Speeds of Sound, Densities, and Isentropic Compressibilities of Poly(propylene glycol)-425 at Temperatures from (293.15 to 373.15) K and Pressures up to 100 MPa

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Experimental speeds of sound and densities are presented for the liquid phase of poly(propylene glycol)-425. The measurements were carried out along nine isotherms from (293.15 to 373.15) K at pressures from saturation condition up to 100 MPa. The speed of sound was measured by a pulse-phase echo ultrasonic device at a frequency of 1 to 5 MHz with an uncertainty of ±0.2%. The density was measured by an acoustic piezometer constructed by the authors with an uncertainty of ±0.3%. The experimental results were used to calculate isobaric thermal expansion coefficient α_p and isentropic compressibility k_S.

Introduction

In recent years, interest to measurement of speed of a sound in heavy organic liquids has considerably increased.[1−4] Interest in the properties of poly(propylene glycol) PPG is as a result of their extensive application in the petrochemical, medicine, and pharmaceutical industries. They represent fragments of many surface-active substances and can serve as modeling objects. However, thermodynamic properties of PPG are not clearly understood. Research of these properties was carried out under narrow-range condition parameters.

In this work, we report speed of sound and density data for PPG-425 in the range of temperature from (293.15 to 373.15) K at high pressure. To our best knowledge, the speed of sound and density of PPG-425 under high pressures has not been reported.

Experimental Section

The speed of sound was measured using a pulse-phase echo ultrasonic device[5] at a frequency of (1 to 5) MHz with an uncertainty of ±0.2%. Dispersion was not observed. For the simultaneous measurement of speed of sound and density, an acoustic piezometer[6] has been developed. This method makes possible measurements of speed of sound and density of a liquid at pressure up to 600 MPa in a temperature range from (223.15 to 523.15) K. The density was measured by the acoustic piezometer with an uncertainty of ±0.3%. The acoustic piezometer was thermostated with a temperature stability of ±0.01 K. The temperature and pressure were measured by the platinum-resistance thermometer and dead-weight pressure gauge MP-2500 with an accuracy of ±0.01 K and 0.01 MPa, respectively.

Figure 1 shows the acoustic piezometer. The speed of sound was determined by the simple relation

$$u = \frac{2L}{\tau_2 - \tau_1} \tag{1}$$

where L is the acoustic path (length of the stationary base) and τ_2 and τ_1 are the total delay time of the second and the first pulses reflected from the diaphragm, respectively. The variation of acoustic path L with temperature and pressure was calculated from the formula

$$L_{P,T} = L_0 \Omega_P \Omega_T \tag{2}$$

where $L_0 = 24.807$ mm is the path length at temperature $T_0 = 293.15$ K and pressure $P_0 = 0.1$ MPa

$$\Omega_T = 1 + \alpha(T/K - 293) \tag{3}$$

$$\Omega_P = 1 - \frac{1 - 2\mu}{E} P \tag{4}$$

where μ, α, E, T, and P are Poisson's coefficient, coefficient of thermal expansion, Young's modulus, absolute temperature, and pressure, respectively. The length of the stationary base at temperature $T_0 = 293.15$ K and pressure $P_0 = 0.1$ MPa was measured by the device IZV-2 (Russia) with a precision of ±0.001 mm. The density was determined by the change of volume at compression of the bellows (eq 1). Change of length of the bellows (moving of the reflector 11) was registered on speed of sound.

According to Bridgman,[7] the change of volume of the bellows at compression can be determined from

$$\Delta V = S_0 \Delta h \tag{5}$$

where Δh is the change of length of the bellows and S_0 is the square of the effective cross-section

$$V = V_0 + S_0 \Delta h \tag{6}$$

$$V = vm \tag{7}$$

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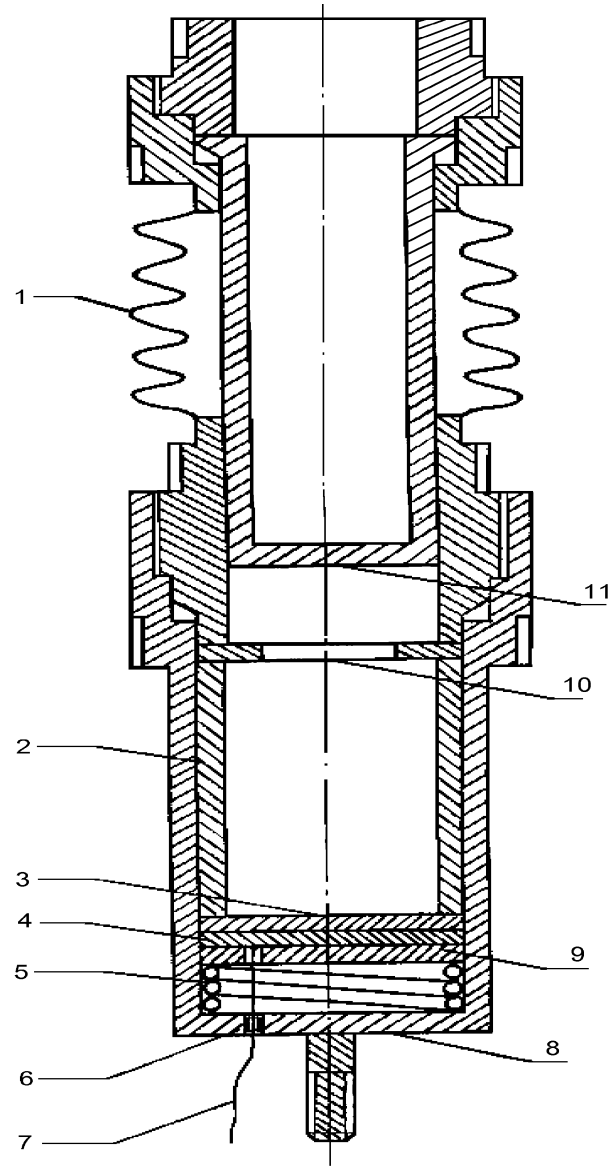

Figure 1. Acoustic piezometer. 1, bellows; 2, stationary base; 3, piezoelectric ceramics; 4, contact plate; 5, spring; 6, lead-in wire; 7, wire; 8, pressurized body; 9, fluoroplastic gasket; 10, diaphragm; 11, reflectors.

where v is specific volume of the liquid, m is the mass of the liquid

$$v = v_0 + \frac{S_0 \Delta h}{m} \tag{8}$$

Therefore

$$\rho^{-1} = \rho_0^{-1} + \frac{S_0 \Delta h}{m} \tag{9}$$

where ρ_0 is the density of liquid at atmospheric pressure, ρ is the density of liquid at some pressure P, and

$$\Delta h = L_0 - L = \frac{u_0\tau_0 - u_i\tau_i}{2} \tag{10}$$

where L_0 and L are the distances from a piezoelectric ceramics (eq 3) up to the reflector at atmospheric pressure P_0 and at some pressure P_i, respectively; u_0 and u_i are the speeds of sound at atmospheric pressure P_0 and at some pressure P_i, respectively; τ_0 and τ_i are propagation times by ultrasound at distances from the reflector and back at atmospheric pressure P_0 and at some pressure P_i, respectively. The initial density at atmospheric pressure P_0 was measured by an Ostwald−Sprengel-type pycnometer, with a volume of approximately 50 cm^3. The uncertainty of the density measurements was estimated to be $\pm 3 \times 10^{-5}$ $g \cdot cm^{-3}$. The effective cross section of the bellows was determined on the basis of measurements of liquid dependence of density on pressure is well known.[8] We have compared our results for speed of sound and density with data reported by other authors. The speeds of sound and densities for pentane, at 293.15 K and 313.15 K, were in good agreement with Rasumihin's[9] data (Table 1).

Table 1. Reference Speed of Sound and Density of Pentane at 293.15 K and 313.15 K

	293.15 K				313.15 K			
	$\rho/(kg \cdot m^3)$		$u/(m \cdot s^{-1})$		$\rho/(kg \cdot m^3)$		$u/(m \cdot s^{-1})$	
P/MPa	exp	lit[a]	exp	lit[a]	exp	lit[a]	exp	lit[a]
0.1	626.4	626	1029	1030	606.3	606	934	934
50	666.9	666	1357	1356	653.3	650	1290	1291
100	702.8	705	1568	1569	689.6	694	1511	1510
150	728.6	730	1731	1730	716.9	717	1686	1685
200	748.7	748	1878	1879	737.7	736	1833	1835
250	764.8	763	1989	1991	754.0	752	1934	1936
300	778.2	779	2104	2105	767.4	768	2049	2050
350	790.0	791	2197	2196	779.0	780	2140	2140
400	800.7	800	2294	2292	789.6	791	2240	2238
450	810.9	811	2381	2380	799.8	800	2301	2300
500	820.6	820	2469	2469	809.7	808	2397	2398
550	830.0	830	2534	2535	819.5	819	2448	2450
600	838.9	840	2606	2608	828.9	830	2538	2540

[a] Reference 9.

The PPG with number-average molecular weights of 425 $g \cdot mol^{-1}$ were manufactured by Merck and were used without further purification. The purity of PPG-425 was checked by gel permeation chromatography. The purity of PPG-425 was 99.7 mol %. The including of the water did not exceed 0.1 mol %. A polydispersity index of PPG-425 was 1.086. Experimental values of density and refractive index at 293.15 K of PPG-425 were $\rho = 1020.1$ $kg \cdot m^{-3}$ and $n_D = 1.4468$, respectively.

Results and Discussion

The experimental results of the speed of sound, u, and density, ρ, in the liquid phase of PPG-425 at various temperatures, T, and pressures P are listed in Tables 2 and 3 and are plotted as a function of temperature and pressure in Figures 2−5, respectively. The data, which is presented in Tables 2 and 3, have been fitted by the following cubic polynomial for each isotherm

$$\boldsymbol{Y} = A_0 + A_1 P/\text{MPa} + A_2(P/\text{MPa})^2 + A_3(P/\text{MPa})^3 \tag{11}$$

where Y is $u/m \cdot s^{-1}$ or $\rho/kg \cdot m^{-3}$, P is pressure, and A_0, A_1, and A_2 are adjustable parameters. All the measured data were used in the fitting process. The values of coefficients, A_i, were calculated by the least-squares method. Standard deviation $\sigma(Y)$ of u and ρ is defined by

$$\sigma(Y) = [\{\sum_{i=1}^{n} (Y_{obs} - Y_{cal})^2\}/\{(n - p)\}]^{1/2} \tag{12}$$

Where Y_{obs} and Y_{cal} are the observed and calculated quantities as defined earlier, n is total number of experimental points, and p is the number of estimated parameters. The

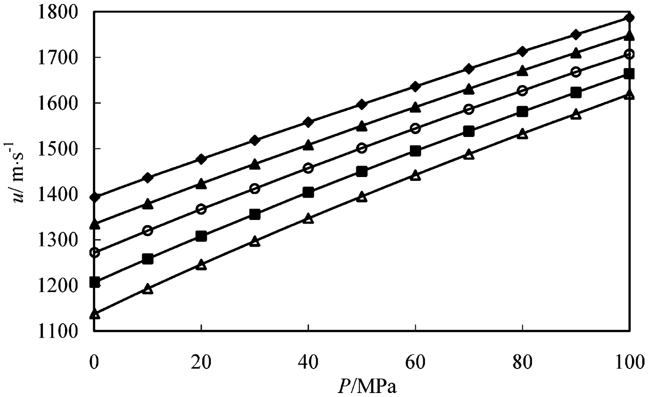

Figure 2. Speed of sound in the liquid phase of PPG-425 as a function of pressure: ◆, 293.15 K; ▲, 313.15 K; ○, 333.15 K; ■, 353.15 K; △, 373.15 K.

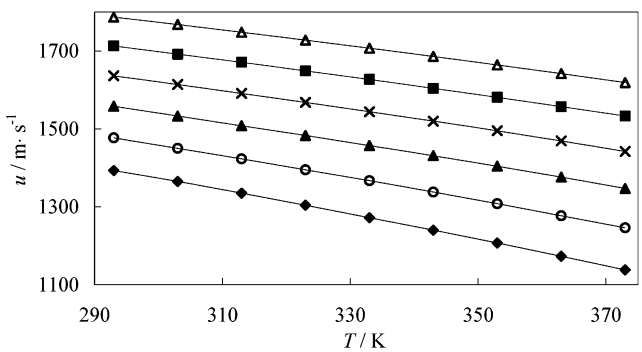

Figure 3. Speed of sound in the liquid phase of PPG-425 as a function of temperature: ◆, $P = 0.1$ MPa; ○, $P = 20$ MPa; ▲, $P = 40$ MPa; ×, $P = 60$ MPa; ■, $P = 80$ MPa; △, $P = 100$ MPa.

values of parameters A_i of eq 11 and standard deviation $\sigma(Y)$ are given in Tables 4 and 5 at temperatures from (293.15 to 373.15) K, respectively. As can be seen from Figures 2−5, the speed of sound and density for PPG-425 monotonically decrease with an increase in temperature along isobars and increase with increase pressure along isotherms. Values of speed of sound and density both change with temperature and with pressure have nonlinear character pronounced along isotherms. And also, the

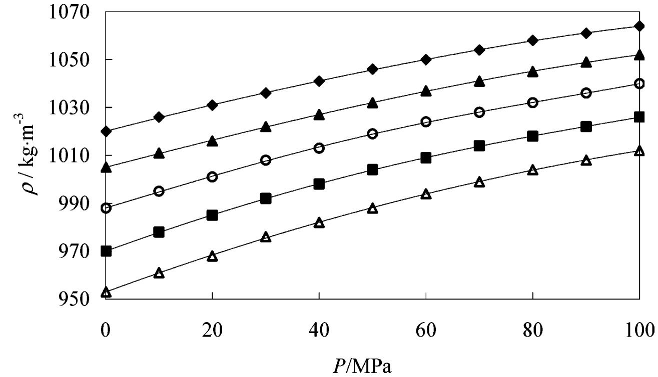

Figure 4. Density in the liquid phase of PPG-425 as a function of pressure: ◆, 293.15 K; ▲, 313.15 K; ○, 333.15 K; ■, 353.15 K; △, 373.15 K.

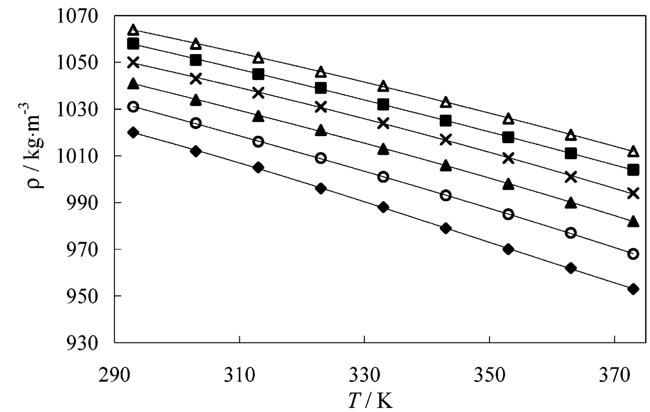

Figure 5. Density in the liquid phase of PPG-425 as a function of temperature: ◆, $P = 0.1$ MPa; ○, $P = 20$ MPa; ▲, $P = 40$ MPa; ×, $P = 60$ MPa; ■, $P = 80$ MPa; △, $P = 100$ MPa.

Table 2. Speed of Sound, *u*, in the Liquid Phase for PPG-425 at Various Temperatures, *T*, and Pressures, *P*

	$u/(\mathrm{m \cdot s^{-1}})$ at T/K								
P/ MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	1393	1365	1335	1304	1272	1240	1207	1173	1138
10	1436	1408	1379	1350	1320	1290	1258	1226	1193
20	1477	1450	1423	1395	1367	1338	1308	1277	1246
30	1518	1492	1466	1439	1412	1384	1356	1327	1297
40	1558	1533	1508	1483	1457	1431	1404	1376	1347
50	1597	1574	1550	1526	1501	1476	1450	1423	1395
60	1636	1614	1591	1568	1544	1520	1495	1469	1442
70	1675	1653	1631	1609	1586	1562	1538	1513	1488
80	1713	1692	1671	1649	1627	1604	1581	1557	1533
90	1750	1730	1710	1689	1668	1646	1623	1600	1576
100	1787	1768	1748	1728	1707	1686	1664	1642	1619

Table 3. Density, *ρ*, in the Liquid Phase for PPG-425 at Various Temperatures, *T*, and Pressures, *P*

	$\rho/(\mathrm{kg \cdot m^{3}})$ at T/K								
P/ MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	1020	1012	1005	996	988	979	970	962	953
10	1026	1018	1011	1003	995	986	978	969	961
20	1031	1024	1016	1009	1001	993	985	977	968
30	1036	1029	1022	1015	1008	1000	992	984	976
40	1041	1034	1027	1021	1013	1006	998	990	982
50	1046	1039	1032	1026	1019	1012	1004	996	988
60	1050	1043	1037	1031	1024	1017	1009	1001	994
70	1054	1047	1041	1035	1028	1021	1014	1006	999
80	1058	1051	1045	1039	1032	1025	1018	1011	1004
90	1061	1055	1049	1043	1036	1029	1022	1015	1008
100	1064	1058	1052	1046	1040	1033	1026	1019	1012

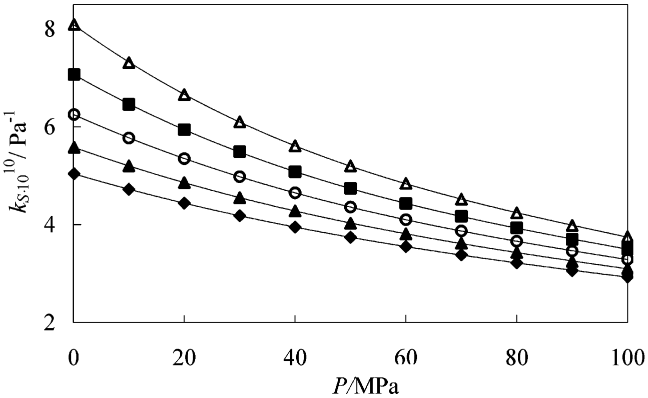

Figure 6. Pressure dependence, *P*, of isentropic compressibilities, k_S, in the liquid phase of PPG-425: ◆, 293.15 K; ▲, 313.15 K; ○, 333.15 K; ■, 353.15 K; △, 373.15 K.

Table 4. Values of the Parameters of Eq 11 and Standard Deviation for Speed of Sound from (293.15 to 373.15) K

T/K	A_0	A_1	A_2	A_3	σ/m·s^{-1}
293	1392.95	4.2908	-4.5294×10^{-3}	1.0430×10^{-5}	1.09
303	1364.64	4.3435	-3.3042×10^{-3}	1.9417×10^{-6}	0.64
313	1334.58	4.4832	-3.5642×10^{-3}	8.6123×10^{-7}	0.53
323	1303.62	4.6554	-4.3565×10^{-3}	2.3164×10^{-6}	0.65
333	1271.77	4.8506	-5.6681×10^{-3}	7.0761×10^{-6}	0.93
343	1239.75	5.0397	-7.0632×10^{-3}	1.3014×10^{-5}	1.54
353	1206.45	5.2263	-7.8678×10^{-3}	1.3537×10^{-5}	0.78
363	1172.47	5.4191	-9.2279×10^{-3}	1.9862×10^{-5}	0.83
373	1137.68	5.5973	-1.0006×10^{-2}	2.1692×10^{-5}	0.84

Table 5. Values of the Parameters of Eq 11 and Standard Deviation for Density from (293.15 to 373.15) K

T/K	A_0	A_1	A_2	A_3	σ/kg·m^{-3}
293	1020.10	0.5650	-8.2609×10^{-4}	-4.3475×10^{-6}	0.60
303	1011.94	0.6352	-2.2343×10^{-3}	5.0315×10^{-6}	0.58
313	1005.00	0.5809	-4.9718×10^{-4}	-6.0768×10^{-6}	0.65
323	995.97	0.7021	-2.0543×10^{-3}	4.1000×10^{-7}	0.63
333	987.82	0.7340	-2.5377×10^{-3}	3.9337×10^{-6}	1.14
343	978.59	0.7995	-3.0433×10^{-3}	4.5753×10^{-6}	1.17
353	969.92	0.8279	-3.3152×10^{-3}	6.3094×10^{-6}	0.53
363	961.65	0.8218	-3.0390×10^{-3}	5.5543×10^{-6}	0.77
373	952.91	0.8230	-2.3534×10^{-3}	2.8624×10^{-7}	0.70

maximal change of speed of sound and density values at change of pressure and temperatures occurs in the range of small pressure and high temperatures.

Isentropic compressibilities k_S of the PPG-425 were calculated from the Laplace equation

$$k_S = \frac{1}{\rho u^2} \qquad (13)$$

where u is the sound velocity and ρ is the density. The values of isentropic compressibilities k_S for PPG-425 as a function of pressure at constant temperatures are plotted in Figure 6. The isobaric thermal expansion coefficient

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \qquad (14)$$

was calculated from numerical differentiation of the density fitting equation. In Figure 7 is given the isobaric thermal expansion coefficient α_p for the PPG-425 as a function of pressure at constant temperatures. The uncertainties of the calculated values are not greater than ±1% for isentropic compressibility k_S and ±5% for isobaric thermal expansion coefficient α_p, respectively.

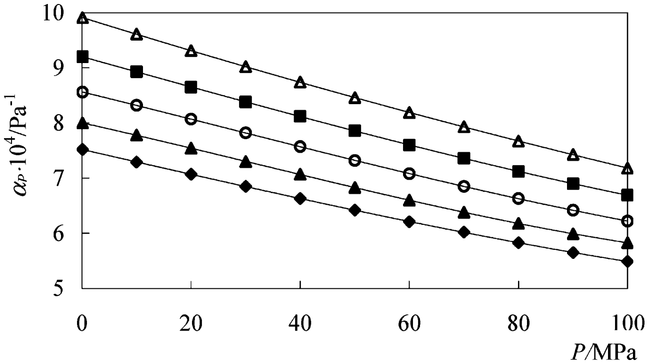

Figure 7. Pressure dependence, *P*, of the isobaric thermal expansion coefficient, α_P, in the liquid phase of PPG-425: ◆, 293.15 K; ▲, 313.15 K; ○, 333.15 K; ■, 353.15 K; △, 373.15 K.

Conclusions

Speeds of sound and densities are presented for the PPG-425 at temperatures from (293.15 to 373.15) K and pressures up to 100 MPa. An acoustic piezometer described in the submitted work has allowed us to obtain the speed of sound and density data with the uncertainty of ±0.2% and ±0.3%, respectively. These dates are a small part of our research program of systematic investigations of thermodynamic properties for organic liquids.

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