Determination of Temperature and Composition Dependence of Refractive Index in Binary Solutions

by

Nicholas W. Dnistrian
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A Thesis Proposal by

Nicholas Dnistrian

Department of Chemical Engineering

Mentor: Dr. R. J. McCluskey

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Abstract:

Refractive index is useful in measuring the composition of binary mixtures and is often used in chemical engineering applications. The temperature-dependence of refractive index is something that is often ignored or circumvented through the use of temperature compensation methods. Initial investigation leads to the idea that refractive index’s variation with temperature may also vary with composition. A model that allows the prediction of the variation of refractive index in binary systems with variation in temperature and composition would allow for a head on approach to composition measurement corrections.

Introduction:

Separation and reaction processes employed by chemical engineers oftentimes require that streams enter process units at precise compositions. It could be that components must enter a reactor at precise stoichiometric ratios. It could also be that if a stream enters a separation tower at the wrong composition there will be undesirable variation in product stream composition. So there are many reasons why precision is needed in determining solution compositions. One effective method of measuring stream composition is with an on-line refractometer. Composition of mixtures can be measured by finding the refractive index of the solution. The mixtures in this investigation will be binary, having two components. This technique has been in use in industry for some time. Using refractive index to measure composition affords several advantages. It is quick, relatively simple, requires a sample size of only a few drops and can be done on-line. Like many physical properties, refractive index varies with temperature. While there are some on-line instruments that can compensate for temperature changes, in batch processes and in experimental applications using this type of instrument can prove problematic due to lack of stream flow (Glasser & Troy, 1958). For these types of applications it would be helpful to have an equation to predict how refractive index changes with temperature, so that an accurate composition of the sample may be calculated. A formula such that, by recording temperature of the refractometer and the refractive index, a
composition corrected for temperature may be obtained. It is the aim of this investigation to derive such an equation from experimental data collection and data analysis.

**Background Information:**

Refractive index is a comparison of the speed of light in two media. The equation to calculate a refractive index is below:

\[ n = \frac{\sin \theta}{\sin \theta'} \]  

(1)

Where \( n \) and \( n' \) are refractive indices and \( \theta \) and \( \theta' \) are angles made with the normal. By convention, one of the substances used for a refractive index reading is air or a vacuum with refractive index equal to one. This simplifies the equation to:

\[ \frac{\sin \theta}{\sin \theta'} = 1 \]  

(2)

However, as long as the refractive index of one of the components is known, the other can be calculated from measurements of the angle of dispersion, \( \theta \). Most Abbe refractometers work on the concept of having one known refractive index and are calibrated with a scale to display the refractive index of the material being tested as compared to a vacuum, giving an absolute measure of refractive index measurement (Stanley, R. C., 1968). From such measurements of the index of refraction of mixtures can be related to their compositions.

Calculation of composition of a binary system from refractive index information is fairly straightforward. The concept is based on an assumption that molar refraction of a mixture is directly proportional to the mole fraction of its components. The exact formula comes from Fucaloro and is shown in equation 3.

\[ R = \sum x_i R_i \]  

(3)

\[ V = \sum x_i V_i \]  

(4)

Where \( R \) is molar refraction, \( V \) is molar volume, \( n \) is the refractive index of the mixture, \( x_i \) is the mole fraction of component \( i \) and \( R_i \) is the refractive index of pure component \( i \). This equation is useful but, is derived from data at one temperature (2002). Molar volume and refraction are
dependent. This is a good place to start with composition calculations but temperature dependence of refractive index must be investigated further to form a comprehensive model.

The temperature compensating refractometers in existence work on several different principals that are not useful in all applications. The major way that these refractometers compensate for the temperature difference is by using a reference liquid that is kept at the same temperature as the stream it is measuring (Glasser & Troy, 1958). This works for processes with steady state streams, but may prove difficult to implement in batch processes or really any process without continuous streams. Furthermore, this process operates under the assumption that all indices of refraction vary uniformly with change in temperature. That is to say that five degrees change in one fluid causes the same change in index of refraction in one fluid or mixture as it would in another. While Glasser & Troy do go into detail about proper design choices in such refractometers, in the instances above, it would be easier to simply predict the behavior of the mixture in absolute means (1958).

Another method of eliminating "the thermal noise that is connected with conventional refractive index detection," is by utilizing spectroscopic refractometry. This method makes use of a spectroscope. The sample is dissolved in solvent and is then analyzed using light of a certain wavelength. This method measures what the authors call a complex index of refraction. It consists of a real part, the type of index of refraction discussed here, and an imaginary part that is a function of the wavelength of light used and the absorbtivity of the sample (Hanning & Roeraade, 1997). This method is accurate and achieves the goal of eliminating the thermal noise that proves so problematic in conventional refractive index detection, and is discussed more in significance. However, this method requires the purchase of new sophisticated spectroscopic refractometers. While this is a simple enough solution, some institutions may prefer to save on new equipment and use a temperature correction for the equipment they already have.
Significance:

Refractive index changes across a very small range as composition of a mixture varies greatly. This makes taking very precise measurements crucial. Sample data for refractive index of isopropanol and water at 15 C shows that for an increase from 80 weight percent isopropanol to 90 weight percent isopropanol the refractive index of the solution only changes from 1.3785 to 1.3797. In other words a 0.087 percent error in refractive index would yield a 10 weight percent error in the measured composition. From various sources, it is found that a change of 4 x 10^-4 per degree is a common ballpark figure for change of refractive index with temperature (Glasser & Troy, 1958 and Grassi & Georgiadis, 1999). If this is so, then a difference in 2 degrees can cause close to a 10 weight percent error of composition reading. This approximation, however is strictly linear, when it can be seen from plotting sample data of refractive index at different constant temperatures that linearity is not the case (Figure 1). As such, there is a need for a simple temperature prediction model so that the kind of errors mentioned in this section may be avoided.

Research Methodology:

In formulating a model to predict the temperature-dependence of refractive index experimental data will be collected and compiled to be analyzed mathematically. The model will first be developed for a solution of isopropanol and water. Once an accurate model is obtained to describe this solutions behavior, refractive index data will be collected for other solutions to see how well the model obtained for isopropanol and water describes other solutions. It is doubtful that the model will work well for all solutions, but their behaviors are likely to be somewhat similar. The hope is to incorporate parameters that can be found for each unique solution to create a general predictive equation. This will involve collecting large amounts of data to ensure accuracy.

The data collected in this investigation will consist of measurements of refractive index made with an abbe refractometer, as described earlier. Each set of data will consist of refractive index measurements of the solution in question taken all at a constant temperature. The
temperatures at which data are measured will be varied within the constraints of the constant temperature bath selected. The concentration of the solutions will be varied by five percent from zero to one hundred percent. A refractive index will be measured at each concentration for a given temperature. It is the hope that by varying the concentration of each solution tested, it can be determined if the magnitude of change in refractive index with change in temperature is also related to concentration of the solution in question. From the data in figure 1, this seems it may be the case.

In this investigation, a Bausch & Lomb ABBE-3L refractometer will be used to make measurements. This model refractometer works on the principles outlined in the background. It utilizes a measuring prism of known refractive index and uses a calibrated scale to make refractive index measurements. The model features a built in thermometer that measures the temperature of the measuring prism, and by extension the sample placed on the prism that is being measured. It also features fittings for use with a constant temperature bath, a crucial feature for these experiments. This will allow for the temperature of the measuring prism and of the sample to be precisely controlled. Before beginning work on data collection the apparatus must be properly calibrated as outlined in the operating manual. Once the refractometer is ready to make measurements, a drop of the sample solution is placed on the prism and allowed to come to the temperature of the measuring prism. Once the thermometer reads the desired temperature, the proper measuring adjustments are made to the apparatus and the refractive index is measured and recorded (Analytical Systems Division).

Enough data must be collected so that values for recorded data can be reported with confidence. In this investigation, measurements will be taken until the measured values fall within a 95% confidence interval. Once enough data is collected to reach the desired confidence level, analysis can begin.

Without knowing what behaviors will be observed, it is difficult to outline the exact procedure that will be followed in analyzing it. Generally speaking, however, regression analysis will be used in an attempt to determine the dependence of a solution's refractive index on
temperature and perhaps also concentration. It will be determined the nature of the dependence, be it polynomial, exponential, logarithmic etc. The coefficients of the equation will also be found in this manner for the various solutions tested.

**Initial Data:**

Some preliminary data were found resembling the remainder of the data to be collected. Figure 1 shows data plotted in the manner it would be presented in the final thesis project. It shows multiple curves of refractive index vs weight percent of one component of a mixture, with the weight percent of the other component being 100 minus the first weight percent. Each curve represents a different temperature at which data was taken. The 15°C data comes from the *CRC Handbook of Chemistry and Physics* (Wolf, Brown & Prentiss, 1982). The 20°C data comes from the *International Critical Tables* (National Research Council, 1930). It is from these data that some initial thoughts may be formed.

![Graph](image)

**Expected Results:**
From preliminary data and investigation into background and theory an initial hypothesis can be formulated. A model with variable parameters can be found to accurately predict the behavior of the refractive index of a binary system as the system's temperature and composition change. The preliminary data leads to this idea of variation with both temperature and composition because of the divergence of the data at the pure isopropanol end, as seen in figure 1. This may not be the case for all systems but hopefully most systems behave similarly and can be described in a manner similar to that described in the hypothesis above.

**Timeline:**

Pending this proposal's approval, work on data collection will continue. For the remainder of the semester data for isopropanol and water will be collected to be used in producing the first prediction model that will be used for comparison with data for additional solutions. Data collection proceeds quickly once the measuring prism is brought to the desired temperature. Different concentrations of a solution can be prepared in advance with simple dilution techniques. Once the solutions are prepared, taking measurements are as simple as placing a drop on the measuring prism verifying that the prism is still at the correct temperature and taking the measurement. Several trials can be performed in the course of a day's work. By using statistical analysis, it can be determined when the 95% confidence in each measured value is reached and analysis can begin. This initial phase of data collection will likely take no longer than 2 to 3 weeks, working in the lab two days a week. In this data collection period, other solutions may be prepared as well to be measured at the same time as isopropanol and water as the refractometer will be at the desired temperature already. This would, in effect, complete the majority of data collection for the project if all the solutions could be measured with sufficient confidence and accuracy. The first priority of this phase will be to collect isopropanol and water data with sufficient confidence. Phase two may begin when the isopropanol water data is sufficient, although this data collection phase may continue until the other solutions are measured with desired confidence. This phase will end in early to mid-April 2011.
The second phase would be analyzing the data to formulate the first predictive model that other data will be compared to. Hopefully an accurate model may be obtained by the end of the spring semester 2011. If work is not finished by the end of the semester, the data will already be collected and can be analyzed into the summer if need be. This phase of the project, therefore, will last until the beginning of May 2011 and into the summer if need be. During the summer there will also be time to begin writing portions of the final thesis that can be written, such as background theory etc.

This brings about the third phase of the project, altering the model or its parameters to describe other solutions. Since the majority, if not all, of the data needed for the investigation will be collected in phase one, this phase can begin as soon as the first model is produced. That is to say likely in summer 2011. However, professional requirements this summer may hinder the availability of time for this phase, and as a result it may not begin in full swing until fall semester 2011. Hopefully, with diligent work this phase will take approximately 2 to 3 months. Lasting until early October 2011. This date could be earlier depending on when this phase begins.

The final phase, phase four, is to finish writing the completed thesis. Since throughout this process pieces of the thesis are being written, this phase should only take until the end of fall semester 2011 to complete. These dates are all somewhat tentative, but represent the best estimation of time usage in this proposal. If the project should move along much faster than planned, work can be begun on a model for ternary systems, mixtures with three components. Ternary system work would progress very similarly to the work outlined here for binary systems.

References:


