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Thermodynamic Properties of Liquid 2,2-Difluoroethanol

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p–V–T data for liquid 2,2-difluoroethanol (DFE) have been obtained in the form of volume ratios at six temperatures, 278.15, 288.15, 298.15, 313.15, 323.15, and 338.15 K, at pressures from atmospheric to 151 MPa or higher. Densities at atomospheric pressure in the same temperature range are also reported. Isothermal compressibilities, isobaric expansivities, and internal pressures have been calculated from the volumetric data. They show that DFE is much less compressible than 2,2,2-trifluoroethanol and indicate that 2-fluoroethanol may be even less compressible.

KEY WORDS: compressibility; 2,2-difluoroethanol; expansivities; internal pressure; *p–V–T* data; 2,2,2-trifluoroethanol.

1. INTRODUCTION

An earlier paper [1] reported volumetric data for 2,2,2-trifluoroethanol (TFE), which in its compressibility and internal pressure, showed a closer similarity to the behavior of methanol than that of ethanol for most of the pressure range (up to 280 MPa). That paper investigated a means of using a modified Tait equation to extrapolate volume ratios well outside the temperature range of the measurements. More recent work [2, 3] has focused on prediction of volumetric data for related groups of compounds by assessment of the contribution of specific functional groups to one of the two coefficients of the Tait equation. For that purpose the Tait equation is expressed as

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

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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 common value of C is established from the experimental data for one or two members of the group and the temperature-dependent value of B related to the number of each of the functional groups (–CH, –CH_2, –Cl, etc.) making up a typical member of the group. The present work aimed to provide data to investigate the use of the earlier work [1] to determine the effect on the volumetric properties of ethanol from progressively substituting fluorine atoms.

2. EXPERIMENTS

The 2,2-difluoroethanol (molecular weight, 0.082050 kg) was obtained from PCR Inc. (Gainesville, FL) and was fractionally distilled from a molecular sieve (Type 4A) to provide a middle fraction for use in the experiments. Densities at atmospheric pressure (0.093 to 0.095 MPa) were measured with a reproducibility of ±0.005 $kg \cdot m^{-3}$ with an Anton Paar Model DMA 602 densimeter calibrated frequently with water and dry nitrogen [4]. The densities were as follows: 278.15 K, 1323.77 $kg \cdot m^{-3}$; 288.15 K, 1309.93 $kg \cdot m^{-3}$; 298.15 K, 1296.01 $kg \cdot m^{-3}$; 313.15 K, 1274.73 $kg \cdot m^{-3}$; 323.15 K, 1260.29 $kg \cdot m^{-3}$; and 338.15 K, 1238.09 $kg \cdot m^{-3}$. Temperatures were measured relative to IPTS-68 with 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]. The pressure measurement system [5] comprises a pressure transducer (380–30 MPa) referenced at each temperature by comparison with a Heise–Bourdon gauge, a Heise–Bourdon gauge (25–10 MPa) and a deadweight gauge (5 and 2.5 MPa); the transducer and analogue gauges had been calibrated with deadweight gauges within a month of the measurements. Because the sample of 2,2-difluoroethanol had a normal freezing point of 243 ± 1 K and freezing pressures were not available, the volumometer measurements at 278.15 K were started at a maximum pressure of 152 MPa.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

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 ±0.1 % at pressures near 0.1 MPa.

Table I. Experimental Pressures and Volume Ratios for 2,2-difluoroethanol

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K							
2.547	0.9983	24.15	0.9853	58.04	0.9680	99.00	0.9509
4.996	0.9968	28.60	0.9828	67.28	0.9638	118.65	0.9436
9.919	0.9937	37.83	0.9779	77.57	0.9594	139.58	0.9365
14.642	0.9908	47.62	0.9729	88.04	0.9551	151.92	0.9325
19.630	0.9878						
$T = 288.15$ K							
2.547	0.9982	28.64	0.9818	87.92	0.9530	176.82	0.9217
4.996	0.9966	38.79	0.9761	98.30	0.9488	198.17	0.9155
9.909	0.9933	48.19	0.9712	117.20	0.9416	218.21	0.9101
14.311	0.9904	57.73	0.9665	137.08	0.9345	239.19	0.9047
19.828	0.9870	68.17	0.9616	158.74	0.9273	252.10	0.9016
24.503	0.9842	77.94	0.9572				
$T = 298.15$ K							
2.547	0.9982	27.63	0.9816	138.43	0.9313	246.37	0.8993
4.996	0.9964	38.07	0.9755	156.92	0.9251	271.20	0.8932
9.998	0.9929	57.49	0.9651	176.52	0.9188	297.26	0.8872
14.980	0.9896	78.24	0.9552	197.02	0.9127	323.35	0.8815
19.617	0.9866	97.96	0.9467	223.47	0.9053	343.73	0.8772
24.238	0.9837	117.38	0.9390				
$T = 313.15$ K							
2.547	0.9979	29.08	0.9787	137.22	0.9266	273.06	0.8860
4.996	0.9959	38.23	0.9730	156.96	0.9195	295.01	0.8807
9.872	0.9921	58.05	0.9617	177.93	0.9126	323.66	0.8743
14.788	0.9885	76.62	0.9522	197.84	0.9064	353.54	0.8680
19.633	0.9850	96.86	0.9429	221.55	0.8995	362.77	0.8661
24.128	0.9820	117.16	0.9344	246.28	0.8928		
$T = 323.15$ K							
2.547	0.9978	29.49	0.9773	136.95	0.9234	272.89	0.8817
4.996	0.9958	37.28	0.9721	158.04	0.9157	298.06	0.8756
9.871	0.9918	57.91	0.9598	176.67	0.9093	322.79	0.8699
14.939	0.9878	77.10	0.9496	198.45	0.9023	348.61	0.8643
19.789	0.9842	97.12	0.9400	221.73	0.8954	375.57	0.8588
23.975	0.9811	117.16	0.9313	248.50	0.8880		
$T = 338.15$ K							
2.547	0.9975	29.88	0.9746	137.23	0.9176	272.26	0.8746
4.995	0.9952	39.45	0.9678	155.98	0.9103	296.55	0.8685
9.921	0.9907	56.12	0.9571	176.07	0.9032	320.81	0.8627
14.840	0.9864	76.30	0.9457	197.43	0.8961	349.77	0.8563
19.997	0.9822	97.00	0.9352	222.28	0.8884	373.25	0.8513
23.947	0.9791	116.40	0.9263	246.27	0.8816		

The secant bulk modulus (SBM), $K\ [=(p-p_{0.1})/(1-k)]$, was represented by third-order equations in p:

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

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 can be obtained using a common C of 0.2150, for which

$$B=390.587-1.0069T+3.95\times10^{-4}T^2 \qquad [278.15\leqslant T(\mathrm{K})\leqslant 338.15] \tag{3}$$

with a standard deviation of 0.64 in B. This equation would be expected to be the most suitable for extrapolation outside the experimental temperature range particularly with the use of the critical temperature [1]. The k for DFE and TFE can be reproduced within experimental error by using for each of them a C of 0.21 in Eq. (1) with

$$B=346.217-0.7525T \qquad \text{for DFE} \tag{4}$$

$$B=224.801-0.5094T \qquad \text{for TFE} \tag{5}$$

The differences between the two sets of B values are given by

$$B(\mathrm{TFE})-B(\mathrm{DFE})=-121.415+0.2439T \tag{6}$$

Malhotra and co-workers [3] found that the B values for a series of fluorinated ethers could be correlated over a wide range of reduced temperature, $T_R=T/T_C$, where T_C is the critical temperature. From data for two fluorinated ethers, 2,2,2-trifluoroethyl-difluoromethylether (RE245) and 1,2,2,2-tetrafluoroethyl-difluoromethylether (RE236) [6], they determined the contribution, δB_F to the overall B of adding an additional -F to a fluorinated linear ether. The δB_F was determined by expressing B in

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

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	$10^2\langle\Delta k/k\rangle$
278.15	1510.54	5.3125	1.1383	−11.497	0.001	132.75	0.2036	0.004
288.15	1417.78	5.6208	6.1202	7.201	0.002	130.13	0.2103	0.009
298.15	1360.81	5.2107	3.9191	2.712	0.004	128.77	0.2172	0.014
313.15	1202.84	5.6891	6.9284	7.486	0.010	116.29	0.2175	0.020
323.15	1148.49	5.2779	5.0502	4.578	0.006	110.24	0.2190	0.017
338.15	1014.10	5.5369	6.6198	6.834	0.011	98.13	0.2177	0.027

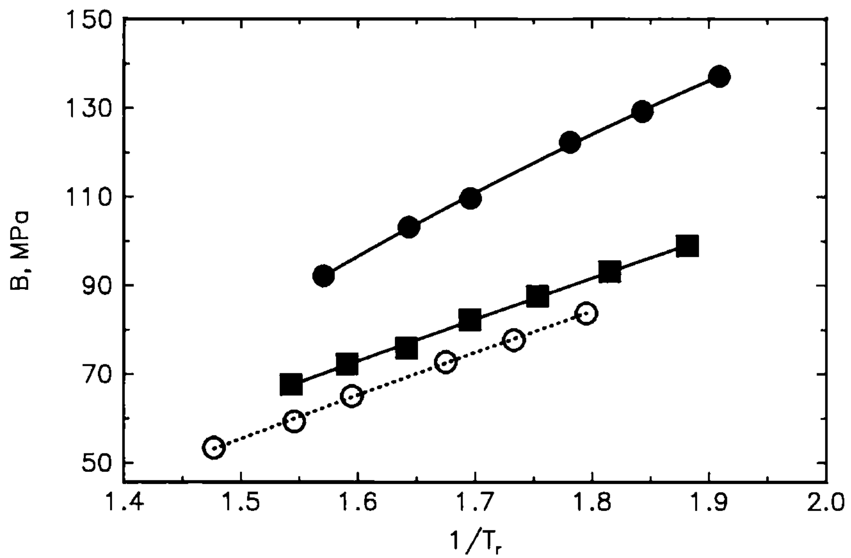

Fig. 1. Variation of B [Eq. (1)] at a fixed C of 0.21: 2,2-difluoroethanol (●); 2,2,2-trifluoroethanol (○); ethanol (■).

terms of $1/T_R$. Figure 1 shows the values of B for DFE and TFE in terms of $1/T_R$ with $C = 0.21$. A value of T_C of 531 K was estimated for DFE from Joback group contributions [7]; a similar estimate for TFE was within 4 K of the experimental value [8]. Included in the figure are values of B for the same C calculated from data for ethanol [9]. The lines drawn through the points are

$$B = -115.940 + 133.032\,(1/T_R) \qquad \text{(DFE)} \qquad (7)$$

$$B = -76.123 + 93.188\,(1/T_R) \qquad \text{(TFE)} \qquad (8)$$

$$B = -88.321 + 95.934\,(1/T_R) \qquad \text{(Ethanol)} \qquad (9)$$

The results for the three compounds suggest that the replacement of one hydrogen of the methyl group of ethanol by a fluorine atom has a major effect on the volumetric properties insofar as they are represented by the B of Eq. (1). The complete replacement of the methyl hydrogens in TFE gives B's which have a similar dependence on $1/T_R$ to those of ethanol; the average δB_F is similar to that found [3] for RE236 with RE245. The data are insufficient to enable the formulation of an equation linking the p–V–T properties of the fluoro-substituted ethanols with those of ethanol through a δB_F evaluated from either the di- or the tri-substituted fluoroethanol.

3.2. Compressibilities and Expansivities

Isothermal compressibilities, κ_T, given in Table III, were calculated from the coefficients in Table II for Eq. (2) by using the relationship

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

They have a probable uncertainty of ±1–2%; comparison with those for TFE, ethanol, and methanol at 278.15 K (Table V of Ref. 1) shows that DFE is the least compressible of the four. Isobaric expansivities, α, also

Table III. Isothermal Compressibilities and Isobaric Expansivities for DFE

	p (MPa)									
Property	0.1	10	20	40	60	80	100	150	200	250
					$T = 278.15$ K					
$10^4\kappa_T\ (\mathrm{MPa})^{-1}$	6.62	6.22	5.86	5.24	4.73	4.32	3.99	3.44		
$10^3\alpha\ (\mathrm{K}^{-1})$	1.03	1.00	0.97	0.92	0.88	0.84	0.80	0.73		
					$T = 288.15$ K					
$10^4\kappa_T\ (\mathrm{MPa})^{-1}$	7.05	6.58	6.16	5.48	4.95	4.52	4.17	3.51	3.05	2.68
$10^3\alpha\ (\mathrm{K}^{-1})$	1.06	1.02	0.99	0.93	0.88	0.84	0.81	0.74		
					$T = 298.15$ K					
$10^4\kappa_T\ (\mathrm{MPa})^{-1}$	7.34	6.87	6.45	5.74	5.17	4.71	4.33	3.62	3.14	2.80
$10^3\alpha\ (\mathrm{K}^{-1})$	1.08	1.04	1.00	0.94	0.89	0.85	0.81	0.74		
					$T = 313.15$ K					
$10^4\kappa_T\ (\mathrm{MPa})^{-1}$	8.31	7.65	7.09	6.19	5.51	4.98	4.57	3.83	3.33	2.95
$10^3\alpha\ (\mathrm{K}^{-1})$	1.13	1.08	1.03	0.96	0.90	0.86	0.82	0.75		
					$T = 323.15$ K					
$10^4\kappa_T\ (\mathrm{MPa})^{-1}$	8.70	8.04	7.46	6.52	5.80	5.23	4.77	3.95	3.41	3.01
$10^3\alpha\ (\mathrm{K}^{-1})$	1.16	1.10	1.05	0.97	0.91	0.87	0.83	0.75		
					$T = 338.15$ K					
$10^4\kappa_T\ (\mathrm{MPa})^{-1}$	9.85	8.97	8.22	7.05	6.18	5.53	5.02	4.14	3.58	3.15
$10^3\alpha\ (\mathrm{K}^{-1})$	1.20	1.13	1.08	0.99	0.92	0.88	0.84	0.76		

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

V_m	π (MPa) at T(K)					
($cm^3 \cdot mol^{-1}$)	278.15	288.15	298.15	313.15	323.15	338.15
59.0	453.6	454.3	454.0	456.0	456.0	456.9
59.5	456.4	456.5	455.7	456.7	456.2	456.1
60.0	456.8	456.8	455.9	456.5	455.8	455.5
60.5	455.4	455.4	454.8	455.4	454.9	454.8
61.0	452.3	452.7	452.6	453.7	453.6	454.2
61.5	447.9	449.0	449.5	451.4	452.0	453.6
62.0	442.5	444.2	445.6	448.6	450.1	453.1

given in Table III, were calculated by fitting the molar volume, V_m, at a chosen pressure to a quadratic in T and differentiating

$$\alpha = (1/V_m)(\partial V_m/\partial T)_p \tag{11}$$

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. (2) using the coefficients from Table II. The α have an estimated error of ± 2–$3\,\%$; they are smaller than those for TFE at the same temperatures.

3.3. Internal Pressures

The internal pressure, π, was calculated as described in Ref. 5 and is given in Table IV. The values are for a smaller range of molar volumes than for TFE but have similar features: at the lower temperatures π plotted against V_m goes through a shallow maximum which is no longer present at 338.15 K; there is no intersection of the various isotherms.

4. CONCLUSION

It would be useful if it were possible to compare the effect on the Tait B coefficient of progressively substituting the methyl hydrogens by fluorine in ethanol with the results of a similar substitution in ethane. For example, a possible comparison would be for 1,1,2-trifluoroethane (FC143) with 1,1,1,2-tetrafluorethane (FC134a) and 1,1,1-trifluoroethane (FC143a) with 1,1-difluoroethane (FC152a) and fluoroethane (FC161). Unfortunately the data available for those compounds are insufficient in their range of pressure at each temperature to enable adequate determination of the Tait coefficients.

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