PVT Properties of Dimethyl(isopropenylethynyl)carbinol at Temperatures from 293 to 363 K and Pressures from 0.1 to 350 MPa, Studied Using the Micro-*PVT* System

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The effect of pressure on the volume of dimethyl(isopropenylethynyl)carbinol, $(CH_3)_2C(OH)C{\equiv}CC(CH_3){=}CH_2$, has been measured over the pressure range (0.1 to 350) MPa and the temperature range (293.15 to 363.15) K using the Micro-*PVT* system, a new universal instrument for measuring the thermodynamic characteristics of materials. Experimental data on the variation of the volume ratio $k = V_p/V_0$ (V_p = sample volume at given pressure P; V_0 = sample volume at 0.1 MPa) with pressure have been approximated by two equations allowing the interpolation and extrapolation of experimental data with an acceptable uncertainty. The temperature dependence of the coefficients of the Tait equation has been studied, enabling the calculation of the volume ratio with an acceptable uncertainty for a wider temperature and pressure range. The isothermal compressibility, the isobaric thermal expansivity, and the increment of isobaric molar heat capacity from its value at 0.1 MPa have been calculated using the experimental data obtained.

Introduction

The research of foams and colloid media and processes in these media is a promising research area.[1−3] Flotation reagents used in the process of ore enrichment should have a high sorption to floatable materials. The application of materials composed of molecules having a succession of double and triple bonds as flotation reagents is promising for increased sorption in sulfide media having defective polycarbon structures. Specialists from Evrofinchermetholding Ltd., Moscow, were the first to synthesize dimethyl(isopropenylethynyl)carbinol (DMIPEC), a chemical product which meets these requirements. Its chemical formula is $(CH_3)_2C(OH)C{\equiv}CC(CH_3){=}CH_2$. DMIPEC was successfully used as a flotation reagent for the enrichment of ores of precious and nonferrous metals and coals. The results achieved have formed the basis for broad research on the physical and chemical properties of this synthesized material to extend its field of application. The results of *PVT* measurement of DMIPEC at eight temperatures over the temperature range (293.15 to 363.15) K and the pressure range (0.1 to 350) MPa are presented in this article.

Experimental Section

DMIPEC was synthesized by means of direct interaction of acetylene with acetone and subsequent dehydration of the reaction product at the stage of rectification. The purity of the synthesized samples was 98.5% and was determined with gas−liquid chromatography using a conventional type gas−liquid chromatograph of “Chrom-5” model with 3.5 m glass column. Hydroquinone, a polymerization inhibitor, with a concentration of 0.1% was added to the material to prevent polymerization. The synthesized material was stored at room temperature in closed canisters.

The Micro-*PVT* system,[4] developed at VNIIGAZ and intended for the measurement of *PVT* properties of liquid and solid materials, was used for the study on the DMIPEC samples. The system includes an electromechanical press and an electronic control unit connected to a personal computer. The Micro-*PVT* system operates with a high degree of automation and accuracy.

Measurements of the thermodynamic properties of materials using the Micro-*PVT* system are based on the so-called “piston in a bottle” method. Samples of the material are placed in a cylindrical high-pressure chamber made of high-strength stainless steel; the pressure is obtained by means of a tightened piston inserted from one of the flanks of the chamber and moved by a stepping motor. Friction problems in sealing are overcome by having a rotating piston, with varying rotational speeds available. The sample volume is determined on the basis of a preliminary calibration and known piston displacement, and the pressure is calculated from the extension of a spring connected with the piston and calibrated with high accuracy; the piston movement and spring extension are controlled with electronic displacement transducers accurate to 0.1 μm. A temperature sensor placed at the other end of the high-pressure chamber measures the temperature in the chamber, and this sensor simultaneously seals the chamber. Data on the sample volume V, its pressure P, and temperature T are recorded by the computer and used for further treatment of the results. The system allows experiments to be carried out in different regimes (isothermal, isochoric, isobaric, quasiadiabatic) and allows the experimental results obtained to be treated in real time, providing

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10.1021/je000355y CCC: $20.00

Table 1. Experimental Data for Volume Ratio $k = V_p/V_0$ for DMIPEC at Temperatures from (293.15 to 363.15) K

P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k
$T = 293.15$ K															
2.146	0.9983	19.774	0.9849	49.730	0.9661	100.155	0.9416	160.438	0.9194	210.803	0.9041	259.523	0.8916	309.664	0.8801
4.229	0.9966	24.848	0.9814	55.832	0.9628	109.925	0.9377	170.631	0.9161	219.885	0.9019	269.671	0.8892	320.826	0.8777
6.027	0.9952	30.303	0.9777	59.977	0.9606	120.514	0.9334	179.749	0.9132	230.442	0.8989	280.119	0.8868	330.350	0.8757
7.941	0.9938	35.371	0.9746	69.751	0.9556	130.102	0.9299	190.530	0.9100	239.711	0.8965	290.619	0.8844	340.004	0.8737
9.883	0.9923	40.563	0.9713	79.867	0.9506	139.722	0.9264	199.134	0.9074	249.547	0.8940	299.343	0.8823	349.479	0.8718
15.527	0.9881	44.973	0.9687	90.354	0.9458	150.491	0.9227								
$T = 303.15$ K															
1.995	0.9984	19.971	0.9844	49.926	0.9647	100.353	0.9395	159.288	0.9171	210.136	0.9015	260.575	0.8882	310.215	0.8767
4.150	0.9966	24.856	0.9810	54.734	0.9620	110.273	0.9353	170.473	0.9134	220.529	0.8986	270.633	0.8857	319.596	0.8745
5.960	0.9950	30.169	0.9771	59.757	0.9592	120.626	0.9311	179.747	0.9105	229.709	0.8961	280.979	0.8833	330.622	0.8721
7.862	0.9935	35.009	0.9739	70.490	0.9536	130.010	0.9277	189.667	0.9074	239.354	0.8937	289.981	0.8811	339.911	0.8703
9.789	0.9919	39.957	0.9708	80.306	0.9487	140.143	0.9238	200.090	0.9043	250.688	0.8906	300.945	0.8787	349.593	0.8683
15.190	0.9879	45.162	0.9675	89.427	0.9443	150.800	0.9202								
$T = 313.15$ K															
1.960	0.9983	19.774	0.9836	49.527	0.9632	99.909	0.9370	160.205	0.9131	209.523	0.8974	260.892	0.8835	310.192	0.8718
3.783	0.9967	25.258	0.9796	55.073	0.9597	109.462	0.9326	170.138	0.9097	219.998	0.8943	270.914	0.8810	319.385	0.8698
6.039	0.9947	30.476	0.9758	59.884	0.9570	120.530	0.9279	179.331	0.9066	230.741	0.8914	279.665	0.8788	330.883	0.8672
8.333	0.9928	35.132	0.9725	69.895	0.9516	130.280	0.9241	190.029	0.9032	240.054	0.8887	290.272	0.8763	340.839	0.8651
10.166	0.9913	39.871	0.9693	80.291	0.9464	140.376	0.9202	199.599	0.9003	249.697	0.8864	299.316	0.8743	350.844	0.8631
15.102	0.9872	44.971	0.9660	90.217	0.9415	149.557	0.9169								
$T = 323.15$ K															
2.107	0.9980	20.022	0.9820	49.902	0.9606	100.505	0.9331	160.880	0.9087	210.032	0.8925	260.486	0.8786	309.725	0.8669
3.904	0.9963	25.037	0.9779	55.233	0.9572	109.762	0.9289	170.014	0.9055	220.489	0.8895	270.184	0.8763	319.185	0.8647
5.922	0.9944	29.963	0.9741	59.715	0.9544	120.415	0.9242	180.178	0.9021	229.477	0.8870	280.061	0.8738	329.890	0.8625
8.097	0.9924	35.163	0.9704	69.949	0.9485	130.952	0.9199	190.654	0.8985	239.801	0.8841	290.329	0.8711	340.003	0.8605
9.819	0.9909	39.716	0.9674	79.978	0.9433	140.651	0.9162	200.060	0.8957	250.581	0.8813	300.709	0.8688	349.196	0.8586
15.140	0.9861	44.739	0.9640	89.866	0.9383	149.859	0.9128								
$T = 333.15$ K															
1.995	0.9981	20.282	0.9809	50.132	0.9585	100.474	0.9304	159.965	0.9055	209.962	0.8887	260.672	0.8744	310.845	0.8621
4.109	0.9958	25.310	0.9767	54.972	0.9553	109.529	0.9260	169.740	0.9020	220.009	0.8857	270.629	0.8718	320.090	0.8598
6.119	0.9939	29.991	0.9728	59.722	0.9523	120.396	0.9212	179.787	0.8985	230.365	0.8827	280.742	0.8691	329.268	0.8578
8.169	0.9919	34.827	0.9689	70.493	0.9458	130.670	0.9168	190.515	0.8949	239.808	0.8801	289.265	0.8672	340.468	0.8552
10.257	0.9899	40.250	0.9652	80.338	0.9403	140.203	0.9129	200.159	0.8918	250.921	0.8771	300.037	0.8646	350.531	0.8531
15.108	0.9856	45.146	0.9619	90.180	0.9354	150.470	0.9091								
$T = 343.15$ K															
1.995	0.9979	19.707	0.9803	50.169	0.9560	100.360	0.9269	160.153	0.9010	209.509	0.8841	259.652	0.8697	309.625	0.8573
4.098	0.9957	25.151	0.9756	55.376	0.9525	110.585	0.9220	170.995	0.8972	219.705	0.8809	269.648	0.8669	320.675	0.8547
6.312	0.9933	30.229	0.9712	59.958	0.9496	120.199	0.9176	179.963	0.8940	230.065	0.8779	280.066	0.8643	330.081	0.8526
8.209	0.9913	34.750	0.9674	70.309	0.9433	130.116	0.9132	190.495	0.8903	239.884	0.8751	290.096	0.8619	339.961	0.8505
10.154	0.9894	39.942	0.9634	79.980	0.9375	139.831	0.9090	199.934	0.8872	250.253	0.8722	300.692	0.8594	349.982	0.8484
15.340	0.9843	45.379	0.9593	90.329	0.9319	149.819	0.9050								
$T = 353.15$ K															
2.096	0.9976	20.247	0.9784	49.988	0.9536	100.490	0.9230	160.359	0.8966	210.064	0.8791	259.756	0.8645	309.585	0.8517
4.139	0.9955	24.915	0.9741	55.572	0.9496	109.635	0.9185	169.864	0.8930	220.050	0.8759	269.742	0.8617	320.398	0.8493
6.255	0.9933	30.368	0.9693	59.977	0.9467	120.041	0.9137	179.884	0.8893	230.382	0.8728	279.658	0.8591	329.943	0.8470
8.030	0.9912	34.882	0.9655	70.046	0.9403	130.683	0.9088	190.168	0.8859	240.996	0.8696	290.063	0.8565	339.715	0.8448
9.873	0.9893	39.803	0.9613	80.405	0.9341	140.481	0.9047	200.536	0.8823	250.209	0.8671	300.620	0.8538	349.621	0.8427
15.090	0.9836	44.906	0.9574	90.393	0.9284	150.296	0.9006								
$T = 363.15$ K															
1.971	0.9976	20.123	0.9765	50.618	0.9501	100.120	0.9190	160.764	0.8914	210.325	0.8736	259.699	0.8586	310.736	0.8453
4.253	0.9947	25.535	0.9711	55.299	0.9465	110.520	0.9136	170.184	0.8878	220.154	0.8704	269.535	0.8559	319.515	0.8431
6.198	0.9922	30.211	0.9668	60.149	0.9431	120.641	0.9088	179.930	0.8840	230.199	0.8671	281.200	0.8528	330.746	0.8407
8.222	0.9898	34.745	0.9629	70.272	0.9364	130.605	0.9042	189.997	0.8806	240.545	0.8641	289.699	0.8506	340.298	0.8387
10.012	0.9876	40.213	0.9583	80.301	0.9303	140.872	0.8996	200.625	0.8769	250.048	0.8613	300.305	0.8479	350.168	0.8364
15.058	0.9820	45.425	0.9540	90.443	0.9243	150.455	0.8956								

Table 2. Densities of DMIPEC at Atmospheric Pressure (0.1 MPa) and Temperatures from (293.15 to 363.15) K

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
293.15	884.1	333.15	851.8
303.15	876.9	343.15	842.9
313.15	869.0	353.15	833.6
323.15	860.6	363.15	823.7

complex information on the thermodynamic parameters of the sample and allowing one to adjust the measurement regime and to improve the accuracy of the experimental results.

The volume of the chamber can be varied from (0.3 to 0.7) cm^3; the pressure can be varied from (0.1 to 500) MPa with an adjustable rate of compression and decompression over the range 0.001 MPa·s^{-1} to 12.5 MPa·s^{-1}. The possibility of obtaining a large number of experimental *PVT* points is an advantage of the Micro-*PVT* system. The number of data points and time intervals are set by the operator or are selected automatically by the system, depending on the requirements of the experiment. The maximum sampling frequency of experimental points is 10 Hz.

The Micro-*PVT* system has been calibrated at the National Engineering Laboratory (Glasgow, Scotland). The uncertainty of temperature measurement, based on temperature sensor calibration on IPTS-90 against a standard platinum resistance thermometer, was estimated to be ±0.03 K over the temperature range (273 to 373) K; the maximum relative error for the measurement of the volume and pressure was estimated to be ±0.2% over the ranges of values used in the experiments.

Table 3. Coefficients for the Dependence of the Volume Ratio on Pressure for DMIPEC at Temperatures from (293.15 to 363.15) K

T/K	C	B/MPa	a_0/MPa	a_1	$-a_2$/GPa^{-1}	a_3/GPa^{-2}	B^*/MPa
293.15	0.2049	108.40	1215.74	5.254	3.06	1.13	110.13
303.15	0.2051	103.39	1159.60	5.296	3.54	1.72	104.89
313.15	0.2071	98.03	1092.95	5.297	4.48	3.77	97.87
323.15	0.2052	89.67	1005.31	5.398	5.22	5.03	90.92
333.15	0.2077	85.93	953.18	5.221	4.31	3.06	85.37
343.15	0.2076	79.95	890.74	5.248	5.25	5.23	79.48
353.15	0.2095	75.44	832.31	5.210	5.46	5.52	73.81
363.15	0.2083	68.79	759.14	5.239	5.61	5.43	67.96

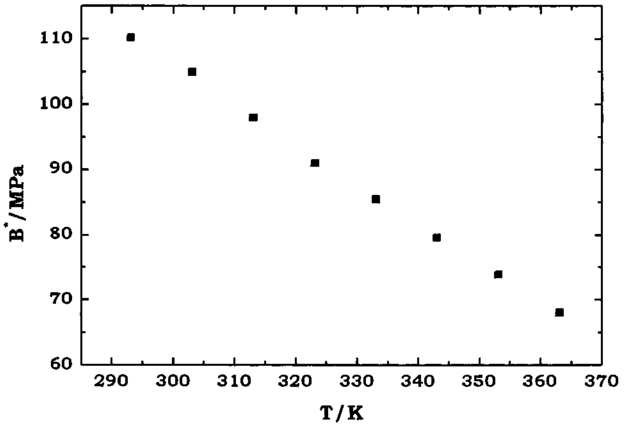

Figure 1. Variation of the coefficient B^* with temperature.

The densities of the samples at atmospheric pressure were measured at different temperatures with an Anton Paar DMA 58 densimeter. The uncertainty of the density measurements was estimated to be ±0.5 $\mathrm{kg \cdot m^{-3}}$. *PVT* curve measurements were carried out on samples using a PETROTEST VC5/5 liquid thermostat. The measurements were carried out under isothermal conditions; the initial volume of the samples was about 0.5 $\mathrm{cm^3}$, and the pressure varied over the range (0.1 to 350) MPa. A thousand experimental points per measurement were obtained for each *PVT* curve.

Results and Discussion

The pressure dependence of the volume ratio $k = V_p/V_0$ (the ratio of the volume V_p at the current pressure P to the initial volume V_0 at a pressure of 0.1 MPa) is a convenient form for the presentation of the effect of pressure on the sample volume. The experimental data obtained for the volume ratio, k, of DMIPEC are given in Table 1 over the temperature range (293.15 to 363.15) K and the pressure range (0.1 to 350) MPa. The total estimated uncertainty of the k measurement was found to be ±0.25%.

The densities of DMIPEC at atmospheric pressure (0.1 MPa) and at the same temperatures are given in Table 2. The densities from this table can be used for the calculation of the pressure dependence of density over the range of measured pressures and temperatures by means of dividing the density at atmospheric pressure from Table 2 by the volume ratio, k, from Table 1 at the required temperature and pressure. The total estimated uncertainty of the density calculation was found to be ±0.3%.

A great number of equations have been developed for the presentation of experimental results of *PVT* measurements. A number of approximation coefficients are used in many of these equations. Malhotra and Woolf[5] have shown that the dependence

$$1 - k = C \log\left(\frac{B + P}{B + 0.1}\right) \qquad (1)$$

which is a Tait integral equation,[6] allows the effect of pressure on the volume of liquids at a given temperature to be approximated with high accuracy and over a wide range of pressures using only two coefficients: C and B. In addition, the experimental results can be extrapolated outside the range of the measurements with an acceptable accuracy using eq 1, including a gas−liquid transition zone. The coefficient C as a rule is practically independent of temperature, and having studied the temperature dependence of the coefficient B, it is possible to obtain an equation which gives the volume ratio to a high accuracy over a large range of temperatures and pressures.

Information on the volume ratio, k, allows one to calculate the secant bulk modulus, K, the pressure dependence of which is usually approximated as follows by a polynomial of third degree:

$$K = \frac{P - P_0}{1 - k} = a_0 + a_1 P + a_2 P^2 + a_3 P^3 \qquad (2)$$

where P_0 refers to atmospheric pressure (0.1 MPa). The coefficients a_0, a_1, a_2, and a_3 are also a convenient method for the presentation of experimental data, and they may be used for the interpolation of experimental results obtained over the measurement range. Unlike eq 1, eq 2 is in general unsuitable for extrapolation outside the pressure range of the experimental data. However, eq 2 is usually a more accurate representation of the experimental data than eq 1.

Experimental results of the measurement of k, presented in Table 1, have been approximated by a least-squares fit using eqs 1 and 2, and the coefficients for such an approximation are given in Table 3 for all temperatures for which measurements have been carried out. The coefficients C and B presented in Table 3 allow an approximation of the experimental data from Table 1 accurate to within ±0.1%. The coefficients a_0, a_1, a_2, and a_3 presented in Table 3 allow an approximation of the experimental data from Table 1 accurate to within ±0.1% for pressures $P \geq$ 50 MPa and accurate to within ±0.15% for lower pressures.

Analysis of the temperature dependence of the coefficient C presented in Table 3 shows that this coefficient depends weakly on temperature, and its average value is 0.2069 ± 0.0017. The experimental data obtained from Table 1 were then approximated by a least-squares fit using eq 1 for a fixed value of $C = 0.2069$ for all temperatures studied, and the values obtained for B^* are presented in Table 3 as well. Using the coefficients $C = 0.2069$ and corresponding B^* values enables the approximation of experimental data from Table 1 accurate to within ±0.15%. The variation of B^* with temperature is presented in Figure 1. It is seen from this figure that B^* decreases linearly with increasing temperature. The approximation coefficients in the equation

$$B^* = B_0 + B_1 T \qquad (3)$$

Table 4. Isothermal Compressibility, k_T, Secant Isothermal Compressibility, k_T*, Isobaric Thermal Expansivity, α, and Increment of Isobaric Molar Heat Capacity, ΔC_p, from Its Value at 0.1 MPa for DMIPEC at Temperatures from (293.15 to 363.15) K

P/MPa	$k_T/10^{-4}$ MPa^{-1}	$k_T^*/10^{-4}$ MPa^{-1}	$\alpha/10^{-3}$ K^{-1}	ΔC_p/J·mol^{-1}·K^{-1}	P/MPa	$k_T/10^{-4}$ MPa^{-1}	$k_T^*/10^{-4}$ MPa^{-1}	$\alpha/10^{-3}$ K^{-1}	ΔC_p/J·mol^{-1}·K^{-1}
$T = 293.15$ K									
0.1	8.22	8.22	0.84	0	125	4.03	5.47	0.57	−18
5	7.87	8.05	0.82	−1	150	3.65	5.16	0.54	−21
10	7.57	7.89	0.81	−3	175	3.35	4.88	0.52	−23
15	7.29	7.73	0.79	−4	200	3.08	4.64	0.50	−24
20	7.04	7.58	0.77	−5	225	2.86	4.43	0.49	−26
30	6.57	7.30	0.74	−6	250	2.66	4.25	0.47	−27
40	6.16	7.04	0.72	−8	275	2.49	4.08	0.46	−29
60	5.49	6.58	0.67	−11	300	2.35	3.93	0.45	−30
80	4.94	6.18	0.63	−13	325	2.21	3.79	0.44	−31
100	4.49	5.84	0.60	−16	350	2.09	3.67	0.43	−32
$T = 303.15$ K									
0.1	8.62	8.62	0.91	0	125	4.19	5.65	0.58	−19
5	8.24	8.43	0.88	−1	150	3.80	5.32	0.56	−22
10	7.92	8.25	0.86	−3	175	3.47	5.03	0.53	−24
15	7.63	8.08	0.83	−4	200	3.19	4.78	0.51	−26
20	7.35	7.91	0.81	−5	225	2.95	4.56	0.49	−27
30	6.86	7.60	0.78	−7	250	2.75	4.37	0.48	−29
40	6.43	7.32	0.75	−8	275	2.58	4.19	0.47	−30
60	5.71	6.83	0.70	−11	300	2.42	4.04	0.46	−31
80	5.14	6.40	0.66	−14	325	2.28	3.90	0.45	−32
100	4.67	6.04	0.62	−16	350	2.16	3.77	0.44	−33
$T = 313.15$ K									
0.1	9.15	9.15	0.98	0	125	4.38	5.91	0.60	−20
5	8.77	8.93	0.94	−2	150	3.97	5.56	0.57	−23
10	8.42	8.73	0.90	−3	175	3.62	5.26	0.54	−25
15	8.10	8.54	0.87	−4	200	3.33	4.99	0.52	−27
20	7.80	8.35	0.85	−5	225	3.08	4.76	0.51	−29
30	7.27	8.01	0.81	−7	250	2.86	4.55	0.49	−30
40	6.79	7.70	0.78	−9	275	2.68	4.37	0.48	−32
60	6.02	7.17	0.73	−12	300	2.51	4.20	0.46	−33
80	5.40	6.71	0.68	−15	325	2.36	4.05	0.45	−34
100	4.90	6.32	0.64	−17	350	2.23	3.91	0.45	−35
$T = 323.15$ K									
0.1	9.94	9.94	1.04	0	125	4.55	6.22	0.63	−21
5	9.45	9.69	0.99	−2	150	4.10	5.83	0.59	−24
10	9.04	9.44	0.96	−3	175	3.74	5.50	0.56	−26
15	8.67	9.22	0.92	−4	200	3.43	5.22	0.54	−28
20	8.32	9.00	0.90	−6	225	3.18	4.97	0.52	−30
30	7.71	8.60	0.85	−8	250	2.95	4.75	0.50	−32
40	7.18	8.24	0.81	−9	275	2.76	4.55	0.49	−33
60	6.32	7.62	0.76	−13	300	2.59	4.37	0.47	−35
80	5.64	7.11	0.71	−16	325	2.44	4.20	0.46	−36
100	5.10	6.68	0.67	−18	350	2.31	4.05	0.45	−37
$T = 333.15$ K									
0.1	10.49	10.49	1.11	0	125	4.76	6.47	0.65	−22
5	10.06	10.21	1.05	−2	150	4.28	6.06	0.61	−25
10	9.61	9.95	1.01	−3	175	3.90	5.71	0.58	−28
15	9.20	9.70	0.97	−5	200	3.58	5.41	0.56	−30
20	8.83	9.47	0.94	−6	225	3.30	5.14	0.53	−32
30	8.15	9.04	0.89	−8	250	3.07	4.91	0.51	−34
40	7.58	8.66	0.85	−10	275	2.86	4.70	0.50	−35
60	6.65	7.99	0.79	−13	300	2.69	4.52	0.48	−36
80	5.93	7.44	0.74	−17	325	2.52	4.35	0.47	−38
100	5.34	6.97	0.69	−19	350	2.39	4.20	0.46	−39
$T = 343.15$ K									
0.1	11.22	11.22	1.18	0	125	4.94	6.78	0.68	−24
5	10.72	10.91	1.11	−2	150	4.45	6.34	0.64	−27
10	10.22	10.61	1.06	−3	175	4.05	5.97	0.60	−29
15	9.78	10.33	1.01	−5	200	3.70	5.64	0.58	−32
20	9.36	10.06	0.98	−6	225	3.42	5.36	0.55	−34
30	8.62	9.58	0.92	−9	250	3.18	5.11	0.53	−35
40	7.99	9.15	0.88	−11	275	2.97	4.89	0.51	−37
60	6.97	8.42	0.82	−14	300	2.78	4.69	0.49	−38
80	6.18	7.81	0.76	−17	325	2.62	4.50	0.48	−39
100	5.56	7.31	0.72	−20	350	2.48	4.33	0.47	−41
$T = 353.15$ K									
0.1	12.01	12.01	1.25	0	125	5.06	7.10	0.70	−25
5	11.40	11.65	1.16	−2	150	4.54	6.62	0.66	−28
10	10.90	11.31	1.10	−4	175	4.14	6.22	0.62	−31
15	10.41	11.00	1.06	−5	200	3.79	5.88	0.59	−33
20	9.90	10.70	1.02	−7	225	3.51	5.58	0.57	−35
30	9.05	10.16	0.96	−9	250	3.27	5.32	0.54	−37
40	8.35	9.69	0.91	−11	275	3.07	5.08	0.52	−39
60	7.23	8.88	0.84	−15	300	2.89	4.87	0.50	−40
80	6.38	8.22	0.79	−18	325	2.73	4.68	0.49	−41
100	5.72	7.67	0.75	−21	350	2.60	4.50	0.48	−43

Table 4 (Continued)

P/MPa	$k_T/10^{-4}$ MPa^{-1}	$k_T^*/10^{-4}$ MPa^{-1}	$\alpha/10^{-3}$ K^{-1}	ΔC_p/J·mol^{-1}·K^{-1}	P/MPa	$k_T/10^{-4}$ MPa^{-1}	$k_T^*/10^{-4}$ MPa^{-1}	$\alpha/10^{-3}$ K^{-1}	ΔC_p/J·mol^{-1}·K^{-1}
				$T = 363.15$ K					
0.1	13.16	13.16	1.31	0	125	5.28	7.48	0.72	−26
5	12.41	12.74	1.21	−2	150	4.73	6.96	0.68	−29
10	11.73	12.33	1.14	−4	175	4.30	6.52	0.64	−32
15	11.15	11.95	1.10	−5	200	3.95	6.15	0.61	−35
20	10.55	11.60	1.06	−7	225	3.65	5.83	0.58	−37
30	9.64	10.97	0.99	−10	250	3.41	5.55	0.56	−39
40	8.85	10.42	0.94	−12	275	3.20	5.30	0.53	−41
60	7.61	9.48	0.87	−16	300	3.03	5.07	0.51	−42
80	6.69	8.73	0.82	−19	325	2.87	4.86	0.50	−43
100	5.97	8.11	0.77	−23	350	2.73	4.68	0.49	−45

were found to be 288.55 MPa and −0.6087 MPa·K^{-1}, respectively, for B_0 and B_1.

The estimate of the accuracy of the value of k using the dependence obtained for $B^*(T)$ (see eq 3) and $C = 0.2069$ allows the calculation of the volume ratio, k, over the pressure range (0.1 to 350) MPa and the temperature range (293.15 to 363.15) K accurate to ±0.25%, and the extrapolation of data outside the measurement range over (0.1 to 700) MPa and (273.15 to 373.15) K accurate to ±0.75%. Outside this range extrapolation probably becomes unreliable.

The values of isothermal compressibility, k_T, presented in Table 4 were calculated using the following expression:

$$k_T = -\{1/[(P - P_0) - K]\}\{1 - (P - P_0)/K(\partial K/\partial P)_T\} \qquad (4)$$

The differentiation was carried out analytically, using data from Table 3 on the approximation of the secant bulk modulus by a cubic polynomial. The data presented in Table 4 show that the isothermal compressibility of DMIPEC increases significantly with increasing temperature. So, k_T equals 8.22×10^{-4} MPa^{-1} at a temperature of 293.15 K and a pressure of 0.1 MPa, and it increases about one and a half times, becoming equal to 13.16×10^{-4} MPa^{-1} for an increase of temperature up to 363.15 K. The accuracy of the determination of k_T is estimated as ±0.4% for pressures $P \geq 50$ MPa, and is perhaps greater for lower pressures.

Strictly speaking, the secant bulk modulus is not a thermodynamic function, since its determination is based on a ratio of finite increments (see eq 2), not on a differentiation. It is used because of its simplicity of calculation and because of the small number of experimental points usually available. The tangent bulk modulus $K^* = -V(\partial P/\partial V)_T$ (or simply bulk modulus) and its inverse value, the isothermal compressibility k_T (see also eq 4), which are calculated by the differentiation of the dependence of volume on pressure, are real thermodynamic values. The Micro-*PVT* system allows the determination of these derivatives with high accuracy due to the large number of experimental points and high accuracy of measurements. The coefficient of secant isothermal compressibility, k_T^* (the inverse of the secant bulk modulus, K, calculated according to eq 2), is given in Table 4 for comparison. The values of k_T and k_T^* coincide only at low pressures, and the difference between them increases with increasing pressure. This is stipulated by the fact that the ratio of finite increments is close to the derivative only for small increments.

Values of isobaric thermal expansivity, α, presented in Table 4, were calculated according to formula

$$\alpha = (\partial \ln V_m/\partial T)_P \qquad (5)$$

where V_m is the molar volume, which was determined on the basis of densities taken from Table 2 and volume ratios, k, calculated according to eq 1 using coefficients from Table 3. The derivative was calculated analytically, for which purpose the dependence of ln V_m on temperature was approximated by a cubic polynomial. The accuracy of the determination of α is estimated as ±0.5% for pressures $P \geq 50$ MPa and is perhaps greater for lower pressures.

The calculated values of isobaric thermal expansivity, α, allowed the calculation of the increment of isobaric molar heat capacity, ΔC_p, from its value at 0.1 MPa according to the following formula:

$$\Delta C_p = C_p - C_p(0.1\ \text{MPa}) = -\int_{0.1}^{P} TM/\rho\{(\partial\alpha/\partial T)_P + \alpha^2\}\, dP \qquad (6)$$

where M is the molar mass and ρ is the density at P. The data obtained are presented in Table 4. The values of α were represented by a quadratic in T to enable analytic differentiation. ΔC_p has an error of about ±2 J·mol^{-1}·K^{-1} for the studied range of pressures.

Conclusion

The *PVT* properties of DMIPEC have been measured for eight temperatures over the temperature range (293.15 to 363.15) K and the pressure range (0.1 to 350) MPa. The data obtained on the volume ratio were approximated by the Tait equation, and the calculated secant bulk modulus was approximated by a cubic polynomial. A dependence for the calculation of DMIPEC volume ratio has been proposed based on the analysis of the temperature dependence of coefficients in the Tait equation for different temperatures and the studied range of pressures. The isothermal compressibility, the isobaric thermal expansivity, and the increment of isobaric molar heat capacity from its value at 0.1 MPa were calculated.

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Received for review November 8, 2000. Accepted January 23, 2001.

JE000355Y