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# Partial Molar Isentropic Compressions of Alkyl Acetates in Water

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The ultrasonic speeds in dilute aqueous solutions of eight alkyl acetates (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, and *tert*-butyl acetates) were measured at (5, 15, 25, 35, and 45) °C by means of a sing-around velocimeter. From these data and density results reported previously, the apparent molar isentropic compressions of the alkyl acetates were evaluated. The results were compared with those for more hydrophilic solutes, alcohols reported earlier, and the effects of chain lengthening and chain branching of the alkyl residues on the compression behavior were discussed.

## Introduction

In a previous study, we have reported the partial molar volumes $V_2$ and their temperature dependences $\partial^2 V_2/\partial T^2$ for eight alkyl acetates with varying alkyl chain length and branching (Sakurai et al., 1996). If the structure of water is enhanced in the vicinity of hydrophobic residues, as is well-known as hydrophobic hydration or iceberg formation (Franks and Reid, 1973), one might expect a characteristic volumetric behavior in aqueous solutions of these hydrophobic solutes. The results, however, showed that no peculiarity has been found in the temperature dependence of the partial molar volumes of these hydrophobic solutes in water. This is in clear contrast to more hydrophilic alcohol + water systems (Sakurai et al., 1994).

One of the decisive factors in determining the partial molar volume of solute is the intrinsic contribution due to a core volume of the solute. Such an intrinsic volume can be regarded as incompressible as a first approximation, and hence the partial molar compression can be a more sensitive measure of the solute−water interactions than the partial molar volume (Høiland, 1986). In this paper we present the results of the ultrasonic speed measurements for dilute aqueous solutions of the alkyl acetates at different temperatures. The partial molar isentropic compressions of the acetates in water were estimated and compared with the results for aqueous alcohol systems reported earlier (Sakurai et al., 1995).

## Experimental Section

The ultrasonic speeds *u* in solution were measured at a frequency of about 5 MHz by using a laboratory-built sing-around velocimeter (Sakurai et al., 1995). The cell constant was determined by measuring the pulse repetition periods for pure water at various temperatures. The ultrasonic speed in water was taken from the table reported by Grosso and Mader (1972). The temperature of the thermostat was maintained within ±0.002 K, and the absolute temperature was determined to 0.02 K with a calibrated quartz thermometer. The accuracy of the ultrasonic speed measurements was believed to be better than ±1 cm·s$^{-1}$ for the dilute solution range studied.

**Table 1. Ultrasonic Speeds *u* (m·s$^{-1}$) in Pure Alkyl Acetates**

| | *t*/°C | | | | |
|---|---|---|---|---|---|
| solutes | 5 | 15 | 25 | 35 | 45 |
| MeAc | 1243.25 | 1196.24 | 1149.53 | 1102.99 | 1056.88 |
| EtAc | 1230.63 | 1184.37 | 1138.62 | 1093.28 | 1048.52 |
| PrAc | 1253.03 | 1208.36 | 1164.27 | 1120.74 | 1077.86 |
| *i*-PrAc | 1193.18 | 1147.65 | 1102.78 | 1058.52 | 1014.96 |
| BuAc | 1275.24 | 1232.58 | 1190.48 | 1148.98 | 1108.15 |
| *i*-BuAc | 1236.43 | 1193.30 | 1150.91 | 1109.01 | 1067.90 |
| *s*-BuAc | 1221.81 | 1179.04 | 1136.81 | 1095.16 | 1054.13 |
| *t*-BuAc | 1181.19 | 1136.56 | 1092.76 | 1049.71 | 1007.43 |

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). The sources and purifications of the alkyl acetates are the same as in our previous work (Sakurai et al., 1996). The ultrasonic speeds in the pure alkyl acetates are given in Table 1. All solutions were prepared by successive addition of a weighed amount of a pure acetate into a speed-measuring cell containing a known quantity of solvent water (ca. 110−200 g). The accuracy of composition of the solution was estimated to be better than 0.1%. The densities $\rho$ of the solutions used for the ultrasonic speed measurements were calculated from $V_2°$ and $B_V$ values reported previously (Sakurai et al., 1996).

## Results and Discussion

The differences in ultrasonic speeds between solutions and pure water at various temperatures are listed in Table

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**Table 2. Ultrasonic Speed Differences and Apparent Molar Isentropic Compressions of Alkyl Acetates in Dilute Aqueous Solutions**

| $t$/°C | $m$/ mol·kg$^{-1}$ | $u - u_1$/ m·s$^{-1}$ | $K_{\phi 2}$/ cm$^3$·mol$^{-1}$·GPa$^{-1}$ | $m$/ mol·kg$^{-1}$ | $u - u_1$/ m·s$^{-1}$ | $K_{\phi 2}$/ cm$^3$·mol$^{-1}$·GPa$^{-1}$ | $m$/ mol·kg$^{-1}$ | $u - u_1$/ m·s$^{-1}$ | $K_{\phi 2}$/ cm$^3$·mol$^{-1}$·GPa$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| Methyl Acetate | | | | | | | | | |
| 5 | 0.028 51 | 2.064 | −17.15 | 0.144 03 | 10.237 | −16.27 | 0.230 52 | 16.141 | −15.57 |
| | 0.058 15 | 4.190 | −16.92 | 0.177 16 | 12.508 | −15.95 | 0.258 63 | 18.023 | −15.35 |
| | 0.085 45 | 6.125 | −16.67 | 0.203 25 | 14.284 | −15.74 | 0.292 91 | 20.304 | −15.12 |
| | 0.114 87 | 8.194 | −16.43 | | | | | | |
| 15 | 0.022 95 | 1.285 | −3.74 | 0.136 58 | 7.478 | −3.04 | 0.237 53 | 12.724 | −2.36 |
| | 0.050 79 | 2.815 | −3.40 | 0.168 46 | 9.147 | −2.77 | 0.268 29 | 14.307 | −2.23 |
| | 0.079 67 | 4.405 | −3.34 | 0.200 71 | 10.834 | −2.59 | 0.296 76 | 15.720 | −2.03 |
| | 0.108 15 | 5.941 | −3.13 | | | | | | |
| 25 | 0.025 19 | 1.059 | 6.19 | 0.144 36 | 5.881 | 6.88 | 0.231 93 | 9.275 | 7.25 |
| | 0.056 29 | 2.345 | 6.40 | 0.180 50 | 7.294 | 7.04 | 0.261 50 | 10.394 | 7.37 |
| | 0.090 61 | 3.725 | 6.70 | 0.206 54 | 8.291 | 7.18 | 0.290 93 | 11.477 | 7.53 |
| | 0.119 67 | 4.894 | 6.80 | | | | | | |
| 35 | 0.029 54 | 0.920 | 13.37 | 0.155 35 | 4.576 | 14.25 | 0.247 38 | 7.077 | 14.67 |
| | 0.061 84 | 1.885 | 13.73 | 0.185 76 | 5.417 | 14.40 | 0.275 34 | 7.811 | 14.79 |
| | 0.088 83 | 2.678 | 13.90 | 0.218 69 | 6.309 | 14.55 | 0.304 56 | 8.567 | 14.90 |
| | 0.126 82 | 3.774 | 14.09 | | | | | | |
| 45 | 0.022 81 | 0.468 | 19.98 | 0.140 76 | 2.758 | 20.44 | 0.232 37 | 4.369 | 20.84 |
| | 0.052 48 | 1.067 | 20.07 | 0.177 71 | 3.428 | 20.59 | 0.268 39 | 4.976 | 20.97 |
| | 0.082 17 | 1.647 | 20.21 | 0.204 03 | 3.884 | 20.72 | 0.296 54 | 5.421 | 21.10 |
| | 0.112 60 | 2.230 | 20.33 | | | | | | |
| Ethyl Acetate | | | | | | | | | |
| 5 | 0.034 74 | 3.171 | −20.99 | 0.146 72 | 13.066 | −19.50 | 0.229 54 | 20.103 | −18.53 |
| | 0.064 81 | 5.892 | −20.74 | 0.176 01 | 15.589 | −19.18 | 0.261 03 | 22.724 | −18.20 |
| | 0.091 82 | 8.269 | −20.17 | 0.203 51 | 17.914 | −18.82 | 0.287 48 | 24.891 | −17.89 |
| | 0.118 94 | 10.667 | −19.92 | | | | | | |
| 15 | 0.028 64 | 2.048 | −4.71 | 0.143 84 | 10.011 | −3.64 | 0.222 21 | 15.157 | −2.87 |
| | 0.059 34 | 4.203 | −4.32 | 0.170 07 | 11.724 | −3.26 | 0.249 45 | 16.879 | −2.56 |
| | 0.088 77 | 6.257 | −4.14 | 0.196 92 | 13.522 | −3.12 | 0.281 66 | 18.905 | −2.26 |
| | 0.115 81 | 8.086 | −3.75 | | | | | | |
| 25 | 0.026 88 | 1.451 | 7.74 | 0.132 22 | 6.945 | 8.47 | 0.220 35 | 11.331 | 9.01 |
| | 0.052 25 | 2.800 | 7.94 | 0.161 77 | 8.449 | 8.61 | 0.251 92 | 12.834 | 9.25 |
| | 0.081 01 | 4.303 | 8.19 | 0.191 75 | 9.940 | 8.80 | 0.281 73 | 14.237 | 9.45 |
| | 0.104 68 | 5.539 | 8.28 | | | | | | |
| 35 | 0.027 13 | 1.095 | 16.69 | 0.138 14 | 5.339 | 17.54 | 0.224 31 | 8.386 | 18.17 |
| | 0.052 02 | 2.074 | 16.94 | 0.166 27 | 6.363 | 17.73 | 0.251 14 | 9.286 | 18.38 |
| | 0.078 02 | 3.077 | 17.16 | 0.192 52 | 7.287 | 17.94 | 0.282 27 | 10.333 | 18.55 |
| | 0.108 22 | 4.221 | 17.37 | | | | | | |
| 45 | 0.025 76 | 0.726 | 24.33 | 0.123 40 | 3.252 | 25.28 | 0.232 45 | 5.765 | 26.06 |
| | 0.049 96 | 1.381 | 24.62 | 0.149 70 | 3.888 | 25.47 | 0.258 36 | 6.330 | 26.21 |
| | 0.073 85 | 2.002 | 24.89 | 0.175 78 | 4.493 | 25.68 | 0.284 34 | 6.885 | 26.35 |
| | 0.097 23 | 2.606 | 25.05 | 0.205 00 | 5.155 | 25.89 | | | |
| Propyl Acetate | | | | | | | | | |
| 5 | 0.016 22 | 1.808 | −26.29 | 0.091 69 | 10.041 | −24.97 | 0.150 80 | 16.274 | −23.92 |
| | 0.035 31 | 3.916 | −25.91 | 0.110 44 | 12.032 | −24.60 | 0.171 01 | 18.352 | −23.52 |
| | 0.053 91 | 5.961 | −25.68 | 0.133 03 | 14.420 | −24.23 | 0.193 56 | 20.649 | −23.10 |
| | 0.072 36 | 7.955 | −25.26 | | | | | | |
| 15 | 0.019 58 | 1.744 | −7.57 | 0.105 64 | 9.087 | −5.75 | 0.167 81 | 14.176 | −4.86 |
| | 0.040 08 | 3.526 | −6.90 | 0.125 75 | 10.748 | −5.43 | 0.188 24 | 15.803 | −4.56 |
| | 0.061 76 | 5.383 | −6.41 | 0.146 41 | 12.441 | −5.14 | 0.204 67 | 17.088 | −4.29 |
| | 0.083 93 | 7.263 | −6.05 | | | | | | |
| 25 | 0.020 24 | 1.392 | 7.06 | 0.096 45 | 6.424 | 8.22 | 0.153 60 | 10.026 | 8.90 |
| | 0.038 61 | 2.630 | 7.42 | 0.115 04 | 7.618 | 8.41 | 0.174 77 | 11.308 | 9.20 |
| | 0.058 53 | 3.965 | 7.60 | 0.134 51 | 8.836 | 8.68 | 0.191 07 | 12.293 | 9.38 |
| | 0.074 18 | 4.987 | 7.88 | | | | | | |
| 35 | 0.017 07 | 0.886 | 18.22 | 0.096 01 | 4.766 | 19.38 | 0.152 65 | 7.342 | 20.17 |
| | 0.036 42 | 1.864 | 18.60 | 0.115 55 | 5.668 | 19.68 | 0.172 53 | 8.202 | 20.45 |
| | 0.057 53 | 2.905 | 18.96 | 0.133 60 | 6.489 | 19.93 | 0.188 03 | 8.832 | 20.76 |
| | 0.077 51 | 3.872 | 19.23 | | | | | | |
| 45 | 0.016 42 | 0.602 | 27.75 | 0.075 60 | 2.623 | 28.78 | 0.134 17 | 4.455 | 29.54 |
| | 0.036 37 | 1.291 | 28.38 | 0.092 57 | 3.172 | 29.00 | 0.151 72 | 4.954 | 29.83 |
| | 0.054 01 | 1.912 | 28.41 | 0.111 39 | 3.763 | 29.24 | 0.170 89 | 5.484 | 30.12 |
| Isopropyl Acetate | | | | | | | | | |
| 5 | 0.018 90 | 2.013 | −21.87 | 0.103 92 | 10.854 | −20.54 | 0.160 68 | 16.562 | −19.68 |
| | 0.040 49 | 4.297 | −21.62 | 0.122 15 | 12.698 | −20.23 | 0.180 40 | 18.507 | −19.37 |
| | 0.059 37 | 6.260 | −21.17 | 0.142 48 | 14.747 | −19.94 | 0.204 69 | 20.875 | −18.99 |
| | 0.081 87 | 8.590 | −20.84 | | | | | | |
| 15 | 0.017 85 | 1.499 | −3.39 | 0.099 28 | 8.114 | −2.12 | 0.161 18 | 12.941 | −1.33 |
| | 0.035 24 | 2.944 | −3.15 | 0.122 12 | 9.919 | −1.85 | 0.180 17 | 14.390 | −1.11 |
| | 0.055 36 | 4.591 | −2.80 | 0.139 09 | 11.247 | −1.65 | 0.202 47 | 16.063 | −0.82 |
| | 0.079 72 | 6.554 | −2.39 | | | | | | |

**Table 2 (Continued)**

| $t$/°C | $m$/mol·kg$^{-1}$ | $u - u_1$/m·s$^{-1}$ | $K_{\phi2}$/cm$^3$·mol$^{-1}$·GPa$^{-1}$ | $m$/mol·kg$^{-1}$ | $u - u_1$/m·s$^{-1}$ | $K_{\phi2}$/cm$^3$·mol$^{-1}$·GPa$^{-1}$ | $m$/mol·kg$^{-1}$ | $u - u_1$/m·s$^{-1}$ | $K_{\phi2}$/cm$^3$·mol$^{-1}$·GPa$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| Isopropyl Acetate | | | | | | | | | |
| 25 | 0.022 14 | 1.428 | 10.49 | 0.100 38 | 6.256 | 11.63 | 0.165 25 | 10.039 | 12.44 |
| | 0.040 49 | 2.591 | 10.75 | 0.122 47 | 7.568 | 11.90 | 0.189 61 | 11.431 | 12.67 |
| | 0.060 26 | 3.817 | 11.10 | 0.144 37 | 8.862 | 12.10 | 0.212 91 | 12.718 | 12.95 |
| | 0.080 73 | 5.075 | 11.35 | | | | | | |
| 35 | 0.019 82 | 0.940 | 21.58 | 0.081 59 | 3.753 | 22.29 | 0.145 66 | 6.479 | 23.06 |
| | 0.039 58 | 1.854 | 21.88 | 0.101 22 | 4.603 | 22.56 | 0.167 38 | 7.369 | 23.29 |
| | 0.059 63 | 2.773 | 22.04 | 0.124 23 | 5.583 | 22.83 | 0.188 29 | 8.196 | 23.54 |
| 45 | 0.019 48 | 0.637 | 30.72 | 0.075 83 | 2.343 | 31.67 | 0.137 45 | 4.071 | 32.33 |
| | 0.038 61 | 1.233 | 31.13 | 0.095 26 | 2.906 | 31.87 | 0.157 74 | 4.594 | 32.58 |
| | 0.055 54 | 1.747 | 31.38 | 0.114 40 | 3.452 | 32.03 | | | |
| Butyl Acetate | | | | | | | | | |
| 5 | 0.006 47 | 0.863 | −33.29 | 0.027 06 | 3.597 | −32.94 | 0.042 92 | 5.677 | −32.46 |
| | 0.013 28 | 1.775 | −33.47 | 0.033 73 | 4.467 | −32.59 | 0.047 45 | 6.266 | −32.30 |
| | 0.019 06 | 2.545 | −33.36 | | | | | | |
| 15 | 0.006 03 | 0.664 | −12.96 | 0.026 73 | 2.875 | −11.35 | 0.041 96 | 4.474 | −10.77 |
| | 0.013 20 | 1.427 | −11.69 | 0.034 77 | 3.715 | −10.91 | 0.047 40 | 5.045 | −10.66 |
| | 0.019 93 | 2.152 | −11.61 | | | | | | |
| 25 | 0.005 31 | 0.451 | 5.34 | 0.020 62 | 1.713 | 6.42 | 0.035 31 | 2.922 | 6.58 |
| | 0.013 74 | 1.154 | 5.88 | 0.028 01 | 2.322 | 6.51 | 0.044 46 | 3.656 | 6.87 |
| 35 | 0.009 73 | 0.627 | 18.92 | 0.022 37 | 1.412 | 19.65 | 0.036 59 | 2.300 | 19.76 |
| | 0.016 18 | 1.034 | 19.21 | 0.028 27 | 1.773 | 19.87 | 0.041 56 | 2.584 | 20.15 |
| 45 | 0.008 26 | 0.382 | 30.28 | 0.016 35 | 0.747 | 30.58 | 0.031 79 | 1.405 | 31.38 |
| | 0.012 55 | 0.568 | 30.83 | 0.024 06 | 1.088 | 30.82 | 0.036 46 | 1.585 | 31.78 |
| | 0.012 90 | 0.589 | 30.60 | 0.026 98 | 1.202 | 31.19 | 0.038 91 | 1.685 | 31.87 |
| Isobutyl Acetate | | | | | | | | | |
| 5 | 0.007 97 | 1.036 | −30.32 | 0.031 66 | 4.091 | −29.76 | 0.045 16 | 5.799 | −29.18 |
| | 0.016 30 | 2.111 | −29.98 | 0.040 34 | 5.187 | −29.31 | 0.050 85 | 6.520 | −29.05 |
| | 0.023 96 | 3.096 | −29.77 | | | | | | |
| 15 | 0.007 64 | 0.802 | −9.05 | 0.028 44 | 2.919 | −7.59 | 0.046 02 | 4.705 | −7.35 |
| | 0.014 67 | 1.537 | −8.93 | 0.033 76 | 3.457 | −7.45 | 0.051 13 | 5.219 | −7.26 |
| | 0.021 74 | 2.240 | −7.84 | 0.040 40 | 4.147 | −7.62 | | | |
| 25 | 0.009 14 | 0.745 | 7.89 | 0.029 56 | 2.371 | 8.63 | 0.043 54 | 3.456 | 9.10 |
| | 0.014 57 | 1.180 | 8.19 | 0.036 41 | 2.905 | 8.87 | 0.048 22 | 3.824 | 9.13 |
| | 0.023 46 | 1.887 | 8.51 | | | | | | |
| 35 | 0.007 65 | 0.468 | 21.27 | 0.027 74 | 1.658 | 22.04 | 0.038 32 | 2.280 | 22.17 |
| | 0.014 50 | 0.869 | 21.97 | 0.033 10 | 1.976 | 22.06 | 0.044 91 | 2.641 | 22.55 |
| | 0.020 60 | 1.240 | 21.81 | | | | | | |
| 45 | 0.007 32 | 0.313 | 32.83 | 0.024 63 | 1.036 | 33.19 | 0.040 11 | 1.640 | 33.82 |
| | 0.009 99 | 0.416 | 33.46 | 0.028 96 | 1.216 | 33.22 | 0.041 24 | 1.664 | 34.12 |
| | 0.014 50 | 0.630 | 32.43 | 0.029 13 | 1.223 | 33.22 | 0.045 57 | 1.826 | 34.27 |
| | 0.015 96 | 0.678 | 32.97 | 0.033 55 | 1.388 | 33.56 | | | |
| *sec*-Butyl Acetate | | | | | | | | | |
| 5 | 0.009 96 | 1.246 | −26.49 | 0.032 82 | 4.056 | −25.43 | 0.052 68 | 6.463 | −24.80 |
| | 0.017 46 | 2.177 | −26.20 | 0.038 86 | 4.790 | −25.21 | 0.060 97 | 7.454 | −24.50 |
| | 0.025 13 | 3.111 | −25.58 | 0.046 20 | 5.689 | −25.12 | | | |
| 15 | 0.007 42 | 0.740 | −5.37 | 0.027 84 | 2.734 | −4.43 | 0.049 89 | 4.850 | −3.83 |
| | 0.013 37 | 1.333 | −5.36 | 0.035 62 | 3.463 | −3.81 | 0.057 06 | 5.537 | −3.73 |
| | 0.021 09 | 2.067 | −4.29 | 0.043 53 | 4.229 | −3.78 | | | |
| 25 | 0.006 17 | 0.467 | 11.74 | 0.027 52 | 2.076 | 11.84 | 0.049 55 | 3.686 | 12.42 |
| | 0.014 31 | 1.085 | 11.64 | 0.035 12 | 2.617 | 12.38 | 0.057 20 | 4.228 | 12.68 |
| | 0.020 32 | 1.543 | 11.56 | 0.044 24 | 3.296 | 12.36 | | | |
| 35 | 0.007 32 | 0.424 | 23.36 | 0.029 71 | 1.652 | 24.65 | 0.048 66 | 2.682 | 24.88 |
| | 0.014 01 | 0.802 | 23.74 | 0.036 59 | 2.016 | 24.92 | 0.054 24 | 2.959 | 25.19 |
| | 0.021 97 | 1.213 | 24.89 | 0.042 76 | 2.350 | 24.99 | | | |
| 45 | 0.006 08 | 0.251 | 33.84 | 0.029 08 | 1.150 | 34.77 | 0.043 78 | 1.671 | 35.52 |
| | 0.015 38 | 0.613 | 34.63 | 0.036 75 | 1.429 | 35.13 | 0.050 12 | 1.871 | 35.98 |
| | 0.022 13 | 0.885 | 34.54 | | | | | | |
| *tert*-Butyl Acetate | | | | | | | | | |
| 5 | 0.009 69 | 1.160 | −22.69 | 0.033 58 | 4.002 | −22.32 | 0.050 18 | 5.922 | −21.52 |
| | 0.017 80 | 2.126 | −22.50 | 0.041 42 | 4.912 | −21.91 | 0.060 07 | 7.065 | −21.24 |
| | 0.025 58 | 3.057 | −22.55 | | | | | | |
| 15 | 0.007 89 | 0.746 | −2.04 | 0.031 31 | 2.925 | −1.36 | 0.051 31 | 4.742 | −0.76 |
| | 0.014 47 | 1.348 | −1.16 | 0.038 08 | 3.539 | −1.06 | 0.058 93 | 5.424 | −0.53 |
| | 0.021 90 | 2.048 | −1.40 | 0.045 19 | 4.175 | −0.73 | | | |
| 25 | 0.008 55 | 0.614 | 14.07 | 0.032 14 | 2.302 | 14.13 | 0.053 52 | 3.797 | 14.48 |
| | 0.016 88 | 1.216 | 13.91 | 0.039 46 | 2.820 | 14.20 | 0.059 42 | 4.214 | 14.48 |
| | 0.023 82 | 1.723 | 13.72 | 0.045 99 | 3.279 | 14.29 | | | |
| 35 | 0.008 04 | 0.418 | 26.87 | 0.027 93 | 1.446 | 26.95 | 0.046 93 | 2.374 | 27.60 |
| | 0.014 32 | 0.734 | 27.28 | 0.035 51 | 1.831 | 27.06 | 0.050 51 | 2.540 | 27.76 |
| | 0.020 92 | 1.088 | 26.83 | 0.042 16 | 2.141 | 27.49 | | | |
| 45 | 0.006 46 | 0.244 | 35.73 | 0.021 72 | 0.806 | 36.08 | 0.036 99 | 13.09 | 37.02 |
| | 0.013 83 | 0.506 | 36.39 | 0.029 90 | 1.078 | 36.66 | 0.044 62 | 15.43 | 37.46 |

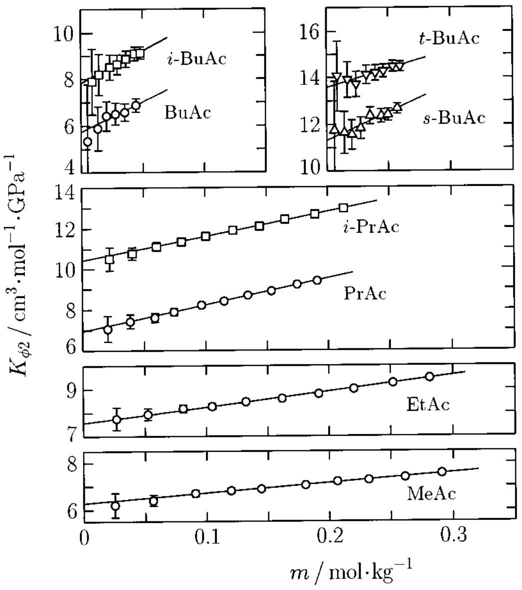

**Figure 1.** Apparent molar isentropic compressions of alkyl acetates at 25 °C.

2. The specific isentropic compression $k_S(=-(\partial v/\partial P)_S)$ of solution can be estimated from the values of $u$ and $\rho$ by the relation

$$k_S = 1/(\rho u)^2 \quad (1)$$

The apparent molar isentropic compression $K_{\phi 2}$ of alkyl acetate in solution is given by

$$K_{\phi 2} = (k_S - k_{S1})/m + k_S M_2 \quad (2)$$

where $m$ is molality, $M_2$ is the molar mass of the acetate, and $k_{S1}$ is the specific compression of solvent water. The estimated $K_{\phi 2}$ values are also summarized in Table 2.

In the concentration range studied, $K_{\phi 2}$ values of alkyl acetates increase linearly with molality; that is

$$K_{\phi 2} = K_{\phi 2}{}^{\circ} + B_K m \quad (3)$$

where the infinite dilution value $K_{\phi 2}{}^{\circ}$ is equal to the limiting partial molar isentropic compression $K_2{}^{\circ}$ and $B_K$ is an experimental parameter.

Figure 1 shows the concentration dependence of the apparent molar isentropic compressions of eight alkyl acetates at 25 °C. The error bars indicate the uncertainty $\delta K_{\phi 2}$ due to errors in ultrasonic speed measurements, $\delta u = \pm 1$ cm·s$^{-1}$ and in density estimations, $\delta\rho = \pm 2 \times 10^{-6}$ g·cm$^{-3}$. The parameters $K_2{}^{\circ}$ and $B_K$ in eq 3 were evaluated by the method of weighted least squares taking into consideration the uncertainty $\delta K_{\phi 2}$. The results are summarized in Table 3, in which the molar isentropic compressions $K_2{}^{*}$ of pure alkyl acetates are also included for comparison.

Although the reliability of the results for butyl acetate isomers is less satisfactory because of the very low solubility in water, it is apparent that the $B_K$ values increase with the chain length of alkyl acetates. This tendency is the same, on the whole, as that observed for alcohols. It should, however, to be noted that the $B_K$ values for the alkyl acetates are positive over the temperature range studied, while negative $B_K$ values were observed at lower temperatures for the shorter-chain alcohols, i.e., methyl, ethyl, and isopropyl alcohols (Sakurai et al., 1995).

**Table 3. Molar Isentropic Compressions $K_2$*, Limiting Partial Molar Isentropic Compressions $K_2{}^{\circ}$, and $B_K$ Parameters for Alkyl Acetates in Water**

| $t$/°C | $K_2{}^{*}$/ cm$^3$·mol$^{-1}$·GPa$^{-1}$ | $K_2{}^{\circ}$/ cm$^3$·mol$^{-1}$·GPa$^{-1}$ | $B_K$/ cm$^3$·kg·mol$^{-2}$·GPa$^{-1}$ |
|---|---|---|---|
| | | Methyl Acetate | |
| 5 | 52.77 | −17.30(0.03)[a] | 7.5(0.1)[a] |
| 15 | 58.56 | −3.78(0.04) | 5.9(0.2) |
| 25 | 65.22 | 6.27(0.03) | 4.3(0.1) |
| 35 | 72.92 | 13.53(0.04) | 4.6(0.1) |
| 45 | 81.82 | 19.86(0.01) | 4.2(0.1) |
| | | Ethyl Acetate | |
| 5 | 68.96 | −21.28(0.06) | 11.8(0.2) |
| 15 | 76.43 | −4.95(0.06) | 9.5(0.3) |
| 25 | 84.95 | 7.56(0.04) | 6.7(0.2) |
| 35 | 94.73 | 16.59(0.03) | 7.0(0.1) |
| 45 | 105.96 | 24.45(0.05) | 6.8(0.2) |
| | | Propyl Acetate | |
| 5 | 79.50 | −26.62(0.03) | 18.1(0.2) |
| 15 | 87.59 | −7.32(0.06) | 14.8(0.3) |
| 25 | 96.74 | 6.93(0.03) | 12.9(0.2) |
| 35 | 107.11 | 18.07(0.06) | 14.0(0.4) |
| 45 | 118.88 | 27.68(0.05) | 14.2(0.4) |
| | | Isopropyl Acetate | |
| 5 | 90.73 | −22.12(0.03) | 15.2(0.2) |
| 15 | 100.63 | −3.46(0.04) | 13.1(0.2) |
| 25 | 111.91 | 10.40(0.05) | 12.0(0.3) |
| 35 | 124.81 | 21.40(0.02) | 11.4(0.2) |
| 45 | 139.60 | 30.72(0.05) | 11.8(0.4) |
| | | Butyl Acetate | |
| 5 | 88.87 | −33.8(0.2) | 32(4) |
| 15 | 97.31 | −12.2(0.2) | 34(5) |
| 25 | 106.77 | 5.7(0.2) | 26(5) |
| 35 | 117.36 | 18.9(0.3) | 29(9) |
| 45 | 129.26 | 29.7(0.2) | 54(6) |
| | | Isobutyl Acetate | |
| 5 | 96.57 | −30.5(0.1) | 30(3) |
| 15 | 106.15 | −8.5(0.3) | 25(8) |
| 25 | 116.88 | 7.8(0.1) | 28(2) |
| 35 | 129.01 | 21.2(0.2) | 27(6) |
| 45 | 142.65 | 31.9(0.2) | 49(6) |
| | | *sec*-Butyl Acetate | |
| 5 | 99.04 | −26.6(0.1) | 34(3) |
| 15 | 108.91 | −4.8(0.3) | 20(7) |
| 25 | 120.02 | 11.3(0.2) | 24(4) |
| 35 | 132.57 | 24.1(0.3) | 20(7) |
| 45 | 146.76 | 33.4(0.2) | 49(6) |
| | | *tert*-Butyl Acetate | |
| 5 | 106.88 | −23.4(0.2) | 36(3) |
| 15 | 118.35 | −1.9(0.2) | 24(4) |
| 25 | 131.35 | 13.6(0.1) | 16(3) |
| 35 | 146.12 | 26.3(0.3) | 28(6) |
| 45 | 162.95 | 35.2(0.3) | 49(8) |

[a] Standard deviations are in parentheses.

The negative excess volume of mixing, which is well-known for many aqueous systems, is ascribed principally to the small size of the water molecules and only indirectly to the structural change of solvent water (Lee, 1983; Sakurai, 1987). The compression behavior is very similar to the volume change; that is, the partial molar isentropic compressions of alkyl acetates are much smaller than the molar compressions of neat acetates and become even negative at lower temperatures. The same is true for the aqueous alcohol systems reported previously (Sakurai et al., 1995). As well as a negative excess volume, the negative compression change on mixing may be also explained primarily by the packing effect due to the difference in size between solute and solvent molecules.

In Figure 2 is shown the temperature dependence of the limiting partial molar isentropic compressions of the $n$-

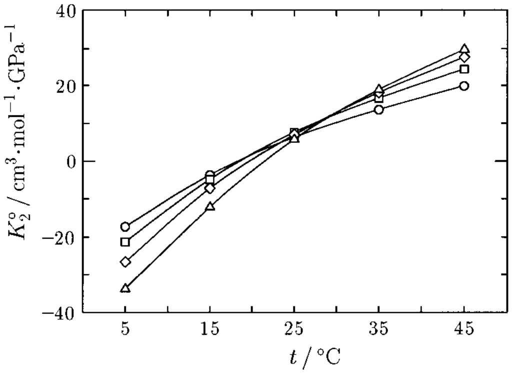

**Figure 2.** Temperature dependence of the limiting partial molar compressions of *n*-alkyl acetates: (○) MeAc; (□) EtAc; (◇) PrAc; (△) BuAc.

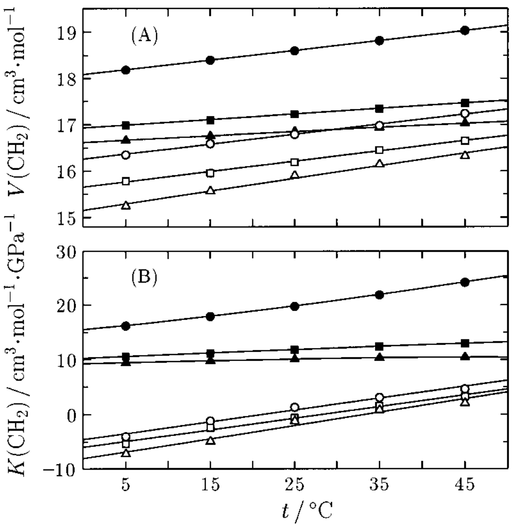

**Figure 3.** Methylene group contributions to the partial molar volumes (A) and partial molar isentropic compressions (B): (○) $N = 1$; (□) $N = 2$; (△) $N = 3$. Filled symbols refer to the corresponding molar quantities for neat alkyl acetates.

alkyl acetates in water. The close analogy between the present results and those for alcohols reported previously is very striking; in both cases the increase in chain length brings about more negative $K_2°$ values at lower temperatures, and more positive values at higher temperatures (Nakajima et al., 1975; Høiland, 1980; Sakurai et al., 1995). This means that the methylene group contribution to the partial molar compression $K°(CH_2)$ is negative at lower temperatures and positive at higher temperatures. The values of $K°(CH_2)$ can be obtained from the subtraction process

$$K°(\mathrm{CH_2}) = K°(N + 1) - K°(N) \qquad (4)$$

where $K°(N)$ refers to the partial molar isentropic compression of *n*-alkyl acetate containing $N$ carbon atoms in the alkyl residue. The $K°(CH_2)$ values for $N = 1$ to 3 are illustrated as a function of temperature in Figure 3B, in which analogous methylene contributions $K^*(CH_2)$ estimated from the molar isentropic compressions of neat alkyl acetates are also described by filled symbols. It should be stressed that a change of sign of the $K°(CH_2)$ itself has no special meaning, but we shall call attention to much smaller $K°(CH_2)$ values at all temperatures and, particularly, to their large temperature dependence compared with $K^*(CH_2)$. A similar behavior can be seen in the methylene contribution to the partial molar volume illustrated in Figure 3A; that is, the $V°(CH_2)$ is smaller and its temperature dependence (partial molar expansion of methylene group) is larger than the molar quantities calculated from the molar volumes of pure alkyl acetates (Sakurai et al., 1996). Both volume and compression properties of the methylene groups of the alkyl acetate series are just the same as those observed for aqueous alcohol systems.

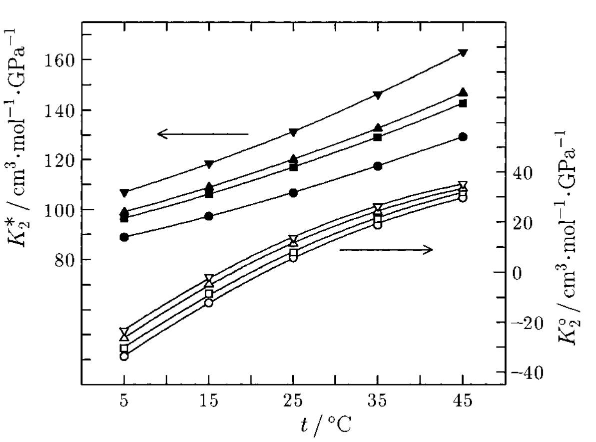

**Figure 4.** Temperature dependences of the molar isentropic compressions $K_2^*$ (filled symbols) and limiting partial molar isentropic compressions $K_2°$ (open symbols) of butyl acetate isomers: (○) BuAc; (□) *i*-BuAc; (△) *s*-BuAc; (▽) *t*-BuAc.

Consequently, it is apparent that the introduction of the methylene group in water results in solutions that have less volume and are more expansive and less compressible. These changes should be associated with the well-known volumetric properties of solvent water; i.e., more volume, less expansive, and more compressive at ambient temperature due to the formation of tetrahedral liquid structure. However, it does not necessarily follow that the structure of water must be altered by the dissolution of hydrophobic groups. The transfer of a nonpolar group from nonpolar medium to water is accompanied by negative volume and compressibility changes that can be attributed to reduced free volume around the nonpolar group because of the small size (Lee, 1983) and strong cohesive energy density of solvent water (Masterton, 1954). Since there is no appreciable interaction between a nonpolar group and water, the application of heat facilitates the increase in the free volume and results in larger partial molar expansion of nonpolar groups.

It is known that many thermodynamic properties of aqueous solutions are influenced by the chain branching of an alkyl chain through its water-structuring effect (Franks and Reid, 1973). The well-known example is *tert*-butyl alcohol. Its dilute solution exhibits outstanding characteristics in partial molar volume and, especially, in thermal expansion behavior (Sakurai, 1987). Strange to say, however, our previous results of various alcohol + water systems showed that the chain branching has only a minor effect on the partial molar compression and its temperature dependence (Sakurai et al., 1995). On the other hand, the temperature dependences of the partial molar volumes of four butyl acetate isomers are almost the same, and furthermore these are very similar to the molar expansions of neat butyl acetates (Sakurai et al., 1996). As can be seen from Figure 4, with increasing chain branching the partial molar isentropic compressions of butyl acetate isomers increase slightly, but not so markedly as the molar compressions for pure butyl acetates. Particularly to be noted is that the difference in the temperature dependences of $K_2°$ is hardly appreciable for the branched isomers. Thus, both temperature profiles of partial molar compressions and volumes suggest that the chain branching of the alkyl acetates brings about only a minor influence on the hydration behavior.

It is also worthwhile to note the difference in the temperature dependences of $K_2°$ and $K_2^*$; that is, the $K_2°$ values decrease steeply as the temperature decreases. Obviously such a nonlinear temperature dependence may not arise from hydrophobic groups−water interactions since $K°(CH_2)$ values increase linearly with temperature (see Figure 3B). In fact, a similar temperature dependence can be found in hydrophilic solutes such as alkali halides (Sakurai et al., 1981) or various amino acids (Kikuchi et al., 1995; Mizuguchi et al., 1997) and in hydrophobic solutes such as alkylbenzenes (Sakurai, unpublished data). The large and nonlinear temperature dependence of the partial molar compression seems to be essentially characteristic for aqueous mixtures regardless of hydrophobic or hydrophilic solutes, although we cannot offer a clear explanation at present.

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