Partial Molar Volumes of Alkyl Acetates in Water

Masao Sakurai,* Kunio Nakamura, and Katsutoshi Nitta

Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060, Japan

The densities of dilute aqueous solutions of eight alkyl acetates (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, *tert*-butyl acetates) were measured at 5, 15, 25, 35, and 45 °C by means of a vibrating tube densimeter. The limiting partial molar volumes and its temperature dependences for the alkyl acetates in water were estimated and compared with those for more hydrophilic solutes, alcohols, reported previously. The results were discussed in terms of the effects of chain length and chain branching of alkyl residues on the solute−solvent interactions.

Introduction

Volumetric behavior of dilute aqueous solutions is useful in the study of solute−water interactions. Especially the effect of nonpolar residues on the structure of water, so-called iceberg formation or hydrophobic hydration, has received considerable attention in the literature (Franks and Reid, 1973), since the hydrophobic interactions may play an important role in protein folding phenomena (Kauzmann, 1959). Although the partial molar volumes of various nonelectrolytes in water have been extensively studied, the volume change accompanying iceberg formation is still uncertain (Sakurai, 1987). One reason for this obscurity may be the few data concerning the really hydrophobic solutes in water, because of the difficulty in estimation of the accurate partial molar quantities due to their low solubilities.

Instead of using nonpolar solutes, more hydrophilic solutes, e.g., alcohols, have often been utilized for the investigation of the effects of alkyl residues on the water structure, regarding the alcohols as "soluble hydrocarbons" rather than as "alkylated water" (Franks and Desnoyers, 1985). On the basis of the study of the temperature dependence of the partial molar volumes of various alcohols in water, however, we have pointed out the relative importance of the hydrogen-bonding interactions between alcohols and water rather than the interactions between nonpolar groups and water (Sakurai et al., 1994a).

Our earlier paper on aqueous benzene and alkylbenzene solutions showed no anomalous volumetric behavior in these hydrocarbon−water systems (Sakurai, 1990). The results suggest that the characteristic volumetric feature found in aqueous solutions of monofunctional nonelectrolytes, such as alcohols, ethers, or amines, may originate from the interactions between polar groups in organic solutes and water molecules, rather than the nonpolar group−water interactions. In the present paper we will report the results of the densities of dilute aqueous solutions of some alkyl acetates, fairly hydrophobic solutes, in order to obtain further information on the hydration behavior of alkyl groups.

Experimental Section

The solution densities ρ were determined with a vibrating tube densimeter (Anton Paar, DMA 60) operated in a phase-locked loop mode using two measuring cells (DMA 601) (Sakurai et al., 1982; Sakurai, 1987). The cell constant at each temperature was determined by the measurements for pure water (Kell, 1975) and dry air. The precision of the measured density values is believed to be better than $\pm 2 \times 10^{-6}$ g·cm^{-3} for the dilute solution range studied. The temperature of the measuring cell of the densimeter was maintained within ±0.002 °C by a laboratory-made controller using a Y-cut quartz as a temperature sensor.

The alkyl acetates used were methyl (MeAc), ethyl (EtAc), propyl (PrAc), isopropyl (*i*-PrAc), butyl (BuAc), isobutyl (*i*-BuAc), *sec*-butyl (*s*-BuAc), and *tert*-butyl acetates (*t*-BuAc). They were purified by fractional distillation and stored over a molecular sieve 3A. The densities of the pure alkyl acetates are given in Table 1. The water was doubly distilled by using a quartz still.

All solutions were prepared by successive additions of pure acetates to a known quantity of solvent water, which was degassed before using to prevent the formation of bubbles during an experiment. The addition was carried out by mass in a mixing chamber connected to the density measuring cell with a Teflon tube and a flow pump.

Results and Discussion

The density differences between solutions and pure water at various temperatures are listed in Table 2. The apparent molar volume $V_{\phi,2}$ of component 2 in solution is given by the relation

$$V_{\phi,2} = (v - v_1)/m + vM_2 \qquad (1)$$

where v and v_1 are the specific volumes ($=1/\rho$) of solution and solvent, respectively, m is the molality, and M_2 is the molar mass of the solute.

For dilute solutions, the variation of $V_{\phi,2}$ with the concentration can be adequately represented by the linear relation

$$V_{\phi,2} = V^\circ_{\phi,2} + B_V m \qquad (2)$$

where the infinite dilution value $V^\circ_{\phi,2}$ is equal to the limiting partial molar volume V°_2 and B_V is an experimental parameter.

Figure 1 shows the concentration dependence of the apparent molar volumes of alkyl acetates in dilute aqueous solutions at 25 °C. The error bars indicate the uncertainty due to a density error of $\delta\rho = \pm 2 \times 10^{-6}$ g·cm^{-3}. It is apparent that a good linear correlation holds in the concentration range studied, although the uncertainty in $V_{\phi,2}$ rapidly increases as the concentration is reduced. The parameters V°_2 and B_V in eq 2 were evaluated by the least-

* To whom correspondence should be addressed. E-mail: sakurai@indy.polymer.hokudai.ac.jp.

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Table 1. Densities (g·cm^{-3}) of Pure Alkyl Acetates

	t/°C						
solutes	5	15	25			35	45
MeAc	0.953 00	0.940 19	0.927 09	0.927 9[a]	0.927 24[b]	0.913 80	0.900 28
EtAc	0.918 44	0.906 51	0.894 37	0.894 55[a]	0.894 28[c]	0.882 10	0.869 65
PrAc	0.904 55	0.893 61	0.882 50	0.883 03[a]	0.880 81[c]	0.871 28	0.859 93
i-PrAc	0.889 19	0.877 81	0.866 27	0.866 8[a]		0.854 57	0.842 73
BuAc	0.896 49	0.886 37	0.876 14	0.876 36[a]	0.876 09[c]	0.865 85	0.855 43
i-BuAc	0.887 02	0.876 63	0.866 17	0.869 5[a]		0.855 62	0.845 01
s-BuAc	0.886 35	0.875 91	0.865 37			0.854 72	0.843 96
t-BuAc	0.882 59	0.871 64	0.860 57			0.849 38	0.838 07

[a] Riddick and Bunger, 1970. [b] Hnědkovský and Cibulka, 1986. [c] Jimenez et al., 1986.

Table 2. Densities and Apparent Molar Volumes of Alkyl Acetates in Dilute Aqueous Solutions

t/ °C	*m*/ mol·kg^{-1}	$10^3(\rho-\rho_1)$/ g·cm^{-3}	$V_{\phi,2}$/ cm^3·mol^{-1}	*m*/ mol·kg^{-1}	$10^3(\rho-\rho_1)$/ g·cm^{-3}	$V_{\phi,2}$/ cm^3·mol^{-1}	*t*/ °C	*m*/ mol·kg^{-1}	$10^3(\rho-\rho_1)$/ g·cm^{-3}	$V_{\phi,2}$/ cm^3·mol^{-1}	*m*/ mol·kg^{-1}	$10^3(\rho-\rho_1)$/ g·cm^{-3}	$V_{\phi,2}$/ cm^3·mol^{-1}
						Methyl Acetate							
5	0.037 55	0.139	70.370	0.206 16	0.782	70.233		0.134 63	0.271	72.254	0.291 24	0.586	72.232
	0.067 60	0.252	70.336	0.236 34	0.899	70.214		0.166 00	0.335	72.244	0.323 95	0.654	72.220
	0.104 24	0.391	70.303	0.266 33	1.017	70.191	35	0.041 19	0.051	73.268	0.194 09	0.242	73.244
	0.136 81	0.516	70.273	0.299 19	1.147	70.167		0.073 75	0.090	73.282	0.229 11	0.285	73.244
	0.171 30	0.649	70.247	0.333 41	1.282	70.146		0.102 00	0.128	73.245	0.258 82	0.322	73.241
15	0.038 80	0.111	71.273	0.206 87	0.593	71.232		0.134 20	0.167	73.252	0.289 93	0.359	73.244
	0.072 29	0.205	71.291	0.234 83	0.674	71.222		0.162 65	0.202	73.252	0.330 52	0.408	73.244
	0.104 09	0.298	71.257	0.265 90	0.763	71.217	45	0.030 49	0.015	74.308	0.190 59	0.100	74.268
	0.141 25	0.404	71.252	0.299 17	0.861	71.201		0.058 56	0.030	74.286	0.226 47	0.117	74.275
	0.173 86	0.498	71.241	0.329 51	0.950	71.190		0.092 65	0.049	74.268	0.257 94	0.132	74.279
25	0.037 40	0.076	72.248	0.195 07	0.394	72.238		0.125 88	0.066	74.271	0.288 44	0.145	74.288
	0.068 13	0.138	72.251	0.277 48	0.459	72.235		0.161 16	0.084	74.273	0.316 62	0.159	74.287
	0.099 64	0.202	72.244	0.261 09	0.526	72.234							
						Ethyl Acetate							
5	0.030 99	0.043	86.718	0.172 30	0.263	86.560		0.115 15	−0.074	89.020	0.253 69	−0.152	88.983
	0.057 61	0.082	86.679	0.202 28	0.313	86.535		0.146 18	−0.093	89.015	0.282 52	−0.166	88.973
	0.086 18	0.125	86.648	0.227 63	0.357	86.510	35	0.031 41	−0.050	90.251	0.167 91	−0.260	90.226
	0.115 73	0.171	86.617	0.258 48	0.411	86.483		0.059 56	−0.094	90.241	0.194 12	−0.300	90.226
	0.144 96	0.218	86.586	0.284 49	0.457	86.463		0.086 60	−0.137	90.249	0.223 76	−0.345	90.227
15	0.025 55	0.007	87.911	0.164 63	0.064	87.790		0.111 44	−0.175	90.240	0.256 02	−0.393	90.224
	0.051 16	0.017	87.852	0.195 59	0.080	87.769		0.140 35	−0.218	90.227	0.283 44	−0.436	90.231
	0.081 69	0.027	87.852	0.221 72	0.093	87.757	45	0.026 68	−0.066	91.505	0.176 67	−0.430	91.499
	0.106 79	0.037	87.835	0.249 55	0.108	87.742		0.053 27	−0.132	91.516	0.206 05	−0.501	91.503
	0.137 91	0.051	87.811	0.284 20	0.127	87.727		0.078 84	−0.194	91.504	0.243 88	−0.594	91.516
25	0.030 46	−0.021	89.062	0.173 53	−0.107	88.997		0.100 23	−0.246	91.502	0.267 82	−0.650	91.512
	0.056 18	−0.038	89.051	0.198 68	−0.121	88.990		0.125 35	−0.307	91.503	0.295 68	−0.718	91.520
	0.088 38	−0.058	89.032	0.225 82	−0.137	88.990		0.151 67	−0.370	91.499			
						Propyl Acetate							
5	0.020 34	−0.007	102.482	0.116 07	−0.023	102.337		0.062 27	−0.171	105.216	0.162 17	−0.433	105.167
	0.038 50	−0.012	102.450	0.133 27	−0.023	102.312		0.082 16	−0.225	105.214	0.181 13	−0.483	105.169
	0.057 72	−0.017	102.433	0.153 90	−0.021	102.275		0.102 37	−0.278	105.197	0.199 85	−0.531	105.164
	0.078 07	−0.020	102.395	0.173 78	−0.020	102.254	35	0.020 70	−0.082	106.765	0.119 48	−0.458	106.675
	0.094 92	−0.021	102.360	0.192 63	−0.019	102.237		0.042 58	−0.166	106.710	0.138 29	−0.528	106.667
15	0.020 83	−0.033	103.817	0.120 93	−0.183	103.760		0.064 65	−0.249	106.671	0.154 46	−0.589	106.669
	0.040 50	−0.065	103.840	0.140 34	−0.211	103.753		0.083 17	−0.321	106.687	0.173 88	−0.661	106.665
	0.058 23	−0.093	103.835	0.158 88	−0.237	103.744		0.102 60	−0.393	106.665	0.190 68	−0.724	106.667
	0.080 35	−0.124	103.784	0.181 73	−0.269	103.736	45	0.017 38	−0.085	108.138	0.097 55	−0.475	108.160
	0.101 92	−0.156	103.775					0.040 30	−0.197	108.149	0.119 16	−0.577	108.144
25	0.020 34	−0.056	105.210	0.122 80	−0.332	105.190		0.060 80	−0.296	108.140	0.143 82	−0.697	108.161
	0.044 21	−0.122	105.224	0.142 57	−0.384	105.185		0.080 19	−0.391	108.158	0.163 94	−0.793	108.162
						Isopropyl Acetate							
5	0.025 19	−0.036	103.570	0.126 37	−0.149	103.331		0.085 03	−0.314	106.184	0.197 48	−0.711	106.133
	0.044 39	−0.060	103.495	0.152 76	−0.173	103.287		0.108 78	−0.398	106.158	0.221 74	−0.795	106.127
	0.064 21	−0.083	103.438	0.177 73	−0.195	103.254	35	0.022 48	−0.107	107.576	0.123 99	−0.585	107.585
	0.086 96	−0.110	103.413	0.201 46	−0.214	103.221		0.042 97	−0.205	107.597	0.145 66	−0.686	107.587
	0.106 21	−0.129	103.365	0.226 03	−0.233	103.192		0.059 71	−0.284	107.591	0.171 93	−0.807	107.584
15	0.024 60	−0.063	104.798	0.132 72	−0.327	104.728		0.078 18	−0.370	107.576	0.194 37	−0.910	107.583
	0.045 20	−0.115	104.787	0.151 82	−0.373	104.726		0.099 97	−0.472	107.576	0.218 86	−1.022	107.583
	0.065 14	−0.165	104.780	0.174 81	−0.424	104.699	45	0.017 55	−0.102	109.080	0.139 87	−0.797	109.041
	0.085 81	−0.217	104.782	0.199 47	−0.478	104.676		0.039 67	−0.227	109.003	0.160 98	−0.918	109.059
	0.109 44	−0.273	104.753	0.227 08	−0.539	104.659		0.057 58	−0.331	109.041	0.181 11	−1.033	109.073
25	0.018 72	−0.071	106.257	0.128 50	−0.470	106.165		0.081 14	−0.464	109.025	0.199 92	−1.137	109.068
	0.044 22	−0.165	106.206	0.150 36	−0.547	106.153		0.100 39	−0.573	109.026	0.222 48	−1.265	109.081
	0.062 12	−0.229	106.168	0.173 97	−0.630	106.145		0.118 94	−0.679	109.039			
						Butyl Acetate							
5	0.005 26	−0.008	117.686	0.027 03	−0.042	117.723		0.016 62	−0.077	121.173	0.033 22	−0.152	121.125
	0.011 47	−0.018	117.736	0.031 41	−0.050	117.762	35	0.006 48	−0.038	122.801	0.026 66	−0.157	122.838
	0.018 44	−0.029	117.740	0.035 61	−0.056	117.743		0.011 52	−0.070	123.018	0.031 93	−0.188	122.840
	0.022 61	−0.036	117.761	0.039 17	−0.061	117.729		0.016 25	−0.096	122.850	0.036 78	−0.216	122.828
15	0.006 51	−0.020	119.349	0.026 33	−0.082	119.395		0.021 18	−0.126	122.895	0.043 69	−0.255	122.796
	0.012 09	−0.039	119.503	0.031 56	−0.099	119.420	45	0.008 91	−0.062	124.410	0.029 41	−0.206	124.477
	0.016 45	−0.052	119.439	0.036 40	−0.113	119.389		0.013 43	−0.095	124.533	0.034 28	−0.241	124.508
	0.021 54	−0.069	119.483	0.041 13	−0.127	119.374		0.019 34	−0.135	124.443	0.038 87	−0.271	124.452
25	0.006 71	−0.031	121.153	0.021 97	−0.101	121.140		0.024 46	−0.172	124.500	0.043 71	−0.304	124.439
	0.011 84	−0.055	121.182	0.026 97	−0.124	121.144							

Table 2 (Continued)

t/°C	m/mol·kg^{-1}	$10^3(\rho-\rho_1)$/g·cm^{-3}	$V_{\phi,2}$/cm^3·mol^{-1}	m/mol·kg^{-1}	$10^3(\rho-\rho_1)$/g·cm^{-3}	$V_{\phi,2}$/cm^3·mol^{-1}	t/°C	m/mol·kg^{-1}	$10^3(\rho-\rho_1)$/g·cm^{-3}	$V_{\phi,2}$/cm^3·mol^{-1}	m/mol·kg^{-1}	$10^3(\rho-\rho_1)$/g·cm^{-3}	$V_{\phi,2}$/cm^3·mol^{-1}
						Isobutyl Acetate							
5	0.007 11	−0.015	118.276	0.029 88	−0.065	118.347		0.017 76	−0.093	121.782	0.038 97	−0.201	121.717
	0.012 26	−0.027	118.370	0.034 23	−0.076	118.394		0.023 63	−0.122	121.712	0.045 45	−0.234	121.711
	0.016 81	−0.038	118.429	0.039 90	−0.089	118.405	35	0.007 06	−0.045	123.317	0.027 53	−0.178	123.424
	0.021 33	−0.046	118.326	0.045 35	−0.100	118.381		0.011 44	−0.074	123.415	0.032 21	−0.208	123.419
	0.024 92	−0.055	118.378					0.016 32	−0.104	123.321	0.036 60	−0.235	123.385
15	0.005 93	−0.023	120.158	0.028 72	−0.110	120.116		0.021 74	−0.140	123.393	0.044 26	−0.281	123.318
	0.011 42	−0.044	120.132	0.033 36	−0.127	120.095	45	0.008 38	−0.064	125.102	0.029 31	−0.225	125.165
	0.017 50	−0.067	120.110	0.039 70	−0.151	120.094		0.015 47	−0.118	125.101	0.035 76	−0.273	125.128
	0.023 44	−0.090	120.123	0.045 34	−0.171	120.064		0.020 10	−0.154	125.140	0.041 59	−0.319	125.170
25	0.066 10	−0.031	121.617	0.028 46	−0.147	121.717		0.025 79	−0.199	125.202	0.047 95	−0.367	125.160
	0.011 54	−0.059	121.653	0.033 43	−0.172	121.700							
						sec-Butyl Acetate							
5	0.007 14	−0.019	118.828	0.032 26	−0.086	118.840		0.020 04	−0.112	122.139	0.044 48	−0.246	122.097
	0.014 02	−0.038	118.879	0.037 68	−0.100	118.830		0.025 93	−0.144	122.108			
	0.020 13	−0.054	118.853	0.044 35	−0.119	118.862	35	0.006 77	−0.045	123.594	0.030 12	−0.201	123.637
	0.026 00	−0.070	118.865					0.013 37	−0.089	123.607	0.036 32	−0.241	123.603
15	0.007 44	−0.031	120.447	0.031 66	−0.132	120.458		0.018 98	−0.127	123.646	0.042 81	−0.284	123.607
	0.012 89	−0.055	120.548	0.038 34	−0.161	120.492		0.024 64	−0.164	123.615			
	0.019 70	−0.083	120.497	0.044 94	−0.187	120.456	45	0.008 04	−0.064	125.432	0.029 84	−0.235	125.369
	0.025 54	−0.107	120.476					0.013 51	−0.108	125.473	0.034 68	−0.273	125.370
25	0.006 64	−0.037	122.111	0.032 18	−0.178	122.090		0.019 17	−0.150	125.306	0.039 29	−0.309	125.367
	0.013 89	−0.077	122.089	0.038 42	−0.213	122.107		0.024 04	−0.188	125.307			
						tert-Butyl Acetate							
5	0.007 31	−0.020	118.903	0.032 01	−0.089	118.955		0.019 13	−0.107	122.143	0.043 58	−0.241	122.096
	0.013 46	−0.037	118.918	0.038 63	−0.107	118.947		0.025 86	−0.145	122.162			
	0.019 30	−0.054	118.969	0.045 13	−0.124	118.927	35	0.006 88	−0.047	123.781	0.030 56	−0.207	123.739
	0.025 78	−0.071	118.927					0.013 43	−0.091	123.728	0.036 71	−0.247	123.698
15	0.007 58	−0.032	120.502	0.031 78	−0.134	120.506		0.019 50	−0.133	123.778	0.043 19	−0.291	123.713
	0.013 18	−0.056	120.530	0.038 86	−0.164	120.513		0.025 37	−0.172	123.741			
	0.018 59	−0.079	120.533	0.045 92	−0.193	120.499	45	0.007 57	−0.059	125.261	0.025 00	−0.195	125.287
	0.024 83	−0.106	120.555					0.013 80	−0.108	125.302	0.031 34	−0.244	125.278
25	0.006 58	−0.038	122.315	0.031 65	−0.176	122.119		0.019 63	−0.154	125.327	0.038 31	−0.296	125.225
	0.013 12	−0.074	122.186	0.037 83	−0.209	122.087							

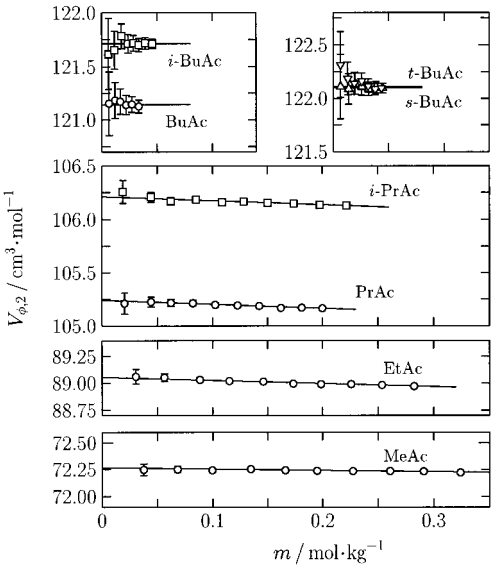

Figure 1. Apparent molar volumes of alkyl acetates at 25 °C.

squares method described in a previous paper (Sakurai et al., 1994b) and are summarized in Table 3. From Figure 1, the very low solubility of butyl acetate isomers leads to large uncertainty in the estimation of the $V_{\phi,2}$ value. In these cases, it was assumed that $B_V = 0$; that is, the apparent molar volumes are equal to the limiting values. We believe that the assumption does not lead to serious error in V_2° values because of the very low concentration range studied.

The precision of our limiting partial molar volumes is believed to be better than 0.1 cm^3·mol^{-1} for most cases. The V_2° values obtained at 25 °C are in good agreement with those from the literature: V_2° = 72.46 cm^3·mol^{-1} (Roux et al., 1978) for methyl acetate and V_2° = 88.97 (Roux et al., 1978), 88.8 (Edward et al., 1977), and 88.93 cm^3·mol^{-1} (Tasker et al., 1983) for ethyl acetate.

It is well-known that the dissolution of nonpolar nonelectrolytes in water brings about a negative volume change; that is, the limiting partial molar volumes of hydrophobic solutes in water are smaller than the solute molar volumes or the partial molar volumes in organic solvents. This is also the case for the alkyl acetate series. Such a negative volume change has been regarded as a characteristic of the hydrophobic hydration (Kauzmann, 1959; Desnoyers and Arel, 1967; Franks and Desnoyers, 1985). As described previously (Sakurai et al., 1994a), however, the negative volume change may not be attributable to hydration effects but may result essentially from the volume change on mixing of the component molecules of different sizes (Lee, 1983).

For all the alkyl acetates studied, the partial molar volumes increase almost linearly with increasing chain length of the alkyl residues; i.e., the contribution of the methylene group to V_2° is almost independent of chain length. This is in contrast to *n*-alcohol series, where $V°$-(CH_2) varies irregularly with chain length (Sakurai et al., 1994a). The chain branching of the alkyl residues causes the increase in the V_2° value. It is often said that the chain branching brings about more effective hydrophobic hydration. It is well-known that *tert*-butyl alcohol (TBA) in dilute aqueous solutions exhibits outstanding characteristics in many physicochemical properties. For instance, with increasing temperature, the partial molar volume of TBA in water passes through a minimum at about 15 °C; that is, partial molar expansion is negative at low temperatures (Sakurai, 1987). In other words, the temperature of maximum density of a dilute TBA solution is higher than that of pure water, 3.98 °C (Wada and Umeda, 1962; Sakurai et al., 1972). Such an anomalous behavior can be seen for isopropyl alcohol (Sakurai, 1988) and, perhaps, for methyl and ethyl alcohols. It should be kept in mind, however, that no peculiarity in the temperature dependence of the partial molar volume can be seen for longer-

Table 3. Limiting Partial Molar Volumes V_2° and Parameter B_V of Alkyl Acetates in Water at 5, 15, 25, 35, and 45 °C

	V_2°/cm^3·mol^{-1}					B_V/cm^3·kg·mol^{-2}				
solute	5 °C	15 °C	25 °C	35 °C	45 °C	5 °C	15 °C	25 °C	35 °C	45 °C
MeAc	70.37	71.30	72.26	73.25	74.26	−0.67	−0.33	−0.13	−0.04	0.09
EtAc	86.72	87.89	89.05	90.23	91.49	−0.91	−0.58	−0.28	−0.03	0.10
PrAc	102.50	103.84	105.24	106.69	108.14	−1.38	−0.59	−0.38	−0.14	0.13
i-PrAc	103.53	104.84	106.21	107.58	109.00	−1.53	−0.79	−0.37	−0.00	0.38
BuAc	117.74	119.40	121.14	122.83	124.47					
i-BuAc	118.38	120.09	121.71	123.37	125.16					
s-BuAc	118.85	120.47	122.10	123.61	125.36					
t-BuAc	118.94	120.51	122.11	123.72	125.26					

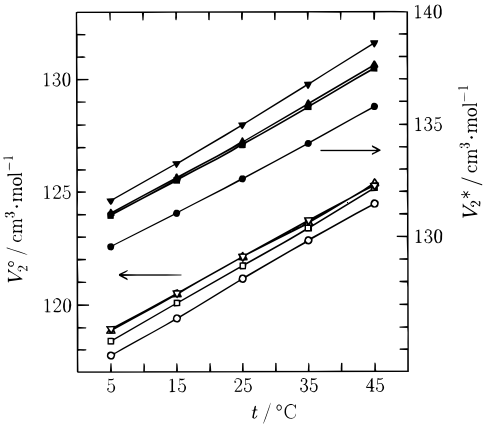

Figure 2. Temperature dependences of the molar volumes V_2* (filled symbols) and limiting partial molar volumes V_2° (open symbols) of butyl acetate isomers: (○) BuAc; (□) *i*-BuAc; (△) *s*-BuAc; (▽) *t*-BuAc.

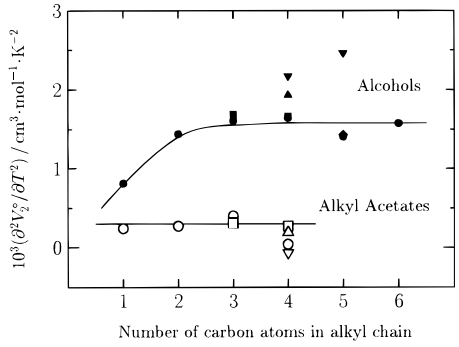

Figure 3. Chain length dependence of the $(\partial^2V_2^\circ/\partial T^2)_P$ values for alkyl acetates (open symbols) and alcohols (filled symbols) at 25 °C: (○) *n*-homologues; (□) *i*-isomers; (△) *s*-isomers; (▽) *t*-isomers.

chain alcohols (Sakurai et al., 1994a) nor for the alkyl acetates studied here.

Figure 2 clearly shows that the partial molar volumes of the four isomers of the butyl acetates exhibit almost the same temperature dependences and furthermore the slopes are very similar to the molar expansions of neat butyl acetates. This is also the case for the other alkyl acetates studied here. A similarity of the temperature dependences of the partial molar volume in water and of the molar volume of neat solute has been reported for the other hydrophobic solutes such as alkylbenzene derivatives (Sakurai, 1990) or dichloromethane (Alexander, 1959).

Helper has suggested that the pressure dependence of the partial molar heat capacity at infinite dilution may serve as a criterion of water-structural effects of various solutes (Hepler, 1969). Thus, on the basis of the relation

$$(\partial C_{P,2}^\circ/\partial P)_T = -T(\partial^2V_2^\circ/\partial T^2)_P \qquad (3)$$

one can estimate the effects by measuring carefully the temperature dependence of the partial molar volume. Figure 3 displays the $(\partial^2V_2^\circ/\partial T^2)_P$ values for the alkyl acetates studied here and for various alcohols reported previously (Sakurai et al., 1994a) as a function alkyl chain length. For the alcohol series the $(\partial^2V_2^\circ/\partial T^2)_P$ values are evidently positive and the substitution of a hydrogen atom on the α-carbon by a methyl group causes larger positive values. On the other hand, for the alkyl acetate series, the $(\partial^2V_2^\circ/\partial T^2)_P$ values are very small and almost independent of the chain length and chain branching.

In conclusion, since the water structure is considered to be largely influenced by the variation of temperature, the results obtained in this study strongly suggest either that the introduction of hydrophobic residue to water brings about little structural change in water (Fernandez-Prini et al., 1985) or that the volumetric behavior is not very sensitive to the hydrophobic hydration.

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