Sound Velocities and Apparent Molar Adiabatic Compressions of Alcohols in Dilute Aqueous Solutions

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The sound velocities in dilute aqueous solutions of 12 alcohols were measured at 5, 15, 25, 35, and 45 °C by means of a sing-around ultrasonic velocimeter. The alcohols used were methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2−methyl-1-propanol, 2-methyl-2-propanol, 1-pentanol, 2-methyl-2-butanol, 2,2-dimethyl-1-propanol, and 1-hexanol. From these data and density results reported previously, the apparent molar adiabatic compressions of the alcohols were evaluated. The effects of chain length and chain branching of alkyl residues on the compression behavior of alcohols in water were discussed.

Introduction

The volumetric behavior of aqueous alcohol solutions has been investigated by many researchers and usually discussed in connection with the structural change of solvent water (*1*). In a previous paper, we have reported the partial molar volumes of alcohols in water at various temperatures and pointed out the relative importance of the hydrogen-bonding interactions between alcohols and water (*2*). Since the structure of water can be largely influenced by the variation of temperature and pressure, the study of the compression behavior of aqueous solutions at different temperatures may provide useful information on solute−solvent interactions.

The partial molar adiabatic compressions of some alcohols in water have been investigated by several researchers. For instances, Nakajima et al. (*3*) in our laboratory have reported some reliable data for 1-alcohols at 5, 25, and 45 °C. It seems, however, that the agreement among different researchers is not necessarily good, and there have been only a few studies on the temperature dependence of the partial molar compression. In this paper we present the results of sound velocity measurements for dilute aqueous solutions of twelve monohydric alcohols having from one to six carbon atoms at 5, 15, 25, 35, and 45 °C by using a sing-around ultrasonic velocimeter.

Experimental Section

The alcohols used are methanol (MeOH), ethanol (EtOH), 1-propanol (*n*-PrOH), 2-propanol (*i*-PrOH), 1-butanol (*n*-BuOH), 2-butanol (*sec*-BuOH), 2-methyl-1-propanol (*i*-BuOH), 2-methyl-2-propanol (*t*-BuOH), 1-pentanol (*n*-PenOH), 2-methyl-2-butanol (*t*-PenOH), 2,2-dimethyl-1-propanol (*neo*-PenOH), and 1-hexanol (*n*-HexOH). These alcohols were purified by fractional distillation and stored over molecular sieves 3A or 4A, except for solid *neo*-PenOH which was purified by crystallization twice. The sound velocities of *n*-HexOH are 1372.59, 1337.65, 1303.16, 1269.09, and 1235.48 m s^{-1} at 5, 15, 25, 35, and 45 °C, respectively. The data for the other liquid alcohols have been reported elsewhere (*4*). The water was doubly distilled by using a quartz still.

The sound velocities in solutions *u* were measured at a frequency of about 5 MHz by using a sing-around veloci-

meter constructed in our laboratory. The values are given relative to the sound velocity in pure solvent u_1 by using the relation

$$1/u = 1/u_1 + (T - T_1)/L \qquad (1)$$

where T and T_1 are the pulse repetition periods for solution and solvent, respectively, and L is the effective path length between two piezoelectric transducers fixed to both sides of the measuring cell. The calibration of L (ca. 7 cm) was based on the sound velocities in pure water at various temperatures reported by Del Grosso and Mader (*5*). The precision of the sound velocity measurements was estimated, in most cases, to be better than ±1 cm s^{-1} for the dilute solution range studied.

The cell of the velocimeter was thermostated in a water bath within ±0.002 °C by a laboratory-made controller using a Y-cut quartz as a temperature sensor. All solutions were prepared by successive addition of a weighed amount of a concentrated stock solution or a pure alcohol into the measuring cell containing a known quantity of solvent water.

Results and Discussion

The specific adiabatic compression of solution is defined as the partial derivative of specific volume *v* with respect to pressure P under isentropic conditions; $k_S = -(\partial v/\partial P)_S$. Then, the k_S values can be estimated from the measurements of sound velocity u and density ϱ ($=1/v$) by the relation

$$k_s = 1/(\varrho u)^2 \qquad (2)$$

In the present work, the density values of the solutions used for the sound velocity measurements were calculated from $V_2°$ and B_V values reported previously (*2*). Then, the apparent molar adiabatic compression of alcohol in solution ϕ_{K_2} is given by

$$\phi_{K_2} = (k_S - k_{S1})/m + k_S M_2 \qquad (3)$$

where m is molality, M_2 is the molar mass of alcohol, and k_{S1} is the specific compression of solvent water. Table 1 summarizes the sound velocity differences between solu-

Table 1. Sound Velocity Differences and Apparent Molar Adiabatic Compressions of Alcohols in Water

m/(mol·kg⁻¹)	$(u-u_1)$/(m·s⁻¹)	ϕ_K/(cm³·GPa⁻¹·mol⁻¹)	m/(mol·kg⁻¹)	$(u-u_1)$/(m·s⁻¹)	ϕ_K/(cm³·GPa⁻¹·mol⁻¹)		m/(mol·kg⁻¹)	$(u-u_1)$/(m·s⁻¹)	ϕ_K/(cm³·GPa⁻¹·mol⁻¹)	m/(mol·kg⁻¹)	$(u-u_1)$/(m·s⁻¹)	ϕ_K/(cm³·GPa⁻¹·mol⁻¹)
						Methanol						
0.055 12	1.176	6.954	0.192 60	4.128	6.805	5 °C	0.312 20	6.714	6.684	0.421 17	9.080	6.583
0.111 79	2.386	6.915	0.237 01	5.087	6.758		0.355 75	7.651	6.658	0.458 44	9.890	6.552
0.154 77	3.318	6.824	0.275 86	5.925	6.724		0.393 48	8.474	6.615	0.490 47	10.595	6.513
0.051 38	0.842	10.063	0.173 19	2.826	10.051	15 °C	0.295 67	4.820	10.004	0.410 45	6.701	9.936
0.091 15	1.485	10.105	0.220 57	3.594	10.044		0.331 78	5.409	9.987	0.449 94	7.350	9.912
0.134 60	2.193	10.084	0.255 63	4.166	10.026		0.372 84	6.082	9.962	0.494 90	8.085	9.891
0.027 53	0.341	12.356	0.198 71	2.424	12.403	25 °C	0.344 11	4.220	12.308	0.476 33	5.835	12.266
0.072 19	0.877	12.481	0.240 82	2.954	12.346		0.376 94	4.624	12.293			
0.119 77	1.464	12.418	0.277 67	3.396	12.353		0.409 83	5.029	12.278			
0.164 39	2.032	12.318	0.307 87	3.773	12.327		0.439 71	5.414	12.242			
0.040 19	0.371	14.020	0.189 62	1.672	14.216	35 °C	0.303 31	2.677	14.178	0.421 22	3.736	14.119
0.091 43	0.814	14.195	0.229 65	2.032	14.186		0.339 43	3.002	14.157	0.458 08	4.057	14.116
0.141 96	1.260	14.196	0.267 73	2.380	14.151		0.379 92	3.371	14.129	0.491 59	4.355	14.105
0.071 73	0.420	15.849	0.213 41	1.264	15.780	45 °C	0.337 98	2.004	15.749	0.453 48	2.692	15.719
0.127 54	0.751	15.818	0.256 43	1.518	15.772		0.378 45	2.238	15.749	0.488 10	2.886	15.725
0.164 90	0.977	15.789	0.301 46	1.785	15.761		0.413 92	2.453	15.734			
						Ethanol						
0.039 16	1.826	−0.654	0.154 65	7.250	−0.980	5 °C	0.260 93	12.261	−1.195	0.366 03	17.225	−1.378
0.080 43	3.765	−0.834	0.187 19	8.777	−1.029		0.294 65	13.856	−1.263	0.406 13	19.118	−1.439
0.119 10	5.579	−0.908	0.225 68	10.595	−1.120		0.331 63	15.597	−1.315	0.439 22	20.681	−1.490
0.044 85	1.713	5.428	0.162 56	6.221	5.238	15 °C	0.271 09	10.383	5.088	0.375 60	14.398	4.943
0.086 42	3.298	5.398	0.196 96	7.534	5.208		0.309 34	11.854	5.030	0.407 66	15.629	4.902
0.124 69	4.767	5.308	0.233 93	8.958	5.137		0.342 07	13.107	4.994	0.440 38	16.889	4.856
0.039 09	1.224	9.818	0.153 45	4.808	9.681	25 °C	0.272 02	8.519	9.563	0.381 03	11.930	9.451
0.079 37	2.486	9.768	0.192 31	6.024	9.644		0.310 37	9.719	9.523	0.415 75	13.007	9.428
0.115 73	3.621	9.749	0.231 38	7.249	9.599		0.347 41	10.878	9.485	0.446 57	13.968	9.400
0.037 32	0.943	13.390	0.158 79	4.005	13.301	35 °C	0.265 20	6.678	13.224	0.364 19	9.147	13.169
0.081 13	2.049	13.355	0.196 97	4.966	13.271		0.295 72	7.441	13.206	0.397 43	9.975	13.148
0.124 90	3.152	13.325	0.232 38	5.853	13.252		0.331 94	8.348	13.180			
0.047 59	0.950	16.444	0.196 61	3.899	16.394	45 °C	0.343 71	6.767	16.353	0.487 63	9.513	16.337
0.087 26	1.738	16.436	0.237 81	4.706	16.384		0.382 10	7.501	16.354			
0.124 42	2.475	16.420	0.273 09	5.393	16.378		0.420 59	8.239	16.346			
0.159 45	3.171	16.393	0.308 83	6.088	16.368		0.452 25	8.843	16.341			

1-Propanol

5 °C

0.030 49	2.217	-10.529	0.135 54	9.820	-10.539	0.236 58	17.073	-10.525	0.322 43	23.196	-10.524
0.067 04	4.862	-10.466	0.173 20	12.531	-10.538	0.264 90	19.098	-10.527	0.352 64	25.337	-10.515
0.102 13	7.406	-10.523	0.206 73	14.946	-10.561	0.293 16	21.111	-10.521	0.383 23	27.499	-10.506

15 °C

0.035 52	2.144	-0.858	0.141 92	8.519	-0.846	0.237 21	14.169	-0.836	0.323 87	19.264	-0.837
0.069 45	4.181	-0.821	0.172 95	10.366	-0.846	0.263 81	15.735	-0.830	0.353 90	21.016	-0.831
0.107 65	6.472	-0.841	0.204 38	12.221	-0.815	0.294 68	17.557	-0.846	0.387 84	22.993	-0.830

25 °C

0.039 25	1.960	6.298	0.138 61	6.877	6.312	0.240 95	11.893	6.282	0.329 90	16.179	6.313
0.070 05	3.491	6.303	0.173 05	8.569	6.308	0.271 16	13.358	6.286	0.356 76	17.465	6.318
0.106 83	5.311	6.309	0.206 23	10.195	6.298	0.302 97	14.884	6.310	0.384 38	18.784	6.321

35 °C

0.036 16	1.486	11.827	0.143 90	5.849	11.917	0.233 20	9.416	11.934	0.325 23	13.021	11.989
0.068 93	2.821	11.873	0.178 15	7.226	11.913	0.263 47	10.609	11.951	0.355 38	14.188	12.008
0.112 49	4.586	11.896	0.207 07	8.380	11.921	0.298 07	11.963	11.974	0.383 55	15.275	12.022

45 °C

0.031 20	1.028	16.766	0.130 23	4.243	16.834	0.225 23	7.260	16.898	0.320 56	10.209	16.985
0.065 23	2.140	16.798	0.159 06	5.161	16.869	0.257 79	8.275	16.928	0.353 18	11.201	17.015
0.097 29	3.182	16.809	0.191 38	6.193	16.874	0.286 90	9.174	16.958	0.389 37	12.289	17.053

2-Propanol

5 °C

0.035 74	2.668	-10.488	0.139 12	10.385	-10.702	0.226 59	16.905	-10.853	0.310 20	23.113	-10.957
0.073 49	5.488	-10.586	0.172 53	12.862	-10.704	0.253 41	18.894	-10.876	0.334 63	24.925	-10.989
0.109 44	8.168	-10.632	0.197 66	14.747	-10.796	0.280 44	20.904	-10.918	0.362 06	26.948	-11.006

15 °C

0.035 34	2.193	-0.751	0.125 59	7.792	-0.939	0.213 36	13.219	-1.071	0.308 34	19.063	-1.188
0.067 30	4.180	-0.855	0.158 21	9.807	-0.973	0.241 75	14.971	-1.113	0.333 75	20.617	-1.210
0.098 90	6.135	-0.874	0.184 84	11.453	-1.014	0.276 45	17.105	-1.152	0.363 74	22.458	-1.252

25 °C

0.037 45	1.942	6.134	0.130 46	6.747	6.031	0.225 76	11.632	5.958	0.315 45	16.201	5.881
0.066 49	3.446	6.092	0.167 40	8.647	5.995	0.258 04	13.278	5.934	0.342 35	17.563	5.862
0.099 42	5.147	6.061	0.197 58	10.193	5.974	0.286 41	14.724	5.907	0.371 57	19.042	5.838

35 °C

0.032 41	1.399	11.531	0.124 18	5.323	11.533	0.220 69	9.409	11.488	0.314 35	13.332	11.444
0.064 08	2.755	11.571	0.156 32	6.688	11.520	0.251 89	10.721	11.472	0.344 08	14.566	11.435
0.095 95	4.121	11.537	0.189 54	8.094	11.505	0.283 73	12.055	11.457	0.370 11	15.640	11.431

45 °C

0.022 87	0.803	16.303	0.116 74	4.065	16.313	0.208 50	7.201	16.325	0.303 54	10.388	16.350
0.052 63	1.843	16.307	0.149 34	5.187	16.310	0.240 79	8.293	16.327	0.332 12	11.338	16.352
0.087 19	3.044	16.310	0.180 12	6.238	16.317	0.275 72	9.463	16.339	0.363 31	12.367	16.358

1-Butanol

5 °C

0.042 49	4.109	-18.764	0.128 66	12.330	-18.350	0.201 39	19.157	-18.022	0.271 97	25.692	-17.729
0.071 99	6.939	-18.609	0.150 77	14.413	-18.235	0.222 12	21.091	-17.951	0.298 05	28.082	-17.618
0.101 42	9.746	-18.471	0.180 17	17.173	-18.107	0.245 45	23.247	-17.838	0.324 82	30.512	-17.485

15 °C

|											
0.034 17	2.747	-5.467	0.125 22	9.959	-5.156	0.200 67	15.822	-4.916	0.269 40	21.071	-4.695
0.066 77	5.339	-5.277	0.151 22	11.992	-5.077	0.223 30	17.560	-4.844	0.292 86	22.840	-4.614
0.097 56	7.784	-5.246	0.175 50	13.877	-4.994	0.247 32	19.394	-4.766	0.316 63	24.628	-4.544

Table 1 (Continued)

Column units: $m/(\mathrm{mol\cdot kg^{-1}})$; $(u-u_1)/(\mathrm{m\cdot s^{-1}})$; $\phi_K/(\mathrm{cm^3\cdot GPa^{-1}\cdot mol^{-1}})$

m	$u-u_1$	ϕ_K	m	ϕ_K	$u-u_1$	m	$u-u_1$	ϕ_K	m	$u-u_1$	ϕ_K
1-Butanol											
25 °C											
0.036 18	2.403	4.345	0.121 74	4.534	8.005	0.197 52	12.857	4.746	0.266 66	17.178	4.981
0.067 23	4.451	4.397	0.147 69	4.589	9.682	0.221 89	14.392	4.825	0.290 37	18.638	5.062
0.095 22	6.280	4.480	0.172 86	4.674	11.290	0.244 40	15.798	4.903	0.315 05	20.151	5.137
35 °C											
0.036 97	2.007	12.173	0.118 69	12.339	6.371	0.197 60	10.453	12.610	0.273 45	14.266	12.860
0.065 63	3.550	12.221	0.146 93	12.439	7.845	0.223 73	11.786	12.678	0.295 44	15.350	12.935
0.093 18	5.022	12.271	0.173 05	12.523	9.197	0.248 97	13.051	12.771	0.321 44	16.616	13.029
45 °C											
0.030 14	1.308	18.868	0.118 91	19.125	5.069	0.202 40	8.462	19.424	0.275 97	11.320	19.727
0.060 39	2.606	18.945	0.146 92	19.215	6.225	0.228 00	9.470	19.528	0.300 56	12.244	19.838
0.091 72	3.931	19.049	0.175 77	19.317	7.398	0.252 28	10.414	19.625	0.325 10	13.163	19.932
2-Methyl-1-propanol											
5 °C											
0.037 45	3.554	−17.584	0.134 34	−17.167	12.625	0.213 84	19.942	−16.853	0.286 29	26.496	−16.536
0.072 53	6.859	−17.434	0.160 23	−17.079	15.024	0.239 23	22.255	−16.754	0.309 45	28.562	−16.419
0.103 94	9.799	−17.303	0.187 88	−16.954	17.565	0.263 02	24.407	−16.650	0.326 65	30.103	−16.362
15 °C											
0.036 30	2.872	−4.792	0.128 11	−4.444	10.018	0.204 98	15.895	−4.228	0.274 90	21.156	−4.038
0.067 11	5.285	−4.638	0.156 67	−4.367	12.214	0.229 92	17.780	−4.157	0.298 65	22.925	−3.975
0.100 01	7.845	−4.526	0.181 33	−4.292	14.097	0.252 28	19.462	−4.097	0.321 78	24.642	−3.920
25 °C											
0.037 67	2.465	4.782	0.133 90	5.011	8.658	0.213 86	13.687	5.210	0.287 05	18.196	5.397
0.068 97	4.494	4.871	0.161 94	5.083	10.433	0.239 27	15.258	5.286	0.310 29	19.608	5.458
0.104 08	6.753	4.950	0.187 36	5.131	12.036	0.263 66	16.765	5.336	0.332 31	20.936	5.519
35 °C											
0.024 34	1.307	12.324	0.117 71	12.526	6.236	0.197 40	10.324	12.736	0.276 71	14.260	12.998
0.057 19	3.058	12.380	0.143 70	12.599	7.580	0.221 92	11.556	12.811	0.300 75	15.438	13.061
0.087 28	4.642	12.475	0.171 44	12.668	9.004	0.249 10	12.908	12.897	0.324 23	16.569	13.141
45 °C											
0.042 20	1.821	18.743	0.132 13	19.040	5.590	0.214 08	8.908	19.272	0.290 08	11.856	19.542
0.072 95	3.128	18.835	0.159 50	19.085	6.720	0.239 88	9.916	19.376	0.314 64	12.772	19.652
0.101 93	4.340	18.947	0.187 34	19.172	7.846	0.266 02	10.928	19.471	0.335 46	13.537	19.747
2-Butanol											
5 °C											
0.029 59	2.959	−20.719	0.111 82	−20.389	11.098	0.191 36	18.888	−20.195	0.270 98	26.591	−19.984
0.055 93	5.572	−20.521	0.143 04	−20.317	14.167	0.218 77	21.551	−20.125	0.296 76	29.072	−19.930
0.081 95	8.149	−20.452	0.166 95	−20.285	16.514	0.245 46	24.133	−20.054	0.324 95	31.761	−19.843
15 °C											
0.031 20	2.614	−7.545	0.120 12	−7.384	9.988	0.200 30	16.553	−7.277	0.275 38	22.619	−7.160
0.063 13	5.258	−7.318	0.147 95	−7.351	12.277	0.226 47	18.679	−7.244	0.300 77	24.655	−7.124
0.092 35	7.692	−7.399	0.174 11	−7.309	14.417	0.251 28	20.680	−7.197	0.325 47	26.623	−7.080

2-Butanol

25 °C	0.029 90	2.109	1.813	0.117 61	8.213	2.000	0.198 17	13.733	2.105	0.274 60	18.886	2.215
	0.059 64	4.188	1.922	0.143 78	10.016	2.032	0.224 09	15.490	2.141	0.301 56	20.679	2.265
	0.091 07	6.376	1.963	0.169 91	11.808	2.062	0.250 89	17.294	2.186	0.326 69	22.347	2.300
35 °C	0.031 77	1.855	9.628	0.121 83	7.043	9.734	0.203 19	11.625	9.874	0.273 21	15.487	10.004
	0.063 37	3.689	9.649	0.154 17	8.879	9.778	0.228 87	13.050	9.922	0.299 30	16.903	10.060
	0.092 31	5.353	9.705	0.179 31	10.293	9.824	0.251 72	14.310	9.963	0.322 23	18.137	10.112
45 °C	0.031 05	1.486	16.060	0.118 15	5.581	16.218	0.196 96	9.175	16.414	0.271 17	12.463	16.604
	0.063 38	3.019	16.115	0.144 94	6.814	16.286	0.223 77	10.373	16.484	0.301 64	13.785	16.685
	0.090 93	4.311	16.180	0.170 38	7.971	16.359	0.245 67	11.345	16.536	0.331 08	15.042	16.773

2-Methyl-2-propanol

5 °C	0.028 50	2.919	−20.855	0.119 38	12.190	−20.880	0.214 55	21.802	−20.789	0.285 74	28.938	−20.739
	0.059 75	6.115	−20.884	0.152 81	15.576	−20.843	0.233 76	23.728	−20.763	0.310 98	31.451	−20.709
	0.089 04	9.095	−20.825	0.184 41	18.765	−20.807	0.255 78	25.940	−20.758	0.338 72	34.209	−20.685
15 °C	0.031 63	2.732	−7.920	0.120 66	10.354	−7.822	0.204 91	17.508	−7.832	0.284 79	24.219	−7.808
	0.057 14	4.922	−7.845	0.148 43	12.717	−7.817	0.231 69	19.766	−7.826	0.310 29	26.348	−7.800
	0.089 34	7.687	−7.877	0.174 66	14.947	−7.830	0.259 29	22.082	−7.812	0.336 91	28.558	−7.782
25 °C	0.035 39	2.576	1.568	0.117 35	8.480	1.644	0.203 99	14.655	1.646	0.284 26	20.293	1.687
	0.063 18	4.585	1.617	0.146 21	10.547	1.637	0.227 25	16.292	1.669	0.309 95	22.085	1.694
	0.088 70	6.426	1.617	0.176 47	12.703	1.640	0.257 64	18.430	1.676	0.338 11	24.039	1.707
35 °C	0.032 09	1.963	8.981	0.119 02	7.207	9.099	0.208 74	12.524	9.173	0.294 03	17.485	9.248
	0.061 51	3.750	9.019	0.152 98	9.235	9.113	0.237 95	14.233	9.199	0.318 20	18.872	9.274
	0.091 34	5.550	9.054	0.181 17	10.903	9.143	0.266 52	15.897	9.219	0.340 64	20.152	9.300
45 °C	0.029 35	1.476	15.546	0.118 77	5.900	15.675	0.214 95	10.533	15.824	0.305 52	14.765	15.989
	0.056 38	2.819	15.643	0.149 54	7.394	15.731	0.246 96	12.044	15.879	0.335 19	16.122	16.049
	0.086 64	4.321	15.641	0.181 23	8.923	15.773	0.278 97	13.542	15.931			

1-Pentanol

5 °C	0.026 92	3.242	−26.852	0.096 94	11.540	−26.051	0.162 02	19.067	−25.270			
	0.047 85	5.745	−26.643	0.120 50	14.296	−25.827	0.183 61	21.531	−25.036			
	0.073 64	8.807	−26.378	0.141 81	16.760	−25.566	0.206 23	24.087	−24.772			
15 °C	0.021 90	2.202	−10.244	0.089 02	8.834	−9.606	0.153 12	15.000	−8.990			
	0.044 47	4.449	−9.989	0.108 94	10.764	−9.393	0.175 46	17.104	−8.753			
	0.064 53	6.431	−9.803	0.129 81	12.779	−9.225	0.196 54	19.072	−8.537			
25 °C	0.021 11	1.746	2.608	0.084 06	6.853	3.101	0.147 95	11.895	3.555			
	0.046 00	3.775	2.908	0.105 37	8.555	3.228	0.168 15	13.446	3.745			
	0.064 01	5.236	3.005	0.129 79	10.480	3.410	0.189 24	15.043	3.954			
35 °C	0.020 39	1.378	12.512	0.061 23	4.089	12.840	0.107 38	7.060	13.286	0.164 68	10.643	13.745
	0.042 64	2.867	12.638	0.084 48	5.607	13.001	0.126 90	8.288	13.474	0.182 30	11.706	13.928

Table 1 (Continued)

m/(mol·kg⁻¹)	$(u - u_1)$/(m·s⁻¹)	ϕ_{KZ}/(cm³·GPa⁻¹·mol⁻¹)	m/(mol·kg⁻¹)	$(u - u_1)$/(m·s⁻¹)	ϕ_{KZ}/(cm³·GPa⁻¹·mol⁻¹)	m/(mol·kg⁻¹)	$(u - u_1)$/(m·s⁻¹)	ϕ_{KZ}/(cm³·GPa⁻¹·mol⁻¹)	m/(mol·kg⁻¹)	$(u - u_1)$/(m·s⁻¹)	ϕ_{KZ}/(cm³·GPa⁻¹·mol⁻¹)
1-Pentanol											
45 °C											
0.028 31	1.529	20.900	0.074 26	3.916	21.495	0.118 30	6.139	21.851			
0.051 65	2.754	21.225	0.094 91	4.975	21.618	0.141 21	7.236	22.157			
2,2-Dimethyl-1-propanol											
5 °C											
0.026 86	3.251	−27.453	0.072 45	8.725	−27.139	0.114 28	13.683	−26.760	0.152 89	18.181	−26.296
0.043 22	5.222	−27.344	0.087 74	10.541	−26.977	0.128 56	15.368	−26.662	0.167 72	19.905	−26.171
0.057 42	6.924	−27.213	0.100 75	12.074	−26.803	0.141 24	16.842	−26.491			
15 °C											
0.023 37	2.356	−10.623	0.071 39	7.180	−10.631	0.112 18	11.222	−10.426	0.152 20	15.125	−10.143
0.038 52	3.879	−10.602	0.086 13	8.647	−10.566	0.126 11	12.597	−10.379			
0.055 96	5.645	−10.771	0.099 52	9.973	−10.494	0.139 39	13.885	−10.249			
25 °C											
0.016 14	1.389	0.319	0.070 25	5.914	1.252	0.115 83	9.662	1.553	0.151 85	12.559	1.849
0.037 93	3.236	0.689	0.086 29	7.242	1.351	0.125 80	10.470	1.630	0.168 31	13.882	1.928
0.054 88	4.625	1.252	0.101 58	8.499	1.451	0.138 50	11.497	1.715			
35 °C											
0.020 90	1.456	10.907	0.068 02	4.701	11.068	0.114 30	7.801	11.410	0.154 59	10.442	11.681
0.037 49	2.624	10.663	0.084 69	5.830	11.169	0.125 91	8.567	11.492			
0.052 14	3.628	10.850	0.099 48	6.818	11.294	0.139 89	9.463	11.672			
45 °C											
0.019 64	1.105	19.233	0.075 22	4.113	19.961	0.125 46	6.750	20.309	0.166 57	8.839	20.606
0.037 40	2.081	19.531	0.091 75	4.999	20.023	0.138 44	7.431	20.342			
0.058 74	3.252	19.625	0.110 40	5.983	20.132	0.150 97	8.067	20.442			
2-Methyl-2-butanol											
5 °C											
0.018 65	2.353	−31.247	0.072 29	9.074	−30.938	0.124 97	15.607	−30.635			
0.039 42	4.967	−31.185	0.090 96	11.398	−30.837	0.140 71	17.548	−30.554			
0.055 66	6.999	−31.049	0.108 41	13.562	−30.738	0.156 50	19.488	−30.467			
15 °C											
0.019 00	2.030	−15.078	0.071 77	7.623	−14.844	0.121 92	12.885	−14.664			
0.036 88	3.933	−15.007	0.088 21	9.354	−14.786	0.137 12	14.465	−14.590			
0.054 12	5.761	−14.937	0.106 12	11.234	−14.727	0.154 01	16.214	−14.508			
25 °C											
0.018 54	1.677	−3.158	0.073 66	6.624	−3.044	0.124 09	11.090	−2.895			
0.038 06	3.436	−3.125	0.089 11	8.000	−3.011	0.139 42	12.433	−2.835			
0.057 20	5.155	−3.101	0.150 71	9.467	−2.939	0.156 09	13.889	−2.779			
35 °C											
0.019 28	1.464	6.469	0.072 85	5.489	6.601	0.122 53	9.160	6.749			
0.038 62	2.923	6.537	0.089 37	6.716	6.651	0.138 73	10.347	6.787			
0.056 06	4.234	6.562	0.105 34	7.898	6.689	0.157 20	11.691	6.839			
45 °C											
0.016 47	1.033	14.662	0.067 29	4.167	14.920	0.119 75	7.349	15.039			
0.032 55	2.027	14.854	0.085 90	5.305	14.946	0.138 89	8.492	15.097			
0.050 91	3.166	14.833	0.103 77	6.391	14.975	0.155 98	9.504	15.153			

1-Hexanol — $m/(\text{mol·kg}^{-1})$, $(u - u_1)$, and ϕ_{K_2}

T	m	$(u - u_1)$	ϕ_{K_2}
5 °C	0.009 54	1.380	-35.295
	0.011 03	1.600	-35.577
	0.017 34	2.498	-34.901
	0.019 71	2.849	-35.240
	0.026 36	3.790	-34.725
	0.028 88	4.142	-34.484
	0.036 00	5.160	-34.438
	0.037 30	5.342	-34.361
	0.045 18	6.439	-33.899
	0.047 04	6.705	-33.916
	0.054 70	7.775	-33.658
	0.056 97	8.083	-33.487
15 °C	0.009 49	1.138	-14.487
	0.010 67	1.270	-13.923
	0.017 84	2.143	-14.635
	0.020 30	2.438	-14.624
	0.028 09	3.353	-14.175
	0.031 82	3.807	-14.357
	0.037 84	4.500	-13.913
	0.042 46	5.055	-14.006
	0.046 99	5.553	-13.459
	0.052 34	6.188	-13.504
	0.054 01	6.362	-13.233
25 °C	0.010 25	1.013	0.853
	0.010 55	1.026	1.798
	0.017 44	1.713	1.186
	0.020 40	1.995	1.430
	0.026 74	2.620	1.291
	0.031 98	3.135	1.239
	0.037 08	3.604	1.718
	0.042 64	4.136	1.812
	0.046 07	4.461	1.897
	0.051 16	4.924	2.225
	0.052 59	5.059	2.249
35 °C	0.007 41	0.593	13.309
	0.011 92	0.950	13.476
	0.016 80	1.335	13.587
	0.021 62	1.709	13.803
	0.025 10	1.996	13.512
	0.030 33	2.388	13.941
	0.032 93	2.600	13.800
	0.036 96	2.901	14.048
	0.042 96	3.371	14.031
	0.045 64	3.550	14.413
45 °C	0.008 58	0.551	23.204
	0.008 91	0.568	23.468
	0.017 76	1.123	23.726
	0.018 56	1.178	23.589
	0.025 81	1.622	23.915
	0.026 29	1.647	24.024
	0.032 51	2.040	23.943
	0.034 47	2.147	24.197
	0.042 38	2.609	24.576
	0.046 33	2.823	24.916
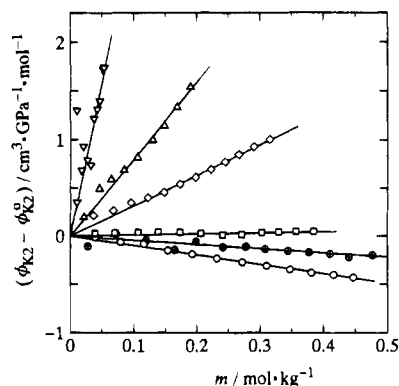
Figure 1. Concentration dependence of the apparent molar adiabatic compressions of 1-alcohols in dilute aqueous solutions at 25 °C; $\oplus$, methanol; $\bigcirc$, ethanol; $\square$, 1-propanol; $\Diamond$, 1-butanol; $\triangle$, 1-pentanol; $\triangledown$, 1-hexanol.

tions and water $(u - u_1)$ and apparent molar adiabatic compressions of the alcohols ϕ_{K_2} for all systems studied.

For sufficiently dilute solutions the concentration dependence of ϕ_{K_2} can be represented by the linear relation

$$\phi_{K_2} = \phi_{K_2}{}^\circ + B_K m \qquad (4)$$

where $\phi_{K_2}{}^\circ$ is equal to the limiting partial molar adiabatic compression K_2° and B_K is an empirical constant. Figure 1 shows the plots of $\phi_{K_2} - \phi_{K_2}{}^\circ$ vs m for 1-alcohols at 25 °C. It is clear that a good linear correlation holds in the concentration range studied. The parameters $\phi_{K_2}{}^\circ$ and B_K were evaluated by the least-squares method described in a previous paper (4). These values together with their standard deviations and the molar adiabatic compressions K_2^* are summarized in Table 2. For the purpose of comparison, some relevant literature values of K_2° (3, 6−12) are also given in Table 2. The precision of our limiting partial molar adiabatic compressions is believed to be better than 0.5 cm³ GPa⁻¹ mol⁻¹ for most cases.

It can be seen that the K_2° values of alcohols in water are much smaller than the K_2^* values and are negative for longer chain homologoues at lower temperatures. It is well-known that partial molar volumes of alcohols in water are always smaller than the molar volumes (1). These negative excess partial molar quantities may be attributed to the fact that the free space around alcohol molecules in water is significantly less than that in pure liquid alcohols owing to the small size (13) and high cohesive energy density of water (14). Furthermore, we have reported that the limiting partial molar compressions of water in various alcohols are appreciably negative (4). In alcohol−water systems, strong associations due to hydrogen bonding between the alcohol and water may be predominantly responsible for the volumetric properties (2).

Figure 2 shows the K_2° values for the 1-alcohol series as a function of temperature. With increasing chain length, the K_2° values decrease at lower temperature, are nearly constant at about 35 °C, and increase slightly at 45 °C. A similar feature has been reported by Nakajima et al. (3) and Hoiland (8). This means that the sign of a methylene group contribution to the partial molar compression K°-(CH_2) changes with temperature. The values of $K^\circ(CH_2)$ can be obtained from the subtraction process

$$K^\circ(CH_2) = K^\circ(N + 1) - K^\circ(N) \qquad (5)$$

where $K^\circ(N)$ refers to the partial molar adiabatic compression of the 1-alcohol containing N carbon atoms. The K°-(CH_2) values estimated at various temperatures are illus-

Table 2. Molar Adiabatic Compressions, Limiting Partial Molar Adiabatic Compressions, and B_K Parameters for Alcohols in Water

$t/°C$	$K_2^*/(cm^3 GPa^{-1} mol^{-1})$	$K_2°/(cm^3 GPa^{-1} mol^{-1})$	$B_K/(cm^3 kg\,GPa^{-1} mol^{-2})$	$K_2°/(cm^3 GPa^{-1} mol^{-1})$ in refs
Methanol				
5	36.12	6.99(0.01)[a]	-0.97(0.02)	7.3,[b] 6.8[c]
15	39.25	10.16(0.01)	-0.54(0.02)	
25	42.63	12.45(0.02)	-0.43(0.06)	12.6,[b] 12.6,[c] 12.5[d]
35	46.42	14.24(0.02)	-0.29(0.04)	
45	50.61	15.83(0.01)	-0.23(0.02)	15.9,[b] 15.8[c]
Ethanol				
5	48.72	-0.71(0.02)	-1.78(0.05)	-0.8,[b] -1.4[c]
15	52.81	5.47(0.01)	-1.40(0.02)	
25	57.29	9.82(0.01)	-0.97(0.02)	10.0,[b] 9.9,[c] 9.9[d]
35	62.24	13.39(0.01)	-0.63(0.02)	
45	67.72	16.43(0.01)	-0.19(0.01)	16.5,[b] 16.3[c]
1-Propanol				
5	55.54	-10.55(0.02)	0.12(0.05)	-10.8,[b] -10.7,[c] -10.8,[e] -21[f]
15	59.93	-0.84(0.01)	0.02(0.03)	
25	64.73	6.27(0.01)	0.10(0.04)	6.3,[b] 6.4,[c] 5.8[g]
35	69.99	11.82(0.01)	0.51(0.03)	11.6[g]
45	75.81	16.71(0.01)	0.85(0.03)	16.9,[b] 17.3[c]
2-Propanol				
5	64.67	-10.50(0.02)	-1.44(0.08)	-4.7,[c] -10.8[e]
15	70.08	-0.77(0.01)	-1.31(0.05)	
25	76.10	6.13(0.01)	-0.80(0.01)	11.0,[c] 6.2,[d] 6.1[g]
35	82.86	11.57(0.01)	-0.41(0.02)	11.2[g]
45	90.56	16.28(0.01)	0.21(0.01)	22.8[c]
1-Butanol				
5	64.22	-18.90(0.01)	4.35(0.05)	-19.0,[b] -20.2,[c] -19.0[e]
15	69.07	-5.55(0.01)	3.18(0.04)	
25	74.34	4.13(0.02)	3.16(0.07)	4.6,[b] 4.7,[c] 4.5[g]
35	80.08	11.94(0.01)	3.34(0.06)	12.2[g]
45	86.41	18.63(0.02)	3.97(0.08)	19.0,[b] 19.1[c]
2-Methyl-1-propanol				
5	71.04	-17.76(0.02)	4.29(0.06)	-14.7[c]
15	76.56	-4.79(0.01)	2.73(0.04)	
25	82.56	4.67(0.01)	2.54(0.03)	9.4[c]
35	89.21	12.16(0.02)	2.99(0.07)	
45	96.54	18.52(0.03)	3.58(0.10)	24.9[c]
2-Butanol				
5	67.20	-20.69(0.01)	2.60(0.05)	-21.6,[c] -20.1[e]
15	72.53	-7.55(0.02)	1.43(0.08)	
25	78.51	1.81(0.01)	1.47(0.03)	7.4,[c] 2.0,[g] 4.9[h]
35	85.27	9.49(0.01)	1.88(0.05)	10.0[g]
45	92.96	15.91(0.01)	2.55(0.04)	28.6[c]
2-Methyl-2-propanol				
5		-20.94(0.01)	0.76(0.05)	-9.7,[c] -20.5[i]
15		-7.87(0.01)	0.26(0.05)	
25		1.58(0.01)	0.36(0.03)	7.5,[c] 3.8[d]
35	107.93	8.96(0.01)	0.96(0.02)	
45	120.47	15.46(0.02)	1.69(0.06)	13.4[c]
1-Pentanol				
5	71.63	-27.24(0.03)	12.00(0.20)	-27.1,[b] -27.1[e]
15	76.82	-10.47(0.03)	9.78(0.16)	
25	82.47	2.41(0.06)	7.98(0.39)	2.6,[b] 2.3[g]
35	88.64	12.30(0.05)	8.89(0.31)	12.4[g]
45	95.40	20.65(0.09)	10.48(0.74)	21.3[b]
2,2-Dimethyl-1-propanol				
5		-27.84(0.07)	9.83(0.51)	
15		-11.03(0.07)	5.63(0.59)	
25		0.69(0.07)	7.40(0.52)	
35		10.50(0.07)	7.88(0.56)	
45		19.26(0.06)	7.94(0.47)	
2-Methyl-2-butanol				
5	83.04	-31.36(0.01)	5.75(0.11)	
15	90.28	-15.16(0.02)	4.20(0.12)	
25	98.16	-3.28(0.01)	3.19(0.12)	
35	106.95	6.40(0.01)	2.74(0.06)	
45	116.88	14.69(0.02)	2.88(0.18)	
1-Hexanol				
5	78.87	-35.79(0.11)	40.0(2.3)	-33.8[c]
15	84.47	-15.27(0.25)	35.4(5.6)	
25	90.56	0.51(0.21)	31.8(4.9)	0.5[g]
35	97.20	13.03(0.21)	26.8(5.7)	13.3[g]
45	104.45	22.74(0.18)	44.3(4.9)	

[a] Standard deviations are in parentheses. [b] Reference 3. [c] Reference 6. [d] Reference 7. [e] Reference 8. [f] Reference 9. [g] Reference 10. [h] Reference 11. [i] Reference 12.
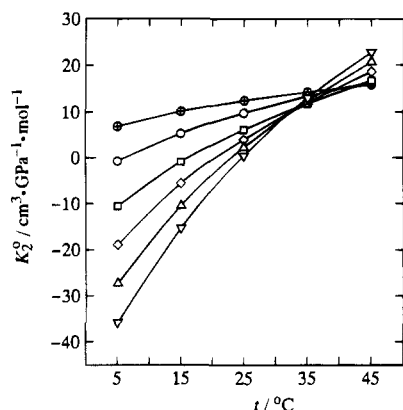
Figure 2. Temperature dependence of the limiting partial molar adiabatic compressions of 1-alcohols in water. The symbols are the same as in Figure 1.
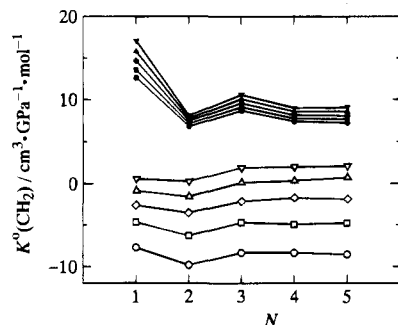

Figure 3. Methylene group contributions to partial molar adiabatic compressions (open symbols) and to molar compressions (filled symbols) as a function of the carbon number of 1-alcohols: $\bigcirc$, 5 °C; $\square$, 15 °C; $\lozenge$, 25 °C; $\triangle$, 35 °C; $\triangledown$, 45 °C.

trated as a function of N in Figure 3, in which analogous methylene contributions $K^*(CH_2)$ estimated from the molar adiabatic compressions of neat alcohols are also described by filled symbols. The $K^\circ(CH_2)$ values are considerably less than $K^*(CH_2)$. As has been described previously, on the other hand, the partial molar expansion of a methylene group is obviously larger than the corresponding molar expansion, except for $N = 1$ due to the exceptional behavior of methyl alcohol (*2, 4*). Thus, the introduction of a methylene group into water results in solutions less compressible and more expansive. It appears to be a fairly natural consequence since there is no appreciable interaction between hydrophobic groups and water.

The temperature dependences of K_2° of the branched isomers of butyl and pentyl alcohols are shown in Figure 4. The K_2° values of *n*- and *i*-PrOH fell virtually on the same smooth curve and are not illustrated. It appears that the chain branching influences both the K_2° values and their temperature dependences only a little. This is in contrast to the results of the partial molar volumes and thermal expansions of these isomers (*2*). It is difficult to explain these conflicting results. However, considering the fact that both partial molar expansions and compressions of buty acetates in water are little affected by chain branching (*15*), the unique expansion properties found for branched-chain alcohols may arise from hydrogen-bonding interactions between alcohols and water, not from so-called hydrophobic hydration.

The concentration dependence of the apparent molar adiabatic compression in dilute solution B_K is shown in Figure 5 as a function of temperature. It is well-known that the corresponding parameter B_V for apparent molar
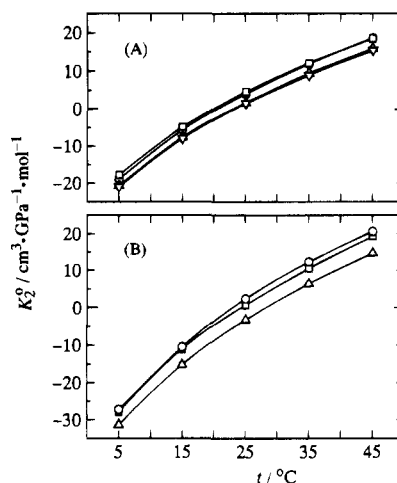
Figure 4. Effects of chain branching on the limiting partial molar adiabatic compressions: (A) $\bigcirc$, 1-butanol; $\square$, 2-methyl-1-propanol; $\triangle$, 2-butanol; $\triangledown$, 2-methyl-2-propanol; (B) $\bigcirc$, 1-pentanol; $\square$, 2,2-dimethyl-1-propanol; $\triangle$, 2-methyl-2-butanol.
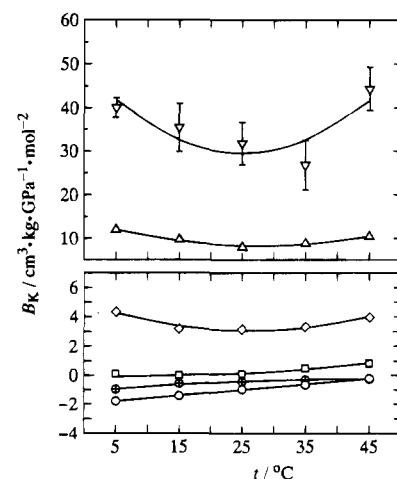
Figure 5. Temperature dependence of the B_K parameter in eq 4 for 1-alcohols. The symbols are the same as in Figure 1. The bars refer to the standard deviations.

volume is negative for aqueous alcohol systems and becomes more negative with decreasing temperature or increasing chain length and chain branching (*2*). On the other hand, complicating features are observed for the compression; that is, for MeOH and EtOH the B_K values are slightly negative and more negative with decreasing temperature in a manner similar to B_V. With the further increase in chain length, however, the B_K becomes positive and increases enormously for *n*-PenOH or *n*-HexOH. The temperature dependence of B_K for these homologues is also peculiar. However, the chain branching brings about smaller B_K values analogously to B_V. These complicating B_K features are not easy to interpret. Further systematic studies must be done on other solute−solvent systems to prove the concentration dependence of the apparent molar compression.

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