Saturated Liquid Densities of Benzene, Cyclohexane, and Hexane from 298.15 to 473.15 K

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The results of measurements of saturated liquid densities using a high-pressure stainless steel pycnometer system over a wide variation of temperature from 298.15 to 473.15 K are presented for benzene, cyclohexane, and hexane. Experimental densities were compared with those predicted by the Spencer–Danner-modified Rackett equation (SDR) and the Hankinson–Brobst–Thompson correlation (HBT). The SDR showed an average deviation of 0.22% while the HBT predicted the densities of the three organic solvents with an average deviation of 0.28%. The data obtained have also been compared with the available data reported in the literature.

Introduction

There has always been a need for reliable densities of organic liquids at elevated temperatures. This is true particularly for those organic solvents commonly used in industrial processes. The shortage of such data is due primarily to experimental difficulties arising from the need to use a sealed measuring system. Pressure–volume–temperature (PVT) measurements of various kinds have been the main source of such data in the past, but values obtained are not generally reliable.

In this study, the densities of benzene, cyclohexane, and hexane were measured over the temperature range 298.15–473.15 K. The experimental density data were compared with predictions made by the Spencer–Danner-modified Rackett equation (*1*) and the Hankinson–Brobst–Thompson correlation (*2*). The experimental results were also compared with the experimental data reported in the literature.

Experimental Section

Materials. Analytical grade benzene, cyclohexane, and hexane were obtained from BDH Limited, Poole, England, with purities of 99.7, 99.5, and 99.7 mol %, respectively. An attempt was made to further purify each of the three samples by means of simple distillation, with the first and last 20% of the distillate being discarded. Precision refractometry indicated that the purity of each product was not significantly enhanced.

Apparatus and Procedure. Measurements of liquid densities were carried out using a 40 cm^3 double-ended 316-stainless steel cylinder with 35-mm female threads on both ends. The volume of the cylinder (i.e., the pycnometer) was calibrated as a function of temperature using mercury as the density standard. The principle of the density measurement involves measurement of a mass of the test fluid contained in a pycnometer of known volume at any desired temperature. The experimental system was designed to operate in a temperature range from ambient to 500 K and at pressures up to 125 bar (*3*).

Schematic diagrams of the experimental apparatus for the density measurements are shown in Figure 1. The setup consisted of six units which could be operated independent of each other. Figure 1b shows the schematic diagram of one assembly used for the density measurement. The two vessels A and B are made of pressure-resistant stainless steel cylinders and have volumes of 150 cm^3 and 40 cm^3, respectively. Cylinder A served as the sample reservoir while cylinder B was the pycnometer for determining the densities of the samples.

For the measurement of the density of the test sample, the pycnometer was first evacuated by connecting it to the vacuum line as shown in Figure 1, after which it was weighed carefully on a Mettler balance PC-2000 with a readability of 0.01 g. The pycnometer was subsequently reconnected back to the system. The test sample was then forced into the pycnometer under pressure from the nitrogen gas in the standard nitrogen cylinder (C). The fluid in the pycnometer was kept in the liquid state by applying a pressure of approximately 15 kPa above the saturation pressure of the fluid at the operating temperature. The saturation pressures of the test samples were estimated from the correlation presented by Reid, Praunitz, and Poling (*4*), which was derived from numerous experimental vapor pressure data of pure compounds including benzene, cyclohexane, and hexane.

A digital pressure gauge (D) with an accuracy of 1% full scale (11 MPa) monitored the pressure in the high-pressure line. The pycnometer was then immersed in a constant-temperature bath which had already attained a steady-state predetermined operating temperature. After thermal equilibrium had been achieved, the density cell was disconnected from the system, properly cleaned, dried, and weighed. The density was then determined from the weight of the sample and the volume of the density cell.

A Tamson TCV-70 constant-temperature bath supplied by Neslab was used for operating temperatures from ambient to 500 K. The bath was designed to maintain a constant and uniform temperature to within ±0.1 K. The bath was provided with an 800-W control heater and a 1750-W booster heater for quick heating. The temperature in the bath could be maintained within constancy and uniformity of ±0.02 K. A Neslab DR-2 digital readout compact thermometer with an independent system that could monitor temperature in the range from 200 to 500 K was obtained for measuring the operating bath temperatures. This system was supplemented with a Fluke Model 2180A RTD digital thermometer which had a temperature range from 100 to 500 K and a resolution of ±0.01 K as a double check on the bath temperature measurement.

Results and Discussion

In order to test the accuracy of the experimental system, the density of doubled distilled water was measured from

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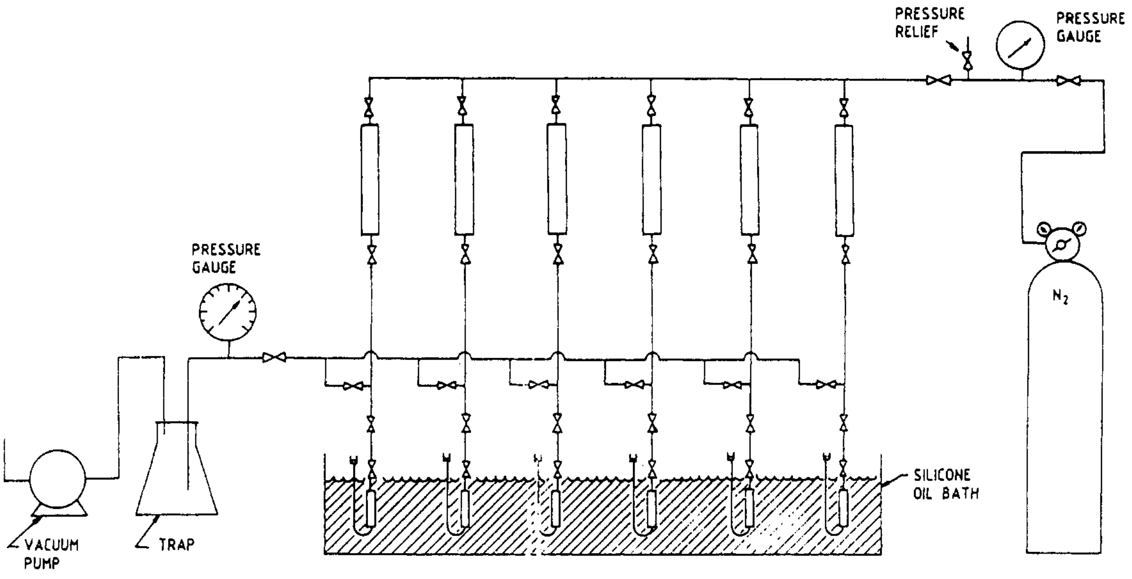
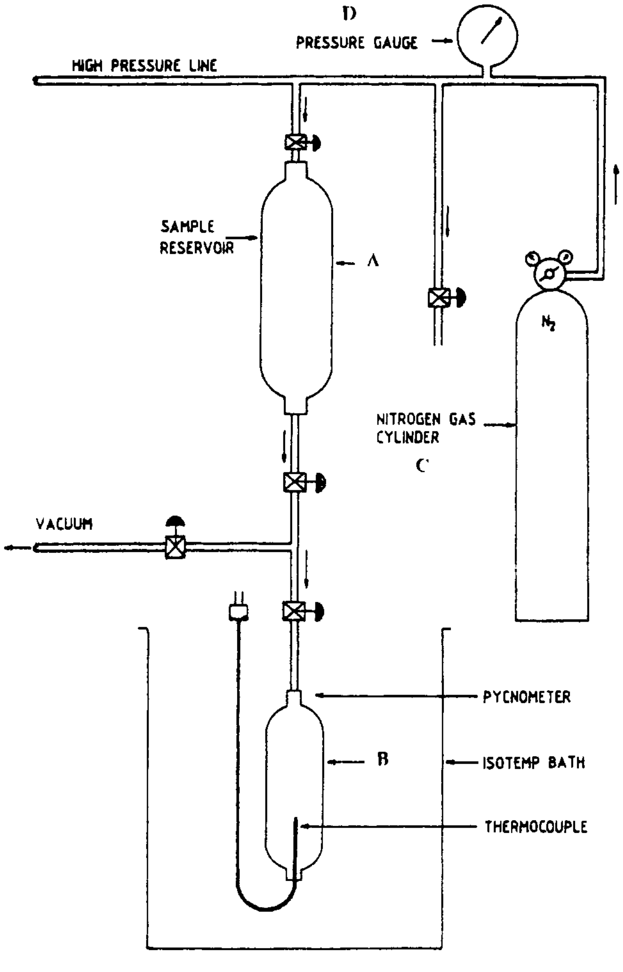


1(a) : Six units



1(b) : A single unit

Figure 1. Schematic diagram of the experimental apparatus.

313.15 to 373.15 K and each observation was repeated. The data obtained were compared with the reliable data reported in the literature (*5, 6*) as shown in Table I. The experimental measurement has been found to differ with the two reported literature values by an average absolute deviation of about 0.06% which does establish the reliability of the system in terms of both its accuracy and reproducibility. The uncertainty in the measurement of density was estimated to be within ±0.06% over the whole range of temperature.

All the experimental results for benzene, cyclohexane, and hexane are summarized in Tables II–IV, respectively, together with the data reported by other researchers. The results

Table I. Comparison of Density, Data Obtained for Distilled Water with the Data Reported in the Literature

	ρ (kg m^{-3})				
T (K)	present work	lit.[a]	% dev from present work	ρ (kg m^{-3}) lit.[b]	% dev from present work
313.15	993.2	992.25	+0.10	992.215	+0.10
	991.7		−0.06		−0.05
333.15	982.2	983.24	−0.11	983.200	−0.10
	982.9		−0.03		−0.03
353.15	971.3	971.83	−0.05	971.799	−0.05
	971.5		−0.03		−0.03
373.5	958.1	958.38	−0.03	958.365	−0.03
	959.1		+0.08		+0.08

[a] Reference 5. [b] Reference 6.

Table II. Densities of Benzene at Different Temperatures (T)

	ρ (kg m^{-3})			ρ (kg m^{-3})	
T (K)	present work	lit.	T (K)	present work	lit.
298.15	873.7	873.6[a]	353.15	814.6	
		873.65[b]	373.15	792.6	
		873.44[c]	393.15	768.5	
		873.7[d]	413.15	743.7	
303.15	868.3	868.29[a]	433.15	718.8	
		868.3[d]	453.15	691.2	
313.15	858.1	857.5[d]	473.15	660.7	
333.15	835.8				

[a] Reference 7. [b] Reference 8. [c] Reference 9. [d] Reference 10.

Table III. Densities of Cyclohexane at Different Temperatures (T)

	ρ (kg m^{-3})			ρ (kg m^{-3})	
T (K)	present work	lit.	T (K)	present work	lit.
298.15	773.9	773.9[a]	373.15	699.2	
		773.62[b]	393.15	677.8	
303.15	769.1	768.7[a]	433.15	631.4	
		768.79[b]	433.15	631.4	
313.15	759.5	759.46[c]	453.15	605.5	
333.15	740.4	740.25[c]	473.15	576.8	
353.15	720.1				

[a] Reference 12. [b] Reference 13. [c] Reference 14.

Table IV. Densities of Hexane at Different Temperatures (T)

	ρ (kg m^{-3})			ρ (kg m^{-3})	
T (K)	present work	lit.	T (K)	present work	lit.
298.15	654.8	655.08[a]	333.15	622.1	
		655.04[b]	353.15	602.3	
		654.8[c]	373.15	581.6	
		654.8[d]	393.15	559.6	
303.15	650.4	650.3[c]	413.15	535.5	
		650.2[d]	433.15	508.7	
313.15	640.9	641.3[c]	453.15	477.3	
		641.0[d]	473.15	438.1	

[a] Reference 9. [b] Reference 15. [c] Reference 10. [d] Reference 16.

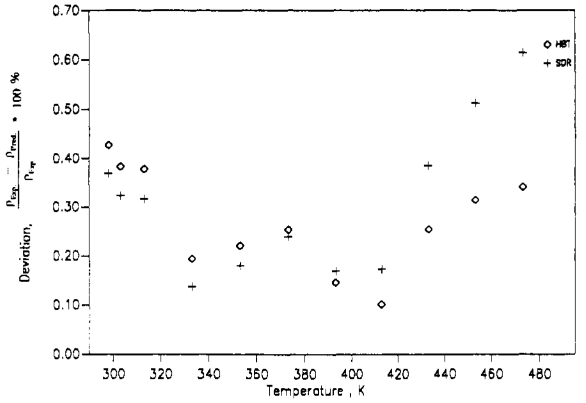


Figure 2. Deviation plot of the prediction of the density of benzene by SDR and HBT from the experimental values.

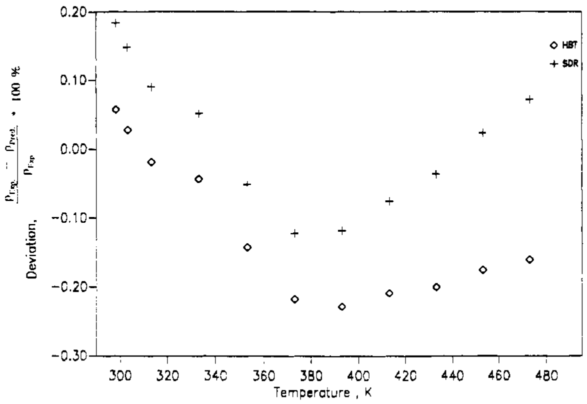


Figure 3. Deviation plot of the prediction of the density of cyclohexane by SDR and HBT from the experimental values.

Table V. Effect of High-Temperature Exposure on the Experimental Density Measurements

	ρ (kg m^{-3})	T (K)
Benzene		
fresh sample	873.7	298.15
after exposure to high temperature	873.5	298.15
Cyclohexane		
fresh sample	773.9	298.15
after exposure to high temperature	773.8	298.15
Hexane		
fresh sample	654.8	298.15
after exposure to high temperature	654.9	298.15

obtained in the present studies for benzene as listed in Table II agree quite well with those reported in the literature (*7–10*). Although Hales and Townsend (*7*) made measurements of liquid densities in the temperature range of 293–490 K, their experimental measurements could only be compared with the results obtained at only two temperatures (298.15 and 303.15 K) as their measurements were carried out at temperatures different from those selected for the present studies. Their data at these two temperatures show a close agreement as shown in Table II.

However, it has been possible to compare the density data of the present work with predictions made by their empirical correlation derived from their experimental measurements. They have been found to fit the experimental data obtained with an average absolute error of 0.177% for the whole range of temperature.

Furthermore, Connoly and Kondalic's correlation (*11*) valid from 400 to 550 K showed a close agreement with our experimental data for the temperature range considered (average absolute error of 0.411%).

The data obtained for cyclohexane at 298.15, 303.15, and 313.15 K as reported in the literature (*12–14*) are also listed in Table III. These measurements are in reasonable agreement with the data obtained. The data for hexane at 298.15, 303.15, and 313.15 K as reported in the literature (*9, 10, 15, 16*) are also listed in Table IV. These values are also in reasonable agreement with the measurements obtained. The comparison of the data at higher temperatures for both cyclohexane and hexane is not possible due to the lack of such measurements for these compounds.

In order to make sure that the test samples were not decomposed or contaminated during studies at high temperatures, measurements of the density at ambient temperature were made for all such samples that had been previously exposed to high temperatures. The data obtained were

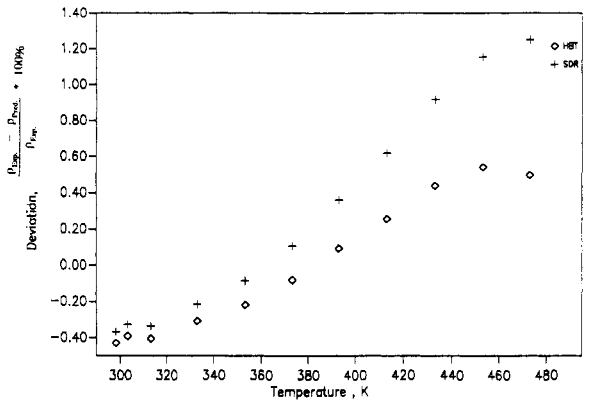


Figure 4. Deviation plot of the prediction of the density of hexane by SDR and HBT from the experimental values.

compared with the density measurement of a fresh sample. From these results no evidence of decomposition or contamination of the specimens was found, as shown in Table V.

The density data were also predicted as a function of temperature by the HBT method and the Spencer–Danner-modified Rackett equation. The Z_{RA} values and the pure component critical property data required to estimate the liquid densities were obtained from the literature (*4*). However, relatively high deviations of 0.25% and 0.29% have been found for the benzene data as predicted by the HBT and the SDR correlations, respectively.

The HBT correlation predicts the experimental density data of cyclohexane and hexane with average absolute deviations of 0.12% and 0.48%, respectively, while the SDR predicted the densities of cyclohexane and hexane with relatively lower deviations of 0.08% and 0.03%, respectively. Figures 2–4 show deviation plots between the measured and the predicted densities for the three pure compounds considered.

The modified Tait equation included in the HBT (i.e., the COSTALD) correlation for predicting the effect of pressure on a liquid was utilized in order to ascertain the effect of the excess pressure (15 kPa approximately) applied in determining the density of the samples. The effect on the saturated liquid densities was found to be negligible (to within 0.009% maximum for benzene, 0.01% maximum for cyclohexane, and 0.04% maximum for hexane).

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Received for review February 1, 1993. Accepted April 16, 1993. The authors wish to acknowledge the King Fahd University of Petroleum & Minerals at Dhahran, Saudi Arabia, for financial support during the course of this research.