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Volumetric and Thermodynamic Properties of Liquid Mixtures of 2-*n*-Butoxyethanol with Water

P. J. Back,[1] **R. Malhotra,**[1] **and L. A. Woolf**[1, 2]

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p–V–T data for six compositions of 2-*n*-butoxyethanol (BE) and water have been obtained in the form of volume ratios at several temperatures in the range 278.15 to 353.13 K at pressures from atmospheric to 347 MPa or higher. One of the compositions is in the region where two phases exist at certain temperatures, while two compositions are near the boundary of that region. Densities at atmospheric pressure in a temperature range similar to that for the *p–V–T* data are also reported. Isothermal compressibilities, isobaric expansivities, and changes in the isobaric heat capacity have been calculated from the volumetric data for pressures up to 300 MPa. The values of normalized volume fluctuations obtained from the data at 0.1 MPa approach those of water for conditions which are close to those for phase separation in this system. Such behavior is not observed at 100 MPa, where such separation is suppressed.

KEY WORDS: compressibility; expansivities; 2-*n*-butoxyethanol; heat capacity; *p–V–T* data; Tait equation; volume fluctuations.

1. INTRODUCTION

Although this system has been studied extensively at pressures close to atmospheric, there are few data for its properties at high pressures. This work was performed principally to provide *p–V–T* data for the study by Mensah-Brown and Wakeham [1] of the effect of pressure on the thermal conductivity of mixtures of 2-*n*-butoxyethanol (BE) and water. Accordingly, two of the six compositions of the present work were close to but

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[1] Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

[2] To whom correspondence should be addressed.

outside opposite sides of the concentration region at which phase separation occurs [2–4] at atmospheric and higher pressures. Another composition was close to that of the lower consolute mixture and measurements for this mixture were made at temperatures extending to close to the lower consolute temperature at 0.1 MPa. (At 0.1 MPa the two-phase region exists for a small range of water-rich compositions at temperatures between about 322.3 and 403.3 K.) An extensive series of density measurements at 0.1 MPa has been made to assist the interpretation of the results at higher pressures. These data have enabled the effect of pressure and temperature on volume fluctuations in the system to be determined. An earlier paper [5] reported *p–V–T* measurements for pure BE.

2. EXPERIMENTAL

The BE was Fluka Chemika HPLC-GC grade material of stated purity <99.9% mol, which, before use, was fractionally distilled under reduced pressure in an argon atmosphere and then stored under helium. 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 $k = V_p/V_{0.1}$, with V_p and $V_{0.1}$, the volumes of a fixed mass of liquid at pressure p and 0.1 MPa, respectively, were measured with an automated bellows volumometer described in detail elsewhere [6].

A summary of the pressure measurement system is given in Ref. 7. Densities at atmospheric pressure (0.093 to 0.095 MPa) were measured for samples taken from the volumometer at the conclusion of the experiments for each composition 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 [8]. Measurements were also made for a series of standard solutions to enable determination of the composition of the volumometer samples.

3. RESULTS AND DISCUSSION

3.1. Volumetric Data

The experimental pressures, temperatures, and volume ratios are given in Tables I–VI for each mole fraction, x_1, of BE. The molecular weights which were used were 0.118767 and 0.0180153 kg · mol for BE and water, respectively. For the system with $x_1 = 0.04826$ the highest temperature used was 322.14 K, which is about 0.1 K below the temperature at 0.1 MPa at which a phase separation is expected [4], which persists to a temperature well above the highest attainable with the present volumometer [6]. The

Table I. Experimental Pressures, Volume Ratios, $k = V_p/V_{0.1}$, and Densities[a] at 0.1 MPa for 2-Butoxyethanol (1) + Water (2), $x_1 = 0.006934$

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 278.15$ K; $\rho(0.1) = 999.46$ kg · m^{-3}							
2.547	0.9989	27.61	0.9883	138.74	0.9501	273.22	0.9148
4.996	0.9978	38.54	0.9841	158.58	0.9442	298.93	0.9091
9.839	0.9957	58.55	0.9766	177.93	0.9388	324.37	0.9036
14.605	0.9937	78.47	0.9695	198.48	0.9333	348.67	0.8987
19.579	0.9916	98.55	0.9627	223.71	0.9268	366.62	0.8951
24.218	0.9897	119.25	0.9561	248.98	0.9205		
$T = 288.15$ K; $\rho(0.1) = 998.04$ kg · m^{-3}							
2.547	0.9989	26.97	0.9887	138.58	0.9505	274.01	0.9153
4.996	0.9978	37.64	0.9846	158.24	0.9448	298.46	0.9098
9.519	0.9959	57.89	0.9770	178.10	0.9393	324.18	0.9043
14.585	0.9937	78.17	0.9699	198.24	0.9339	348.82	0.8993
19.955	0.9915	97.96	0.9632	224.32	0.9272	370.04	0.8950
23.522	0.9901	118.42	0.9567	248.48	0.9213		
$T = 298.14$ K; $\rho(0.1) = 995.61$ kg · m^{-3}							
2.547	0.9988	28.03	0.9879	139.10	0.9498	273.84	0.9148
4.996	0.9977	38.61	0.9838	158.67	0.9441	299.38	0.9091
10.155	0.9954	58.65	0.9763	178.36	0.9386	322.68	0.9041
14.535	0.9935	78.66	0.9692	199.31	0.9331	348.33	0.8989
20.055	0.9912	98.93	0.9624	224.32	0.9267	374.21	0.8938
23.011	0.9900	119.14	0.9559	248.47	0.9208		
$T = 313.14$ K; $\rho(0.1) = 990.28$ kg · m^{-3}							
2.547	0.9988	27.58	0.9880	139.16	0.9493	273.34	0.9143
4.996	0.9977	39.07	0.9834	158.62	0.9436	298.75	0.9085
9.938	0.9955	58.76	0.9759	179.09	0.9378	323.95	0.9031
15.454	0.9931	78.51	0.9689	198.96	0.9325	346.87	0.8985
19.429	0.9914	98.56	0.9620	223.97	0.9261	374.55	0.8930
23.547	0.9897	118.60	0.9556	249.13	0.9200		
$T = 323.14$ K; $\rho(0.1) = 985.76$ kg · m^{-3}							
2.547	0.9988	28.24	0.9872	138.72	0.9480	273.74	0.9124
4.996	0.9976	37.89	0.9832	158.76	0.9421	297.55	0.9070
9.396	0.9955	57.90	0.9754	179.08	0.9363	322.84	0.9015
14.535	0.9932	78.62	0.9678	198.64	0.9310	349.30	0.8960
19.404	0.9910	98.43	0.9610	224.14	0.9244	373.67	0.8912
23.646	0.9892	118.31	0.9544	248.75	0.9183		

[a] Value at 338.13 K measured; values at other temperatures except 278.15 K interpolated from data at each temperature given in Table VIII. Value at 278.15 K obtained from extrapolation of the values at the higher temperatures.

Table I. (*Continued*)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 338.13$ K; $\rho(0.1) = 977.79$ kg · m^{-3}							
2.547	0.9988	28.05	0.9873	139.14	0.9473	273.95	0.9113
4.996	0.9976	38.76	0.9829	159.10	0.9412	298.77	0.9056
9.568	0.9955	58.76	0.9750	179.23	0.9354	323.71	0.9003
14.860	0.9931	78.84	0.9675	198.62	0.9301	346.31	0.8957
19.554	0.9910	99.26	0.9603	223.70	0.9235	377.89	0.8894
23.571	0.9892	118.94	0.9537	249.24	0.9172		

Table II. Experimental Pressures, Volume Ratios, $k = V_p/V_{0.1}$, and Densities[a] at 0.1 MPa for 2-Butoxyethanol (1) + Water (2), $x_1 = 0.015965$

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 288.15$ K; $\rho(0.1) = 997.18$ kg · m^{-3}							
2.547	0.9989	27.61	0.9883	138.74	0.9501	273.22	0.9148
4.996	0.9978	38.54	0.9841	158.58	0.9442	298.93	0.9091
9.839	0.9957	58.55	0.9766	177.93	0.9388	324.37	0.9036
14.605	0.9937	78.47	0.9695	198.48	0.9333	348.67	0.8987
19.579	0.9916	98.55	0.9627	223.71	0.9268	366.62	0.8951
24.218	0.9897	119.25	0.9561	248.98	0.9205		
$T = 298.14$ K; $\rho(0.1) = 993.98$ kg · m^{-3}							
2.547	0.9989	26.97	0.9887	138.58	0.9505	274.01	0.9153
4.996	0.9978	37.64	0.9846	158.24	0.9448	298.46	0.9098
9.519	0.9959	57.89	0.9770	178.10	0.9393	324.18	0.9043
14.585	0.9937	78.17	0.9699	198.24	0.9339	348.82	0.8993
19.955	0.9915	97.96	0.9632	224.32	0.9272	370.04	0.8950
23.522	0.9901	118.42	0.9567	248.48	0.9213		
$T = 313.14$ K; $\rho(0.1) = 987.48$ kg · m^{-3}							
2.547	0.9988	28.03	0.9879	139.10	0.9498	273.84	0.9148
4.996	0.9977	38.61	0.9838	158.67	0.9441	299.38	0.9091
10.155	0.9954	58.65	0.9763	178.36	0.9386	322.68	0.9041
14.535	0.9935	78.66	0.9692	199.31	0.9331	348.33	0.8989
20.055	0.9912	98.93	0.9624	224.32	0.9267	374.21	0.8938
23.011	0.9900	119.14	0.9559	248.47	0.9208		

[a] Value at 313.14 K measured; values at other temperatures interpolated.

Table II. (*Continued*)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 323.14$ K; $\rho(0.1) = 982.28$ kg $\cdot$ m^{-3}							
2.547	0.9988	27.58	0.9880	139.16	0.9493	273.34	0.9143
4.996	0.9977	39.07	0.9834	158.62	0.9436	298.75	0.9085
9.938	0.9955	58.76	0.9759	179.09	0.9378	323.95	0.9031
15.454	0.9931	78.51	0.9689	198.96	0.9325	346.87	0.8985
19.429	0.9914	98.56	0.9620	223.97	0.9261	374.55	0.8930
23.547	0.9897	118.60	0.9556	249.13	0.9200		
$T = 338.13$ K; $\rho(0.1) = 973.47$ kg $\cdot$ m^{-3}							
2.547	0.9988	28.24	0.9872	138.72	0.9480	273.74	0.9124
4.996	0.9976	37.89	0.9832	158.76	0.9421	297.55	0.9070
9.396	0.9955	57.90	0.9754	179.08	0.9363	322.84	0.9015
14.535	0.9932	78.62	0.9678	198.64	0.9310	349.30	0.8960
19.404	0.9910	98.43	0.9610	224.14	0.9244	373.67	0.8912
23.646	0.9892	118.31	0.9544	248.75	0.9183		
$T = 348.13$ K; $\rho(0.1) = 967.04$ kg $\cdot$ m^{-3}							
2.547	0.9988	28.05	0.9873	139.14	0.9473	273.95	0.9113
4.996	0.9976	38.76	0.9829	159.10	0.9412	298.77	0.9056
9.568	0.9955	58.76	0.9750	179.23	0.9354	323.71	0.9003
14.860	0.9931	78.84	0.9675	198.62	0.9301	346.31	0.8957
19.554	0.9910	99.26	0.9603	223.70	0.9235	377.89	0.8894
23.571	0.9892	118.94	0.9537	249.24	0.9172		

Table III. Experimental Pressures, Volume Ratios, $k = V_p/V_{0.1}$, and Densities[a] at 0.1 MPa for 2-Butoxyethanol (1) + Water (2), $x_1 = 0.048263$

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 288.15$ K; $\rho(0.1) = 986.97$ kg $\cdot$ m^{-3}							
2.547	0.9988	27.94	0.9874	139.37	0.9487	273.67	0.9147
4.996	0.9976	38.31	0.9831	159.42	0.9430	298.50	0.9093
9.381	0.9955	58.53	0.9754	178.79	0.9377	321.35	0.9046
14.835	0.9930	78.57	0.9682	199.18	0.9324	335.24	0.9019
19.159	0.9911	98.09	0.9616	224.51	0.9261	348.96	0.8992
23.199	0.9894	118.85	0.9549	248.98	0.9203		

[a] Value at 313.14 K measured; values at other temperatures interpolated.

Table III. (*Continued*)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 298.14$ K; $\rho(0.1) = 981.65$ kg · m^{-3}							
2.547	0.9987	28.21	0.9871	138.58	0.9483	274.05	0.9137
4.996	0.9976	38.50	0.9828	158.56	0.9425	297.65	0.9086
9.145	0.9956	59.01	0.9748	178.92	0.9369	321.47	0.9036
14.364	0.9932	78.95	0.9676	199.03	0.9317	332.95	0.9013
19.424	0.9909	99.00	0.9607	224.14	0.9254	347.48	0.8985
23.701	0.9890	119.03	0.9543	249.47	0.9193		
$T = 313.14$ K; $\rho(0.1) = 972.92$ kg · m^{-3}							
2.547	0.9987	27.85	0.9868	138.15	0.9471	274.06	0.9119
4.996	0.9975	38.11	0.9824	158.58	0.9411	298.19	0.9065
9.410	0.9953	57.90	0.9744	178.33	0.9356	323.80	0.9012
15.000	0.9926	77.81	0.9670	199.01	0.9301	349.11	0.8961
19.735	0.9904	97.97	0.9600	223.80	0.9238	373.48	0.8913
23.776	0.9886	118.16	0.9533	248.79	0.9177		
$T = 322.14$ K; $\rho(0.1) = 966.92$ kg · m^{-3}							
2.547	0.9987	28.02	0.9863	138.24	0.9460	273.28	0.9105
4.996	0.9974	38.31	0.9818	159.10	0.9398	299.41	0.9047
9.317	0.9952	59.05	0.9733	178.82	0.9342	323.99	0.8995
15.202	0.9923	78.76	0.9659	199.32	0.9286	346.57	0.8950
19.649	0.9902	96.71	0.9595	224.55	0.9221	379.42	0.8885
23.666	0.9883	117.07	0.9527	249.85	0.9160		

Table IV. Experimental Pressures, Volume Ratios, $k = V_p/V_{0.1}$, and Densities[a] at 0.1 MPa for 2-Butoxyethanol (1) + Water (2), $x_1 = 0.17484$

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 288.15$ K; $\rho(0.1) = 957.48$ kg · m^{-3}							
2.547	0.9986	28.68	0.9855	138.92	0.9449	274.16	0.9104
4.996	0.9973	38.65	0.9810	158.79	0.9391	299.23	0.9051
9.716	0.9948	59.37	0.9723	179.85	0.9332	323.87	0.9001
14.727	0.9922	78.93	0.9649	199.99	0.9279	347.22	0.8955
19.564	0.9898	99.44	0.9576	225.23	0.9217	367.62	0.8917
23.726	0.9878	119.31	0.9510	249.55	0.9159		

[a] Value at 313.14 K measured; values at other temperatures except 353.13 K interpolated. Value at 353.13 K extrapolated from $\rho(0.1)$ at lower temperatures.

Table IV. (*Continued*)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 298.14$ K; $\rho(0.1) = 950.36$ kg · m^{-3}							
2.547	0.9986	28.63	0.9850	138.74	0.9434	275.32	0.9079
4.996	0.9972	39.48	0.9799	159.22	0.9372	299.53	0.9027
9.677	0.9946	59.22	0.9714	179.07	0.9316	324.23	0.8976
14.725	0.9920	79.08	0.9636	199.85	0.9260	347.53	0.8930
19.471	0.9895	99.27	0.9563	224.80	0.9197	372.99	0.8883
23.969	0.9873	118.81	0.9497	250.00	0.9137		
$T = 313.14$ K; $\rho(0.1) = 939.14$ kg · m^{-3}							
2.547	0.9985	29.29	0.9837	139.67	0.9401	275.35	0.9039
4.996	0.9970	39.74	0.9785	160.08	0.9338	301.17	0.8983
9.660	0.9943	59.72	0.9695	179.62	0.9281	324.93	0.8933
14.905	0.9913	79.52	0.9613	200.05	0.9225	346.91	0.8889
19.979	0.9885	99.98	0.9536	225.75	0.9158	371.87	0.8841
24.416	0.9862	120.02	0.9466	250.74	0.9097		
$T = 323.14$ K; $\rho(0.1) = 930.96$ kg · m^{-3}							
2.547	0.9984	28.07	0.9835	139.65	0.9380	273.59	0.9015
4.996	0.9968	39.44	0.9777	159.54	0.9317	299.79	0.8956
9.808	0.9939	59.44	0.9683	178.87	0.9259	324.64	0.8903
14.610	0.9910	78.49	0.9602	199.08	0.9202	347.17	0.8857
20.104	0.9879	99.24	0.9521	224.38	0.9134	371.39	0.8810
23.746	0.9859	119.53	0.9448	249.97	0.9070		
$T = 338.13$ K; $\rho(0.1) = 918.81$ kg · m^{-3}							
2.547	0.9982	28.83	0.9819	139.14	0.9346	274.69	0.8966
4.996	0.9966	39.65	0.9760	159.48	0.9279	300.24	0.8907
10.165	0.9932	59.17	0.9663	179.35	0.9218	324.73	0.8854
15.144	0.9900	79.08	0.9574	199.29	0.9160	347.98	0.8805
20.604	0.9867	99.43	0.9491	225.09	0.9089	371.96	0.8758
24.223	0.9845	119.38	0.9416	249.24	0.9027		
$T = 353.13$ K; $\rho(0.1) = 906.36$ kg · m^{-3}							
2.547	0.9981	30.17	0.9800	139.28	0.9312	275.00	0.8917
4.996	0.9963	39.04	0.9749	159.07	0.9244	300.10	0.8859
9.712	0.9930	58.84	0.9645	179.39	0.9178	325.43	0.8803
14.620	0.9897	78.67	0.9552	199.89	0.9116	360.16	0.8731
19.254	0.9867	98.47	0.9467	224.29	0.9047	385.66	0.8682
23.639	0.9839	119.26	0.9385	248.92	0.8982		

Table V. Experimental Pressures, Volume Ratios, $k = V_p/V_{0.1}$, and Densities[a] at 0.1 MPa for 2-Butoxyethanol (1) + Water (2), $x_1 = 0.50247$

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 288.15$ K; $\rho(0.1) = 925.01$ kg · m^{-3}							
2.547	0.9984	26.59	0.9844	136.07	0.9389	273.03	0.9020
4.996	0.9969	37.47	0.9787	156.69	0.9324	296.73	0.8967
8.948	0.9944	57.25	0.9692	176.48	0.9265	318.89	0.8921
14.777	0.9910	76.99	0.9606	197.25	0.9206	338.33	0.8882
19.112	0.9885	96.86	0.9528	221.66	0.9142	350.10	0.8859
23.804	0.9859	116.64	0.9455	247.64	0.9078		
$T = 298.14$ K; $\rho(0.1) = 917.07$ kg · m^{-3}							
2.547	0.9983	26.73	0.9834	136.35	0.9363	271.14	0.8989
4.996	0.9967	36.03	0.9783	156.73	0.9297	294.34	0.8937
9.612	0.9937	56.82	0.9678	176.14	0.9237	320.00	0.8883
14.692	0.9905	76.28	0.9590	196.51	0.9179	343.17	0.8836
20.125	0.9873	95.88	0.9509	220.50	0.9114	357.39	0.8808
24.138	0.9849	117.37	0.9429	245.92	0.9049		
$T = 313.14$ K; $\rho(0.1) = 904.65$ kg · m^{-3}							
2.547	0.9982	38.63	0.9758	158.05	0.9254	295.19	0.8883
4.996	0.9965	58.53	0.9653	177.00	0.9194	320.19	0.8828
9.701	0.9934	78.82	0.9557	196.84	0.9134	346.40	0.8774
14.469	0.9903	97.61	0.9476	222.47	0.9062	367.26	0.8732
19.224	0.9872	118.05	0.9395	247.47	0.8996		
24.092	0.9843	138.24	0.9322	271.89	0.8936		
$T = 323.14$ K; $\rho(0.1) = 895.70$ kg · m^{-3}							
2.547	0.9980	29.56	0.9792	135.87	0.9293	271.39	0.8897
4.996	0.9961	37.48	0.9743	155.37	0.9225	294.68	0.8842
9.796	0.9926	56.09	0.9637	177.44	0.9154	319.51	0.8787
14.278	0.9894	75.73	0.9539	197.05	0.9095	341.87	0.8739
19.756	0.9856	95.67	0.9449	222.53	0.9023	355.17	0.8712
24.335	0.9825	115.81	0.9367	247.29	0.8957		
$T = 338.13$ K; $\rho(0.1) = 882.55$ kg · m^{-3}							
2.547	0.9978	30.05	0.9772	136.24	0.9248	270.39	0.8840
4.996	0.9958	37.41	0.9724	157.17	0.9171	296.41	0.8777
9.986	0.9918	56.52	0.9610	177.63	0.9102	321.25	0.8720
14.568	0.9882	77.14	0.9502	197.05	0.9041	347.08	0.8664
19.734	0.9844	96.87	0.9409	222.31	0.8967	372.21	0.8613
24.230	0.9812	116.72	0.9324	246.52	0.8901		

[a] Value at 288.15 K measured; values at other temperatures interpolated.

Table V. (*Continued*)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 348.13$ K; $\rho(0.1) = 873.55$ kg · m^{-3}							
2.547	0.9977	25.59	0.9793	137.14	0.9215	270.27	0.8800
4.996	0.9956	39.78	0.9695	156.15	0.9143	295.80	0.8738
9.489	0.9918	56.37	0.9594	176.32	0.9072	320.22	0.8682
14.596	0.9876	77.04	0.9482	195.55	0.9010	349.32	0.8619
19.823	0.9835	96.58	0.9387	222.82	0.8927	376.44	0.8565
23.608	0.9807	116.10	0.9300	246.71	0.8861		

Table VI. Experimental Pressures, Volume Ratios, $k = V_p/V_{0.1}$, and Densities[a] at 0.1 MPa for 2-Butoxyethanol (1) + Water (2), $x_1 = 0.75398$

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 288.15$ K; $\rho(0.1) = 912.45$ kg · m^{-3}							
2.547	0.9983	27.14	0.9832	136.14	0.9360	272.40	0.8982
4.996	0.9967	36.97	0.9777	156.60	0.9293	296.77	0.8928
10.046	0.9934	56.81	0.9677	176.16	0.9233	319.01	0.8881
14.597	0.9906	76.64	0.9587	196.73	0.9174	332.61	0.8853
19.642	0.9875	96.81	0.9503	221.04	0.9108	350.21	0.8818
23.516	0.9853	116.67	0.9428	246.73	0.9043		
$T = 298.14$ K; $\rho(0.1) = 904.40$ kg · m^{-3}							
2.547	0.9982	27.38	0.9818	136.36	0.9328	271.13	0.8945
4.996	0.9964	36.72	0.9764	156.81	0.9259	294.27	0.8892
9.496	0.9933	56.38	0.9660	176.24	0.9198	319.54	0.8837
14.657	0.9898	75.99	0.9567	196.62	0.9138	334.34	0.8807
19.448	0.9867	95.82	0.9482	220.88	0.9071	349.47	0.8777
24.074	0.9838	117.25	0.9398	246.34	0.9005		
$T = 313.14$ K; $\rho(0.1) = 891.91$ kg · m^{-3}							
2.547	0.9980	26.74	0.9806	135.64	0.9286	272.45	0.8884
4.996	0.9960	36.71	0.9743	155.48	0.9217	296.51	0.8828
9.905	0.9923	56.42	0.9632	176.69	0.9147	318.35	0.8779
14.617	0.9889	76.71	0.9530	196.78	0.9086	337.32	0.8739
19.533	0.9854	95.84	0.9444	222.71	0.9012	347.92	0.8717
23.881	0.9825	116.90	0.9357	247.69	0.8946		

[a] Value at 288.15 K measured; values at other temperatures interpolated.

Table VI. (*Continued*)

p (MPa)	k	p (MPa)	k	p (MPa)	k	p (MPa)	k
$T = 323.14$ K; $\rho(0.1) = 882.85$ kg · m^{-3}							
2.547	0.9979	30.95	0.9768	137.18	0.9251	270.53	0.8851
4.996	0.9959	37.12	0.9729	158.30	0.9175	296.62	0.8788
9.404	0.9923	58.16	0.9605	176.52	0.9115	321.56	0.8732
14.040	0.9888	77.80	0.9503	196.25	0.9053	347.22	0.8677
19.746	0.9846	96.80	0.9415	221.55	0.8979	372.57	0.8626
23.640	0.9818	117.40	0.9328	246.06	0.8913		
$T = 338.13$ K; $\rho(0.1) = 869.72$ kg · m^{-3}							
2.547	0.9976	26.34	0.9780	137.19	0.9199	271.72	0.8782
4.996	0.9954	37.57	0.9700	156.30	0.9128	296.75	0.8721
9.546	0.9914	60.30	0.9559	176.78	0.9056	321.34	0.8664
14.538	0.9872	76.28	0.9471	196.24	0.8993	350.70	0.8599
19.647	0.9831	95.97	0.9374	221.33	0.8917	377.54	0.8545
24.088	0.9797	115.83	0.9286	247.93	0.8843		
$T = 348.13$ K; $\rho(0.1) = 860.72$ kg · m^{-3}							
2.547	0.9975	27.03	0.9763	136.16	0.9169	270.78	0.8739
4.996	0.9951	40.53	0.9665	158.27	0.9084	295.23	0.8678
9.770	0.9907	57.62	0.9555	178.26	0.9012	322.95	0.8615
14.577	0.9864	77.54	0.9442	197.16	0.8950	348.37	0.8560
19.612	0.9822	96.56	0.9345	221.73	0.8874	371.92	0.8512
24.002	0.9786	117.27	0.9249	247.67	0.8801		

compositions $x_1 = 0.01596$ and 0.17484 lie just outside opposite sides of the phase boundary at 0.1 MPa for all of the temperatures at which measurements were made. 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. The k can be represented within the experimental accuracy by either the modified Tait equation, Eq. (1), or the secant bulk modulus (SBM), $K\ [= (p - p_{0.1})/(1 - k)]$ represented by third-order equations, with the pressure p in MPa:

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

$$K = a_0 + a_1 p + a_2 p^2 + a_3 p^3 \tag{2}$$

for which the coefficients are given in Table VII together with the B and C for Eq. (1). Equation (1) is particularly suitable for extrapolation of the k, while Eq. (2) is the more accurate representation of them.

Table VII. Coefficients of the SBM Equation (1) and Tait Equation (2) for 2-Butoxyethanol (1) + Water (2)

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 $\langle \Delta k/k \rangle$
				$x_1 = 0.006934$				
278.15	2116.1	3.5587	1.1533	0.864	0.001	275.28	0.3024	0.004
288.15	2204.5	3.4670	0.6938	0.097	0.000	288.86	0.3049	0.004
298.14	2266.8	3.3604	0.2430	−0.718	0.001	301.41	0.3095	0.003
313.14	2282.2	3.4440	0.1613	−1.434	0.002	301.78	0.3069	0.001
323.14	2232.3	4.2308	4.7340	6.693	0.004	295.95	0.3033	0.004
338.13	2181.5	4.0366	2.8051	2.754	0.001	280.76	0.2957	0.004
				$x_1 = 0.015965$				
288.15	2229.8	4.842	7.4326	10.041	0.010	298.41	0.3017	0.008
298.14	2261.5	4.68	6.4865	8.419	0.008	303.38	0.3032	0.007
313.14	2172.7	5.366	8.7853	11.065	0.011	285.86	0.2921	0.014
323.14	2155.7	5.126	7.4863	9.126	0.009	279.63	0.2898	0.013
338.13	2053.9	5.53	9.0905	11.319	0.011	262.66	0.2829	0.017
348.13	2068.4	4.944	7.0157	9.078	0.010	260.75	0.2845	0.009
				$x_1 = 0.048263$				
288.15	2037.5	6.203	11.0725	14.483	0.010	237.56	0.2565	0.019
298.14	2014.9	5.942	9.5419	11.895	0.007	233.51	0.2562	0.019
313.14	1940.3	5.959	9.0921	10.464	0.009	225.41	0.2555	0.023
322.15	1879	6.063	9.5401	11.079	0.010	217.18	0.2534	0.024
				$x_1 = 0.174838$				
288.15	1804.49	6.1338	8.0790	8.665	0.006	185.44	0.2277	0.023
298.14	1742.70	5.9582	7.2421	7.392	0.004	177.87	0.2271	0.023
313.14	1626.56	5.8914	6.9369	6.842	0.003	164.88	0.2256	0.026
323.14	1541.15	5.9886	7.5225	7.734	0.005	155.89	0.2243	0.028
338.13	1425.89	5.9228	7.3022	7.345	0.005	143.31	0.2229	0.031
353.13	1335.83	5.8405	7.6226	8.276	0.010	134.78	0.2244	0.026
				$x_1 = 0.50247$				
288.15	1556.68	5.5222	4.9581	4.363	0.002	147.72	0.2160	0.014
298.14	1474.42	5.3738	4.1441	2.888	0.004	139.11	0.2154	0.017
313.14	1416.53	4.8229	2.6844	1.416	0.004	136.10	0.2232	0.005
323.14	1270.42	5.1641	3.0279	0.708	0.008	117.67	0.2128	0.025
338.13	1158.81	5.4158	5.2998	4.743	0.005	109.96	0.2157	0.021
348.13	1101.39	5.3720	5.7321	5.885	0.007	104.45	0.2165	0.015
				$x_1 = 0.75398$				
288.15	1474.78	5.2201	3.5763	2.265	0.004	138.12	0.2154	0.011
298.14	1359.65	5.5712	5.5040	5.226	0.003	127.64	0.2134	0.016
313.14	1233.09	5.6078	5.8030	5.486	0.003	115.60	0.2124	0.021
323.14	1176.90	5.3344	4.6528	3.722	0.003	110.12	0.2138	0.019
338.13	1060.24	5.3739	5.1529	4.467	0.005	99.03	0.2129	0.023
348.13	994.24	5.5315	6.7450	7.467	0.012	93.63	0.2137	0.017

Table VIII. Density, $\rho(0.1)$ ($\mathrm{kg\cdot m^{-3}}$), for 2-Butoxyethanol (1) + Water (2) at 0.1 MPa[a]

x_1	$\rho(0.1)$	x_1	$\rho(0.1)$	x_1	$\rho(0.1)$	x_1	$\rho(0.1)$
$T = 288.15$ K							
0	999.099	0.089473	974.891	0.547147	922.300	0.981108	904.930
0.001029	998.894	0.181828	956.366	0.593933	919.769	0.983576	904.874
0.004977	998.276	0.253201	946.504	0.647469	917.090	0.987263	904.775
0.009685	997.764	0.301138	941.169	0.701593	914.625	0.991718	904.603
0.014887	997.293	0.367068	934.964	0.746787	912.734	0.995811	904.516
0.019844	996.576	0.398020	932.369	0.799255	910.711	0.999082	904.423
0.024946	995.110	0.429165	930.061	0.845623	909.081	1	904.412
0.030290	993.246	0.451091	928.405	0.888320	907.693		
0.049564	986.538	0.506773	924.714	0.950764	905.795		
$T = 298.14$ K							
0	997.044	0.046803	982.183	0.177416	949.924	0.690536	907.086
0.009580	995.173	0.048806	981.449	0.500554	917.188	0.739515	904.988
0.016045	993.963	0.055023	979.246	0.546072	914.416	0.790745	902.984
0.019560	992.874	0.168653	951.406	0.447247	920.803	1	896.289
$T = 313.14$ K							
0	992.215	0.016434	987.276	0.060760	968.050	0.181133	937.994
0.000867	991.956	0.019012	986.096	0.099029	955.935	0.195990	935.490
0.005138	990.763	0.029864	980.916	0.109725	953.042	0.398337	912.258
0.009684	989.560	0.030015	980.846	0.123603	949.615	0.597712	899.069
0.010581	989.331	0.038631	976.943	0.156050	942.648	0.814771	889.602
0.015712	987.588	0.050930	971.809	0.162370	941.413	1	883.775
0.016140	987.406						
$T = 322.14$ K							
0	988.484	0.100194	948.861	0.398706	904.264	0.743263	884.186
0.004905	986.869	0.153267	936.012	0.450261	900.219	0.799071	882.019
0.010066	985.213	0.175431	931.675	0.498866	896.828	0.901330	878.535
0.015785	982.863	0.199358	927.494	0.544753	893.961	0.949541	877.059
0.020219	980.584	0.298737	913.974	0.695576	886.226	1	875.649
0.050531	965.990	0.380309	905.843				
$T = 338.13$ K							
0	980.554	0.251227	906.199	0.69338	872.279	0	980.554
0.009910	976.546	0.251227	906.214	0.739574	870.310	0.003099	979.311
0.015785	973.558	0.251227	906.188	0.796714	868.076	0.007016	977.752
0.049652	969.549	0.444835	886.627	0.900325	864.560	0.010040	976.494
0.049652	969.555	0.444835	886.646	0.900325	864.576	0.014057	974.542
0.170700	919.613	0.496084	882.972	0.949831	863.054	0.015959	973.476
0.200314	914.166	0.544611	879.912	1	861.658	0.019678	970.870
0.251227	906.385	0.693380	872.267			1	861.751
$T = 348.13$ K							
0	974.848	0.015827	967.125	0.499217	873.765	1	852.730
0.010037	970.322	0.196789	906.378	0.752993	860.760		

[a] Density of water adjusted for local isotopic composition.

3.2. Densities at 0.1 MPa

The densities of the standard solutions at 0.1 MPa used for determination of the composition of the volumometer samples are given in Table VIII. These measurements were made over a sufficient range of concentrations to enable an accurate comparison with literature data. The results were compared with the literature data by using the densities to obtain excess molar volumes, V_m^E. These were expressed as $V_m^E/[x_1(1-x_1)]$ and plotted against $(1-2x_1)$. Figure 1 shows the present data for $V_m^E/[x_1(1-x_1)]$ at the six lowest compositions, excluding $x_1=0$ (see Table VIII), at 298.14 K, with those from Refs. 9, 11, and 12. Figure 2 extends the comparison at 298.14 K to the higher compositions for the same references as in Fig. 1 except Ref. 9, where the data are not available. The values from Roux et al. [10] were not included in the figures because they are mostly in close coincidence with either the present results or those of the other references. The comparisons were also made at 288.15 K with the results of Ref. 9 and at 313.14 K with those of Ref. 10. The agreement with the present data at all temperatures was generally within the combined experimental uncertainties, although it is evident from Fig. 1 that there is some scatter in the values of Koga et al. [9], and at the lower compositions their data lie above those from the other sources. At those compositions the data of Roux et al. [10] (not shown) are closer to those of the other data. The densities of the volumometer samples at 0.1 MPa, $\rho_{0.1}$, were determined at the temperatures identified in Tables I–VI with a precision of $2\times10^{-6}\rho_{0.1}$ and an estimated accuracy of $2\times10^{-5}\rho_{0.1}$. These were

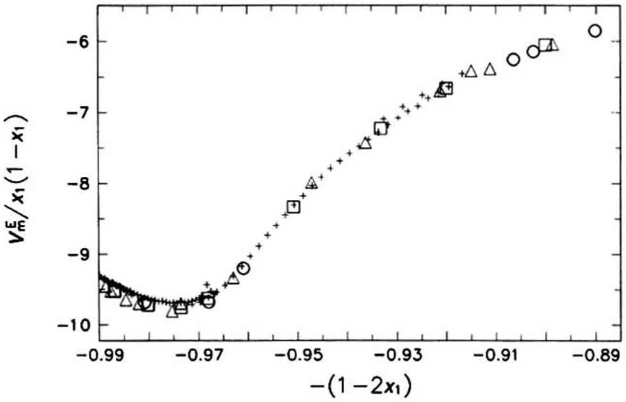

Fig. 1. Excess molar volumes for 2-*n*-butoxyethanol (1) + water at 0.1 MPa and 298.14 K for mole fractions $x_1 \leqslant 0.055$. (○) This work; (△) Ref. 11; (□) Ref. 12; (+) Ref. 9.

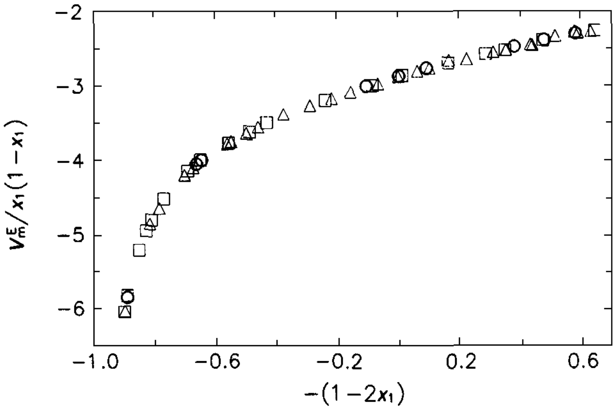

Fig. 2. Excess molar volumes for 2-*n*-butoxyethanol (1) + water at 0.1 MPa and 298.14 K for mole fractions $x_1 \geqslant 0.055$. Symbols as in the legend to Fig. 1.

used to determine the corresponding x_1 from fits of a Redlich–Kister type for the standard solutions in Table VIII, although a cubic spline was used for the fit because the usual polynomial in $(1-2x_1)$ did not provide a good fit. Those x_1 were used to calculate the densities given in Tables I–VI at the other experimental temperatures by using a cubic spline fit of a Redlich–Kister type for the $V_m^E/[x_1(1-x_1)]$ at those temperatures. At 353.13 K, for $x_1 = 0.17484$ the density was estimated from an extrapolation of a cubic fit of the densities at the lower temperatures. A similar procedure was used to estimate the density at 278.15 K for $x_1 = 0.006934$. The compositions are estimated to have an accuracy of $0.0001 \cdot x_1$.

3.3. Isothermal Compressibilities

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

$$\kappa_T = -[1/(p-K)][1-(p/K)(\partial K/\partial p)_T] \tag{3}$$

They have a probable uncertainty of ±1–2%. Koga et al. [13] calculated κ_T as 0.1 MPa and 298.14 K from speed-of-sound and other measurements; their corresponding value is within the lower bound of our probable uncertainty at $x_1 = 0.006934$ but smaller by an amount exceeding the combined maximum uncertainties at $x_1 = 0.01596$. The isobaric κ_T for $x_1 = 0.007$ and 0.01596 initially are less than, and have a similar temperature dependence

Table IX. Isothermal Compressibilities (κ_T; MPa^{-1}), Molar Volumes (V_m; $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$), Isobaric Expansivities (α; K^{-1}), Volume Fluctuations ($\langle (\Delta V/V)^2 \rangle$), and Change in Molar Heat Capacity (ΔC_p; $\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$) in 2-Butoxyethanol (1) + Water (2)

	p (MPa)								
	0.1	20	40	60	100	150	200	250	300
(a) $x_1 = 0.0069337$									
$T = 278.15$ K									
$10^4\kappa_T$	4.72	4.47	4.23	4.02	3.66	3.28	2.98	2.72	2.50
V_m	18.719	18.549	18.388	18.237	17.959	17.651	17.377	17.132	16.910
$10^3\alpha$	0.120	0.157	0.189	0.217	0.264	0.311	0.347	0.374	0.393
$-\Delta C_p$	0.0	0.8	1.5	2.1	3.1	4.1	4.7	5.2	5.5
$\langle (\Delta V/V)^2 \rangle$	0.0584	0.0557	0.0532	0.0510	0.0471	0.0430	0.0396	0.0367	0.0342
$T = 288.15$ K									
$10^4\kappa_T$	4.53	4.30	4.09	3.90	3.56	3.20	2.91	2.67	2.46
V_m	18.746	18.582	18.426	18.280	18.010	17.709	17.441	17.199	16.981
$10^3\alpha$	0.203	0.229	0.252	0.272	0.307	0.342	0.369	0.389	0.404
$-\Delta C_p$	0.0	0.9	1.6	2.2	3.3	4.2	4.9	5.4	5.8
$\langle (\Delta V/V)^2 \rangle$	0.0580	0.0555	0.0532	0.0511	0.0473	0.0433	0.0400	0.0371	0.0347
$T = 298.14$ K									
$10^4\kappa_T$	4.41	4.20	4.00	3.82	3.49	3.15	2.87	2.64	2.45
V_m	18.791	18.631	18.479	18.335	18.069	17.772	17.507	17.267	17.049
$10^3\alpha$	0.286	0.300	0.314	0.327	0.350	0.374	0.391	0.404	0.415
$-\Delta C_p$	0.0	0.9	1.7	2.3	3.4	4.4	5.2	5.7	6.0
$\langle (\Delta V/V)^2 \rangle$	0.0582	0.0558	0.0537	0.0516	0.0479	0.0440	0.0407	0.0379	0.0357
$T = 313.14$ K									
$10^4\kappa_T$	4.38	4.16	3.96	3.78	3.45	3.12	2.84	2.63	2.46
V_m	18.893	18.733	18.581	18.438	18.173	17.878	17.614	17.375	17.156
$10^3\alpha$	0.410	0.408	0.409	0.410	0.415	0.421	0.425	0.428	0.431
$-\Delta C_p$	0.0	1.0	1.8	2.5	3.6	4.7	5.5	6.1	6.4
$\langle (\Delta V/V)^2 \rangle$	0.0604	0.0579	0.0555	0.0534	0.0495	0.0454	0.0420	0.0394	0.0373
$T = 323.14$ K									
$10^4\kappa_T$	4.48	4.20	3.97	3.77	3.45	3.13	2.87	2.63	2.39
V_m	18.979	18.816	18.663	18.519	18.254	17.957	17.690	17.449	17.231
$10^3\alpha$	0.492	0.480	0.472	0.466	0.458	0.452	0.447	0.443	0.442
$-\Delta C_p$	0.0	1.0	1.9	5.6	3.8	4.9	5.8	6.3	6.7
$\langle (\Delta V/V)^2 \rangle$	0.0634	0.0600	0.0572	0.0547	0.0507	0.0468	0.0436	0.0405	0.0372
$T = 338.13$ K									
$10^4\kappa_T$	4.58	4.31	4.07	3.85	3.50	3.15	2.88	2.64	2.44
V_m	19.134	18.966	18.808	18.659	18.387	18.085	17.815	17.571	17.349
$10^3\alpha$	0.616	0.588	0.566	0.549	0.523	0.499	0.481	0.466	0.458
$-\Delta C_p$	0.0	1.1	2.0	2.8	4.1	5.3	6.2	6.8	7.2
$\langle (\Delta V/V)^2 \rangle$	0.0673	0.0638	0.0608	0.0581	0.0535	0.0490	0.0454	0.0423	0.0395

Table IX. (*Continued*)

	p (MPa)								
	0.1	20	40	60	100	150	200	250	300
(b) $x_1 = 0.015965$									
$T = 288.15$ K									
$10^4\kappa_T$	4.48	4.17	3.92	3.70	3.38	3.09	2.85	2.64	2.40
V_m	19.669	19.501	19.344	19.197	18.928	18.625	18.350	18.100	17.873
$10^3\alpha$	0.316	0.309	0.307	0.309	0.318	0.333	0.348	0.358	0.363
$-\Delta C_p$	0.0	0.8	1.5	2.2	3.4	4.7	5.7	6.6	7.4
$\langle(\Delta V/V)^2\rangle$	0.0546	0.0512	0.0485	0.0462	0.0428	0.0397	0.0373	0.0349	0.0322
$T = 298.14$ K									
$10^4\kappa_T$	4.42	4.13	3.88	3.68	3.36	3.06	2.83	2.62	2.40
V_m	19.732	19.565	19.409	19.263	18.995	18.693	18.420	18.171	17.944
$10^3\alpha$	0.382	0.373	0.369	0.367	0.369	0.376	0.383	0.389	0.390
$-\Delta C_p$	0.0	0.8	1.6	2.3	3.5	4.9	6.0	6.9	7.7
$\langle(\Delta V/V)^2\rangle$	0.0555	0.0523	0.0496	0.0473	0.0438	0.0406	0.0381	0.0357	0.0332
$T = 313.14$ K									
$10^4\kappa_T$	4.60	4.24	3.94	3.71	3.36	3.05	2.83	2.62	2.40
V_m	19.862	19.689	19.528	19.380	19.109	18.806	18.531	18.281	18.052
$10^3\alpha$	0.482	0.470	0.461	0.454	0.445	0.439	0.436	0.434	0.431
$-\Delta C_p$	0.0	0.9	1.7	2.4	3.8	5.2	6.4	7.4	8.2
$\langle(\Delta V/V)^2\rangle$	0.0609	0.0566	0.0531	0.0503	0.0462	0.0427	0.0401	0.0377	0.0350
$T = 323.14$ K									
$10^4\kappa_T$	4.64	4.28	3.99	3.76	3.40	3.08	2.84	2.63	2.41
V_m	19.968	19.792	19.629	19.478	19.202	18.895	18.618	18.365	18.135
$10^3\alpha$	0.548	0.534	0.522	0.512	0.496	0.482	0.471	0.464	0.459
$-\Delta C_p$	0.0	0.9	1.8	2.5	4.0	5.5	6.7	7.7	8.6
$\langle(\Delta V/V)^2\rangle$	0.0624	0.0581	0.0547	0.0518	0.0475	0.0438	0.0409	0.0384	0.0357
$T = 338.13$ K									
$10^4\kappa_T$	4.87	4.45	4.12	3.85	3.46	3.13	2.88	2.67	2.44
V_m	20.148	19.962	19.793	19.636	19.352	19.037	18.753	18.495	18.260
$10^3\alpha$	0.648	0.630	0.614	0.599	0.573	0.545	0.524	0.509	0.500
$-\Delta C_p$	0.0	1.0	1.9	2.7	4.3	5.9	7.2	8.3	9.2
$\langle(\Delta V/V)^2\rangle$	0.0679	0.0626	0.0585	0.0551	0.0503	0.0462	0.0432	0.0405	0.0375
$T = 348.13$ K									
$10^4\kappa_T$	4.83	4.46	4.16	3.91	3.53	3.19	2.92	2.68	2.44
V_m	20.282	20.095	19.923	19.763	19.472	19.149	18.859	18.597	18.360
$10^3\alpha$	0.714	0.695	0.676	0.657	0.624	0.588	0.559	0.539	0.527
$-\Delta C_p$	0.0	1.0	2.0	2.9	4.5	6.1	7.5	8.7	9.7
$\langle(\Delta V/V)^2\rangle$	0.0690	0.0643	0.0604	0.0573	0.0525	0.0482	0.0448	0.0417	0.0384

Table IX. (*Continued*)

	p (MPa)								
	0.1	20	40	60	100	150	200	250	300
(c) $x_1 = 0.048263$									
$T = 288.15$ K									
$10^4\kappa_T$	4.91	4.43	4.06	3.77	3.36	3.02	2.77	2.54	2.29
V_m	23.150	22.936	22.743	22.566	22.247	21.896	21.582	21.297	21.042
$10^3\alpha$	0.502	0.494	0.484	0.474	0.457	0.444	0.438	0.435	0.424
$-\Delta C_p$	0.0	0.8	1.4	2.0	3.1	4.3	5.3	6.1	6.8
$\langle(\Delta V/V)^2\rangle$	0.0508	0.0463	0.0428	0.0401	0.0362	0.0331	0.0307	0.0286	0.0260
$T = 298.14$ K									
$10^4\kappa_T$	4.96	4.49	4.12	3.83	3.41	3.05	2.78	2.55	2.31
V_m	23.275	23.058	22.861	22.680	22.355	21.998	21.681	21.393	21.135
$10^3\alpha$	0.561	0.545	0.530	0.516	0.495	0.478	0.466	0.457	0.444
$-\Delta C_p$	0.0	0.8	1.5	2.1	3.2	4.5	5.6	6.4	7.1
$\langle(\Delta V/V)^2\rangle$	0.0528	0.0483	0.0447	0.0419	0.0378	0.0343	0.0318	0.0296	0.0271
$T = 313.14$ K									
$10^4\kappa_T$	5.15	4.64	4.25	3.93	3.47	3.09	2.82	2.60	2.38
V_m	23.484	23.257	23.051	22.864	22.529	22.163	21.838	21.545	21.278
$10^3\alpha$	0.649	0.620	0.597	0.580	0.553	0.529	0.509	0.491	0.472
$-\Delta C_p$	0.0	0.9	1.6	2.3	3.5	4.8	6.0	6.9	7.6
$\langle(\Delta V/V)^2\rangle$	0.0571	0.0520	0.0480	0.0448	0.0402	0.0364	0.0337	0.0314	0.0291
$T = 322.15$ K									
$10^4\kappa_T$	5.32	4.77	4.35	4.01	3.53	3.14	2.86	2.63	2.40
V_m	23.630	23.394	23.183	22.990	22.647	22.274	21.942	21.643	21.372
$10^3\alpha$	0.701	0.665	0.638	0.618	0.588	0.560	0.535	0.511	0.490
$-\Delta C_p$	0.0	0.9	1.7	2.4	3.6	5.0	6.2	7.2	8.0
$\langle(\Delta V/V)^2\rangle$	0.0603	0.0546	0.0502	0.0468	0.0418	0.0378	0.0350	0.0326	0.0301
(d) $x_1 = 0.174838$									
$T = 288.15$ K									
$10^4\kappa_T$	5.54	4.93	4.46	4.09	3.55	3.09	2.78	2.53	2.30
V_m	37.103	36.719	36.377	36.067	35.523	34.941	34.433	33.980	33.573
$10^3\alpha$	0.75	0.71	0.67	0.64	0.60	0.56	0.53	0.51	0.49
$-\Delta C_p$	0.0	0.8	1.4	2.0	3.0	4.1	5.0	5.8	6.4
$\langle(\Delta V/V)^2\rangle$	0.0358	0.0322	0.0294	0.0272	0.0239	0.0212	0.0193	0.0178	0.0164

Table IX. (*Continued*)

	p (MPa)								
	0.1	20	40	60	100	150	200	250	300
(d) $x_1 = 0.174838$									
$T = 298.14$ K									
$10^4\kappa_T$	5.73	5.11	4.61	4.22	3.64	3.16	2.83	2.57	2.33
V_m	37.381	36.981	36.624	36.303	35.739	35.139	34.618	34.155	33.740
$10^3\alpha$	0.78	0.73	0.69	0.66	0.62	0.57	0.54	0.52	0.50
$-\Delta C_p$	0.0	0.8	1.5	2.1	3.2	4.4	5.3	6.1	6.7
$\langle(\Delta V/V)^2\rangle$	0.0380	0.0342	0.0312	0.0288	0.0253	0.0223	0.0202	0.0186	0.0171
$T = 313.14$ K									
$10^4\kappa_T$	6.14	5.43	4.88	4.44	3.81	3.28	2.92	2.64	2.40
V_m	37.827	37.395	37.012	36.670	36.073	35.443	34.899	34.419	33.988
$10^3\alpha$	0.82	0.77	0.73	0.70	0.65	0.60	0.56	0.53	0.51
$-\Delta C_p$	0.0	0.9	1.6	2.3	3.4	4.7	5.7	6.5	7.2
$\langle(\Delta V/V)^2\rangle$	0.0423	0.0378	0.0343	0.0315	0.0275	0.0241	0.0218	0.0200	0.0184
$T = 323.14$ K									
$10^4\kappa_T$	6.48	5.69	5.07	4.60	3.92	3.36	2.99	2.70	2.44
V_m	38.159	37.702	37.299	36.941	36.321	35.669	35.109	34.614	34.172
$10^3\alpha$	0.85	0.80	0.76	0.72	0.67	0.62	0.58	0.54	0.52
$-\Delta C_p$	0.0	0.9	1.7	2.4	3.6	4.9	6.0	6.9	7.6
$\langle(\Delta V/V)^2\rangle$	0.0457	0.0405	0.0365	0.0334	0.0290	0.0253	0.0229	0.0209	0.0192
$T = 338.13$ K									
$10^4\kappa_T$	7.01	6.09	5.40	4.86	4.10	3.50	3.09	2.78	2.52
V_m	38.664	38.165	37.730	37.346	36.686	36.000	35.414	34.898	34.439
$10^3\alpha$	0.90	0.84	0.79	0.76	0.70	0.64	0.60	0.56	0.53
$-\Delta C_p$	0.0	1.0	1.8	2.6	3.9	5.3	6.5	7.4	8.1
$\langle(\Delta V/V)^2\rangle$	0.0510	0.0449	0.0402	0.0366	0.0314	0.0273	0.0245	0.0224	0.0205
$T = 353.13$ K									
$10^4\kappa_T$	7.48	6.46	5.70	5.12	4.30	3.66	3.22	2.89	2.58
V_m	39.195	38.657	38.191	37.781	37.081	36.355	35.737	35.196	34.719
$10^3\alpha$	0.95	0.88	0.83	0.79	0.73	0.67	0.62	0.58	0.55
$-\Delta C_p$	0.0	1.1	2.0	2.8	4.2	5.7	7.0	7.9	8.7
$\langle(\Delta V/V)^2\rangle$	0.0560	0.0491	0.0438	0.0398	0.0341	0.0295	0.0265	0.0241	0.0218

Table IX. (*Continued*)

	p (MPa)								
	0.1	20	40	60	100	150	200	250	300
(e) $x_1 = 0.50247$									
$T = 288.15$ K									
$10^4\kappa_T$	6.42	5.69	5.11	4.64	3.94	3.35	2.94	2.62	2.37
V_m	73.880	72.997	72.214	71.515	70.304	69.041	67.968	67.032	66.201
$10^3\alpha$	0.86	0.81	0.76	0.72	0.64	0.58	0.55	0.52	0.49
$-\Delta C_p$	0.0	1.5	2.6	3.6	5.4	7.5	9.2	10.5	11.6
$\langle(\Delta V/V)^2\rangle$	0.0208	0.0187	0.0169	0.0155	0.0134	0.0116	0.0104	0.0094	0.0086
$T = 298.14$ K									
$10^4\kappa_T$	6.78	5.99	5.36	4.85	4.09	3.44	3.00	2.68	2.43
V_m	74.519	73.581	72.753	72.016	70.747	69.436	68.330	67.369	66.515
$10^3\alpha$	0.89	0.83	0.78	0.73	0.66	0.60	0.56	0.53	0.50
$-\Delta C_p$	0.0	1.6	2.8	3.8	5.7	7.9	9.7	11.1	12.2
$\langle(\Delta V/V)^2\rangle$	0.0225	0.0202	0.0182	0.0167	0.0143	0.0123	0.0109	0.0099	0.0091
$T = 313.14$ K									
$10^4\kappa_T$	7.06	6.28	5.65	5.13	4.34	3.64	3.15	2.79	2.52
V_m	75.542	74.548	73.665	72.875	71.514	70.110	68.935	67.921	67.027
$10^3\alpha$	0.94	0.87	0.81	0.76	0.69	0.62	0.58	0.54	0.51
$-\Delta C_p$	0.0	1.7	3.0	4.1	6.2	8.6	10.5	12.0	13.2
$\langle(\Delta V/V)^2\rangle$	0.0243	0.0219	0.0200	0.0183	0.0158	0.0135	0.0119	0.0107	0.0098
$T = 323.14$ K									
$10^4\kappa_T$	7.87	6.85	6.05	5.41	4.46	3.68	3.17	2.83	2.59
V_m	76.296	75.190	74.229	73.385	71.960	70.519	69.326	68.298	67.382
$10^3\alpha$	0.97	0.89	0.83	0.78	0.71	0.64	0.59	0.55	0.52
$-\Delta C_p$	0.0	1.8	3.2	4.4	6.5	9.0	11.0	12.6	13.8
$\langle(\Delta V/V)^2\rangle$	0.0277	0.0245	0.0219	0.0198	0.0167	0.0140	0.0123	0.0111	0.0103
$T = 338.13$ K									
$10^4\kappa_T$	8.62	7.37	6.43	5.71	4.69	3.88	3.35	2.97	2.65
V_m	77.432	76.214	75.173	74.269	72.752	71.220	69.949	68.856	67.896
$10^3\alpha$	1.02	0.92	0.86	0.80	0.73	0.66	0.61	0.56	0.53
$-\Delta C_p$	0.0	2.0	3.4	4.7	7.0	9.7	11.9	13.5	14.9
$\langle(\Delta V/V)^2\rangle$	0.0313	0.0272	0.0240	0.0216	0.0181	0.0153	0.0135	0.0121	0.0110
$T = 348.13$ K									
$10^4\kappa_T$	9.07	7.71	6.70	5.93	4.86	4.02	3.46	3.04	2.68
V_m	78.229	76.940	75.843	74.894	73.307	71.710	70.388	69.257	68.274
$10^3\alpha$	1.05	0.95	0.88	0.82	0.75	0.68	0.62	0.57	0.54
$-\Delta C_p$	0.0	2.1	3.6	5.0	7.4	10.2	12.5	14.2	15.6
$\langle(\Delta V/V)^2\rangle$	0.0336	0.0290	0.0256	0.0229	0.0192	0.0162	0.0142	0.0127	0.0114

Table IX. (*Continued*)

	p (MPa)								
	0.1	20	40	60	100	150	200	250	300
(f) $x_1 = 0.75398$									
$T = 288.15$ K									
$10^4\kappa_T$	6.78	6.01	5.39	4.88	4.12	3.46	3.01	2.68	2.43
V_m	102.503	101.210	100.066	99.046	97.288	95.472	93.945	92.621	91.448
$10^3\alpha$	0.89	0.81	0.74	0.70	0.63	0.57	0.53	0.49	0.46
$-\Delta C_p$	0.0	2.2	4.0	5.6	8.5	11.5	14.0	15.9	17.7
$\langle(\Delta V/V)^2\rangle$	0.0158	0.0142	0.0129	0.0118	0.0101	0.0087	0.0077	0.0069	0.0064
$T = 298.14$									
$10^4\kappa_T$	7.35	6.40	5.66	5.09	4.26	3.57	3.11	2.76	2.47
V_m	103.414	102.014	100.793	99.718	97.882	95.996	94.411	93.038	91.831
$10^3\alpha$	0.92	0.83	0.77	0.72	0.65	0.59	0.54	0.50	0.47
$-\Delta C_p$	0.0	2.3	4.2	5.9	9.0	12.2	14.7	16.8	18.6
$\langle(\Delta V/V)^2\rangle$	0.0176	0.0155	0.0139	0.0127	0.0108	0.0092	0.0082	0.0074	0.0067
$T = 313.14$									
$10^4\kappa_T$	8.10	6.95	6.09	5.42	4.48	3.73	3.23	2.87	2.56
V_m	104.862	103.309	101.975	100.811	98.848	96.854	95.189	93.752	92.491
$10^3\alpha$	0.96	0.87	0.80	0.75	0.68	0.61	0.56	0.52	0.49
$-\Delta C_p$	0.0	2.5	4.5	6.4	9.7	13.1	15.9	18.1	20.0
$\langle(\Delta V/V)^2\rangle$	0.0201	0.0175	0.0155	0.0140	0.0118	0.0100	0.0088	0.0080	0.0072
$T = 323.14$									
$10^4\kappa_T$	8.49	7.29	6.37	5.66	4.65	3.84	3.31	2.93	2.63
V_m	105.937	104.293	102.882	101.654	99.593	97.515	95.796	94.319	93.021
$10^3\alpha$	0.99	0.90	0.83	0.78	0.70	0.63	0.57	0.53	0.50
$-\Delta C_p$	0.0	2.6	4.8	6.8	10.2	13.8	16.7	19.0	21.1
$\langle(\Delta V/V)^2\rangle$	0.0215	0.0188	0.0166	0.0150	0.0125	0.0106	0.0093	0.0083	0.0076
$T = 338.13$									
$10^4\kappa_T$	9.42	7.95	6.87	6.04	4.90	4.02	3.45	3.04	2.71
V_m	107.535	105.700	104.151	102.819	100.610	98.408	96.597	95.049	93.694
$10^3\alpha$	1.04	0.94	0.86	0.81	0.73	0.65	0.59	0.55	0.52
$-\Delta C_p$	0.0	2.8	5.2	7.3	11.0	14.9	18.0	20.5	22.6
$\langle(\Delta V/V)^2\rangle$	0.0246	0.0212	0.0185	0.0165	0.0137	0.0115	0.0100	0.0090	0.0081
$T = 348.13$ K									
$10^4\kappa_T$	10.05	8.36	7.15	6.26	5.07	4.17	3.58	3.13	2.74
V_m	108.660	106.699	105.064	103.668	101.365	99.067	97.174	95.560	94.170
$10^3\alpha$	1.07	0.96	0.89	0.83	0.75	0.67	0.61	0.56	0.53
$-\Delta C_p$	0.0	3.0	5.5	7.7	11.6	15.7	18.9	21.5	23.8
$\langle(\Delta V/V)^2\rangle$	0.0268	0.0227	0.0197	0.0175	0.0145	0.0122	0.0107	0.0095	0.0084

to, those of pure water [14]. The decrease with increase in temperature of the κ_T for the first composition does not persist much above 313.14 K, and for $x_1 = 0.01596$ the κ_T have increased to exceed those for water before that temperature is reached. The isobaric κ_T for [acetonitrile (1) + water] [15] and [methanol (1) + water] [14] have κ_T which remain below those for water to much higher compositions: $0.1 < x_1 < 0.2$ for (acetonitrile + water) and $0.25 < x_1 < 0.35$ for (methanol + water).

3.3. Volume Fluctuations

Table IX includes normalized volume fluctuations [16], $\langle(\Delta V/V)^2\rangle$, defined by Eq. (4)

$$\langle(\Delta V/V)^2\rangle = RT\kappa_T/V_\mathrm{m} \tag{4}$$

where V_m is the molar volume, to extend those obtained by Koga and Westh [17] at 0.1 MPa and 298.14 K. The $\langle(\Delta V/V)^2\rangle$ have an estimated error of ±1–2%. The V_m in Table IX were calculated as a function of temperature at chosen pressures from the densities at 0.1 MPa and the volume

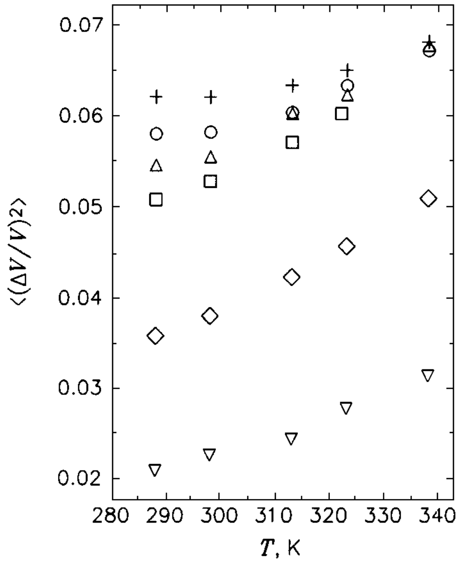

Fig. 3. Temperature dependence of normalized volume fluctuations, $\langle(\Delta V/V)^2\rangle$, in 2-*n*-butoxyethanol (1) + water at 0.1 MPa. (○) $x_1 = 0.007$; (△) $x_1 = 0.016$; (□) $x_1 = 0.05$; (◇) $x_1 = 0.175$; (▽) $x_1 = 0.502$; (+) water.

ratios from Eq. (2) using the coefficients from Table VII. The $\langle(\Delta V/V)^2\rangle$ for five of the six compositions and those for water calculated from the data of Easteal and Woolf [14] are shown in Fig. 3 at 0.1 MPa. The value at $x_1 = 0.016$ at 298 K is greater than the corresponding value in Ref. 17 by about 0.0028, an amount which exceeds the combined maximum uncertainties and, taken with the other data at that temperature from Table IX, gives no indication of the inflection point which Koga and Westh obtained near that composition. Figure 3 shows that, as the temperature increases, the $\langle(\Delta V/V)^2\rangle$ for $x_1 = 0.007$, 0.016, and 0.05 increase rapidly and move toward those for water. At the highest temperature, which is close to the phase boundary for $x_1 = 0.016$, the $\langle(\Delta V/V)^2\rangle$ for $x_1 = = 0.007$, 0.016, and water are virtually coincident. A similar trend appears to be present in the data for $x_1 = 0.175$, for which the phase boundary is closest at about 358 K. Koga [18] proposed a mixing scheme of three regions for this system with a transition between them which depends on the temperature and composition: region I, $x_1 < 0.017$ at 298 K, where the hydrogen bond network of water is enhanced by the BE; region II, $0.017 < x_1 < 0.46$ at 298 K, typified by water-rich and BE-rich clusters; and region III, $x_1 > 0.46$ at 298 K,

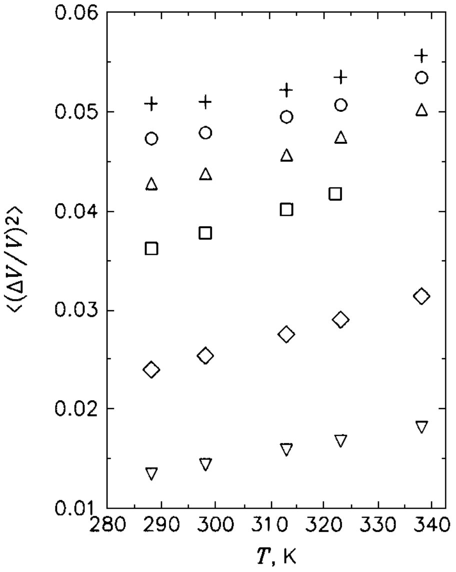

Fig. 4. Temperature dependence of normalized volume fluctuations, $\langle(\Delta V/V)^2\rangle$, in 2-*n*-butoxyethanol (1) + water at 100 MPa. Symbols as in the legend to Fig. 3.

where micelles are significant. The rapid change in $\langle(\Delta V/V)^2\rangle$ for $x_1 \approx 0.016$ shown in Fig. 3 begins close to the temperature of 298 K identified by Koga [18] as the temperature for transition of this composition from I to II at 0.1 MPa. In contrast, his data indicate that the I–II transition at the same pressure for $x_1 \approx 0.007$ was near 348 K. Figure 4 shows that the movement of the $\langle(\Delta V/V)^2\rangle$ of the mixtures towards those for water seen in Fig. 3 is not detectable at 100 MPa. The suppression of the phase separation [2, 3] before this pressure is reached would be expected from the influence of pressure in disrupting the hydrogen bond structure in region I, and adversely affecting the formation and stability of clusters and micelles in regions II and III.

3.5. Isobaric Expansivities

Isobaric expansivities, α, also given in Table IX, were calculated by fitting the V_m at a chosen pressure to a quadratic in T and differentiating analytically

$$\alpha = (\partial \ln V_m/\partial T)_p \tag{5}$$

The α have an estimated error of ±2–4%. The values at 0.1 MPa at $x_1 = 0.5025$ and 0.7540 for 298.14 and 323.14 K agree within 1% with those interpolated from the data of Onken [19]. A direct comparison with the measurements of Davies et al. [20] is not possible, as their data are not true thermal expansivities.

3.4. Isobaric Molar Heat Capacity, C_p

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

$$\Delta C_p = C_p - C_p\,(0.1\text{ MPa}) = -\int_{0.1\text{ MPa}}^{p} (TM/\rho)\{(\partial\alpha/\partial T)_p + \alpha^2\}\,dp \tag{6}$$

where C_p (0.1 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 expressed by a quadratic equation in T to enable analytic differentiation. The error in the ΔC_p is estimated to be $\pm 1\ \mathrm{J \cdot (mol \cdot K^{-1})}$. The change in the C_p with either temperature or pressure is not very large at low x_1 but increases more rapidly at higher compositions. Apparent molal heat capacities and molar heat capacities at 0.1 MPa are available [10, 21] for some of the temperatures and compositions of the data in Table IX.

4. CONCLUSION

The volumetric data have provided values for the normalized volume fluctuations in this system over an extensive range of temperature, pressure, and composition. The magnitude of the fluctuations moves close to those for the major component, water, as the phase boundary is approached. The inflection point in the normalized volume fluctuations at low x_1 at 0.1 MPa and 298 K observed by Koga and Westh [15] has not been detected.

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