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ELLIPSOMETRIC MEASUREMENT OF LIQUID FILM THICKNESS

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ABSTRACT

The immediate objective of this research is to measure liquid film thickness from the two equilibrium phases of a monotectic system in order to estimate the film pressure of each phase. Thus liquid film thicknesses on the inside walls of the prism cell above the liquid level have been measured ellipsometrically for the monotectic system of succinonitrile and water. The thickness varies with temperature and composition of each phase.

The preliminary results from both layers at 60° angle of incidence show nearly uniform thickness from about 21° to 23°C. The thickness increases with temperature but near 30°C the film appears foggy and scatters the laser beam. As the temperature of the cell is raised beyond room temperature it becomes increasingly difficult to equalize the temperature inside and outside the cell. But the fogging may also be an indication that solution, not pure water, is adsorbed onto the substrate.

Nevertheless, our preliminary results suggest that ellipsometric measurement is feasible and necessary to measure more accurately and rapidly the film thickness and to improve thermal control of the prism walls.

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Introduction

Considerable interest in monotectic systems within NASA and in materials science in general during the last decade or so is evidenced by the large number of publications on this subject. A few of them are listed in the reference section.[1,2,3,4] Succinonitrile is a transparent organic compound and freezes like metals with small entropies of melting.[5]

The monotectic system of succinonitrile-water has been subjected to considerable investigations not only due to its transparency but also due to a convenient temperature range to work with for its solution and solidification. Its upper consolution temperature of near 56°C and monotectic temperature of close to 19°C make the system[2] nearly ideal for various experiments.

In our current investigation attempts have been made to estimate the thickness of liquid films formed on the inner wall of a prism cell from each of the two separate layers: water-rich and succinonitrile-rich layers of the monotectic system. Several other monotectic systems including succinonitrile-ethanol, succinonitrile-glycerol and succinonitrile-phenanthrene will be subjected to similar investigations. The reason for this study is to assess Cahn's critical wetting theory[6] in a quantitative manner by determining solid-liquid interfacial tension input to Young's equation

$$\gamma_{L_2S} = \gamma_{L_1S} + \gamma_{L_1L_2} \cos \theta$$

where θ is the contact angle and γ is the interfacial energy corresponding to the interface denoted by the subscript pair. The liquid film from these solutions may be formed by condensation of the vapor or by van der Waals adsorption of the liquid along the wall. Thus, it becomes necessary to estimate partial pressures of each component for each solution equilibrated at different temperatures. This task is pursued by Frazier and coworkers[7] at the Marshall Space Flight Center.

Experiment

Since ellipsometric measurement of film thickness requires refractive indices of medium, liquid and substrate, it is absolutely imperative that these values be available or estimated accurately at the particular wavelength, in our case, 632.8 nm of He-Ne laser. Unfortunately these quantities are not available and therefore must be estimated with some degree of accuracy at various temperatures.

Refractive indices are very sensitive to temperature[8] and composition of the liquid. Therefore, index measurements were made using two different devices, a prism spectrometer and the ellipsometer with He-Ne laser. There was some variance between the two apparatuses, as shown in Table 1, which may be due to thermal sensitivity of the prism spectrometer. The table was not completed for all the listed temperatures due to the lack of temperature control device for the prism spectrometer. Thermal control stability on the solution in the prism cell was ± 0.1°C, although it was difficult to achieve this stability on the prism wall at temperatures other than ambient temperature. This was the case because circulation of the bath water around the wall on which film thicknesses were measured would not be permitted since it would obstruct the measurement.

Table 1. Indices of Refraction for Succinonitrile-rich Phase

T°C	Ellipsometer	Prism Spectrometer
18.9	1.42114	
19.2		1.42043
19.6		1.42069
19.9	1.41871	
21.0		1.42017
22.0		1.41945
24.0	1.41990	
24.6		1.41763
25.5		1.41661
26.0	1.42003	
28.0	1.41416	
29.0	1.41135	
30.0	1.41096	
31.0	1.41036	

For the ellipsometric work, prism cells of three different angles of incidence were specifically designed for refractive index and thickness measurements. As stated earlier, the inner wall temperature of the prism could not be controlled as accurately as the solution temperature in the cell. Refractive indices of water from the literature[8] are compared with those estimated ellipsometrically in our experiment in Table 2. The agreement between the two is excellent near room temperature. In this measurement the refractive index of the cell prism glass was assumed constant over the temperature range.

Table 2. Indices of Refraction for Water

T°C	Ellipsometer	Ref. 8*	Deviation %
16.0	1.32880	1.33245	0.3
18.0	1.32977	1.33229	0.2
22.0	1.33197	1.33194	0.002
25.0	1.33119	1.33165	0.03
29.0	1.33099	1.33121	0.02
40.0	1.32970	1.32977	0.005

*Temperature was rounded to 3 digits for this table.

The manually operated ellipsometer (leased from the Marshall Space Flight Center) has been used very extensively, but is very time-consuming and tedious. A temperature shift during a long reading period was entirely possible unless the room and the water jacket were at the same ambient temperature.

Preliminary Result

Liquid film thickness and refractive indices are presented in Figs. 1 and 2 for the monotectic system of succinonitrile and water (SN-water) at the 60° incident angle. Both water-rich and succinonitrile-rich (SN-rich) phases show variation of thickness with temperature. Variations are small between 21° and 23°C. At higher temperatures, film thickness increases, while at lower temperatures thickness decreases. The two layers gave rise to the same thickness near the monotectic temperature. Formation of foggy film as the cell temperature was raised beyond room temperature may indicate precipitation of the conjugate phase within the adsorbed film itself if indeed the film composition is similar to the liquid solution composition, rendering the film quite foggy. The fogging is one of the most consistent problems that should be dealt with. Similar results were obtained with the cells of different glass and angles of incidence.

In calculation of thickness, experimental values of index of refraction for the solution phases obtained in this lab were used. No literature data are available for the solution. Measurements were usually made on a large drop of the phase placed at the floor corner away from the prism wall to minimize capillary migration of the liquid along the wall. Condensation of the vapor onto the wall is the main mechanism of film formation when the wall is not in contact with the sample solution. This allows use of the Gibbs adsorption equation to determine film pressure of liquid films formed from adsorbed phase.

The variation of the index with temperature for both conjugate phases of each succinonitrile-water solution is as anticipated because at higher temperatures there will be more homogeneous mixing between the two components. This trend was shown by both the hollow-prism spectrometer and the ellipsometer. Thus, the succinonitrile-rich phase has a decreasing index as the temperature is raised. In fact, the graph of indices, Fig. 1, is a combination of two separate data from the prism spectrometer and ellipsometer. The result is rather remarkable for the two entirely different instruments. On the other hand, the index of the water-rich phase varies very little with temperature near 23° to 25°C but slowly decreases again above this temperature range. Under nearly identical conditions, variance between the two spectrometers is usually less than 0.1%, still a remarkable agreement.

A preliminary calculation of film pressure was also attempted by utilizing the estimated film thickness and partial pressure data[7] for the two components, succinonitrile and water, obtained elsewhere. The result was obviously too large when the specific surface was replaced by the total inner walls (24 cm^2) of the sample cell. Since for the flat surface of prism glass specific area has not been defined, some new parameters need to be defined and estimated for the Gibbs adsorption equation to calculate film pressure. One parameter under consideration in our laboratory is the quantity defined as the total empty volume of the cell divided by the total inner surface area of the available space.

Conclusion

Much work remains to be done including more precise control of the sample cell and accurate measurement of film thickness with a fully automated ellipsometer system. This system requires a new design of prism cells so that the difficulty of observing liquid film formation on the vertical wall can be eliminated. The liquid film itself on the cell ceiling will be less dependent on any capillary adsorption of liquid. Partial pressures and composition of each component vapor phase should also be estimated.

Acknowledgements

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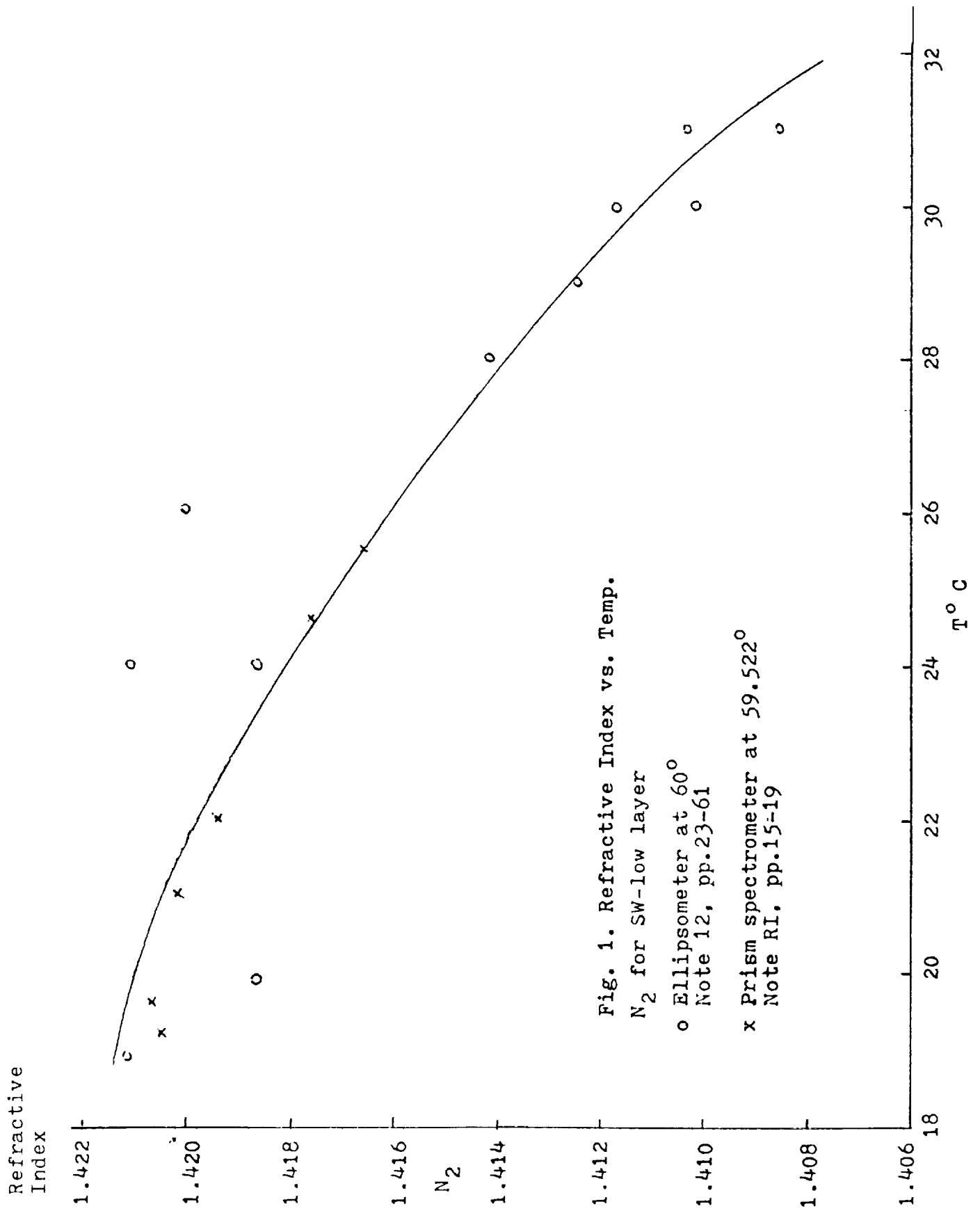8. Stanley, E.M.; J. Chem. Eng. Data, 1971, 16, 454.

Fig. 1. Refractive Index vs. Temp. N_2 for SW-low layer

o Ellipsometer at $60°$
  Note 12, pp.23-61

x Prism spectrometer at $59.522°$
  Note RI, pp.15-19

Fig. 2. Thickness vs. Temp.

SW-Low Layer(o) and SW-Top Layer (x)

Thickness vs. Temp. at 4 mm

Lab notes: SW-12-70 to SW-12-88

BK-7-1 glass $\theta_i = 60^\circ$