PVTx measurements and partial molar volume for water-hydrocarbon mixtures in the near-critical and supercritical conditions[1]

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Abstract

By means of a constant-volume piezometer, measurements have been made of the PVTx properties of water-hydrocarbon (n-heptane, n-octane, and benzene) mixtures at near-critical and supercritical conditions. The measurements cover the pressure range from 5 to 40 MPa and densities between 20 and 450 $kg \cdot m^{-3}$ for six compositions from 0 to 0.614 mole fraction of hydrocarbon. Tests on the piezometer and consistency tests on the measurements suggest that the results are free from significant "dead volume" error. The experimental errors of the present PVTx measurements are estimated to be within ±10mK in temperature, ±0.15% in density, ±2 kPa in pressure, and ±0.002 mole fraction in composition.Good agreement was obtained with values reported in the literature for pure components (water, n-heptane, n-octane, and benzene), measured using other techniques. Values of partial molar volumes and Krichevskii parameter have been obtained from these measurements.

Analysis of the results for dilute water- hydrocarbon mixtures show that partial molar volume of hydrocarbon (solute) near the critical point of pure water (solvent) exhibit remarkable anomalies. The experimental results have been interpreted in terms of the modern molecular thermodynamic models for the partial molar volumes of the solute near the solvent critical point and Kirkwood-Buff fluctuation theory of solutions in terms of direct correlation function integral.

Keywords:: Apparent molar volume;Critical state; Density; Excess molar volume; Partial molar volume; Piezometer; Pressure; Supercritical fluid; Water

Introduction

Water, the most important solvent in nature, has surprising properties as a reaction medium in its supercritical state. The remarkable anomalous properties of supercritical fluids in general, as well as supercritcal water in particular, are widely used as a solvent or reaction medium for a number of technological applications [1]. Supercritical fluids are of fundamental importance in geology and mineralogy (for hydrothermal synthesis), in chemistry, in the oil and gas industries (e. g. in tertiary oil recovery), for some new separation techniques, especially in supercritical fluid extraction, for regeneration of sorbents used in wastewater treatment, for hazardous waste decontamination of soils or equipment, and oxidation of hazardous chemicals.

Binary aqueous fluid mixtures with hydrocarbons are interesting combinations of polar and non-polar molecules. The near-critical local environment (microstructure) around an infinitely dilute solute can be dramatically different from the bulk average. This is associated with the divergence of the solute partial molar volume at the solvent's critical point. The aim of this work was to use PVTx measurements of dilute water+hydrocarbon mixtures near the critical point of pure water to study the anomalous critical behavior of the partial molar volume of hydrocarbon in the critical point of pure water (solvent).

Very little has been published concerning the PVTx properties of water+hydrocarbon mixtures at near- and supercritical conditions due to the experimental difficulties in their measurement. In previous papers. [2-4] we reported PVTx data of five water-hydrocarbon binary mixtures (water-methane, -n-hexane, -n-heptane, -n-octane, -benzene) at supercritical conditions. The new PVTx for water-n-heptane, water+n-octane, and water+benzene systems in the immediate vicinity of the solvent's critical point provide additional information on the effects of temperature, pressure, and composition on the PVT relation in such systems, which could lead to improved understanding of the process near the solvent's critical point. However, the PVTx data for the system water-hydrocarbon at near- and supercritical conditions are scarce. A

number of phase equilibrium (PTx) studies have been made on water-n-alkane mixtures [5-7]. Most of the measurements were performed at temperatures up to the critical point of pure water.

2. Experiments

Since the experimental apparatus and procedure have been reported in [2-4], only a brief explanation is given here. Experimental methods were similar to those described in [2-4], except that a smoler (≈36.8 cm^3) piezometer was used. The volume of the piezometer have been carefully calibrated by using standard fluid (pure water) with a well known PVT [8] at temperature T_0=673 K and at pressure P_0=39 MPa. The volume at these conditions was V_{PoTo}=36.880 ±0.003 cm^3.The temperature in the air thermostat was controlled authomatically to within ±5mK. The main part of the apparatus consisted of an air thermostat, a piezometer, lines for filling and extracting samples, temperature control and temperature measuring devices, and pressure measuring instruments. The air thermostat has double walls and it has an inside volume of 65 dm^3. Guard heaters have been located between the walls of the thermostat for setting the desired temperature inside the thermostat. The regulating heater was mounted inside the thermostat to avoid thermal losses. The temperature is measured by a 10 Ω platinum resistance thermometer. The uncertainty in the temperature measurement when local temperature gradients and temperature stability are taken into account is less than ±10 mK. To minimize temperature gradients in the air thermostat two electrically driven high-speed fans were provided. The cylindrical piezometer was made from a heat- and corrosion-resistant high-strength alloy (EI-437B4). On one of the ends of the piezometer a diaphragm-type null indicator is mounted and on the other end, a high pressure valve. The diaphragm (40 mm in diameter and 0.08 mm thick) was made from type 321 stainless steel. The pressure measurements have an uncertainty of ±2 kPa. To reach equilibrium fast, the electric heater was switched on and the sample was stirred with a steel ball bearing which was rotated rapidly in the sample by a mechanical rotation of

the piezometer. The volume V_{PT} of the piezometer was corrected for its variation with temperature T and pressure P.

Taking into account the errors of temperature, pressure and concentration measurements, the total experimental uncertainty of density, $\overline{\delta\rho}$ not more ±0.2%.

3. Results

In Tables I-III, the some of the experimental results for water+n-heptane, water+n-octane, and water+benzene binary mixtures are presented on critical isotherm (T_C=647.05 K). Some of the these measured results are also shown in Figures 1-4. Measurements have been made at critical isotherm (T_C=647.05 K), at pressures from 5 to 40 MPa, and at six hydrocarbon mole fractions from 0 to 0.614 for each system. Figure 3 shows the molar volume V_m of a water+hydrocarbon mixtures at critical isotherm-isobar (T_C=647.05 K and P_C=22.035 MPa) as a function of composition.

The measurements of pure components (water, n-heptane, n-octane, and benzene) were carried out in order to confirm the reliability of the present apparatus. In order to check the apparatus, density measurements on the pure components have been carried out also on three isotherms (573, 623, and 648 K). From Figure 5 can be seen that the test measurements for benzene are in excellent agreement, namely clearly within ±0.3%, with the densities measured [9]. The excellent agreement between the densities measured with the our piezometer and the values from the [9] and may be considered as proof of principle for the technique.

4. Discussion

The partial molar volumes $\overline{V}_i$, i=1,2, are obtained from the slope of tangent $(\partial V_m/\partial x)_{PT}$ as follows [10].The measurements of the molar volumes $V_m(P,T,x)$ at critical isotherm-isobar (T_C=674.05 K and P_C=22.035 MPa) have been correlated as a function of the concentration x by equation:

$$V_m(x) = V_0 e^{-x} \sum_{i=1}^{N} \frac{x^{i-\gamma/\beta\delta}}{(i-\gamma/\beta\delta)} + (1-x)V_{mc}(P_c, T_c) + xV_{12}, \qquad (1)$$

where γ=1.24, β=0.325, and δ=4.83 are universal critical exponents; N=2; $V_{mc}(P_c,T_c)$ =55.838 $cm^3 \cdot mol^{-1}$ is the critical volume of pure water; V_o and V_{12} are nonuniversal adjustable parameters. From our experimental PVTx data at critical isotherm-isobar we have deduced values for V_o and V_{12}. Our results are: V_o =19.385, V_{12}=113.341$cm^3 \cdot mol^{-1}$ for water+benzene, V_o =25.070, V_{12}=189.581 $cm^3 \cdot mol^{-1}$ for water+ n-heptane , and V_o =30.044, V_{12}=230.872 $cm^3 \cdot mol^{-1}$ for water+ n-octane mixtures. From (1) we derivatived $(\partial V_m/\partial x)_{PT}$ which yields the partial molar volumes $\overline{V}_1$ and $\overline{V}_2$. On the critical isotherm-isobar in the limit $x \to 0$, $(\partial V_m/\partial x)_{PT}$, as a follows from (1), diverges as $x^{-\gamma/\beta\delta}$. Consequently, $\overline{V}_2^{\infty}$ behave as $x^{-\gamma/\beta\delta}$ which good agreement with the nonclassical limiting behavior [11]. The classical (mean field theory) predict the behave of $\overline{V}_2^{\infty}$ as $x^{-2/3}$. In Figures 6,7, the partial molar volumes for hydrocarbons derived from our experimental molar volumes are shown as a function of concentration and pressure at the critical isotherm.In the vicinity of the solvent's critical point $T \to T_C$, the partial molar volume of an infinitly dilute solute ($x \to 0$) in a binary mixture is given by [12]: $\overline{V}_2^{\infty} = \rho^{-1} K_T \delta$, where $\delta = \rho kT\left(1 - C_{12}^{\infty}\right)$ is the infinite dilution limit of the rate of change of pressure upon solute addition at constant temperature, volume, and solvent mass. Partial molar volume of solute $\overline{V}_2^{\infty}$ can be expressed as [12]: $\overline{V}_2^{\infty} = kT K_T\left(1 - C_{12}^{\infty}\right)$, where $C_{12}^{\infty} = \rho \int c_{12}^{\infty}(r)dr$, is the DCFI (solute-solvent direct correlation function integral), $c_{12}^{\infty}(r)$, is the direct correlation function (DCF). This equation is an identity and follows from reformulating the Kirkwood-Buff fluctuation theory of solutions [13] in terms of direct correlation function [14]: $C_{12}^{\infty} = 1 - \dfrac{\delta}{\rho kT}$,

where $\delta = \left(\dfrac{\partial P}{\partial x}\right)_{V,T}^{C} + K_T^{-1}$ (2).

At asymptotically near the critical point, $T \to T_C$, the $K_T \propto (T - T_C)^{-\gamma} \to +\infty$, and $\delta \to \left(\frac{\partial P}{\partial x}\right)^C_{V,T}$, where $\left(\frac{\partial P}{\partial x}\right)^C_{V,T}$ is the Krichevsii parameter. In terms of a long-ranged fluctuation integral the partial molar volume of an infinitly dilute solute can be written as [15]: $\rho\overline{V}_2^\infty = \rho kT K_T - G_{12}$, where $G_{12} = \rho\int_0^\infty (g_{12}^\infty - 1)4\pi r^2 dr$ is the statistical excess number of solvent molecules surrounding an infinity dilute solute molecule with respect to a uniform distribution at bulk conditions. The partial molar volume at infinite dilution $V_2^\infty \to \pm\infty$ and cluster size $G_{12} \to \pm\infty$ diverge strongly as K_T near the solvent's critical point.

The divergence of G_{12} is the result of the long-range (critical) part of distribution function $g_{ij}(r)$, not the short-range solvation part. Note that G_{12} can be either positive or negative. The sign of the solute's partial molar volume $V_2^\infty \to \pm\infty$ and cluster size $G_{12} \to \pm\infty$ divergences are determined by the value of the DCFI C_{12}^∞ and of δ,($\rho kT - \delta$). From our PVTx experimental data for C_{12}^∞ using Eq. (2) we obtain (see Fig. 8): $0 \le C_{12}^\infty \le 1$, $\overline{V}_2^\infty \to +\infty$ and $G_{12} \to \pm\infty$. It can be seen from Fig. 8 that the water+n-octane system exhibit weakly attractive behavior in the near-critical region.

The initial slopes of the critical line, are related with Krichevskii parameter as follows:

$$\delta^C = \left(\frac{\partial P}{\partial x}\right)^C_{V,T} = \left(\frac{\partial P_C}{\partial x}\right)^C_{CRL} - \left(\frac{dP_S}{dT}\right)^C_{CXC}\left(\frac{\partial T_C}{\partial x}\right)^C_{CRL}, \qquad (3)$$

where $\left(\frac{\partial P_C}{\partial x}\right)_{CRL}$, $\left(\frac{\partial T_C}{\partial x}\right)^C_{CRL}$ are the initial slopes of the critical lines, $\left(\frac{dP_S}{dT}\right)^C_{CXC}$ >0 is the slope of the solvent's vapor-pressure curve evaluated at the critical point of the solvent (always positive). The regimes near-critical behavior of mixtures depends

the signs and the magnitudes of the derivatives (initial slopes of the critical lines and vapor-pressure curve at the critical point) in these equation (3). The values of the Krichevskii parameter for the water+hydrocarbon mixtures was estimated from Eq. (3) using critical lines (T_C-x, P_C-x) and vapor-pressure P_S-T experimental data [16]. The results of this estimate together with values derived from our PVTx measurements were:

Systems	$\left(\frac{\partial P}{\partial x}\right)^c_{VT}$, MPa from PVTx measurements	$\left(\frac{\partial P}{\partial x}\right)^c_{VT}$, MPa from initial slopes of the critical lines
Water+benzene	52.4223	52.1684
Water+n-heptane	115.1093	230.4061
Water+n-octane	127.4525	-

5. Conclusion

New measurements of the PVTx of water+n-heptane, water+n-octane, and water+benzen mixtures are reported. The measurements were performed by means of a constant-volume piezometer in a precision thermostat. The measurements cover the pressure range from 5 to 40 MPa and density between 20 and 450 kg·m^{-3} for six compositions from 0 to 0.614 mole fraction of hydrocarbon. All measurements was made at critical isotherm T_C=647.05 K. The accuracy of the present results was estimated as : molar density- ±0.15%, pressure- ±2 kPa, temperature- ±10 mK, and concentration- ±0.002 mole fraction. For pure benzene at isotherms 573 K, 623 K and 648 K it was found that the experimental data of [9] were consistent with the present results. Using our experimental results, the partial molar volumes were determined. The nonclassical anomalous critical behavior of the partial molar volume of hydrocarbons near the critical point pure water (solvent) was found.

Acknowledgments

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Table I. Measurements of PVTx for Water+Benzene Mixtures at Critical Isotherm:

P, Pressure (MPa), ρ, Density (kg ·m^{-3}), V_m, Molar Volume (cm^3·mol^{-1})

T_C=647.05 K

P	ρ	V_m	P	ρ	V_m	P	ρ	V_m
x=0.028 mole fraction			x=0.043 mole fraction			x=0.063 mole fraction		
4.618	18.480	1064.954	4.695	19.581	1052.808	3.508	16.037	1359.757
9.241	40.536	485.505	9.369	42.897	480.561	5.424	24.380	894.448
15.077	78.323	251.271	13.599	69.850	295.125	8.593	40.564	537.591
21.263	161.713	121.699	16.500	95.177	216.591	12.890	67.143	324.782
25.404	410.311	47.964	19.800	135.750	151.856	17.537	108.301	201.354
28.490	484.011	40.661	25.293	339.791	60.668	21.282	167.917	129.867
34.655	542.676	36.265	29.672	465.4007	44.294	25.352	307.127	71.003
			37.676	541.279	38.085	27.185	374.552	58.221
						33.646	484.691	44.991
x=0.075 mole fraction			x=0.222 mole fraction			x=0.439 mole fraction		
5.424	25.086	896.808	5.424	34.276	915.062	5.060	46.726	950.221
8.593	41.801	538.195	8.593	56.371	556.397	9.981	104.021	426.839
14.235	79.324	283.611	17.537	151.472	207.065	17.390	223.588	198.581
17.537	110.502	203.590	22.328	229.857	136.453	22.217	313.728	141.525
21.610	176.650	127.354	25.228	287.579	109.064	28.533	406.631	109.191
23.105	211.529	106.355	36.491	451.191	69.515	35.509	471.866	94.095
31.127	444.505	50.612						
36.787	504.305	44.610						

Table II. Measurements of PVTx for Water+N-Heptane Mixtures at Critical Isotherm:

P, Pressure (MPa), ρ, Density (kg ·m^{-3}), V_m, Molar Volume (cm^3·mol^{-1})

T_C=647.05 K

P	ρ	V_m	P	ρ	V_m	P	ρ	V_m
x=0.028 mole fraction			x=0.048 mole fraction			x=0.082 mole fraction		
4.737	19.832	1023.060	4.881	22.090	992.906	4.983	24.376	1016.482
13.082	66.405	305.535	12.208	64.973	337.566	11.424	64.294	385.374
18.930	123.567	164.194	17.891	117.355	186.894	14.474	88.593	279.674
21.820	180.412	112.458	21.943	178.111	123.141	20.215	153.341	161.583
24.194	279.970	72.468	25.516	296.998	73.848	22.481	191.640	129.291
28.343	421.399	48.147	30.612	419.054	52.339	23.926	221.739	111.741
38.334	524.269	38.699	37.997	492.557	44.528	28.348	320.847	77.225
						39.071	448.249	55.276
x=0.173 mole fraction			x=0.474 mole fraction			x=0.706 mole fraction		
4.713	29.915	1076.601	4.733	53.956	1055.454	4.700	77.193	984.847
10.398	73.271	439.545	8.026	98.131	580.326	9.144	172.630	440.383
15.900	127.198	253.197	12.060	158.705	358.830	15.241	288.9626	263.091
24.147	239.063	134.718	16.776	231.513	245.982	23.746	377.099	201.600
30.417	327.625	98.302	26.939	347.803	163.737	39.046	454.710	167.191
41.137	420.867	76.523	40.294	427.211	133.302			

Table III. Measurements of PVTx for Water+N-Octane Mixtures at Critical Isotherm:

P, Pressure (MPa), ρ, Density (kg ·m^{-3}), V_m, Molar Volume (cm^3·mol^{-1})

T_C=647.05 K

P	ρ	V_m	P	ρ	V_m	P	ρ	V_m
x=0.031 mole fraction			x=0.048 mole fraction			x=0.078 mole fraction		
4.607	19.660	1070.122	5.109	23.508	961.626	4.603	22.642	1125.437
7.763	35.569	591.492	7.413	34.887	647.984	9.854	54.347	468.880
11.426	54.218	388.047	12.305	63.481	356.110	15.993	105.487	241.564
17.841	107.324	196.033	18.295	123.711	182.735	20.470	164.622	154.791
21.722	176.384	119.280	21.808	184.707	122.390	22.717	208.561	122.180
23.565	244.522	86.042	25.222	289.895	77.981	24.142	243.363	104.708
26.922	368.389	57.111	27.030	345.599	65.412	27.232	321.304	79.308
28.690	410.816	51.213	36.503	480.168	47.080	38.257	460.100	55.384
38.268	507.826	41.430						
x=0.263 mole fraction			x=0.425 mole fraction			x=0.614 mole fraction		
5.143	43.356	998.612	5.154	63.473	928.248	4.894	84.134	916.358
9.559	87.762	493.332	9.463	127.773	461.118	9.473	190.134	405.486
15.207	149.715	289.189	14.991	222.786	264.462	14.971	301.701	255.5406
20.203	224.189	193.123	22.375	328.275	179.479	22.430	385.128	200.184
36.796	402.703	107.513	33.562	415.971	141.641	36.618	460.692	167.350
			43.211	459.470	128.231			

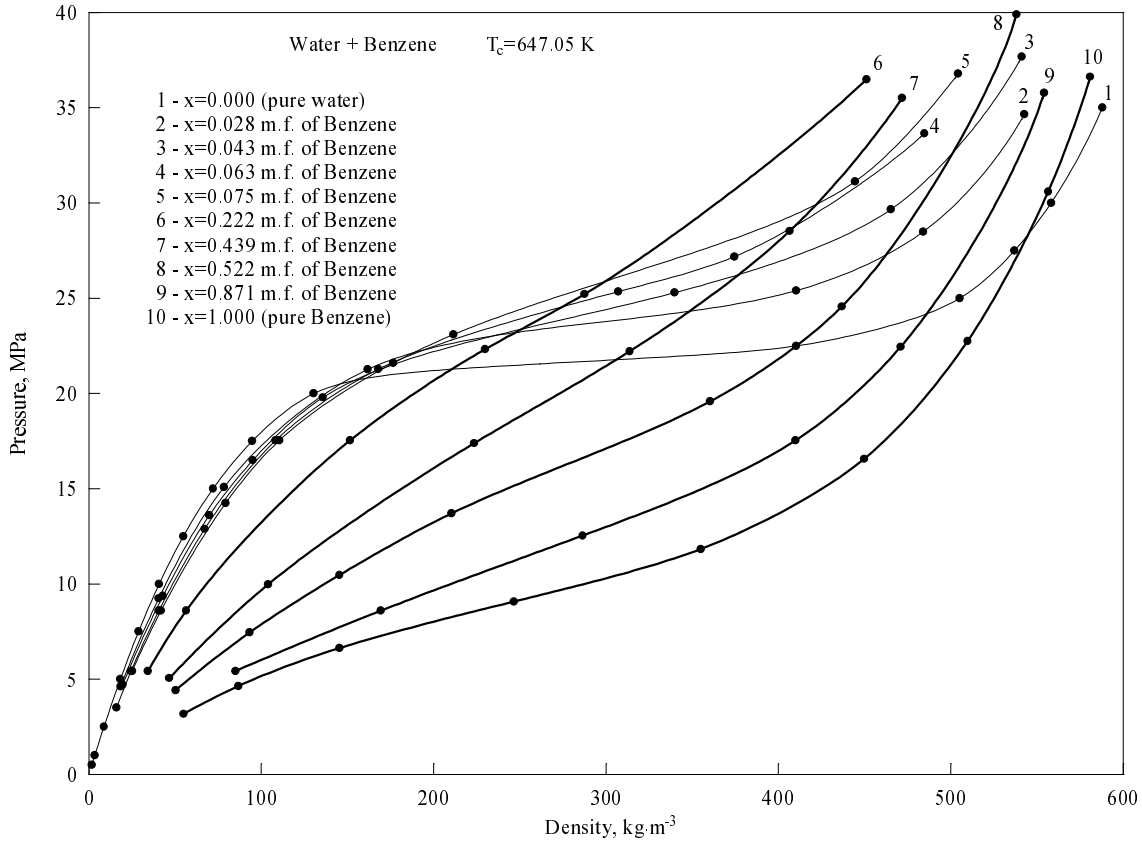

Figure 1. The pressure P of the mixture water-benzene as a function of density ρ at critical isotherm 647.05 K for various compositions.

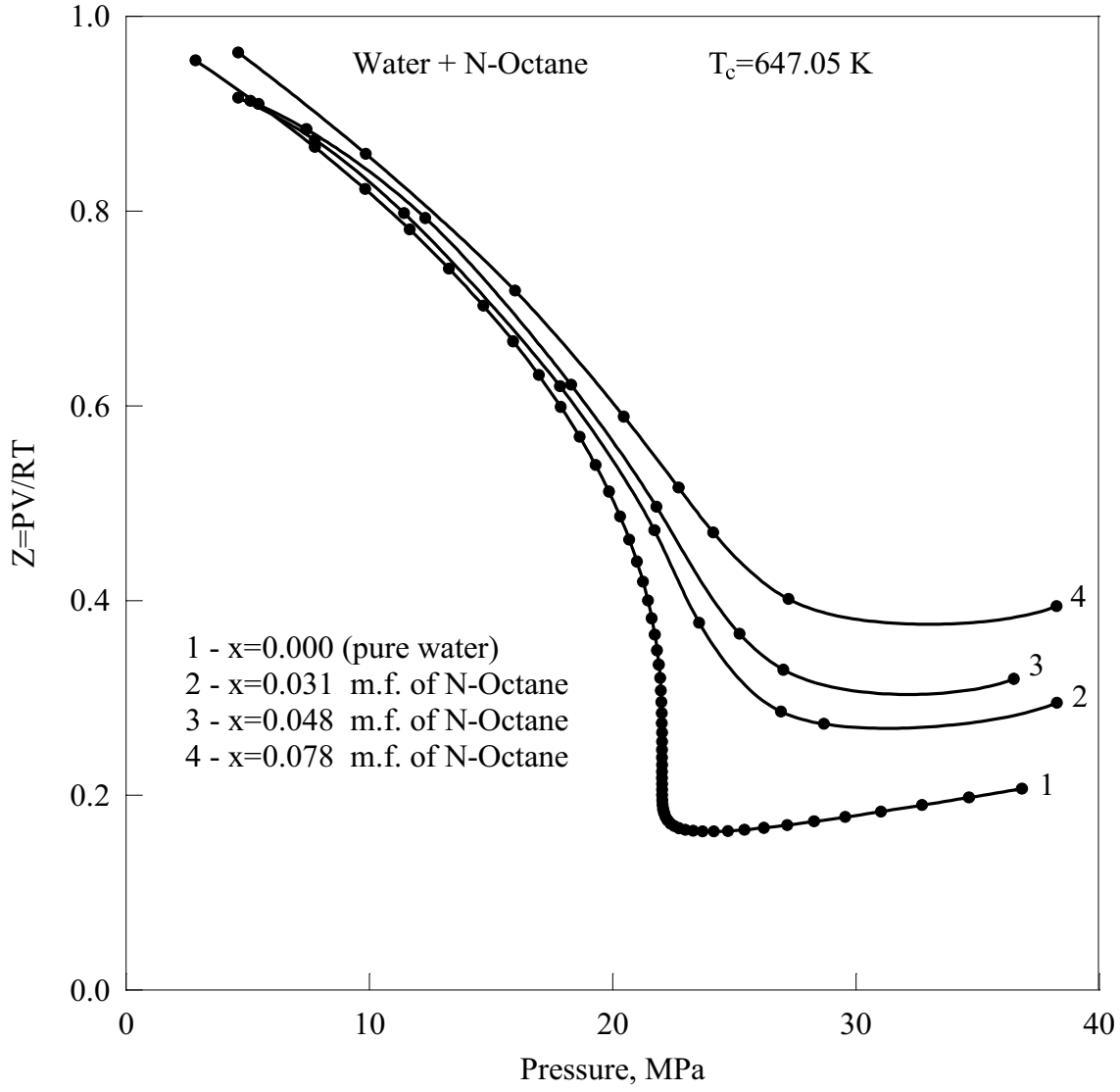

Figure 2. Compressibility factor $Z=PV_m/RT$ as a function of pressure P for water-n-octane mixtures at critical isotherm 647.05 K for various compositions.

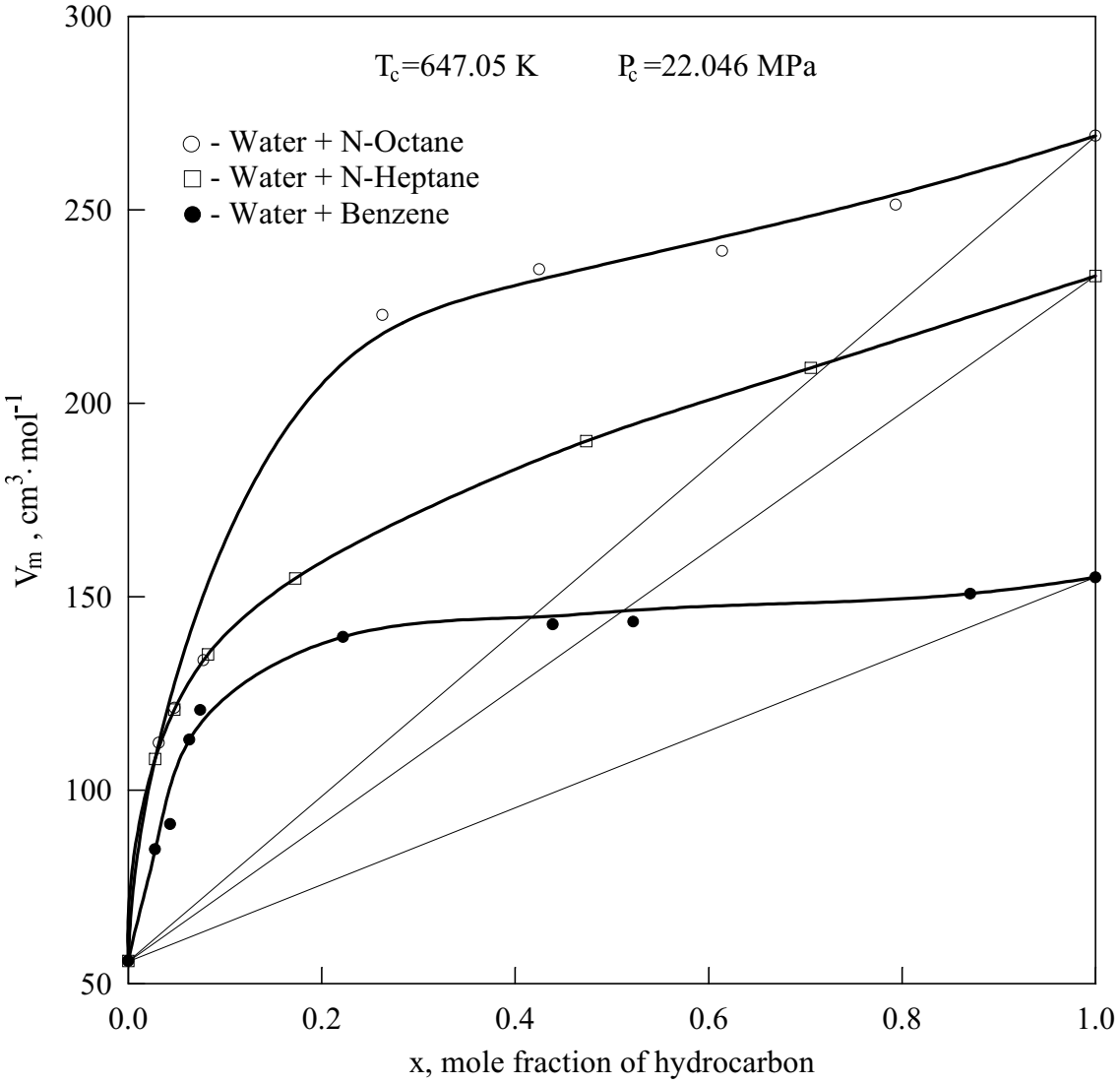

Figure 3. Molar volume V_m as a function of composition x for water+hydrocarbon mixtures at critical isotherm-isobar.

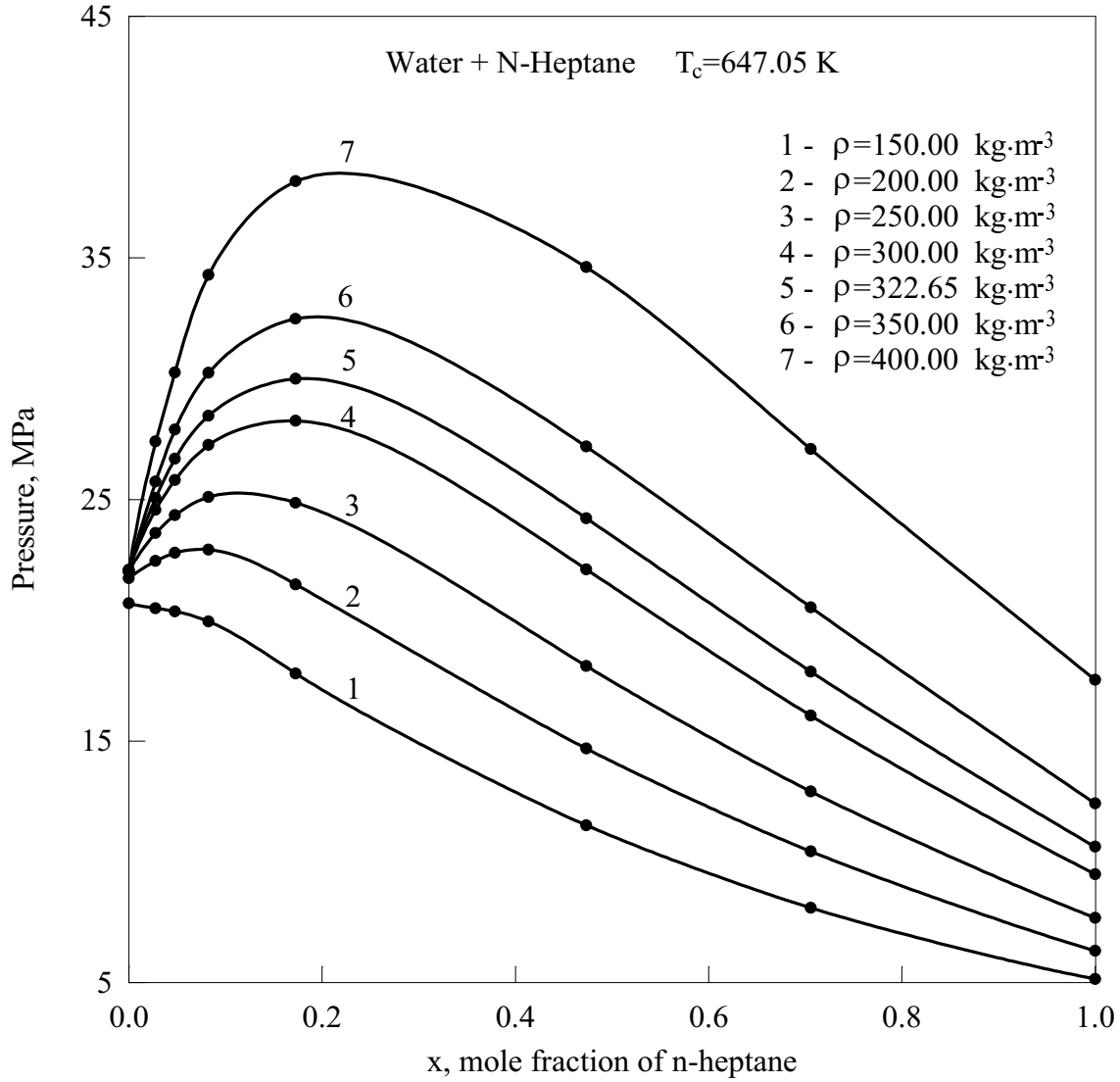

Figure 4. The pressure P of the mixture water-n-heptane as a function of composition x at critical isotherm 647.05 K for various near-critical isochores.

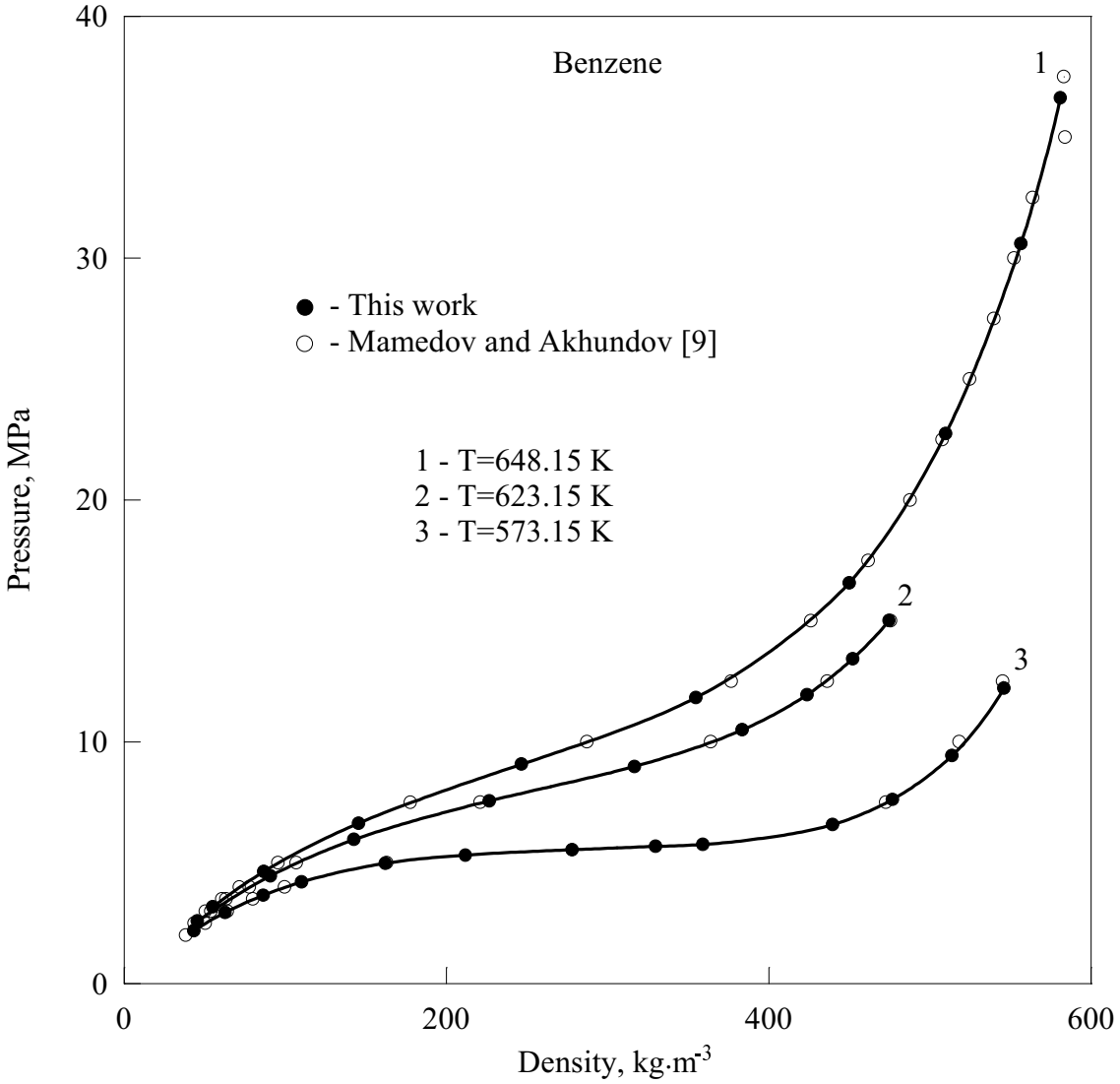

Figure 5. Test measurements of densities of benzene taken with the apparatus in comparison with experimental densities of other authors [9].

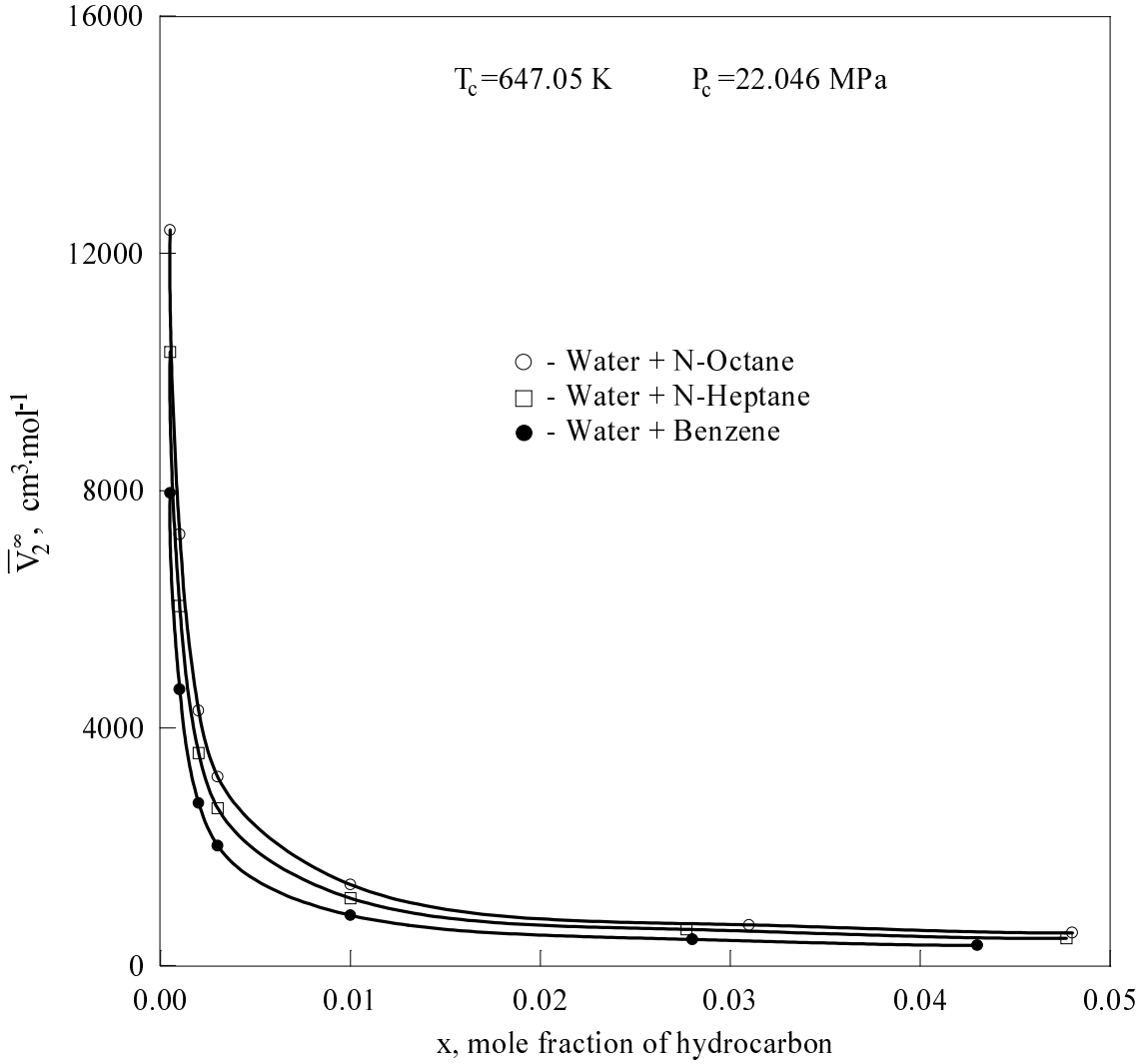

Figure 6. Partial critical isothermal-isobaric molar volume $\overline{V}_2^\infty$ as a function of composition.

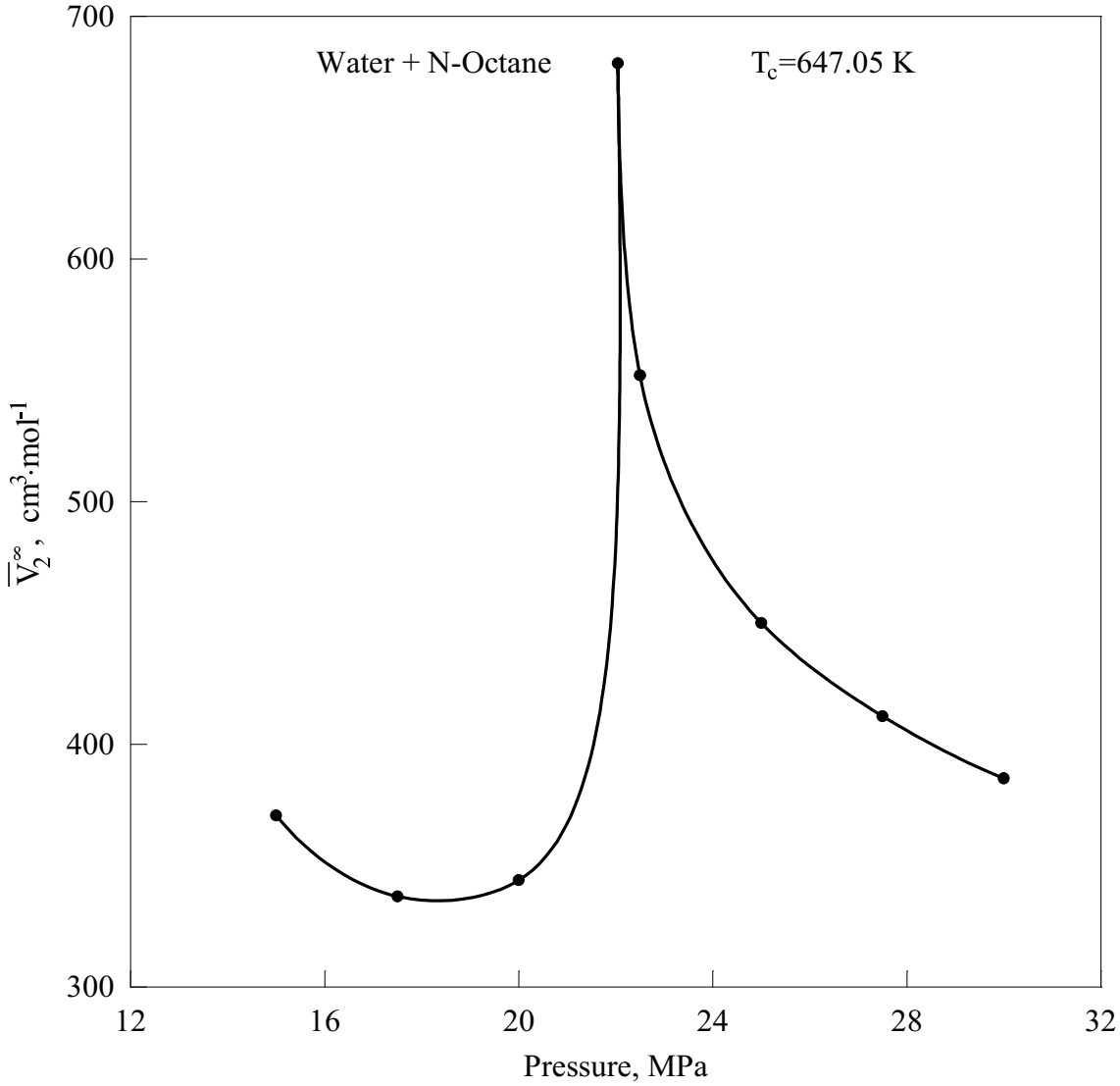

Figure 7. The partial molar volume $\overline{V}_2^{\infty}$ of the water+n-octane mixture as a function of pressure at critical isotherm 647.05 K.

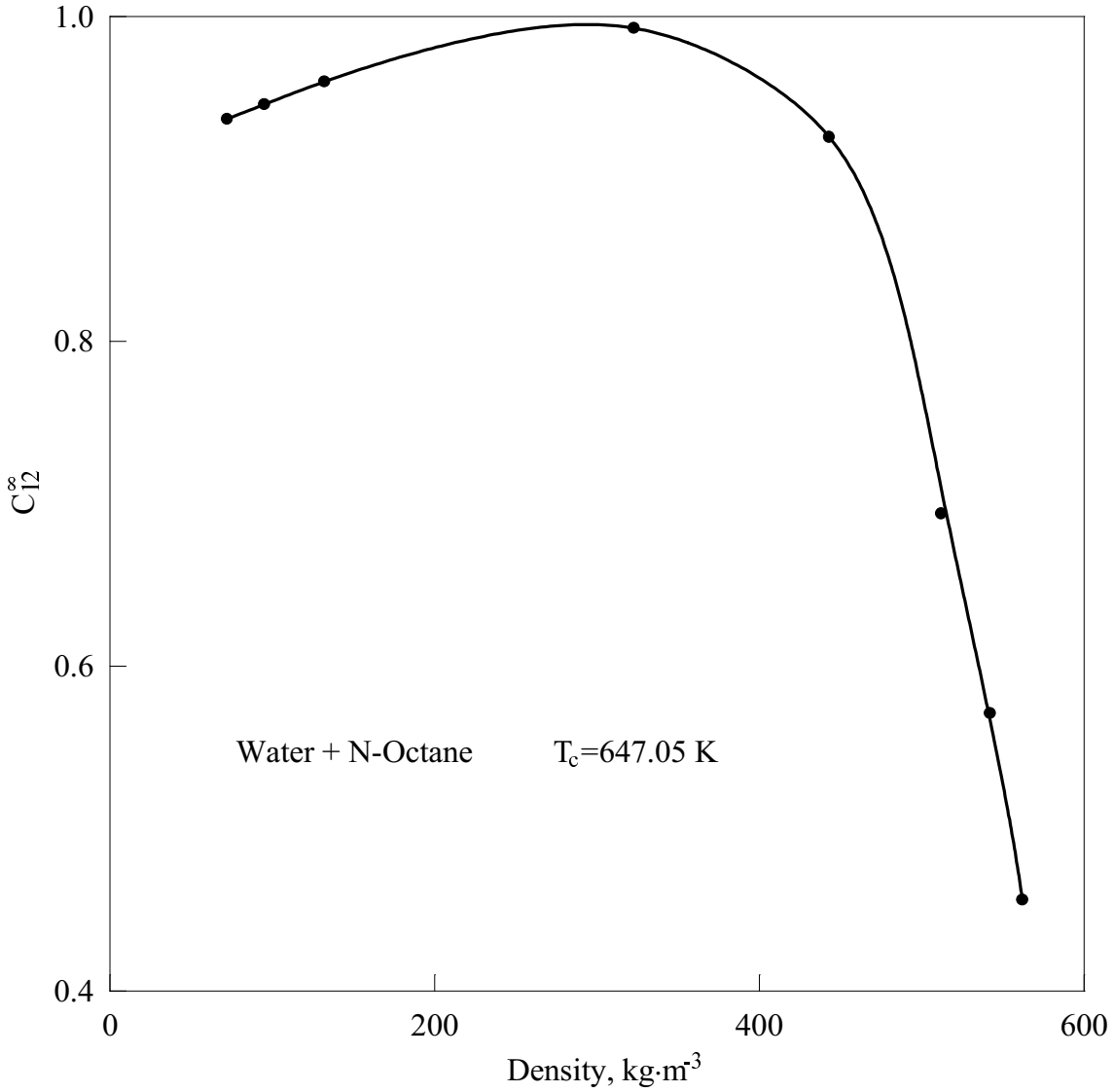

Figure 8. The solute-solvent (n-octane-water) direct correlation function integral as a function of density at critical isotherm 647.05 K.