J. Chem. Eng. Data **2007,** *52,* 989−1002

Temperature Dependence of Limiting Activity Coefficients, Henry's Law Constants, and Related Infinite Dilution Properties of Branched (C3 and C4) Alkanols in Water. Measurement, Critical Compilation, Correlation, and Recommended Data

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Limiting activity coefficients (γ_1^∞) of lower branched alkanols (2-propanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol) in water were measured at several temperatures covering the range from the melting to the normal boiling point of water. Four experimental techniques (namely, headspace analysis, inert gas stripping, Rayleigh distillation, and the method of circulation still) were employed for the purpose. A comprehensive review is further presented of experimental data on the limiting activity coefficients (γ_1^∞), infinite dilution partial molar excess enthalpies ($\bar{H}_1^{E,\infty}$), and heat capacities ($\bar{C}_{p,1}^{E,\infty}$) of these aqueous solutes. For each alkanol, the compiled data were critically evaluated and together with the data measured in this work correlated with a suitable model equation providing adequate simultaneous description of the equilibrium measurements and the calorimetric information. As a result, a recommended thermodynamically consistent temperature dependence of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ of superior accuracy was established in the range from the melting point to the normal boiling point of water. In addition, by employing literature data on the respective residual properties of the pure alkanols, analogous recommendations were derived also for the temperature dependence of the Henry's law constants, hydration enthalpies, and hydration heat capacities. Variation of these various infinite dilution thermodynamic properties of aqueous branched alkanols with temperature and alkanol branching is briefly discussed.

Introduction

Lower alkanols are large volume production chemicals that find widespread usage as solvents, chemical intermediates, and oxygenated fuel additives. In their production, use, and environmental fate, these volatile organic compounds interact frequently with water. The thermodynamic properties of their highly dilute aqueous solutions, such as alkanol-limiting activity coefficients (γ_1^∞) or Henry's law constants in water (K_H), are of essential importance to model and predict phase and chemical equilibria, kinetic solvent effects, and other phenomena involved in these processes. For theoretical reasons, in particular for understanding the hydrophobic effect, accurate knowledge of the thermodynamic quantities of the dissolution and hydration of alkanols and their variation with temperature is of extreme interest because alkanols represent a unique set of compounds formally derived from water by adding aliphatic groups.

Recently, we have conducted a detailed study of limiting activity coefficients and Henry's law constants of (C1−C5) 1-alkanols in water as a function of temperature and established for them a highly reliable recommended temperature dependence.[1,2] In this work, we extend the scope of our investigation focusing on branched (C3 and C4) alkanols. For these solutes in water, we report here the results of our systematic and accurate measurements of limiting activity coefficients that were performed by several suitable experimental techniques and cover the temperature range from (273 to 373) K. The present experimental work is further amended by a comprehensive compilation and critical evaluation of literature experimental data on limiting activity coefficient and related thermal dissolution properties—limiting partial molar excess enthalpy ($\bar{H}_1^{E,\infty}$) and heat capacity ($\bar{C}_{p,1}^{E,\infty}$). All the data, measured in this work and taken from literature, are subsequently processed by a simultaneous thermodynamically consistent correlation. The treatment results in a recommended temperature dependence of these infinite dilution properties that has superior accuracy and is valid in the range from the melting to the normal boiling temperature of water. Analogous recommendations are further generated for the temperature dependence of the Henry's law constants, hydration enthalpies, and heat capacities. Finally, an overview of these various infinite dilution properties is presented, and their variation with temperature and alkanol branching is discussed.

Experimental Section

Materials. Analar grade 2-propanol, 2-butanol, and 2-methyl-1-propanol obtained from Lachema (Czech Republic) were fractionally distilled on a 1 m long packed column, while 2-methyl-2-propanol (p.a.) supplied by Reanal (Hungary) was fractionally recrystallized using a Vigreaux column. The purity of the final products was better than 99.9 % as determined by GC with DB-WAX capillary or Carbowax 20 M packed columns. Before measurements, all alkanols were dried and stored over 0.4 nm Merck molecular sieves. Water was distilled and subsequently treated by a Milli-Q Water Purification System (Millipore, Milford, MA).

Apparatus and Procedure. Four experimental techniques were employed to measure γ_1^∞ values in this work, viz., headspace analysis (HSA), inert gas stripping (IGS), Rayleigh distillation (RDIST), and the method of circulation still (CIRC).

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10.1021/je600567z CCC: $37.00

Table 1. Parameters of the Cox Vapor Pressure Equation[a] for Pure Alkanols[7]

alkanol	range/K	A_0	$A_1 \times 10^3$	$A_2 \times 10^6$	$A_3 \times 10^9$	T_0/K
2-propanol	190−372	2.951030	−1.161868	1.975221	−2.984829	355.363
2-butanol	190−382	2.898364	0.2283123	−3.948154	3.701043	372.635
2-methyl-1-propanol	180−382	2.965308	−1.082450	1.758035	−3.229507	381.014
2-methyl-2-propanol	299−370	2.259168	6.973582	−27.09966	29.51366	355.469

[a] $\ln(p^s/p_0) = (1 - (T_0/T)) \exp(A_0 + A_1(T/\mathrm{K}) + A_2(T/\mathrm{K})^2 + A_3(T/\mathrm{K})^3)$; $p_0 = 101\,325$ Pa.

Table 2. Experimental Limiting Activity Coefficients of Branched Alkanols (1) in Water (2) Determined in This Work

T/K	γ_1^∞	$s(\gamma_1^\infty)$	technique[a]	T/K	γ_1^∞	$s(\gamma_1^\infty)$	technique[a]	T/K	γ_1^∞	$s(\gamma_1^\infty)$	technique[a]
					2-Propanol						
283.15	5.37	0.16	RHSA	333.15	11.8	0.4	RDIST	363.15	12.9	0.4	CIRC
293.15	6.89	0.21	RHSA	353.15	12.5	0.4	CIRC	371.15	13.1	0.4	CIRC
308.15	8.84	0.27	RHSA								
					2-Butanol						
273.35	13.7	0.4	RHSA	313.15	30.8	0.9	IGS	333.15	36.9	1.1	HSA
283.15	17.9	0.5	RHSA	313.15	31.3	0.9	HSA	343.15	38.0	1.1	RDIST
293.15	22.6	0.7	RHSA	323.15	33.8	1.0	HSA	353.15	38.4	1.2	RDIST
293.15	22.5	0.7	HSA	323.15	34.4	1.0	IGS	363.15	40.4	1.2	CIRC
303.15	26.8	0.8	HSA	333.15	35.7	1.1	IGS	371.15	37.8	1.1	CIRC
303.15	26.8	0.8	IGS								
					2-Methyl-1-propanol						
273.35	31.6	1.0	RHSA	303.15	50.3	1.5	HSA	333.15	58.3	1.8	HSA
283.15	36.8	1.1	RHSA	313.15	54.1	1.6	HSA	363.15	54.3	1.6	CIRC
293.15	44.3	1.3	HSA	323.15	57.6	1.7	HSA	371.15	52.2	1.6	CIRC
298.15	47.4	1.4	RHSA								
					2-Methyl-2-propanol						
299.15	13.1	0.4	HSA	323.15	19.9	0.6	RDIST	353.15	25.4	0.8	CIRC
303.15	14.4	0.4	HSA	333.15	21.8	0.7	RDIST	363.15	26.3	0.8	CIRC
313.15	16.9	0.5	HSA	343.15	23.5	0.7	RDIST	371.15	27.4	0.8	CIRC

[a] HSA, headspace analysis; RHSA, relative headspace analysis; CIRC, circulation equilibrium still; RDIST, Rayleigh distillation; IGS, inert gas stripping.

Since we have used these methods previously and described the respective instrumentation and experimental procedures in detail, given here are only some particulars that are specific to the present application. For a full account of our experimental techniques, we refer the reader to our previous papers.[3−6]

All the methods involve the use of gas chromatography: here, we employed computer-driven gas chromatographs, a Hewlett-Packard HP 5890 II or an Agilent 6890 Plus, allowing us to automate our experiments to a great extent. The HSA measurements for the present systems were carried out at alkanol mole fractions below 0.001. A wide-bore 15 m long DB-WAX capillary column at oven temperatures from (30 to 50)°C or a packed Porapak Q (80/100 mesh) column at 200 °C were used for the GC analysis. In some cases, the headspace method was applied in its relative variant (RHSA). Contrary to the conventional HSA, in which the GC detector is typically calibrated by the saturated vapor above the pure solute, in RHSA the calibration is accomplished using the vapor phase above the same highly dilute solution as that under study but at some different temperature where γ_1^∞ has been already accurately determined by another technique. The IGS method was applied here much less than the HSA, mostly because its applicability is inherently related to more enhanced solute volatilities than those exhibited by the present systems. In the present measurements we used a small stripping cell of 13/17 mL (liquid loading/total volume) and the DB-WAX capillary column specified above. The RDIST method was applied from (323 to 353) K, a temperature range that is suitable for aqueous solutions. To perform the GC analyses, a 0.5 m long Chromosorb 103 (80/100 mesh) packed column at oven temperatures from (160 to 190) °C or a 15 m long wide-bore HP Plot U capillary column at 160 °C were used depending on the solute. Samples were injected by a HP 7673 automatic sampler, typically with 10 replicates each. The CIRC measurements carried out in this work cover mostly the temperature region (353 to 373) K. The analysis of the samples was done by gas chromatography in the same manner as in the case of the RDIST method.

Results of Measurements

The primary VLE measurements carried out by the outlined techniques were processed to obtain the values of limiting activity coefficients as described in our papers cited above. The saturated vapor pressures of pure solutes were calculated from the Cox equation, whose parameters recently obtained by Růžička et al.[7] are given in Table 1. Water vapor pressures were calculated from the reference equation of Wagner and Pruss.[8] The gas phase nonideality was accounted for by the truncated virial equation of state, the second virial coefficients being obtained from the Hayden−O'Connell correlation with parameters from Prausnitz et al.[9] and CDATA.[10] For the systems and conditions under study, the gas phase nonideality corrections are in most cases quite small, typically of the order of a few tenths of percent and always less than 2 %.

The limiting activity coefficients obtained by us in this work using the various measurement techniques are listed in Table 2, along with their estimated standard uncertainties. The uncertainty estimates correspond to standard deviations and comprise errors from all possible sources combined through the error propagation law. As seen from Table 2, the uncertainty of the determined γ_1^∞ values does not exceed 3 %.

Table 3. Parameters of Equation 1[a] Obtained by Simultaneous Correlation of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ Data, Overall Standard Deviation of Fit *s*, Weighted Root-Mean-Square Deviations (WRMSD) of Individual Properties, and Temperature T_{max} at Which γ_1^∞ is Maximum

						WRMSD[c]			T_{max}
alkanol	*A*	*B*	*C*	*D*	s^b	$\ln \gamma_1^\infty$	$\bar{H}_1^{E,\infty}$	$\bar{C}_{p,1}^{E,\infty}$	K
2-propanol	−0.94215	5.6462	−58.8740	−3.0937	1.01	1.14	1.12	0.52	380.0
2-butanol	−1.6966	8.2748	−69.2759	−3.0264	0.92	1.05	0.93	0.59	361.1
2-methyl-1-propanol	−3.3156	11.0223	−65.1637	−2.8295	0.89	1.00	1.26	0.46	338.9
2-methyl-2-propanol	−1.6351	8.3544	−59.9247	−2.6566	0.90	0.97	1.03	0.66	389.1

[a] Recommended temperature dependence for limiting activity coefficient. [b] $s = [S_{min}/(n-4)]^{1/2}$; *S* given by eq 2.

[c] $$\mathrm{WRMSD} = \left(\frac{1}{n_Y}\sum_{i=1}^{n_Y}\frac{[Y_i(\mathrm{exptl}) - Y_i(\mathrm{calcd})]^2}{s^2(Y_i)}\right)^{1/2}, \; Y = \ln \gamma_1^\infty, \bar{H}_1^{E,\infty}, \bar{C}_{p,1}^{E,\infty}.$$

Table 4. Recommended Values of Excess Thermodynamic Functions at Infinite Dilution[a] for Branched Lower Alkanols in Water at 298.15 K Together with Their Standard Uncertainties

		$\bar{G}_1^{E,\infty}$	$\bar{H}_1^{E,\infty}$	$\bar{C}_{p,1}^{E,\infty}$
alkanol	γ_1^∞	kJ·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
2-propanol	7.65 ± 0.06	5.05 ± 0.02	−13.09 ± 0.02	212 ± 2
2-butanol	25.0 ± 0.2	7.98 ± 0.02	−13.02 ± 0.04	256 ± 2
2-methyl-1-propanol	47.4 ± 0.3	9.57 ± 0.02	−9.20 ± 0.05	256 ± 2
2-methyl-2-propanol	12.3 ± 0.1	6.23 ± 0.02	−17.42 ± 0.02	247 ± 2

[a] Calculated from eq 1 with parameters from Table 3.

Table 5. Parameters of Equation 8[a] Obtained by Simultaneous Treatment of K_H, $\Delta_{hyd}H_1^\infty$, and $\Delta_{hyd}C_{p,1}^\infty$ along with the Respective Standard Deviation of Fit s_{rel}

alkanol	*A*	*B*	*C*	*D*	$s_{rel}{}^b$
2-propanol	61.0445	−69.8548	−58.7948	12.6022	0.010
2-butanol	70.4890	−81.3780	−70.9743	14.9529	0.005
2-methyl-1-propanol	68.0466	−78.7577	−69.5854	14.9952	0.008
2-methyl-2-propanol	72.5737	−82.3846	−70.4649	14.0467	0.006

[a] Recommended temperature dependence for Henry's law constant. [b] $s_{rel} = [S_{min}/(n-4)]^{1/2}$.

$$S = \sum_{i=1}^{n_G}\left[\frac{K_{H,i}(\mathrm{calcd})}{K_{H,i}(\mathrm{exptl})} - 1\right]^2 + \sum_{i=1}^{n_H}\left[\frac{\Delta_{hyd}H_{1,i}^\infty(\mathrm{calcd})}{\Delta_{hyd}H_{1,i}^\infty(\mathrm{exptl})} - 1\right]^2 + \sum_{i=1}^{n_C}\left[\frac{\Delta_{hyd}C_{p,1,i}^\infty(\mathrm{calcd})}{\Delta_{hyd}C_{p,1,i}^\infty(\mathrm{exptl})} - 1\right]^2, \; n_G = n_H = n_C = 21.$$

Table 6. Recommended Values of Hydration Thermodynamic Functions[a] for Lower Branched Alkanols in Water at 298.15 K and Their Comparison with Those Given by Plyasunov and Shock[76] (in parentheses)[b]

	K_H	$\Delta_{hyd}G_1^\infty$	$\Delta_{hyd}H_1^\infty$	$\Delta_{hyd}C_{p,1}^\infty$
alkanol	kPa	kJ·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
2-propanol	44.3	−2.02	−58.66	279
	(45.1 ± 1.8)	(−1.98 ± 0.10)	(−58.5 ± 0.2)	(272 ± 15)
2-butanol	58.2	−1.34	−62.86	342
	(56.3 ± 6)	(−1.42 ± 0.27)	(−62.8 ± 0.2)	(340 ± 15)
2-methyl-1-propanol	72.5	−0.796	−59.91	329
	(65.4 ± 6)	(−1.05 ± 0.23)	(−60.2 ± 0.2)	(330 ± 15)
2-methyl-2-propanol	69.1	−0.916	−64.37	352
	(70.3 ± 4.8)	(−0.87 ± 0.17)	(−64.1 ± 0.3)	(353 ± 10)

[a] Calculated from eq 8 with parameters from Table 5. [b] Converted from the molality scale used in ref 76 to the mole fraction scale used in the present work.

Data Compilation and Survey

Besides the γ_1^∞ data measured in this work (42 values), we compiled additional data on γ_1^∞ and related thermal dissolution properties $\bar{H}_1^{E,\infty}$ and $\bar{C}_{p,1}^{E,\infty}$ of (C3 and C4) branched alkanols from the literature (266 data points from 60 literature references). All of these values are listed in Tables 7 to 9, respectively. Only original experimental values were considered in this collection. Those extrapolated from measurements on concentrated solution were disregarded. The distribution of the data points among the alkanols studied is roughly uniform, varying from 67 for 2-methyl-2-propanol to 93 for 2-propanol.

The majority of the collected information concerns limiting activity coefficients for which 148 data points are available. The collected γ_1^∞ data file covers beside values of γ_1^∞ directly reported in the literature (more than 80 % of values) also those derived by us from reported closely related experimental VLE quantities such as the Henry's law constants or gas−liquid partition coefficients. As to the distribution of γ_1^∞ data with respect to temperature, it is characteristic that many data were measured at 298.15 K. For 2-propanol and 2-methyl-1-propanol, temperatures higher than 298.15 K are fairly covered also whereas at subambient temperatures the data are generally scarce. Note that in Table 7 are also listed some results previously obtained in this laboratory, namely, those from our earlier RDIST measurements for 2-methyl-1-propanol[3] and from our recent measurements by the non-steady gas−liquid chromatography.[33] The measurements carried out by this laboratory thus represent the most systematic and complete contribution to the determination of $\gamma_1^\infty(T)$ for (C3 and C4) branched alkanols in water (52 values, 35 % of all γ_1^∞ available).

The existing $\bar{H}_1^{E,\infty}$ data (49 data points) cover well the range of near-ambient temperatures, most of them being at 298.15 K. $\bar{H}_1^{E,\infty}$ values at temperatures higher than 323.15 K are scarce and originate from only three laboratories.[54,56,62] Data on limiting partial molar excess heat capacities (111 data points) appear to be relatively numerous, but they resulted from a limited number of studies. As concerns the temperature dependence, systematic measurements have been carried out only recently.[64,67] Note that the determination of $\bar{C}_{p,1}^{E,\infty}$ is not direct but requires both the heat capacities of dilute aqueous solutions (leading to the infinite dilution partial molar heat capacity $\bar{C}_{p,1}^\infty$) and the heat capacity of the pure solute $C_{p,1}^{L,\bullet}$ to be measured. When only $\bar{C}_{p,1}^\infty$ values were reported, values of $\bar{C}_{p,1}^{E,\infty}$ were derived by us using recommended $C_{p,1}^{L,\bullet}$ data.[70−72]

Data Evaluation and Correlation

The quality of the information gathered in Tables 7 to 9 is not at all uniform. The collected data differ in their accuracy and show in some cases significant disparity, inconsistency or scatter. In order to resolve this issue and establish reliable and accurate recommended data, we subjected all the collected

Table 7. Experimental Values of Limiting Activity Coefficients of Branched (C3 and C4) Alkanols (1) in Water (2) Together with their Standard Uncertainty, Technique of Measurement, and Vapor-Phase Nonideality Treatment

T/K	ln γ_1^∞	s(ln γ_1^∞)	technique[a]	vapor[b]	ref	T/K	ln γ_1^∞	s(ln γ_1^∞)	technique[a]	vapor[b]	ref
					2-Propanol						
298.15	2.041	0.1	DDST	IDEAL	Butler et al.[11]	313.15	2.523[c]	0.2	VPC	IDEAL	Kolb et al.[25]
298.15	1.878	0.1	TENS	VIR+A	Pierotti et al.[12]	333.15	2.616[c]	0.2	VPC	IDEAL	Kolb et al.[25]
333.15	2.252	0.1	TENS	VIR+A	Pierotti et al.[12]	343.15	2.654[c]	0.2	VPC	IDEAL	Kolb et al.[25]
353.15	2.612	0.05	TENS	IDEAL	Slocum and Dodge[13]	353.15	2.680[c]	0.2	VPC	IDEAL	Kolb et al.[25]
363.15	2.616	0.05	TENS	IDEAL	Slocum and Dodge[13]	288.15	2.557	0.5	TENS	VIR	Pividal et al.[26]
373.15	2.639	0.05	TENS	IDEAL	Slocum and Dodge[13]	310.15	2.084[c]	0.1	HSA	IDEAL	Kaneko et al.[27]
373.15	2.536	0.2	EBUL	IDEAL	Kojima et al.[14]	298.15	2.028	0.03	HSA	unknown	Sherman et al.[28][d]
298.15	2.097	0.05	GLC	VIR	Larkin and Pemberton[15]	298.15	2.041[c]	0.1	HSA	IDEAL	Merk and Riederer[29]
298.15	2.029	0.05	HSA	IDEAL	Rytting et al.[16]	298.15	2.342[c]	0.2	WWC	IDEAL	Altschuh et al.[30]
298.15	2.096	0.05	GLC	VIR	Mash and Pemberton[17]	298.15	2.140[c]	0.1	IGS	IDEAL	Kim et al.[31]
298.15	1.533[c]	0.5	HSA	IDEAL	Mazza[18]	283.15	1.641	0.05	IGS	IDEAL	Fukuchi et al.[32]
310.2	2.280[c]	0.05	GLC	IDEAL	Kühne et al.[19]	293.15	1.977	0.05	IGS	IDEAL	Fukuchi et al.[32]
328.15	2.506	0.05	IGS	IDEAL	Lee[20]	298.15	2.105	0.05	IGS	IDEAL	Fukuchi et al.[32]
298.15	2.019	0.02	TENS	VIR	Nord et al.[21]	303.15	2.213	0.05	IGS	IDEAL	Fukuchi et al.[32]
308.15	2.182	0.02	TENS	VIR	Nord et al.[21]	313.15	2.380	0.05	IGS	IDEAL	Fukuchi et al.[32]
273.15	1.477[c]	0.1	HSA	IDEAL	Snider and Dawson[22]	328.15	2.416	0.03	NSGLC	IDEAL	Dohnal and Ondo[33]
298.15	2.036[c]	0.1	HSA	IDEAL	Snider and Dawson[22]	283.15	1.681	0.03	RHSA	VIR	this work
317.85	2.175	0.1	EBUL	VIR	Bergmann and Eckert[23]	293.15	1.930	0.03	RHSA	VIR	this work
328.05	2.262	0.1	EBUL	VIR	Bergmann and Eckert[23]	308.15	2.179	0.03	RHSA	VIR	this work
337.55	2.251	0.1	EBUL	VIR	Bergmann and Eckert[23]	333.15	2.468	0.03	RDIST	VIR	this work
349.15	2.398	0.1	EBUL	VIR	Bergmann and Eckert[23]	353.15	2.526	0.03	CIRC	VIR	this work
357.75	2.451	0.1	EBUL	VIR	Bergmann and Eckert[23]	363.15	2.557	0.03	CIRC	VIR	this work
298.15	2.048	0.1	NSGLC	IDEAL	Landau et al.[24]	371.15	2.573	0.03	CIRC	VIR	this work
					2-Butanol						
298.15	3.219	0.05	DDST	IDEAL	Butler et al.[11]	308.15	3.550	0.1	HSA	IDEAL	Whitehead and Sandler[38]
298.15	3.186[e]	0.05	DDST	IDEAL	Butler and Reid[34]	328.15	3.603	0.03	NSGLC	IDEAL	Dohnal and Ondo[33]
308.15	3.364[e]	0.05	DDST	IDEAL	Butler and Reid[34]	273.35	2.617	0.03	RHSA	VIR	this work
298.15	3.211	0.1	TENS	VIR+A	Pierotti et al.[12]	283.15	2.885	0.03	RHSA	VIR	this work
333.15	3.481	0.1	TENS	VIR+A	Pierotti et al.[12]	293.15	3.118	0.03	RHSA	VIR	this work
298.15	3.270	0.05	GLC	VIR	Larkin and Pemberton[15]	293.15	3.114	0.03	HSA	VIR	this work
298.15	3.258[g]	0.03	TENS	IDEAL	Cabani et al.[35]	303.15	3.288	0.03	HSA	VIR	this work
298.15	3.211	0.05	HSA	IDEAL	Rytting et al.[16]	303.15	3.288	0.03	IGS	VIR	this work
298.15	3.270	0.05	GLC	VIR	Mash and Pemberton[17]	313.15	3.428	0.03	IGS	VIR	this work
310.2	3.472[c]	0.05	GLC	IDEAL	Kühne et al.[19]	313.15	3.444	0.03	HSA	VIR	this work
273.15	2.734[c]	0.1	HSA	IDEAL	Snider and Dawson[22]	323.15	3.520	0.03	HSA	VIR	this work
298.15	3.077[c]	0.1	HSA	IDEAL	Snider and Dawson[22]	323.15	3.538	0.03	IGS	VIR	this work
293.15	3.035	0.03	HSA	VIR	Sagert and Lau[36]	333.15	3.575	0.03	IGS	VIR	this work
298.15	3.109	0.1	NSGLC	IDEAL	Landau et al.[24]	333.15	3.608	0.03	HSA	VIR	this work
323.18	3.570	0.05	TENS	IDEAL	Fischer and Gmehling[37]	343.15	3.638	0.03	RDIST	VIR	this work
298.15	3.270	0.03	HSA	unknown	Sherman et al.[28][d]	353.15	3.648	0.03	RDIST	VIR	this work
298.15	3.360[c]	0.1	HSA	IDEAL	Merk and Riederer[29]	363.15	3.699	0.03	CIRC	VIR	this work
298.15	3.219	0.05	HSA	IDEAL	Whitehead and Sandler[38]	371.15	3.632	0.03	CIRC	VIR	this work
303.15	3.520	0.1	HSA	IDEAL	Whitehead and Sandler[38]						

Table 7. (Continued)

T/K	$\ln \gamma_1^\infty$	$s(\ln \gamma_1^\infty)$	technique[a]	vapor[b]	ref	T/K	$\ln \gamma_1^\infty$	$s(\ln \gamma_1^\infty)$	technique[a]	vapor[b]	ref
2-Methyl-1-propanol											
298.15	3.766	0.05	DDST	IDEAL	Butler et al.[11]	298.15	4.181	0.1	IGS	IDEAL	Sancho et al.[42]
298.15	3.852	0.02	GLC	VIR	Larkin and Pemberton[15]	298.15	3.848[c]	0.1	HSA	IDEAL	Merk and Riederer[29]
373.15	3.484[f]	0.5	CIRC	IDEAL	Hakuta et al.[39]	303.15	3.963	0.02	HSA	VIR	Hovorka et al.[3]
298.15	3.795	0.05	HSA	IDEAL	Rytting et al.[16]	323.15	4.034	0.02	RDIST	VIR	Hovorka et al.[3]
298.15	3.879	0.02	GLC	VIR	Mash and Pemberton[17]	323.15	4.052	0.02	RDIST	VIR	Hovorka et al.[3]
310.2	3.996[c]	0.03	GLC	IDEAL	Kühne et al.[19]	333.15	4.109	0.02	RDIST	VIR	Hovorka et al.[3]
298.15	3.578[c]	0.2	HSA	IDEAL	Snider and Dawson[22]	343.15	4.088	0.02	RDIST	VIR	Hovorka et al.[3]
293.15	3.793	0.02	HSA	VIR+A	Sagert and Lau[36]	353.15	4.048	0.02	RDIST	VIR	Hovorka et al.[3]
323.72	3.466[f]	0.5	CIRC	IDEAL	Ikari et al.[40]	328.15	4.038	0.03	NSGLC	IDEAL	Dohnal and Ondo[33]
338.4	3.632[f]	0.5	CIRC	IDEAL	Ikari et al.[40]	273.35	3.453	0.03	RHSA	VIR	this work
373.14	3.728[f]	0.5	CIRC	IDEAL	Ikari et al.[40]	283.15	3.605	0.03	RHSA	VIR	this work
310.15	3.624[c]	0.5	HSA	IDEAL	Kaneko et al.[27]	293.15	3.791	0.03	HSA	VIR	this work
298.15	4.615[c]	0.5	IGS	IDEAL	Shiu and Mackay[41]	298.15	3.859	0.03	RHSA	VIR	this work
298.15	3.484[c]	0.5	WWC	IDEAL	Altschuh et al.[30]	303.15	3.918	0.03	HSA	VIR	this work
298.15	3.835	0.03	HSA	IDEAL	Whitehead and Sandler[38]	313.15	3.991	0.03	HSA	VIR	this work
303.15	3.912	0.03	HSA	IDEAL	Whitehead and Sandler[38]	323.15	4.054	0.03	HSA	VIR	this work
308.15	3.940	0.03	HSA	IDEAL	Whitehead and Sandler[38]	333.15	4.066	0.03	HSA	VIR	this work
298.15	3.892	0.03	HSA	unknown	Sherman et al.[28][d]	363.15	3.995	0.03	CIRC	VIR	this work
323.15	4.062	0.03	TENS	IDEAL	Fischer and Gmehling[37]	371.15	3.955	0.03	CIRC	VIR	this work
2-Methyl-2-propanol											
298.15	2.468	0.1	DDST	IDEAL	Butler et al.[11]	303.15	2.526	0.05	HSA	IDEAL	Whitehead and Sandler[38]
298.15	2.313	0.2	TENS	VIR+A	Pierotti et al.[12]	308.15	2.728	0.05	HSA	IDEAL	Whitehead and Sandler[38]
333.15	2.839	0.2	TENS	VIR+A	Pierotti et al.[12]	298.15	2.201[c]	0.2	WWC	IDEAL	Altschuh et al.[30]
298.15	2.507	0.03	GLC	VIR	Larkin and Pemberton[15]	328.15	3.030	0.03	NSGLC	IDEAL	Dohnal and Ondo[33]
298.15	2.557	0.03	HSA	IDEAL	Rytting et al.[16]	299.15	2.573	0.03	HSA	VIR	this work
298.15	2.501	0.03	GLC	VIR	Mash and Pemberton[17]	303.15	2.667	0.03	HSA	VIR	this work
310.2	2.779[c]	0.03	GLC	IDEAL	Kühne et al.[19]	313.15	2.827	0.03	HSA	VIR	this work
298.15	2.667[c]	0.1	HSA	IDEAL	Snider and Dawson[22]	323.15	2.991	0.03	RDIST	VIR	this work
293.15	2.434	0.03	HSA	VIR+A	Sagert and Lau[36]	333.15	3.082	0.03	RDIST	VIR	this work
323.13	2.955	0.05	TENS	IDEAL	Fischer and Gmehling[37]	343.15	3.157	0.03	RDIST	VIR	this work
298.15	2.477[e]	0.03	TENS	VIR	Koga et al.[43]	353.15	3.235	0.03	CIRC	VIR	this work
298.15	2.477	0.03	HSA	unknown	Sherman et al.[28][d]	363.15	3.270	0.03	CIRC	VIR	this work
298.15	2.501[c]	0.03	HSA	IDEAL	Merk and Riederer[29]	371.15	3.311	0.03	CIRC	VIR	this work
298.15	2.468	0.05	HSA	IDEAL	Whitehead and Sandler[38]						

[a] CIRC, circulation equilibrium still; DDST, differential distillation; EBUL, ebulliometry; GLC, measurement of retention time in gas−liquid chromatography; HSA, headspace analysis; IGS, inert gas stripping; NSGLC, non-steady-state gas−liquid chromatography; RHSA, relative headspace analysis; RDIST, Rayleigh distillation; VPC, vapor-phase calibration; TENS, tensimetry; WWC, wetted-wall column. [b] IDEAL, ideal gas; VIR, virial equation of state; VIR+A, virial equation of state with Amagat's law. [c] Limiting activity coefficient calculated from liquid/vapor or vapor/liquid distribution coefficient reported in the cited source. [d] Secondary reference citing an original unavailable source (e.g., thesis). [e] Limiting activity coefficient calculated from dilute range $P-x$ data reported in the cited source. [f] Limiting activity coefficient calculated from relative volatility in highly dilute solutions reported in the cited source. [g] Limiting activity coefficient calculated from solution Gibbs energy reported in the cited source.

information to critical evaluation and processed it by a thermodynamically consistent treatment.

The essentials of the procedure are the same as described previously.[3] For each solute, the equilibrium (γ_1^∞) and calorimetric ($\bar{H}_1^{E,\infty}$ and $\bar{C}_{p,1}^{E,\infty}$) data were fitted simultaneously with a suitable, sufficiently flexible model equation describing their temperature dependence. Like for lower 1-alkanols treated recently,[2] also for the branched alkanols studied in this work the following four-parameter equation

$$\ln \gamma_1^\infty = A + B/\tau + C \exp(D\tau)/\tau \tag{1}$$

Table 8. Experimental Values of Limiting Partial Molar Excess Enthalpies of Branched (C3 and C4) Alkanols (1) in Water (2) Together with their Standard Uncertainty and Technique of Measurement

$\frac{T}{\mathrm{K}}$	$\frac{\bar{H}_1^{E,\infty}}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{s(\bar{H}_1^{E,\infty})}{\mathrm{kJ \cdot mol^{-1}}}$	technique[a]	ref	$\frac{T}{\mathrm{K}}$	$\frac{\bar{H}_1^{E,\infty}}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{s(\bar{H}_1^{E,\infty})}{\mathrm{kJ \cdot mol^{-1}}}$	technique[a]	ref
				2-Propanol					
298.15	−13.40	0.4	BATCH	Lama and Lu[44]	298.15	−12.5[b]	0.3	FLOW	Denda et al.[51]
277.88	−17.72	0.1	BATCH	Alexander and Hill[45]	298.15	−13.09	0.03	FLOW	Dohnal et al.[52]
288.07	−15.20	0.1	BATCH	Alexander and Hill[45]	298.15	−13.3[b]	0.3	BATCH	Davis et al.[53]
298.1	−12.98	0.05	BATCH	Alexander and Hill[45]	283.15	−15.09	0.5	FLOW	Pfeffer et al.[54]
308.2	−11.07	0.05	BATCH	Alexander and Hill[45]	298.15	−12.76	0.3	FLOW	Pfeffer et al.[54]
298.15	−13.08	0.1	BATCH	Arnett et al.[46]	323.15	−8.17	0.2	FLOW	Pfeffer et al.[54]
299.65	−13.26	0.3	BATCH	Brower et al.[47]	343.15	−4.73	0.2	FLOW	Pfeffer et al.[54]
298.15	−12.90	0.4	BATCH	Krishnan and Friedman[48]	363.15	−2.21	0.1	FLOW	Pfeffer et al.[54]
298.15	−13.10	0.04	BATCH	Rouw and Somsen[49]	298.15	−13.1	0.03	TITR	Tanaka et al.[55]
298.15	−12.69	0.3	BATCH	Korolev et al.[50]					
				2-Butanol					
298.15	−13.19	0.1	BATCH	Arnett et al.[46]	298.15	−13.02	0.06	BATCH	Rouw and Somsen[49]
299.65	−11.99	0.7	BATCH	Brower et al.[47]	298.15	−12.62	0.8	BATCH	Bury and Treiner[57]
303.15	−11.723	0.4	BATCH	Belousov and Ponner[56]	278.15	−17.22	0.8	TITR	Andersson and Olofsson[58]
328.15	−5.862	0.4	BATCH	Belousov and Ponner[56]	298.15	−12.99	0.8	TITR	Andersson and Olofsson[58]
348.15	−2.093	0.4	BATCH	Belousov and Ponner[56]	317.15	−9.29	0.8	TITR	Andersson and Olofsson[58]
298.15	−12.895	0.1	BATCH	Cabani et al.[35]					
				2-Methyl-1-propanol					
298.15	−9.32	0.1	BATCH	Arnett et al.[46]	348.15	3.349	0.6	BATCH	Belousov and Ponner[56]
299.65	−9.683	0.6	BATCH	Brower et al.[47]	298.15	−9.22	0.1	BATCH	Rouw and Somsen[49]
303.15	−7.536	0.6	BATCH	Belousov and Ponner[56]	298.15	−9.18	0.1	FLOW	Hovorka et al.[59]
328.15	−2.512	0.6	BATCH	Belousov and Ponner[56]					
				2-Methyl-2-propanol					
298.15	−17.17	0.2	BATCH	Arnett and McKelvey[60]	298.15	−17.44	0.02	BATCH	Sköld et al.[61]
298.15	−17.21	0.3	BATCH	Krishnan and Friedman[48]	298.15	−17.31	0.05	BATCH	Rouw and Somsen[49]
299.2	−17.04	0.1	BATCH	Alexander and Hill[45]	300.05	−16.9	0.3	BATCH	Koga[62]
308.2	−14.92	0.1	BATCH	Alexander and Hill[45]	303.15	−16.03	0.3	BATCH	Koga[62]
298.15	−17.46	0.1	BATCH	Arnett et al.[46]	318.32	−12.82	0.3	BATCH	Koga[62]
299.65	−17.47	0.5	BATCH	Brower et al.[47]	332.64	−10.03	0.3	BATCH	Koga[62]

[a] BATCH, batch dissolution calorimetry; FLOW, flow mixing calorimetry; TITR, titration microcalorimetry. [b] $\bar{H}_1^{E,\infty}$ calculated from H^E data for the lowest solute concentrations reported in the cited literature.

giving

$$\bar{H}_1^{E,\infty} = RT_0[B - C\exp(D\tau)(D\tau - 1)]$$

and

$$\bar{C}_{p,1}^{E,\infty} = -RCD^2\tau\exp(D\tau)$$

where $\tau = T/T_0$ and $T_0 = 298.15$ K, yielded superior performance and was used for the purpose. The adjustable parameters A, B, C, and D were calculated by the simultaneous correlation of all available data using the weighted least-squares method. The minimized objective function was as follows:

$$S = \sum_{i=1}^{n_G}[\ln \gamma_{1,i}^{\infty}(\mathrm{exp}) - \ln \gamma_{1,i}^{\infty}(\mathrm{calcd})]^2/s^2(\ln \gamma_{1,i}^{\infty}) + \sum_{i=1}^{n_H}[\bar{H}_{1,i}^{E,\infty}(\mathrm{exp}) - \bar{H}_{1,i}^{E,\infty}(\mathrm{calcd})]^2/s^2(\bar{H}_{1,i}^{E,\infty}) + \sum_{i=1}^{n_C}[\bar{C}_{p,1,i}^{E,\infty}(\mathrm{exp}) - \bar{C}_{p,1,i}^{E,\infty}(\mathrm{calcd})]^2/s^2(\bar{C}_{p,1,i}^{E,\infty}) \quad (2)$$

Table 9. Experimental Values of Limiting Partial Molar Excess Heat Capacities of Branched (C3 and C4) Alkanols (1) in Water (2) Together with Their Standard Uncertainty and Technique of Measurement

T	$\bar{C}_{p,1}^{E,\infty}$	$s(\bar{C}_{p,1}^{E,\infty})$			T	$\bar{C}_{p,1}^{E,\infty}$	$s(\bar{C}_{p,1}^{E,\infty})$		
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	technique[a]	ref	K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	technique[a]	ref
2-Propanol									
298.15	232	20	INDIRECT	Arnett et al.[46]	333.15	166[b]	6	SCAN	Origlia-Luster and Woolley[64]
283.15	236	7	FLOW	Roux et al.[63]	338.15	160[b]	6	SCAN	Origlia-Luster and Woolley[64]
298.15	201	7	FLOW	Roux et al.[63]	343.15	155[b]	6	SCAN	Origlia-Luster and Woolley[64]
278.15	252[b]	6	SCAN	Origlia-Luster and Woolley[64]	348.15	149[b]	6	SCAN	Origlia-Luster and Woolley[64]
283.15	239[b]	6	SCAN	Origlia-Luster and Woolley[64]	353.15	144[b]	6	SCAN	Origlia-Luster and Woolley[64]
288.15	230[b]	6	SCAN	Origlia-Luster and Woolley[64]	358.15	139[b]	6	SCAN	Origlia-Luster and Woolley[64]
293.15	221[b]	6	SCAN	Origlia-Luster and Woolley[64]	363.15	134[b]	10	SCAN	Origlia-Luster and Woolley[64]
298.15	214[b]	6	SCAN	Origlia-Luster and Woolley[64]	368.15	129[b]	10	SCAN	Origlia-Luster and Woolley[64]
303.15	206[b]	6	SCAN	Origlia-Luster and Woolley[64]	373.15	125[b]	10	SCAN	Origlia-Luster and Woolley[64]
308.15	199[b]	6	SCAN	Origlia-Luster and Woolley[64]	378.15	121[b]	10	SCAN	Origlia-Luster and Woolley[64]
313.15	192[b]	6	SCAN	Origlia-Luster and Woolley[64]	383.15	117[b]	10	SCAN	Origlia-Luster and Woolley[64]
318.15	186[b]	6	SCAN	Origlia-Luster and Woolley[64]	388.15	113[b]	10	SCAN	Origlia-Luster and Woolley[64]
323.15	179[b]	6	SCAN	Origlia-Luster and Woolley[64]	393.15	110[b]	10	SCAN	Origlia-Luster and Woolley[64]
328.15	173[b]	6	SCAN	Origlia-Luster and Woolley[64]	298.15	211	3	FLOW	Fenclová et al.[65]
2-Butanol									
298.15	285	20	INDIRECT	Arnett et al.[46]	338.15	192[b]	8	SCAN	Origlia and Woolley[67]
298.15	250[b]	3	FLOW	Jolicoeur and Lacroix[66]	343.15	185[b]	8	SCAN	Origlia and Woolley[67]
278.15	298[b]	8	SCAN	Origlia and Woolley[67]	348.15	177[b]	8	SCAN	Origlia and Woolley[67]
283.15	288[b]	8	SCAN	Origlia and Woolley[67]	353.15	171[b]	8	SCAN	Origlia and Woolley[67]
288.15	278[b]	8	SCAN	Origlia and Woolley[67]	358.15	165[b]	8	SCAN	Origlia and Woolley[67]
293.15	268[b]	8	SCAN	Origlia and Woolley[67]	363.15	159[b]	8	SCAN	Origlia and Woolley[67]
298.15	258[b]	8	SCAN	Origlia and Woolley[67]	368.15	154[b]	8	SCAN	Origlia and Woolley[67]
303.15	249[b]	8	SCAN	Origlia and Woolley[67]	373.15	150[b]	10	SCAN	Origlia and Woolley[67]
308.15	240[b]	8	SCAN	Origlia and Woolley[67]	378.15	146[b]	10	SCAN	Origlia and Woolley[67]
313.15	231[b]	8	SCAN	Origlia and Woolley[67]	383.15	143[b]	10	SCAN	Origlia and Woolley[67]
318.15	222[b]	8	SCAN	Origlia and Woolley[67]	388.15	141[b]	10	SCAN	Origlia and Woolley[67]
323.15	214[b]	8	SCAN	Origlia and Woolley[67]	393.15	139[b]	10	SCAN	Origlia and Woolley[67]
328.15	206[b]	8	SCAN	Origlia and Woolley[67]	298.15	258	3	FLOW	Fenclová et al.[65]
333.15	198[b]	8	SCAN	Origlia and Woolley[67]					
2-Methyl-1-propanol									
298.15	284	20	INDIRECT	Arnett et al.[46]	333.15	205[b]	8	SCAN	Origlia and Woolley[67]
298.15	252[b]	3	FLOW	Jolicoeur and Lacroix[66]	338.15	198[b]	8	SCAN	Origlia and Woolley[67]
298.15	255	3	FLOW	Hovorka et al.[68]	343.15	191[b]	8	SCAN	Origlia and Woolley[67]
278.15	292[q]	8	SCAN	Origlia and Woolley[67]	348.15	184[b]	8	SCAN	Origlia and Woolley[67]
283.15	283[b]	8	SCAN	Origlia and Woolley[67]	353.15	178[b]	8	SCAN	Origlia and Woolley[67]
288.15	275[b]	8	SCAN	Origlia and Woolley[67]	358.15	172[b]	8	SCAN	Origlia and Woolley[67]

Table 9. (Continued)

T / K	$\bar{C}_{p,1}^{\mathrm{E},\infty}$ / $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$	$s(\bar{C}_{p,1}^{\mathrm{E},\infty})$ / $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$	technique[a]	ref	T / K	$\bar{C}_{p,1}^{\mathrm{E},\infty}$ / $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$	$s(\bar{C}_{p,1}^{\mathrm{E},\infty})$ / $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$	technique[a]	ref
2-Methyl-1-propanol (Continued)									
293.15	267[b]	8	SCAN	Origlia and Woolley[67]	363.15	166[b]	8	SCAN	Origlia and Woolley[67]
298.15	259[b]	8	SCAN	Origlia and Woolley[67]	368.15	161[b]	8	SCAN	Origlia and Woolley[67]
303.15	251[b]	8	SCAN	Origlia and Woolley[67]	373.15	156[b]	10	SCAN	Origlia and Woolley[67]
308.15	243[b]	8	SCAN	Origlia and Woolley[67]	378.15	151[b]	10	SCAN	Origlia and Woolley[67]
313.15	235[b]	8	SCAN	Origlia and Woolley[67]	383.15	147[b]	10	SCAN	Origlia and Woolley[67]
318.15	227[b]	8	SCAN	Origlia and Woolley[67]	388.15	143[b]	10	SCAN	Origlia and Woolley[67]
323.15	219[b]	8	SCAN	Origlia and Woolley[67]	393.15	140[b]	10	SCAN	Origlia and Woolley[67]
328.15	212[b]	8	SCAN	Origlia and Woolley[67]	298.15	257	3	FLOW	Fenclová et al.[65]
2-Methyl-2-propanol									
298.15	283	20	INDIRECT	Arnett et al.[46]	333.15	197[b]	10	SCAN	Origlia and Woolley[67]
298.15	245[b]	3	FLOW	Jolicoeur and Lacroix[66]	338.15	191[b]	10	SCAN	Origlia and Woolley[67]
298.15	244	8	DROP	Sköld et al.[61]	343.15	186[b]	10	SCAN	Origlia and Woolley[67]
298.15	254	10	FLOW	De Visser et al.[69]	348.15	181[b]	10	SCAN	Origlia and Woolley[67]
313.15	219	10	FLOW	De Visser et al.[69]	353.15	177[b]	10	SCAN	Origlia and Woolley[67]
328.15	195	10	FLOW	De Visser et al.[69]	358.15	172[b]	10	SCAN	Origlia and Woolley[67]
338.15	191[b]	20	FLOW	De Visser et al.[69]	363.15	168[b]	10	SCAN	Origlia and Woolley[67]
298.15	252[b]	8	SCAN	Origlia and Woolley[67]	368.15	165[b]	10	SCAN	Origlia and Woolley[67]
303.15	242[b]	8	SCAN	Origlia and Woolley[67]	373.15	161[b]	10	SCAN	Origlia and Woolley[67]
308.15	232[b]	8	SCAN	Origlia and Woolley[67]	378.15	158[b]	10	SCAN	Origlia and Woolley[67]
313.15	224[b]	8	SCAN	Origlia and Woolley[67]	383.15	155[b]	10	SCAN	Origlia and Woolley[67]
318.15	216[b]	8	SCAN	Origlia and Woolley[67]	388.15	152[b]	10	SCAN	Origlia and Woolley[67]
323.15	209[b]	8	SCAN	Origlia and Woolley[67]	393.15	151[b]	10	SCAN	Origlia and Woolley[67]
328.15	203[b]	8	SCAN	Origlia and Woolley[67]	298.15	249	3	FLOW	Fenclová et al.[65]

[a] DROP, drop calorimetry; FLOW, flow calorimetry; SCAN, scanning calorimetry; INDIRECT, integral heat method. [b] Calculated from partial molar heat capacity at infinite dilution reported in the cited source; molar heat capacities of pure solute were taken from Zábranský et al.[70−72]

with data being weighted according to their standard uncertainties $s(\ln \gamma_1^{\infty})$, $s(\bar{H}_1^{\mathrm{E},\infty})$, and $s(\bar{C}_{P,1}^{\mathrm{E},\infty})$. These uncertainties correspond to standard deviations (68 % probability level) and comprise contributions from all possible sources of error, both random and systematic. Only discrete values of uncertainties corresponding to several predefined uncertainty levels were assigned to γ_1^{∞} data.[73] Although no such uncertainty levels were used for thermal data, values of uncertainties rounded to just one significant digit were preferred.

The first estimates of the uncertainties came from information given in the original source of data. The judgment was based on our own experience with various experimental methods and on their detailed analyses concerning the error propagation and applicability. As a rule, comparison of correlation deviations to the initially assigned uncertainties indicated that true uncertainties of some data were significantly greater than those assumed, probably because of systematic errors. Thus, the values of uncertainties were subsequently readjusted by trial and error in order to obtain coherence of all data in the statistical sense. As a main coherence criterion, the residual sum of squares $S_{\min}$ was required to range within statistically plausible bounds (i.e., within the respective critical values of χ^2):

$$\chi^2_{\alpha/2}(n-p) < S_{\min} < \chi^2_{1-\alpha/2}(n-p) \tag{3}$$

where $n = n_{\mathrm{G}} + n_{\mathrm{H}} + n_{\mathrm{C}}$ is the total number of data points, p is the number of fitted parameters (here $p = 4$), and α is the significance level ($\alpha = 0.05$). In addition to this global condition of coherence, the statistical behavior of individual weighted residuals was also considered; here, an improbably big magnitude of the weighted residual signaled the necessity to increase the uncertainty of the given data point. As a rule, the uncertainty was increased for those data where the available information or our own experience suggested that an enhanced error is probable.

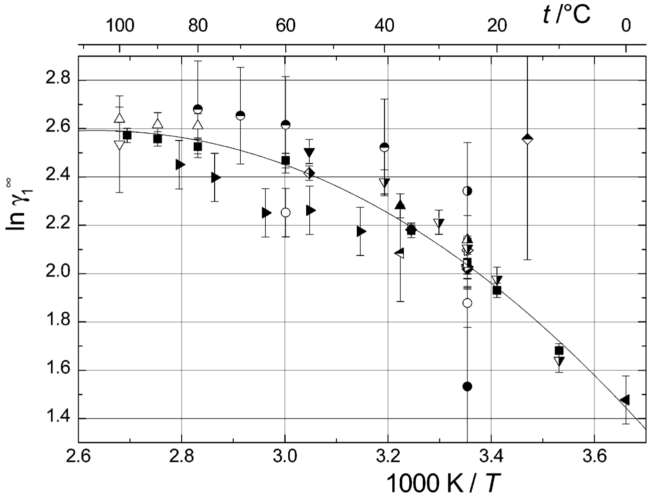

Figure 1. Limiting activity coefficient ln γ_1^∞ of 2-propanol (1) in water (2) as a function of temperature. Experimental values are from Table 7: □, ref 11; ○, ref 12; △, ref 13; ▽, ref 14; ◇, ref 15; left-facing open triangle, ref 16; right-facing open triangle, ref 17; ●, ref 18; ▲, ref 19; ▼, ref 20; ◆, ref 21; left-facing solid triangle, ref 22; right-facing solid triangle, ref 23; ⬒, ref 24; ◓, ref 25; upper solid diamond, ref 26; left-facing upper solid open triangle, ref 27; right-facing upper solid triangle, ref 28; ◨, ref 29; ◑, ref 30; ◭, ref 31; ⧨, ref 32; right side solid diamond, ref 33; ■, this work. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 1.

The outlined procedure enabled us to discriminate between existing data and to establish a thermodynamically consistent temperature dependence of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$. The final values of uncertainties assigned to the data are given in Tables 7 to 9. The values of parameters of eq 1, together with the overall standard deviations of fit *s* and other fit characteristics, are listed in Table 3.

Results of Correlations and Discussion

Data Assessment. The values of limiting activity coefficients for the four branched alkanols in water are displayed, together with their fits by eq 1, in the van't Hoff coordinates in Figures 1 to 4. As seen, most data agree quite well, exhibiting a reasonable scatter, but there are also some data deviating grossly ($>$ 0.2 in ln γ_1^∞) from the fits. According to the evaluation policy we adopted, such data were not strictly rejected but rather labeled with a larger uncertainty, which reduced appropriately their statistical weight in the treatment. The grossly deviating points, which are indisputably subject to large errors, are encountered especially for 2-propanol and 2-methyl-1-propanol. They involve the tensimetric measurement of Pividal et al.,[26] the inert gas stripping measurements of Shiu and Mackay[41] and Sancho et al.;[42] the headspace analysis measurements of Mazza,[18] Kaneko et al.,[27] and Snider and Dawson;[22] and the circulation still measurements of Ikari et al.[40] and Hakuta et al.[39] In addition, the results from environmental screening of air−water partitioning of Altschuh et al.[30] by the wetted-wall column technique belong also to those grossly deviating.

Apart from the outliers mentioned, most other data are in a good agreement, supporting the stability of the recommended fit. Among the γ_1^∞ data that show the closest agreement and the smallest deviations from the recommended fit are especially those of Nord et al.[21] and Fischer and Gmehling[37] (tensimetry); Rytting et al.;[16] Sherman et al.;[28] and in most cases Whitehead and Sandler[38] (headspace analysis), Pemberton et al.,[15,17] and Kühne et al.[19] (GLC); Butler et al.[11,34] (differential distillation) and those measured in this laboratory (applicability optimized use of various techniques).

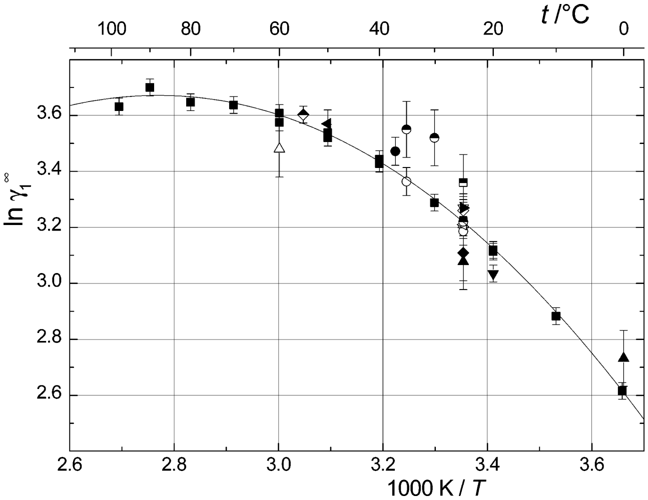

Figure 2. Limiting activity coefficient ln γ_1^∞ of 2-butanol (1) in water (2) as a function of temperature. Experimental values are from Table 7: □, ref 11; ○, ref 34; △, ref 12; ▽, ref 15; ◇, ref 35; left-facing open triangle, ref 16; right-facing open triangle, ref 17; ●, ref 19; ▲, ref 22; ▼, ref 36; ◆, ref 24; left-facing solid triangle, ref 37; right-facing solid triangle, ref 28; ⬒, ref 29; ◓, ref 38; upper solid diamond, ref 33; ■, this work. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 1.

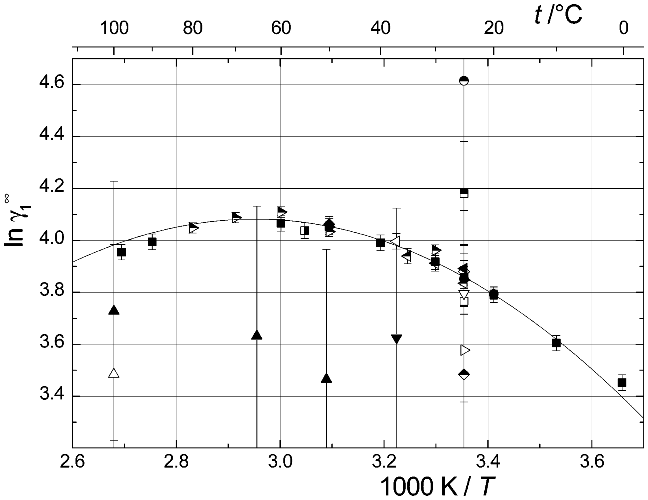

Figure 3. Limiting activity coefficient ln γ_1^∞ of 2-methyl-1-propanol (1) in water (2) as a function of temperature. Experimental values are from Table 7: □, ref 11; ○, ref 15; △, ref 39; ▽, ref 16; ◇, ref 17; left-facing open triangle, ref 19; right-facing open triangle, ref 22; ●, ref 36; ▲, ref 40; ▼, ref 27; ◆, ref 37; left-facing solid triangle, ref 28; right-facing solid triangle, ref 29; ⬒, ref 42; ◓, ref 41; upper solid diamond, ref 30; left-facing upper solid triangle, ref 38; right-facing upper solid triangle, ref 3; ◨, ref 33; ■, this work. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 1.

Compared to the measurements of limiting activity coefficients, the calorimetric determinations of dissolution thermal properties appear to be considerably less scattered, as seen from Figures 5 to 8. At 298.15 K, where most calorimetric measurements were done, very good accord is generally observed. Although the determinations of $\bar{H}_1^{E,\infty}$ as a function of temperature are not abundant, one can note mutual agreement between the early measurements[45,56] and the more recent ones[54,62,58] and consistency with the data on the dissolution heat capacity.

Regarding $\bar{C}_{p,1}^{E,\infty}$, the only data clearly in error are those resulting from the earliest determinations by Arnett et al.,[46] their $\bar{C}_{p,1}^{E,\infty}$ values being systematically too high. On the other hand,

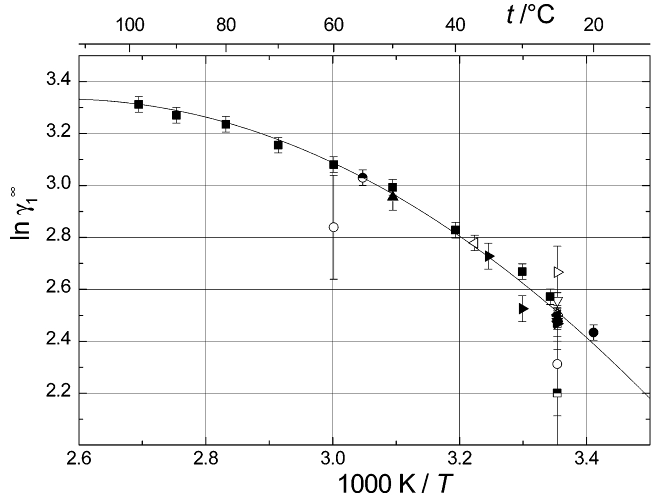

Figure 4. Limiting activity coefficient $\ln \gamma_1^\infty$ of 2-methyl-2-propanol (1) in water (2) as a function of temperature. Experimental values are from Table 7: □, ref 11; ○, ref 12; △, ref 15; ▽, ref 16; ◇, ref 17; left-facing open triangle, ref 19; right-facing open triangle, ref 22; ●, ref 36; ▲, ref 37; ▼, ref 43; ◆, ref 28; left-facing closed triangle, ref 29; right-facing closed triangle, ref 38; ⬒, ref 30; ◓, ref 33; ■, this work. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{\mathrm{E},\infty}$, and $\bar{C}_{p,1}^{\mathrm{E},\infty}$ data by eq 1.

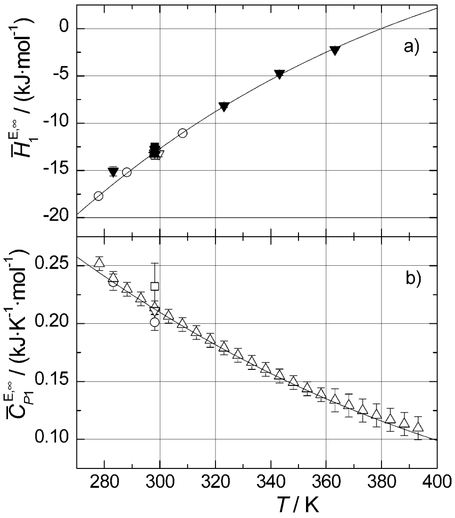

Figure 5. Limiting partial molar excess enthalpy $\bar{H}_1^{\mathrm{E},\infty}$ (a) and heat capacity $\bar{C}_{p,1}^{\mathrm{E},\infty}$ (b) of 2-propanol (1) in water (2) as a function of temperature. Experimental $\bar{H}_1^{\mathrm{E},\infty}$ values are from Table 8: □, ref 44; ○, ref 45; △, ref 46; ▽, ref 47; ◇, ref 48; left-facing open triangle, ref 49; right-facing open triangle, ref 50;[50] ■, ref 51; ●, ref 52; ▲, ref 53; ▼, ref 54; ◆, ref 55. Experimental $\bar{C}_{p,1}^{\mathrm{E},\infty}$ values are from Table 9: □, ref 46; ○, ref 63; △, ref 64; ▽, ref 65. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{\mathrm{E},\infty}$, and $\bar{C}_{p,1}^{\mathrm{E},\infty}$ data by eq 1.

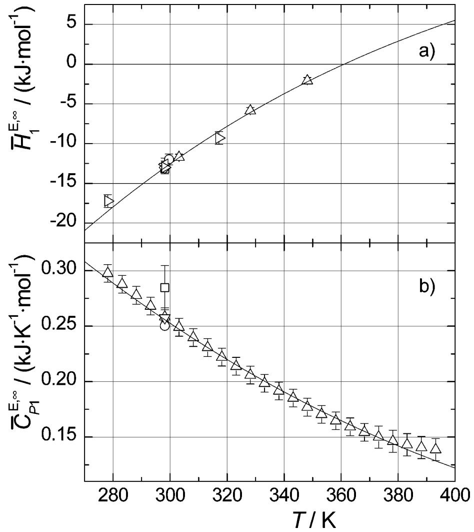

Figure 6. Limiting partial molar excess enthalpy $\bar{H}_1^{\mathrm{E},\infty}$ (a) and heat capacity $\bar{C}_{p,1}^{\mathrm{E},\infty}$ (b) of 2-butanol (1) in water (2) as a function of temperature. Experimental $\bar{H}_1^{\mathrm{E},\infty}$ values are from Table 8: □, ref 46; ○, ref 47; △, ref 56; ▽, ref 35; ◇, ref 49; left-facing open triangle, ref 57; right-facing open triangle, ref 58. Experimental $\bar{C}_{p,1}^{\mathrm{E},\infty}$ values are from Table 9: □, ref 46; ○, ref 66; △, ref 67; ▽, ref 65. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{\mathrm{E},\infty}$, and $\bar{C}_{p,1}^{\mathrm{E},\infty}$ data by eq 1.

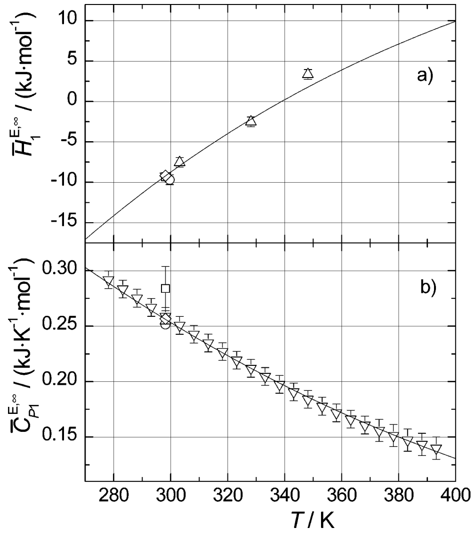

Figure 7. Limiting partial molar excess enthalpy $\bar{H}_1^{\mathrm{E},\infty}$ (a) and heat capacity $\bar{C}_{p,1}^{\mathrm{E},\infty}$ (b) of 2-methyl-1-propanol (1) in water (2) as a function of temperature. Experimental $\bar{H}_1^{\mathrm{E},\infty}$ values are from Table 8: □, ref 46; ○, ref 47; △, ref 56; ▽, ref 49; ◇, ref 59. Experimental $\bar{C}_{p,1}^{\mathrm{E},\infty}$ values are from Table 9: □, ref 46; ○, ref 66; △, ref 68; ▽, ref 67; ◇, ref 65. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{\mathrm{E},\infty}$, and $\bar{C}_{p,1}^{\mathrm{E},\infty}$ data by eq 1.

exceptional in both the extent and quality are the data on $\bar{C}_{p,1}^{\mathrm{E},\infty}(T)$ derived from measurements of Origlia and Woolley,[64,67] which are available for all of the four alkanols studied. Fairly good agreement of these data is seen with the only other systematic determination of $\bar{C}_{p,1}^{\mathrm{E},\infty}(T)$ performed earlier by de Visser et al.[69] for 2-methyl-2-propanol.

Recommended $\gamma_1^\infty(T)$ and $K_H(T)$ Data. Equation 1 with parameters from Table 3 yields for available data a thermodynamically consistent description of superior quality. We consider it to establish the recommended temperature dependence of γ_1^∞ as well as of its derivative properties, $\bar{H}_1^{\mathrm{E},\infty}$ and $\bar{C}_{p,1}^{\mathrm{E},\infty}$, in the range from the melting point to the normal boiling point of water. Note, however, that for 2-methyl-2-propanol the values of γ_1^∞ and other dissolution properties calculated from eq 1 at temperatures below its melting point (298 K) refer to the hypothetical subcooled liquid standard state. The relative standard uncertainty (68 % confidence level) of the recommended values, as inferred by the error propagation from the parameter variance−covariance matrix, does not exceed (1 to 2) % for γ_1^∞ and (2 to 3) % for $\bar{H}_1^{\mathrm{E},\infty}$ or $\bar{C}_{p,1}^{\mathrm{E},\infty}$. The recommended values at 298.15 K are of the highest accuracy and are listed for a quick reference and illustration in Table 4. The recommended temperature dependence of γ_1^∞ is believed to be reliable even in a moderate extrapolation toward higher tem-

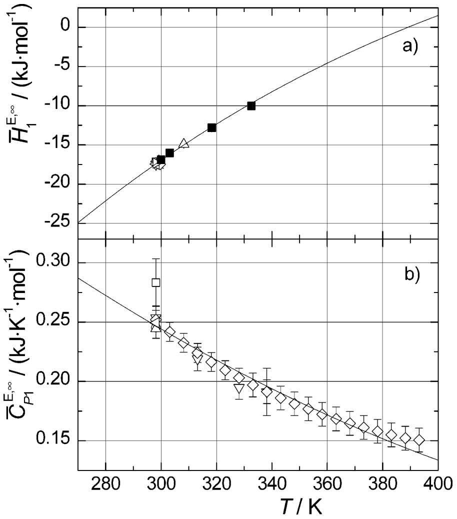

Figure 8. Limiting partial molar excess enthalpy $\bar{H}_1^{E,\infty}$ (a) and heat capacity $\bar{C}_{p,1}^{E,\infty}$ (b) of 2-methyl-2-propanol (1) in water (2) as a function of temperature. Experimental $\bar{H}_1^{E,\infty}$ values are from Table 8: □, ref 60; ○, ref 48; △, ref 45; ▽, ref 46; ◇, ref 47; left-facing open triangle, ref 61; right-facing open triangle, ref 49; ■, ref 62. Experimental $\bar{C}_{p,1}^{E,\infty}$ values are from Table 9: □, ref 46; ○, ref 66; △, ref 61; ▽, ref 69; ◇, ref 67; left-facing open triangle, ref 65. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 1.

peratures (e.g., at 400 K the probable uncertainty of the calculated γ_1^∞ values is estimated to about 3 %).

To obtain the recommendation for the temperature dependence of the Henry's law constants and the related hydration properties, the dependence $\gamma_1^\infty(T)$ was combined with reliable data on respective pure solute properties using the following relations:

$$K_H = \gamma_1^\infty p_1^s \varphi_1^s \exp[v_1^L(p_2^s - p_1^s)/(RT)] \tag{4}$$

$$\Delta_{hyd}G_1^\infty = RT \ln(K_H/p^\circ) \tag{5}$$

$$\Delta_{hyd}H_1^\infty = \bar{H}_1^{E,\infty} - \Delta_{vap}H^\circ \tag{6}$$

$$\Delta_{hyd}C_{p,1}^\infty = \bar{C}_{p,1}^\infty - C_{p,1}^{G,\circ} = \bar{C}_{p,1}^{E,\infty} + (C_{p,1}^{L,\bullet} - C_{p,1}^{G,\circ}) \tag{7}$$

where p_i^s are pure component vapor pressures; v_1^L is the pure liquid solute molar volume; φ_1^s is the fugacity coefficient of the pure solute saturated vapor; $\Delta_{vap}H^\circ$ is the pure solute vaporization enthalpy to the standard state ideal gas (standard vaporization enthalpy); $C_{p,1}^{L,\bullet}$ and $C_{p,1}^{G,\circ}$ are the pure solute heat capacities at the liquid state and the ideal gas standard state, respectively; and $\bar{C}_{p,1}^\infty$ is the solute partial molar heat capacity at infinite dilution in water. These hydration quantities correspond to a transfer of the solute from the pure ideal gas state at standard pressure $p^\circ = 100$ kPa to a hypothetical infinitely dilute solution of unity solute mole fraction ($x_1 = 1$).

The vapor pressures of 1-alkanols were calculated from the Cox equation with parameters from Table 1. Their fugacity coefficients were calculated from truncated virial equation of state with the second virial coefficients estimated by the Hayden and O'Connell correlation.[74] The liquid densities were obtained from CDATA.[10] The standard vaporization enthalpies were obtained from the temperature dependence of standard vaporization internal energies (cohesive energies) given by Majer and Svoboda.[75]

The selected data on the pure alkanols studied may be considered to be the best of those presently available, yet they were noted to exhibit a slight mutual inconsistency in some cases. Extrapolations necessary to cover the temperature range of interest and uncertainties in the vapor phase nonideality corrections are at least partially responsible for these problems. It is obvious that any uncertainty and/or inconsistency in pure solute property data are translated into the calculated values of hydration properties.

In order to establish the recommended temperature dependence of hydration properties in a thermodynamically consistent analytical form, we fitted the data on K_H, $\Delta_{hyd}H_1^\infty$, and $\Delta_{hyd}C_{p,1}^\infty$ simultaneously to the following equation:

$$\ln K_H = A + B/\tau + C \ln \tau + D\tau \tag{8}$$

Equation 8 was used instead of an analogous form of eq 1, because for hydration properties the latter equation was found to perform significantly worse than the former. Yet, eq 8 is a compromise to fit the rather nonlinear $\Delta_{hyd}C_{p,1}^\infty(T)$ dependence encountered. Values of the hydration properties at 21 equidistant temperatures (5 K increment) covering the temperature range of interest were used as input data for the fit. To provide a simplified way of data weighing, the sum of squares of relative deviations was minimized.

The calculated parameters of eq 8, along with the corresponding relative standard deviations of fit s_{rel} are listed for the branched alkanols studied in Table 5. It is seen that eq 8 fits the hydration data quite well, the relative standard deviation being within 1 %. The values of s_{rel} may suggest the probable level of uncertainty for the recommended hydration properties calculated from eq 8, except for $\Delta_{hyd}C_{p,1}^\infty$ at the ends of the temperature interval (273 K, 373 K) where one should allow for uncertainties of (2 to 3) % mainly due to the compromised linear fit of $\Delta_{hyd}C_{p,1}^\infty$ provided by eq 8. An increased uncertainty (1.5 %) is also probable for $\Delta_{hyd}H_1^\infty$ of 2-methyl-2-propanol at higher temperatures close to 373 K and for all its properties at temperatures below its melting point. Nevertheless, for estimation of the Henry's law constants, even moderate extrapolations by eq 8 toward higher temperatures are believed to be reliable (e.g., at 400 K the probable uncertainty of the calculated K_H values is estimated to about 5 %). The values of thermodynamic functions of hydration at 298.15 K calculated from eq 8 are compared with recent recommendations by Plyasunov and Shock[76] in Table 6. In general, a very good agreement is observed for all the branched alkanols and properties studied. The present values, especially of K_H ($\Delta_{hyd}G_1^\infty$), should be however preferred as they are significantly more accurate.

Variation of Properties with Temperature and Alkanol Branching

Having established the thermodynamically consistent and accurate temperature dependence for various infinite dilution properties of the branched (C3 and C4) alkanols in water, we will be now commenting on their essential features, in particular on their variation with temperature and alkanol branching. The results for the respective 1-alkanols used for comparison are taken from our previous work.[2]

In Figure 9, the recommended $\gamma_1^\infty(T)$ and $K_H(T)$ for all (C3 and C4) alkanol isomers are plotted in the van't Hoff coordinates. As seen in Figure 9a, going from 273 K the values of ln γ_1^∞ rise with temperature, following concave courses which at a higher T display a maximum. For 2-propanol and 2-methyl-

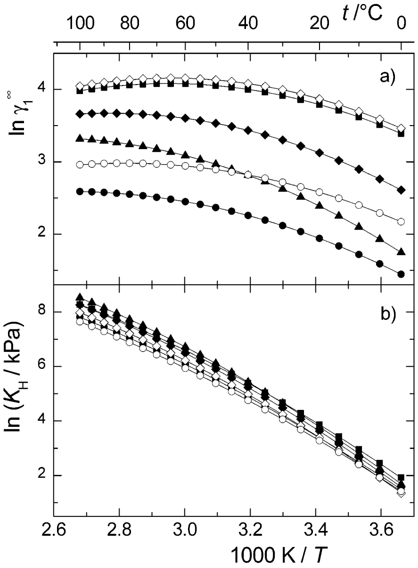

Figure 9. Recommended temperature dependence for limiting activity coefficients γ_1^∞ (a) and Henry's law constants K_H (b) of (C3 and C4) alkanols (1) in water (2): ○, 1-propanol; ●, 2-propanol; ◇, 1-butanol; ◆, 2-butanol; ■, 2-methyl-1-propanol; ▲, 2-methyl-2-propanol.

2-propanol, the maximum appears slightly above the normal boiling temperature of water. The temperature corresponding to the maximum, T_{max} (see Table 4 here and in ref 2), increases with the branching of the alkanol isomer and follows the hydroxyl group position sequence: primary < secondary < tertiary. At a constant T, the branching of alkanol is in all instances seen to decrease the value of limiting activity coefficient. However, when the branching occurs solely on the aliphatic chain of alkanol, without affecting the position of hydroxyl group, the decrease in ln γ_1^∞ is only subtle (2-methyl-1-propanol vs 1-butanol), whereas when the hydroxyl group position changes from primary to secondary (2-propanol vs 1-propanol or 2-butanol vs 1-butanol) and then to tertiary (2-methyl-2-propanol vs 2-butanol), the decrease is considerable and about of the same magnitude for each of the steps. The effect of alkanol branching on the value of γ_1^∞ is the largest at 273 K, with increasing temperature it diminishes monotonically, suggesting that at higher temperatures γ_1^∞ values for the isomeric alkanols converge. Note that at lower temperatures (T < 313 K) the branching effect for 2-methyl-2-propanol is so strong that this causes this butanol isomer to behave more ideally in aqueous solution than 1-propanol does.

The Henry's law constants (Figure 9b) for (C3 and C4) alkanols exhibit also a concave rise with temperature, but the curves are seen to be still quite steep at 373 K. Their reliable extrapolation to 423 K by eq 8 shows no maximum to occur within this range. Due to the large scale of Figure 9b dictated by the temperature range considered, the curves for (C3 and C4) alkanols are clustered and details are barely visible. The effect of branching on K_H values is opposite to that on γ_1^∞ (i.e., the branched isomers have higher K_H values). This reversal is due to the fact that the branching increases the alkanol vapor pressure to a greater extent than it decreases its limiting activity coefficient. The differences in K_H values of isomeric (C3 and C4) alkanols are smallest at 273 K and increase with temperature, 2-methyl-1-propanol however being an exception.

Figures 10 and 11 give a graphical overview of the variation of thermodynamic functions of dissolution and hydration with temperature and branching. The pattern of thermodynamic behavior resembles in many respects that of aqueous hydrophobic solutes: large negative entropy changes and large positive heat capacity changes accompanying the processes of dissolution and hydration at lower temperatures are two of the characteristic features of the hydrophobic phenomenon. They are generally considered to indicate a striking structure enhancement due to reorganization of water molecules around the solute.[77] On the other hand, the dual hydrophobic−hydrophilic character of the alkanol molecules is also manifested. The dissolution and hydration of alkanols at ambient temperatures are strongly exothermic processes mainly because the hydroxyl group of the alkanols is capable of efficient hydrogen bonding with the solvent water. Although the heat capacities of dissolution and hydration diminish with temperature, their values

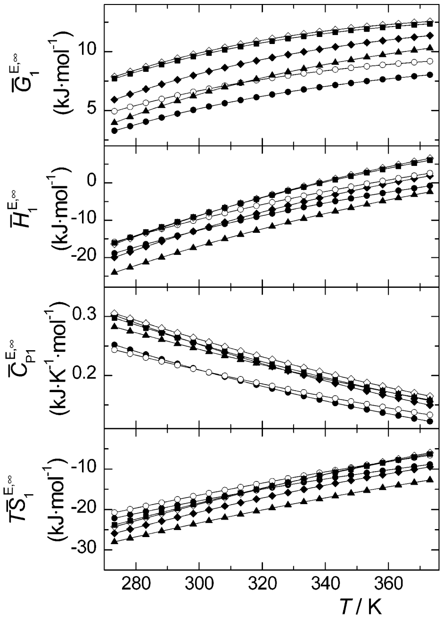

Figure 10. Variation of limiting partial molar excess functions $\bar{Y}_1^{E,\infty}$ (Y = G, H, C_p, TS) of (C3 and C4) alkanols (1) in water (2) with temperature and branching: ○, 1-propanol; ●, 2-propanol; ◇, 1-butanol; ◆, 2-butanol; ■, 2-methyl-1-propanol; ▲, 2-methyl-2-propanol.

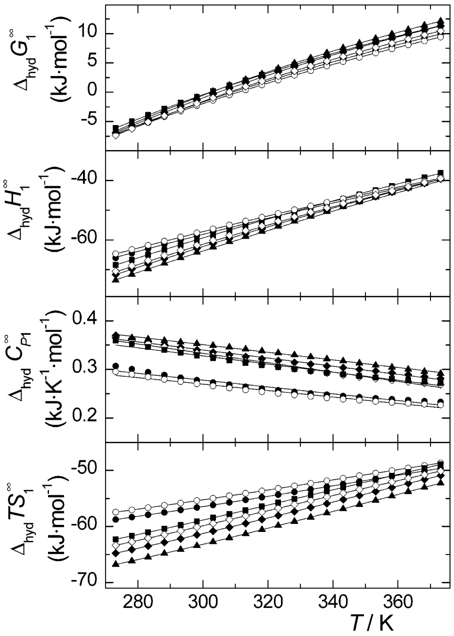

Figure 11. Variation of thermodynamic functions of hydration $\Delta_{hyd}Y_1^\infty$ (Y = G, H, C_p, TS) of (C3 and C4) alkanols (1) in water (2) with temperature and branching: ○, 1-propanol; ●, 2-propanol; ◇, 1-butanol; ◆, 2-butanol; ■, 2-methyl-1-propanol; ▲, 2-methyl-2-propanol.

remain still positive and large at 373 K; hence, in the temperature range considered, the respective enthalpies and entropies are rapidly increasing functions of T.

The values of $\bar{C}_{p,1}^{\mathrm{E},\infty}$ and $\Delta_{\mathrm{hyd}}C_{p,1}^{\infty}$ of (C3 and C4) alkanols are seen to be mainly determined by the number of carbon atoms of the alkanol as compared to which the branching has a lesser effect. On the other hand, the effect of branching on dissolution and hydration enthalpy and entropy of C3 and C4 alkanols is relatively stronger but complicated and rather difficult to resolve. Nevertheless, at least three specific observations can be made: (i) Among (C3 and C4) alkanols, 2-methyl-2-propanol exhibits the most negative values of all these functions, indicating the strongest hydrogen bonding with water and the highest degree of ordering of its aqueous solution. (ii) $\bar{H}_1^{\mathrm{E},\infty}$ at lower temperatures (below ambient) and $\bar{S}_1^{\mathrm{E},\infty}$ at higher temperatures (close 373 K) for (C3 and C4) alkanols appear to be determined by the position of hydroxyl group (primary, secondary, tertiary) and not by the number of carbon atoms in the alkanol molecule. (iii*)* both $\Delta_{\mathrm{hyd}}H_1^{\infty}(T)$ and $T\Delta_{\mathrm{hyd}}S_1^{\infty}(T)$ converge for all (C3 and C4) alkanols with increasing temperature and cross at higher temperatures, the crossover occurring with the exception of 2-methyl-1-propanol at essentially same points. It is noteworthy that the respective crossover temperatures for this last observation, 383 K ($\Delta_{\mathrm{hyd}}H_1^{\infty}$) and 423 K ($\Delta_{\mathrm{hyd}}S_1^{\infty}$), are the same as those found previously for 1-alkanols.[2]

As a result of a rather delicate balance of the large enthalpic and entropic contributions, $\bar{G}_1^{\mathrm{E},\infty}$ and $\Delta_{\mathrm{hyd}}G_1^{\infty}$ of (C3 and C4) alkanols in the given temperature range exhibit a monotonically increasing temperature dependence. The entropy and enthalpy contributions largely compensate each other, and it is only for $\bar{G}_1^{\mathrm{E},\infty}$ at temperatures higher than T_{max} where both act in the positive direction. Concerning $\Delta_{\mathrm{hyd}}G_1^{\infty}$, it is worthy to notice the closely similar values for all C3 and C4 alkanols at temperatures near the melting point of water (cf. $K_{\mathrm{H}}(T)$).

Conclusions

The recommended temperature dependence of limiting activity coefficients and Henry's law constants established in this work for (C3 and C4) branched alkanols in water greatly improves our knowledge of gas−liquid partitioning of these aqueous solutes. The present results, together with the analogous ones reported for (C1−C5) 1-alkanols previously,[2] compose a very accurate picture of the entire infinite dilution thermodynamic behavior of these important systems, thus opening new possibilities for its detailed theoretical analysis and generalization. In addition, the results contribute to the establishment of a database on hydration properties of organic nonelectrolytes within an international project[78] (2005−2007) conducted under the auspices of IUPAC and IAPWS.

Literature Cited

(1) Vrbka, P.; Fenclová, D.; Laštovka, V. Dohnal, V. Measurement of infinite dilution activity coefficients of 1-alkanols (C1−C5) in water as a function of temperature. *Fluid Phase Equilib.* **2005**, *237*, 123−129.

(2) Dohnal, V.; Fenclová, D.; Vrbka, P. Temperature dependences of limiting activity coefficients, Henry's law constants, and derivative infinite dilution properties of lower (C1−C5) 1-alkanols in water. Critical compilation, correlation, and recommended data. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1621−1651.

(3) 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.

(4) Hovorka, Š.; Dohnal, V. Determination of air−water partitioning of volatile halogenated hydrocarbons by the inert gas stripping method. *J. Chem. Eng. Data* **1997**, *42*, 924−933.

(5) Dohnal, V.; Horáková, I. A new variant of the Rayleigh distillation method for the determination of limiting activity coefficients. *Fluid Phase Equilib.* **1991**, *68*, 173−185.

(6) Dohnal, V.; Fenclová, D. Air−water partitioning and aqueous solubility of phenols. *J. Chem. Eng. Data* **1995**, *40*, 478−483.

(7) Růžička, K.; Fulem, M.; Diky, V. V.; Růžička, V. Vapor pressures, enthalpies of vaporization and heat capacities of C1 to C5 alkanols at ambient and subambient temperatures. *Proceedings of the Thermo International Three-Conference Event*, Boulder, CO, July 30−August 4, 2006; pp 527−528.

(8) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(9) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R. O'Connell, J. P. *Computer Calculations for Multicomponent Vapor−Liquid and Liquid−Liquid Equilibrium*; Prentice Hall: Englewood Cliffs, NJ, 1980.

(10) *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.

(11) Butler, J. A. V.; Ramchandani, C. N.; Thomson, D. W. The solubility of non-electrolytes. Part I. The free energy of hydration of some aliphatic alcohols. *J. Chem. Soc.* **1935**, 280−285.

(12) Pierotti, G. J.; Deal, C. H.; Derr, E. L. Activity coefficients and molecular structure. *Ind. Eng. Chem.* **1959**, *51*, 95−102.

(13) Slocum, E. W.; Dodge, B. A. Activity coefficient at infinite dilution: 2-propanol−water system. *AIChE J.* **1964**, *10*, 364−368.

(14) Kojima, K.; Tochigi, K.; Seki, H.; Watase, K. Determination of vapor−liquid equilibria from boiling point curves. *Kagaku Kogaku* **1968**, *32*, 149−153.

(15) Larkin, J. A.; Pemberton, R. C. Thermodynamic properties of binary mixtures of water + alkanols. *Proceedings of the Third International Conference on Chemical Thermodynamics*, Baden, Austria, September 3−7, 1973; pp 163−170.

(16) Rytting, J. H.; Huston, L. P.; Higuchi, T. Thermodynamic group contributions for hydroxyl, amino, and methylene groups. *J. Pharm. Sci.* **1978**, *67*, 615−618.

(17) Mash, C. J.; Pemberton, R. C. Activity coefficients at very low concentrations for organic solutes in water determined by an automatic chromatographic method. *NPL Rep. Chem. U.K. Natl. Phys. Lab., Div. Chem. Stand.* **1980**, *111*, 1−24.

(18) Mazza, G. Relative volatilities of some onion flavour components. *J. Food Technol.* **1980**, *15*, 35−41.

(19) Kühne, R.; Bocek, K.; Scharfenberg, P.; Frank, R. Hydrophobicity and hydrophobic interactions. II. Differentiation of surface area effects on several thermodynamic transfer data of hydrophobic solutes. *Eur. J. Med. Chem.* **1981**, *16*, 7−12.

(20) Lee, H. J. Accurate determination of activity coefficients at infinite dilution by measuring the stripping rates of solutes in liquid mixtures. *Hwahak Konghak* **1983**, *21*, 317−324.

(21) Nord, L.; Tucker, E. E.; Christian, S. D. Liquid−vapor equilibrium of dilute aqueous solutions of ethanol and 2-propanol. *J. Solution Chem.* **1984**, *13*, 849−867.

(22) Snider, J. R.; Dawson, G. A. Tropospheric light alcohols, carbonyls, and acetonitrile: concentrations in the Southwestern United States and Henry's law data. *J. Geophys. Res.* **1985**, *90*, 3797−3805.

(23) Bergmann, D. L.; Eckert, C. A. Measurement of limiting activity coefficients for aqueous systems by differential ebulliometry. *Fluid Phase Equilib.* **1991**, *63*, 141−150.

(24) Landau, I.; Belfer, A. J.; Locke, D. C. Measurement of limiting activity coefficients using non-steady-state gas chromatography. *Ind. Eng. Chem. Res.* **1991**, *30*, 1900−1906.

(25) Kolb, B.; Welter, C.; Bichler, C. Determination of partition coefficients by automatic equilibrium headspace gas chromatography by vapor phase calibration. *Chromatographia* **1992**, *34*, 235−240.

(26) Pividal, K. A.; Birtigh, A.; Sandler, S. I. Infinite dilution activity coefficients for oxygenate systems determined using a differential static cell. *J. Chem. Eng. Data* **1992**, *37*, 484−487.

(27) Kaneko, T.; Wang, P.-Y.; Sato, A. Partition coefficients of some acetate esters and alcohols in water, blood, olive oil, and rat tissues. *Occup. Environ. Med.* **1994**, *51*, 68−72.

(28) Sherman, S. R.; Trampe, D. B.; Bush, D. M.; Schiller, M.; Eckert, C. A.; Dallas, A. J.; Li, J.; Carr, P. W. Compilation and correlation of limiting activity coefficients of nonelectrolytes in water. *Ind. Eng. Chem. Res.* **1996**, *35*, 1044−1058.

(29) Merk, S.; Riederer, M. Sorption of volatile C1 to C6 alkanols in plant cuticles. *J. Exp. Bot.* **1997**, *48*, 1095−1104.

(30) Altschuh, J.; Bruggemann, R.; Santl, H.; Eichinger, G.; Piringer, O. G. Henry's law constants for a diverse set of organic chemicals: experimental determination and comparison of estimation methods. *Chemosphere* **1999**, *39*, 1871−1887.

(31) Kim, B. R.; Kalis, E. M.; DeWulf, T.; Andrews, K. M. Henry's law constants for paint solvents and their implications on volatile organic compound emissions from automotive painting. *Water Environ. Res.* **2000**, *72*, 65−74.

(32) Fukuchi, K.; Miyoshi, K.; Watanabe, T.; Yonezawa, S.; Arai, Y. Measurement and correlation of infinite dilution activity coefficients of alkanol or ether in aqueous solution. *Fluid Phase Equilib.* **2002**, *194*−*197*, 937−945.

(33) Dohnal, V.; Ondo, D. Refined non-steady-state gas−liquid chromatography for accurate determination of limiting activity coefficients of VOCs in water. Application to C1−C5 alkanols. *J. Chromatogr. A* **2005**, *1097*, 157−164.

(34) Butler, J. A. V.; Reid, W. S. The Solubility of non-electrolytes. Part III. The entropy of hydration. *J. Chem. Soc.* **1936**, 1171−1173.

(35) Cabani, S.; Conti, G.; Mollica, V.; Lepori, L. Thermodynamic study of dilute aqueous solutions of organic compounds. Part 4. Cyclic and straight chain secondary alcohols. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1943−1952.

(36) Sagert, N. H.; Lau, D. W. P. Limiting activity coefficients for butyl alcohols in water, *n*-octane, and carbon tetrachloride. *J. Chem. Eng. Data* **1986**, *31*, 475−478.

(37) Fischer, K.; Gmehling, J. P. $P-x$ and γ^{∞} data for the different binary butanol−water systems at 50 °C. *J. Chem. Eng. Data* **1994**, *39*, 309−315.

(38) Whitehead, P. G.; Sandler, S. I. Headspace gas chromatography for measurement of infinite dilution activity coefficients of C4 alcohols in water. *Fluid Phase Equilib.* **1999**, *157*, 111−120.

(39) Hakuta, T.; Negishi, A.; Goto, T.; Kato, J.; Ishizaka, S. Vapor−liquid equilibria of some pollutants in aqueous and saline solutions. Part I: Experimental results. *Desalination* **1977**, *21*, 11−21.

(40) Ikari, A.; Hatate, Y.; Yanagida, K.; Eta, M. Vapor−liquid equilibria of a minute amount of *n*-propyl, isobutyl, and isoamyl alcohols in aqueous ethanol solution under reduced pressure. *Kagaku Kogaku Ronbunshu* **1990**, *16*, 1101−1104.

(41) Shiu, W. Y.; Mackay, D. Henry's law constants of selected aromatic hydrocarbons, alcohols, and ketones. *J. Chem. Eng. Data* **1997**, *42*, 27−30.

(42) Sancho, M. F.; Rao, M. A.; Downing, D. L. Infinite dilution activity coefficients of apple juice aroma compounds. *J. Food Eng.* **1997**, *34*, 145−158.

(43) Koga, Y.; Siu, W. W. Y.; Wong, T. Y. H. Excess partial molar free energies and entropies in aqueous *tert*-butyl alcohol solutions at 25 °C. *J. Phys. Chem.* **1990**, *94*, 7700−7706.

(44) Lama, R. F.; Lu, B. C. Y. Excess thermodynamic properties of aqueous alcohol solutions. *J. Chem. Eng. Data* **1965**, *10*, 216−219.

(45) Alexander, D. M.; Hill, D. J. T. The heats of solution of alcohols in water. *Aust. J. Chem.* **1969**, *22*, 347−356.

(46) Arnett, E. M.; Kover, W. B.; Carter, J. V. Heat capacities of organic compounds in solution. I. Low molecular weight alcohols in water. *J. Am. Chem. Soc.* **1969**, *91*, 4028−4034.

(47) Brower, K. R.; Peslak, J., Jr.; Elrod, J. A correlation of molecular flexibility with volume and heat of mixing of organic solutes with water and glycol−water mixture. *J. Phys. Chem.* **1969**, *73*, 207−211.

(48) Krishnan, C. V.; Friedman, H. L. Solvation enthalpies of various nonelectrolytes in water, propylene carbonate, and dimethyl sulfoxide. *J. Phys. Chem.* **1969**, *73*, 1572−1580.

(49) Rouw, A. C.; Somsen, G. The solvation of some alcohols in binary solvents: enthalpies of solution and enthalpies of transfer. *J. Chem. Thermodyn.* **1981**, *13*, 67−76.

(50) Korolev, V. P.; Batov, D. V.; Krestov, G. A. Izotopnyj effekt v ental'piyakh gidratatsii zhidkikh neelektrolitov. *Zh. Fiz. Khim.* **1985**, *59*, 212−214.

(51) Denda, M.; Touhara, H.; Nakanishi, K. Excess molar enthalpies for (water + a fluoroalkanol). *J. Chem. Thermodyn.* **1987**, *19*, 539−542.

(52) Dohnal, V.; Roux, A. H.; Hynek, V. Limiting partial molar excess enthalpies by flow calorimetry: some organic solvents in water. *J. Solution Chem.* **1994**, *23*, 889−900.

(53) Davis, M. I.; Rubio, J. B.; Douheret, G. Excess molar enthalpies of 2-propanol + water at 25 °C. *Thermochim. Acta* **1995**, *259*, 177−185.

(54) Pfeffer, T.; Löwen, B.; Schulz, S. Calorimetric measurement of the partial molar excess enthalpy at infinite dilution and its meaning for the calculation of the concentration and temperature dependence of the molar excess enthalpy. *Fluid Phase Equilib.* **1995**, *106*, 139−167.

(55) Tanaka, S. H.; Yoshihara, H. I.; Ho, A. W. C.; Lau, F. W.; Westh, P.; Koga, Y. Excess partial molar enthalpies of alkane-mono-ols in aqueous solutions. *Can. J. Chem.* **1996**, *74*, 713−721.

(56) Belousov, V. P.; Ponner, V. Teploty smesheniia zhidkostei-VI. *Vestn. Leningr. Univ.* **1970**, 111−115.

(57) Bury, R.; Treiner, C. Heats of solution of aliphatic and aromatic, linear, branched, and cyclic alcohols in aqueous sodium dodecyl sulfate micelles at 298 K. *J. Colloid Interface Sci.* **1985**, *103*, 1−10.

(58) Andersson, B.; Olofsson, G. Partial molar enthalpies of solution as indicators of interactions in mixtures of 2-butoxyethanol and 2-butanol in water. *J. Solution Chem.* **1988**, *17*, 1169−1182.

(59) Hovorka, Š.; Roux, A. H.; Roux-Desgranges, G.; Dohnal, V. Limiting partial molar excess enthalpies of selected organic compounds in water at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 954−959.

(60) Arnett, E. M.; McKelvey, D. R. Enthalpies of transfer from water to dimethyl sulfoxide for some ions and molecules. *J. Am. Chem. Soc.* **1966**, *88*, 2598−2599.

(61) 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.

(62) Koga, Y. Excess partial molar enthalpies of *tert*-butanol in water−*tert*-butanol mixtures. *Can. J. Chem.* **1988**, *66*, 1187−1193.

(63) 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.

(64) 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.

(65) Fenclová, D.; Perez-Casas, S.; Costas, M.; Dohnal, V. Partial molar heat capacities and partial molar volumes of all of the isomeric (C3−C5) alkanols at infinite dilution in water at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1833−1838.

(66) Jolicoeur, 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.

(67) 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*, 451−468.

(68) 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.

(69) 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.

(70) Zábranský, M.; Růžička, V.; Majer, V.; Domalski, E. S. Heat capacity of liquids: critical review and recommended values. Vol. I. *J. Phys. Chem. Ref. Data Monogr.* **1996**, *6*, 1−810.

(71) Zábranský, M.; Růžička, V.; Majer, V.; Domalski, E. S. Heat capacities of liquids: critical review and recommended values. Vol. II. *J. Phys. Chem. Ref. Data Monogr.* **1996**, *6*, 1−781.

(72) 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.

(73) Dohnal, V.; Vrbka, P. Limiting activity coefficients in the 1-alkanol + *n*-alkane systems: survey, critical evaluation and recommended values, interpretation in terms of association models. *Fluid Phase Equilib.* **1997**, *133*, 73−87.

(74) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

(75) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds, Critical Review and Data Compilation*; Blackwell: Oxford, 1985.

(76) 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.

(77) Frank, H. S.; Evans, M. W. Free volume and entropy in condensed systems. III. Entropy in binary liquid mixtures, partial molal entropy in dilute solutions, structure and thermodynamics in aqueous electrolytes. *J. Phys. Chem.* **1945**, *13*, 507−532.

(78) www.iupac.org/projects/2004/2004-036-1-100.html.

Received for review December 14, 2006. Accepted February 16, 2007. This work was supported by the Ministry of Education of the Czech Republic (Grant MSM 604 613 7307).

JE600567Z