J. Chem. Eng. Data 1982, 27, 16-18

Refractive Index of Liquids under High Pressure

Toshiharu Takagi* and Hiroshi Teranishi

Department of Chemistry, Kyoto Technical University, Matsugasaki Sakyoku Kyoto, 606 Japan

In order to measure the variation of the refractive index of liquids with pressures up to 50 MPa, a Michelson-type interferometer for 632.8-nm light is constructed. The pressure variations of the refractive indexes for mesitylene, benzene, and carbon tetrachloride which were measured and reported in the literature confirm the reliability of the interferometer. Measurements are performed on benzene, toluene, chlorobenzene, and nitrobenzene at several temperatures and pressures up to 50 MPa, with an estimated accuracy of better than ±0.000 08.

Introduction

The value of the refractive index of a liquid under high pressure is important to know in investigations of pressure effects. Waxler and Weir (*9*) measured the refractive indexes of benzene, carbon tetrachloride, and water at several temperatures and pressures up to about 110 MPa. Langer and Montalvo (*2*) also reported values for isopentane and mesitylene at room temperature and pressures up to 700 MPa. Since the refractive index of a liquid usually is largely dependent on pressure at low pressures, it is necessary to measure the values at narrow pressure intervals. However, in their studies, the measured pressure intervals were nearly 25 MPa or wider.

In this work, in order to determine refractive indexes in detail, especially at low pressures, we constructed an optical interferometer which can be used up to 100 MPa. Comparing the observed values of the refractive index for benzene and carbon tetrachloride with those values derived by Richard (*4*) using $p-V-T$ relations and the Lorentz-Lorenz function, we confirmed that at high pressures the present interferometer method was convenient and accurate. The new experimental data reported here are refractive indexes of pure organic liquids, i.e., benzene, toluene, chlorobenzene, and nitrobenzene, measured at 293.15, 303.15, and 313.15 K at 5-MPa intervals up to 50 MPa.

Experimental Section

Materials. G. R. grade compounds purchased from Wako Pure Chemical Industrials, Co., were used without further purification. The observed physical constants of each material are listed in Table I.

Table I. Physical Constants of Pure Liquids at 303.15 K

compd	density, g cm^{-3}	n_D
benzene	0.867 73	1.4948
carbon tetrachloride	1.574 79	1.4567
mesitylene	0.856 91	1.4943
toluene	0.858 01	1.4916
chlorobenzene	1.095 62	1.5192
nitrobenzene	1.193 31	1.5478

Apparatus. The variation of refractive index with pressure was measured by using Michelson's interferometer method. A schematic diagram of the liquid interferometer including the pressure-generating mechanism is shown in Figure 1. The light beam from a 1.5 mW He-Ne laser was separated into two beams by the half-mirror M2; one of the beams was passed through a reference cell, and the other through a high-pressure sample cell. Both beams, after being reflected by a mirror (M1 or M3) and passed again through each cell, returned to M2 once again, and interference occurs. After being magnified by a lens (L2), they displayed an interference fringe, i.e., Newton's ring, on a slit board (S6).

When the temperature or the pressure in the pressure vessel was changed, the liquid density, that is, the apparent optical path length inside the interferometer, was changed and, as a result, caused a displacement of interference fringes on the slit board. For the detection and recording of the displacement of the interference fringe pattern, which passed over the slit position, a phototransistor and a pen recorder were used, respectively.

Figure 2 shows the detail of the optical pressure sample cell, which was constructed of stainless steel. Two optical windows of quartz 6 mm in thickness and 12 mm in diameter were mounted parallel to each other and about 2.5 mm apart by using a couple of Teflon spacers. The pressure was set by using O-rings of fluorine-containing rubber.

The pressure applied to the sample was generated by means of a hand oil pump, and transmitted through mercury in H_g cylinder of about 40 cm^3 in volume. At each experimental position, the pressure was measured by a precise Bourdon gauge (Nagano Keiki, Ltd., 10A-2), full scale 98 MPa and minimum scale 0.2 MPa, which was calibrated by a deadweight tester and was accurate within 0.12% of scale up to 50 MPa. Thermostated water was circulated around the two vessels for maintaining the temperature within ±0.03 K during the experiment.

Procedures. After the pressure in the vessel was raised above the maximum pressure and kept there for about 20 min to allow sufficient time for attaining thermal equilibrium, measurements were started by decreasing the pressure at a slow constant rate of about 0.05 MPa min^{-1} or less. The pressure and the fringe pattern, which appeared as a roughly sine-shaped curve along with pressure changes, were recorded by the pen recorder. The position corresponding to each measured pressure was marked as a sharp peak on the recorder chart. When the pressure-reducing speed was faster than this value, the interference fringe showed a deformed pattern; therefore, the displacement of the pattern as a function of pressure change had poor reproducibility.

Results and Discussion

Refractive-Index Calculation. The change of the refractive index, Δn, at various temperatures and pressures is calculated with the following equation:

$$\Delta n = \Delta m \lambda / (2l \sin \theta) \qquad (1)$$

where Δm is the number of fringes passing the reference mark (slit position). In this study, the wavelength of the light source is 632.8 nm for the He-Ne laser, but it is difficult to obtain directly the exact values of the optical path length, l, and the angle of the incident light beam, θ. Langer and Montalvo (*2*) have measured the refractive indexes for pure liquid mesitylene under high pressure by an interferometric method using 632.8-nm light with an accuracy of better than ±0.0001; their reported values at 295.15 K are 1.4946 under atmospheric pressure and 1.510 69 at 49 MPa. And so, in order to obtain

0021-9568/82/1727-0016$01.25/0 © 1982 American Chemical Society

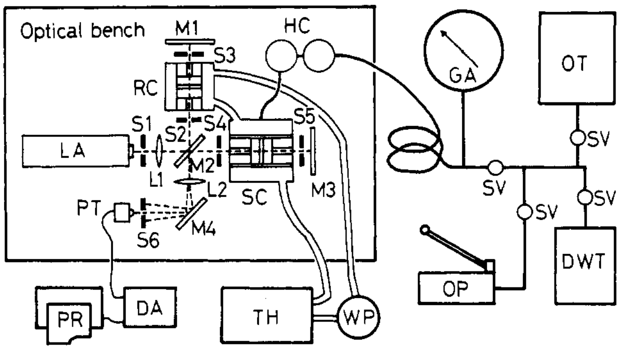

Figure 1. Block diagram of refractive-index apparatus: (LA) He-Ne laser, 632.8 nm, 1.5 mW; (RC) reference cell; (SC) sample cell; (M1, M4) mirrors; (L1, L2) lenses; (S1, S6) slits; (HC) H_g cylinder; (PT) phototransistor; (PR) pen recorder; (DA) dc amplifier; (TH) thermostat; (WP) water pump; (GA) gauge; (OT) oil tank; (SV) stop valve; (OP) oil pump; (DWT) deadweight tester.

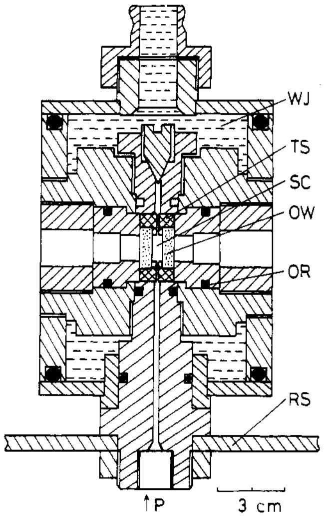

Figure 2. High-pressure sample cell: (WJ) water jacket; (TS) Teflon spacer; (SC) sample chamber; (OW) optical window; (OR) O-ring; (RS) rock stand.

the values of l and θ in eq 1, the authors measured, at 295.15 K, Δm of mesitylene for pressures ranging from atmospheric pressure to 49.0 MPa, and they obtained 243.6 as the value of Δm. From this value, eq 1 may be expressed as follows:

$$n = (6.628 \times 10^{-5})(\Delta m - c) \qquad (2)$$

where c is a correction term for the strain on the optical windows due to pressure. This value is determined by observing the change of interference fringe (Newton ring) number within a constant area on the slit board with pressure, and c obtained over the same pressure range was found to be expressed by an equation of the form

$$c = (1.88 \times 10^{-2})p - (2.3 \times 10^{-6})p^2 \qquad (p \text{ in MPa}) \quad (3)$$

Comparison with Other Data. As preliminary work, the refractive indexes of benzene and carbon tetrachloride were measured at 298.15 K under pressures up to 50 MPa, and the results of Δn for some pressure intervals Δp are listed in Table II. Richard (*4*) recently indicated that the values of Δn can conveniently be calculated by combining the Lorentz–Lorenz function and the equation of state and that, for these liquids, Δn values for 632.8 nm estimated at 298.15 K were compatible with those observed by Waxler et al. (*9*) under pressures up to about 100 MPa. And so, the estimated and observed values of these studies are listed in Table II in order to check the reliability of the present values. As can be seen clearly in the table, the values observed with the interferometer in the present investigation agree closely with the values reported in ref *4* and *9* within the usual experimental error for the present pressure range. Moreover, at each experimental condition, the values of Δm were reproduced within an accuracy of 1.1 fringes on repeated runs. Consequently, it is found that the probable uncertainty in the measurements of refractive index is estimated, taking into account the observed errors of temperature and pressure, to be less than ±0.000 08 over the whole range of the experiment.

Table II. Comparison of the Observed Refractive Indexes with Literature Values for 632.8 nm at 298.15 K

		$10^3\Delta n$		
compd	Δp, MPa	this work	Richard[a]	Waxler[b]
benzene	24.91	11.46	11.73	11.63
	48.80	20.92	21.07	21.08
carbon tetrachloride	27.59	13.06	13.12	12.91
	52.26	22.43	22.54	22.38

[a] Reference *4*, calculated values. [b] Interpolated values, as were given in ref *4*, from observed values of Waxler (*9*).

Table III. Refractive Indexes of Pure Liquids for 632.8 nm

p, MPa	293.15 K	303.15 K	313.15 K
	Benzene		
0.1	1.4981	1.4912	1.4849
5	1.5004	1.4939	1.4876
10	1.5025	1.4962	1.4901
15	1.5047	1.4985	1.4925
20	1.5066	1.5007	1.4949
25	1.5087	1.5029	1.4972
30	1.5107	1.5049	1.4994
35	1.5125	1.5071	1.5016
40	1.5142	1.5094	1.5036
45	1.5159	1.5109	1.5056
50	1.5173	1.5128	1.5075
	Chlorobenzene		
0.1	1.5193	1.5152	1.5104
5	1.5218	1.5176	1.5133
10	1.5240	1.5198	1.5156
15	1.5259	1.5220	1.5177
20	1.5278	1.5240	1.5197
25	1.5295	1.5259	1.5216
30	1.5313	1.5276	1.5233
35	1.5328	1.5292	1.5249
40	1.5343	1.5308	1.5264
45	1.5355	1.5322	1.5277
50	1.5367	1.5334	1.5288
	Toluene		
0.1	1.4925	1.4874	1.4817
5	1.4947	1.4899	1.4844
10	1.4969	1.4921	1.4869
15	1.4990	1.4944	1.4892
20	1.5011	1.4966	1.4914
25	1.5030	1.4986	1.4937
30	1.5049	1.5005	1.4958
35	1.5068	1.5025	1.4978
40	1.5087	1.5042	1.4998
45	1.5103	1.5058	1.5016
50	1.5119	1.5075	1.5034
	Nitrobenzene		
0.1	1.5476	1.5426	1.5381
5	1.5500	1.5449	1.5409
10	1.5522	1.5471	1.5432
15	1.5541	1.5492	1.5453
20	1.5556	1.5512	1.5473
25	1.5576	1.5529	1.5491
30	1.5594	1.5547	1.5508
35	1.5610	1.5563	1.5524
40	1.5624	1.5576	1.5538
45	1.5638	1.5589	1.5551
50	1.5651	1.5601	1.5562

Refractive Indexes of Pure Liquids. The experimental values of the refractive indexes of pure benzene, toluene,

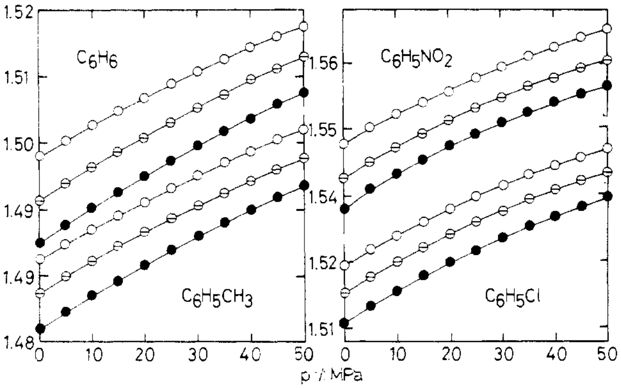

Figure 3. Refractive indexes of liquids for 632.8 nm at (○) 293.15, (⊖) 303.15, and (●) 313.15 K.

chlorobenzene, and nitrobenzene for 632.8-nm light are listed in Table III. As to the refractive indexes of various organic liquids at atmospheric pressure, it is known that they slightly decrease as the wavelength of the measuring light increases (*1*, *3*, *5*). However, the values for the wavelength of 632.8 nm, corresponding to the light source of the He-Ne laser, have been scarcely measured, except for the report of Langer and Montalvo (*2*), where the refractive index of mesitylene for 632.8 nm is reported as 1.4946 at 295.15 K and atmospheric pressure. And so, we at first estimated by the least-squares method the refractive index of mesitylene for 632.8 nm at 293.15 K from data for several wavelengths at 293.15 K reported in the literatures (*1*, *3*, *5*), and, to check the estimated values, we measured change in the refractive index with temperature over the range 293.15-295.15 K. The value at 295.15 K thus obtained is 1.4944, and this value is found to coincide with that of Langer and Montalvo (*2*). Thus, for all of the present samples, the values at 0.1 MPa in Tables III are estimated values which are determined by the same method described above.

For each compound, the observed refractive indexes increase parabolically with increasing pressure throughout the experimental range, as shown in Figure 3. From these results, it is found that the values for the temperature and pressure dependence of the refractive index, $(\partial n/\partial T)_p$ and $(\partial n/\partial p)_T$, decrease with an increase of pressure and have a tendency similar to that of the specific volume on pressure, which was estimated from the pressure dependence at ultrasonic speed, as described in our previous papers (*6*-*8*).

Literature Cited

(1) Forziati, A. F. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1950**, *44*, 373.
(2) Langer, D. W.; Montalvo, R. A. *J. Chem. Phys.* **1968**, *49*, 2836.
(3) "Landolt-Bornstein Tabellen"; Springer-Verlag: West Berlin, 1962; 6 Aufl., 8 Teil, Zahlenwerte und Funktion.
(4) Richard, A. J. *J. Chem. Phys.* **1960**, *72*, 4063.
(5) Savkovic-Stevanovic, J.; Simonovic, C. *J. Chem. Eng. Data* **1976**, *21*, 456.
(6) Takagi, T. *Rev. Phys. Chem. Jpn.* **1976**, *46*, 10.
(7) Takagi, T. *Rev. Phys. Chem. Jpn.* **1976**, *46*, 17.
(8) Takagi, T. *J. Chem. Thermodyn.* **1980**, *12*, 277.
(9) Waxler, R. M.; Weir, C. E. *J. Res. Natl. Bur. Stand., Sect. A* **1963**, *67*, 163.

Received for review April 20, 1980. Revised manuscript received September 14, 1981. Accepted October 1, 1981.

Hydrates of Methane + *n*-Butane Below the Ice Point

V. T. John
Department of Chemical Engineering, Columbia University in the City of New York, New York, New York 10027

G. D. Holder*
Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Three-phase vapor (V)-ice (I)-hydrate (H) and four-phase vapor-ice-hydrate-liquid hydrocarbon (L_2) equilibrium conditions were measured for mixtures of methane and *n*-butane, at temperatures below the ice point. One purpose of the experiments was to determine whether pure *n*-butane gas can form hydrates; the results led to the conclusion that *n*-butane cannot form hydrates under its own vapor pressure. The experimental results can also serve as a basis for evaluating the accuracy of models for predicting hydrate phase equilibrium (*1*). The experimental method followed to nucleate hydrates at temperatures below 273.15 K is a variation of the procedure used to form hydrates at higher temperatures.

Introduction

Gas hydrates are a form of clathrate compounds formed by water and gases of low molecular weight. Hydrates crystallize in either of two structures, commonly known as structures I and II, each of which contains two characteristic interstitial vacancies referred to as large and small cavities. The crystal lattice is made up of water molecules that are strongly hydrogen bonded. Gas molecules are enclosed in cavities formed by these lattice structures and interact with the water molecules of a cavity through dispersion forces. The formation of structure I or II is dependent on the relative stabilities of the two structures when a given gas (or gas mixture) is enclathrated at the thermodynamic conditions in effect.

Determination of gas hydrate equilibrium is important from the standpoint of assessing the potential of recovering gas from hydrate reservoirs, and in gas processing and pipeline operations. In such determinations, it is useful to establish whether the heavier components of natural gas, such as the propanes and the butanes, contribute to the hydrate formation process. The enclathration of such relatively large molecules tends to strongly stabilize the hydrate structure and thereby lower the equilibrium pressure considerably. In understanding hydrate formation, it is important to determine which large molecules can form hydrates at pressures below their vapor pressure at a given temperature. Several studies have been conducted on the formation of hydrates from pure *n*-butane or from gas mixtures containing *n*-butane; Ng and Robinson (*2*) have presented a detailed bibliography of these studies. There has been conflicting evidence, however, on the role of n-butane in hydrate formation. A systematic study of hydrate formation in

0021-9568/82/1727-0018$01.25/0