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Volumetric and Thermodynamic Properties of Liquid 2-Fluoroethanol

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p-V-T data for liquid 2-fluoroethanol (FE) have been obtained in the form of volume ratios at six temperatures (278.15, 288.15, 298.14, 313.14, 323.14, and 338.130 K) at pressures from atmospheric to 314 MPa or higher. Freezing pressures have also been measured in the temperature range from the normal freezing point to 288 K. Densities at atmospheric pressure in the same temperature range as that for the p-V-T data are also reported. Isothermal compressibilities, isobaric expansivities, changes in the isobaric heat capacity, and internal pressures have been calculated from the volumetric data. Representation of the volume ratios for FE, 2,2-difluoroethanol, 2,2,2-trifluoroethanol, and ethanol by a form of the modified Tait equation shows that the effect of the progressive substitution of fluorine into ethanol cannot be represented by a simple correlation.

KEY WORDS: compressibility; expansivities; 2-fluoroethanol; heat capacity; internal pressure; p-V-T data; Tait equation.

1. INTRODUCTION

Previous papers reported volumetric data for 2,2,2-trifluoroethanol (TFE) [1] and 2,2-difluoroethanol (DFE) [2]. The latter publication investigated a method [3] for predicting volumetric data for related groups of compounds which uses the contribution of specific functional groups to one of the two coefficients of the modified Tait equation. For that purpose the Tait equation is expressed as

$$1 - k = C \log[(B + p)/(B + p_{0.1})] \tag{1}$$

where $k = V_p/V_{0.1}$, with V_p, and $V_{0.1}$, the volumes of a fixed mass of liquid at pressure p and 0.1 MPa, respectively. For each group of compounds a

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common value of C is established from the experimental data for one or two members of the group and the reduced temperature-dependent value of B related to the number of each of the functional groups ($-CH_3$, $>CH_2$, $-F$, etc.) present in a typical member of the group. The data for DFE and TFE did not provide a conclusive result for the effect on the volumetric properties of ethanol from progressively replacing hydrogen atoms in the methyl group with fluorine atoms. It was suggested [2] that p–V–T data for 2-fluoroethanol (FE) might clarify the situation. The lack of such measurements in the literature led to this work.

2. EXPERIMENTS

The 2-fluoroethanol (molecular weight, 0.064060 kg) was obtained from Fluorochem Ltd. (Derbyshire, U.K.). It had a stated purity of 95% and was fractionally distilled from a molecular sieve (Type 4A) to provide a middle fraction (boiling range, 275–276 K at 0.0941 MPa) for use in the experiments. Because volume ratios are relatively insensitive to small levels of impurities there was no determination of the purity. The solid–liquid transition under pressure occurred over a very narrow range of temperature, which does not suggest any significant proportion of impurities. Densities at atmospheric pressure (0.093 to 0.095 MPa) were measured with a reproducibility of, $\pm 0.005\ \mathrm{kg \cdot m^{-3}}$ with an Anton Paar Model DMA 602 densimeter calibrated frequently with water and dry nitrogen [4]. The densities were $1125.45\ \mathrm{kg \cdot m^{-3}}$ at 278.15 K, $1146.10\ \mathrm{kg \cdot m^{-3}}$ at 288.15 K, $1103.63\ \mathrm{kg \cdot m^{-3}}$ at 298.14 K, $1086.88\ \mathrm{kg \cdot m^{-3}}$ at 313.14 K, $1075.48\ \mathrm{kg \cdot m^{-3}}$ at 323.14 K, and $1057.98\ \mathrm{kg \cdot m^{-3}}$ at 338.13 K. Temperatures were measured relative to IPTS-68 and converted to ITS90; they had an accuracy of ±0.01 K and were constant within ±0.005 K. Volume ratios were measured with an automated bellows volumometer described in detail elsewhere [5]. A summary of the pressure measurement system is given in Ref. 2. To determine the maximum pressure for the volumometer measurements freezing pressures were measured using the technique described by Easteal and co-workers [6]. The results were referred to the literature value of the normal freezing point [7] of 246.8 K.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

The freezing pressures at temperature T_m for FE are represented with a standard deviation of 0.174 K by

$$T_m = 246.656 + 0.1240p - 5.39 \times 10^{-5} p^2 \tag{2}$$

for the range $0.1 < p < 450$ MPa.

Table I. Experimental Pressures and Volume Ratios, $k = V_p/V_{0.1}$, for 2-Fluoroethanol

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
2.547	0.9985	28.23	0.9847	117.59	0.9483	222.65	0.9178
4.996	0.9971	38.56	0.9797	137.47	0.9418	248.84	0.9115
9.741	0.9944	58.53	0.9707	156.65	0.9359	271.45	0.9064
14.152	0.9920	77.65	0.9629	176.68	0.9301	298.41	0.9005
19.032	0.9894	96.97	0.9555	197.71	0.9243	314.89	0.8971
23.851	0.9869						
$T = 288.15$ K							
2.547	0.9984	27.86	0.9841	137.96	0.9392	247.70	0.9085
4.996	0.9970	38.10	0.9789	156.78	0.9332	272.98	0.9026
9.868	0.9941	57.55	0.9697	176.61	0.9273	296.50	0.8974
14.592	0.9914	77.67	0.9611	197.35	0.9214	322.83	0.8918
19.433	0.9887	98.02	0.9531	221.91	0.9149	342.41	0.8879
23.763	0.9863	118.21	0.9458				
$T = 298.14$ K							
2.449	0.9984	26.87	0.9838	137.89	0.9366	272.50	0.8991
4.996	0.9968	37.40	0.9782	158.20	0.9300	295.76	0.8939
9.785	0.9938	56.75	0.9686	177.60	0.9241	321.53	0.8884
13.805	0.9914	76.26	0.9598	198.00	0.9182	344.52	0.8836
19.811	0.9878	97.56	0.9511	222.06	0.9116	361.18	0.8803
23.466	0.9857	117.03	0.9438	247.57	0.9051		
$T = 313.14$ K							
2.547	0.9982	29.25	0.9809	136.79	0.9325	271.04	0.8935
4.996	0.9965	37.50	0.9762	156.86	0.9257	296.73	0.8875
9.724	0.9932	56.36	0.9661	178.03	0.9189	321.83	0.8820
13.759	0.9906	76.57	0.9565	198.14	0.9129	348.10	0.8765
19.674	0.9868	95.71	0.9482	221.84	0.9061	371.42	0.8717
23.962	0.9841	116.43	0.9400	246.79	0.8995		
$T = 323.14$ K							
2.547	0.9980	29.39	0.9795	136.72	0.9292	270.90	0.8893
4.996	0.9962	38.66	0.9739	157.97	0.9217	296.21	0.8833
9.622	0.9928	56.74	0.9639	176.81	0.9155	321.12	0.8776
15.026	0.9889	76.38	0.9541	196.56	0.9094	347.04	0.8721
19.530	0.9859	96.58	0.9451	222.07	0.9021	367.57	0.8679
23.436	0.9833	116.82	0.9368	246.83	0.8954		
$T = 338.13$ K							
2.547	0.9979	29.02	0.9780	137.79	0.9239	272.03	0.8826
4.996	0.9958	39.05	0.9715	156.88	0.9169	297.54	0.8763
9.942	0.9919	57.92	0.9604	196.64	0.9036	322.08	0.8706
14.532	0.9883	77.29	0.9502	221.65	0.8961	355.03	0.8634
19.909	0.9844	96.92	0.9409	248.28	0.8887	385.83	0.8571
23.669	0.9817	116.61	0.9324				

The experimental pressures and volume ratios are given in Table I. The volume ratios are expected to have an accuracy of ± 0.03–$0.05\,\%$ for pressures above 50 MPa, increasing to $\pm 0.1\,\%$ at pressures near 0.1 MPa. The secant bulk modulus (SBM), $K[=(p-p_{0.1})/(1-k)]$ was represented by third-order equations in p:

$$K=a_0+a_1p+a_2p^2+a_3p^3 \tag{3}$$

for which the coefficients are given in Table II, together with the B and C for Eq. (1).

Another set of B values which adequately represent the experimental k within the experimental error can be obtained using a common C of 0.2230 for which

$$B=498.78-1.4786T+1.004\times 10^{-3}T^2 \tag{4}$$

for the range $278.15 \leqslant T \leqslant 338.15$ K, with a standard deviation of 0.53 in B. Equation (4) would be expected to be the most suitable for interpolation, or extrapolation outside the experimental temperature range. To enable a comparison of the Tait equation representation of FE with that used for DFE and TFE it is necessary to use a common C of 0.21; for FE the corresponding B values produce k that differ from the actual by more than the experimental error (but within 0.09% at worst). Figure 1 shows the B's for the three fluoroethanols and ethanol [8] as a function of the reciprocal of the reduced temperature $T_r = T/T_c$, with T_c the critical temperature estimated as 537.2 K using the Joback group contribution method [9]. (The critical temperatures of all four compounds are between 499 and 537 K.)

Table II. Coefficients of the Tait Equation, Eq. (1), and SBM Equation, Eq. (3), for 2-Fluoroethanol

T (K)	B (MPa)	C	$10^2\langle \Delta k/k \rangle$	a_0 (MPa)	a_1	$-a_2$ (GPa^{-1})	a_3 (GPa^{-2})	$10^2\langle \Delta k/k \rangle$
278.15	164.82	0.2216	0.011	1695.27	5.4568	5.1556	5.065	0.002
288.15	157.96	0.2237	0.011	1615.90	5.2032	3.9635	3.002	0.003
298.14	149.64	0.2242	0.014	1524.78	5.1888	3.9584	2.862	0.003
313.14	136.19	0.2242	0.018	1386.50	5.1815	4.1899	3.171	0.005
323.15	125.51	0.2220	0.022	1277.71	5.4571	5.6739	5.368	0.004
338.13	115.25	0.2235	0.020	1171.38	5.2670	5.1708	4.665	0.007

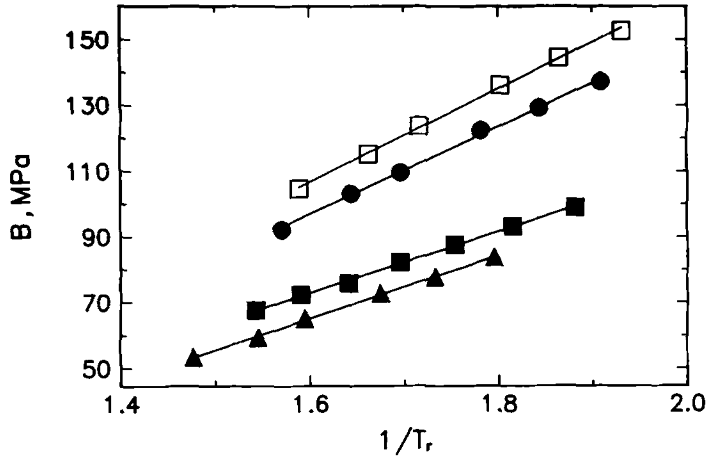

Fig. 1. Variation of B [Eq. (1)] with reciprocal of the reduced temperature for a fixed C of 0.21: 2-fluoroethanol (□); 2,2-difluoroethanol (●); ethanol (■); 2,2,2-trifluoroethanol (△).

Equations (5)–(8) represent the lines drawn through the points in Fig. 1.

$$\text{FE:} \quad B = -119.88 + 141.62(1/T_R) \tag{5}$$

$$\text{DFE:} \quad B = -115.94 + 133.03(1/T_R) \tag{6}$$

$$\text{TFE:} \quad B = -76.12 + 93.19(1/T_R) \tag{7}$$

$$\text{Ethanol:} \quad B = -88.32 + 95.93(1/T_R) \tag{8}$$

The respective standard deviations are 0.78, 0.92, 0.52, and 0.43. The similar slopes of the lines for ethanol and TFE in Fig. 1 suggest that their two sets of B's can be combined, using a common gradient but with allowance for the different intercepts, to extend the reduced temperature range for each compound. The difference between the intercepts, B(TFE)-B(ethanol), of 12.2 can be interpreted as implying a change of 4 units in B(ethanol) for each -F which replaces a methyl proton. However, although the difference between the intercepts for DFE and FE also is very close to 4, the relationship breaks down if an attempt is made to predict the B of either of those compounds from that of either ethanol or TFE using 4 as the contribution for the substitution of each -F. The implication is that the mono- or disubstitution of $-\mathrm{F}$ into $-\mathrm{CH_3}$ has a greater effect on the volumetric properties than the full substitution. The partial substitutions also affect other physical properties, such as the normal boiling point more markedly than does the total replacement. It would be expected that the asymmetry of the partially fluorosubstituted methyl group would affect the coupling of rotational and translational motion and this would be reflected in the extent and strength of the hydrogen bonding in which the hydroxyl groups of the alcohol participate [10].

Table III. Isothermal Compressibilities, Isobaric Expansivities, and Changes in Molar Heat Capacity at Constant Pressure for 2-Fluoroethanol

	p (MPa)									
Property	0.1	10	20	40	60	80	100	150	200	250
					$T = 278.15$ K					
$10^4\kappa_T$	5.90	5.57	5.28	4.79	4.39	4.06	3.78	3.25	2.87	2.57
$10^3\alpha$	0.95	0.92	0.89	0.84	0.80	0.77	0.74	0.68	0.63	0.60
$-\Delta C_p$	0	0.6	1.0	1.8	2.4	2.9	3.3	4.2	5.0	5.4
					$T = 288.15$ K					
$10^4\kappa_T$	6.18	5.85	5.54	5.02	4.59	4.23	3.93	3.35	2.95	2.64
$10^3\alpha$	0.98	0.94	0.91	0.86	0.81	0.78	0.75	0.68	0.64	0.60
$-\Delta C_p$	0	0.6	1.1	1.9	2.5	3.1	3.5	4.6	5.3	5.7
					$T = 298.14$ K					
$10^4\kappa_T$	6.55	6.18	5.84	5.26	4.79	4.40	4.07	3.46	3.03	2.71
$10^3\alpha$	1.00	0.96	0.93	0.87	0.83	0.79	0.76	0.69	0.64	0.60
$-\Delta C_p$	0	0.6	1.2	2.0	2.7	3.2	3.7	4.8	5.6	6.0
					$T = 313.14$ K					
$10^4\kappa_T$	7.21	6.75	6.35	5.67	5.13	4.68	4.32	3.63	3.17	2.83
$10^3\alpha$	1.04	1.00	0.96	0.90	0.85	0.80	0.77	0.70	0.65	0.60
$-\Delta C_p$	0	0.7	1.3	2.2	2.9	3.5	4.0	5.2	6.0	6.5
					$T = 323.14$ K					
$10^4\kappa_T$	7.82	7.26	6.77	5.98	5.35	4.86	4.47	3.75	3.27	2.91
$10^3\alpha$	1.07	1.02	0.98	0.91	0.86	0.81	0.78	0.71	0.65	0.60
$-\Delta C_p$	0	0.7	1.3	2.3	3.0	3.7	4.2	5.5	6.3	6.8
					$T = 338.13$ K					
$10^4\kappa_T$	8.53	7.89	7.34	6.43	5.73	5.18	4.74	3.95	3.42	3.03
$10^3\alpha$	1.11	1.06	1.01	0.93	0.88	0.83	0.79	0.71	0.66	0.61
$-\Delta C_p$	0	0.8	1.4	2.5	3.3	4.0	4.7	5.9	6.8	7.4

3.2. Compressibilities and Expansivities

Isothermal compressibilities, κ_T, given in Table III, were calculated from the coefficients in Table II for Eq. (3) using the relationship

$$\kappa_T = -[1/(p-K)][1-(p/K)(\partial K/\partial p)_T] \qquad (10)$$

They have a probable uncertainty of ±1–2%; comparison with those for DFE, TFE, and ethanol at 278.15 K (Table V of Ref. 1) shows that FE, followed by DFE, are the least compressible of the four. Isobaric expansivities, α, also given in Table III, were calculated by fitting the molar volume, V_m, at a chosen pressure to a quadratic in T and differentiating

$$\alpha = (1/V_m)(\partial V_m/\partial T)_p \qquad (11)$$

The V_m were calculated as a function of temperature at chosen pressures from the densities at atmospheric pressure and the volume ratios from Eq. (3) using the coefficients from Table II. The α have an estimated error of ±2–4%; they are smaller than those for either DFE or TFE at the same temperatures.

3.3. Isobaric Molar Heat Capacity, C_p

The effect of pressure on the isobaric molar heat capacity is given by

$$\Delta C_p = C_p - C_p(0.1\ \text{MPa}) = -\int_{0.1\ \text{MPa}}^{p} (TM/\rho)\{(\partial\alpha/\partial T)_p + \alpha^2\}\, dp \qquad (12)$$

where $C_p(0.1\ \text{MPa})$ is the isobaric molar heat capacity at 0.1 MPa, M is the molar mass, and ρ is the density of the liquid at p. The α were

Table IV. Internal Pressure, π (MPa), of 2-Fluoroethanol

V_m	π (MPa) at T (K)					
(cm^3·mol^{-1})	278.15	288.15	298.14	313.14	323.14	338.13
53.8	435	435	435	435	436	435
54.3	441	441	441	441	442	441
54.8	446	446	445	446	446	446
55.3	449	449	449	449	450	449
55.8	452	452	452	452	453	452
56.3	454	454	454	454	455	454
56.9	455	455	455	456	456	456

expressed by a quadratic equation in T to enable analytic differentiation. The error in the ΔC_p is estimated to be ±6–8%. There is only a small change in the C_p with either temperature or pressure.

3.4. Internal Pressures

The internal pressure, π, was calculated as described in Ref. 5 and is given in Table IV. The isochores are independent of temperature within the estimated error of ±2 MPa.

4. CONCLUSION

The results indicate that the group- contribution-volume-ratio method [3] is not suitable, in its present form, for correlating and predicting the volumetric properties of liquids in which specific interactions, such as hydrogen bonding in the present case, are affected by substitution of additional or different functional groups/atoms into the molecule.

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