The Influence of Chemical Composition on the Refractive Index Thermal Coefficient of Liquids

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ABSTRACT

Liquids have been shown to be very effective in the design of apochromatic lenses. The incorporation of abnormal liquids is complicated by their large thermal coefficients of refractive index (dn/dT). To make a glass-liquid design thermally stable, two liquids with different dn/dT and dispersions are typically used. This paper, which extends previously reported investigations of liquid dn/dT dependencies in the visible spectrum (SPIE Volume 2512, 1995), explores the dependence of dn/dT, abnormal dispersion, and composition for a number of liquids.

The optical property measurements were made at the Vavilov State Optical Institute, St. Petersburg, Russia, in collaboration with the Lockheed Martin Advanced Technology Center, Palo Alto, California.

Key Words: liquids, dispersion, refractometry, refractive index, chromatic aberration, apochromatic design.

INTRODUCTION

During the last ten years more and more scientific attention has been attracted to new and unique classes of optical materials for designing refractive optical systems[1-6]. One such optical material class is that of optical liquids. The essence of the uniqueness of optical liquids is that some liquids appear to have great abnormal dispersion properties, as compared with those of traditional optical materials (i.e., glasses or crystals). It is the abnormal dispersion of a material incorporated into the optical design of a lens system that can be used to cause the system to be apochromatic.

Abnormal dispersion, which physically originates from the shape of the dispersion curve for a material in the visible spectral region, can be mathematically defined in terms of Buchdahl dispersion coefficients. In Figure 1, the primary and secondary Buchdahl dispersion coefficients for a number of Schott optical glasses and optical liquids are presented. In this Figure, both liquids with well known compositions and liquids whose composition is proprietary to Lockheed Martin(#295990, #400513, #550206 and #642134) are plotted.

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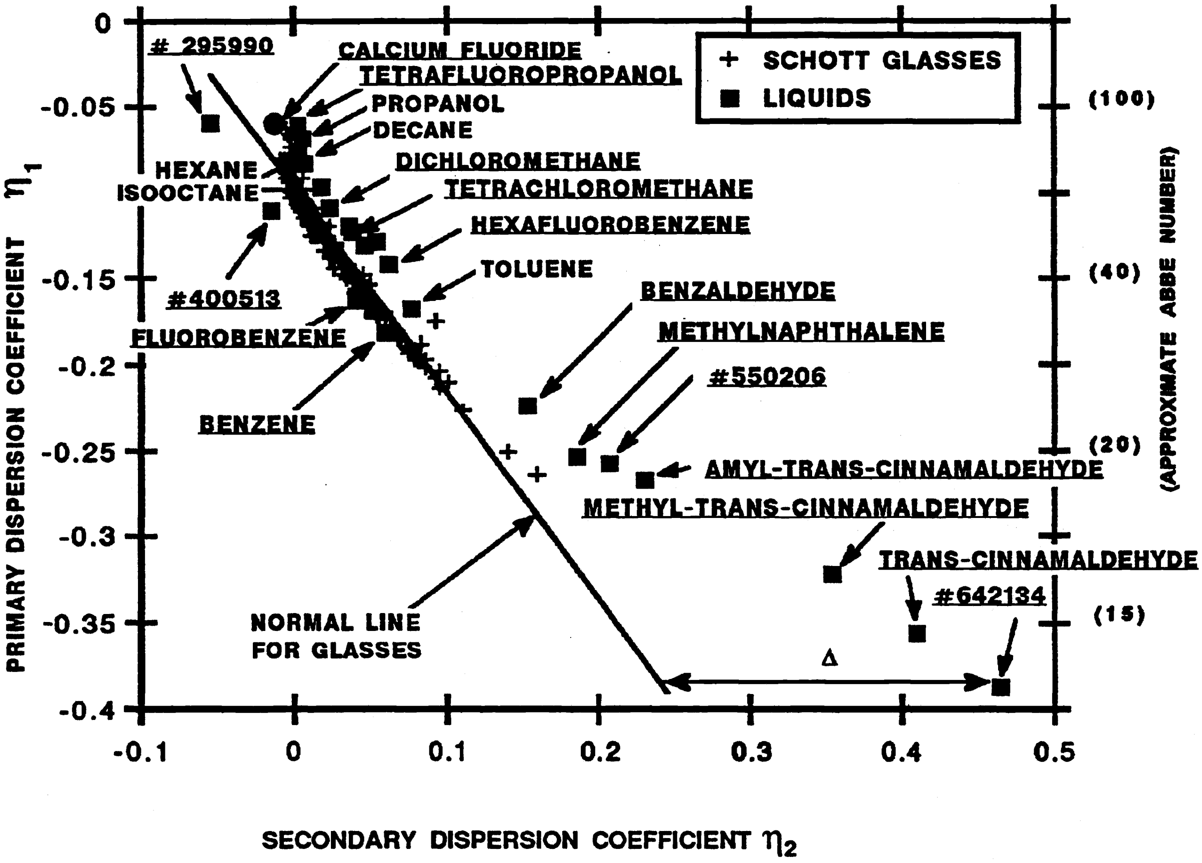


Figure 1

The abnormal dispersion of an optical material is characterized with the following parameter:

$$\Delta = | \eta_2 \text{ (material) } - \eta_1 \text{(normal line)} |$$

In the Buchdahl dispersion map, the "Normal line" is the location of optical materials that are referred to as having normal dispersion. To be normally dispersive, an optical material has a common (or normal) correlation between the refractive index and dispersion over the visible spectral region. Most of the optical glasses are material types that are known to have normal dispersion.

The greater the value of Δ for a particular material, the more effectively the lens system chromatic aberration can be corrected, by incorporating this particular material. As it can be seen from Figure 1, optical liquids have large values of Δ . This means they are very abnormal. The reason for the unique abnormal dispersion property of optical liquids is the physical-chemical and structural features associated with these optical liquids.

The incorporation of abnormal liquids is complicated by their large thermal coefficients of refractive index (dn/dT)[7]. To make a glass-liquid lens design thermally stable, two liquids with different dn/dT and dispersions are typically used. Knowledge of the dependencies of dn/dT versus composition of the mixed liquids will allow a proper selection of liquid materials to achieve thermally stable optical designs. This paper extends previously reported investigations of dn/dT dependencies of liquids in the visible spectrum[6].

EXPERIMENTAL PROCEDURE

The experimental procedure used in obtaining these measurements has been described in detail previously[3-6]. The refractive indices of each liquid, under consideration, was measured at three different temperatures (i.e., room temperature (RT), RT+9°C, and RT-9°C). To measure the refractive indices, two high-precision goniometers of the same type and two identical thermal stabilization cells were used. One set of these instruments (i.e., a goniometer and thermal stabilization cell) was used to get measurements over the visible spectral region, and the other set was used to obtain measurements for the ultraviolet (UV) and infrared (IR) regions. Using the special thermal stabilization cell[3-6] allows the temperature of the liquids to be controlled to ±0.02° C, and measured to an accuracy of ±0.01° C. Refractive indices were measured with an accuracy of ±0.00001 over the UV and visible regions, up to 1.5 μm. At 1.6 μm, the refractive indices were measured with an accuracy of ±0.00005 . The data obtained was linearized by a least squares fit, and the values of dn/dT were then calculated. The accuracy of the dn/dT calculation is ±0.00001 .

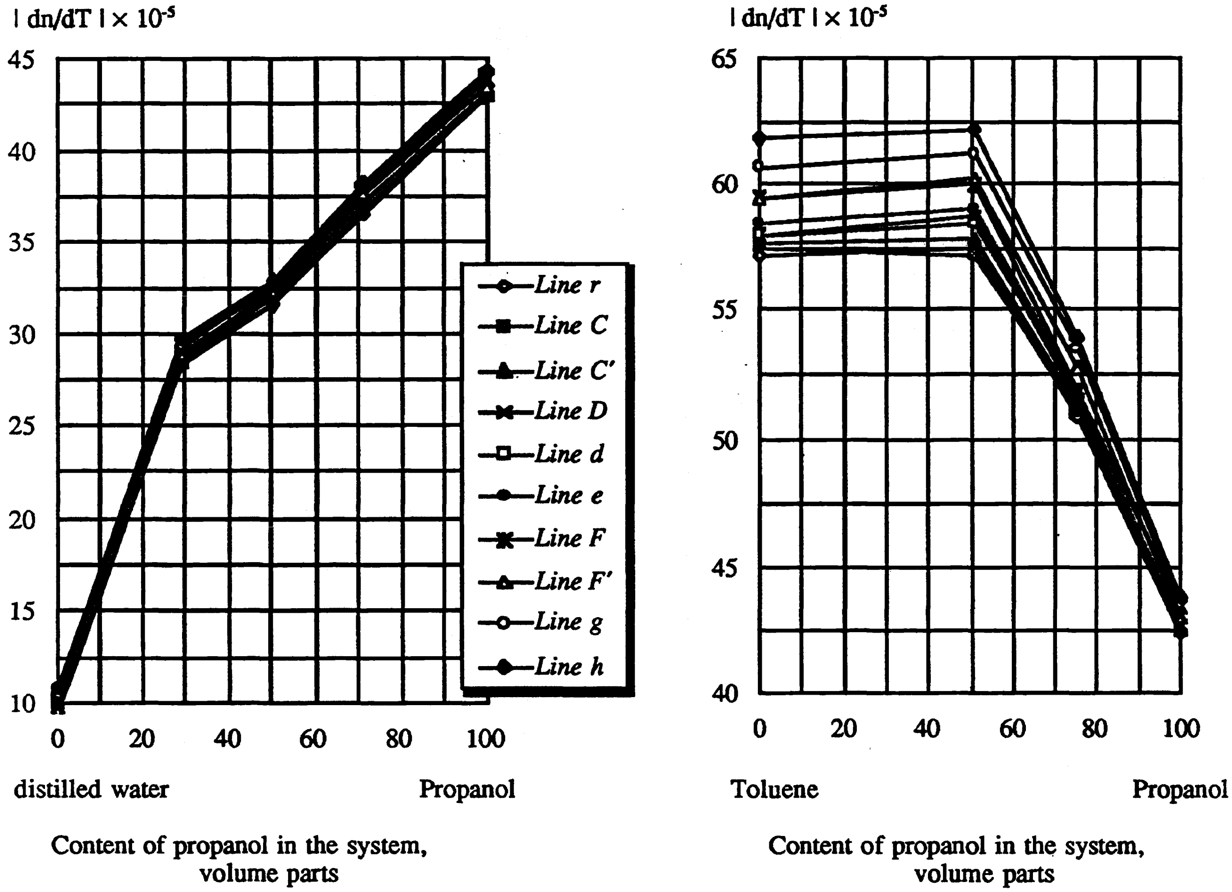
RESULTS

Figures 2, and 3 show the "thermal coefficients of refractive index (dn/dT) versus composition" for several different liquids. In these Figures, the ordinate axis is dn/dT, and the abscissa axis is the composition of the mixed liquids. The dn/dT data presented was calculated for 10 spectral lines over the visible region.

The ultimate goal of the present work is to gain an understanding of how the values of dn/dT change for a solution of mixed liquids. For this purpose, liquids were chosen which have very different values of dn/dT and at the same time could be dissolved into each other, while still varying the percentage composition of the two components in the final solution of the mixed liquids. Liquids are well known to have negative dn/dT and large by absolute value comparison with other optical materials. This negative dn/dT is due to the fact that these liquids have a rather large value of thermal expansion. The values for dn/dT of an overwhelming majority of liquids range from $40\times10^{-5}K^{-1}$ to $90\times10^{-5}K^{-1}$. Unique exceptions to this characteristic are distilled water (i.e., dn/dT about 10×10^{-5}) and Glycerol (i.e., dn/dT about 20×10^{-5})[7].

In Figure 2, the dn/dT data for the two component system of "distilled water - Propanol" is shown. As can be seen, this two component system appears to have an almost linear dn/dT versus the volume percentage content of Propanol in the system, for all 10 spectral lines, where Propanol content is represented by volume. Expressing the composition of the liquid system in appropriate units is the most important aspect for understanding the results, from a physical-chemical and optical properties point of view. In Figures 2 and 3, the composition of two component systems are shown by volume percentages, which is the most conventional way to display characteristics for these types of systems in refractometry studies.

The dn/dT curve shown in Figure 2 could be considered as linear. The shape of this curve is close to typical curves for refractive index (n) versus the composition for two component systems. In Ref.7, all curves of "n as a function of volume percentage of a component liquid", in two component systems, can be divided into three large groups. The biggest group includes systems having very small deviations from linear dependency of "n" versus the composition of a system.



a) b)

Figure 2. Diagram dn/dT versus composition for two component systems:
a) distilled water - Propanol;
b) Toluene - Propanol.

dn/dT data presented were calculated at 10 spectral lines over the visible region: r (λ=0.7065 μm), C (0.6563 μm), C' (0.6439 μm), D (0.5893 μm), d (0.5876 μm), e (0.5461 μm), F (0.4861 μm), F' (0.4800 μm), g (0.4358 μm), h (0.4047 μm).

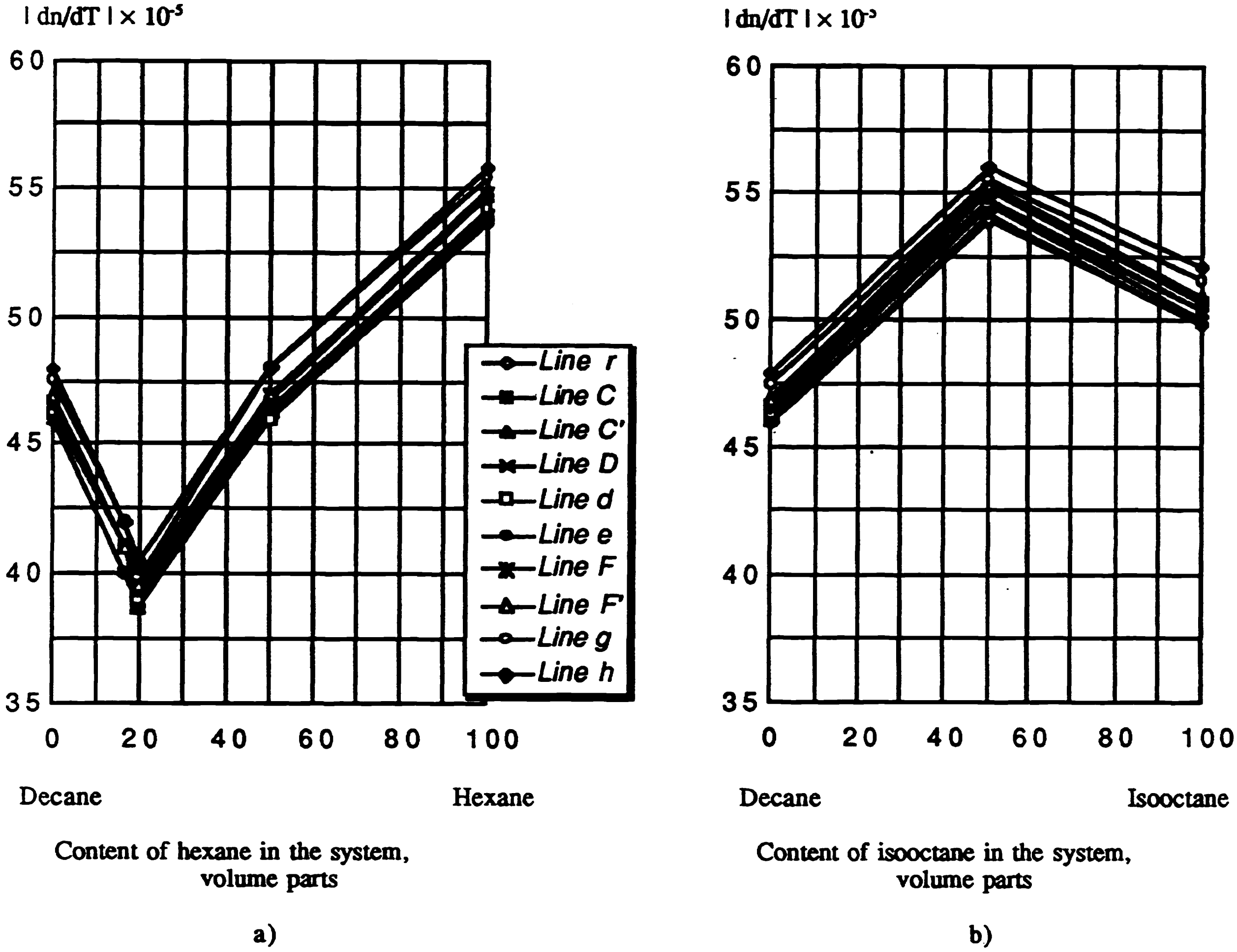


Figure 3. Diagram dn/dT versus composition for two component systems:

a) Decane - Hexane;

b) Decane - Isooctane.

dn/dT data presented were calculated at 10 spectral lines over the visible region: r (λ=0.7065 μm), C (0.6563 μm), C' (0.6439 μm), D (0.5893 μm), d (0.5876 μm), e (0.5461 μm), F (0.4861 μm), F' (0.4800 μm), g (0.4358 μm), h (0.4047 μm).

Most of the two component systems have maximum points on the curves for "n versus volume percentage composition". So therefore maximum points are also expected on the two component system curves for "dn/dT versus composition". Two component systems were found with maximum points on the curves of "dn/dT versus volume percentage composition", which is explained by the fact that the value of thermal expansion coefficient of these two component systems is increased as compared to those thermal expansion coefficients of each of the system's components. The most interesting examples of such systems are shown in Figures 2-b and 3-b. In these systems, the maximum dn/dT points were found to correspond to the stable azeotropic composition of the mixture[8] .

It appears that two component systems with a minimum point exist, on the curve of dn/dT versus volume percentage composition curve. In Figure 3-a, dn/dT data is presented for the two component system of "Decane - Hexane". The dn/dT for the system with a ratio of components at 1:4 is significantly lower than those of both starting components: for example, at the spectral line e (λ =0.5461 μm) dn/dT of the mixture is 39×10^{-5}, and dn/dT of the components are 47×10^{-5} (Decane) and 55×10^{-5} (Hexane).

The abnormal dispersion properties of both pure components are not very high as compared with those of other optical liquids (i.e., all liquids studied within this project are presented in Figure 1). Therefore, it is unexpected that the mixture of "Decane - Hexane" would show very abnormal dispersion properties. To characterize the abnormal dispersion of the newly studied liquids, the primary (η_1) and secondary (η_2) Buchdahl dispersion coefficients of this two component system were calculated.

	Pure Decane	Two component system with ratio of components 1:4	Pure Hexane
η_1	- 0.096	- 0.096	- 0.095
η_2	0.015	0.017	0.018

As can be seen from the Table, the abnormal dispersion of the mixture, at the minimum dn/dT point, is practically the same as for both pure components. It means that mixing these two components, which results in significantly decreasing the dn/dT, does not result in changing the dispersion curve shape of the mixture as compared to those characteristics of the starting components.

CONCLUSIONS

The dependence of both the thermal coefficients of refractive index (dn/dT) and abnormal dispersion versus the volume percentage composition for a number of liquids has been investigated in the visible spectral region.

Three types of diagrams "dn/dT as a function of content of a component" in two component systems were found to exist. It has been shown that mixing two components can result in significantly decreasing the dn/dT of the mixture over the visible spectral region, while at the same time the mixing does not result in a change of the abnormal dispersion properties of the mixture, as compared to those characteristics of the starting components.

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