PVT Property Measurements for the Liquids Propyl Acetate, Butyl Acetate, and 1-Methylethyl Acetate from (278 to 338) K and (0.1 to 380) MPa

Rakesh Malhotra and Lawrence A. Woolf*

Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

The effect of pressure on the volume in the liquid phase for three acetates, propyl, butyl, and 1-methylethyl (isopropyl), 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. Densities of the liquids at 0.1 MPa have been determined for the same temperatures. 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 three acetates and with literature data for methyl and ethyl acetates. The comparison permits volumetric data for all five liquids to be generated with reasonable accuracy from those for propyl acetate by making an allowance for the number of -CH_2 groups in the alkyl part of the acetate; the prediction is least accurate for methyl acetate and 1-methylethyl acetate. Isothermal compressibilities, isobaric expansivities, and the change in the isobaric heat capacity from its value at 0.1 MPa have been calculated from the volumetric data.

Introduction

This work is part of an experimental program which explores the limitations of a simple scheme for predicting the volumetric properties of a series of related compounds (Malhotra and Woolf, 1995) over an extensive range of pressure and temperature. The present results complement the earlier measurements for methyl acetate (Kumagai and Iwasaki, 1978) and ethyl acetate (Kumagai and Iwasaki, 1979) which have, however, a lower maximum pressure of 157 MPa compared to 380 MPa in this work and a different temperature range of (−20 to +40) °C compared to (5 to 65) °C.

Experimental Section

The acetates 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 butyl acetate the distillation was at reduced pressure. The boiling point range was ±0.1 K for each except 1-methylethyl acetate for which the range was 1.2 K. The purity of each purified liquid was not measured although the densities at atmospheric pressure and 25 °C are lower than those in the literature (Riddick *et al.*, 1986). 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, ρ(0.1 MPa), were measured using an Anton Paar Model DMA60 digital densimeter with a DMA602HT external cell; this was frequently and carefully calibrated (Malhotra and Woolf, 1994). Temperatures were measured with a platinum resistance thermometer and adjusted to ITS-90. They were held constant to ±0.005 K and have an accuracy of ±0.01 K; the procedure for measuring the densities employs a short term temperature stability corresponding to a density equivalent of $\pm 2 \times 10^{-3}$ kg·m^{-3} or better (Malhotra and Woolf, 1991a, 1994). The overall reproducibility of the density is estimated to be ±0.005 kg·m^{-3}.

* To whom correspondence should be addressed.

Table 1. Experimental Pressures and Volume Ratios $k = V_p/V(0.1\ \text{MPa})$ for Propyl Acetate 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	29.82	0.9756	149.49	0.9154	275.51	0.8770
4.996	0.9954	39.81	0.9688	174.76	0.9064	300.47	0.8708
10.054	0.9910	59.83	0.9565	200.13	0.8981	326.60	0.8647
15.297	0.9867	79.10	0.9461	225.26	0.8905	352.92	0.8591
20.215	0.9828	99.50	0.9362	250.67	0.8835	368.33	0.8562
24.475	0.9795	124.54	0.9252				
			T = 288.15 K				
2.547	0.9975	28.10	0.9751	150.54	0.9100	275.70	0.8709
4.996	0.9951	40.25	0.9662	175.38	0.9009	299.98	0.8649
10.130	0.9903	59.99	0.9533	201.02	0.8923	326.96	0.8586
15.198	0.9858	79.90	0.9419	225.68	0.8847	348.22	0.8539
20.050	0.9816	100.50	0.9315	250.51	0.8776	366.20	0.8503
23.820	0.9785	124.55	0.9206				
			T = 298.14 K				
2.547	0.9973	39.47	0.9644	150.46	0.9055	276.08	0.8653
4.996	0.9947	59.89	0.9504	174.17	0.8965	300.42	0.8591
9.815	0.9898	79.90	0.9385	200.55	0.8873	326.21	0.8528
14.600	0.9852	100.68	0.9276	225.03	0.8796	350.36	0.8473
23.895	0.9769	125.53	0.9160	249.79	0.8724	375.90	0.8420
28.154	0.9733						
			T = 313.14 K				
2.547	0.9969	28.07	0.9702	150.21	0.8981	274.76	0.8567
4.996	0.9940	39.12	0.9607	175.01	0.8883	299.59	0.8502
9.924	0.9884	79.82	0.9327	199.95	0.8793	349.82	0.8380
19.875	0.9780	125.23	0.9091	250.05	0.8635	377.23	0.8321
29.930	0.9740						
			T = 323.14 K				
2.547	0.9967	40.07	0.9577	149.57	0.8932	275.50	0.8503
4.996	0.9937	59.12	0.9427	175.42	0.8827	300.15	0.8438
10.251	0.9874	79.99	0.9287	200.72	0.8734	325.99	0.8373
15.495	0.9815	100.74	0.9167	225.70	0.8650	349.96	0.8316
20.475	0.9762	125.12	0.9042	250.09	0.8575	376.34	0.8258
28.549	0.9681						
			T = 338.13 K				
2.547	0.9962	28.96	0.9636	149.84	0.8846	274.73	0.8407
4.996	0.9927	44.26	0.9488	175.12	0.8739	300.35	0.8337
15.074	0.9794	80.18	0.9217	200.03	0.8643	323.85	0.8276
20.120	0.9733	100.36	0.9094	224.98	0.8557	347.81	0.8217
23.940	0.9690	124.56	0.8966	249.56	0.8479	381.45	0.8143

An automated bellows volumometer (Easteal and Woolf, 1985; Malhotra and Woolf, 1993) was used for the high-pressure volumetric measurements which are reported in

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Table 2. Experimental Pressures and Volume Ratios $k = V_P/V(0.1\text{MPa})$ for Butyl Acetate 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	0.9978	29.44	0.9770	126.06	0.9271	251.14	0.8868
4.996	0.9957	40.60	0.9696	151.14	0.9175	276.09	0.8804
9.465	0.9919	60.48	0.9578	176.54	0.9087	300.52	0.8745
15.218	0.9874	80.67	0.9473	201.01	0.9010	323.26	0.8693
20.221	0.9836	100.92	0.9377	226.74	0.8935	336.25	0.8666
24.834	0.9802						
			T = 288.15 K				
2.547	0.9976	29.02	0.9757	150.06	0.9139	274.85	0.8757
5.000	0.9953	39.46	0.9683	175.07	0.9049	300.77	0.8694
10.003	0.9909	60.13	0.9554	200.19	0.8966	323.61	0.8640
14.975	0.9866	79.67	0.9447	225.03	0.8891	350.00	0.8582
20.095	0.9825	99.78	0.9349	250.26	0.8821	373.31	0.8535
24.253	0.9792	125.32	0.9237				
			T = 298.14 K				
2.547	0.9974	31.02	0.9726	150.77	0.9094	274.24	0.8708
5.000	0.9950	39.81	0.9661	175.52	0.9003	300.06	0.8643
9.617	0.9906	59.40	0.9532	200.39	0.8919	325.86	0.8582
14.788	0.9859	78.96	0.9420	225.03	0.8843	350.40	0.8527
20.095	0.9813	100.52	0.9310	250.01	0.8772	385.93	0.8454
24.895	0.9774	125.60	0.9197				
			T = 313.14 K				
2.547	0.99711	30.40	0.9702	150.06	0.9028	275.49	0.8621
5.000	0.99441	39.98	0.9625	174.80	0.8932	300.66	0.8557
9.793	0.98933	59.74	0.9485	199.98	0.8844	326.28	0.8494
14.718	0.98438	79.74	0.9363	224.90	0.8764	351.74	0.8435
19.870	0.97947	100.01	0.9255	250.49	0.8689	390.36	0.8355
24.658	0.97512	124.96	0.9135				
			T = 323.14 K				
2.547	0.9968	29.50	0.9687	150.66	0.8976	275.08	0.8564
5.000	0.99382	39.66	0.9602	175.92	0.8876	299.96	0.8498
9.622	0.98848	60.46	0.9450	200.68	0.8789	325.99	0.8434
14.945	0.98272	80.48	0.9324	225.35	0.8709	349.82	0.8380
19.741	0.97785	100.21	0.9213	250.46	0.8633	372.09	0.8331
24.439	0.97334	125.96	0.9085				
			T =338.13 K				
2.547	0.99642	27.78	0.9670	149.94	0.8901	275.35	0.8474
4.996	0.99311	40.27	0.9554	174.61	0.8801	299.82	0.8408
9.710	0.98705	59.72	0.9400	199.62	0.8709	325.69	0.8343
15.265	0.98038	79.34	0.9268	224.64	0.8625	349.27	0.8288
20.028	0.97504	100.17	0.9145	250.17	0.8546	370.45	0.8240
24.358	0.97045	123.84	0.9021				

Table 3. Experimental Pressures and Volume Ratios $k = V_P/V(0.1\text{MPa})$ for 1-Methylethyl Acetate 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	0.9973	30.65	0.9724	140.47	0.9128	276.31	0.8696
4.996	0.9948	40.47	0.9651	160.36	0.9052	301.82	0.8632
9.775	0.9902	60.53	0.9520	180.66	0.8980	326.12	0.8576
14.890	0.9854	80.75	0.9405	201.69	0.8910	350.17	0.8524
20.100	0.9809	100.65	0.9304	226.20	0.8835	361.21	0.8500
23.970	0.9776	120.68	0.9212	251.39	0.8763		
			T = 288.15 K				
2.547	0.9971	27.93	0.9724	139.67	0.9080	274.25	0.8638
4.996	0.9944	39.83	0.9629	160.17	0.8998	300.86	0.8569
9.874	0.9892	59.77	0.9491	180.35	0.8923	323.43	0.8516
15.000	0.9841	79.74	0.9370	200.72	0.8854	348.31	0.8460
19.905	0.9795	99.28	0.9266	225.16	0.8777	360.03	0.8434
23.800	0.9760	119.81	0.9167	250.00	0.8704		
			T = 298.14 K				
2.547	0.9968	29.09	0.9692	139.18	0.9033	275.05	0.8576
4.996	0.9938	38.90	0.9610	159.11	0.8950	300.11	0.8510
9.943	0.9881	59.44	0.9460	179.61	0.8873	325.35	0.8449
14.850	0.9829	79.44	0.9335	200.39	0.8800	349.52	0.8394
19.574	0.9781	99.09	0.9225	225.16	0.8721	375.53	0.8337
23.820	0.9740	119.08	0.9125	250.29	0.8646		
			T = 313.14 K				
2.547	0.9964	27.82	0.9670	140.10	0.8947	274.73	0.8479
4.996	0.9931	40.75	0.9551	159.62	0.8863	299.58	0.8411
9.835	0.9869	59.31	0.9405	179.58	0.8784	325.63	0.8346
14.800	0.9809	79.58	0.9268	199.95	0.8711	350.62	0.8289
19.925	0.9751	99.72	0.9150	225.33	0.8626	374.61	0.8235
24.131	0.9707	119.85	0.9044	250.18	0.8550		
			T = 323.14 K				
2.547	0.9961	28.02	0.9641	139.53	0.8892	274.90	0.8409
4.996	0.9925	42.25	0.9503	159.50	0.8803	299.71	0.8341
9.578	0.9861	59.47	0.9361	179.39	0.8722	325.63	0.8275
14.975	0.9790	79.38	0.9222	199.61	0.8647	348.31	0.8222
19.674	0.9733	99.72	0.9097	224.72	0.8562	376.24	0.8159
23.945	0.9685	119.54	0.8990	249.35	0.8484		
			T = 338.13 K				
2.547	0.9955	27.51	0.9602	139.48	0.8796	274.38	0.8298
4.996	0.9914	41.55	0.9452	159.12	0.8704	299.55	0.8227
9.914	0.9836	58.75	0.9298	179.34	0.8620	324.23	0.8164
14.800	0.9765	79.61	0.9141	199.94	0.8541	350.19	0.8105
19.850	0.9697	98.87	0.9017	224.48	0.8455	383.85	0.8028
23.795	0.9647	119.27	0.8899	249.58	0.8373		

Tables 1−3. This determines the effect of pressure on the volume of a fixed mass of liquid at constant temperature as the ratio of its volume at the experimental pressure, P, to the volume at a lower reference pressure usually chosen as 0.1 MPa. Pressures above 25 MPa were measured with a pressure transducer; the lower pressures were read from a Heise-Bourdon analogue gauge except for those below 5 MPa which were generated with a dead weight gauge. Both the pressure transducer and Heise-Bourdon gauge had been calibrated with a dead weight gauge with an accuracy of ±0.05%. 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 1−3. They can be used with the $\rho(0.1\text{ MPa})$ of Table 4 to obtain densities of the compressed liquid. The k's were represented by either of eqs 1 or 2 with the coefficients,

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

$$1 - k = C \log[(B + P)/(B + 0.1)] \qquad (2)$$

given in Table 5, obtained by a least squares fit. K is the secant bulk modulus, and eq 1 provides the most accurate representation of the experimental k. Equation 2, the modified Tait equation, is particularly useful for extrapolation outside the experimental temperature and pressure range for liquids (Malhotra and Woolf, 1991b), including the liquid−vapor coexistence region (Malhotra and Woolf,

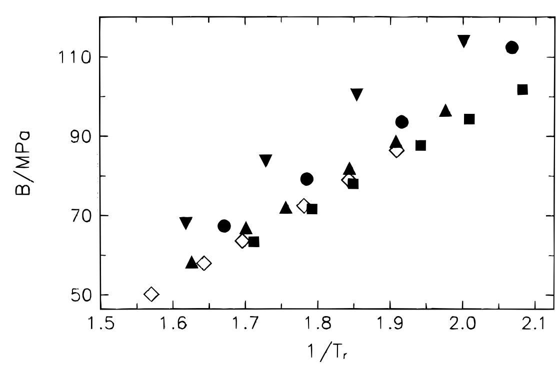

Figure 1. Variation of B of eq 2 with C = 0.21 for (▽) methyl acetate, (●) ethyl acetate, (△) propyl acetate, (◇) 1-methylethyl acetate, and (■) butyl acetate.

Table 4. Densities, ρ (kg·m^{-3}), for Propyl Acetate, Butyl Acetate, and 1-Methylethyl Acetate at 0.1 MPa

	T/K					
	278.15	288.15	298.14	313.14	323.14	338.13
propyl acetate	904.87	893.85	882.76	865.87	854.47	837.02
butyl acetate	896.41	886.21	876.02	860.50	850.11	834.10
1-methylethyl acetate	889.50	878.12	866.59	848.92	837.02	818.74

Table 5. Coefficients of Eqs 1 and 2 and Standard Deviation of Their Fit to the Volume Ratio $k = V_p/V(0.1\text{MPa})$ for Propyl Acetate, Butyl Acetate, and 1-Methylethyl Acetate

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]	$10^2\langle\Delta k/k\rangle$
					Propyl Acetate					
278.15	1065.90	5.4979	6.3289	6.574	0.007	102.01	0.2167	0.023	101.31	0.057
288.15	989.38	5.1996	5.1585	4.980	0.004	92.88	0.2158	0.014	93.14	0.043
298.14	913.46	5.2000	5.3276	4.978	0.009	86.91	0.2174	0.022	86.08	0.046
313.14	802.27	5.2021	5.6656	5.393	0.012	76.40	0.2167	0.031	75.87	0.066
323.14	765.78	4.7413	3.8616	2.943	0.008	71.46	0.2185	0.014	70.55	0.019
338.13	660.12	4.8823	4.8792	4.359	0.016	61.77	0.2168	0.029	61.57	0.045
					Butyl Acetate					
278.15	1123.40	5.4503	5.8708	6.016	0.004	105.88	0.2148	0.017	105.23	0.045
288.15	1040.30	5.4327	5.8652	5.736	0.007	98.62	0.2153	0.022	97.62	0.051
298.14	970.97	5.3188	5.5168	5.143	0.010	92.02	0.2158	0.024	90.80	0.047
313.14	867.67	5.1943	5.3170	4.854	0.012	82.06	0.2161	0.026	80.82	0.044
323.14	785.03	5.5225	7.4463	8.241	0.023	75.50	0.2157	0.034	74.30	0.073
338.13	700.12	5.2526	6.3116	6.444	0.015	65.88	0.2140	0.033	65.81	0.075
					1-Methylethyl Acetate					
278.15	938.48	5.7076	7.5217	8.321	0.011	89.34	0.2132	0.030	88.24	0.069
288.15	860.82	5.5701	7.1516	7.764	0.014	81.69	0.2134	0.030	80.64	0.066
298.14	784.80	5.6445	7.7421	8.497	0.023	75.19	0.2134	0.040	74.04	0.085
313.14	697.92	5.3399	6.7308	7.072	0.018	66.01	0.2138	0.036	65.02	0.067
323.14	637.45	5.2535	6.6044	6.900	0.019	59.96	0.2133	0.039	59.29	0.070
338.13	556.83	5.0662	6.2537	6.534	0.021	51.66	0.2129	0.035	51.36	0.061

[a] These data are for a C fixed at 0.217 (propyl acetate), 0.215 (butyl acetate), and 0.213 (1-methylethyl acetate).

Table 6. Isothermal Compressibility, κ_T, Isobaric Expansivity, α, and Changein Molar Heat Capacity, ΔC_p, for Propyl Acetate

P/MPa	0.1	20	40	60	100	150	200	250	300	350
				T = 278.15 K						
$\kappa_T/10^{-4}$ MPa^{-1}	9.37	7.89	6.82	6.01	4.91	4.06	3.50	3.08	2.72	2.38
$\alpha/10^{-3}$ K^{-1}	1.20	1.08	0.99	0.92	0.80	0.71	0.65	0.60	0.55	0.51
ΔC_p/J·mol^{-1}·K^{-1}	0	−2	−4	−5	−7	−9	−10	−12	−13	−14
				T = 288.15 K						
$\kappa_T/10^{-4}$ MPa^{-1}	10.10	8.48	7.29	6.40	5.17	4.22	3.60	3.15	2.78	2. 45
$\alpha/10^{-3}$ K^{-1}	1.23	1.10	1.00	0.93	0.81	0.72	0.65	0.60	0.56	0.52
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−5	−5	−7	−8	−9	−9	−9	−10
				T = 298.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	10.94	9.06	7.71	6.72	5.37	4.36	3.72	3.26	2.89	2.55
$\alpha/10^{-3}$ K^{-1}	1.27	1.12	1.02	0.93	0.82	0.72	0.66	0.61	0.57	0.53
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−5	−6	−8	−9	−9	−9	−10	−10
				T = 313.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	12.45	10.06	8.42	7.24	5.70	4.58	3.89	3.40	3.01	2.64
$\alpha/10^{-3}$ K^{-1}	1.31	1.15	1.03	0.95	0.83	0.73	0.67	0.62	0.58	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−6	−7	−8	−9	−10	−10	−10	−11
				T = 323.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	13.04	10.64	8.94	7.68	6.00	4.76	3.99	3.46	3.07	2.75
$\alpha/10^{-3}$ K^{-1}	1.35	1.17	1.05	0.96	0.84	0.74	0.68	0.63	0.58	0.55
ΔC_p/J·mol^{-1}·K^{-1}	0	−4	−6	−7	−9	−10	−10	−11	−11	−12
				T = 338.13 K						
$\kappa_T/10^{-4}$ MPa^{-1}	15.13	11.90	9.74	8.23	6.32	4.97	4.17	3.62	3.19	2.81
$\alpha/10^{-3}$ K^{-1}	1.39	1.20	1.06	0.97	0.85	0.75	0.69	0.64	0.59	0.56
ΔC_p/J·mol^{-1}·K^{-1}	0	−4	−6	−8	−10	−11	−11	−11	−12	−13

1993). 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 measurements and a corresponding set of B's calculated; those B's and the accuracy of the fit are given in the second last and last columns of Table 5. 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 5 indicates 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 for methyl and ethyl acetates. (The B's for the methyl and ethyl acetates with $C = 0.21$ at (253.15, 273.15, 293.15, and 313.14) K are (113.85, 100.34, 83.71, and 67.97) MPa and (112.41, 93.55, 79.19, and 67.33) MPa, respectively.) A linear fit to the B's of each acetate gives

$$\text{propyl } B = -118.028 + 108.476/T_r \quad (3)$$

$$\text{butyl } B = -114.570 + 104.006/T_r \quad (4)$$

$$\text{isopropyl } B = -116.807 + 106.322/T_r \quad (5)$$

$$\text{methyl } B = -124.962 + 120.222/T_r \quad (6)$$

$$\text{ethyl } B = -123.369 + 113.719/T_r \quad (7)$$

with standard deviations of 0.49, 0.22, 0.18, 2.48, and 1.02, respectively. The T_c's were from the compilation by Riddick *et al.* (1986). The larger error in the fit of the ethyl and methyl acetates may reflect a greater uncertainty in the

Table 7. Isothermal Compressibility, κ_T, Isobaric Expansivity, α, and Change in Molar Heat Capacity, ΔC_p, for Butyl Acetate

P/MPa	0.1	20	40	60	100	150	200	250	300
				T = 278.15 K					
$\kappa_T/10^{-4}$ MPa^{-1}	8.89	7.56	6.57	5.82	4.78	3.96	3.41	3.00	2.65
$\alpha/10^{-3}$ K^{-1}	1.12	1.02	0.94	0.87	0.78	0.70	0.64	0.59	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−2	−3	−5	−5	−5	−6	−6	−6
				T = 288.15 K					
$\kappa_T/10^{-4}$ MPa^{-1}	9.60	8.07	6.95	6.11	4.97	4.08	3.51	3.09	2.74
$\alpha/10^{-3}$ K^{-1}	1.15	1.03	0.94	0.87	0.78	0.7	0.64	0.58	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−2	−4	−4	−5	−6−	−6	−6	−6
				T = 298.14 K					
$\kappa_T/10^{-4}$ MPa^{-1}	10.29	8.58	7.34	6.42	5.17	4.22	3.61	3.18	2.82
$\alpha/10^{-3}$ K^{-1}	1.17	1.04	0.95	0.88	0.78	0.69	0.63	0.58	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−4	−5	−5	−6−	−6	−6	−6
				T = 313.14 K					
$\kappa_T/10^{-4}$ MPa^{-1}	11.51	9.45	7.99	6.92	5.49	4.44	3.78	3.31	2.93
$\alpha/10^{-3}$ K^{-1}	1.21	1.06	0.95	0.88	0.77	0.69	0.63	0.58	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−4	−5	−6	−6	−7	−7	−7
				T = 323.14 K					
$\kappa_T/10^{-4}$ MPa^{-1}	12.72	10.12	8.38	7.18	5.66	4.6	3.94	3.44	2.99
$\alpha/10^{-3}$ K^{-1}	1.24	1.07	0.96	0.88	0.77	0.69	0.62	0.57	0.53
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−4	−5	−6	−7	−7	−7	−7
				T = 338.13 K					
$\kappa_T/10^{-4}$ MPa^{-1}	14.26	11.18	9.15	7.76	6.01	4.79	4.06	3.53	3.09
$\alpha/10^{-3}$ K^{-1}	1.28	1.09	0.97	0.88	0.77	0.68	0.62	0.57	0.53
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−5	−6	−7	−7	−8	−8	−8

Table 8. Isothermal Compressibility, κ_T, Isobaric Expansivity, α, and Change in Molar Heat Capacity, ΔC_p, for 1-Methylethyl Acetate

P/MPa	0.1	20.	40	60	100	150	200	250	300	350
				T = 278.15 K						
$\kappa_T/10^{-4}$ MPa^{-1}	10.64	8.71	7.37	6.41	5.15	4.23	3.64	3.19	2.79	2.39
$\alpha/10^{-3}$ K^{-1}	1.26	1.12	1.02	0.94	0.84	0.75	0.68	0.62	0.58	0.53
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−5	−6	−7	−8	−8	−8	−9	−9
				T = 288.15 K						
$\kappa_T/10^{-4}$ MPa^{-1}	11.60	9.38	7.87	6.79	5.40	4.40	3.77	3.29	2.88	2.46
$\alpha/10^{-3}$ K^{-1}	1.30	1.14	1.03	0.95	0.84	0.75	0.68	0.62	0.58	0.53
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−5	−6	−7	−8	−8	−9	−9	−10
				T = 298.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	12.72	10.07	8.32	7.11	5.59	4.54	3.89	3.41	2.97	2.53
$\alpha/10^{-3}$ K^{-1}	1.34	1.17	1.05	0.96	0.84	0.74	0.67	0.62	0.58	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−3	−5	−6	−8	−9	−9	−9	−10	−10
				T = 313.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	14.30	11.17	9.12	7.72	5.98	4.79	4.06	3.54	3.09	2.64
$\alpha/10^{-3}$ K^{-1}	1.40	1.20	1.06	0.97	0.84	0.74	0.67	0.62	0.58	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−4	−6	−7	−8	−9	−10	−10	−10	−11
				T = 323.14 K						
$\kappa_T/10^{-4}$ MPa^{-1}	15.66	12.01	9.69	8.13	6.23	4.94	4.18	3.63	3.16	2.70
$\alpha/10^{-3}$ K^{-1}	1.44	1.22	1.08	0.97	0.84	0.74	0.67	0.62	0.58	0.54
ΔC_p/J·mol^{-1}·K^{-1}	0	−4	−6	−7	−9	−10	−10	−11	−11	−12
				T = 338.13 K						
$\kappa_T/10^{-4}$ MPa^{-1}	17.92	13.42	10.63	8.81	6.63	5.20	4.37	3.77	3.26	2.77
$\alpha/10^{-3}$ K^{-1}	1.50	1.25	1.09	0.98	0.84	0.73	0.66	0.61	0.58	0.55
ΔC_p/J·mol^{-1}·K^{-1}	0	−4	−6	−8	−10	−11	−11	−11	−12	−13

experimental results on which the B values are based but could also be a consequence of the effect of temperature on the hydrogen-bonded liquid structure of these lower alcohols. Equations 3−5 with eq 2 will reproduce the k values of Tables 1−3 within ±0.1%. The similarity of the slopes suggests that it may be possible to represent the B for the normal 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 propyl acetate as the reference compound so that

$$B = -118.028 + 108.476/T_r - 4.59(C_{n,R} - 3) \quad (8)$$

with $C_{n,R}$ the number of carbon atoms in the alkyl group of the acetate. The value of 4.59 MPa for the contribution of the -CH_2 group is an approximate average of the change in B in going from ethyl acetate to propyl acetate, and propyl acetate to butyl acetate for a range of $1/T_r$ from 1.8 to 1.85. No allowance has been made for the different configuration of 1-methylethyl acetate, the isomer of propyl acetate. Equation 8 reproduces the experimental k for butyl acetate with an overall standard deviation of ±0.06% and a maximum deviation of 0.14%; for ethyl acetate the corresponding numbers are ±0.08% and 0.19%, for 1-methylethyl acetate ±0.21% and 0.5%, and methyl acetate ±0.3% and 0.6%. The inference to be drawn from these results is that eq 8 is suitable for generating k with reasonable precision for all five acetates for the reduced temperature range from 0.48 to 0.64. Lacking other data, it would be reasonable to anticipate that eq 8 would provide useful estimates of k for acetates with longer normal alkyl groups.

The isothermal compressibilities, κ_T, given in Tables 6−8 have been calculated from eq 1 using the relation

$$\kappa_T = -\{1/(P - K)\}\{1 - (P/K)(\partial K/\partial P)_T\} \qquad (9)$$

with the differentiation performed analytically. The κ_T data in the tables show that 1-methylethyl acetate is the most compressible of the three liquids.

The isobaric thermal expansivity, α, is defined by

$$\alpha = (\partial \ln V_m/\partial T)_P \qquad (10)$$

with V_m the molar volume. The V_m values at pressures above 0.1 MPa were determined by multiplying the V_m data at 0.1 MPa, determined from the densities in Table 4, by the k obtained from eq 1 using the coefficients of Table 5. The α values given in Tables 6−8 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 densities at 0.1 MPa for propyl acetate in Table 1 differ from those in the literature (TRC Tables, 1996) by amounts between about (−0.01 and ±0.1)%; the literature data are larger than those of Table 4 at temperatures below 298.14 K where they are close to coincidence and then become smaller at the higher temperatures. For butyl acetate the experimental and literature densities (TRC Tables, 1996) agree within 0.01% at the two highest temperatures but differ by as much as ±0.2% at the lower temperatures. Geiseler *et al.* (1973) purified their 1-methylethyl acetate by distillation and obtained a density at 293.15 K which is 0.07% smaller than the value (872.4 $kg \cdot m^{-3}$) interpolated from the data in Table 1. However, the densities for this ester in the TRC Tables (1996) are always larger than the present results by amounts ranging from 1.2% at 278.15 K to 0.22% at 313.14 K. The α's obtained from the densities of the TRC Tables agree within ±(1−2)% with those in Table 6 for (298.14, 313.14, and 323.14) K and at 313.14 K for those in Table 7. The comparison is always poor for 1-methylethyl acetate (Table 8).

The α values enable calculation of the change in the isobaric molar heat capacity

$$\Delta C_P = C_p - C_p(0.1\ \text{MPa}) = -\int_{0.1}^{P} (TM/\rho\{(\partial\alpha/\partial T)_p + \alpha^2\}\ dP \qquad (11)$$

where M is the molar mass and ρ the density at P. The α values were represented by a quadratic in T to enable analytic differentiation. The ΔC_P's given in Tables 6−8 are estimated to have an error of ±(1 to 2) $J \cdot mol^{-1} \cdot K^{-1}$ based on previous work for *n*-heptane (Malhotra and Woolf, 1991c). Their variation with pressure is small in comparison to C_p(0.1 MPa) (Riddick *et al.*, 1986; Geiseler *et al.*, 1973).

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