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PVT Property Measurements for the Liquids Ethyl Propionate and Ethyl Butyrate from (278 to 338) K and (0.1 to 380) MPa

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The effect of pressure on the volume in the liquid phase for two ethyl alkanoic acid esters, the propionate and butyrate, has been measured relative to the volume at 0.1 MPa with a bellows volumometer for pressures up to 380 MPa over the temperature range (278.15 to 338.13) K. The experimental volume ratios have been represented by two sets of equations to enable interpolation and extrapolation of volumetric properties. One set enables intercomparison of the volume ratios for the two esters and with literature data for ethyl acetate. The comparison permits volumetric data for all three liquids to be generated with reasonable accuracy from those for ethyl propionate by making an allowance for the number of $-CH_2$ groups in the alkanoic acid segment of the ester. A small modification of the predictive method enables calculation, with lesser accuracy, of volumetric data for methyl, propyl, and butyl acetates. Isothermal compressibilities, isobaric expansivities, and the change in the isobaric heat capacity from its value at 0.1 MPa have been calculated for both esters from the volumetric data.

Introduction

In a recent paper Malhotra and Woolf (1996) used volumetric measurements for several alkyl acetates to develop a simple equation that reproduced the measurements with an overall accuracy of a few tenths of a percent. The equation was based on a modified Tait equation

$$1 - k = C \log[(B + P)/(B + 0.1)] \qquad (1)$$

where the volume ratio $k = V_P/V(0.1\ \text{MPa})$, P is the pressure, and B and C are parameters of the fit. A temperature independent value for C of 0.21 was determined for the model system, propyl acetate, and the corresponding values of B for the temperature range of the experimental measurements fitted to a linear equation in the reciprocal of the reduced temperature, $T_r = T/T_c$ where T_c is the critical temperature

$$B = -118.028 + 108.476/T_r - 4.59(C_{n,R} - 3) \qquad (2)$$

The third term in eq 2 enables the equation to be used for other alkyl acetates where $C_{n,R}$ is the number of carbon atoms in the alkyl group of the acetate. Equation 2 was least accurate for the isomer 1-methylethyl acetate.

The present measurements provide data for two esters, ethyl propionate and ethyl butyrate, where the composition of the alkyl alcohol group is fixed while that of the alkanoic acid head group is varied. These data are complemented by those of Kumagai and Iwasaki (1979) for ethyl acetate which have, however, a lower maximum pressure of 157 MPa (380 MPa in this work) and a different temperature range of −20 to +40 °C (5 to 65 °C).

Experimental Section

Both esters were from Aldrich with a stated purity of 99%. They were distilled in an argon atmosphere through a helices-packed column to obtain a middle fraction; for ethyl butyrate the distillation was at reduced pressure. The boiling point range was ±0.1 K for each. The purity of each purified liquid was not measured. It is general experience that the volume ratios used here to measure the effect of pressure on the liquid are affected only within the experimental error by small amounts of impurities. Densities at atmospheric pressure, $\rho(0.1\ \text{MPa})$, were measured with an Anton Paar Model DMA60 digital densimeter with a DMA602HT external cell; they are estimated to have a reproducibility of $\pm 0.005\ \text{kg·m}^{-3}$ (Malhotra and Woolf, 1996, and references therein). The densities $\rho(0.1\ \text{MPa})$ at (278.15, 288.15, 298.14, 313.14, 323.14, and 338.13) K were (907.008, 895.707, 884.359, 867.094, 855.456, and 837.671) kg·m^{-3} for ethyl propionate and (894.605, 884.176, 873.668, 857.765, 847.031, and 830.781) kg·m^{-3} for ethyl butyrate. A literature compilation (Riddick *et al.*, 1986) gives 895.74 kg·m^{-3} for the density of ethyl propionate at 15 °C and (884.40 and 873.94) kg·m^{-3} for ethyl butyrate at (15 and 25) °C.

An automated bellows volumometer (Malhotra and Woolf, 1996, and references therein) was used for the high-pressure volumetric measurements which are reported in Table 1. The volume ratios are estimated to have an accuracy of ±0.05% at and above 50 MPa and ±0.1% below that pressure.

Results and Discussion

The volume ratios, $k = V_{P}/V(0.1\ \text{MPa})$, are given in Tables 1 and 2. They can be used with the $\rho(0.1\ \text{MPa})$ to obtain densities of the compressed liquid. The k were represented by either eq 1 or 3 with the coefficients, given

$$K = P/(1 - k) = a_0 + a_1P + a_2P^2 + a_3P^3 \qquad (3)$$

in Table 3, obtained by a least squares fit. K is the secant bulk modulus, and as can be seen in Table 3, eq 3 provides a more accurate representation of the experimental k than eq 1. Equation 1, however, is the more reliable of the two representations of k for extrapolation outside the experimental temperature and pressure range for liquids (Malhotra and Woolf, 1991). For that purpose a value of C is chosen, usually close to the average, to represent those determined independently for all the temperatures of the

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Table 1. Experimental Pressures and Volume Ratios $k = V_P/V(0.1\ \text{MPa})$ for Ethyl Propionate at Temperatures from 278.15 K to 338.13 K

P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k
$T = 278.15$ K							
2.547	0.9976	27.66	0.9769	150.78	0.9144	275.93	0.8762
4.996	0.9954	40.28	0.9682	176.03	0.9054	300.78	0.8701
10.353	0.9907	60.43	0.9558	201.31	0.8971	326.10	0.8641
14.850	0.9869	80.63	0.9449	226.04	0.8897	350.42	0.8590
19.900	0.9828	101.00	0.9350	251.49	0.8826	365.30	0.8564
23.620	0.9800	125.59	0.9243				
$T = 288.15$ K							
2.547	0.9974	29.83	0.9738	150.28	0.9101	276.02	0.8707
4.996	0.9950	40.78	0.9658	175.93	0.9005	300.37	0.8645
10.450	0.9899	59.57	0.9536	200.00	0.8924	325.07	0.8586
15.495	0.9854	79.35	0.9423	225.54	0.8845	349.28	0.8532
19.775	0.9818	101.13	0.9313	250.69	0.8774	368.59	0.8492
23.790	0.9785	125.69	0.9202				
$T = 298.14$ K							
2.547	0.9972	28.37	0.9729	150.43	0.9051	274.25	0.8654
4.996	0.9946	39.79	0.9640	174.96	0.8958	300.04	0.8588
9.840	0.9897	59.14	0.9506	200.58	0.8869	325.78	0.8526
14.715	0.9850	79.12	0.9386	225.04	0.8792	350.32	0.8470
20.075	0.9801	100.50	0.9273	249.95	0.8719	370.88	0.8427
24.162	0.9765	124.71	0.9160				
$T = 313.14$ K							
2.547	0.9969	28.79	0.9693	150.52	0.8974	275.33	0.8559
4.996	0.9939	37.99	0.9614	175.25	0.8876	300.48	0.8494
10.125	0.9881	59.08	0.9455	200.25	0.8785	324.58	0.8434
15.114	0.9827	79.36	0.9325	225.12	0.8704	350.00	0.8374
19.890	0.9778	100.72	0.9206	249.45	0.8631	372.07	0.8327
24.121	0.9737	125.49	0.9084				
$T = 323.14$ K							
2.547	0.9966	28.47	0.9674	149.92	0.8923	275.36	0.8496
4.996	0.9934	44.04	0.9535	174.19	0.8824	300.04	0.8431
9.864	0.9874	59.53	0.9416	200.38	0.8726	323.87	0.8370
15.139	0.9813	78.70	0.9288	224.86	0.8644	350.22	0.8306
19.790	0.9762	100.59	0.9161	249.78	0.8568	376.15	0.8251
23.920	0.9719	124.79	0.9038				
$T = 338.13$ K							
2.547	0.9961	28.34	0.9635	149.50	0.8833	276.58	0.8388
4.996	0.9925	39.33	0.9526	176.03	0.8722	301.65	0.8320
9.578	0.9861	59.85	0.9352	201.61	0.8625	326.57	0.8256
15.495	0.9783	80.45	0.9206	225.95	0.8542	349.73	0.8201
20.475	0.9723	100.56	0.9082	251.64	0.8461	369.07	0.8156
23.920	0.9684	125.70	0.8946				

Table 2. Experimental Pressures and Volume Ratios $k = VP/V(0.1\ \text{MPa})$ for Ethyl Butyrate at Temperatures from 278.15 K to 338.13 K

P/MPa	k	P/MPa	k	P/MPa	k	P/MPa	k
$T = 278.15$ K							
2.547	0.9977	28.64	0.9769	150.55	0.9161	275.02	0.8787
4.996	0.9955	39.62	0.9695	175.22	0.9075	299.16	0.8728
9.593	0.9916	59.10	0.9576	199.89	0.8995	326.00	0.8667
13.407	0.9885	80.24	0.9462	225.24	0.8920	351.46	0.8612
20.700	0.9828	100.77	0.9364	249.85	0.8852	371.44	0.8573
23.695	0.9805	125.35	0.9259				
$T = 288.15$ K							
2.547	0.9975	31.42	0.9732	150.39	0.9119	275.44	0.8733
4.996	0.9952	39.49	0.9674	175.43	0.9028	301.29	0.8669
10.419	0.9902	59.50	0.9545	200.61	0.8944	324.01	0.8616
15.371	0.9859	78.91	0.9437	225.55	0.8869	350.40	0.8557
20.225	0.9818	99.52	0.9334	250.78	0.8798	370.91	0.8516
23.745	0.9790	124.13	0.9224				
$T = 298.14$ K							
2.547	0.9973	39.93	0.9650	150.60	0.9073	275.15	0.8680
4.996	0.9948	59.92	0.9515	175.91	0.8979	300.57	0.8616
15.297	0.9850	79.37	0.9402	200.45	0.8895	325.32	0.8557
20.075	0.9807	100.71	0.9291	223.42	0.8823	350.17	0.8500
23.800	0.9775	124.95	0.9179	249.85	0.8747	372.96	0.8453
28.82	0.9734						
$T = 313.14$ K							
2.547	0.9970	28.60	0.9708	149.30	0.9008	274.66	0.8597
4.996	0.9942	39.80	0.9616	174.85	0.8909	300.74	0.8529
10.125	0.9885	59.37	0.9475	200.78	0.8818	325.98	0.8468
15.198	0.9833	80.14	0.9346	225.65	0.8738	350.19	0.8413
20.455	0.9782	99.95	0.9237	249.95	0.8666	377.95	0.8353
23.770	0.9751	125.24	0.9113				
$T = 323.14$ K							
2.547	0.9967	28.22	0.9689	150.47	0.8953	274.72	0.8538
4.996	0.9937	38.96	0.9595	175.02	0.8855	299.52	0.8472
9.899	0.9878	58.60	0.9446	199.81	0.8767	324.50	0.8410
15.050	0.9821	79.14	0.9312	225.13	0.8684	348.52	0.8355
20.035	0.9769	99.55	0.9195	250.15	0.8608	375.18	0.8296
23.970	0.9730	124.73	0.9068				
$T = 338.13$ K							
2.547	0.9963	28.41	0.9655	149.66	0.8878	275.22	0.8445
4.996	0.9929	39.28	0.9552	174.74	0.8774	300.60	0.8375
9.751	0.9866	59.69	0.9386	200.17	0.8680	325.17	0.8313
14.860	0.9803	79.80	0.9247	224.55	0.8597	349.77	0.8257
19.950	0.9745	100.44	0.9123	247.80	0.8525	378.69	0.8192
23.950	0.9701	125.21	0.8992				

measurements and a corresponding set of B's calculated; those B's and the accuracy of the fit are given in the second to last and last columns of Table 3. To enable comparison and prediction of volume ratios for related compounds, it is convenient to choose the same value of C for each substance and to express the corresponding B in terms of the reduced temperature, $T_r = T/T_c$ where T_c is the critical temperature. The C given for each ester in Table 3 indicate a suitable C of 0.21. The variation of the B's for this value with the reciprocal of the reduced temperature is shown in Figure 1 which includes the data of Kumagai and Iwasaki (1979) for ethyl acetate. (The B's for ethyl acetate with $C = 0.21$ at (253.15, 273.15, 293.15, and 313.14) K are (112.41, 93.55, 79.19, and 67.33) MPa, respectively.) A linear fit to the B's of each ethyl ester gives

$$\text{propionate} \qquad B = -121.758 + 110.829/T_r \tag{4}$$

$$\text{butyrate} \qquad B = -113.408 + 104.265/T_r \tag{5}$$

$$\text{acetate} \qquad B = -123.369 + 113.719/T_r \tag{6}$$

with standard deviations of 0.18, 0.13, and 1.02, respectively. The T_c values (546.1, 566.0, and 523.3 K) for the propionate, butyrate, and acetate, respectively, were from the compilation by Riddick *et al.* (1986). Equations 4−6 with eq 1 will reproduce the k of Tables 1 and 2 within ±0.1%. The similarity of the slopes in eqs 4−6 suggests that it may be possible to represent the B for the normal ethyl esters by a common equation which allows for changes in the composition of the alkyl group. Because the data for ethyl acetate do not extend to as high a pressure as those of the present work, it is appropriate to choose ethyl propionate as the reference compound so that

$$B = -121.758 + 110.829/T_r - 3.8(C_{n,A} - 3) \tag{7}$$

with $C_{n,A}$ the number of carbon atoms in the head group of the alkanoic acid. The value of 3.8 MPa for the contribution of each $-CH_2$ group is an approximate average of the change in B in going from ethyl acetate to the propionate, and from the latter to the butyrate, for a range of $1/T_r$ from 1.8 to 1.9. Equation 7 reproduces the experimental k for ethyl acetate with an overall standard deviation of ±0.07% and a maximum deviation of 0.17%; for ethyl propionate the corresponding numbers are ±0.05% and 0.18, and for ethyl butyrate, ±0.08% and 0.21%. The conclusion to be drawn from these results is that eq 7 is suitable for generating k with reasonable precision for all three ethyl esters for the reduced temperature range from 0.48−0.62. Lacking other data it would be reasonable to anticipate that eq 7 would provide useful estimates of k for ethyl esters with longer normal alkyl head groups of the alkanoic acid.

Table 3. Coefficients of Eqs 1 and 3 and the Standard Deviation of Their Fit to the Volume Ratio $k = VP/V(0.1\ \mathrm{MPa})$ for Ethyl Propionate and Ethyl Butyrate

T/K	a_0/MPa	a_1	$-a_2$/GPa^{-1}	a_3/GPa^{-2}	$10^2\langle\Delta k/k\rangle$	B/MPa	C	$10^2\langle\Delta k/k\rangle$	B/MPa^a	$10^2\langle\Delta k/k\rangle$
					Ethyl Propionate					
278.15	1051.11	5.5780	6.8145	7.417	0.008	100.47	0.2160	0.025	99.58	0.059
288.15	981.42	5.3932	6.2455	6.497	0.012	94.53	0.2184	0.022	92.23	0.041
298.14	904.33	5.2413	5.5249	5.291	0.009	85.66	0.2163	0.023	84.85	0.047
313.14	794.74	5.2020	5.7275	5.585	0.012	75.00	0.2156	0.028	74.67	0.058
323.14	733.86	5.0958	5.5015	5.237	0.015	69.15	0.2161	0.030	68.66	0.053
338.13	639.33	5.0335	5.6977	5.622	0.014	59.88	0.2153	0.029	59.80	0.058
					Ethyl Butyrate					
278.15	1092.52	5.3703	5.4163	5.118	0.005	103.09	0.2152	0.019	102.20	0.044
288.15	1008.27	5.3584	5.5414	5.216	0.006	95.06	0.2148	0.023	94.47	0.051
298.14	938.02	5.2717	5.4778	5.207	0.009	88.54	0.2155	0.022	87.62	0.042
313.14	831.90	5.3258	6.2631	6.444	0.014	79.11	0.2160	0.024	77.91	0.050
323.14	762.75	5.3170	6.3891	6.559	0.016	72.24	0.2148	0.030	71.68	0.066
338.13	680.80	5.1572	6.1129	6.257	0.018	64.20	0.2154	0.028	63.53	0.054

[a] These data are for a C fixed at 0.216 (ethyl propionate) and 0.215 (ethyl butyrate).

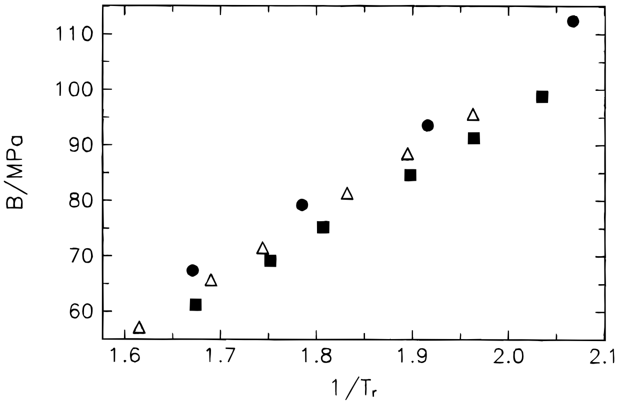

Figure 1. Variation of B of eq 1 with $C = 0.21$ for (●) ethyl acetate, (△) ethyl propionate, and (■) ethyl butyrate.

It is interesting to note that esters with the same empirical formula have similar representations of their B's for the same value of C (0.21); this can be seen by comparing eqs 4 and 5 with eqs 8 and 9 (Malhotra and Woolf, 1996)

propyl acetate $$B = -118.028 + 108.476/T_r \tag{8}$$

butyl acetate $$B = -114.570 + 104.006/T_r \tag{9}$$

The similarities between the Tait B coefficient representations of the various esters with the same C (=0.21) as seen with eqs 4−6, 8, and 9) raises the possibility of using one equation of the form of eq 1 or 7 to reproduce the volumetric properties of the several esters. The obvious equation is that obtained by combining eqs 2 and 7

$$B = -120 + 109.6/T_r - 4.2(C_{n,T} - 3) \tag{10}$$

with $C_{n,T}$ the total number of carbon atoms in the compound. The k are generated with an average standard deviation of 0.16% and a maximum deviation of −0.4% for methyl acetate (Kumagai and Iwasaki, 1978), (0.23 and 0.3)% for ethyl acetate, (0.37 and 0.85)% for propyl acetate, (0.35 and 0.7)% for butyl acetate, (0.33 and 0.82)% for ethyl propionate, and (0.24 and 0.48)% for ethyl butyrate. For 1-methylethyl acetate the results are (0.6 and 1.2)%.

The isothermal compressibilities, κ_T, isobaric thermal expansivity, α, and change in the isobaric molar heat

Table 4. Isothermal Compressibility, κ_T, Isobaric Expansivity, α, and Change in Molar Heat Capacity, ΔC_P, for Ethyl Propionate

	P/MPa									
	0.1	20	40	60	100	150	200	250	300	350
				T = 278.15 K						
$\kappa_T/10^{-4}$ MPa^{-1}	9.50	7.97	6.86	6.04	4.93	4.08	3.52	3.09	2.72	2.35
α/10^{-3} K^{-1}	1.23	1.11	1.02	0.95	0.84	0.75	0.69	0.65	0.61	0.56
$-\Delta C_P$/J mol^{-1} K^{-1}	0	2	4	4	5	6	6	6	5	5
				T = 288.15 K						
$\kappa_T/10^{-4}$ MPa^{-1}	10.18	8.48	7.27	6.37	5.16	4.24	3.64	3.20	2.82	2.46
α/10^{-3} K^{-1}	1.26	1.13	1.03	0.95	0.84	0.75	0.69	0.64	0.60	0.56
$-\Delta C_P$/J mol^{-1} K^{-1}	0	2	4	4	5	6	6	6	5	5
				T = 298.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	11.05	9.12	7.75	6.74	5.38	4.37	3.73	3.26	2.89	2.54
α/10^{-3} K^{-1}	1.29	1.14	1.03	0.95	0.84	0.75	0.68	0.63	0.59	0.55
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	4	5	6	6	6	6	6	5
				T = 313.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	12.57	10.14	8.47	7.28	5.72	4.60	3.90	3.40	3.00	2.62
α/10^{-3} K^{-1}	1.34	1.16	1.04	0.95	0.84	0.74	0.67	0.62	0.58	0.55
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	4	5	6	7	7	7	6	6
				T = 323.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	13.61	10.85	8.98	7.66	5.96	4.76	4.02	3.50	3.08	2.70
α/10^{-3} K^{-1}	1.37	1.18	1.05	0.96	0.83	0.74	0.67	0.62	0.57	0.54
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	5	5	7	7	7	7	6	6
				T = 338.13 K						
$\kappa_T/10^{-4}$ MPa^{-1}	15.62	12.11	9.83	8.27	6.33	5.00	4.21	3.65	3.19	2.76
α/10^{-3} K^{-1}	1.42	1.20	1.06	0.959	0.83	0.73	0.66	0.61	0.56	0.54
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	5	6	7	8	8	7	7	6

Table 5. Isothermal Compressibility, κ_T, Isobaric Expansivity, α, and Change in Molar Heat Capacity, ΔC_P, for Ethyl Butyrate

	P/MPa									
	0.1	20	40	60	100	150	200	250	300	350
					$T = 278.15$ K					
$\kappa_T/10^{-4}$ MPa^{-1}	9.14	7.76	6.73	5.95	4.86	4.00	3.44	3.03	2.70	2.39
$\alpha/10^{-3}$ K^{-1}	1.16	1.04	0.96	0.89	0.79	0.71	0.65	0.59	0.55	0.52
$-\Delta C_P$/J mol^{-1} K^{-1}	0	2	4	5	6	7	7	8	8	9
					$T = 288.15$ K					
$\kappa_T/10^{-4}$ MPa^{-1}	9.91	8.30	7.13	6.26	5.06	4.14	3.55	3.12	2.77	2.46
$\alpha/10^{-3}$ K^{-1}	1.18	1.05	0.96	0.89	0.80	0.71	0.65	0.59	0.55	0.52
$-\Delta C_P$/J mol^{-1} K^{-1}	0	2	4	5	6	7	8	8	9	9
					$T = 298.14$ K					
$\kappa_T/10^{-4}$ MPa^{-1}	10.65	8.84	7.54	6.58	5.27	4.29	3.66	3.21	2.84	2.51
$\alpha/10^{-3}$ K^{-1}	1.21	1.07	0.97	0.90	0.80	0.71	0.65	0.59	0.55	0.52
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	4	5	7	8	8	9	9	10
					$T = 313.14$ K					
$\kappa_T/10^{-4}$ MPa^{-1}	12.01	9.73	8.16	7.04	5.58	4.52	3.85	3.36	2.95	2.56
$\alpha/10^{-3}$ K^{-1}	1.25	1.09	0.98	0.90	0.80	0.71	0.64	0.59	0.55	0.52
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	4	6	7	8	9	9	10	11
					$T = 323.14$ K					
$\kappa_T/10^{-4}$ MPa^{-1}	13.09	10.43	8.64	7.38	5.78	4.65	3.95	3.45	3.02	2.61
$\alpha/10^{-3}$ K^{-1}	1.27	1.10	0.99	0.91	0.80	0.71	0.64	0.59	0.55	0.52
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	5	6	7	9	9	10	11	11
					$T = 338.13$ K					
$\kappa_T/10^{-4}$ MPa^{-1}	14.67	11.48	9.38	7.94	6.13	4.88	4.13	3.58	3.13	2.69
$\alpha/10^{-3}$ K^{-1}	1.31	1.12	1.00	0.91	0.80	0.71	0.64	0.59	0.55	0.52
$-\Delta C_P$/J mol^{-1} K^{-1}	0	3	5	6	8	9	10	11	11	12

capacity, ΔC_P, given in Tables 4 and 5 show the similarity between the esters having the same empirical formula noted above (Tables 6 and 7, Malhotra and Woolf, 1996). The κ_T were calculated from eq 3 using the relation

$$\kappa_T = -\{1/(P - K)\}\{1 - (P/K)(\partial K/\partial P)_T\} \qquad (10)$$

with the differentiation performed analytically. The α are defined by

$$\alpha = (\partial \ln V_m/\partial T)_P \qquad (11)$$

with V_m the molar volume. The V_m at pressures above 0.1 MPa were determined by multiplying the V_m at 0.1 MPa by the k obtained from eq 1 using the coefficients of Table 3. The α values given in Tables 4 and 5 were obtained by analytical differentiation of the ln V_m expressed as a quadratic in T. The estimated fractional uncertainties in α are ±(0.02 to 0.03) for $P \geq 50$ MPa and possibly greater below that pressure. The α values enable calculation of the change in the isobaric molar heat capacity, ΔC_P,

$$\Delta C_P = C_P - C_P(0.1\ \text{MPa}) = TM\int_{0.1}^{P}\{(\partial\alpha/\partial T)_P + \alpha^2\}/\rho\,\mathrm{d}P \qquad (12)$$

where M is the molar mass and ρ is the density at P. The α values were represented by a quadratic in T to enable analytic differentiation. The ΔC_P given in Tables 4 and 5 are estimated to have an error of ±(1 to 2) J·mol^{-1}·K^{-1}. Their variation with pressure is small in comparison to C_P(0.1 MPa) at 25 °C which is (196 and 228) J·mol^{-1}·K^{-1} for ethyl propionate and ethyl butyrate, respectively (Riddick *et al.*, 1986).

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