

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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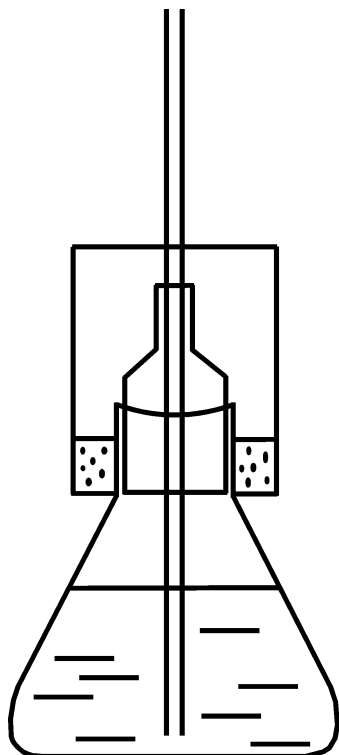


Figure 1. Sample flask with a simple presaturation arrangement.

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			
	0.01575	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-methyl-1-butanol	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-1-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 ³ , 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

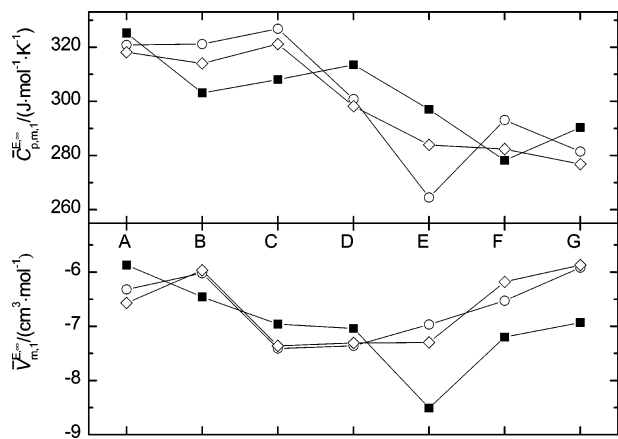


Figure 2. Comparison of experimental partial molar excess quantities at infinite dilution (■) with the predictions by group contribution methods of Cabani (○) and Plyasunov and Shock (◇) for isomeric pentanols: A, 1-pentanol; B, 2-methyl-1-butanol; C, 3-methyl-1-butanol; D, 2-pentanol; E, 2-methyl-2-butanol;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

Literature Cited

- Hovorka, Š.; Dohnal, V.; Roux, A. H.; Roux-Desgranges, G. Determination of Temperature Dependence of Limiting Activity Coefficients for a Group of Moderately Hydrophobic Organic Solutes in Water. *Fluid Phase Equilib.* **2002**, *201*, 135–164.
- Vrbka, P.; Hovorka, Š.; Dohnal, V.; Arlt, W. Excess Thermodynamic Properties of Highly Dilute Solutions of 1-Alkanols (C1–

- C4) in Water. In *Proceedings of the 15th International Conference on Chemical Thermodynamics*, Porto, Portugal, July 26–August 1, 1998; pp C1–15.
- Makhatadze, G. I.; Privalov, P. L. Heat Capacity of Alcohols in Aqueous Solutions in the Temperature Range from 5 to 125 °C. *J. Solution Chem.* **1989**, *18*, 927–936.
- Jolicouer, C.; Lacroix, G. Thermodynamic Properties of Aqueous Organic Solutes in Relation to Their Structure. Part III. Apparent Molal Volumes and Heat Capacities of Low Molecular Weight Alcohols and Polyols at 25 °C. *Can. J. Chem.* **1976**, *54*, 624–631.
- Origlia, M. L.; Woolley, E. M. Apparent Molar Volumes and Apparent Molar Heat Capacities of Aqueous Solutions of Isomeric Butanols at Temperatures from 278.15 K to 393.15 K and at the Pressure 0.35 MPa. *J. Chem. Thermodyn.* **2001**, *33*, 451–469.
- Origlia-Luster, M. L.; Woolley, E. M. Apparent Molar Volumes and Apparent Molar Heat Capacities of Dilute Aqueous Solutions of Ethanol, 1-Propanol, and 2-Propanol at Temperatures from 278.15 K to 393.15 K and at the Pressure 0.35 MPa. *J. Chem. Thermodyn.* **2003**, *35*, 1101–1118.
- 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.
- 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.
- Fortier, J.-L.; Benson, G. C. Excess Heat Capacities of Binary Liquid Mixtures Determined with a Picker Flow Microcalorimeter. *J. Chem. Thermodyn.* **1976**, *8*, 411–423.
- Picker, P.; Leduc, P. A.; Philip, P. R.; Desnoyers, J. E. Heat Capacity of Solutions by Flow Microcalorimetry. *J. Chem. Thermodyn.* **1971**, *3*, 631–642.
- Zábranský, M.; Růžička, V.; Majer, V.; Domalski, E. S. Heat Capacity of Liquids: Volume I: Critical Review and Recommended Values. *J. Phys. Chem. Ref. Data, Monogr.* **1996**, *6*, 1–810.
- Zábranský, M.; Růžička, V.; Domalski, E. S. Heat Capacity of Liquids: Critical Review and Recommended Values. Supplement I. *J. Phys. Chem. Ref. Data* **2001**, *30*, 1199–1689.
- Hales, J. L.; Ellender, J. H. Liquid Densities from 293 to 490 K of Nine Aliphatic Alcohols. *J. Chem. Thermodyn.* **1976**, *8*, 1177–1184.
- CDATA: *Database of Thermodynamic and Transport Properties for Chemistry and Engineering*; Department of Physical Chemistry, Institute of Chemical Technology; Distributed by FIZ Chemie GmbH, Berlin: Prague, 1991.
- Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley-Interscience: New York, 1986.
- Domalski, E. S.; Hearing, E. D. Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805–1159.
- Sakurai, M.; Nakamura, K.; Nitta, K. Volumetric Properties of Dilute Aqueous Alcohol Solutions at Different Temperatures. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1580–1587.
- Hoiland, H.; Vikingstad, E. Partial Molal Volumes and Additivity of Group Partial Molal Volumes of Alcohols in Aqueous Solution at 25 and 35 °C. *Acta Chem. Scand., Ser. A* **1976**, *30*, 182–186.
- Alexander, D. M. Apparent Molar Volumes of Alcohols in Dilute Aqueous Solution. *J. Chem. Eng. Data* **1959**, *4*, 252–254.
- Roux, G.; Roberts, D.; Perron, G.; Desnoyers, J. E. Microheterogeneity in Aqueous-Organic Solutions: Heat Capacities, Volumes and Expansibilities of Some Alcohols, Aminoalcohol and Tertiary Amines in Water. *J. Solution Chem.* **1980**, *9*, 629–647.
- Hovorka, Š.; Roux, A. H.; Roux-Desgranges, G.; Dohnal, V. Limiting Partial Molar Excess Heat Capacities and Volumes of Selected Organic Compounds in Water at 25 °C. *J. Solution Chem.* **1999**, *28*, 1289–1305.
- Franks, F.; Smith, H. T. Precision Densities of Dilute Aqueous Solutions of the Isomeric Butanols. *J. Chem. Eng. Data* **1968**, *13*, 538–541.
- Cabani, S.; Conti, G.; Lepori, L. Volumetric Properties of Aqueous Solutions of Organic Compounds. III. Aliphatic Secondary Alcohols, Cyclic Alcohols, Primary, Secondary, and Tertiary Amines. *J. Phys. Chem.* **1974**, *78*, 1030–1034.
- de Visser, C.; Perron, G.; Desnoyers, J. E. The Heat Capacities, Volumes, and Expansibilities of tert-Butyl Alcohol - Water Mixtures from 6 to 65 °C. *Can. J. Chem.* **1977**, *55*, 856–862.
- Edward, J. T.; Farrel, P. G.; Shahidi, F. Partial Molar Volumes of Organic Compounds in Carbon Tetrachloride. IV. Ketones, Alcohols, and Ethers. *Can. J. Chem.* **1979**, *57*, 2585–2592.
- Sakurai, M. Partial Molar Volumes in Aqueous Mixtures of Nonelectrolytes. III. t-Pentyl Alcohol. *J. Solution Chem.* **1989**, *18*, 37–44.
- Hallén, D.; Nilsson, S.-O.; Rothschild, W.; Wadsö, I. Enthalpies and Heat Capacities for n-Alkan-1-ols in H₂O and D₂O. *J. Chem. Thermodyn.* **1986**, *18*, 429–442.

- (28) Sköld, R.; Suurkuusk, J.; Wadsö, I. Thermochemistry of Solutions of Biochemical Model Compounds. 7. Aqueous Solutions of Some Amides, t-Butanol and Pentanol. *J. Chem. Thermodyn.* **1976**, *8*, 1075–1080.

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