the two. We find the density and viscosity at the intersections of the index contours with the boundaries, and also search the composition space by discretization. The minimum and maximum values found are accepted as the final minima and maxima.

A large number of points (on the order of 100) are chosen for \( \gamma \) in the range \([\gamma_{\min}(n), \gamma_{\max}(n)]\). For each density ratio, the range of accessible viscosity ratios is determined as follows. First, consider a line segment in a rectangular region of the \( \rho_{\text{polar}} - \rho_{\text{oil}} \) plane, as shown in Figure 7. The boundaries of the rectangle (determined as described above) depend on \( n \), and the slope of the line is \( \gamma \). Depending on \( n \) and \( \gamma \), there are four qualitatively different possibilities, denoted by lines 1, 2, 3, and 4. The range of \( \rho_{\text{oil}} \) corresponding to the end points of the line is divided into 100 intervals. For every given combination \( \gamma \) and \( \rho_{\text{oil}} \), we compute \( \rho_{\text{polar}} = \gamma \rho_{\text{oil}} \). Then for the given combination of \( n \) and \( \rho_{\text{oil}} \), the composition \((y_1, y_2)\) is evaluated from (1a) and (1b) using the method of resultants\(^9\) to solve the pair of bivariate polynomials, in order to ensure that all of the compositions are found. For the cases considered, only one acceptable composition\(^*\) was found, and the corresponding value of \( \mu_{\text{oil}} \) is computed and stored. Similarly, \( \mu_{\text{polar}} \) is computed for each combination of \( n \) and \( \rho_{\text{polar}} = \gamma \rho_{\text{oil}} \) and stored. Finally, for each \( n \) and \( \gamma \), the viscosity range is evaluated as \( \phi_{\min}(n, \gamma) = \min(\mu_{\text{polar}})/\max(\mu_{\text{oil}}) \) and \( \phi_{\max}(n, \gamma) = \max(\mu_{\text{polar}})/\min(\mu_{\text{oil}}) \).

\(^*\) A composition is acceptable if it a) is real, b) lies in the admissible range of composition (within the ternary triangle in every case, and on the correct side of the saturation curve for the aqueous phase), and c) corresponds to the desired values of index and density.
For each $n$, one thus obtains a region of accessible density ratios and viscosity ratios, one of which is shown in Figure 8.

Figure 9 shows an overlay of several such regions, each for a different value of the index. The combination of density ratios and viscosity ratios available with this fluid pair is the union of those regions, and can be easily understood as the exterior envelope of the curves shown.

**Aqueous/oil pair.** A similar analysis was performed for the aqueous/oil pair. The principal difference is that the components of the aqueous phase are not fully miscible over the entire composition space, and so the traverses and analysis must account for the saturation curve as shown in Figure 5.
CHAPTER 6
A SURROGATE FOR LIQUID CO\textsubscript{2} AND WATER

6.1 POLAR PHASE-OIL PHASE PAIR FOR SURROGATE

An important class of liquid/liquid systems in which a surrogate approach is of great interest is that in which the pressure is necessarily very high. An important example is the CO\textsubscript{2}-H\textsubscript{2}O system, which is of interest in understanding transport in porous geological formations into which CO\textsubscript{2} has been injected for storage\textsuperscript{92}, as well as in understanding the fate of CO\textsubscript{2} that has escaped from natural vents in the ocean\textsuperscript{93} or from sub-seabed storage.\textsuperscript{94} Here, the availability of a surrogate system not only allows for optical diagnostics, but also enables experiments to be conducted without the cost and limitations of building and operating a high-pressure flow facility. The availability of a pair of surrogate liquids with the same density and viscosity ratios, that can be used at normal pressure, and which can be index-matched at wavelengths appropriate for optical diagnostics, is therefore of considerable interest.

Here, we focus on the CO\textsubscript{2}-H\textsubscript{2}O system at a typical deep-ocean temperature of 0°C. For illustrative purposes, we consider pure water rather than seawater. In this case, at fixed temperature, the density and viscosity depend only on pressure. We use data for CO\textsubscript{2} density and viscosity from van der Gulik\textsuperscript{95}. For water, we use the density data of from Kell and Whalley\textsuperscript{96}, and viscosity data from Schmelzer\textsuperscript{97}.

For the chosen surrogate system of the polar and oil phase, there is a significant range of overlap for the CO\textsubscript{2}-H\textsubscript{2}O system at 0°C as function of pressure, for which density and viscosity ratios could be matched. The overlap between the “real” and “surrogate” in the ratio-ratio plane is maximized at \( n = 1.4012 \), the index value shown in Figure 10. Here the surrogate phases allow for matching of the index at combinations of the density ratio and viscosity ratio corresponding to the CO\textsubscript{2}-water system at pressures between 2.5 MPa to 10.3 MPa, and from 13.8 MPa to 50.0 MPa. There is less overlap at
other values of the index (and indeed, no overlap for many values of $n$), thus illustrating the value of the “extra” degree of freedom provided by using two ternary solutions (as opposed to one ternary and one binary). We also note that the availability of four degrees of freedom can allow not only for matching the index of the two surrogate fluids along with the density and viscosity ratios of CO$_2$-H$_2$O system, but also matching the index to that of a transparent solid. In the present case, $n = 1.4012$ provides an excellent match to PDMS.$^{98}$

6.2 AQUEOUS PHASE-OIL PHASE PAIR FOR SURROGATE

Figure 11 shows the corresponding overlap between the CO$_2$-water data and the accessible regions of density ratio and viscosity ratio for the aqueous/oil pair. Here, the blue curve represents the situation in which the ternary aqueous phase serves as the surrogate for the liquid CO$_2$ and the ternary oil phase serves as the surrogate for water. But there is no scientific reason why the roles cannot be reversed, so the red curve shows the situation in which the ternary aqueous phase serves as the surrogate for water and the ternary oil phase serves as the surrogate for liquid CO$_2$. It is easily seen that two curves are related by the relation $\phi_{\text{red}} \rightarrow 1/\phi_{\text{blue}}$, $\gamma_{\text{red}} \rightarrow 1/\gamma_{\text{blue}}$. While the blue curve does not intersect the accessible range of $\gamma$ and $\phi$, the red curve does, showing that the surrogate system has the capability to match the density and viscosity ratios of the CO$_2$-water system at $0^\circ$C over at least the range 9.95 MPa to 21.0 MPa. We note that computations with finer increments of $\Delta n$ would increase this range of pressure to some extent.
CHAPTER 7
COMPATIBILITY TEST FOR POLAR AND OIL PHASES

After the conclusion of all the analysis, a simple experiment was performed in which one composition of the oil phase and one composition of the polar phase were prepared and brought together (by emulsification). The main purpose of this experiment was to check for solubility of any of the components in the opposite phase. If solubility appeared to be low, we would then measure index, density, and viscosity to see how much the measured properties were affected by interphase equilibration, and how well the polynomials approximated the properties (particularly the index) in regions of the composition space relatively far from points were solutions were data was available from our experiments with the oil phase, or from the literature values of Blanco et al and García-Abuin et al. Samples would then be submitted for analysis at the Mass Spectrometry Center of the UIUC School of Chemical Sciences in order to quantitatively assess solubility.

To prepare the polar phase, a 250 ml Griffin beaker and stirring bar were weighed and tared, and 44.92 g of NMP was added. Water was gradually added until the balance read 61.27 g. It was observed that the reading on the balance fell quite smoothly from 61.27 g to 61.15 g in less than three minutes. It was also observed that a significant amount of condensation appeared on the side walls of the beaker. The beaker was also warm to the touch. These facts strongly suggested that there is an appreciable heat of mixing associated with addition of NMP to water, which caused the water to evaporate, thereby altering the intended composition of the solution.

Mass addition ceased, but the mass of solution was measured at regular intervals. About five minutes after the addition ceased, the mass of the solution stabilized at a reading of 61.15 g. The loss of water was accounted for and appropriate masses of NMP,
water, and ethanol were added to achieve a mass fraction composition of (0.200, 0.400, 0.400).

About 100 ml of the prepared polar phase was poured into a 250 ml screw-top Erlenmeyer Flask, and about 100 ml of a solution of a heavier oil phase (with mass fractions 0.1877, 0.1877, and 0.6246 of LSO, HSO, and 1-BO, respectively) prepared during the earlier series of oil phase measurements was added to it. The cap of the flask was immediately screwed down. A significant cloudiness developed upon pouring. The oil phase quickly settled to the bottom of the flask. The cloudiness cleared within two minutes from the bottom and the top, being confined to a progressively thinner layer in between. A sharp interface between the two phases was visualized by the presence of a few bubbles, some very small particles (that had possibly been in the flask) and, of course, a difference in refractive index. The position of the interface was noted on the flask.

The flask was then shaken vigorously to form a very fine emulsion with a very large number of small droplets, in order to promote interphase mass transfer. Once again, the solution clarified with a sharp interface, this time within 10 minutes. Visual observation revealed that the position of the interface had dropped appreciably. This led to the conclusion that a measurable amount of one of the oil-phase components had dissolved into the polar phase.

A more thorough literature search than had been conducted previously revealed a relatively new synthetic procedure\textsuperscript{99} in which NMP is a solvent in which alkylzinc compounds can be prepared by direct reaction of alkyl bromides (and specifically 1-bromooctane) with zinc dust at room temperature. This solubility showed that the NMP + water + ethanol polar phase was not a good choice as a counter-phase for our oil phase. Beyond the issue of solubility of the 1-BO in this polar phase, we note that the heat of solution of NMP with water\textsuperscript{75,77} (-5.05 kcal/mol at infinite dilution of NMP) is negative, so that heat is released. For ethanol, heat is evolved when small amounts of ethanol are
added to NMP and heat is absorbed when small of amounts of NMP are added to ethanol\textsuperscript{76}. When heat is evolved, the result can be in measurable evaporation during the mixing process, especially when one of the components has a significant vapor pressure. This calls into question the solution compositions for which Blanco et. al.\textsuperscript{39} and García-Abuín\textsuperscript{74} reported their measurements. (We note that those authors made no reference to either the heat of mixing, or to any precautions taken to avoid evaporation.)
All of our index measurements were performed using 589 nm as the wavelength, with imperfect temperature control, and for each phase as a system of known composition of the three nominal components. Here, we discuss potential errors associated with each of these issues, and how each can be ameliorated if it is significant.

8.1 DEPENDENCE OF INDEX MISMATCH ON WAVELENGTH

For every material for which measurements have been made, the index depends on wavelength\(^\text{100}\). Of the components or solutions we have considered, pure water and ethanol are the only two for which index data have been reported as a function of wavelength. For water, Sellmeier fits by Daimon and Masumura to their data at 57 wavelengths in the range \(181 \text{ nm} < \lambda < 1129 \text{ nm}\) show that the index at 20°C varies from 1.333358 at 589 nm to 1.335381 at 532 nm (the Nd:YAG laser wavelength typically used in PIV). For ethanol, least-squares fits of the data of Moreels et al.\(^\text{101}\) to a Cauchy equation (Eq. 5 of Rheims et al.\(^\text{102}\)) show that for 20°C the index varies from 1.361604 at 589 nm to 1.363665 at 532 nm. Absent data for the wavelength dependence of the index of the other components (not to mention the possibility that wavelength dependence of index for any of their ternary solutions is not an additive function of the dependences for each component), we can say that the index is expected to be a monotonically decreasing function of wavelength for all components, and so that if the indexes of the two phases are matched at 589 nm, the index mismatch at other wavelengths will result from a difference in the magnitudes (but presumably not the signs) of the derivatives \(\partial n_{\text{polar}} / \partial \lambda\) and \(\partial n_{\text{oil}} / \partial \lambda\).

In any particular application, the degree to which the indexes of the two phases must be matched will typically depend on the details of the optical diagnostics. Since the
index mismatch at any wavelength will depend on the compositions of the two phases, and since the index mismatch at the wavelength of interest can be determined interferometrically, a practical solution to the problem will be to adjust the composition along a curve of constant \( \rho_{\text{polar}} / \rho_{\text{oil}} \), and \( \mu_{\text{polar}} / \mu_{\text{oil}} \). Such curves, for the isolated ternary solutions, can be constructed using the polynomial fits developed in Chapter 4.

We also note that the four degrees of freedom provided by the four composition variables allow, in principle, for one to achieve desired values of the density and viscosity ratios, while simultaneously matching the indexes of the two solutions at two wavelengths. This is of interest in planar laser-induced fluorescence, where one is concerned about both the planarity of the excitation sheet at one wavelength and straight-line propagation of the fluorescence at the emission wavelength. While one might decide to strike a balance between the degree of index mismatch at the two wavelengths, such a compromise might not be necessary. We have not explored this possibility.

8.2 DEPENDENCE OF INDEX MISMATCH ON TEMPERATURE

For water and ethanol, the dependence of index on temperature is well known. At 589 nm, the index of water decreases from 1.333358 at 20°C to 1.332972 at 24°C\(^{103}\), while for ethanol, the decrease is from 1.361604 at 20°C to 1.358972 at 25°C\(^{101}\). In those situations when the optical diagnostic approach employed requires close matching of index, it will be necessary to control the temperature accordingly in order to avoid a) departures from the temperature at which the index has been matched, and b) spatiotemporal variation of temperature within the facility. The flexibility provided by the four degrees of freedom in the current approach will allow the first issue to be addressed (as discussed for wavelength dependence of \( n \)), provided that the temperature is known and can be maintained steady and uniform. The extent to which spatiotemporal variation of temperature within the facility will be a problem will need to be assessed on a case-by-case basis.
8.3 EFFECTS OF NONZERO SOLUBILITY

Since no liquid is completely insoluble in any other liquid, each of the components of each phase will have a nonzero solubility in the opposite phase. When the two phases are brought together in a flow facility, the two phases will undergo compositional equilibration over time, with each component diffusing across the interface between the phases. At equilibrium, the compositions of the two phases will depend on the relative amounts of the six components, weakly on temperature, and very weakly on pressure.
CHAPTER 9
OTHER TERNARY SYSTEMS

In this section, we discuss how the approach can be extended, both to other pairs of ternary liquids and to other four-degree-of-freedom systems, as well as to systems with additional degrees of freedom.

First, as mentioned in Chapter 2, a wider range of $\mu_{\text{polar}}/\mu_{\text{oil}}$ can be had by using different silicone oils in the oil phase. It is expected that this will translate into a larger domain in the $\rho_{\text{polar}}/\rho_{\text{oil}} - \mu_{\text{polar}}/\mu_{\text{oil}}$ plane. A larger range of density or index (or both) in the oil phase can also be achieved by replacing 1-bromo-octane in the oil phase. Before we settled on 1-bromo-octane, we considered perfluoro-hexyloctane and several other fluorinated alkanes with very low index (less than water) and relatively high density ($>1.3\text{g/mL}$) that are currently used as ophthalmic tamponades. But we could not identify a source willing to provide bulk material (even at a purity less than suitable for medical applications) at a reasonable price. The value of that approach would have been to significantly extend the range of matchable $n$ on the low end, with significant “cost” at the high end.

In the polar phase, glycerol can be substituted for the diol we used, reducing the cost of the polar phase, and providing additional range for the polar-phase viscosity. The data of Li et al.\textsuperscript{40} show that CsBr is considerably more soluble in pure glycerol than in our diol, and strongly suggest that the same will be true for NaBr. If that is indeed the case, then replacing the diol with glycerol will presumably expand the range of accessible viscosity ratios, with the potential “costs” being those associated with use of a more hygroscopic liquid. Another issue with glycerol is that its viscosity is considerably more sensitive to temperature than is that of the diol. That is a potential advantage if one wants to use temperature as an additional degree of freedom, and a disadvantage if temperature control in an experimental facility is problematic.
Additional degrees of freedom can be realized with two ternary phases (or, for that matter, with other six-component systems) if the dependence of the index, density, and viscosity on temperature or wavelength is measured and accounted for, say, in a polynomial fit. As noted above, there are some 35 different ternary systems for which index, density, and viscosity measurements have been reported simultaneously in a single paper, to higher precision than our measurements. For many of those systems, measurements of all three properties have been reported at more than one temperature, and so the measurements are not particularly onerous. The data can then be fitted to appropriate temperature-dependent generalizations of Eqs. 1(a-c), and the temperature can be chosen as an additional variable, thus providing a fifth degree of freedom. When one or both of the phases has a component (in the case of the polar phase, the diol) whose viscosity depends strongly on temperature, this can allow for significant temperature variation in the accessible part of the $\rho_{\text{polar}}/\rho_{\text{oil}} - \mu_{\text{polar}}/\mu_{\text{oil}}$ plane.

Our work on the aqueous/oil pair suggests that replacement of CsBr by NaBr as the salt would be advantageous. (The more popular choice of NaI was rejected because of its known, room-temperature, uncatalyzed reaction with 1-bromoocctane to form 1-iodooctane and NaBr. This reaction, which in a system using 1,2-propanediol + NaI + water and LSO + HSO + 1-bromoocctane might occur at the interface, is also thought to be a problem for ZnI$_2$.) Sodium bromide is much less expensive and considerably more soluble in water than is CsBr, and we expect that it will be more soluble in the diol, both contributing to a considerable increase in the size of the region in the ternary triangle wherein the three components are fully miscible.

All of the components considered can be handled safely in the laboratory, in bulk, with normal precautions. The diol is on the US FDA's list of "Generally Recognized as Safe" materials, and is widely used in foods and beverages. It has a much lower vapor pressure than ethanol (0.08 mm Hg at 20°C, versus 44.6 mm Hg for ethanol) and is considerably less flammable. The salt is also relatively nontoxic. While it should not be
taken internally, it has a long history of use in human and veterinary medicine, and has physiological effects similar to the active ingredient (potassium bromide) in the over-the-counter preparation known as Bromo Seltzer prior to its 1975 reformulation. It finds extensive use in dense drilling fluids used by the oil industry. The 1-bromooctane has a low vapor pressure (0.34 mm Hg at 20°C), and the major hazard associated with it is toxicity to aquatic life. The silicone oils are quite inert, and are routinely handled with minimal safety measures.
CHAPTER 10
CONCLUSIONS

For a ternary solution consisting of light silicone oil + heavy silicone oil + 1-bromooctane and a counter-phase solution consisting of either N-methyl-2-pyrrolidone + water + ethanol, or 1,2-propanediol + CsBr + water, we have shown how the compositions of a pair of phases can be chosen to match their index of refraction, and to simultaneously achieve a range of density ratios and viscosity ratios of interest in two-phase flow studies. We have shown that both of these solution pairs provide overlap with the density ratio and viscosity ratio of liquid CO$_2$-water over a range of pressure at 0°C in the latter system.

For the N-methyl-2-pyrrolidone + water + ethanol counter-phase, measurable dissolution of 1-bromooctane into the polar phase appeared to have occurred. There is good reason to believe that the other counter-phase (1,2-propanediol + CsBr + water) will not have solubility problems with the oil phase, and the much lower cost and greater solubility of NaBr in water (and probably 1,2-propanediol) suggests that 1,2-propanediol + NaBr + water will be a good counter-phase for our light silicone oil + heavy silicone oil + 1-bromooctane oil phase.
REFERENCES

1. Adrian, R. J., “Particle-Imaging Techniques for Experimental Fluid Mechanics,” 


Figure 1. Cost-minimizing sequencing of solution preparation and measurement. Each color represents a single “traverse” originating from a point on a binary boundary of the ternary composition triangle, and terminating at a “break point” (P, R, S, T, Q) or at “turn point” E. The arrows denote the direction of traverse as liquid is added.

Figure 2. Compositions at which index, density, and viscosity measurements were made.
Figure 3. Contours of (a) refractive index, (b) density in g/mL, and (c) dynamic viscosity in mPa·s for the oil phase, determined from the bicubic polynomials fitted to data at the 120 compositions at which measurements were made in the present work. $y_1$, $y_2$, and $y_3$ are the mass fractions of LSO, HSO, and 1-BO, respectively.
Figure 4. Contours of (a) refractive index, (b) density in g/mL, and (c) dynamic viscosity in mPa s, for the polar phase, determined from the bicubic polynomials fitted to data at the 58 compositions at which Blanco et al. (2012) and García-Abuin et al. (2011) measured properties. $x_1$, $x_2$, and $x_3$ are the mole fractions of NMP, water, and ethanol, respectively.
Figure 5. Contours of (a) refractive index, (b) density in g/mL, and (c) dynamic viscosity in mPa s, for the polar phase, determined from the bicubic polynomials fitted to the experimental data of Li et al.\textsuperscript{40}. \(w_1\), \(w_2\), and \(w_3\) are the mass fractions of 1,2-propanediol, CsBr, and water, respectively.
Figure 6. Limiting case of accessible ratios of density and viscosity for (a) $n = 1.3946$, the smallest matchable value of the index, and (b) $n = 1.4493$, the largest matchable value of the index.
Figure 7. Graphical illustration of the procedure by which the upper and lower values of \( \rho_{\text{polar}} \) and \( \rho_{\text{oil}} \) are determined for a given value of \( \rho_{\text{polar}} / \rho_{\text{oil}} \) at each \( n \).

Figure 8. Accessible region of density and viscosity ratio for \( n = 1.4100 \). The kinks in the lower and upper bound correspond to the points where a value of \( \gamma_{\min}(n) \) or \( \gamma_{\max}(n) \) switches from one line to another in the \( \rho_{\text{polar}} - \rho_{\text{oil}} \) plane as shown in Figure 7.
Figure 9. Boundaries of the accessible regions in the $\frac{\rho_{\text{polar}}}{\rho_{\text{oil}}} - \frac{\mu_{\text{polar}}}{\mu_{\text{oil}}}$ for 18 values of the index. At the two limiting values of the index (1.3946 and 1.4493), the region collapses to a curve, as shown in Figures 6a and 6b.

Figure 10. - - - : density ratio ($\frac{\rho_{\text{CO}_2}}{\rho_{\text{H}_2\text{O}}}$) and viscosity ratio ($\frac{\mu_{\text{CO}_2}}{\mu_{\text{H}_2\text{O}}}$) at 0°C parametrized by pressure; --- : boundary of accessible region of density ratio ($\frac{\rho_{\text{polar}}}{\rho_{\text{oil}}}$) and viscosity ratio ($\frac{\mu_{\text{polar}}}{\mu_{\text{oil}}}$) for the polar and oil phases, index-matched at $n = 1.4012$. 

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Figure 11. Overlap between the density ratio/viscosity ratio curve for CO$_2$-water and the accessible region of density ratio and viscosity ratio for the surrogate aqueous/oil pair. Each black boundary delimits the combinations of density and viscosity ratios accessible for a given $n$ in the range of $n$ in which the index values of the two phases overlap. The nine values of $n$ for which boundaries are shown lie between 1.395 and 1.435, with a uniform increment of 0.005. The blue curve represents the situation in which the aqueous and oil phases serve as surrogates for CO$_2$ and water, respectively, and the red curve the situation in which the aqueous and oil phases serve as surrogates for water and CO$_2$, respectively. Those two curves are related by the relation $\phi_{red} \rightarrow 1/\phi_{blue}$, $\gamma_{red} \rightarrow \gamma_{blue}$. 
### TABLES

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**Table 1.** Experimental measurements of index, density, and absolute viscosity for the ternary oil phase, light silicone oil (1) + heavy silicone oil (2) + 1-bromooctane (3)
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**Table 1.** (cont.) Experimental measurements of index, density, and absolute viscosity for the ternary oil phase, light silicone oil (1) + heavy silicone oil (2) + 1-bromooctane (3).
<table>
<thead>
<tr>
<th>$y_1$</th>
<th>$y_2$</th>
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<th>Index</th>
<th>Density (g/mL)</th>
<th>Viscosity (mPa-s)</th>
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Table 1. (cont.) Experimental measurements of index, density, and absolute viscosity for the ternary oil phase, light silicone oil (1) + heavy silicone oil (2) + 1-bromooctane (3).
<table>
<thead>
<tr>
<th>$y_1$</th>
<th>$y_2$</th>
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<th>Index</th>
<th>Density (g/mL)</th>
<th>Viscosity (mPa-s)</th>
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**Table 1.** Experimental measurements of index, density, and absolute viscosity for the ternary oil phase, light silicone oil (1) + heavy silicone oil (2) + 1-bromooctane (3).

<table>
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<tr>
<th>$i$</th>
<th>Index Coefficients ($n_i$)</th>
<th>Density Coefficients ($\rho_i$)</th>
<th>Viscosity Coefficients ($a_i$)</th>
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<td>1.43629259\times10^{-2}</td>
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**Table 2.** Coefficients of the bicubic polynomials least-squares fitted to the experimental index, density, and viscosity data for the oil phase.