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Densities, Molar Volumes, Thermal Expansion Coefficients, and Isothermal Compressibilities of Organic Acids from 293.15 K to 323.15 K and at Pressures up to 25 MPa

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Densities of seven straight-chain organic acids, including acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, and octanoic acid, have been measured by using a vibrating-tube densimeter in the temperature range from 293.15 K to 323.15 K and pressure range from 0.1 MPa to 25.0 MPa. Molar volumes of these organic acids have been obtained from the measured densities and fitted to polynomials as a function of temperature and pressure. Thermal expansion coefficients and isothermal compressibilities have been derived as a function of temperature and pressure.

Introduction

To design chemical reactors and separation equipment efficiently, it is necessary to have data on fluid properties over a wide range of temperatures and pressures. In this work, densities are measured of straight-chain organic acids from acetic acid to octanoic acid for temperatures of 293.15 K to 323.15 K and pressures up to 25 MPa. Thermal expansion coefficients and isothermal compressibilities are also reported. These properties are correlated with temperature and pressure for each organic acid.

$P-\rho-T$ data of some carboxylic acids (C_8-C_{16}) have been measured. Densities of straight-chain organic acids from acetic acid to octanoic acid were measured by Bernardo-Gil *et al.* in the temperature range 20−50 °C at atmospheric pressure. However, to our knowledge, no literature data on isothermal compressibilities of organic acids within the experimental range in this work are available.

Experimental Section

Materials. The chemicals used in this work were acetic acid (Riedel-de Haën, >99.8 mass %), propanoic acid (Fluka, >99.5 mass %), butanoic acid (Fluka, >99.5 mass %), pentanoic acid (Merck, >99.0 mass %), hexanoic acid (Riedel-de Haën, >99.0 mass %), heptanoic acid (Merck, >99.0 mass %), and octanoic acid (Riedel-de Haën, >99.5 mass %). All of the chemicals were used without further purification.

Apparatus and Procedure. In this work all densities were measured with a vibrating-tube densimeter (Anton Paar, Model DMA 60/512P), with a resolution of 1×10^{-5} $g\cdot cm^{-3}$. The densimeter was equipped with a thermostat that could keep the temperature within ±0.01 °C (Haake, Model F3-K).

The sample was filled into the sample tube and the pressure increased by a syringe pump (Isco, Model 100DX). The pressure of system was measured by a pressure gauge (Heise, Model CMM, 0−27.6 MPa) with an accuracy of ±0.02 MPa. The densimeter was calibrated with nitrogen and water, and all the measurements were made by reference to water. The densities of nitrogen and water were taken from the literature (Jacobsen *et al.*, 1972; Keenan *et al.*, 1969). The estimated accuracy of density measurements is $\pm 5 \times 10^{-4}$ $g\cdot cm^{-3}$.

Table 1. Densities ρ of Organic Acids at 298.15 K and 0.1 MPa

	$\rho/(g\cdot cm^{-3})$			
compound	this work	Bernardo-Gil *et al.*	Korpela	Riddick *et al.*
acetic acid	1.0427	1.0443	1.0434	1.04392
propanoic acid	0.9882	0.9872	0.9878	0.98808
butanoic acid	0.9528	0.9595		0.9532
pentanoic acid	0.9339	0.9340		0.9345
hexanoic acid	0.9212	0.9180		0.9230
heptanoic acid	0.9124	0.9143		
octanoic acid	0.9073	0.9061		0.9066

Results and Discussion

As listed in Table 1, the densities of the carboxylic acids measured at 298.15 K and 0.1 MPa were compared with those reported in the literature (Bernardo-Gil *et al.*, 1990; Korpela, 1971; Riddick *et al.*, 1986). The results of this study show good agreement with previous work. The densities of the carboxylic acids measured from 293.15 K to 323.15 K in the pressure range of 0.1 MPa to 25.0 MPa are listed in Table 2.

The molar volumes V_m can be calculated by the following equation

$$V_m = M_W/\rho \quad (1)$$

where M_W is the molar mass and ρ is the density. The molar volumes V_m are fitted to the following second-degree polynomial T and P

$$V_m(T,P)/(cm^3\cdot mol^{-1}) = a_0 + a_1(T/K) + a_2(T/K)^2 + a_3(P/MPa) + a_4(P/MPa)^2 + a_5(P/MPa)(T/K) \quad (2)$$

where a_i are adjustable parameters. The values of a_i are obtained by least-squares methods with all points weighted equally. The standard deviations are calculated by using the following equation

$$\sigma(V_m) = [\Sigma(V_{m,exp} - V_{m,cal})^2/(n - p)]^{1/2} \quad (3)$$

where n is the number of measurements and p is the number of parameters. The thermal expansion coefficients α_P and isothermal compressibilities κ_T are derived by using

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Table 2. Experimental Densities ρ of Organic Acids under Various Temperatures T and Pressures P

	ρ/(g·cm^{-3})						
P/MPa	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
			Acetic Acid				
0.1	1.0483	1.0427	1.0371	1.0314	1.0258	1.0202	1.0145
0.2	1.0483	1.0428	1.0372	1.0316	1.0260	1.0203	1.0146
0.5	1.0485	1.0431	1.0375	1.0319	1.0263	1.0207	1.0150
1.0	1.0490	1.0436	1.0381	1.0324	1.0268	1.0212	1.0155
2.0	1.0500	1.0446	1.0391	1.0335	1.0279	1.0223	1.0167
5.0	1.0529	1.0475	1.0421	1.0366	1.0311	1.0256	1.0200
10.0	1.0574	1.0522	1.0468	1.0415	1.0361	1.0307	1.0253
15.0	1.0615	1.0564	1.0512	1.0458	1.0406	1.0353	1.0301
20.0	1.0650	1.0600	1.0550	1.0499	1.0447	1.0396	1.0345
25.0	1.0677	1.0629	1.0580	1.0530	1.0481	1.0432	1.0382
			Propanoic Acid				
0.1	0.9934	0.9882	0.9829	0.9774	0.9721	0.9667	0.9613
0.2	0.9935	0.9883	0.9830	0.9776	0.9722	0.9668	0.9614
0.5	0.9938	0.9886	0.9833	0.9779	0.9725	0.9671	0.9617
1.0	0.9943	0.9891	0.9838	0.9784	0.9730	0.9677	0.9623
2.0	0.9952	0.9900	0.9847	0.9794	0.9741	0.9687	0.9634
5.0	0.9979	0.9928	0.9876	0.9823	0.9771	0.9719	0.9666
10.0	1.0022	0.9973	0.9922	0.9871	0.9819	0.9769	0.9717
15.0	1.0063	1.0015	0.9966	0.9915	0.9866	0.9816	0.9766
20.0	1.0103	1.0056	1.0008	0.9959	0.9911	0.9863	0.9814
25.0	1.0138	1.0094	1.0048	1.0000	0.9953	0.9907	0.9860
			Butanoic Acid				
0.1	0.9576	0.9528	0.9479	0.9429	0.9379	0.9329	0.9279
0.2	0.9577	0.9529	0.9480	0.9430	0.9380	0.9331	0.9280
0.5	0.9579	0.9532	0.9483	0.9433	0.9383	0.9334	0.9284
1.0	0.9583	0.9536	0.9487	0.9438	0.9388	0.9339	0.9289
2.0	0.9592	0.9545	0.9496	0.9448	0.9398	0.9349	0.9299
5.0	0.9617	0.9571	0.9523	0.9475	0.9426	0.9378	0.9329
10.0	0.9658	0.9613	0.9567	0.9520	0.9472	0.9425	0.9378
15.0	0.9698	0.9655	0.9610	0.9563	0.9517	0.9472	0.9426
20.0	0.9741	0.9697	0.9654	0.9608	0.9563	0.9519	0.9475
25.0	0.9782	0.9739	0.9698	0.9653	0.9610	0.9567	0.9524
			Pentanoic Acid				
0.1	0.9383	0.9339	0.9294	0.9247	0.9202	0.9157	0.9111
0.2	0.9384	0.9340	0.9295	0.9249	0.9203	0.9158	0.9112
0.5	0.9386	0.9342	0.9297	0.9251	0.9206	0.9160	0.9114
1.0	0.9390	0.9346	0.9301	0.9256	0.9210	0.9165	0.9119
2.0	0.9398	0.9355	0.9310	0.9265	0.9220	0.9174	0.9129
5.0	0.9421	0.9378	0.9335	0.9290	0.9246	0.9201	0.9156
10.0	0.9460	0.9418	0.9375	0.9332	0.9289	0.9245	0.9202
15.0	0.9498	0.9458	0.9416	0.9373	0.9331	0.9289	0.9247
20.0	0.9540	0.9500	0.9459	0.9418	0.9377	0.9336	0.9295
25.0	0.9584	0.9545	0.9505	0.9465	0.9424	0.9385	0.9344
			Hexanoic Acid				
0.1	0.9254	0.9212	0.9170	0.9126	0.9083	0.9040	0.8996
0.2	0.9255	0.9214	0.9171	0.9127	0.9084	0.9041	0.8997
0.5	0.9257	0.9216	0.9173	0.9130	0.9087	0.9043	0.9000
1.0	0.9261	0.9220	0.9177	0.9134	0.9091	0.9048	0.9005
2.0	0.9268	0.9227	0.9185	0.9142	0.9099	0.9056	0.9013
5.0	0.9290	0.9249	0.9208	0.9166	0.9124	0.9082	0.9039
10.0	0.9326	0.9287	0.9247	0.9205	0.9164	0.9123	0.9082
15.0	0.9363	0.9325	0.9286	0.9245	0.9205	0.9165	0.9125
20.0	0.9404	0.9366	0.9328	0.9289	0.9250	0.9211	0.9172
25.0	0.9449	0.9412	0.9375	0.9336	0.9298	0.9260	0.9222
			Heptanoic Acid				
0.1	0.9166	0.9124	0.9082	0.9040	0.8998	0.8958	0.8916
0.2	0.9166	0.9125	0.9083	0.9041	0.9000	0.8959	0.8917
0.5	0.9168	0.9126	0.9085	0.9043	0.9002	0.8961	0.8919
1.0	0.9171	0.9130	0.9089	0.9047	0.9006	0.8965	0.8924
2.0	0.9179	0.9137	0.9097	0.9055	0.9014	0.8973	0.8932
5.0	0.9199	0.9159	0.9119	0.9078	0.9038	0.8997	0.8957
10.0	0.9234	0.9195	0.9156	0.9116	0.9077	0.9038	0.8998
15.0	0.9270	0.9232	0.9195	0.9155	0.9117	0.9079	0.9040
20.0	0.9311	0.9273	0.9236	0.9198	0.9161	0.9123	0.9086
25.0	0.9357	0.9320	0.9284	0.9246	0.9209	0.9173	0.9136
			Octanoic Acid				
0.1	0.9113	0.9073	0.9033	0.8991	0.8951	0.8910	0.8870
0.2	0.9113	0.9073	0.9033	0.8992	0.8952	0.8911	0.8871
0.5	0.9115	0.9075	0.9035	0.8994	0.8954	0.8914	0.8873
1.0	0.9118	0.9078	0.9038	0.8998	0.8958	0.8914	0.8877
2.0	0.9125	0.9086	0.9046	0.9006	0.8966	0.8925	0.8885
5.0	0.9144	0.9106	0.9067	0.9027	0.8988	0.8949	0.8909
10.0	0.9178	0.9141	0.9103	0.9064	0.9025	0.8987	0.8948
15.0	0.9213	0.9177	0.9140	0.9102	0.9065	0.9027	0.8990
20.0	0.9253	0.9218	0.9181	0.9144	0.9108	0.9071	0.9035
25.0	0.9299	0.9264	0.9229	0.9192	0.9156	0.9120	0.9084

Table 3. Coefficients a_i and Standard Deviation $\sigma(V_m)$ of Eq 2

compound	a_0	$10^2 \times a_1$	$10^4 \times a_2$	$10^1 \times a_3$	$10^4 \times a_4$	$10^4 \times a_5$	$\sigma(V_m)$
acetic acid	47.787	0.4304	0.9596	0.6085	5.7042	−4.0048	0.0037
propanoic acid	61.866	0.7186	1.2336	0.9634	3.8027	−5.6659	0.0038
butanoic acid	78.073	0.1766	1.5622	1.1418	1.2823	−6.6412	0.0064
pentanoic acid	91.241	1.6022	1.5018	1.2292	−1.3590	−7.1633	0.0092
hexanoic acid	107.94	0.5568	1.8556	1.3094	−3.8111	−7.6444	0.0126
heptanoic acid	112.66	7.1253	0.9888	1.4353	−6.2018	−8.3036	0.0149
octanoic acid	131.23	4.5128	1.6062	1.5806	−8.3929	−8.9780	0.0171

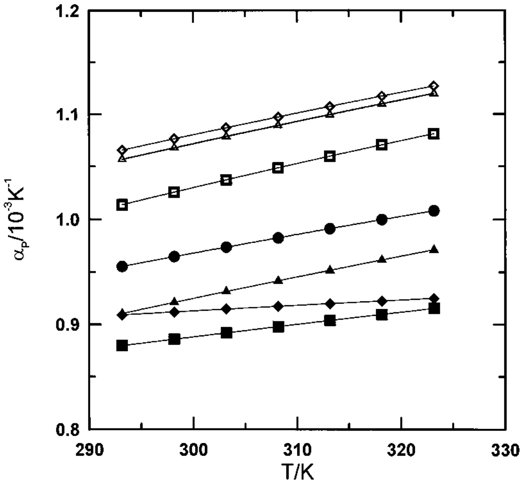

Figure 1. Thermal expansion coefficient versus temperature at 0.1 MPa: △, acetic acid; ◇, propanoic acid; □, butanoic acid; ●, pentanoic acid; ▲, hexanoic acid; ◆, heptanoic acid; ■, octanoic acid.

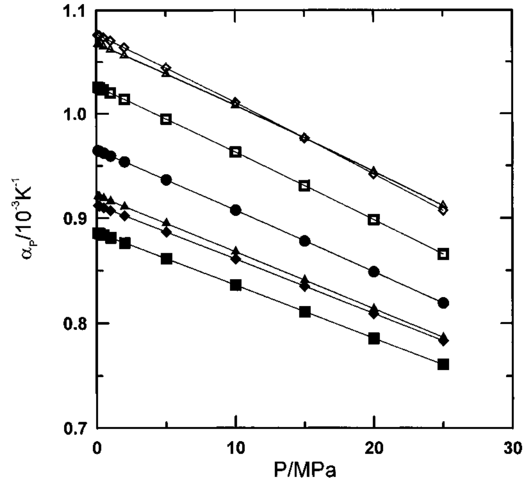

Figure 2. Thermal expansion coefficient versus temperature at 298.15 K: △, acetic acid; ◇, propanoic acid; □, butanoic acid; ●, pentanoic acid; ▲, hexanoic acid; ◆, heptanoic acid; ■, octanoic acid.

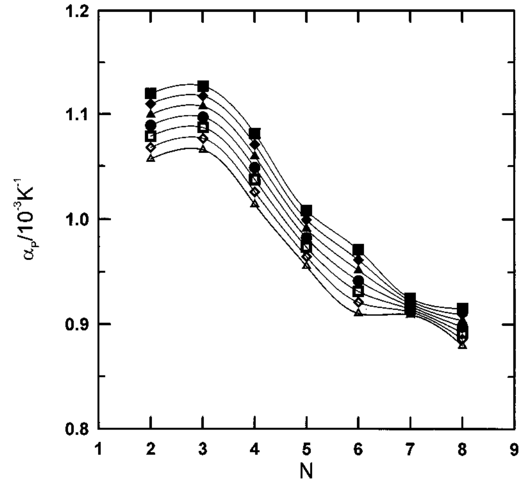

Figure 3. Thermal expansion coefficient versus *N* at 0.1 MPa: △, 293.15 K; ◇, 298.15 K; □, 303.15 K; ●, 308.15 K; ▲, 308.15 K; ◆, 313.15 K; ■, 318.15 K.

the following relations:

$$\alpha_P = V_m^{-1} (\partial V_m/\partial T)_P \qquad (4)$$

$$\kappa_T = - V_m^{-1} (\partial V_m/\partial P)_T \qquad (5)$$

From eqs 2, 4 and 5, we can get the thermal expansion coefficients α_P and isothermal compressibilities κ_T by using the following relations:

$$\alpha_P = (a_1 + 2a_2T + a_5P)/(a_0 + a_1T + a_2T^2 + a_3P + a_4P^2 + a_5PT) \qquad (6)$$

$$\kappa_T = - (a_3 + 2a_4P + a_5T)/(a_0 + a_1T + a_2T^2 + a_3P + a_4P^2 + a_5PT) \qquad (7)$$

The values of the parameters a_i, along with the standard deviations σ, are listed in Table 3. The estimated uncertainties of α_P and κ_T were 1×10^{-5} K^{-1} and 1×10^{-5} MPa^{-1}, respectively.

Thermal expansion coefficients for these organic acids are shown in Figures 1 and 2. They show that the thermal expansion coefficients increase as the temperature increases at constant pressure and decrease as the pressure increases at constant temperature.

The relationships between thermal expansion coefficients and numbers of carbon atoms are shown in Figure 3 at 0.1 MPa and Figure 4 at 298.15 K. The thermal expansion coefficients decrease as the number of carbon atoms increase at constant pressure (except for $N = 2$, 3) and decrease with increasing numbers of carbon atoms at constant temperature.

The isothermal compressibilities increase with increase in temperature as shown in Figure 5. In Figure 6, the isothermal compressibilities decrease as the pressure increases for acetic acid, propanoic acid, and butanoic acid. On the other hand, for pentanoic acid, hexanoic acid, heptanoic acid, and octanoic acid, it is exactly the opposite.

The relationships between isothermal compressibilities and numbers of carbon atoms at 0.1 MPa are shown in Figure 7. The isothermal compressibilities decrease as the numbers of carbon atoms increase at 0.1 MPa.

In Figure 8, the isothermal compressibilities decrease with an increase in the number of carbon atoms at constant temperature when the pressure is under 5.0 MPa. When the pressure increases, it changes gradually to increase with an increase in the number of carbons atoms at constant temperature.

In many works about thermal expansion coefficients and isothermal compressibilities (Banipal *et al.*, 1992), as in the phenomenon seen in Figures 3, 4, 7, and 8, there is no visible numerical relationship between these properties and number of carbon atoms. The dramatic changes in the

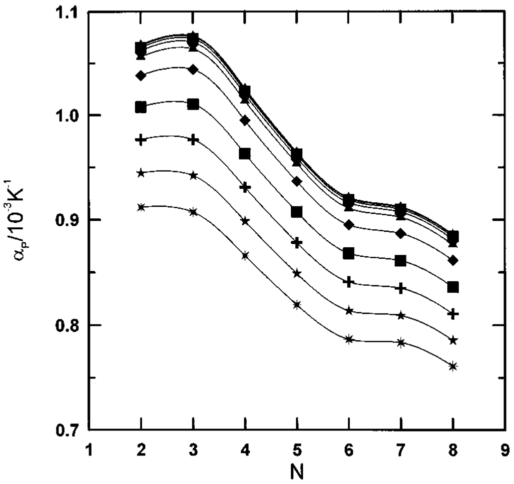

Figure 4. Thermal expansion coefficient versus *N* at 298.15 K: △, 0.1 MPa; ◇, 0.2 MPa; □, 0.5 MPa; ●, 1.0 MPa; ▲, 2.0 MPa; ◆, 5.0 MPa; ■, 10.0 MPa; +, 15.0 MPa; ★, 20.0 MPa, *, 25.0 MPa.

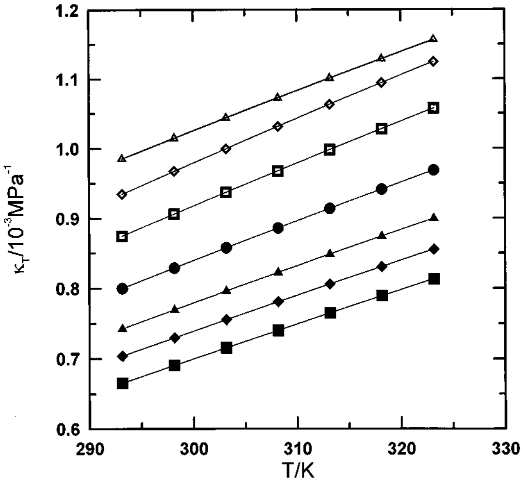

Figure 5. Isothermal compressibility versus temperature at 0.1 MPa: △, acetic acid; ◇, propanoic acid; □, butanoic acid; ●, pentanoic acid; ▲, hexanoic acid; ◆, heptanoic acid; ■, octanoic acid.

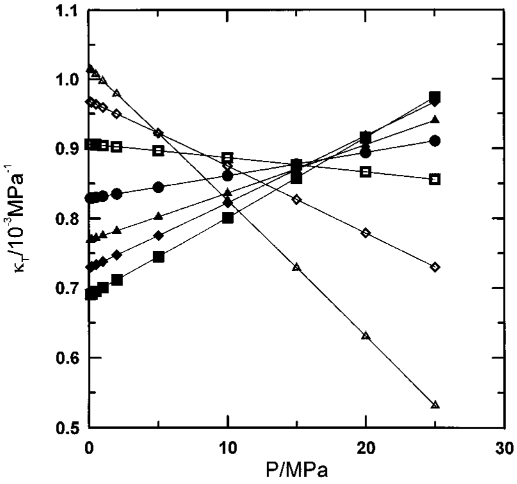

Figure 6. Isothermal compressibility versus temperature at 298.15 K: △, acetic acid; ◇, propanoic acid; □, butanoic acid; ●, pentanoic acid; ▲, hexanoic acid; ◆, heptanoic acid; ■, octanoic acid.

values of a_1 and a_2 in Table 3 also explain this phenomenon. A further study on the correlation of this relationship is needed.

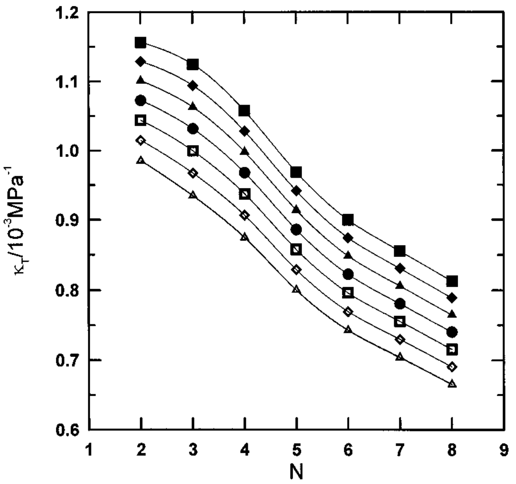

Figure 7. Isothermal compressibility versus *N* at 0.1 MPa: △, 293.15 K; ◇, 298.15 K; □, 303.15 K; ●, 308.15 K; ▲, 308.15 K; ◆, 313.15 K; ■, 318.15 K.

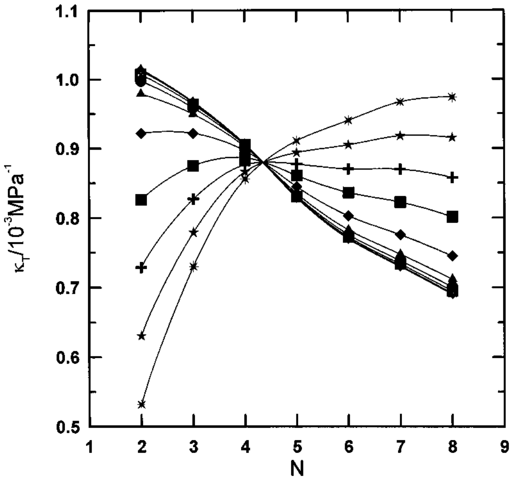

Figure 8. Isothermal compressibility versus *N* at 298.15 K: △, 0.1 MPa; ◇, 0.2 MPa; □, 0.5 MPa; ●, 1.0 MPa; ▲, 2.0 MPa; ◆, 5.0 MPa; ■, 10.0 MPa; +, 15.0 MPa; ★, 20.0 MPa; *, 25.0 MPa.

Conclusion

Throughout this study it can be seen that the densities of the carboxylic acids increase as the pressure increases, the temperature decreases, or the carbon numbers decrease. The thermal expansion coefficients are exactly the opposite to the densities. The isothermal compressibilities increase with increase in temperature and increase as the pressure increases for acetic acid, propanoic acid, and butanoic acid, but the opposite occurs for pentanoic acid, hexanoic acid, heptanoic acid, and octanoic acid. It also decreases with an increase in the number of carbon atoms when the pressure is under 5.0 MPa and changes gradually to increase with an increase in the number of carbon atoms at higher pressure.

A simple equation can be used to express the relationships between molar volumes, temperature, and pressure for these carboxylic acids: $V_m = a_0 + a_1T + a_2T^2 + a_3P + a_4P^2 + a_5PT$. It can be used for interpolation and derivation of other properties within the experimental temperature and pressure ranges. It is also a simple equation to determine the values of thermal expansion coefficients and isothermal compressibilities in these ranges.

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