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Partial Molar Heat Capacities and Partial Molar Volumes of All of the Isomeric (C3 to C5) Alkanols at Infinite Dilution in Water at 298.15 K

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Apparent molar heat capacities and apparent molar volumes were measured for all isomeric C₃ to C₅ alkanols in their dilute aqueous solutions at 298.15 K using a differential flow microcalorimeter in conjunction with a vibrating-tube densimeter. Molar volumes and molar heat capacities of the pure alkanols (except for 2-methyl-2-propanol and 2,2-dimethyl-1-propanol, which are solid at 298.15 K) were determined using the same instrumentation. The concentration dependence of the apparent properties allowed the determination, through extrapolation, of the infinite dilution partial molar volumes $\bar{V}_{m,1}^{\infty}$ and heat capacities $\bar{C}_{p,m,1}^{\infty}$ of these alkanols in water. These values, combined with the respective pure liquid properties, produced the limiting partial molar excess quantities ($\bar{V}_{m,1}^{E,\infty}$, $\bar{C}_{p,m,1}^{E,\infty}$). The present measurements agree well with available literature values. The group contribution schemes of Cabani et al. (Cabani, S.; Gianni, P.; Mollica, V.; Lepori, L. Group Contribution to the Thermodynamic Properties of Non-Ionic Organic Solutes in Dilute Aqueous Solution. *J. Solution Chem.* **1981**, *10*, 563–595) and of Plyasunov and Shock (Plyasunov, A. V.; Shock, E. L. Thermodynamic Functions of Hydration of Hydrocarbons at 298.15 K and 0.1 MPa. *Geochim. Cosmochim. Acta* **2000**, *64*, 439–468) were used to predict the limiting partial molar properties. It was found that the predictions of both schemes are very good.

1. Introduction

Most organic compounds exhibit much larger heat capacities in their dilute aqueous solutions than in the pure liquid or ideal gas states. The greatly enhanced heat capacities of dissolution or hydration of organic compounds are of interest for both theory and practice because they sensitively reflect induced water structuring around the solute molecules and directly determine the curvature of van't Hoff plots for limiting activity coefficients or Henry's law constants as functions of temperature. The present work is part of our broader thermodynamic study of dilute aqueous solutions of alkanols, the aim of which is to obtain reliable temperature dependences of limiting activity coefficients or Henry's law constants in the range from the normal melting point to the normal boiling point of water. The procedure of choice¹ for this purpose consists of a simultaneous thermodynamic treatment of limiting activity coefficients and infinite dilution thermal data on both the enthalpy and the heat capacity.

In this work, the heat capacities and densities of dilute aqueous solutions of isomeric C₃ to C₅ alkanols at 298.15 K were accurately measured, and the respective infinite dilution partial molar, dissolution, and hydration quantities were determined. Reliable values of limiting partial molar excess heat capacities (dissolution heat capacities) are important for a high-quality representation of the temperature dependence of limiting activity coefficients because its course for studied alkanols in water displays a maximum in the temperature region of interest.² Although heat

capacity measurements in dilute aqueous solutions for all short-chain linear alkanols and some branched alkanols have been reported in the literature,^{3–6} this work provides a systematic study of the effects of alkanol branching and fills data gaps encountered for pentanol isomers. The performance of existing group contribution schemes^{7,8} to predict infinite dilution partial molar heat capacities and volumes was tested against the newly measured values.

2. Experimental Section

2.1. Materials. The alkanols were all obtained from Aldrich with a stated purity of 99 mass % or better with the exception of 2-pentanol, 3-pentanol, and 3-methyl-2-butanol, for which the purity was 98 mass %. The samples of optically active alkanols (2-butanol, 2-pentanol, 2-methyl-1-butanol, and 3-methyl-2-butanol) were racemic mixtures of the respective stereoisomers. The alkanol samples were used without further purification other than being stored over 0.4-nm Merck molecular sieves to remove water. Heptane (J. T. Baker, purity 99.3 mass %) was used as a reference liquid for heat capacity measurements. Water was distilled and subsequently treated with a Milli-Q water purification system (Millipore). Prior to each experiment, the liquids were carefully degassed by filtering under vacuum.

2.2. Apparatuses and Procedure. Volumetric heat capacities were measured using a Picker flow microcalorimeter (Sodev Inc., Sherbooke, P. Q., Canada) and were transformed to a molar basis through densities obtained with a vibrating-tube densimeter (Sodev Inc.). The instrumentation and procedures have been described in detail in the literature.^{9,10} In the flow calorimeter, the volumetric heat capacity of the liquid flowing through the working cell is measured against that of the reference cell. The primary

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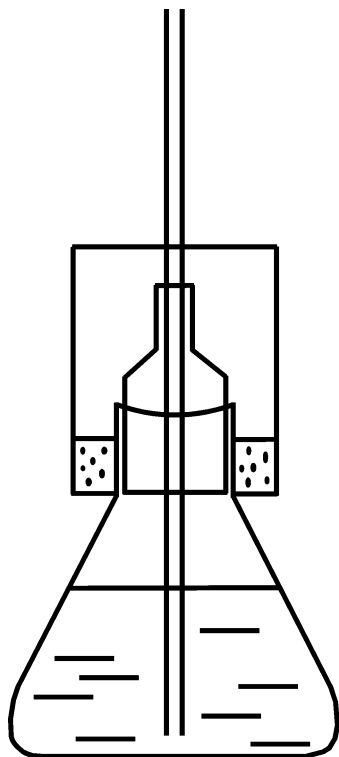


Figure 1. Sample flask with a simple presaturation arrangement.

reference for the volumetric heat capacity measurement of pure compounds was *n*-heptane ($1.5240 \text{ J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3}$).⁹ In the dilute concentration range, the heat capacity of each solution was determined using pure water as a reference ($4.16828 \text{ J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3}$).¹¹ The densimeter was calibrated with water and dry nitrogen as references. The calorimeter and the densimeter were connected in series, and their temperature was controlled to $\pm 0.003 \text{ K}$ using a CT-L thermostat (Sodev Inc.).

The solutions (20 cm^3) were prepared carefully by mass and kept in tightly sealed glass flasks whose volume was only slightly greater to minimize evaporation losses. The uncertainty in the mole fraction resulting from weighing was $\pm 1 \times 10^{-6}$. For each alkanol studied, at least seven or eight dilute sample solutions of varying concentration were prepared. The maximum alkanol mole fraction was 0.02 or less, depending on solubility. When the samples are pumped into the calorimeter, there is a substantial increase of the vapor space in the sample flask. To avoid possible composition changes of the samples due to gas–liquid partitioning, the air coming into the flask is presaturated using the simple arrangement shown in Figure 1. Here, a cylindrical cap is placed over the neck of the sample flask, and the sample is exhausted through the Teflon tube passing through a small hole in its top. The bottom of the cap consists of a foam rubber annulus fitting the flask neck and is wetted with a small portion of the sample. The air coming into the sample flask is forced to pass through this porous wet material, being thus saturated with the sample vapor.

The apparent molar volumes $V_{\phi,1}$ and apparent molar heat capacities $C_{\phi,1}$ of the solute (component 1) were calculated using the following equations

$$V_{\phi,1} = \frac{V_m - x_2 V_{m,2}}{x_1} \quad (1)$$

$$C_{\phi,1} = \frac{C_{p,m} - x_2 C_{p,m,2}}{x_1} \quad (2)$$

Table 1. Densities and Molar Heat Capacities of Pure Alkanols at 298.15 K^a

| alkanol | $\rho/(\text{g}\cdot\text{cm}^{-3})$ | | ref | $C_{p,m}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ | | |
|---------------------|--------------------------------------|---------|-----|--|--------------------|-----|
| | exptl | lit | | exptl | lit | ref |
| 1-propanol | 0.79952 | 0.79960 | 13 | 144.3 | 143.8 | 11 |
| 2-propanol | 0.78072 | 0.78093 | 13 | 155.2 | 155.2 | 11 |
| 1-butanol | 0.80562 | 0.80575 | 13 | 177.1 | 177.1 | 11 |
| 2-butanol | 0.80207 | 0.80244 | 13 | 197.8 | 196.8 | 11 |
| 2-methyl-1-propanol | 0.79763 | 0.79775 | 14 | 181.9 | 180.9 | 12 |
| 2-methyl-2-propanol | | 0.78122 | 14 | | 218.6 | 11 |
| 1-pentanol | 0.81068 | 0.81080 | 13 | 208.8 | 208.1 | 11 |
| 2-pentanol | 0.80455 | 0.80539 | 14 | 235.3 | 232.4 | 12 |
| 3-pentanol | 0.81530 | 0.81552 | 14 | 254.6 | 251.1 | 12 |
| 2-methyl-1-butanol | 0.81454 | 0.81484 | 14 | 215.0 | 209.2 ^b | 12 |
| 3-methyl-1-butanol | 0.80418 | 0.80455 | 14 | 209.3 | 207.8 | 12 |
| 2-methyl-2-butanol | 0.80401 | 0.80419 | 14 | 251.1 | 247.7 | 12 |
| 3-methyl-2-butanol | 0.81231 | 0.81380 | 15 | 249.5 | 248.2 | 12 |

^a Experimental results and comparison with literature data.

^b Extrapolated value.

where x_i is the mole fraction of component i , V_m is the molar volume of the solution, $V_{m,2}$ is the molar volume of the pure solvent (water), and $C_{p,m}$ and $C_{p,m,2}$ are the molar heat capacities of the solution and the pure solvent, respectively. In the dilute region studied, the apparent molar properties $V_{\phi,1}$ and $C_{\phi,1}$ exhibited a practically linear dependence with alkanol mole fraction x_1 . Hence, the results could be represented by the following equations

$$V_{\phi,1} = \bar{V}_{m,1}^{\infty} + b_v x_1 \quad (3)$$

$$C_{\phi,1} = \bar{C}_{p,m,1}^{\infty} + b_c x_1 \quad (4)$$

and their parameters could be obtained by means of linear regression, the intercepts being in eq 3 the limiting partial molar volume $\bar{V}_{m,1}^{\infty}$ and in eq 4 the limiting partial molar heat capacity $\bar{C}_{p,m,1}^{\infty}$ of the alkanol in water.

The limiting partial molar excess properties of alkanol in water that represent the volume or heat capacity change of the dissolution process (transfer of 1 mol of alkanol from the pure liquid state to the infinitely dilute aqueous solution) were evaluated by subtracting the molar property for the pure liquid solute from the corresponding limiting partial molar property:

$$\bar{V}_{m,1}^{E,\infty} = \bar{V}_{m,1}^{\infty} - V_{m,1} \quad (5)$$

$$\bar{C}_{p,m,1}^{E,\infty} = \bar{C}_{p,m,1}^{\infty} - C_{p,m,1} \quad (6)$$

In an analogous manner, the heat capacity change due to hydration (transfer of 1 mol of alkanol from the pure ideal gas to the infinitely dilute aqueous solution) was obtained as follows

$$\Delta_{\text{hyd}} C_{p,m,1}^{\infty} = \bar{C}_{p,m,1}^{\infty} - C_{p,m,1}^{\circ} \quad (7)$$

where $C_{p,m,1}^{\circ}$ is the molar heat capacity of the alkanol in the ideal gas state. Reliable values for $C_{p,m,1}^{\circ}$ were taken from the literature.

Taking into account various possible sources of error, the estimated standard uncertainty of measurement is less than $0.05 \text{ cm}^3\cdot\text{mol}^{-1}$ for the molar volumes of pure solutes and $0.3 \text{ cm}^3\cdot\text{mol}^{-1}$ for the partial molar volumes and partial molar excess volumes at infinite dilution. The standard uncertainty of the molar heat capacities as well as the infinite dilution partial molar heat capacities is less than 1%, whereas that of the transfer heat capacities ($\bar{C}_{p,m,1}^{E,\infty}$ and $\Delta_{\text{hyd}} C_{p,m,1}^{\infty}$) is about 1–2%.

Table 2. Experimental Apparent Molar Volumes $V_{\phi,1}$ and Heat Capacities $C_{\phi,1}$ for Dilute Aqueous Solutions of Alkanols at 298.15 K

| alkanol(1) | x_1 | $V_{\phi,1}/(\text{cm}^3\cdot\text{mol}^{-1})$ | $C_{\phi,1}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ | x_1 | $V_{\phi,1}/(\text{cm}^3\cdot\text{mol}^{-1})$ | $C_{\phi,1}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ |
|-------------------------|----------|--|---|----------|--|---|
| 1-propanol | 0.000792 | 70.819 | 354.42 | 0.008272 | 70.353 | 357.52 |
| | 0.002096 | 70.790 | 355.26 | 0.011848 | 70.149 | 357.93 |
| | 0.002978 | 70.673 | 355.58 | 0.017324 | 69.914 | 359.62 |
| | 0.006166 | 70.480 | 357.10 | 0.020891 | 69.809 | 359.58 |
| 2-propanol | 0.001072 | 71.697 | 367.07 | 0.005976 | 71.410 | 368.11 |
| | 0.001923 | 71.649 | 367.49 | 0.009312 | 71.360 | 369.03 |
| | 0.003078 | 71.477 | 366.68 | 0.014368 | 70.978 | 370.44 |
| | 0.004130 | 71.455 | 367.21 | 0.016651 | 70.906 | 371.11 |
| 1-butanol | 0.001656 | 86.590 | 446.61 | 0.009163 | 86.064 | 450.11 |
| | 0.003814 | 86.443 | 448.47 | 0.014147 | 85.780 | 453.94 |
| | 0.005524 | 86.283 | 449.13 | 0.016037 | 85.715 | 456.09 |
| | 0.006663 | 86.246 | 448.68 | | | |
| 2-butanol | 0.001648 | 86.076 | 454.92 | 0.009049 | 85.971 | 461.19 |
| | 0.002440 | 86.266 | 456.81 | 0.010471 | 85.798 | 462.53 |
| | 0.003665 | 86.154 | 457.95 | 0.014109 | 85.498 | 464.52 |
| | 0.006146 | 86.033 | 459.80 | 0.014610 | 85.505 | 465.34 |
| 2-methyl-1-propanol | 0.006234 | 85.951 | 460.52 | 0.017660 | 85.337 | 466.62 |
| | 0.008153 | 85.959 | 461.21 | | | |
| | 0.001575 | 86.655 | 440.55 | 0.009083 | 86.095 | 444.42 |
| | 0.001810 | 86.553 | 438.56 | 0.011426 | 86.027 | 445.14 |
| 2-methyl-2-propanol | 0.003631 | 86.420 | 440.31 | 0.016465 | 85.815 | 449.41 |
| | 0.006044 | 86.290 | 443.60 | | | |
| | 0.000883 | 87.501 | 468.89 | 0.006409 | 87.118 | 473.61 |
| | 0.001796 | 87.635 | 469.39 | 0.008670 | 86.940 | 475.71 |
| 1-pentanol | 0.002923 | 87.346 | 469.79 | 0.011530 | 86.842 | 477.87 |
| | 0.004051 | 87.193 | 471.04 | 0.017164 | 86.366 | 481.18 |
| | 0.001069 | 102.716 | 534.21 | 0.002474 | 102.401 | 534.47 |
| | 0.001645 | 102.561 | 534.09 | 0.002743 | 102.379 | 535.60 |
| 2-pentanol | 0.001775 | 102.536 | 535.54 | 0.003049 | 102.388 | 533.91 |
| | 0.001916 | 102.560 | 533.47 | 0.003529 | 102.265 | 535.28 |
| | 0.002185 | 102.497 | 535.92 | | | |
| | 0.001235 | 102.456 | 550.36 | 0.003519 | 102.280 | 552.36 |
| 3-pentanol | 0.002163 | 102.336 | 550.19 | 0.004937 | 102.051 | 552.21 |
| | 0.001831 | 102.306 | 550.75 | 0.005900 | 102.053 | 553.92 |
| | 0.002785 | 102.222 | 550.90 | 0.006950 | 101.870 | 555.54 |
| | 0.000803 | 101.146 | 544.99 | 0.003282 | 100.860 | 550.25 |
| 2-methyl-1-butanol | 0.001033 | 101.059 | 544.69 | 0.005357 | 100.677 | 551.37 |
| | 0.001252 | 101.138 | 547.38 | 0.005689 | 100.590 | 554.08 |
| | 0.001864 | 100.963 | 548.81 | 0.006773 | 100.647 | 554.31 |
| | 0.002399 | 100.991 | 549.35 | | | |
| 3-methyl-1-butanol | 0.000842 | 101.763 | 518.37 | 0.002361 | 101.378 | 519.20 |
| | 0.000975 | 101.867 | 519.10 | 0.002467 | 101.580 | 520.35 |
| | 0.001072 | 101.544 | 519.77 | 0.002771 | 101.368 | 517.91 |
| | 0.001376 | 101.813 | 517.25 | 0.002868 | 101.417 | 519.06 |
| 2-methyl-2-butanol | 0.001398 | 101.574 | 518.15 | 0.002988 | 101.587 | 519.95 |
| | 0.001540 | 101.485 | 517.70 | 0.003068 | 101.653 | 518.53 |
| | 0.002056 | 101.642 | 520.16 | 0.003107 | 101.636 | 519.58 |
| | 0.002325 | 101.403 | 519.98 | 0.003446 | 101.502 | 520.10 |
| 3-methyl-2-butanol | 0.000488 | 102.695 | 518.69 | 0.001362 | 102.656 | 519.98 |
| | 0.000691 | 102.677 | 516.77 | 0.001742 | 102.772 | 520.87 |
| | 0.001002 | 102.295 | 519.03 | 0.002039 | 102.575 | 519.92 |
| | 0.001048 | 102.795 | 520.00 | 0.002063 | 102.627 | 520.52 |
| 2,2-dimethyl-1-propanol | 0.001190 | 102.479 | 518.57 | 0.002225 | 102.332 | 520.92 |
| | 0.001204 | 102.383 | 519.87 | | | |
| | 0.001660 | 101.039 | 550.18 | 0.006999 | 100.533 | 558.27 |
| | 0.001774 | 100.898 | 550.96 | 0.009307 | 100.389 | 562.27 |
| 3-methyl-2-butanol | 0.002795 | 100.898 | 553.46 | 0.012131 | 100.109 | 566.74 |
| | 0.005273 | 100.710 | 555.84 | 0.013551 | 99.990 | 569.14 |
| | 0.000786 | 101.264 | 528.29 | 0.005029 | 100.696 | 530.66 |
| | 0.001489 | 101.117 | 528.64 | 0.006358 | 100.542 | 532.08 |
| 2,2-dimethyl-2-propanol | 0.001981 | 101.086 | 529.35 | 0.007481 | 100.445 | 532.41 |
| | 0.004452 | 100.705 | 529.89 | 0.008252 | 100.314 | 533.23 |
| | 0.001702 | 102.147 | 510.70 | 0.003563 | 101.996 | 512.88 |
| | 0.002268 | 102.070 | 511.35 | 0.004331 | 101.981 | 513.67 |
| 2,2-dimethyl-1-propanol | 0.002665 | 101.997 | 512.67 | 0.004832 | 101.941 | 514.94 |
| | 0.003113 | 102.050 | 512.71 | | | |

3. Results and Discussion

The measured densities and molar heat capacities for pure compounds at 298.15 K, except for 2-methyl-2-propanol ($T_{\text{mmp}} = 298.8$ K) and 2,2-dimethyl-1-propanol ($T_{\text{mmp}} = 327$ K), which are solid at 298.15 K, are listed in Table 1 together with values from the literature. The experimental heat capacities were compared with recom-

mended values as established by the critical assessment of all available literature data.^{11,12} The agreement is excellent especially for propanols and butanols. For pentanols, the agreement is not as good, but it should be taken into account that the reference values are less reliable because the available underlying measurements are not very numerous and not as accurate as for the lower

Table 3. Partial Molar Volumes $\bar{V}_{m,1}^\infty$ (This Work and Literature) and Partial Molar Excess Volumes $\bar{V}_{m,1}^{E,\infty}$ of Alkanols at Infinite Dilution in Water at 298.15 K^a

| alkanol(1) | $\bar{V}_{m,1}^\infty$ ^b | $s(\bar{V}_{m,1}^\infty)$ ^b | $\bar{V}_{m,1}^\infty(\text{lit})$ ^b | $\bar{V}_{m,1}^{E,\infty}$ ^b |
|-------------------------|-------------------------------------|--|--|---|
| 1-propanol | 70.8 | 0.03 | 70.5 ⁶ , 70.71 ¹⁷ , 70.8 ³ , 70.75 ¹⁸ , 70.66 ¹⁹ , 70.63 ⁴ | -4.3 |
| 2-propanol | 71.7 | 0.04 | 71.7 ⁶ , 71.82 ¹⁷ , 71.79 ²⁰ , 71.93 ¹⁸ | -5.3 |
| 1-butanol | 86.7 | 0.02 | 86.4 ⁵ , 86.59 ²¹ , 86.63 ¹⁷ , 86.5 ³ , 86.62 ¹⁸ , 86.48 ⁴ , 86.6 ²² | -5.4 |
| 2-butanol | 86.3 | 0.05 | 86.4 ^{c,5} , 86.2 ^{d,5} , 86.55 ¹⁷ , 86.64 ¹⁸ , 86.53 ⁴ , 86.66 ²³ , 86.54 ²² | -6.1 |
| 2-methyl-1-propanol | 86.7 | 0.04 | 86.6 ⁵ , 86.71 ²¹ , 86.46 ¹⁷ , 86.75 ⁴ , 86.75 ²² | -6.3 |
| 2-methyl-2-propanol | 87.6 | 0.05 | 87.7 ⁵ , 87.81 ¹⁷ , 87.86 ²⁴ , 87.73 ⁴ , 87.86 ²² | -7.3 |
| 1-pentanol | 102.9 | 0.03 | 102.62 ¹⁷ , 102.3 ³ , 102.1 ²⁵ , 102.62 ¹⁸ , 102.88 ⁴ | -5.9 |
| 2-pentanol | 102.5 | 0.04 | 102.5 ²⁵ , 102.55 ¹⁸ | -7.0 |
| 3-pentanol | 101.2 | 0.03 | 101.14 ⁴ , 101.28 ²³ | -6.9 |
| 2-methyl-1-butanol | 101.8 | 0.10 | 101.3 ²⁵ | -6.5 |
| 3-methyl-1-butanol | 102.7 | 0.15 | 101.7 ²⁵ | -7.0 |
| 2-methyl-2-butanol | 101.1 | 0.03 | 101.37 ¹⁷ , 101.38 ²⁶ , 101.15 ²⁰ | -8.5 |
| 3-methyl-2-butanol | 101.3 | 0.03 | 100.5 ²⁵ | -7.2 |
| 2,2-dimethyl-1-propanol | 102.2 | 0.04 | 102.29 ¹⁷ , 102.32 ²⁰ , 101.87 ⁴ | |

^a The standard deviations $s(\bar{V}_{m,1}^\infty)$ were calculated using eq 3 to fit the concentration dependence of the apparent molar volumes.
^b cm³·mol⁻¹. ^c R-(-)-2-butanol. ^d S-(+)-2-butanol.

Table 4. Partial Molar Heat Capacities $\bar{C}_{p,m,1}^\infty$ (This Work and Literature), Partial Molar Excess Heat Capacities $\bar{C}_{p,m,1}^{E,\infty}$, and Molar Heat Capacities of Hydration $\Delta_{\text{hyd}}C_{p,m,1}^\infty$ of Alkanols at Infinite Dilution in Water at 298.15 K^a

| alkanol(1) | $\bar{C}_{p,m,1}^\infty$ ^b | $s(\bar{C}_{p,m,1}^\infty)$ ^b | $\bar{C}_{p,m,1}^\infty(\text{lit})$ ^b | $\bar{C}_{p,m,1}^{E,\infty}$ ^b | $\Delta_{\text{hyd}}C_{p,m,1}^\infty$ ^b |
|-------------------------|---------------------------------------|--|--|---|--|
| 1-propanol | 354.9 | 0.3 | 358.3 ⁶ , 355.2 ³ , 351 ²⁷ , 352.9 ⁴ | 210.6 | 267.8 |
| 2-propanol | 366.5 | 0.2 | 368.7 ⁶ , 362.3 ²⁰ | 211.2 | 276.8 |
| 1-butanol | 445.4 | 0.6 | 445.0 ⁵ , 441.5 ²¹ , 445.9 ³ , 441 ²⁷ , 437 ⁴ | 268.3 | 335.4 |
| 2-butanol | 455.2 | 0.4 | 449.1 ⁴ , 455.9 ^{c,5} , 454.5 ^{d,5} | 257.5 | 342.7 |
| 2-methyl-1-propanol | 438.5 | 0.6 | 439.7 ⁵ , 435.5 ²¹ , 432.5 ⁴ | 256.6 | 328.5 |
| 2-methyl-2-propanol | 468.1 | 0.3 | 470.6 ⁵ , 463.6 ²⁴ , 464 ⁴ , 463 ²⁸ | 249.4 | 357.0 |
| 1-pentanol | 534.1 | 1.0 | 539.5 ³ , 532 ²⁷ , 523.8 ⁴ , 530 ²⁸ | 325.2 | 401.2 |
| 2-pentanol | 548.8 | 0.5 | | 313.5 | 413.4 |
| 3-pentanol | 544.8 | 0.7 | 539.8 ⁴ | 290.3 | 409.4 |
| 2-methyl-1-butanol | 518.1 | 0.7 | | 303.1 | 385.2 |
| 3-methyl-1-butanol | 517.4 | 0.7 | | 308.0 | 384.4 |
| 2-methyl-2-butanol | 548.1 | 0.4 | 538.8 ²⁰ | 297.0 | 414.1 |
| 3-methyl-2-butanol | 527.7 | 0.3 | | 278.2 | 393.8 |
| 2,2-dimethyl-1-propanol | 508.8 | 0.5 | 503.6 ²⁰ , 503.5 ⁴ | | 376.6 |

^a Standard deviations $s(\bar{C}_{p,m,1}^\infty)$ were calculated using eq 4 to fit the concentration dependence of the apparent molar heat capacities.
^b J·K⁻¹·mol⁻¹. ^c R-(-)-2-butanol. ^d S-(+)-2-butanol.

alkanols. For 2-methyl-1-butanol, the reference value was obtained by extrapolation from data at temperatures above 303 K.

Experimental apparent molar volumes $V_{\phi,1}$ and heat capacities $C_{\phi,1}$ for dilute aqueous solutions of alkanols as a function of their mole fraction x_1 at 298.15 K are given in Table 2. Linear extrapolation of $V_{\phi,1}$ and $C_{\phi,1}$ to infinite dilution through eqs 3 and 4 led to limiting partial molar volumes $\bar{V}_{m,1}^\infty$ or heat capacities $\bar{C}_{p,m,1}^\infty$. These resulting limiting quantities are collected in Tables 3 and 4, together with their standard deviations $s(\bar{V}_{m,1}^\infty)$ and $s(\bar{C}_{p,m,1}^\infty)$ determined from the fit and the corresponding limiting partial molar excess properties $\bar{V}_{m,1}^{E,\infty}$ and $\bar{C}_{p,m,1}^{E,\infty}$. Table 4 also lists the heat capacities of hydration calculated using eq 7, where we combined the present $\bar{C}_{p,m,1}^\infty$ values with literature values for alkanol ideal gas heat capacities.¹⁶ To

achieve the best accuracy, the excess properties were calculated from eqs 5 and 6 using the pure component property values measured in this work, the two alkanols that are solid at 298.15 K being the exceptions. For 2-methyl-2-propanol, we used the literature values of pure component properties given in Table 1 that necessarily correspond to the subcooled liquid. In the case of 2,2-dimethyl-1-propanol, the excess properties were not evaluated because the extrapolation needed to obtain properties of the subcooled liquid would be prohibitively long.

Tables 3 and 4 also present a detailed comparison of our measurements with those available in the literature. The comparison is done through the limiting partial molar properties because these are the results usually reported in the literature. The differences between our values and those from literature are very small, not exceeding 1% for

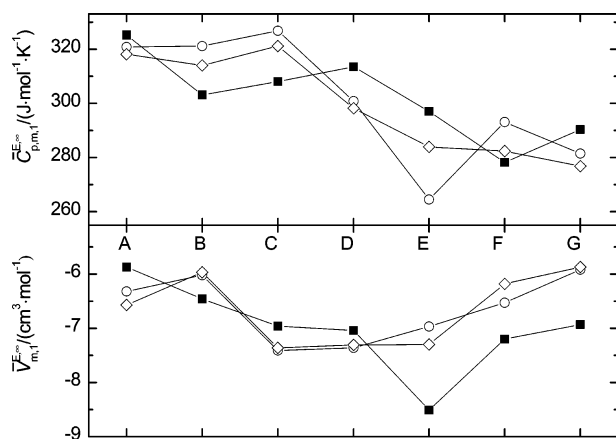


Figure 2. Comparison of experimental partial molar excess quantities at infinite dilution (■) with the predictions by group contribution methods of Cabani (○) and Plyasunov and Shock (◇) for isomeric pentanols: A, 1-pentanol; B, 2-methyl-1-butanol; C, 3-methyl-1-butanol; D, 2-pentanol; E, 2-methyl-2-butanol; F, 3-methyl-2-butanol; G, 3-pentanol.

$\bar{V}_{m,1}^{\infty}$ and 2% for $\bar{C}_{p,m,1}^{\infty}$. The largest deviations are typically encountered for the older measurements of Jolicœur and Lacroix,⁴ which appear to give slightly but systematically lower $\bar{C}_{p,m,1}^{\infty}$ values than those obtained from more recent measurements. On average, the deviations between the present and literature values are about 0.5% and 1% for $\bar{V}_{m,1}^{\infty}$ and $\bar{C}_{p,m,1}^{\infty}$, respectively, which clearly demonstrate the accuracy and reliability of our measurements.

The limiting partial molar excess volumes of all the alkanols in water at 298.15 K are negative. The values of $\bar{V}_{m,1}^{\infty}$ decrease with the number of carbon atoms for 1-alkanols, and they are always more negative for branched isomers than for corresponding 1-alkanols.

As expected, the presented limiting partial molar excess heat capacities at 298.15 K are positive and large. Except for propanols, where the $\bar{C}_{p,m,1}^{\infty}$ values of both isomers practically coincide, the branching is seen to decrease $\bar{C}_{p,m,1}^{\infty}$ appreciably. The hydration heat capacities are on average 30% larger than the dissolution heat capacities.

Group contribution schemes were tested in their ability to reproduce the present experimental results. The classical method of Cabani et al.⁷ and its recent updated modification developed by Plyasunov and Shock⁸ for aqueous hydrocarbons and alkanols were employed. We found the two methods to perform equally well, both predicting $\bar{V}_{m,1}^{\infty}$ with an average deviation of 0.6% and $\bar{C}_{p,m,1}^{\infty}$ with average deviations of 2.6% (Cabani) and 2.2% (Plyasunov). It appears then that for the alkanols under consideration the quality of prediction approaches the experimental error. However, at the level of the more sensitive excess properties, Figure 2 shows that the above-indicated effects of branching are not predicted quantitatively.

Supporting Information Available:

Densities and volumetric heat capacities of dilute aqueous solutions of alkanols. These values represent primary experimental data measured. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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