Refractive Indices of Transparent Solvents

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Values of refractive index have been obtained from observations of critical angle at a Suprasil–solvent interface over the energy range 2.1–6.2 eV for the solvents *n*-hexane and methyl-, ethyl-, and isopropyl alcohol. Measurements were made at room temperature to an accuracy of ±0.001. These data are required in the proper interpretation of various optical measurements.

Introduction

In this paper we are presenting the refractive indices of some common solvents over their energy range of transparency from 2.1 eV (5900 Å) in the visible up to 6.2 eV (2000 Å) in the region of the ultraviolet absorption edge. These data, required in the proper interpretation of, for example, fluorescence spectra, are not available in the literature over as wide an energy range and/or with the necessary accuracy. Our method of obtaining refractive indices involves critical angle measurements using a liquid cell with a semicylindrical window. The values of solvent refractive indices obtained in this way are accurate to ±0.001.

The only comprehensive study of refractive indices of liquids over an extended energy range already published in the literature was performed by Voellmy (*5*) in 1927. The highest photon energy to which Voellmy made measurements was 5.77 eV (2150 Å) although for some liquids measurements were only made up to 3.87 eV (3200 Å). In most cases it is possible to obtain the refractive indices of transparent solvents by our technique to higher energies than were reported by Voellmy. Some observations of refractive index as a function of photon energy have appeared in the literature more recently. These are for a few selected energies in the visible region and do not extend Voellmy's observations to higher energies. They are, in each case, consistent with Voellmy's observations within the limits of experimental accuracy.

Experimental Techniques

The experimental techniques used for measuring refractive index have been described previously (*3*, *4*). The solvents were reagent grade and were used without further purification. Each liquid under investigation was contained in a closed cell, one side of which consisted of a transparent semicylinder. Photons entered the semicylinder along a radius and hence normal to the curved surface, were reflected at the plane semicylinder–liquid interface, and exited from the semicylinder along a radius. If the refractive index of the material of the semicylinder, n_s, is greater than that of the liquid, n, for a given photon energy, then $n/n_s = \sin \theta_c$ where the critical angle, θ_c, is defined as the angle which marks the onset of total reflection. Thus if n_s is known and θ_c measured, n can be calculated. In practice, n_s is measured for the material of the semicylinder with the cell empty.

For the observations reported here, a Suprasil (high-purity fused silica) semicylinder was used. This was cleaned initially with soap and water and then dipped in concentrated solutions of chromic acid and sodium hydroxide to remove any soap or oil films. It was then rinsed thoroughly with distilled water and flushed with isopropyl alcohol. Finally, the semicylinder was flushed with freshly distilled Freon 113 from a vapor degreasing bath. This cleaning procedure was used before measuring the refractive index of the semicylinder and also before the measurement of the refractive indices of each of the solvents. Scans of reflectance as a function of angle of incidence at the plane semicylinder–air and semicylinder–liquid interface were recorded for selected wavelengths over the range from 2000 to 5900 Å. The source of photons was a dc discharge in H_2. When the solvent is completely transparent, as in the present case, its extinction coefficient, k, is zero, and ideally the critical angle should be sharply defined. However, the observed reflectance vs. angle of incidence curves do not show a perfectly defined critical angle as predicted by Fresnel's equations due to the limitations of instrumental resolution. This effect was taken into account when estimating values of θ_c from our experimental reflectance vs. angle of incidence curves. The refractive indices obtained for the Suprasil semicylinder and the four solvents, *n*-hexane and methyl, ethyl, and isopropyl alcohol, are given in Table I as functions of incident photon wavelength.

Table I. Refractive Index, n, as a Function of Photon Wavelength, λ

	n				
λ, Å	Suprasil	*n*-Hexane	Methyl alcohol	Ethyl alcohol	Isopropyl alcohol
2000	1.551	1.482	1.423	1.467	1.482
2100	1.535	1.464	1.405	1.450	1.464
2200	1.525	1.452	1.392	1.435	1.451
2300	1.518	1.441	1.383	1.423	1.441
2400	1.512	1.433	1.377	1.415	1.433
2600	1.502	1.421	1.367	1.404	1.421
2800	1.493	1.411	1.359	1.396	1.413
3000	1.487	1.405	1.353	1.390	1.406
3200	1.482	1.399	1.348	1.385	1.401
3400	1.478	1.395	1.344	1.381	1.397
3600	1.475	1.392	1.342	1.378	1.393
3800	1.472	1.389	1.339	1.375	1.390
4000	1.469	1.386	1.337	1.373	1.388
4500	1.465	1.382	1.333	1.368	1.383
5000	1.461	1.378	1.331	1.365	1.380
5500	1.459	1.376	1.329	1.363	1.378
5900	1.458	1.375	1.329	1.362	1.377

It might be mentioned that use of a semicylindrical window enables a direct observation of θ_c, since photons enter and leave the semicylinder normal to the curved surface and hence are not refracted at these interfaces. Since the location of θ_c does not depend on a proper normalization of the variation of reflectance with angle of incidence, reflections at the curved surfaces do not affect the location of θ_c. For the same reason our technique can be used even when the solvent is fluorescent. In Voellmy's work, absorption by low-lying singlet π states apparently limited some of his results; e.g., for benzene his observations cutoff at 4.59 eV (2700 Å), whereas our technique can yield the refractive index of benzene up to the absorption edge at 5.64 eV (2200 Å) (*2*). Furthermore, the observed location of θ_c is relatively insensitive to surface imperfections at the semicylinder–liquid interface. The uncertainty in the absolute refractive index values obtained by this method is estimated to be ±0.001 over the whole wavelength range studied. This uncertainty arises mainly in the treatment of the instrumental resolution in estimating θ_c from the experimental reflectance vs. angle of incidence scans. All observations were made at a room temperature of 22 ± 1 °C. Where values of

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n are available in the literature (*1*, *5*), they agree with those in Table I within the stated experimental accuracies.

The solvents studied for this note all have relatively low refractive indices, enabling a Suprasil semicylinder to be used. For solvents with relatively large refractive indices, such as benzene and toluene, a semicylinder of some material having a larger refractive index such as sapphire must be used.

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Literature Cited

(1) "Handbook of Chemistry and Physcis", 57th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1976.
(2) Inagaki, T., *J. Chem. Phys.*, **59**, 5207–5208 (1973).
(3) MacRae, R. A., Williams, M. W., Arakawa, E. T., *J. Chem. Phys.*, **61**, 861–865 (1974).
(4) Painter, L. R., Birkhoff, R. D., Arakawa, E. T., *J. Chem. Phys.*, **51**, 243–251 (1969).
(5) Voellmy, H., *Z. Phys. Chem.*, **127**, 305–357 (1927).

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Pressure–Volume–Temperature Relationships of Refrigerant 500 Gas

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The compressibility factors have been measured using a Burnett-type apparatus on Refrigerant 500 from 298.15 to 413.15 K and from 0.2 to about 7 bar. Refrigerant 500 is a minimum-boiling azeotrope of 26.2 wt % 1,1-difluoroethane (Refrigerant 152a) and 73.8 wt % of difluorodichloromethane (Refrigerant 12). The apparatus was calibrated with high-purity helium. The uncertainties in the measurements were estimated as follows: temperature, ±0.01 K; pressure, ±1 × 10^{-4} bar; compressibility factor, ±0.1%. The second virial coefficients are reported for helium and second and third virial coefficients for Refrigerant 500.

A Burnett-type apparatus (*3*) was fabricated and used to obtain compressibility factors of Refrigerant 500 gas at temperatures 298.15 K and from 313.15 to 413.15 K at 20 K intervals. The pressures at each temperature extended from about half the saturation pressure to about 0.2 bar. Refrigerant 500 is a minimum boiling azeotrope of 26.2 wt % 1,1-difluoroethane (Refrigerant 152a) and 73.8 wt % of difluorodichloromethane (Refrigerant 12). Recent applications of minimum boiling azeotropes to the vapor compression refrigeration systems have indicated their superiority over their pure constituents under identical conditions (*2*, *7*). While retaining the merits of pure component refrigerants, the use of minimum boiling azeotropes has resulted in increased capacity, attainment of lower temperatures, and as a consequence improved coefficient of performance.

The only literature *P*–*V*–*T* data for Refrigerant 500 are reported by Sinka and Murphy (*10*), which extend from 322 to 478 K, 14 to 58 bar, and 17 × 10^{-3} to 149 × 10^{-3} m^3 mol^{-1}.

Emphasis in this work has been on the low pressure *P*–*V*–*T* data primarily to obtain reliable values of second virial coefficients and to extend the range of existing *P*–*V*–*T* data on R-500 in the low pressure region.

Experimental Section

Materials Used. Helium of 99.99 mol % purity was obtained from the Low Temperature Laboratory, Indian Institute of Technology Kanpur, Kanpur, India. The purity was checked by gas–liquid chromatography and was found to comply with the above specifications. R-500 was of 99.95 mol % stated purity made by Du Pont and was supplied by the Universal Commercial Co., Bombay, India. It was used without further purification.

Apparatus. The Burnett apparatus used in this investigation was basically similar in design to that used by Anderson et al. (*1*) with some important modifications. The compressibility cell was machined from type 316 stainless steel. The finished cell was 0.1 m o.d. by 0.38 m long. The sample chamber V_I, 0.06 m o.d. by 0.245 m long (approximate volume, 888 × 10^{-6} m^3), and the expansion volume V_{II}, 0.06 m o.d. by 0.105 m long (approximate volume, 380 × 10^{-6} m^3), were bored from the opposite ends of the cell block. Eubank and Kerns (*4*) in their recent analysis of adsorption and molecular association in the Burnett apparatus have recommended the following modifications: (a) Type 303 stainless steel for the construction of the compressibility cell should be avoided as it gives a poor finish and consequently leads to adsorption, (b) elimination of usual tapers at the bottom of V_I and V_{II}, and (c) the surface of the cell should be superfinished. These modifications were incorporated in the design of the present apparatus. An excellent finish of the cell surface was obtained by special lapping process provided at the Indian Ordinance Factory, Kanpur, India.

Temperature Measurement. Temperatures were measured with chromel–constantan thermocouples (Thermoelectric Co.) which were directly exposed to the experimental gas. The emf was measured by a Type K-3 Universal potentiometer (Leeds and Northrup) and a L&N 2430 DC galvanometer assembly. Four thermocouples were used; two were placed in the cell, the third was located inside the oil bath very close to the compressibility cell wall, and the fourth, a movable one, was used to check the temperature gradient inside the bath. All the thermocouples were calibrated against a 25-Ω platinum resistance thermometer and a resistance bridge assembly (both L&N). The uncertainty in the temperature measurement was estimated to be ±0.01 K.

Pressure Measurement. Pressures from 3 to 29 bar were measured by a Ruska dead-weight gauge and from 0.14 to 2 bar by a Ruska air piston gauge. The pressure balance was achieved through a Ruska differential pressure indicator (DPI). The DPI was a low-temperature DPI and hence had to be placed outside the bath, in a small insulated enclosure which was maintained at 298.15 ±1 K. The uncertainty in the final pressure measurement was estimated to be 1 × 10^{-4} bar. Atmospheric pressures were read with a mercury barometer with an accuracy of ±6.8 × 10^{-7} bar.

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