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

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Limiting activity coefficients (γ_1^∞) of six branched pentanols (2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol) in water were measured at several temperatures covering the range from the melting to the normal boiling point of water. Five experimental techniques, namely, inert gas stripping, headspace analysis in two variants, the classical and the relative, 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 ($\bar{H}_1^{\mathrm{E},\infty}$), and heat capacities ($\bar{C}_{p,1}^{\mathrm{E},\infty}$) of these aqueous solutes. Since $\bar{H}_1^{\mathrm{E},\infty}$ data for 2-methyl-1-butanol in water are lacking in the literature, they were also determined in this work. For each pentanol isomer, 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^∞, $\bar{H}_1^{\mathrm{E},\infty}$, and $\bar{C}_{p,1}^{\mathrm{E},\infty}$ 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 pure pentanols, 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 with temperature and pentanol branching is briefly discussed. Furthermore, the performance of five predictive approaches to estimate $\gamma_1^\infty(T)$ of aqueous pentanols was tested.

Introduction

This work is a part of our systematic study on gas−liquid partitioning and related infinite dilution thermodynamic properties of aqueous alkanols. Recently, we have presented results for the temperature dependence of limiting activity coefficients (γ_1^∞) and Henry's law constants (K_H) of (C1 to C5) 1-alkanols[1] and (C3 and C4) branched alkanols.[2] As a logical continuation, we focus here further on branched pentanols. These substances belong to important chemicals with many industrial applications, serving in particular as extraction solvents, reaction media, and precursors to agrochemicals, pharmaceuticals, flavorings, liquid crystals, and dyes.[3] Pentanols are naturally produced during fermentation and appear to be the most abundant odor and flavor components of all fermented beverages.[4] Great potential of pentanols lies in their prospective application as biofuels. Compared to ethanol, the traditional biofuel, branched pentanols offer more favorable physical properties, namely, higher energy density, lower hygroscopicity, and higher octane numbers. Currently, new efficient microbial strains for the production of pentanol isomers are under development using metabolic engineering.[5,6] In their production and use, pentanols often interact with water, which makes the thermodynamic characterization of their aqueous dissolution and/or hydration of essential importance. Accurate data on respective infinite dilution properties are needed also for the improvement of predictive schemes and for development and testing of solution theories.

In this paper we deal with all branched pentanol isomers with the exception of 2,2-dimethyl-1-propanol. This rather rare chemical is solid at room temperature (mp 326 K).[3] We report here results of our systematic and accurate measurements of limiting activity coefficients which were performed by several suitable experimental techniques and cover the temperature range from (273.15 to 373.15) K. The experimental work is further amended by a comprehensive compilation and critical evaluation of literature experimental data on the limiting activity coefficient and related thermal dissolution properties: limiting partial molar excess enthalpy, $\bar{H}_1^{\mathrm{E},\infty}$, and heat capacity, $\bar{C}_{p,1}^{\mathrm{E},\infty}$. Since $\bar{H}_1^{\mathrm{E},\infty}$ data for 2-methyl-1-butanol in water are lacking in the literature, they were also determined in this work. All of 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 which 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. Furthermore, an overview of these various infinite dilution properties is presented, and their variation with temperature and pentanol branching is discussed. Finally, the performance of several predictive approaches to estimate $\gamma_1^\infty(T)$ of aqueous pentanols is tested.

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Table 1. Parameters of the Cox Vapor-Pressure Equation[a] for Pure Pentanols[13]

pentanol	range/K	A_0	$A_1 \cdot 10^3$	$A_2 \cdot 10^6$	$A_3 \cdot 10^9$	T_0/K
2-pentanol	230 to 393	2.896438	0.4724126	−4.818971	4.345597	392.551
3-pentanol	210 to 373	2.924432	0.5161572	−5.710232	5.402471	388.727
2-methyl-1-butanol	130 to 403	3.031190	−1.519705	3.472505	−5.909514	402.247
3-methyl-1-butanol	170 to 415	3.017163	−1.272462	1.987468	−3.332212	404.822
2-methyl-2-butanol	265 to 376	2.730588	2.109314	−10.48545	10.14333	375.374
3-methyl-2-butanol	230 to 385	2.830356	1.335370	−8.471038	8.593542	385.160

[a] $\ln(p^s/p_0) = (1 - T_0/T)\exp(A_0 + A_1(T/\mathrm{K}) + A_2(T/\mathrm{K})^2 + A_3(T/\mathrm{K})^3)$, $p_0 = 101.325$ kPa.

Experimental Section

Materials. 2-Pentanol (98 %), 3-pentanol (98 %), 2-methyl-1-butanol (99 + %), 3-methyl-1-butanol (99 + %), and 3-methyl-2-butanol (98 %) were all supplied by Aldrich. 2-Methyl-2-butanol (99.5 %) was received from Merck. All of these chemicals were used without further purification. Since the methods used for the determination of limiting activity coefficients in this work employed gas chromatography as the analytical tool, the solute purity was monitored in all of our experiments. The purity of the solutes was found to be at least as that specified by the suppliers or better. Moreover, as gas chromatography itself is a separation method, it can be well-assumed that any solute impurities that would possibly affect the measured value of limiting activity coefficient are separated in the course of the chromatographic process. Water was distilled and subsequently treated by a Milli-Q water purification system (Millipore, Milford, MA).

Apparatus and Procedure. To measure the limiting activity coefficients, five experimental techniques were employed in this work: inert gas stripping (IGS),[7] headspace analysis in two variants, the classical (HSA)[8] and the relative (RHSA),[2] Rayleigh distillation (RDIST),[9] and the method of circulation still (CIRC).[10] Since we have used these methods previously and described the respective instrumentation and experimental procedures in detail, given here is only the information regarding the sample analysis. For a full account of our experimental techniques and their application to alkanol−water systems we refer the reader to our previous papers.[2,7−11] Vapor-phase compositions of HSA, RHSA, and IGS samples were determined using a Hewlett-Packard 5890 II gas chromatograph equipped with a flame ionization detector (FID) and a wide-bore DB-WAX (J&W Scientific, USA) capillary column (15 m, 0.53 mm i.d., df = 1 μm). Depending on the pentanol isomer, the carrier gas (N_2) flow rates were from (5 to 17) $\mathrm{mL \cdot min^{-1}}$ and oven temperatures from (45 to 120) °C to provide optimal peak separation and short times of analyses. An Agilent 6890 Plus gas chromatograph with an FID detector was used to perform the analyses of the liquid samples in RDIST and CIRC methods. To analyze these samples, a capillary column HP-Plot U (15 m, 0.53 mm i.d., df = 20 μm) was used and operated at a 6 $\mathrm{mL \cdot min^{-1}}$ N_2 carrier gas flow rate in the isothermal mode. The oven temperatures were from (150 to 180) °C. Liquid samples were injected using an Agilent 7683 AutoInjector.

To determine the missing data on limiting partial molar excess enthalpy for 2-methyl-1-butanol in water, a refined flow mixing microcalorimetric setup with a fully automatic control of the entire experimental sequence was used. The setup consists of a modified model 4400 isothermal differential heat conduction microcalorimeter (CSC, Provo, USA) equipped with flow mixing cells and a highly asymmetric pumping system capable of delivering accurately small mass flow rates of one component. Mixing enthalpies of highly dilute aqueous pentanol solutions were measured as a function of composition, and the limiting partial molar excess enthalpy was then determined by extrapolation to infinite dilution. The instrument and procedure, along with due verification of their performance, have been described in detail elsewhere.[12]

Results of Measurements

The primary air−water partitioning measurements carried out by the various 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; its parameters, recently obtained by Fulem and Růžička,[13] are given in Table 1. Water vapor pressures were calculated from the reference equation of Wagner and Pruss.[14] 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.[15] and CDATA.[16] The pure liquid molar volumes to calculate the Poynting correction were taken also from CDATA. For the systems and conditions under study the gas phase nonideality corrections are quite small and do not typically exceed 1 %.

The values of limiting activity coefficients obtained by us in this work 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 is mostly within 3 %. The experimental values of limiting partial molar excess enthalpies determined for 2-methyl-1-butanol are given, together with their standard uncertainties, in Table 3.

Data Compilation and Survey

Besides the γ_1^∞ and $\bar{H}_1^{\mathrm{E},\infty}$ data measured in this work (80 and 3 values, respectively) we compiled additional data on γ_1^∞ and related thermal dissolution properties $\bar{H}_1^{\mathrm{E},\infty}$ and $\bar{C}_{p,1}^{\mathrm{E},\infty}$ of branched pentanols from the literature (63 data points from 27 literature references). All available values are listed in a form suitable for correlational processing in Tables 4 to 6. Only original experimental values were considered in this collection, those extrapolated from measurements on concentrated solution or obtained by estimation were disregarded. Compared to (C1 to C5) 1-alkanols and (C3 and C4) branched alkanols studied previously, the literature information for branched pentanols is much less abundant. In addition note that among the literature results in Tables 4 to 6 are also some which have been reported by this laboratory earlier.[12,24,39] Taking them into account, the measurements carried out by this laboratory thus represent the most systematic and complete contribution to the determination of $\gamma_1^\infty(T)$ for branched pentanols in water (98 values, 67 % of all available).

The majority of the collected information concerns limiting activity coefficients for which 123 data points are available. The collected γ_1^∞ data file covers, besides values of γ_1^∞ directly reported in the literature, also those derived by us from reported

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

pentanol (1)	T/K	γ_1^∞	$s(\gamma_1^\infty)$	technique[a]
2-pentanol	273.35	58.8	2.9	RHSA
	283.15	73.9	2.2	RHSA
	293.15	89.2	2.7	RHSA
	293.15	86.1	2.6	HSA
	303.15	104	3	HSA
	303.15	103	3	IGS
	313.15	119	4	HSA
	323.15	129	4	HSA
	333.15	134	4	HSA
	343.15	134	4	RDIST
	353.15	124	4	RDIST
	363.15	130	7	CIRC
	371.15	118	6	CIRC
3-pentanol	273.35	48.7	1.5	RHSA
	283.15	63.1	1.9	RHSA
	293.15	75.6	2.3	RHSA
	303.15	88.7	2.7	IGS
	313.15	101	3	IGS
	323.15	108	3	IGS
	333.15	116	3	IGS
	343.15	111	6	RDIST
	353.15	120	6	RDIST
	363.15	117	6	CIRC
	371.15	104	5	CIRC
2-methyl-1-butanol	273.35	86.3	4.3	RHSA
	283.15	117	4	RHSA
	293.15	138	4	RHSA
	293.15	134	4	HSA
	303.15	158	5	HSA
	303.15	151	5	IGS
	313.15	163	5	IGS
	313.15	173	5	HSA
	323.15	180	5	HSA
	323.15	173	5	IGS
	333.15	170	5	IGS
	333.15	179	5	HSA
	343.15	169	5	RDIST
	353.15	160	5	RDIST
	363.15	162	8	CIRC
3-methyl-1-butanol	273.35	94.9	2.8	RHSA
	283.15	126	4	RHSA
	293.15	148	4	RHSA
	293.15	146	4	HSA
	303.15	161	5	HSA
	303.15	164	5	RHSA
	313.15	173	5	IGS
	313.15	175	5	HSA
	323.15	179	5	HSA
	323.15	184	6	IGS
	333.15	182	5	IGS
	333.15	178	5	HSA
	343.15	179	5	RDST
	353.15	164	5	RDST
	371.15	149	4	CIRC
2-methyl-2-butanol	273.35	18.3	1.8	RHSA
	283.15	24.5	0.7	RHSA
	293.15	31.7	1.0	RHSA
	293.15	34.6	1.7	HSA
	303.15	41.3	1.2	HSA
	303.15	39.2	1.2	RHSA
	313.15	49.0	1.5	HSA
	313.15	46.5	1.4	IGS
	323.15	52.3	1.6	IGS
	323.15	56.9	1.7	HSA
	333.15	59.3	1.8	HSA
	333.15	61.4	1.8	IGS
	343.15	64.2	1.9	RDIST
	353.15	67.1	2.0	RDIST
	361.25	75.4	3.8	CIRC
	371.45	73.9	3.7	CIRC
3-methyl-2-butanol	273.35	43.5	1.3	RHSA
	283.15	61.5	1.8	RHSA
	293.15	73.9	2.2	RHSA
	303.15	86.5	2.6	RHSA
	313.15	96.6	2.9	IGS
	323.15	104	3	IGS
	333.15	110	3	IGS
	343.15	111	3	RDIST
	353.15	107	5	RDIST
	371.15	108	5	CIRC

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

Table 3. Experimental Limiting Partial Molar Excess Enthalpies of 2-Methyl-1-butanol (1) in Water (2) Determined in This Work

T / K	$\bar{H}_1^{\mathrm{E},\infty}$ / $\mathrm{kJ \cdot mol^{-1}}$	$s(\bar{H}_1^{\mathrm{E},\infty})$ / $\mathrm{kJ \cdot mol^{-1}}$
288.15	−11.18	0.2
298.15	−8.27	0.1
308.15	−5.38	0.05

closely related experimental vapor−liquid equilibrium quantities such as the Henry's law constants or gas−liquid partition coefficients. The data were determined by eight different experimental techniques.

The existing $\bar{H}_1^{\mathrm{E},\infty}$ data are scarce (13 data points) and, except for our present measurements for 2-methyl-1-butanol, are all limited to 298.15 K. Older literature data were measured by the batch dissolution calorimetry, while the newer data from this laboratory were obtained using the isothermal flow mixing calorimetry. Data on limiting partial molar excess heat capacities (10 data points) are still scarcer and result from only four studies. They were obtained almost exclusively at 298.15 K using the Picker flow microcalorimeter. Note that the determination of $\bar{C}_{p,1}^{\mathrm{E},\infty}$ 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 $C_{p,1}^{\mathrm{L},\bullet}$ to be measured. When only $\bar{C}_{p,1}^{\infty}$ values were reported, values of $\bar{C}_{p,1}^{\mathrm{E},\infty}$ were derived by us using recommended $C_{p,1}^{\mathrm{L},\bullet}$ data.[42−44]

Data Evaluation and Correlation

The quality of the information gathered in Tables 4 to 6 is not uniform. The collected data differ in their accuracy and show in some cases significant disparity, inconsistency, or scatter. To resolve this issue and establish reliable and accurate recommended data, we subjected all of the collected information to critical evaluation and processed it by a thermodynamically consistent treatment.

The essentials of the procedure are the same as described previously.[8] For each solute, the equilibrium (γ_1^∞) and calorimetric ($\bar{H}_1^{\mathrm{E},\infty}$ and $\bar{C}_{p,1}^{\mathrm{E},\infty}$) data were fitted simultaneously with a suitable, sufficiently flexible model equation describing their temperature dependence. Like for the (C1 to C5) 1-alkanols and the branched (C3 and C4) alkanols treated recently,[1,2] also for the branched pentanols studied in this work we employed for the purpose the following four-parameter equation

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

giving

$$\bar{H}_1^{\mathrm{E},\infty} = RT_0[B - C\exp(D\tau)(D\tau - 1)] \quad \text{and}$$
$$\bar{C}_{p,1}^{\mathrm{E},\infty} = -RCD^2\tau \exp(D\tau)$$

where $\tau = T/T_0$ and $T_0 = 298.15$ K. Existing data for the branched pentanols are however insufficient to determine all four parameters in eq 1. Note that in particular parameters C and D cannot be evaluated simultaneously since the $\bar{C}_{p,1}^{\mathrm{E},\infty}$ data for the branched pentanols are available at a single temperature (298.15 K) only. To overcome the problem of missing $\bar{C}_{p,1}^{\mathrm{E},\infty}(T)$ data and to enable the application of eq 1 also for the branched pentanols, we made use of our empirical finding that the values of the temperature derivative $(\partial\bar{C}_{p,1}^{\mathrm{E},\infty}/\partial T)(T_0)$ and the values of $\bar{C}_{p,1}^{\mathrm{E},\infty}(T_0)$ for the previously studied alkanols appear to be fairly well-correlated as shown in Figure 1. The correlation allowed us to predict for each branched pentanol $(\partial\bar{C}_{p,1}^{\mathrm{E},\infty}/\partial T)(T_0)$ from the known $\bar{C}_{p,1}^{\mathrm{E},\infty}(T_0)$ and then to calculate parameter D from equation

Table 4. Experimental Values of Limiting Activity Coefficients of Six Branched Pentanols (1) in Water (2) Together with Their Relative Standard Uncertainty, Technique of Measurement, and Vapor-Phase Nonideality Treatment

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-Pentanol						
298.15	4.635	0.1	DDST	IDEAL	Butler et al.[17]	293.15	4.491	0.03	RHSA	VIR	this work
298.15	4.574	0.05	GLC	VIR	Mash and Pemberton[18]	293.15	4.456	0.03	HSA	VIR	this work
310.2	4.785[c]	0.03	GLC	IDEAL	Kühne et al.[19]	303.15	4.644	0.03	HSA	VIR	this work
343.15	4.579[d]	0.2	CIRC	IDEAL	Zou and Prausnitz[20]	303.15	4.635	0.03	IGS	VIR	this work
353.15	4.678[d]	0.2	CIRC	IDEAL	Zou and Prausnitz[20]	313.15	4.779	0.03	HSA	VIR	this work
363.15	4.798[d]	0.2	CIRC	IDEAL	Zou and Prausnitz[20]	323.15	4.860	0.03	HSA	VIR	this work
298.15	4.638[c]	0.1	HSA	IDEAL	Merk and Riederer[21]	333.15	4.898	0.03	HSA	VIR	this work
310.15	4.860[c]	0.2	HSA	IDEAL	van Ruth et al.[22]	343.15	4.898	0.03	RDIST	VIR	this work
310.15	4.595	0.2	HSA	IDEAL	van Ruth et al.[23]	353.15	4.820	0.03	RDIST	VIR	this work
328.15	4.836[e]	0.03	NSGLC	IDEAL	Dohnal and Ondo[24]	363.15	4.868	0.05	CIRC	VIR	this work
273.35	4.074	0.05	RHSA	VIR	this work	371.15	4.771	0.05	CIRC	VIR	this work
283.15	4.303	0.03	RHSA	VIR	this work						
					3-Pentanol						
298.15	4.439[f]	0.05	TENS	IDEAL	Cabani et al.[25]	313.15	4.615	0.03	IGS	VIR	this work
310.2	4.691[c]	0.05	GLC	IDEAL	Kühne et al.[19]	323.15	4.682	0.03	IGS	VIR	this work
328.15	4.762	0.03	NSGLC	IDEAL	Dohnal and Ondo[24]	333.15	4.754	0.03	IGS	VIR	this work
273.35	3.886	0.03	RHSA	VIR	this work	343.15	4.710	0.05	RDIST	VIR	this work
283.15	4.145	0.03	RHSA	VIR	this work	353.15	4.787	0.05	RDIST	VIR	this work
293.15	4.325	0.03	RHSA	VIR	this work	363.15	4.762	0.05	CIRC	VIR	this work
303.15	4.485	0.03	IGS	VIR	this work	371.15	4.644	0.05	CIRC	VIR	this work
					2-Methyl-1-butanol						
310.2	5.178[c]	0.05	GLC	IDEAL	Kühne et al.[19]	303.15	5.017	0.03	IGS	VIR	this work
308.32	5.370	0.2	IGS	IDEAL	Carelli et al.[26]	313.15	5.094	0.03	IGS	VIR	this work
323.24	5.297	0.2	IGS	IDEAL	Carelli et al.[26]	313.15	5.153	0.03	HSA	VIR	this work
338.07	5.232	0.1	IGS	IDEAL	Carelli et al.[26]	323.15	5.193	0.03	HSA	VIR	this work
298.15	5.298	0.2	IGS	IDEAL	Sancho et al.[27]	323.15	5.153	0.03	IGS	VIR	this work
328.15	5.303	0.1	NSGLC	IDEAL	Dohnal and Ondo[24]	333.15	5.136	0.03	IGS	VIR	this work
273.35	4.458	0.05	RHSA	VIR	this work	333.15	5.187	0.03	HSA	VIR	this work
283.15	4.762	0.03	RHSA	VIR	this work	343.15	5.130	0.03	RDIST	VIR	this work
293.15	4.927	0.03	RHSA	VIR	this work	353.15	5.075	0.03	RDIST	VIR	this work
293.15	4.898	0.03	HSA	VIR	this work	363.15	5.088	0.05	CIRC	VIR	this work
303.15	5.063	0.03	HSA	VIR	this work						
					3-Methyl-1-butanol						
298.15	5.252	0.1	DDST	IDEAL	Butler et al.[17]	293.15	4.997	0.03	RHSA	VIR	this work
374.15	4.504[g]	0.5	CIRC	IDEAL	Hakuta et al.[28]	293.15	4.984	0.03	HSA	VIR	this work
310.2	5.242[c]	0.03	GLC	IDEAL	Kühne et al.[19]	303.15	5.081	0.03	HSA	VIR	this work
323.72	4.644[g]	0.5	CIRC	IDEAL	Ikari et al.[29]	303.15	5.100	0.03	RHSA	VIR	this work
338.40	4.771[g]	0.5	CIRC	IDEAL	Ikari et al.[29]	313.15	5.153	0.03	IGS	VIR	this work
373.15	4.754[g]	0.5	CIRC	IDEAL	Ikari et al.[29]	313.15	5.165	0.03	HSA	VIR	this work
298.15	5.338	0.1	HSA	unknown	Dallas and Carr[h][30]	323.15	5.187	0.03	HSA	VIR	this work
310.15	5.108[c]	0.05	HSA	IDEAL	Kaneko et al.[31]	323.15	5.215	0.03	IGS	VIR	this work
298.15	5.328	0.2	IGS	IDEAL	Sancho et al.[27]	333.15	5.204	0.03	IGS	VIR	this work
310.15	5.130	0.1	HSA	IDEAL	van Ruth et al.[22]	333.15	5.182	0.03	HSA	VIR	this work
310.15	5.118	0.1	HSA	IDEAL	van Ruth et al.[23]	343.15	5.187	0.03	RDIST	VIR	this work
328.15	5.263	0.03	NSGLC	IDEAL	Dohnal and Ondo[24]	353.15	5.100	0.03	RDIST	VIR	this work
273.35	4.553	0.03	RHSA	VIR	this work	371.15	5.004	0.03	CIRC	VIR	this work
283.15	4.836	0.03	RHSA	VIR	this work						
					2-Methyl-2-butanol						
298.15	3.555	0.1	DDST	IDEAL	Butler et al.[17]	293.15	3.544	0.05	HSA	VIR	this work
298.15	3.567[d]	0.05	DDST	IDEAL	Butler and Reid[32]	303.15	3.721	0.03	HSA	VIR	this work
308.15	3.775[d]	0.05	DDST	IDEAL	Butler and Reid[32]	303.15	3.669	0.03	RHSA	VIR	this work
310.2	3.884[c]	0.03	GLC	IDEAL	Kühne et al.[19]	313.15	3.892	0.03	HSA	VIR	this work
283.3	3.578	0.5	TENS	IDEAL	Fischer et al.[33]	313.15	3.839	0.03	IGS	VIR	this work
303.32	4.071	0.5	TENS	IDEAL	Fischer et al.[33]	323.15	3.957	0.03	IGS	VIR	this work
328.29	4.358	0.5	TENS	IDEAL	Fischer et al.[33]	323.15	4.041	0.03	HSA	VIR	this work
343.25	4.240	0.2	TENS	IDEAL	Fischer et al.[33]	333.15	4.083	0.03	HSA	VIR	this work
298.15	3.600[c]	0.1	HSA	IDEAL	Merk and Riederer[21]	333.15	4.117	0.03	IGS	VIR	this work
328.15	4.191	0.05	NSGLC	IDEAL	Dohnal and Ondo[24]	343.15	4.162	0.03	RDIST	VIR	this work
273.35	2.907	0.1	RHSA	VIR	this work	353.15	4.206	0.03	RDIST	VIR	this work
283.15	3.199	0.03	RHSA	VIR	this work	361.25	4.323	0.05	CIRC	VIR	this work
293.15	3.456	0.03	RHSA	VIR	this work	371.45	4.303	0.05	CIRC	VIR	this work
					3-Methyl-2-butanol						
310.2	4.577[c]	0.03	GLC	IDEAL	Kühne et al.[19]	313.15	4.571	0.03	IGS	VIR	this work
328.15	4.644[e]	0.03	NSGLC	IDEAL	Dohnal and Ondo[24]	323.15	4.644	0.03	IGS	VIR	this work
273.35	3.773	0.03	RHSA	VIR	this work	333.15	4.700	0.03	IGS	VIR	this work
283.15	4.119	0.03	RHSA	VIR	this work	343.15	4.710	0.03	RDIST	VIR	this work
293.15	4.303	0.03	RHSA	VIR	this work	353.15	4.673	0.05	RDIST	VIR	this work
303.15	4.460	0.03	RHSA	VIR	this work	371.15	4.682	0.05	CIRC	VIR	this work

[a] CIRC, circulation equilibrium still; DDST, differential distillation; GLC, measurement of retention time in gas−liquid chromatography; HSA, headspace analysis; IGS, inert gas stripping; NSGLC, nonsteady state gas−liquid chromatography; RHSA, relative headspace analysis; RDIST, Rayleigh distillation; TENS, tensimetry. [b] IDEAL, ideal gas; VIR, virial equation of state. [c] Limiting activity coefficient calculated from liquid/vapor or vapor/liquid distribution or Henry coefficient reported in the cited source. [d] Limiting activity coefficient calculated from dilute range $P-x$ data reported in the cited source. [e] Limiting activity coefficient from original source recalculated with the most recent solute vapor pressure data.[13] [f] Limiting activity coefficient calculated from the solution Gibbs energy reported in the cited source. [g] Limiting activity coefficient calculated from relative volatility in highly dilute solutions reported in the cited source. [h] Secondary reference citing an original unavailable source (e.g., thesis).

$$D = T_0(\partial \bar{C}_{p,1}^{\mathrm{E},\infty}/\partial T)(T_0)/\bar{C}_{p,1}^{\mathrm{E},\infty}(T_0) - 1 \qquad (2)$$

which follows from eq 1. Surprisingly, values of parameter D obtained in this manner for individual branched pentanols closely clustered all around $D = -3.20$, and hence this value was taken for all branched pentanols as uniform.

The remaining adjustable parameters A, B, and C were calculated by the simultaneous correlation of all available data using the weighted least-squares method. The minimized objective function was as follows

$$S = \sum_{i=1}^{n_\mathrm{G}} [\ln \gamma_{1,i}^{\infty}(\mathrm{exp}) - \ln \gamma_{1,i}^{\infty}(\mathrm{calc})]^2/s^2(\ln \gamma_{1,i}^{\infty}) + \sum_{i=1}^{n_\mathrm{H}} [\bar{H}_{1,i}^{\mathrm{E},\infty}(\mathrm{exp}) - \bar{H}_{1,i}^{\mathrm{E},\infty}(\mathrm{calc})]^2/s^2(\bar{H}_{1,i}^{\mathrm{E},\infty}) + \sum_{i=1}^{n_\mathrm{C}} [\bar{C}_{p,1,i}^{\mathrm{E},\infty}(\mathrm{exp}) - \bar{C}_{p,1,i}^{\mathrm{E},\infty}(\mathrm{calc})]^2/s^2(\bar{C}_{p,1,i}^{\mathrm{E},\infty}) \qquad (3)$$

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.[50] Although no such uncertainty levels were used for thermal data, values of uncertainties rounded to just one significant digit were preferred.

Table 5. Experimental Values of Limiting Partial Molar Excess Enthalpies of Six Branched Pentanols (1) in Water (2) Together with Their Standard Uncertainty and Technique of Measurement

T / K	$\bar{H}_1^{\mathrm{E},\infty}$ / kJ·mol^{-1}	$s(\bar{H}_1^{\mathrm{E},\infty})$ / kJ·mol^{-1}	technique[a]	ref
		2-Pentanol		
298.00	−11.82	0.1	BATCH	Nishino et al.[34]
298.15	−10.36	1.5	BATCH	Bury and Treiner[35]
298.15	−12.15	0.05	FLOW	Dohnal and Řehák[12]
		3-Pentanol		
298.15	−11.92	1.0	BATCH	Bury and Treiner[35]
298.15	−12.81	0.1	BATCH	Cabani et al.[25]
		2-Methyl-1-butanol		
288.15	−11.18	0.2	FLOW	this work
298.15	−8.27	0.1	FLOW	this work
308.15	−5.38	0.05	FLOW	this work
		3-Methyl-1-butanol		
298.15	−8.23	0.05	FLOW	Dohnal and Řehák[12]
		2-Methyl-2-butanol		
298.15	−18.57	0.5	BATCH	Arnett et al.[36]
298.15	−17.96	0.2	BATCH	Krishnan and Friedman[37]
298.15	−18.29	0.2	BATCH	Rouw and Somsen[38]
		3-Methyl-2-butanol		
298.15	−12.61	0.04	FLOW	Dohnal and Řehák[12]

[a] BATCH, batch dissolution calorimetry; FLOW, flow mixing calorimetry.

Table 6. Experimental Values of Limiting Partial Molar Excess Heat Capacities of Six Branched Pentanols (1) in Water (2) Together with Their Standard Uncertainty and Technique of Measurement

T / K	$\bar{C}_{p,1}^{\mathrm{E},\infty}$ / J·K^{-1}·mol^{-1}	$s(\bar{C}_{p,1}^{\mathrm{E},\infty})$ / J·K^{-1}·mol^{-1}	technique[a]	ref
		2-Pentanol		
298.15	313.5	3	FLOW	Fenclová et al.[39]
		3-Pentanol		
298.15	288.7[b]	3	FLOW	Jolicoeur and Lacroix[40]
298.15	290.3	3	FLOW	Fenclová et al.[39]
		2-Methyl-1-butanol		
298.15	303.1	3	FLOW	Fenclová et al.[39]
		3-Methyl-1-butanol		
298.15	308.0	3	FLOW	Fenclová et al.[39]
		2-Methyl-2-butanol		
298.15	313	30	INDIRECT	Arnett et al.[36]
283.15	334[b]	10	FLOW	Roux et al.[41]
298.15	291[b]	10	FLOW	Roux et al.[41]
298.15	297.0	3	FLOW	Fenclová et al.[39]
		3-Methyl-2-butanol		
298.15	278.2	3	FLOW	Fenclová et al.[39]

[a] FLOW, flow 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.[42−44]

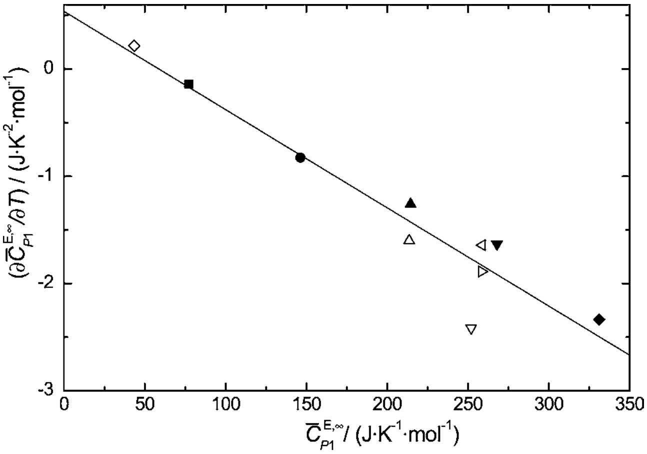

Figure 1. Correlation between the limiting partial molar excess heat capacity $\bar{C}_{p,1}^{\mathrm{E},\infty}$ and its temperature derivative $\partial \bar{C}_{p,1}^{\mathrm{E},\infty}/\partial T$ for alkanols (1) in water (2) at 298.15 K: ■, methanol;[45] ●, ethanol;[46] ▲, 1-propanol;[46] △, 2-propanol;[46] ▼, 1-butanol;[47] right-pointing triangle, 2-butanol;[47] left-pointing triangle, 2-methyl-1-propanol;[47] ▽, 2-methyl-2-propanol;[47] ◆, 1-pentanol;[48] ◇, ethylene glycol.[49]

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, a 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 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, that is, within the respective critical values of χ^2

$$\chi^2_{\alpha/2}(n - p) < S_{\min} < \chi^2_{1-\alpha/2}(n - p) \qquad (4)$$

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 $p = 3$), 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

Table 7. 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 the Fit s, Weighted Root-Mean-Square Deviations (WRMSD) of Individual Properties, and the Temperature T_{max} at Which γ_1^∞ is Maximum

						WRMSD[c]			T_{max}
pentanol	A	B	C	D	s[b]	$\ln \gamma_1^\infty$	$\bar{H}_1^{E,\infty}$	$\bar{C}_{p,1}^{E,\infty}$	K
2-pentanol	−2.36559	10.6376	−90.6646	−3.20	1.07	0.99	1.28	0.38	343
3-pentanol	−1.36742	9.1975	−83.6095	−3.20	1.32	1.30	1.05	0.35	351
2-methyl-1-butanol	−3.0074	11.5574	−87.0341	−3.20	1.07	1.06	0.70	0.35	329
3-methyl-1-butanol	−3.22362	11.9055	−88.9382	−3.20	1.17	1.15	0.04	0.22	328
2-methyl-2-butanol	−0.405078	7.47793	−85.9353	−3.20	1.25	1.26	1.27	0.49	379
3-methyl-2-butanol	−1.06290	8.71245	−80.5647	−3.20	1.24	1.17	0.41	0.46	353

[a] Recommended temperature dependence for limiting activity coefficient. [b] $s = [S_{min}/(n - 3)]^{1/2}$; S is given by eq 3. [c] WRMSD $= \{(1/n_Y)\sum_{i=1}^{n_Y}[Y_i(\text{exp}) - Y_i(\text{calc})]^2/s^2(Y_i)\}^{1/2}$, $Y = \ln \gamma_1^\infty, \bar{H}_1^{E,\infty}, \bar{C}_{p,1}^{E,\infty}$.

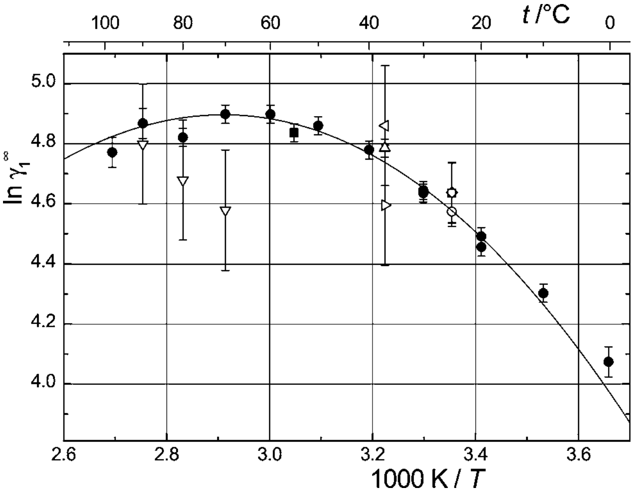

Figure 2. Limiting activity coefficient $\ln \gamma_1^\infty$ of 2-pentanol (1) in water (2) as a function of temperature. Experimental values are from Table 4: □, Butler et al.;[17] ○, Mash and Pemberton;[18] △, Kühne et al.;[19] ▽, Zou and Prausnitz;[20] ◇, Merk and Riederer;[21] left-pointing triangle, van Ruth et al.;[22] right-pointing triangle, van Ruth et al.;[23] ■, Dohnal and Ondo;[24] ●, 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.

or our own experience suggested that an enhanced error is probable.

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 4 to 6. The values of parameters of eq 1, together with the overall standard deviations of the fit s and other fit characteristics, are listed in Table 7.

Results of Correlations and Discussion

Data Assessment. The values of limiting activity coefficients for the six branched pentanols in water are displayed, together with their fits by eq 1, in the van't Hoff coordinates in Figures 2 to 7. As seen, most data agree mutually quite well, exhibiting a reasonable scatter, but there are also some data deviating grossly (> 0.2 in $\ln \gamma_1^\infty$) 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, involve in particular the CIRC measurements of Hakuta et al.[28] and Ikari et al.[29] for 3-methyl-1-butanol and the IGS measurements of Sancho et al.[27] for 2-methyl-1-butanol and 3-methyl-1-butanol. Note that analogous measurements by these authors done for (C3 and C4) branched alkanols have also been found to be substantially in error.[2] Further data belonging to those grossly deviating result from the IGS measurements of Carelli et al.[26] (2-methyl-1-butanol, 308.32 K), the HSA measurements of Dallas and Carr[30] (3-methyl-1-butanol), the CIRC measurements of Zou and Prausnitz[20] (2-pentanol, 343.15 K), and the tensimetric measurements of Fischer et al.[33] (2-methyl-2-butanol, except for 343.25 K).

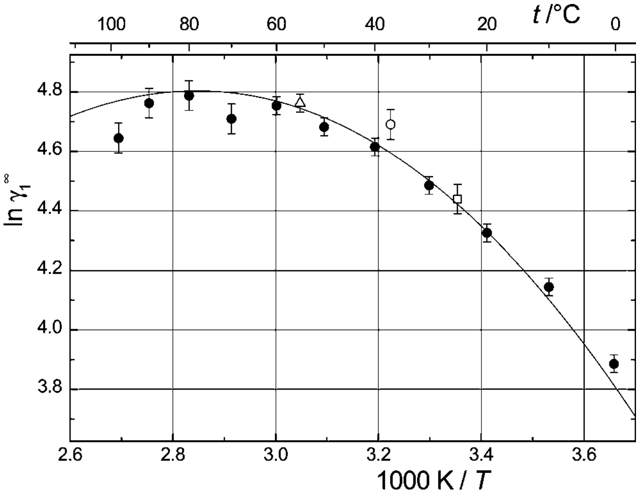

Figure 3. Limiting activity coefficient $\ln \gamma_1^\infty$ of 3-pentanol (1) in water (2) as a function of temperature. Experimental values are from Table 4: □, Cabani et al.;[25] ○, Kühne et al.;[19] △, Dohnal and Ondo;[24] ●, this work. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 1.

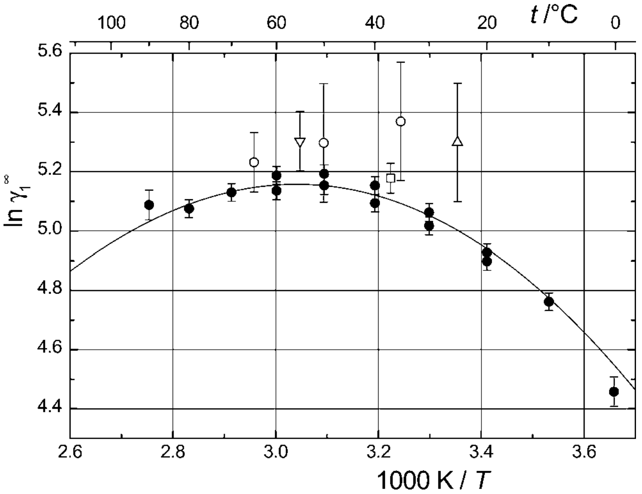

Figure 4. Limiting activity coefficient $\ln \gamma_1^\infty$ of 2-methyl-1-butanol (1) in water (2) as a function of temperature. Experimental values are from Table 4: □, Kühne et al.;[19] ○, Carelli et al.;[26] △, Sancho et al.;[27] ▽, Dohnal and Ondo;[24] ●, this work. The line indicates the recommended 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.

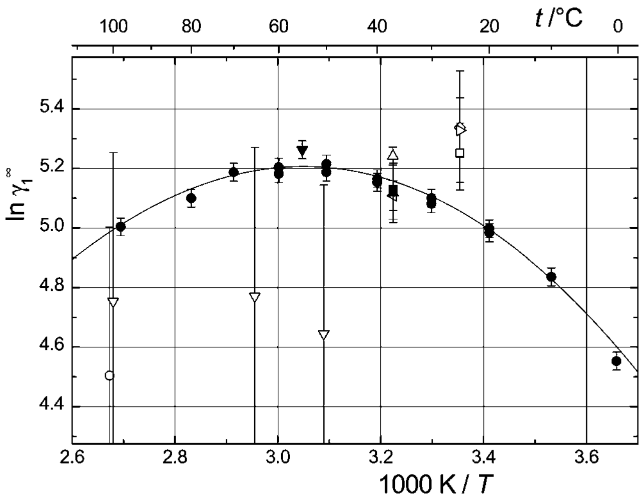

Figure 5. Limiting activity coefficient ln γ_1^∞ of 3-methyl-1-butanol (1) in water (2) as a function of temperature. Experimental values are from Table 4: □, Butler et al.;[17] ○, Hakuta et al.;[28] △, Kühne et al.;[19] ▽, Ikari et al.;[29] ◇, Dallas and Carr;[30] left-pointing triangle, Kaneko et al.;[31] right-pointing triangle, Sancho et al.;[27] ■, van Ruth et al.;[22] ▲, van Ruth et al.;[23] ▼, Dohnal and Ondo;[24] ●, 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.

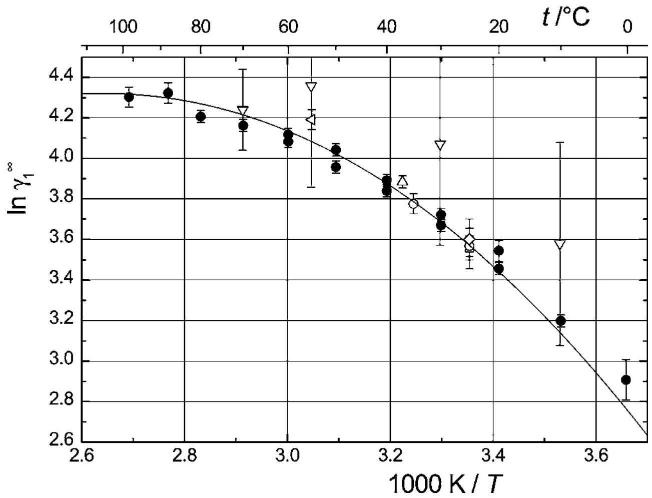

Figure 6. Limiting activity coefficient ln γ_1^∞ of 2-methyl-2-butanol (1) in water (2) as a function of temperature. Experimental values are from Table 4: □, Butler et al.;[17] ○, Butler and Reid;[32] △, Kühne et al.;[19] ▽, Fischer et al.;[33] ◇, Merk and Riederer;[21] left-pointing triangle, Dohnal and Ondo;[24] ●, 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.

Apart from the outliers mentioned, most other data are in a good accord supporting the stability of the recommended fit. Among the γ_1^∞ data which show the closest agreement and the smallest deviations from the recommended fit are those of Kühne et al.[19] and Mash and Pemberton[18] (GLC), Merk and Riederer[21] and Kaneko et al.[31] (HSA), Cabani et al.[25] (tensimetry), in most cases Butler et al.[17,32] (differential distillation), and those measured in this laboratory (applicability optimized use of various techniques).

Calorimetric data, which compared to the measurements of limiting activity coefficients are much less abundant, were matched by the simultaneous fit in general very well (not shown). Appreciable disparities were observed only in the case of $\bar{H}_1^{E,\infty}$ measurements of Bury and Treiner[35] (2-pentanol) and of Arnett et al.[36] (2-methyl-2-butanol).

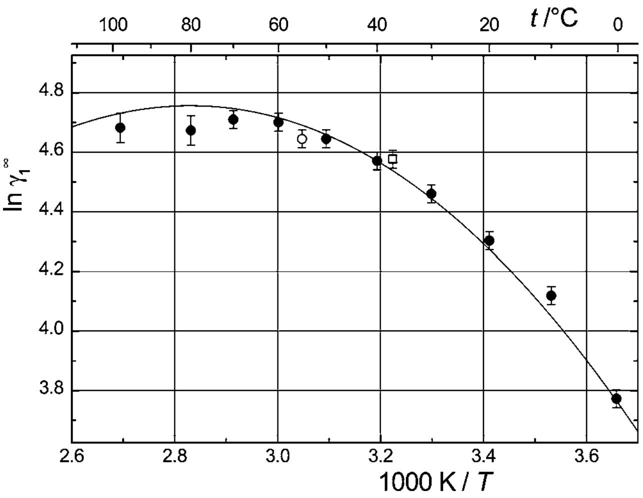

Figure 7. Limiting activity coefficient ln γ_1^∞ of 3-methyl-2-butanol (1) in water (2) as a function of temperature. Experimental values are from Table 4: □, Kühne et al.;[19] ○, Dohnal and Ondo;[24] ●, this work. The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 1.

Table 8. Recommended Values of Excess Thermodynamic Functions at Infinite Dilution[a] for Branched Pentanols in Water at 298.15 K Together with Their Standard Uncertainties

pentanol	γ_1^∞	$\bar{G}_1^{E,\infty}$ kJ·mol^{-1}	$\bar{H}_1^{E,\infty}$ kJ·mol^{-1}	$\bar{C}_{p,1}^{E,\infty}$ J·K^{-1}·mol^{-1}
2-pentanol	97.2 ± 0.8	11.34 ± 0.02	−12.11 ± 0.05	315 ± 3
3-pentanol	83.3 ± 1.1	10.96 ± 0.03	−12.68 ± 0.12	290 ± 3
2-methyl-1-butanol	149 ± 1	12.40 ± 0.02	−8.29 ± 0.05	302 ± 3
3-methyl-1-butanol	157 ± 1	12.53 ± 0.02	−8.23 ± 0.06	309 ± 3
2-methyl-2-butanol	35.5 ± 0.4	8.85 ± 0.03	−17.93 ± 0.16	298 ± 3
3-methyl-2-butanol	78.7 ± 0.9	10.82 ± 0.03	−12.59 ± 0.05	280 ± 4

[a] Calculated from eq 1 with parameters from Table 7.

Recommended $\gamma_1^\infty(T)$ and $K_H(T)$ Data. Equation 1 with parameters from Table 7 yields for available data a thermodynamically consistent description of superior quality and we consider it to establish the recommended temperature dependence of γ_1^∞, as well as of its derivative properties, $\bar{H}_1^{E,\infty}$ and $\bar{C}_{p,1}^{E,\infty}$, in the range from the melting point to the normal boiling point of water. The relative standard uncertainty (68 % confidence level) of the recommended values, as inferred by the error propagation from the parameter variance−covariance matrix, is typically within 2 % for γ_1^∞ and 3 % for $\bar{H}_1^{E,\infty}$ or $\bar{C}_{p,1}^{E,\infty}$. The recommended values at 298.15 K are of the highest accuracy and are listed for a quick reference and illustration in Table 8. The recommended temperature dependence of γ_1^∞ is believed to be reliable even in a moderate extrapolation toward higher temperatures: for example, at 400 K the probable uncertainty of the calculated γ_1^∞ values is estimated to be within 5 %.

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

$$K_H = \gamma_1^\infty p_1^s \varphi_1^s \exp[\upsilon_1^L(p_2^s - p_1^s)/(RT)] \tag{5}$$

$$\Delta_{hyd}G_1^\infty = RT\ln(K_H/p^\circ) \tag{6}$$

$$\Delta_{hyd}H_1^\infty = \bar{H}_1^{E,\infty} - \Delta_{vap}H^\circ \tag{7}$$

$$\Delta_{hyd}C_{p,1}^\infty = \bar{C}_{p,1}^\infty - C_{p,1}^{G,\circ} = \bar{C}_{p,1}^{E,\infty} + (C_{p,1}^{L,\bullet} - C_{p,1}^{G,\circ}) \tag{8}$$

where p_i^s are pure component vapor pressures, υ_1^L is the pure liquid solute molar volume, φ_1^s is the fugacity coefficient of the

Table 9. Parameters of Equation 9[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 the Fit s_{rel}

pentanol	A_H	B_H	C_H	D_H	s_{rel}[b]
2-pentanol	80.2291	−98.8349	−95.0135	22.9685	0.007
3-pentanol	79.8735	−98.8842	−95.5499	23.4663	0.002
2-methyl-1-butanol	75.4977	−91.2766	−85.539	20.0469	0.006
3-methyl-1-butanol	76.3869	−98.2137	−98.5165	26.0376	0.010
2-methyl-2-butanol	81.8832	−102.239	−99.3669	24.704	0.005
3-methyl-2-butanol	78.2757	−98.7862	−97.6753	25.1365	0.006

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

$$S = \sum_{i=1}^{n_G} [K_{H,i}(\text{calc})/K_{H,i}(\text{exp}) - 1]^2 + \sum_{i=1}^{n_H} [\Delta_{hyd}H_{1,i}^\infty(\text{calc})/\Delta_{hyd}H_{1,i}^\infty(\text{exp}) - 1]^2 + \sum_{i=1}^{n_C} [\Delta_{hyd}C_{p,1,i}^\infty(\text{calc})/\Delta_{hyd}C_{p,1,i}^\infty(\text{exp}) - 1]^2$$

pure solute saturated vapor, $\Delta_{vap}H^\circ$ is the pure solute vaporization enthalpy to the standard state of ideal gas (standard vaporization enthalpy), $C_{p,1}^{L,*}$ 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 pure solutes (Table 1) and their fugacity coefficients and liquid molar volumes needed for the evaluation of K_H according to eq 5 are available for the entire temperature range of interest [(273.15 to 373.15) K] and were obtained in the same way as described above in the section Results of Measurements. Thermal properties of some pure pentanol isomers, however, are available only at a single temperature, 298.15 K, or in narrower near-ambient temperature ranges, this fact limiting accordingly the temperatures at which the hydration thermal properties can be calculated. The standard vaporization enthalpies were obtained by correcting the experimental vaporization enthalpies for the vapor-phase nonideality.[51] The heat capacities of pure liquids were taken from the compilation of Zábranský et al.[42−44] and those of ideal gas from CDATA.[16]

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

$$\ln(K_H/\text{kPa}) = A_H + B_H/\tau + C_H \ln \tau + D_H\tau \qquad (9)$$

giving

$$\Delta_{hyd}H_1^\infty = RT_0(B_H - C_H\tau - D_H\tau^2) \quad \text{and}$$
$$\Delta_{hyd}C_{p,1}^\infty = -R(C_H + 2D_H\tau)$$

Equation 9 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 9 is a compromise to fit the rather nonlinear $\Delta_{hyd}C_{p,1}^\infty(T)$ dependence encountered. Values of the hydration properties at equidistant temperatures (5 K increment) covering the temperature ranges of available data 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 9, along with the corresponding relative standard deviations of fit s_{rel}, are listed for the branched pentanols studied in Table 9. It is seen that eq 9 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 9, except for $\Delta_{hyd}H_1^\infty$ and $\Delta_{hyd}C_{p,1}^\infty$ near the ends of the temperature interval (273.15 K, 373.15 K) where one should allow for uncertainties of 3 % and 5 %, respectively, mainly due to the compromised linear fit of $\Delta_{hyd}C_{p,1}^\infty$ provided by eq 9. Nevertheless, for estimation of the Henry's law constants, even moderate extrapolations by eq 9 toward higher temperatures are believed to be reliable: for example, 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 9 are compared with recent recommendations by Plyasunova et al.[52] in Table 10. In general, a very good agreement is observed for all of the branched pentanols 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 Pentanol Branching

In Figure 8 the recommended $\gamma_1^\infty(T)$ and $K_H(T)$ dependences for all studied pentanol isomers are plotted in the van't Hoff coordinates. The results for 1-pentanol used for comparison are taken from our previous work.[1] As seen in Figure 8a, going from 273.15 K the values of ln γ_1^∞ rise with temperature,

Table 10. Recommended Values of Hydration Thermodynamic Functions[a] for Branched Pentanols in Water at 298.15 K and Their Comparison with Those Given by Plyasunova et al.[52] (in parentheses)[b]

	K_H	$\Delta_{hyd}G_1^\infty$	$\Delta_{hyd}H_1^\infty$	$\Delta_{hyd}C_{p,1}^\infty$
pentanol	kPa	kJ·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
2-pentanol	78.5 ± 1.0	−0.601 ± 0.03	−66.41 ± 0.5	408 ± 5
	(81.4 ± 6.6)	(−0.51 ± 0.20)	(−65.3 ± 1.0)	(403 ± 14)
3-pentanol	86.1 ± 1.4	−0.371 ± 0.04	−66.44 ± 0.6	404 ± 5
	(100.7 ± 16)	(0.018 ± 0.40)	(−66.4 ± 1.0)	(405 ± 15)
2-methyl-1-butanol	71.4 ± 1.2	−0.836 ± 0.04	−63.92 ± 0.3	378 ± 5
	(70.1 ± 11)	(−0.88 ± 0.40)	(−62.2 ± 2.0)	(386 ± 15)
3-methyl-1-butanol	67.4 ± 1.1	−0.978 ± 0.04	−63.79 ± 0.4	386 ± 5
	(75.3 ± 9)	(−0.70 ± 0.30)	(−63.1 ± 2.0)	(386 ± 15)
2-methyl-2-butanol	77.3 ± 0.9	−0.637 ± 0.03	−68.36 ± 0.3	415 ± 5
	(89.9 ± 16)	(−0.26 ± 0.44)	(−68.5 ± 0.4)	(409 ± 10)
3-methyl-2-butanol	102.0 ± 1.2	0.052 ± 0.03	−65.06 ± 0.4	394 ± 5

[a] Calculated from eq 9 with parameters from Table 9. [b] Converted from the molality scale used in ref 52 to the mole fraction scale used in the present work.

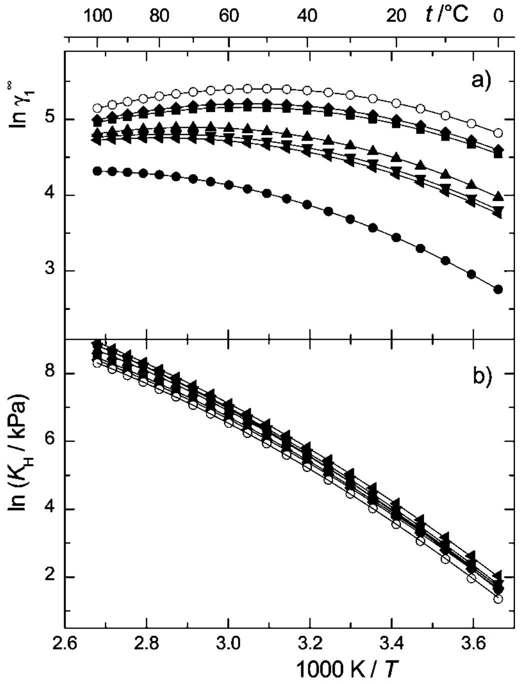

Figure 8. Recommended temperature dependence for limiting activity coefficients γ_1^∞ (a) and Henry's law constants K_H (b) of isomeric pentanols (1) in water (2): -○-, 1-pentanol; -◆-, 3-methyl-1-butanol; -■-, 2-methyl-1-butanol; -▲-, 2-pentanol; -▼-, 3-pentanol; left-pointing triangle, 3-methyl-2-butanol; -●-, 2-methyl-2-butanol.

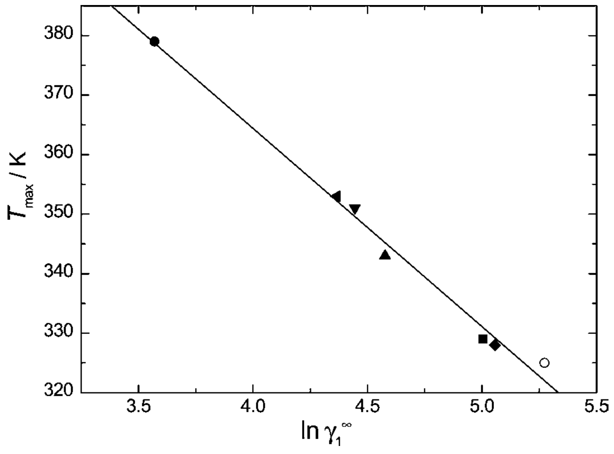

Figure 9. Correlation between the limiting activity coefficient ln γ_1^∞ at 298.15 K and the temperature T_{max} at which ln $\gamma_1^\infty(T)$ attains maximum for isomeric pentanols (1) in water (2): ○, 1-pentanol; ◆, 3-methyl-1-butanol; ■, 2-methyl-1-butanol; ▲, 2-pentanol; ▼, 3-pentanol; left-pointing triangle, 3-methyl-2-butanol; ●, 2-methyl-2-butanol.

following concave courses which at a higher T display a maximum. For 2-methyl-2-butanol, the maximum appears slightly above the normal boiling temperature of water. The temperature corresponding to the maximum, T_{max} (see Table 7 here and Table 4 in ref 1), increases with the branching of the pentanol isomer and follows the sequence: 1-pentanol < 3-methyl-1-butanol < 2-methyl-1-butanol < 2-pentanol < 3-pentanol < 3-methyl-2-butanol < 2-methyl-2-butanol. Note that this sequence reflects an increasing compactness of the isomeric pentanol molecule as measured simply by the number of bonds through which the five pentanol carbon atoms are linked to the hydroxyl group. At a constant T, the branching of alkanol is seen to decrease the value of limiting activity coefficient in the exactly reverse sequence. Figure 9 discloses that the values of T_{max} and ln γ_1^∞(298.15 K) are even closely correlated. When

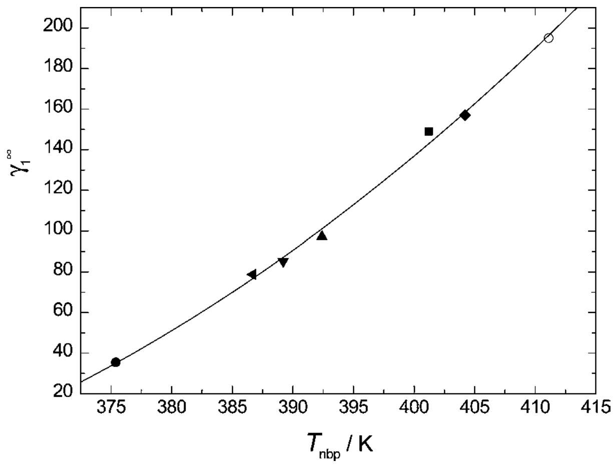

Figure 10. Correlation between the limiting activity coefficient γ_1^∞ of isomeric pentanols (1) in water (2) at 298.15 K and the normal boiling point temperature T_{nbp} of these solutes: ○, 1-pentanol; ◆, 3-methyl-1-butanol; ■, 2-methyl-1-butanol; ▲, 2-pentanol; ▼, 3-pentanol; left-pointing triangle, 3-methyl-2-butanol; ●, 2-methyl-2-butanol.

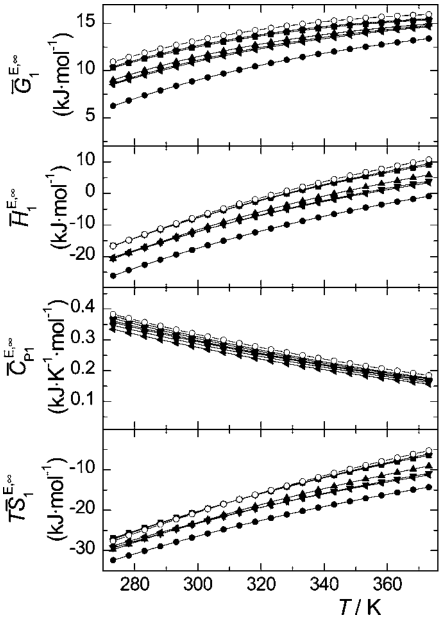

Figure 11. Variation of limiting partial molar excess functions $\bar{Y}_1^{E,\infty}$ (Y = G, H, C_p, TS) of isomeric pentanols (1) in water (2) with temperature and branching: -○-, 1-pentanol; -◆-, 3-methyl-1-butanol; -■-, 2-methyl-1-butanol; -▲-, 2-pentanol; -▼-, 3-pentanol; left-pointing triangle, 3-methyl-2-butanol; -●-, 2-methyl-2-butanol.

the branching occurs solely on the aliphatic chain of pentanol, without affecting the position of hydroxyl group, the decrease in ln γ_1^∞ is only subtle, whereas when the hydroxyl group position changes from primary to secondary and then to tertiary, the decrease is considerable and about of the same magnitude for each of the steps. Since structure compactness of isomeric molecules is an important parameter affecting also various pure component properties of isomers, it is quite understandable that the limiting activity coefficient of isomeric pentanols in water is correlated well also with the normal boiling point temperature of these solutes as shown in Figure 10. Like for (C3 and C4) alkanols studied previously, also for pentanols the effect of branching on the value of γ_1^∞ is the largest at 273.15 K, and with increasing temperature diminishes monotonically, suggesting that at higher temperatures γ_1^∞ values for the isomeric alkanols converge. Note that at lower temperatures ($T < 333$ K) the branching effect for 2-methyl-2-butanol is so strong that

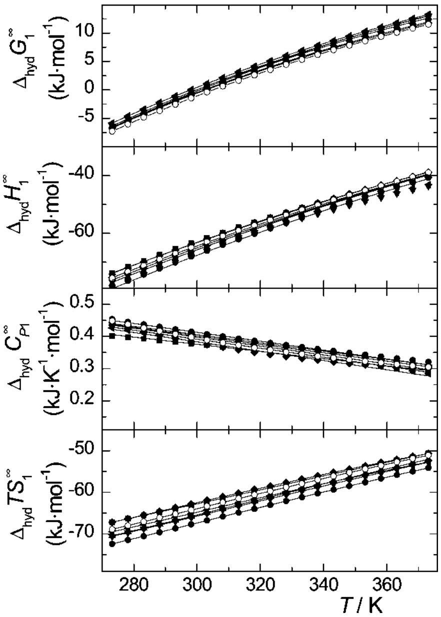

Figure 12. Variation of thermodynamic functions of hydration $\Delta_{\text{hyd}}Y_1^\infty$ ($Y = G, H, C_p, TS$) of isomeric pentanols (1) in water (2) with temperature and branching: -○-, 1-pentanol; -◆-, 3-methyl-1-butanol; -■-, 2-methyl-1-butanol; -▲-, 2-pentanol; -▼-, 3-pentanol; left-pointing triangle, 3-methyl-2-butanol; -●-, 2-methyl-2-butanol.

causes this pentanol isomer to behave more ideally in aqueous solution than 1-butanol does.

The Henry's law constants (Figure 8b) for isomeric pentanols exhibit also a concave rise with temperature, but the curves are seen to be still quite steep at 373.15 K, and their reliable extrapolation to 423.15 K by eq 9 shows no maximum to occur within this range. Because of the large scale of Figure 8b dictated by the temperature range considered, the curves are clustered, and details are barely visible. The effect of branching on K_H values is opposite to that on γ_1^∞, that is, 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. With the exception of 2-methyl-2-butanol, the K_H values of isomeric pentanols follow the sequence that was observed for $T_{\max}$.

Figures 11 and 12 give a graphical overview of the variation of thermodynamic functions of pentanols' dissolution and hydration with temperature and branching. The pattern of thermodynamic behavior is in many respects typical for aqueous amphiphilic solutes: while 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, the strongly exothermic character of these processes indicate that the hydroxyl group of pentanols is capable of efficient hydrogen bonding with the solvent water. As a result of a rather delicate balance of the large enthalpic and entropic contributions, $\bar{G}_1^{E,\infty}$ and $\Delta_{\text{hyd}}G_1^\infty$ of pentanols in the given temperature range exhibit monotonically increasing temperature dependences. The entropy and enthalpy contributions largely compensate each other, and it is only for $\bar{G}_1^{E,\infty}$ at temperatures higher than $T_{\max}$ where both act in the positive direction. Although the heat capacities of dissolution and hydration diminish with temperature, their values remain still positive and large at 373.15 K, and hence, in the temperature range considered, the respective enthalpies and entropies are rapidly increasing functions of T.

The effect of branching on temperature derivative properties seems less pronounced and, except for $\bar{H}_1^{E,\infty}$ and $\bar{S}_1^{E,\infty}$, is rather difficult to resolve. Both the dissolution enthalpy and the dissolution entropy are however clearly seen to decrease (to become more negative) as the position of the hydroxy group changes in the sequence primary > secondary > tertiary, following thus the same trend as that observed for γ_1^∞ ($\bar{G}_1^{E,\infty}$).

Performance of Predictive Approaches

The recommended $\gamma_1^\infty(T)$ data we established for aqueous pentanols enable us to test for the given class of systems the predictive performance of existing estimation methods. Five predictive approaches were examined in this work, namely, the modified universal quasichemical activity coefficient (UNIFAC), the linear free energy relationship (LFER) correlation of Abraham and Acree,[53] the group contribution method of Cabani et al.,[54] and the group contribution schemes of the first order and the second order due to Plyasunov et al.[55] To predict $\gamma_1^\infty(T)$ dependences, the leading method for prediction of activity coefficients, the modified UNIFAC (Dortmund), was applied with the latest parameter values published in open literature (fourth[56] and fifth revision[57]). This method distinguishes three positions of the hydroxy group (primary, secondary, and tertiary) but disregards the branching of alkyl chain. In the case of the other methods, which are destined primarily for prediction of hydration properties at 298.15 K, the $\gamma_1^\infty(T)$ dependences were constructed using the predicted $\Delta_{\text{hyd}}G_1^\infty$(298.15 K), $\Delta_{\text{hyd}}H_1^\infty$(298.15 K), and $\Delta_{\text{hyd}}C_{p,1}^\infty$(298.15 K) values. The first-order methods of Cabani and Plyasunov make no distinction between four pentanol isomers (2-pentanol, 3-pentanol, 2-methyl-1-butanol, and 3-methyl-1-butanol) predicting for all of them the same values of hydration quantities; the predicted γ_1^∞ values differ just because of differing vapor pressures of these isomers. Results of the predictions are summarized in the form of the $\ln \gamma_1^\infty$ root-mean-square deviations (rmsd's) in Table 11. As seen from this table, the quality of the predictions varied considerably among the tested methods. The modified UNIFAC gave the largest deviations. It failed particularly for 2-methyl-2-butanol

Table 11. Performance of Various Prediction Methods in the Estimation of Limiting Activity Coefficients of Aqueous Pentanols

	modified UNIFAC	Abraham LFER	Cabani	Plyasunov first-order	Plyasunov second-order
pentanol isomer	rmsd in $\ln \gamma_1^{\infty a}$				
1-pentanol	0.475	0.371	0.272	0.189	0.174
2-pentanol	0.303	0.215	0.133	0.111	0.101
3-pentanol	0.348	0.338	0.049	0.063	0.027
2-methyl-1-butanol	0.270	0.278	0.283	0.195	0.110
3-methyl-1-butanol	0.305	0.389	0.344	0.255	0.171
2-methyl-2-butanol	0.731	0.254	0.062	0.151	0.149
3-methyl-2-butanol	0.368	0.280	0.121	0.026	0.032
all pentanol isomers	0.427	0.289	0.211	0.155	0.123

[a] Based on 21 equidistant points in the range from (273.15 to 373.15) K.

for which predicted about twice higher γ_1^∞ values and for 1-pentanol for which predicted (except at subambient temperatures) about 50 % lower γ_1^∞ values than those obtained experimentally. A closer inspection of the UNIFAC results further revealed that also its predictions for all secondary pentanols at lower temperatures are rather poor (too high). Compared to the modified UNIFAC, the LFER of Abraham gave better and more uniform predictions without any major failure. Significantly still better performance was observed for the classical method of Cabani which was able to estimate γ_1^∞ of pentanols with an average deviation of about 20 %. Clearly the best were the group contributions schemes developed recently by Plyasunov. It appears that the predictions by his second-order scheme yield for some isomeric pentanols an accuracy approaching almost the experimental uncertainty.

Conclusion

Through our systematic measurements and comprehensive literature search we gathered in this work extensive information on air−water partitioning and related thermal properties of branched pentanol isomers in water. Critical evaluation and thermodynamically consistent treatment of the information enabled us to establish reliable recommended temperature dependences for the limiting activity coefficients, Henry's law constants, and dissolution and hydration enthalpies and heat capacities of these aqueous solutes in the range from the melting point to the normal boiling point of water. Several general features in the variation of these properties with temperature and pentanol molecule branching could be identified. The properties of aqueous pentanols appear to be reasonably predictable using a second-order group contribution scheme. To our best knowledge, this work together with our previous papers on (C1 to C5) 1-alkanols and (C3 and C4) branched alkanols represent one of the most systematic experimental studies on infinite dilution thermodynamics of isomeric amphiphilic solutes in water to the date.

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