Temperature Dependences of Limiting Activity Coefficients, Henry's Law Constants, and Derivative Infinite Dilution Properties of Lower (C_1–C_5) 1-Alkanols in Water. Critical Compilation, Correlation, and Recommended Data

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A comprehensive review is 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 lower 1-alkanols (C_1–C_5) in water. For each alkanol, the compiled data are critically evaluated and correlated with a suitable model equation providing adequate simultaneous description of the equilibrium measurements and the calorimetric information. As a result, recommended thermodynamically consistent temperature dependences of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ of superior accuracy are 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 1-alkanols, analogous recommendations are also derived for the temperature dependences of the Henry's law constants, hydration enthalpies, and hydration heat capacities. Evolution of the various infinite dilution thermodynamic properties of aqueous 1-alkanols with temperature and homologous series is briefly discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2203355]

Key words: 1-alkanols; water; limiting activity coefficient; Henry's law constant; thermodynamic functions of dissolution and hydration; temperature dependence; recommended data.

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1. Introduction

Lower alkanols belong to common large scale production chemicals which are used in a variety of applications as solvents and chemical intermediates and nowadays also increasingly consumed as oxygenated fuel additives. During their production and use the alkanols often interact with water. In order to model and predict phase and chemical equilibria, kinetic solvent effects, and other phenomena involved in these processes, thermodynamic properties of highly dilute aqueous solutions of alkanols, such as alkanol limiting activity coefficients or Henry's law constants in water, are of great importance. Accurate knowledge of thermodynamic quantities of the dissolution and hydration of alkanols and their evolution with temperature is of extreme interest for theoretical reasons, in particular for understanding the hydrophobic effect, because alkanols represent a unique set of homologous compounds formally derived from water by adding aliphatic groups.

A large number of experimental determinations of infinite dilution thermodynamic properties of aqueous alkanols have been reported in the literature. A review of hydration quantities at 298.15 K presented by Plyasunov and Shock[1] in 2000 for nonpolyaromatic hydrocarbons and alkanols indicates that for lower 1-alkanols underlying data are especially abundant and, compared to other solutes considered, relatively unconflicting. However, being at a single temperature, these data can neither be checked for thermodynamic consistency, nor reliably extrapolated in temperature. Our closer inspection of data as functions of temperature has revealed excessive scatter of limiting activity coefficients reported in the literature and a lack of their consistency with thermal data. With the aim to establish a truly reliable recommendation for limiting activity coefficients of C_1–C_5 1-alkanols

valid in a broader temperature range we have measured ample and accurate underlying data spread from 273 to 373 K.[2]

In this work, we then present for lower (C_1–C_5) 1-alkanols in water a comprehensive compilation and critical evaluation of all literature experimental data on limiting activity coefficient, limiting partial molar excess enthalpy and heat capacity, and their simultaneous processing with data measured in our laboratory. The treatment results in recommended temperature dependences of these infinite dilution properties of a significantly improved accuracy which are valid in the range from the freezing to the normal boiling temperatures of water. Analogous recommendations are further presented for the temperature dependences of the Henry's law constants, hydration enthalpies, and heat capacities and the evolution of these various infinite dilution properties with temperature and 1-alkanol homologous series is discussed.

2. Thermodynamic Background

Limiting activity coefficient is a fundamental thermodynamic quantity which measures the solution nonideality and, as a correction factor to the Raoult's law, governs dilute-range fluid-phase equilibria. Its value closely reflects solute–solvent interactions, representing thus for aqueous organic solutes a convenient measure of their hydrophobicity. By definition, the limiting activity coefficient γ_1^∞ of a solute(1) in a solvent(2) is directly related to the solute partial molar excess Gibbs energy (excess chemical potential) at infinite dilution

$$\bar{G}_1^{E,\infty} = RT \ln \gamma_1^\infty. \tag{1}$$

Through its temperature derivatives, the limiting activity coefficient is further linked to infinite dilution partial molar excess enthalpy

$$\bar{H}_1^{E,\infty} = -RT^2(d \ln \gamma_1^\infty/dT) \tag{2}$$

and infinite dilution partial molar excess heat capacity

$$\bar{C}_{p,1}^{E,\infty} = (d\bar{H}_1^{E,\infty}/dT). \tag{3}$$

As the infinite dilution partial molar excess quantities $\bar{Y}_1^{E,\infty}$ ($Y=G,H,C_p$) correspond to a transfer of the solute from its pure liquid state to a hypothetical infinitely dilute solution of unity solute mole fraction ($x_1=1$), they are equal to the values of thermodynamic quantities of the (dis)solution at infinite dilution $\Delta_{sol}Y_1^\infty$. Both these denotations ($\bar{Y}_1^{E,\infty}, \Delta_{sol}Y_1^\infty$) are thus used as synonyms further in this article.

Beside the limiting activity coefficient based on Raoult's law, the concept of Henry's law has been frequently used to characterize the vapor–liquid equilibrium of aqueous organic solutes. In this work, we adopt the following thermodynamically rigorous definition of Henry's law constant

$$K_H = \lim_{x_1 \to 0} (f_1^L/x_1), \tag{4}$$

where f_1^L is the fugacity of a given organic solute and x_1 is its mole fraction in the aqueous solution. Henry's law constant and the limiting activity coefficient are related through

$$K_H = \gamma_1^\infty p_1^s \varphi_1^s \exp[v_1^L(p_2^s - p_1^s)/(RT)], \tag{5}$$

where p_i^s are pure component vapor pressures, v_1^L is the pure liquid solute molar volume, and φ_1^s is the fugacity coefficient of the pure solute saturated vapor. For less volatile solutes and/or at ambient or lower temperatures, both φ_1^s and the exponential Poynting correction approach unity and a good approximation can be disregarded. Several alternative definitions of Henry's law constant[3] are used in the literature and hence care must be exercised to avoid confusion and misinterpretation of the data. The Henry's law constant is closely related to the infinite dilution hydration Gibbs energy

$$\Delta_{hyd}G_1^\infty = RT \ln(K_H/p^0) \tag{6}$$

and through its temperature derivatives to infinite dilution hydration enthalpy and heat capacity

$$\Delta_{hyd}H_1^\infty = -RT^2(d \ln K_H/dT), \tag{7}$$

$$\Delta_{hyd}C_{p,1}^\infty = (d\,\Delta_{hyd}H_1^\infty/dT). \tag{8}$$

These infinite dilution hydration quantities correspond to a transfer of the solute from the pure ideal gas state at standard pressure p^0=100 kPa to a hypothetical infinitely dilute solution of unity solute mole fraction ($x_1=1$).

The infinite dilution hydration quantity $\Delta_{hyd}Y_1^\infty$ ($Y=G,H,C_p$) can be generally obtained from the infinite dilution solution quantity by adding to the latter the respective residual property of the pure solute

$$\Delta_{hyd}Y_1^\infty = \Delta_{sol}Y_1^\infty + \Delta_{res}Y_1^\bullet. \tag{9}$$

By definition, the residual property $\Delta_{res}Y_1^\bullet$ accounts for the difference between the state of pure solute at a given pressure and that of its ideal gas at the standard pressure p^0.

Then, it follows for the infinite dilution hydration enthalpy

$$\Delta_{hyd}H_1^\infty = \Delta_{sol}H_1^\infty - \Delta_{vap}H^0, \tag{10}$$

where $\Delta_{vap}H^0$ is the pure solute vaporization enthalpy to the standard state ideal gas (standard vaporization enthalpy), and for the infinite dilution hydration heat capacity

$$\Delta_{hyd}C_{p,1}^\infty = \bar{C}_{p,1}^\infty - C_{p,1}^{G,0} = \Delta_{sol}C_{p,1}^\infty + (C_{p,1}^{L,\bullet} - C_{p,1}^{G,0}) \tag{11}$$

where $C_{p,1}^{L,\bullet}$ and $C_{p,1}^{G,0}$ 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.

Hereafter in this article, when referring to the infinite dilution hydration or (dis)solution properties, the adjective "infinite dilution" will be mostly omitted for the sake of brevity.

3. Data Compilation and Survey

Data on γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ of C_1-C_5 1-alkanols in water (601 data points compiled from 93 literature references) are listed in Tables 1–3, respectively (Tables1a–1e, 2a–2e, and 3a–3e). Only original experimental values were considered in this collection, those extrapolated from measurements on concentrated solution, calculated from simulations or estimated by group contribution or structure-property correlations were disregarded. In general, the collected data spread over the temperature range from 273 to 373 K; at temperatures higher than 373 K there are only a few values which mostly have a lower accuracy. With the exception of 1-pentanol (57 data points), the distribution of the data points among the other alkanols is roughly uniform, varying from 123 for 1-propanol to 153 for ethanol.

The majority of the collected information concerns limiting activity coefficients for which 327 data points are available [Tables 1a–1e]. The values of γ_1^∞ were extracted from the Prague Limiting Activity Coefficient Inquiry Database (PLACID). For the sake of completeness, the contents of this database developed and maintained by our laboratory were freshly updated on the basis of a thorough ad hoc search of the literature. According to the PLACID policy, the collected γ_1^∞ data file covers not only values of γ_1^∞ directly reported in the literature (more than 80% of values) but also those derived by us from reported closely related experimental vapor–liquid equilibrium (VLE) quantities such as the Henry's law constants, or gas–liquid partition coefficients.

As seen from Tables 1a–1e the γ_1^∞ data were determined using a variety of specialized vapor-liquid equilibrium techniques. Nonanalytical methods (ebulliometry, tensimetry) as well as analytical ones (retention measurements in gas–liquid chromatography, headspace analysis, rate measurements on continuous gas–liquid separation processes, and various distillation methods) were employed. The γ_1^∞ data were often calculated from these VLE measurements assuming the ideal behavior of gas phase. In most such cases, the error caused by this approximation does not exceed 2% and is within the measurement uncertainty. The determination of γ_1^∞ from primary VLE measurements requires generally the knowledge of the pure solute vapor pressure. For higher boiling solutes (1-butanol, 1-pentanol) at subambient temperatures the p_1^s data are largely uncertain which enhances the uncertainty in the determination of γ_1^∞. Note however that a convenient application of the headspace technique using the calibration by pure solute saturated vapor effectively avoids the problem.[56] As to the distribution of γ_1^∞ data with respect to temperature, it is characteristic that many data were measured at 298.15 K, fairly covered are also temperatures higher than 298.15 K, whereas at subambient temperatures the data are very scarce. Systematic measurements of γ_1^∞ of C_1-C_5 1-alkanols in water as a function of temperature have appeared only recently.[30,33–35,43] The most complete contribution to this end has been provided by this laboratory[2] (77 values, 24% of all γ_1^∞ available).

Data on the infinite dilution thermal properties were collected through a careful search of the literature. Limiting partial molar excess enthalpies (151 data points) are listed in Tables 2a–2e. The existing data 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 two laboratories.[73,76,80,83] The $\bar{H}_1^{E,\infty}$ values were obtained directly by measuring the heats of dissolution of aqueous alkanols at high dilution, possibly extrapolating the results to infinite dilution. Either batch or flow isothermal heat-of-mixing calorimeters were employed. Limiting partial molar excess heat capacities (123 data points) are listed in Tables 3a–3e. 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. In some studies, measurements on both dilute solutions and pure solute were carried out using the same apparatus and chemical samples and the resulting $\bar{C}_{p,1}^{E,\infty}$ was reported. This is considered a preferred procedure here as it minimizes possible inconsistency between the combined data. Alternatively, 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.[90–92] Flow C_p calorimetry or scanning calorimetry are typically used for the measurements. Although the collected $\bar{C}_{p,1}^{E,\infty}$ data appear to be relatively numerous, they resulted from a limited number of studies. As concerns the temperature dependence, relevant measurements were done only in two laboratories.[89,93,94,98]

4. Data Evaluation and Correlation

The quality of the information gathered in Tables 1–3 is not at all uniform. A brief inspection of the collected data shows that they greatly differ in their accuracy, showing sometimes significant disparity, inconsistency, and scatter. In order to resolve this issue and establish reliable and accurate recommended data, all the collected information was subjected to a critical evaluation and processed by a thermodynamically consistent treatment.

The essentials of the procedure are the same as described previously.[56] For each solute, the γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data were fitted simultaneously with a suitable, sufficiently flexible model equation describing their temperature dependence. In this work, two alternative four-parameter fitting equations were used (i)

$$\ln \gamma_1^\infty = A + B/\tau + C \ln \tau + D\tau, \tag{12}$$

giving

$$\bar{H}_1^{E,\infty} = RT_0(B - C\tau - D\tau^2),$$

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

or (ii)

TABLE 1a. Experimental values of limiting activity coefficients of methanol(1) in water(2) together with their 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]	Reference
300.45	0.788	0.5	GLC	IDEAL	Hardy[4]
298.15	0.425	0.1	TENS	VIR+A	Pierotti *et al.*[5]
333.15	0.647	0.1	TENS	VIR+A	Pierotti *et al.*[5]
373.15	0.793	0.1	TENS	VIR+A	Pierotti *et al.*[5]
313.15	0.593	0.2	GLC	IDEAL	Hofstee *et al.*[6]
333.15	0.756	0.2	GLC	IDEAL	Hofstee *et al.*[6]
298.15	0.372[c]	0.1	IGS	IDEAL	Burnett[7]
293.15	0.990	0.5	GLC	VIR	Pecsar and Martin[8]
303.15	0.928	0.5	GLC	VIR	Pecsar and Martin[8]
313.15	0.833	0.5	GLC	VIR	Pecsar and Martin[8]
373.15	0.811	0.1	EBUL	IDEAL	Kojima *et al.*[9]
373.15	0.963	0.05	CIRC	VIR+A	Dalager[10]
339.58	0.820	0.1	EBUL	VIR+A	Kojima and Kato[11]
352.78	0.824	0.1	EBUL	VIR+A	Kojima and Kato[11]
361.83	0.824	0.1	EBUL	VIR+A	Kojima and Kato[11]
373.15	0.824	0.1	EBUL	VIR+A	Kojima and Kato[11]
407.14	0.820	0.2	EBUL	VIR+A	Kojima and Kato[11]
425.49	0.806	0.2	EBUL	VIR+A	Kojima and Kato[11]
444.11	0.765	0.2	EBUL	VIR+A	Kojima and Kato[11]
458.60	0.756	0.2	EBUL	VIR+A	Kojima and Kato[11]
297.45	0.751	0.2	GLC	IDEAL	Shaffer and Daubert[12]
298.15	0.507	0.03	GLC	VIR	Larkin and Pemberton[13]
298.15	0.425	0.05	HSA	IDEAL	Rytting *et al.*[14]
298.15	0.495	0.03	GLC	VIR	Mash and Pemberton[15]
298.15	1.778	1.0	MBEA	IDEAL	Schmidt[16]
326.15	0.525	1.0	MBEA	IDEAL	Schmidt[16]
298.15	0.487	0.01	TENS	IDEAL	Christian *et al.*[17]
308.15	0.572	0.01	TENS	IDEAL	Christian *et al.*[17]
328.15	0.756	0.05	IGS	IDEAL	Lee[18]
298.1	0.501	0.1	IGS	IDEAL	Lebert and Richon[19]
298.15	0.495	0.02	IGS	IDEAL	Richon *et al.*[20]
273.15	0.223[c]	0.1	HSA	IDEAL	Snider and Dawson[21]
298.15	0.385[c]	0.1	HSA	IDEAL	Snider and Dawson[21]
373.15	0.859	0.1	EBUL	VIR+A	Ochi and Kojima[22]
317.85	0.378	0.2	EBUL	VIR	Bergmann and Eckert[23]
328.45	0.399	0.2	EBUL	VIR	Bergmann and Eckert[23]
337.65	0.464	0.2	EBUL	VIR	Bergmann and Eckert[23]
348.25	0.419	0.2	EBUL	VIR	Bergmann and Eckert[23]
357.75	0.577	0.2	EBUL	VIR	Bergmann and Eckert[23]
298.15	0.554	0.1	NSGLC	IDEAL	Landau *et al.*[24]
293.15	0.519	0.1	TENS	VIR	Pividal *et al.*[25]
303.15	0.571	0.1	TENS	VIR	Pividal *et al.*[25]
313.15	0.652	0.1	TENS	VIR	Pividal *et al.*[25]
298.15	0.378	0.1	HSA	IDEAL	Li and Carr[26]
373.35	0.824	0.1	EBUL	Unknown	Gmehling *et al.*[27] [e]
298.15	0.531	0.05	TENS	IDEAL	Bader and Gasem[28]
298.15	0.451[c]	0.05	HSA	IDEAL	Merk and Riederer[29]
333.05	0.765	0.05	CIRC	VIR	Christensen[30]
342.35	0.833	0.05	CIRC	VIR	Christensen[30]
353.05	0.892	0.05	CIRC	VIR	Christensen[30]
362.95	0.904	0.05	CIRC	VIR	Christensen[30]
372.55	0.944	0.05	CIRC	VIR	Christensen[30]
313.15	0.527[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
313.15	0.741[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
323.15	0.494[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
323.15	0.572[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
333.15	0.682[c]	0.1	PRV	IDEAL	Chai and Zhu[31]

TABLE 1a. Experimental values of limiting activity coefficients of methanol(1) in water(2) together with their standard uncertainty, technique of measurement, and vapor phase nonideality treatment.—Continued

T (K)	$\ln \gamma_1^\infty$	$s(\ln \gamma_1^\infty)$	Technique[a]	Vapor[b]	Reference
333.15	0.627[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
343.15	0.747[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
343.15	0.735[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
353.15	0.910[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
353.15	0.782[c]	0.1	PRV	IDEAL	Chai and Zhu[31]
298.15	0.704[c]	0.05	WWC	IDEAL	Altschuh *et al.*[32]
313.15	0.645[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
323.15	0.736[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
333.15	0.826[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
343.15	0.914[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
298.2	0.542	0.1	GLC	VIR	Tochigi *et al.*[34]
323.2	0.728	0.1	GLC	VIR	Tochigi *et al.*[34]
333.2	0.815	0.1	GLC	VIR	Tochigi *et al.*[34]
283.15	0.344	0.03	IGS	IDEAL	Fukuchi *et al.*[35]
293.15	0.438	0.03	IGS	IDEAL	Fukuchi *et al.*[35]
298.15	0.604	0.05	IGS	IDEAL	Fukuchi *et al.*[35]
303.15	0.751	0.1	IGS	IDEAL	Fukuchi *et al.*[35]
313.15	0.842	0.1	IGS	IDEAL	Fukuchi *et al.*[35]
328.15	0.723	0.03	NSGLC	IDEAL	Dohnal and Ondo[36]
273.35	0.207	0.02	HSA	VIR	Vrbka *et al.*[2]
283.15	0.336	0.02	HSA	VIR	Vrbka *et al.*[2]
293.15	0.438	0.02	HSA	VIR	Vrbka *et al.*[2]
303.15	0.536	0.02	TENS	VIR	Vrbka *et al.*[2]
308.15	0.588	0.02	TENS	VIR	Vrbka *et al.*[2]
313.15	0.631	0.02	TENS	VIR	Vrbka *et al.*[2]
318.15	0.668	0.02	TENS	VIR	Vrbka *et al.*[2]
323.15	0.703	0.02	TENS	VIR	Vrbka *et al.*[2]
328.15	0.737	0.02	TENS	VIR	Vrbka *et al.*[2]
333.15	0.770	0.02	TENS	VIR	Vrbka *et al.*[2]
358.15	0.837	0.03	CIRC	VIR	Vrbka *et al.*[2]
363.15	0.867	0.03	CIRC	VIR	Vrbka *et al.*[2]
368.15	0.880	0.03	CIRC	VIR	Vrbka *et al.*[2]
372.15	0.875	0.03	CIRC	VIR	Vrbka *et al.*[2]

[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; MBEA: molecular beams; NSGLC: nonsteady state gas-liquid chromatography; PRV: phase ratio variation; RDIST: Rayleigh distillation; VPC: vapor phase calibration; TENS: tensimetry; and WWC: wetted-wall column.
[b]IDEAL: ideal gas; VIR: virial equation of state; and 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]Gas/liquid partition coefficients calculated at experimental temperatures using the van't Hoff equation reported in the cited source.
[e]Secondary reference citing an original unavailable source (e.g., thesis).

$$\ln \gamma_1^\infty = A + B/\tau + C \exp(D\tau)/\tau \tag{13}$$

giving

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

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

where $\tau = T/T_0$ and $T_0 = 298.15$ K.

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

$$S = \sum_{i=1}^{n_G} [\ln \gamma_{1,i}^\infty(\text{exp}) - \ln \gamma_{1,i}^\infty(\text{calc})]^2/s^2(\ln \gamma_{1,i}^\infty) + \sum_{i=1}^{n_H} [\bar{H}_{1,i}^{E,\infty}(\text{exp}) - \bar{H}_{1,i}^{E,\infty}(\text{calc})]^2/s^2(\bar{H}_{1,i}^{E,\infty}) + \sum_{i=1}^{n_C} [\bar{C}_{p,1,i}^{E,\infty}(\text{exp}) - \bar{C}_{p,1,i}^{E,\infty}(\text{calc})]^2/s^2(\bar{C}_{p,1,i}^{E,\infty}), \tag{14}$$

with data being weighted according to their probable uncertainties $s(\ln \gamma_1^\infty)$, $s(\bar{H}_1^{E,\infty})$, and $s(\bar{C}_{P,1}^{E,\infty})$. The uncertainties correspond to standard deviations (68% probability level) and comprise contributions from all possible sources of error, both random and systematic. To comply with the policy of

TABLE 1b. Experimental values of limiting activity coefficients of ethanol(1) in water(2) together with their 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]	Reference
298.15	1.247	0.1	TENS	VIR+A	Pierotti *et al.*[5]
333.15	4.504	0.2	TENS	VIR+A	Pierotti *et al.*[5]
373.15	1.647	0.2	TENS	VIR+A	Pierotti *et al.*[5]
298.15	1.188[c]	0.2	IGS	IDEAL	Burnett[7]
293.15	1.873	0.5	GLC	VIR	Pecsar and Martin[8]
303.15	1.816	0.5	GLC	VIR	Pecsar and Martin[8]
313.15	1.705	0.5	GLC	VIR	Pecsar and Martin[8]
373.15	1.761	0.1	EBUL	IDEAL	Kojima *et al.*[9]
373.15	1.869	0.05	CIRC	VIR+A	Dalager[10]
338.43	1.735	0.1	EBUL	VIR+A	Kojima and Kato[11]
354.82	1.726	0.1	EBUL	VIR+A	Kojima and Kato[11]
361.83	1.726	0.1	EBUL	VIR+A	Kojima and Kato[11]
373.15	1.703	0.1	EBUL	VIR+A	Kojima and Kato[11]
411.49	1.595	0.2	EBUL	VIR+A	Kojima and Kato[11]
437.49	1.530	0.2	EBUL	VIR+A	Kojima and Kato[11]
467.48	1.482	0.2	EBUL	VIR+A	Kojima and Kato[11]
297.45	1.556	0.2	GLC	IDEAL	Shaffer and Daubert[12]
298.15	1.365	0.03	GLC	VIR	Larkin and Pemberton[13]
298.15	1.126[c]	0.2	HSA	IDEAL	Rohrschneider[37]
298.15	1.316	0.05	HSA	IDEAL	Rytting *et al.*[14]
288.15	1.353[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg[38]
293.15	1.188[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg[38]
298.15	1.197[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg[38]
298.15	1.366	0.05	GLC	VIR	Mash and Pemberton[15]
283.15	1.157	0.2	MBEA	IDEAL	Schmidt[16]
328.15	1.671	0.05	IGS	IDEAL	Lee[18]
298.1	1.185	0.2	IGS	IDEAL	Lebert and Richon[19]
298.15	1.363	0.02	TENS	VIR	Nord *et al.*[39]
308.15	1.478	0.02	TENS	VIR	Nord *et al.*[39]
273.15	0.875[c]	0.1	HSA	IDEAL	Snider and Dawson[21]
298.15	1.311[c]	0.1	HSA	IDEAL	Snider and Dawson[21]
298.15	1.267	0.1	IGS	IDEAL	Richon *et al.*[20]
373.15	1.760	0.1	EBUL	VIR+A	Ochi and Kojima[22]
298.15	1.324	0.05	HSA	IDEAL	Park *et al.*[40]
298.15	1.394	0.1	NSGLC	IDEAL	Landau *et al.*[24]
283.15	1.477	0.5	TENS	VIR	Pividal *et al.*[25]
293.15	1.571	0.5	TENS	VIR	Pividal *et al.*[25]
313.15	1.643	0.1	TENS	VIR	Pividal *et al.*[25]
333.15	1.721	0.05	TENS	VIR	Pividal *et al.*[25]
298.15	1.335	0.05	HSA	IDEAL	Li and Carr[26]
318.15	1.889	0.2	TENS	VIR	Rarey and Gmehling[41]
343.15	1.807[e]	0.1	TENS	VIR	Rarey and Gmehling[41]
373.35	1.792	0.1	EBUL	Unknown	Gmehling *et al.*[27,f]
298.15	1.316[c]	0.1	HSA	IDEAL	Merk and Riederer[29]
298.15	1.250	0.02	IGS	IDEAL	Sancho *et al.*[42]
322.05	1.656	0.05	CIRC	VIR	Christensen[30]
333.25	1.749	0.05	CIRC	VIR	Christensen[30]
343.15	1.812	0.05	CIRC	VIR	Christensen[30]
353.05	1.813	0.05	CIRC	VIR	Christensen[30]
362.85	1.904	0.05	CIRC	VIR	Christensen[30]
372.25	1.847	0.05	CIRC	VIR	Christensen[30]
298.15	1.654[c]	0.1	WWC	IDEAL	Altschuh *et al.*[32]
313.15	1.495[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
323.15	1.569[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
333.15	1.644[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
343.15	1.719[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
283.15	1.163	0.03	IGS	IDEAL	Fukuchi *et al.*[35]

TABLE 1b. Experimental values of limiting activity coefficients of ethanol(1) in water(2) together with their standard uncertainty, technique of measurement, and vapor phase nonideality treatment.—Continued

T (K)	$\ln \gamma_1^\infty$	$s(\ln \gamma_1^\infty)$	Technique[a]	Vapor[b]	Reference
293.15	1.340	0.03	IGS	IDEAL	Fukuchi *et al.*[35]
298.15	1.421	0.03	IGS	IDEAL	Fukuchi *et al.*[35]
303.15	1.486	0.03	IGS	IDEAL	Fukuchi *et al.*[35]
313.15	1.558	0.03	IGS	IDEAL	Fukuchi *et al.*[35]
303.25	1.615	0.1	IGS	VIR	Atik *et al.*[43]
313.25	1.673	0.1	IGS	VIR	Atik *et al.*[43]
323.25	1.712	0.1	IGS	VIR	Atik *et al.*[43]
333.25	1.751	0.1	IGS	VIR	Atik *et al.*[43]
343.25	1.785	0.1	IGS	VIR	Atik *et al.*[43]
328.15	1.690	0.03	NSGLC	IDEAL	Dohnal and Ondo[36]
273.35	0.932	0.03	HSA	VIR	Vrbka *et al.*[2]
283.15	1.141	0.03	HSA	VIR	Vrbka *et al.*[2]
303.15	1.421	0.02	TENS	VIR	Vrbka *et al.*[2]
308.15	1.488	0.02	TENS	VIR	Vrbka *et al.*[2]
313.15	1.539	0.02	TENS	VIR	Vrbka *et al.*[2]
318.15	1.579	0.02	TENS	VIR	Vrbka *et al.*[2]
323.15	1.615	0.02	TENS	VIR	Vrbka *et al.*[2]
328.15	1.649	0.02	TENS	VIR	Vrbka *et al.*[2]
333.15	1.668	0.02	TENS	VIR	Vrbka *et al.*[2]
358.15	1.775	0.03	CIRC	VIR	Vrbka *et al.*[2]
363.15	1.792	0.03	CIRC	VIR	Vrbka *et al.*[2]
368.15	1.808	0.03	CIRC	VIR	Vrbka *et al.*[2]
372.15	1.825	0.03	CIRC	VIR	Vrbka *et al.*[2]

[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; MBEA: molecular beams; NSGLC: nonsteady state gas-liquid chromatography; PRV: phase ratio variation; RDIST: Rayleigh distillation; VPC: vapor phase calibration; TENS: tensimetry; and WWC: wetted-wall column.
[b]IDEAL: ideal gas; VIR: virial equation of state; and 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]Gas/liquid partition coefficients calculated at experimental temperatures using the van't Hoff equation reported in the cited source.
[e]Limiting activity coefficient calculated from dilute range P-x data reported in the cited source.
[f]Secondary reference citing an original unavailable source (e.g., thesis).

PLACID, only discrete values of uncertainties corresponding to several predefined uncertainty levels (accuracy grades) were assigned to γ_1^∞ data.[100] 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 were based on information given in the original source of data. Various indications were taken into consideration like the author's statement of uncertainty or precision, type of experimental method, instrumentation and procedure used, approximations adopted, properties of the system and conditions, purities of samples, etc. The judgment was grounded in our own experience with various experimental methods and on their detailed analyses concerning 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

$$\chi^2_{\alpha/2}(n-p) < S_{\min} < \chi^2_{1-\alpha/2}(n-p), \tag{15}$$

where $n=n_G+n_H+n_C$ 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 signalized the necessity to increase the uncertainty of the given data point.

Due to experimental difficulties, measurements in a highly dilute range are easily subject to systematic error. Considerable errors can arise especially in VLE determinations; concurrent adsorption phenomena, improper sample manipulation or use of experimental techniques beyond their applicability ranges are some of the usual causes. The sources of systematic error can sometimes be hypothesized, but only rarely identified unambiguously. Nevertheless, to account for an observed data disparity or inconsistency, the uncertainty was increased for those data where the available information or our own experience suggested that an enhanced error is probable.

The outlined procedure enabled us to discriminate efficiently between existing data and to establish thermodynamically consistent temperature dependences of γ_1^∞, $\bar{H}_1^{E,\infty}$, and

TABLE 1c. Experimental values of limiting activity coefficients of 1-propanol(1) in water(2) together with their 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]	Reference
298.15	2.667	0.1	DDST	IDEAL	Butler *et al.*[44]
298.15	2.460	0.2	TENS	VIR+A	Pierotti *et al.*[5]
333.15	2.734	0.2	TENS	VIR+A	Pierotti *et al.*[5]
373.15	2.879	0.1	TENS	VIR+A	Pierotti *et al.*[5]
298.15	2.510[c]	0.1	IGS	IDEAL	Burnett [7]
293.15	3.178	0.5	GLC	VIR	Pecsar and Martin [8]
303.15	3.258	0.5	GLC	VIR	Pecsar and Martin [8]
313.15	3.091	0.5	GLC	VIR	Pecsar and Martin [8]
373.15	2.963	0.2	EBUL	IDEAL	Kojima *et al.*[9]
297.25	2.845	0.2	GLC	IDEAL	Shaffer and Daubert [12]
298.15	2.622	0.03	GLC	VIR	Larkin and Pemberton [13]
288.15	2.588[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg [38]
293.15	2.501[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg [38]
298.15	2.485[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg [38]
298.15	2.646	0.05	HSA	IDEAL	Rytting *et al.*[14]
298.15	2.625	0.03	GLC	VIR	Mash and Pemberton [15]
328.15	2.919	0.05	IGS	IDEAL	Lee [18]
298.1	2.389	0.2	IGS	IDEAL	Lebert and Richon [19]
298.15	2.416	0.2	IGS	IDEAL	Richon *et al.*[20]
273.15	2.187	0.1	HSA	IDEAL	Snider and Dawson [21]
298.15	2.695	0.1	HSA	IDEAL	Snider and Dawson [21]
323.72	2.460[e]	0.2	CIRC	IDEAL	Ikari *et al.*[45]
338.4	2.603[e]	0.2	CIRC	IDEAL	Ikari *et al.*[45]
373.14	2.773[e]	0.2	CIRC	IDEAL	Ikari *et al.*[45]
298.15	2.708	0.1	NSGLC	IDEAL	Landau *et al.*[24]
298.15	2.651	0.05	HSA	IDEAL	Li and Carr [26]
298.15	2.602[c]	0.1	HSA	IDEAL	Merk and Riederer [29]
298.15	1.992[c]	0.5	WWC	IDEAL	Altschuh *et al.*[32]
313.15	2.842[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
323.15	2.902[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
333.15	2.966[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
343.15	3.031[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
353.15	3.093[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
363.15	3.171[c,d]	0.1	HSA	IDEAL	Gupta *et al.*[33]
298.2	2.625	0.1	GLC	VIR	Tochigi *et al.*[34]
323.2	2.809	0.1	GLC	VIR	Tochigi *et al.*[34]
333.2	2.896	0.1	GLC	VIR	Tochigi *et al.*[34]
283.15	2.140	0.2	IGS	IDEAL	Fukuchi *et al.*[35]
293.15	2.332	0.2	IGS	IDEAL	Fukuchi *et al.*[35]
298.15	2.460	0.1	IGS	IDEAL	Fukuchi *et al.*[35]
303.15	2.580	0.1	IGS	IDEAL	Fukuchi *et al.*[35]
313.15	2.728	0.05	IGS	IDEAL	Fukuchi *et al.*[35]
328.15	2.939	0.03	NSGLC	IDEAL	Dohnal and Ondo [36]
273.35	2.186	0.03	HSA	VIR	Vrbka *et al.*[2]
283.15	2.416	0.03	HSA	VIR	Vrbka *et al.*[2]
293.15	2.603	0.03	HSA	VIR	Vrbka *et al.*[2]
303.15	2.728	0.02	TENS	VIR	Vrbka *et al.*[2]
308.15	2.779	0.02	TENS	VIR	Vrbka *et al.*[2]
313.15	2.815	0.02	TENS	VIR	Vrbka *et al.*[2]
318.15	2.862	0.02	TENS	VIR	Vrbka *et al.*[2]
323.15	2.896	0.02	TENS	VIR	Vrbka *et al.*[2]
328.15	2.923	0.02	TENS	VIR	Vrbka *et al.*[2]
333.15	2.944	0.02	TENS	VIR	Vrbka *et al.*[2]
358.15	3.001	0.05	CIRC	VIR	Vrbka *et al.*[2]
363.15	2.970	0.05	CIRC	VIR	Vrbka *et al.*[2]
368.15	2.929	0.05	CIRC	VIR	Vrbka *et al.*[2]
372.15	2.939	0.05	CIRC	VIR	Vrbka *et al.*[2]

[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; MBEA: molecular beams; NSGLC: nonsteady state gas-liquid chromatography; PRV: phase ratio variation; RDIST: Rayleigh distillation; VPC: vapor phase calibration; TENS: tensimetry; and WWC: wetted-wall column.
[b]IDEAL: ideal gas; VIR: virial equation of state; and 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]Gas/liquid partition coefficients calculated at experimental temperatures using the van't Hoff equation reported in the cited source.
[e]Limiting activity coefficient calculated from relative volatility in highly dilute solutions reported in the cited source.

TABLE 1d. Experimental values of limiting activity coefficients of 1-butanol(1) in water(2) together with their 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]	Reference
298.15	3.968	0.1	DDST	IDEAL	Butler *et al.*[44]
298.15	3.875	0.2	TENS	VIR+A	Pierotti *et al.*[5]
333.15	3.867	0.2	TENS	VIR+A	Pierotti *et al.*[5]
313.15	3.902	0.2	GLC	IDEAL	Hofstee *et al.*[6]
333.15	4.083	0.2	GLC	IDEAL	Hofstee *et al.*[6]
298.15	3.795	0.1	IGS	IDEAL	Burnett[7]
298.15	4.007[c]	0.2	HSA	IDEAL	Buttery *et al.*[46]
298.15	3.922	0.03	GLC	VIR	Larkin and Pemberton[13]
343.15	4.083	0.1	EBUL	IDEAL	Tochigi and Kojima[47]
353.15	4.047	0.1	EBUL	IDEAL	Tochigi and Kojima[47]
363.15	4.016	0.1	EBUL	IDEAL	Tochigi and Kojima[47]
373.15	3.989	0.1	EBUL	IDEAL	Tochigi and Kojima[47]
298.15	3.967	0.05	HSA	IDEAL	Rytting[14]
288.15	3.892[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg[38]
293.15	3.839[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg[38]
298.15	3.852[c]	0.1	IGS	IDEAL	Ioffe and Vitenberg[38]
303.15	4.402[c]	0.5	HSA	IDEAL	Friant and Suffet[48]
298.15	3.944	0.05	GLC	VIR	Mash and Pemberton[15]
343.15	4.217	0.1	EBUL	VIR	Lobien and Prausnitz[49]
353.15	3.839	0.2	EBUL	VIR	Lobien and Prausnitz[49]
372.15	3.300	0.5	EBUL	VIR	Lobien and Prausnitz[49]
298.1	3.809	0.1	IGS	IDEAL	Lebert and Richon[19]
273.15	3.694[c]	0.1	HSA	IDEAL	Snider and Dawson[21]
298.15	3.901[c]	0.1	HSA	IDEAL	Snider and Dawson[21]
293.15	3.723	0.1	HSA	VIR+A	Sagert and Lau[50]
373.15	4.480	0.5	EBUL	VIR+A	Ochi and Kojima[22]
298.15	3.983	0.05	NSGLC	IDEAL	Landau *et al.*[24]
313.15	4.495[c]	0.2	VPC	IDEAL	Kolb *et al.*[51]
333.15	4.373[c]	0.2	VPC	IDEAL	Kolb *et al.*[51]
343.15	4.378[c]	0.2	VPC	IDEAL	Kolb *et al.*[51]
353.15	4.293[c]	0.2	VPC	IDEAL	Kolb *et al.*[51]
298.15	3.976	0.03	HSA	IDEAL	Li and Carr[26]
323.23	4.366	0.2	TENS	IDEAL	Fischer and Gmehling[52]
298.15	4.075[c]	0.2	HSA	IDEAL	Merk and Riederer[29]
298.15	3.875	0.05	HSA	IDEAL	Whitehead and Sandler[53]
303.15	3.945	0.05	HSA	IDEAL	Whitehead and Sandler[53]
308.15	3.676	0.5	HSA	IDEAL	Whitehead and Sandler[53]
298.15	3.982[c]	0.1	WWC	IDEAL	Altschuh *et al.*[32]
298.45	3.934[c]	0.03	HSA	IDEAL	Iraci *et al.*[54]
313.15	4.293[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
323.15	4.292[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
333.15	4.300[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
343.15	4.318[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
353.15	4.338[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
363.15	4.376[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
298.2	4.011	0.05	GLC	VIR	Tochigi *et al.*[34]
323.2	4.072	0.05	GLC	VIR	Tochigi *et al.*[34]
333.2	4.113	0.05	GLC	VIR	Tochigi *et al.*[34]
298.15	4.050[c]	0.1	IGS	IDEAL	Kim *et al.*[55]
323.15	4.117	0.02	RDIST	VIR	Hovorka *et al.*[56]
323.15	4.132	0.02	RDIST	VIR	Hovorka *et al.*[56]
333.15	4.200	0.03	RDIST	VIR	Hovorka *et al.*[56]
333.15	4.165	0.02	RDIST	VIR	Hovorka *et al.*[56]
333.15	4.176	0.02	RDIST	VIR	Hovorka *et al.*[56]
343.15	4.156	0.02	RDIST	VIR	Hovorka *et al.*[56]
353.15	4.140	0.02	RDIST	VIR	Hovorka *et al.*[56]
328.15	4.121	0.03	NSGLC	IDEAL	Dohnal and Ondo[36]

TABLE 1d. Experimental values of limiting activity coefficients of 1-butanol(1) in water(2) together with their standard uncertainty, technique of measurement, and vapor phase nonideality treatment.—Continued

T (K)	$\ln \gamma_1^\infty$	$s(\ln \gamma_1^\infty)$	Technique[a]	Vapor[b]	Reference
273.35	3.484	0.03	HSA	IDEAL	Vrbka *et al.*[2]
283.15	3.699	0.03	HSA	IDEAL	Vrbka *et al.*[2]
293.15	3.879	0.03	HSA	IDEAL	Vrbka *et al.*[2]
303.15	3.978	0.02	TENS	VIR	Vrbka *et al.*[2]
308.15	4.047	0.02	TENS	VIR	Vrbka *et al.*[2]
313.15	4.076	0.02	TENS	VIR	Vrbka *et al.*[2]
318.15	4.098	0.02	TENS	VIR	Vrbka *et al.*[2]
323.15	4.119	0.02	TENS	VIR	Vrbka *et al.*[2]
323.15	4.072	0.05	HSA	IDEAL	Vrbka *et al.*[2]
323.15	4.084	0.05	HSA	IDEAL	Vrbka *et al.*[2]
328.15	4.140	0.02	TENS	VIR	Vrbka *et al.*[2]
333.15	4.149	0.02	TENS	VIR	Vrbka *et al.*[2]
372.15	4.027	0.03	CIRC	VIR	Vrbka *et al.*[2]

[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; MBEA: molecular beams; NSGLC: nonsteady state gas-liquid chromatography; PRV: phase ratio variation; RDIST: Rayleigh distillation; VPC: vapor phase calibration; TENS: tensimetry; and WWC: wetted-wall column.
[b]IDEAL: ideal gas; VIR: virial equation of state; and 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]Gas/liquid partition coefficients calculated at experimental temperatures using the van't Hoff equation reported in the cited source.

TABLE 1e. Experimental values of limiting activity coefficients of 1-pentanol(1) in water(2) together with their 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]	Reference
298.15	5.366	0.1	DDST	IDEAL	Butler *et al.*[44]
298.15	5.130	0.2	TENS	VIR+A	Pierotti *et al.*[5]
333.15	5.242	0.2	TENS	VIR+A	Pierotti *et al.*[5]
298.15	5.286	0.05	GLC	VIR	Larkin and Pemberton[13]
298.15	5.359	0.05	HSA	IDEAL	Rytting *et al.*[14]
298.15	5.283	0.05	GLC	VIR	Mash and Pemberton[15]
298.1	5.257	0.1	IGS	IDEAL	Lebert and Richon[19]
298.15	5.418	0.1	HSA	IDEAL	Li and Carr[26]
298.15	5.527[c]	0.2	HSA	IDEAL	Merk and Riederer[29]
313.15	5.294[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
323.15	5.301[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
333.15	5.320[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
343.15	5.350[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
353.15	5.385[c,d]	0.1	PRV	IDEAL	Gupta *et al.*[33]
363.15	5.435[c,d]	0.2	PRV	IDEAL	Gupta *et al.*[33]
298.2	5.118	0.2	GLC	VIR	Tochigi *et al.*[34]
333.2	5.242	0.2	GLC	VIR	Tochigi *et al.*[34]
343.2	5.159	0.2	GLC	VIR	Tochigi *et al.*[34]
328.15	5.366	0.05	NSGLC	IDEAL	Dohnal and Ondo[36]
273.35	4.796	0.03	HSA	VIR	Vrbka *et al.*[2]
283.15	5.050	0.03	HSA	VIR	Vrbka *et al.*[2]
293.15	5.215	0.03	HSA	VIR	Vrbka *et al.*[2]
303.15	5.313	0.03	IGS	VIR	Vrbka *et al.*[2]
313.15	5.398	0.03	IGS	VIR	Vrbka *et al.*[2]
323.15	5.438	0.03	IGS	VIR	Vrbka *et al.*[2]
333.15	5.398	0.03	RDIST	VIR	Vrbka *et al.*[2]
343.15	5.328	0.03	RDIST	VIR	Vrbka *et al.*[2]
353.15	5.313	0.03	CIRC	VIR	Vrbka *et al.*[2]
363.15	5.198	0.05	CIRC	VIR	Vrbka *et al.*[2]
371.15	5.130	0.05	CIRC	VIR	Vrbka *et al.*[2]

[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; MBEA: molecular beams; NSGLC: nonsteady state gas-liquid chromatography; PRV: phase ratio variation; RDIST: Rayleigh distillation; VPC: vapor phase calibration; TENS: tensimetry; and WWC: wetted-wall column.
[b]IDEAL: ideal gas; VIR: virial equation of state; and 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]Gas/liquid partition coefficients calculated at experimental temperatures using the van't Hoff equation reported in the cited source.

TABLE 2a. Experimental values of limiting partial molar excess enthalpies of methanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{H}_1^{E,\infty}$ (kJ mol^{-1})	$s(\bar{H}_1^{E,\infty})$ (kJ mol^{-1})	Technique[a]	Reference
298.15	−7.33	0.1	BATCH	Aveyard and Lawrence[57]
298.15	−7.12	0.25	BATCH	Lama and Lu[58]
298.15	−7.29	0.2	BATCH	Arnett and McKelvey[59]
298.15	−7.352	0.1	BATCH	Bertrand *et al.*[60]
298.15	−7.344	0.1	BATCH	Arnett *et al.*[61]
298.15	−7.104	0.1	BATCH	Reid *et al.*[62]
299.65	−7.75	0.4	BATCH	Brower *et al.*[63]
298.15	−7.24	0.1	BATCH	Krishnan and Friedman[64]
277.9	−8.767	0.07	BATCH	Alexander and Hill[65]
288.07	−8.009	0.07	BATCH	Alexander and Hill[65]
298.13	−7.264	0.05	BATCH	Alexander and Hill[65]
308.2	−6.506	0.05	BATCH	Alexander and Hill[65]
298.15	−6.97	0.3	FLOW	Murakami *et al.*[66]
298.15	−7.33	0.05	BATCH	Rouw and Somsen[67]
298.15	−7.29	0.05	FLOW	Nilsson and Wadsö[68]
298.15	−7.34	0.05	FLOW	Nilsson and Wadsö[68]
298.15	−7.05	0.15	BATCH	Korolev *et al.*[69]
283.87	−8.43	0.02	BATCH	Hallén *et al.*[70]
298.46	−7.28	0.01	BATCH	Hallén *et al.*[70]
315.6	−6.03	0.02	BATCH	Hallén *et al.*[70]
288.15	−8.09	0.06	FLOW	Hallén *et al.*[70]
298.15	−7.29	0.04	FLOW	Hallén *et al.*[70]
308.15	−6.56	0.08	FLOW	Hallén *et al.*[70]
318.15	−5.85	0.06	FLOW	Hallén *et al.*[70]
298.15	−7.000	0.15	FLOW	Trampe and Eckert[71]
298.15	−7.04	0.15	FLOW	Dohnal *et al.*[72]
283.15	−8.51	0.2	FLOW	Pfeffer *et al.*[73]
298.15	−7.29	0.2	FLOW	Pfeffer *et al.*[73]
323.15	−5.50	0.1	FLOW	Pfeffer *et al.*[73]
343.15	−4.01	0.1	FLOW	Pfeffer *et al.*[73]
363.15	−2.46	0.1	FLOW	Pfeffer *et al.*[73]

[a]BATCH, batch dissolution calorimetry; FLOW, flow mixing calorimetry; and TITR, titration microcalorimetry.

TABLE 2b. Experimental values of limiting partial molar excess enthalpies of ethanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{H}_1^{E,\infty}$ (kJ mol^{-1})	$s(\bar{H}_1^{E,\infty})$ (kJ mol^{-1})	Technique[a]	Reference
298.15	−10.0	0.2	BATCH	Aveyard and Lawrence[57]
298.15	−9.6	0.5	BATCH	Lama and Lu[58]
298.15	−9.965	0.2	BATCH	Bertrand *et al.*[60]
298.15	−10.26	0.2	BATCH	Arnett and McKelvey[59]
298.15	−10.13	0.1	BATCH	Aveyard and Mitchell[74]
298.15	−10.26	0.1	BATCH	Franks and Watson[75]
298.15	−10.187	0.1	BATCH	Arnett[61]
299.65	−9.50	0.4	BATCH	Brower[63]
277.91	−13.234	0.1	BATCH	Alexander and Hill[65]
288.07	−11.585	0.1	BATCH	Alexander and Hill[65]
298.11	−10.124	0.08	BATCH	Alexander and Hill[65]
308.2	−8.771	0.07	BATCH	Alexander and Hill[65]
298.15	−10.13	0.1	BATCH	Krishnan and Friedman[64]
298.15	−10.125	0.1	BATCH	Reid *et al.*[62]
273.15	−14.53	0.5	BATCH	Belousov and Makarova[76]
298.15	−10.43	0.5	BATCH	Belousov and Makarova[76]
328.15	−6.76	0.6	BATCH	Belousov and Makarova[76]
348.15	−3.73	0.5	BATCH	Belousov and Makarova[76]
300	−10.2	0.5	BATCH	Pannell[77]
307	−8.7	0.5	BATCH	Pannell[77]
298.15	−9.97	0.3	FLOW	Landgren *et al.*[78]
298.15	−10.2[b]	0.1	BATCH	Costigan *et al.*[79]
298.15	−10.19	0.05	BATCH	Rouw and Somsen[67]
298.15	−10.15	0.05	FLOW	Nilsson and Wadsö[68]
298.15	−10.14	0.05	FLOW	Nilsson and Wadsö[68]
298.15	−9.75	0.4	BATCH	Korolev *et al.*[69]
283.87	−12.36	0.03	BATCH	Hallén *et al.*[70]
298.43	−10.12	0.01	BATCH	Hallén *et al.*[70]
315.51	−7.68	0.02	BATCH	Hallén *et al.*[70]
288.15	−11.69	0.07	FLOW	Hallén *et al.*[70]
298.15	−10.15	0.05	FLOW	Hallén *et al.*[70]
308.15	−8.71	0.06	FLOW	Hallén *et al.*[70]
318.15	−7.38	0.09	FLOW	Hallén *et al.*[70]
298.15	−10.020	0.15	FLOW	Trampe and Eckert[71]
298.15	−10.17	0.07	FLOW	Dohnal *et al.*[72]
283.15	−12.25	0.3	FLOW	Pfeffer *et al.*[73]
298.15	−10.20	0.3	FLOW	Pfeffer *et al.*[73]
323.15	−6.64	0.1	FLOW	Pfeffer *et al.*[73]
343.15	−3.79	0.1	FLOW	Pfeffer *et al.*[73]
363.15	−1.68	0.05	FLOW	Pfeffer *et al.*[73]

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

TABLE 2c. Experimental values of limiting partial molar excess enthalpies of 1-propanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{H}_1^{E,\infty}$ (kJ mol^{-1})	$s(\bar{H}_1^{E,\infty})$ (kJ mol^{-1})	Technique[a]	Reference
298.15	−9.21	0.75	BATCH	Aveyard and Lawrence[57]
298.15	−10.38	0.2	BATCH	Arnett and McKelvey[59]
298.15	−9.21	0.75	BATCH	Aveyard and Mitchell[74]
298.15	−10.128	0.1	BATCH	Arnett *et al.*[61]
299.65	−10.12	0.7	BATCH	Brower *et al.*[63]
298.15	−10.17	0.13	BATCH	Krishnan and Friedman[64]
277.88	−14.679	0.12	BATCH	Alexander and Hill[65]
288.07	−12.280	0.1	BATCH	Alexander and Hill[65]
298.11	−10.186	0.08	BATCH	Alexander and Hill[65]
308.2	−8.114	0.08	BATCH	Alexander and Hill[65]
298.15	−9.71	0.5	BATCH	Belousov *et al.*[80]
323.15	−5.28	0.4	BATCH	Belousov *et al.*[80]
348.15	−1.47	0.4	BATCH	Belousov *et al.*[80]
298.15	−10.12	0.03	BATCH	Rouw and Somsen[67]
298.15	−10.22	0.04	FLOW	Nilsson and Wadsö[68]
298.15	−9.81	0.25	BATCH	Korolev *et al.*[69]
283.88	−13.27	0.02	BATCH	Hallén *et al.*[70]
298.44	−10.10	0.02	BATCH	Hallén *et al.*[70]
315.6	−6.69	0.03	BATCH	Hallén *et al.*[70]
288.15	−12.37	0.07	FLOW	Hallén *et al.*[70]
308.15	−8.12	0.04	FLOW	Hallén *et al.*[70]
318.15	−6.18	0.06	FLOW	Hallén *et al.*[70]
298.15	−9.88[b]	0.25	FLOW	Denda *et al.*[81]
298.15	−9.900	0.15	FLOW	Trampe and Eckert[71]
298.15	−9.71	0.25	FLOW	Dohnal *et al.*[72]
283.15	−13.97	0.35	FLOW	Pfeffer *et al.*[73]
298.15	−10.46	0.25	FLOW	Pfeffer *et al.*[73]
323.15	−5.50	0.13	FLOW	Pfeffer *et al.*[73]
343.15	−2.10	0.11	FLOW	Pfeffer *et al.*[73]
363.15	0.77	0.12	FLOW	Pfeffer *et al.*[73]
298.15	−10.164	0.02	TITR	Olofsson *et al.*[82]

[a]BATCH, batch dissolution calorimetry; FLOW, flow mixing calorimetry; and TITR, titration microcalorimetry.

[b]$\bar{H}_1^{E,\infty}$ calculated from H^E data for the lowest solute concentrations reported in the cited literature.

TABLE 2d. Experimental values of limiting partial molar excess enthalpies of 1-butanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{H}_1^{E,\infty}$ (kJ mol^{-1})	$s(\bar{H}_1^{E,\infty})$ (kJ mol^{-1})	Technique[a]	Reference
298.15	−8.16	1	BATCH	Aveyard and Lawrence[57]
298.15	−9.04	0.25	BATCH	Arnett and McKelvey[59]
298.15	−9.00	0.4	BATCH	Aveyard and Mitchell[74]
298.15	−9.416	0.1	BATCH	Arnett *et al.*[61]
298.15	−9.21	0.4	BATCH	Krishnan and Friedman[64]
277.87	−15.018	0.12	BATCH	Alexander and Hill[65]
288.07	−11.928	0.12	BATCH	Alexander and Hill[65]
298.13	−9.370	0.08	BATCH	Alexander and Hill[65]
303.13	−8.039	0.08	BATCH	Alexander and Hill[65]
308.18	−6.774	0.08	BATCH	Alexander and Hill[65]
299.65	−10.08	0.7	BATCH	Brower *et al.*[63]
303.15	−9.63	1.2	BATCH	Belousov and Ponner[83]
328.15	−2.30	0.6	BATCH	Belousov and Ponner[83]
348.15	0.50	1.2	BATCH	Belousov and Ponner[83]
303.15	−7.8	0.5	FLOW	Goodwin and Newsham[84]
298.15	−9.24	0.05	BATCH	Rouw and Somsen[67]
298.15	−9.32	0.05	FLOW	Nilsson and Wadsö[68]
298.15	−9.31	0.05	FLOW	Nilsson and Wadsö[68]
298.15	−8.22	0.5	BATCH	Bury and Treiner[85]
283.86	−13.20	0.1	BATCH	Hallén *et al.*[70]
298.43	−9.20	0.1	BATCH	Hallén *et al.*[70]
315.61	−4.88	0.1	BATCH	Hallén *et al.*[70]
288.15	−11.96	0.1	FLOW	Hallén *et al.*[70]
298.15	−9.32	0.1	FLOW	Hallén *et al.*[70]
308.15	−6.75	0.1	FLOW	Hallén *et al.*[70]
318.15	−4.29	0.1	FLOW	Hallén *et al.*[70]
298.15	−8.740	0.5	FLOW	Trampe and Eckert[71]
283.15	−13.22	0.35	FLOW	Pfeffer *et al.*[73]
298.15	−9.37	0.2	FLOW	Pfeffer *et al.*[73]
323.15	−3.36	0.15	FLOW	Pfeffer *et al.*[73]
343.15	0.99	0.14	FLOW	Pfeffer *et al.*[73]
363.15	3.95	0.5	FLOW	Pfeffer *et al.*[73]
298.15	−9.20	0.1	FLOW	Hovorka *et al.*[86]

[a]BATCH, batch dissolution calorimetry; FLOW, flow mixing calorimetry; and TITR, titration microcalorimetry.

TABLE 2e. Experimental values of limiting partial molar excess enthalpies of 1-pentanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{H}_1^{E,\infty}$ (kJ mol^{-1})	$s(\bar{H}_1^{E,\infty})$ (kJ mol^{-1})	Technique[a]	Reference
298.15	−6.36	1	BATCH	Aveyard and Lawrence[57]
298.15	−8.08	0.4	BATCH	Aveyard and Mitchell[74]
298.15	−7.821	0.1	BATCH	Arnett *et al.*[61]
298.15	−7.66	0.4	BATCH	Krishnan and Friedman[64]
298.15	−7.7	0.1	BATCH	Rouw and Somsen[67]
298.15	−6.65	0.8	BATCH	Bury and Treiner[85]
298.43	−7.84	0.08	BATCH	Hallén *et al.*[70]
288.15	−11.31	0.08	FLOW	Hallén *et al.*[70]
298.15	−7.99	0.08	FLOW	Hallén *et al.*[70]
308.15	−4.82	0.08	FLOW	Hallén *et al.*[70]
318.15	−1.86	0.08	FLOW	Hallén *et al.*[70]
283.15	−12.58	0.5	FLOW	Pfeffer *et al.*[73]
298.15	−8.07	0.5	FLOW	Pfeffer *et al.*[73]
323.15	−1.10	0.5	FLOW	Pfeffer *et al.*[73]
343.15	3.65	0.75	FLOW	Pfeffer *et al.*[73]
363.15	7.45	0.75	FLOW	Pfeffer *et al.*[73]

[a]BATCH, batch dissolution calorimetry; FLOW, flow mixing calorimetry; and TITR, titration microcalorimetry.

TABLE 3a. Experimental values of limiting partial molar excess heat capacities of methanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{C}_{p,1}^{E,\infty}$ (J K^{-1} mol^{-1})	$s(\bar{C}_{p,1}^{E,\infty})$ (J K^{-1} mol^{-1})	Technique[a]	Reference
298.15	96.7	10	INDIRECT	Arnett *et al.*[61]
298.15	77[b]	3	FLOW	Jolicoeur and Lacroix[87]
288.15	80[c]	5	FLOW	Benson and D'Arcy[88]
308.15	72[c]	5	FLOW	Benson and D'Arcy[88]
278.15	77.5[b]	3	SCAN	Makhatadze and Privalov[89]
298.15	77.2[b]	3	SCAN	Makhatadze and Privalov[89]
323.15	72.6[b]	3	SCAN	Makhatadze and Privalov[89]
348.15	67.2[b]	3	SCAN	Makhatadze and Privalov[89]
373.15	61.6[b]	3	SCAN	Makhatadze and Privalov[89]
398.15	54.8[b]	3	SCAN	Makhatadze and Privalov[89]

[a]DROP: drop calorimetry; FLOW: flow calorimetry; SCAN: scanning calorimetry; and 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.* (Refs. 90–92).
[c]Calculated from dilute range C_p^E data reported in the cited source.

TABLE 3b. Experimental values of limiting partial molar excess heat capacities of ethanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{C}_{p,1}^{E,\infty}$ (J K^{-1} mol^{-1})	$s(\bar{C}_{p,1}^{E,\infty})$ (J K^{-1} mol^{-1})	Technique[a]	Reference
298.15	164	10	INDIRECT	Arnett *et al.*[61]
298.15	148[b]	3	FLOW	Jolicoeur and Lacroix[87]
288.15	160[c]	10	FLOW	Benson and D'Arcy[88]
278.15	173.7	4	SCAN	Makhatadze and Privalov[93]
298.15	150.3	4	SCAN	Makhatadze and Privalov[93]
323.15	130.8	4	SCAN	Makhatadze and Privalov[93]
348.15	116.5	4	SCAN	Makhatadze and Privalov[93]
373.15	106.7	4	SCAN	Makhatadze and Privalov[93]
398.15	99.4	4	SCAN	Makhatadze and Privalov[93]
278.15	167[b]	5	SCAN	Origlia-Luster and Woolley[94]
283.15	160[b]	5	SCAN	Origlia-Luster and Woolley[94]
288.15	155[b]	5	SCAN	Origlia-Luster and Woolley[94]
293.15	150[b]	5	SCAN	Origlia-Luster and Woolley[94]
298.15	146[b]	5	SCAN	Origlia-Luster and Woolley[94]
303.15	143[b]	5	SCAN	Origlia-Luster and Woolley[94]
308.15	139[b]	5	SCAN	Origlia-Luster and Woolley[94]
313.15	136[b]	5	SCAN	Origlia-Luster and Woolley[94]
318.15	132[b]	5	SCAN	Origlia-Luster and Woolley[94]
323.15	129[b]	5	SCAN	Origlia-Luster and Woolley[94]
328.15	126[b]	5	SCAN	Origlia-Luster and Woolley[94]
333.15	123[b]	5	SCAN	Origlia-Luster and Woolley[94]
338.15	119[b]	5	SCAN	Origlia-Luster and Woolley[94]
343.15	116[b]	5	SCAN	Origlia-Luster and Woolley[94]
348.15	113[b]	5	SCAN	Origlia-Luster and Woolley[94]
353.15	110[b]	5	SCAN	Origlia-Luster and Woolley[94]
358.15	106[b]	8	SCAN	Origlia-Luster and Woolley[94]
363.15	103[b]	8	SCAN	Origlia-Luster and Woolley[94]
368.15	100[b]	8	SCAN	Origlia-Luster and Woolley[94]
373.15	96[b]	8	SCAN	Origlia-Luster and Woolley[94]
378.15	93[b]	10	SCAN	Origlia-Luster and Woolley[94]
383.15	89[b]	10	SCAN	Origlia-Luster and Woolley[94]
388.15	85[b]	10	SCAN	Origlia-Luster and Woolley[94]
393.15	81[b]	10	SCAN	Origlia-Luster and Woolley[94]

[a]DROP: drop calorimetry; FLOW: flow calorimetry; SCAN: scanning calorimetry; and 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.* (Refs. 90–92).
[c]Calculated from dilute range C_p^E data reported in the cited source.

TABLE 3c. Experimental values of limiting partial molar excess heat capacities of 1-propanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{C}_{p,1}^{E,\infty}$ (J K^{-1} mol^{-1})	$s(\bar{C}_{p,1}^{E,\infty})$ (J K^{-1} mol^{-1})	Technique[a]	Reference
298.15	236	14	INDIRECT	Arnett *et al.*[61]
298.15	209[b]	3	FLOW	Jolicoeur and Lacroix[87]
288.15	224[c]	10	FLOW	Benson and D'Arcy[88]
308.15	193[c]	10	FLOW	Benson and D'Arcy[88]
278.15	243.7	5	SCAN	Makhatadze and Privalov[93]
298.15	211.4	5	SCAN	Makhatadze and Privalov[93]
323.15	181.2	5	SCAN	Makhatadze and Privalov[93]
348.15	155.3	5	SCAN	Makhatadze and Privalov[93]
373.15	133.0	5	SCAN	Makhatadze and Privalov[93]
398.15	117.7[d]	7	SCAN	Makhatadze and Privalov[93]
278.15	241[b]	4	SCAN	Origlia-Luster and Woolley[94]
283.15	233[b]	4	SCAN	Origlia-Luster and Woolley[94]
288.15	227[b]	4	SCAN	Origlia-Luster and Woolley[94]
293.15	220[b]	4	SCAN	Origlia-Luster and Woolley[94]
298.15	214[b]	4	SCAN	Origlia-Luster and Woolley[94]
303.15	209[b]	4	SCAN	Origlia-Luster and Woolley[94]
308.15	203[b]	4	SCAN	Origlia-Luster and Woolley[94]
313.15	197[b]	4	SCAN	Origlia-Luster and Woolley[94]
318.15	192[b]	4	SCAN	Origlia-Luster and Woolley[94]
323.15	186[b]	4	SCAN	Origlia-Luster and Woolley[94]
328.15	181[b]	4	SCAN	Origlia-Luster and Woolley[94]
333.15	175[b]	4	SCAN	Origlia-Luster and Woolley[94]
338.15	169[b]	4	SCAN	Origlia-Luster and Woolley[94]
343.15	164[b]	4	SCAN	Origlia-Luster and Woolley[94]
348.15	158[b]	4	SCAN	Origlia-Luster and Woolley[94]
353.15	153[b]	4	SCAN	Origlia-Luster and Woolley[94]
358.15	148[b]	4	SCAN	Origlia-Luster and Woolley[94]
363.15	143[b]	4	SCAN	Origlia-Luster and Woolley[94]
368.15	137[b]	4	SCAN	Origlia-Luster and Woolley[94]
373.15	132[b]	4	SCAN	Origlia-Luster and Woolley[94]
378.15	128[b]	6	SCAN	Origlia-Luster and Woolley[94]
383.15	123[b]	6	SCAN	Origlia-Luster and Woolley[94]
388.15	118[b]	6	SCAN	Origlia-Luster and Woolley[94]
393.15	114[b]	6	SCAN	Origlia-Luster and Woolley[94]
298.15	210.6	3	FLOW	Fenclová *et al.*[95]

[a]DROP: drop calorimetry; FLOW: flow calorimetry; SCAN: scanning calorimetry; and 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.* (Refs. 90–92).
[c]Calculated from dilute range C_p^E data reported in the cited source.
[d]Note that in the article of Makhatadze and Privalov (Ref. 93) there was a misprint of this value.

TABLE 3d. Experimental values of limiting partial molar excess heat capacities of 1-butanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{C}_{p,1}^{E,\infty}$ (J K^{-1} mol^{-1})	$s(\bar{C}_{p,1}^{E,\infty})$ (J K^{-1} mol^{-1})	Technique[a]	Reference
298.15	300	40	INDIRECT	Arnett *et al.*[61]
298.15	260[b]	3	FLOW	Jolicoeur and Lacroix[87]
298.15	262.5[b]	3	FLOW	Roux-Desgranges *et al.*[96]
278.15	309.2	6	SCAN	Makhatadze and Privalov[93]
298.15	268.9	6	SCAN	Makhatadze and Privalov[93]
323.15	224.1	6	SCAN	Makhatadze and Privalov[93]
348.15	191.1	6	SCAN	Makhatadze and Privalov[93]
373.15	158.5	6	SCAN	Makhatadze and Privalov[93]
398.15	137.3	8	SCAN	Makhatadze and Privalov[93]
298.15	264.9	3	FLOW	Hovorka *et al.*[97]
278.15	299[b]	7	SCAN	Origlia and Woolley[98]
283.15	291[b]	7	SCAN	Origlia and Woolley[98]
288.15	283[b]	7	SCAN	Origlia and Woolley[98]
293.15	275[b]	7	SCAN	Origlia and Woolley[98]
298.15	268[b]	7	SCAN	Origlia and Woolley[98]
303.15	260[b]	7	SCAN	Origlia and Woolley[98]
308.15	253[b]	7	SCAN	Origlia and Woolley[98]
313.15	245[b]	7	SCAN	Origlia and Woolley[98]
318.15	238[b]	7	SCAN	Origlia and Woolley[98]
323.15	231[b]	7	SCAN	Origlia and Woolley[98]
328.15	224[b]	7	SCAN	Origlia and Woolley[98]
333.15	216[b]	7	SCAN	Origlia and Woolley[98]
338.15	210[b]	7	SCAN	Origlia and Woolley[98]
343.15	203[b]	7	SCAN	Origlia and Woolley[98]
348.15	196[b]	7	SCAN	Origlia and Woolley[98]
353.15	190[b]	7	SCAN	Origlia and Woolley[98]
358.15	184[b]	7	SCAN	Origlia and Woolley[98]
363.15	178[b]	7	SCAN	Origlia and Woolley[98]
368.15	172[b]	7	SCAN	Origlia and Woolley[98]
373.15	167[b]	7	SCAN	Origlia and Woolley[98]
378.15	162[b]	9	SCAN	Origlia and Woolley[98]
383.15	158[b]	9	SCAN	Origlia and Woolley[98]
388.15	153[b]	9	SCAN	Origlia and Woolley[98]
393.15	150[b]	9	SCAN	Origlia and Woolley[98]
298.15	268.3	3	FLOW	Fenclová *et al.*[95]

[a]DROP: drop calorimetry; FLOW: flow calorimetry; SCAN: scanning calorimetry; and 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.* (Refs. 90–92).

TABLE 3e. Experimental values of limiting partial molar excess heat capacities of 1-pentanol(1) in water(2) together with their standard uncertainty and technique of measurement.

T (K)	$\bar{C}_{p,1}^{E,\infty}$ (J K^{-1} mol^{-1})	$s(\bar{C}_{p,1}^{E,\infty})$ (J K^{-1} mol^{-1})	Technique[a]	Reference
298.15	350	40	INDIRECT	Arnett *et al.*[61]
298.15	321.6	7	DROP	Sköld *et al.*[99]
298.15	316[b]	7	FLOW	Jolicoeur and Lacroix[87]
278.15	376.2	8	SCAN	Makhatadze and Privalov[93]
298.15	331.2	8	SCAN	Makhatadze and Privalov[93]
323.15	270.9	8	SCAN	Makhatadze and Privalov[93]
348.15	227.1	8	SCAN	Makhatadze and Privalov[93]
373.15	188.4	8	SCAN	Makhatadze and Privalov[93]
398.15	160.2	10	SCAN	Makhatadze and Privalov[93]
298.15	325.2	5	FLOW	Fenclová *et al.*[95]

[a]DROP: drop calorimetry; FLOW: flow calorimetry; SCAN: scanning calorimetry; and 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.* (Refs. 90–92).

TABLE 4. Parameters of Eqs. (12) and (13)[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]			
Alkanol	Equation	A	B	C	D	s[b]	$\ln \gamma_1^\infty$	$\bar{H}_1^{E,\infty}$	$\bar{C}_{p,1}^{E,\infty}$	T_{max} (K)
Methanol	(12)	12.6189	−15.2558	−15.4431	3.1336	1.01	0.98	1.08	0.83	407.6
	(13)	−2.1668	6.0946	−17.6001	−1.6350	1.01	0.98	1.08	0.82	407.4
Ethanol	(12)	23.4136	−33.0367	−39.9238	10.9860	1.07	1.14	0.83	1.08	380.0
	(13)	−2.2437	6.9054	−34.0965	−2.3357	1.06	1.14	0.76	0.97	380.1
1-Propanol	(12)	32.1594	−48.6020	−63.5959	19.0952	0.99	0.96	1.12	0.87	354.2
	(13)	−2.5530	8.6101	−52.3154	−2.7321	0.94	0.96	1.03	0.74	354.9
1-Butanol	(12)	39.4357	−59.6265	−80.0069	24.1291	1.03	1.08	0.99	0.90	337.3
	(13)	−3.7993	11.8850	−66.0410	−2.7677	0.98	1.08	0.94	0.68	337.6
1-Pentanol	(12)	47.1186	−74.3247	−103.610	32.4801	1.13	0.85	1.44	1.16	324.8
	(13)	−4.0383	13.3418	−89.4745	−3.0999	1.02	0.86	1.33	0.69	325.1

[a]Recommended temperature dependence for limiting activity coefficient.
[b]$s=[S_{min}/(n-4)]^{1/2}$; S given by Eq. (14).
[c]$\mathrm{WRMSD}=((1/n_Y)\Sigma_{i=1}^{n_Y}[Y_i(\exp)-Y_i(\mathrm{calc})]^2/s^2(Y_i))^{1/2}$, $Y=\ln \gamma_1^\infty$ $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$.

$\bar{C}_{p,1}^{E,\infty}$. The final values of uncertainties assigned to the data are given in Tables 1–3. The values of parameters of Eqs. (12) and (13), together with the overall standard deviations of fit s and other fit characteristics, are listed in Table 4.

5. Results and Discussion

5.1. Fitting Model Discrimination

Both fitting equations, Eqs. (12) and (13) correlate the data for all five systems within the assigned uncertainties, the overall standard deviations of fit being closely around unity. For Eq. (13) the values of s turn out to be systematically lower than those for Eq. (12). Nevertheless, the differences are quite small and when one compares the weighted root mean square (rms) deviations in $\ln \gamma_1^\infty$ yielded by the two equations, the performances of both equations appear to be practically equivalent. Indeed, the courses of $\ln \gamma_1^\infty(T)$ are within the ranges of underlying data almost indistinguishable

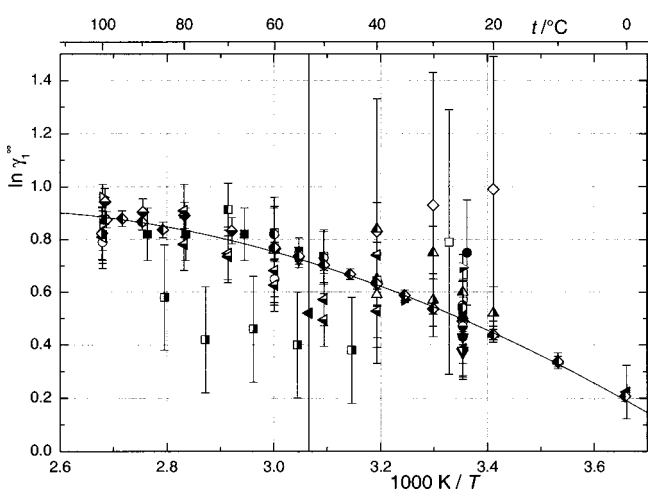

FIG. 1. Limiting activity coefficient $\ln \gamma_1^\infty$ of methanol(1) in water(2) as a function of temperature. Experimental values are from Table 1a: □, Hardy;[4] ○, Pierotti *et al.*;[5] △, Hofstee *et al.*;[6] ▽, Burnett;[7] ◇, Pecsar and Martin;[8] ◁, Kojima *et al.*;[9] ▷, Dalager;[10] ■, Kojima and Kato;[11] ●, Shaffer and Daubert;[12] ▲, Larkin and Pemberton;[13] ▼, Rytting *et al.*;[14] ◆, Mash and Pemberton;[15] ◀, Schmidt;[16] ▶, Christian *et al.*;[17] ▬, Lee;[18] ◓, Lebert and Richon;[19] ◆, Richon *et al.*;[20] ◁, Snider and Dawson;[21] ▷, Ochi and Kojima;[22] ◨, Bergmann and Eckert;[23] ◑, Landau *et al.*;[24] ◭, Pividal *et al.*;[25] ◮, Li and Carr;[26] ◆, Gmehling *et al.*;[27] ▬, Bader and Gasem;[28] ◒, Merk and Riederer;[29] ◆, Christensen;[30] ◁, Chai and Zhu;[31] ▷, Altschuh *et al.*;[32] ◨, Gupta *et al.*;[33] ◐, Tochigi *et al.*;[34] ◭, Fukuchi *et al.*;[35] ◮, Dohnal and Ondo;[36] ◆, Vrbka *et al.*[2] 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. (13).

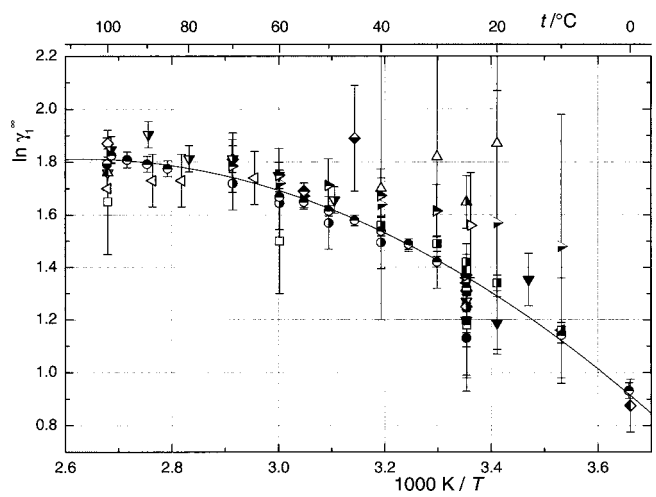

FIG. 2. Limiting activity coefficient $\ln \gamma_1^\infty$ of ethanol(1) in water(2) as a function of temperature. Experimental values are from Table 1b: □, Pierotti *et al.*;[5] ○, Burnett;[7] △, Pecsar and Martin;[8] ▽, Kojima *et al.*;[9] ◇, Dalager;[10] ◁, Kojima and Kato;[11] ▷, Shaffer and Daubert;[12] ■, Larkin and Pemberton;[13] ●, Rohrschneider;[37] ▲, Rytting *et al.*;[14] ▼, Ioffe and Vitenberg;[38] ◆, Mash and Pemberton;[15] ◀, Schmidt;[16] ▶, Lee;[18] ▬, Lebert and Richon;[19] ◁, Nord *et al.*;[39] ◆, Snider and Dawson;[21] ▼, Richon *et al.*;[20] ◭, Ochi and Kojima;[22] ◐, Park *et al.*;[40] ◨, Landau *et al.*;[24] ▷, Pividal *et al.*;[25] ◁, Li and Carr;[26] ◆, Rarey and Gmehling;[41] ◒, Gmehling *et al.*;[27] ▬, Merk and Riederer;[29] ◆, Sancho *et al.*;[42] ▼, Christensen;[30] ◭, Altschuh *et al.*;[32] ◑, Gupta *et al.*;[33] ◨, Fukuchi *et al.*;[35] ▷, Atik *et al.*;[43] ◆, Dohnal and Ondo;[36] ◓, Vrbka *et al.*[2] 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. (13).

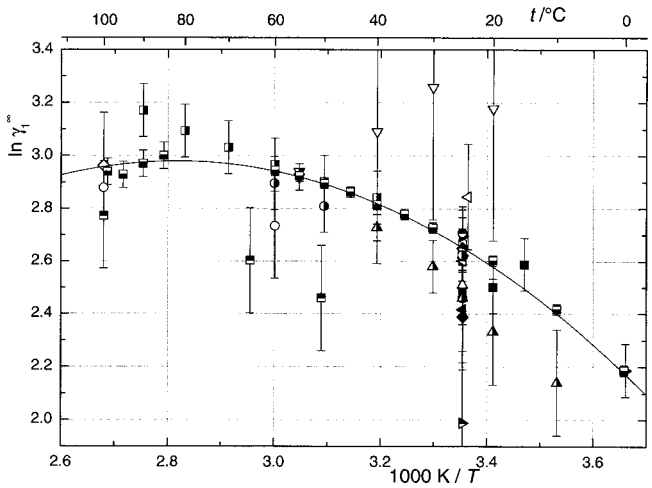

FIG. 3. Limiting activity coefficient $\ln\gamma_1^\infty$ of 1–propanol(1) in water(2) as a function of temperature. Experimental values are from Table 1c: □, Butler *et al.*;[44] ○, Pierotti *et al.*;[5] △, Burnett;[7] ▽, Pecsar and Martin;[8] ◇, Kojima *et al.*;[9] ◁, Shaffer and Daubert;[12] ▷, Larkin and Pemberton;[13] ■, Ioffe and Vitenberg;[38] ●, Rytting *et al.*;[14] ▲, Mash and Pemberton;[15] ▼, Lee;[18] ◆, Lebert and Richon;[19] ◀, Richon *et al.*;[20] ▶, Snider and Dawson;[21] ⬒, Ikari *et al.*;[45] ◓, Landau *et al.*;[24] ⬘, Li and Carr;[26] ◁, Merk and Riederer;[29] ▷, Altschuh *et al.*;[32] ◨, Gupta *et al.*;[33] ◑, Tochigi *et al.*;[34] ◭, Fukuchi *et al.*;[35] ▽, Dohnal and Ondo;[38] ⬓, Vrbka *et al.*[2] 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. (13).

and, as seen from Table 4, also the values of characteristic temperature, T_{max}, corresponding to the maximum γ_1^∞ (i.e., to $\bar{H}_1^{E,\infty}=0$), nearly coincide for the two fits. However, when the

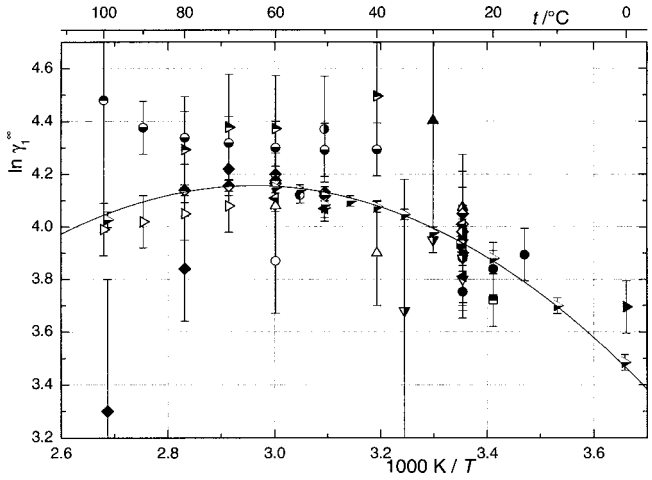

FIG. 4. Limiting activity coefficient $\ln\gamma_1^\infty$ of 1-butanol(1) in water(2) as a function of temperature. Experimental values are from Table 1d: □, Butler *et al.*;[44] ○, Pierotti *et al.*;[5] △, Hofstee *et al.*;[6] ▽, Burnett;[7] ◇, Buttery *et al.*;[46] ◁, Larkin and Pemberton;[13] ▷, Tochigi and Kojima;[47] ■, Rytting *et al.*;[14] ●, Ioffe and Vitenberg;[38] ▲, Friant and Suffet;[48] ▼, Mash and Pemberton;[15] ◆, Lobien and Prausnitz;[49] ◀, Lebert and Richon;[19] ▶, Snider and Dawson;[21] ⬒, Sagert and Lau;[50] ◓, Ochi and Kojima;[22] ◁, Landau *et al.*;[24] ▷, Kolb *et al.*;[51] ◨, Li and Carr;[26] ◑, Fischer and Gmehling;[52] ◭, Merk and Riederer;[29] ▽, Whitehead and Sandler;[53] ◑, Altschuh *et al.*;[32] ⬓, Iraci *et al.*;[54] ◒, Gupta *et al.*;[33] ⬘, Kim *et al.*;[55] ◁, Tochigi *et al.*;[34] ⬘, Hovorka and Dohnal;[56] ◐, Dohnal and Ondo;[36] ▷, Vrbka *et al.*[2] 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. (13).

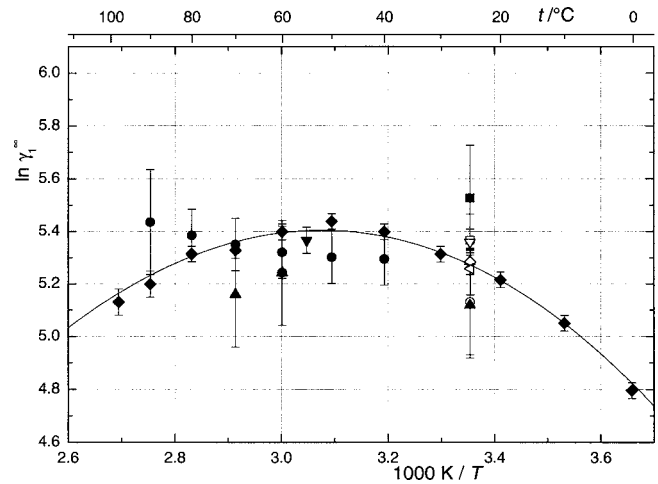

FIG. 5. Limiting activity coefficient $\ln\gamma_1^\infty$ of 1-pentanol(1) in water(2) as a function of temperature. Experimental values are from Table 1e: □, Butler *et al.*[44]; ○, Pierotti *et al.*[5]; △, Larkin and Pemberton[13]; ▽, Rytting *et al.*[14]; ◇, Mash and Pemberton[15]; ◁, Lebert and Richon[19]; ■, Merk and Riederer[29]; ●,, Gupta *et al.*[33]; ▲, Tochigi *et al.*[34]; ▼, Dohnal and Ondo[36]; ◆, Vrbka *et al.*[2] 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. (13).

two fits are compared in $\bar{H}_1^{E,\infty}$, the situation starts to change, and in $\bar{C}_{p,1}^{E,\infty}$ the difference is already quite apparent. Going from methanol to 1-pentanol, the experimental $\bar{C}_{p,1}^{E,\infty}(T)$ dependences become increasingly nonlinear and convex, which causes Eq. (12) with its linear $\bar{C}_{p,1}^{E,\infty}(T)$ to give only compromised fits. Equation (13) designed by us to cope with just this issue gives a definite better representation of $\bar{C}_{p,1}^{E,\infty}(T)$ data for 1-alkanols in water, as evidenced by the comparison of weighted rms deviations of $\bar{C}_{p,1}^{E,\infty}$ given in Table 4. The difference between fits by Eqs. (12) and (13) increases with the chain length of the 1-alkanol and starts to show up in only moderate temperature extrapolations of the fits. Although for methanol the values of $\ln\gamma_1^\infty$, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ calculated at 400 K from Eqs. (12) and (13) do not effectively differ, for 1-pentanol the derivative properties deviate discernibly, being respectively 15.4 and 15.2 kJ mol^{-1} ($\bar{H}_1^{E,\infty}$), and 137 and 150 J K^{-1} mol^{-1} ($\bar{C}_{p,1}^{E,\infty}$). At higher temperatures (>475 K), even negative $\bar{C}_{p,1}^{E,\infty}$ values for 1-pentanol result from Eq. (12) linear extrapolation, which is an obvious artifact lacking any justification. As a consequence, the correlations provided by Eq. (13) are considered superior to those by Eq. (12).

5.2. Data Assessment

The values of limiting activity coefficients for the five 1-alkanols in water are displayed, together with their fits by Eq. (13), in the van't Hoff coordinates in Figs. 1–5. As seen, the data exhibit a considerable scatter, some 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 appropriately reduced their statistical weight in the treatment. Older

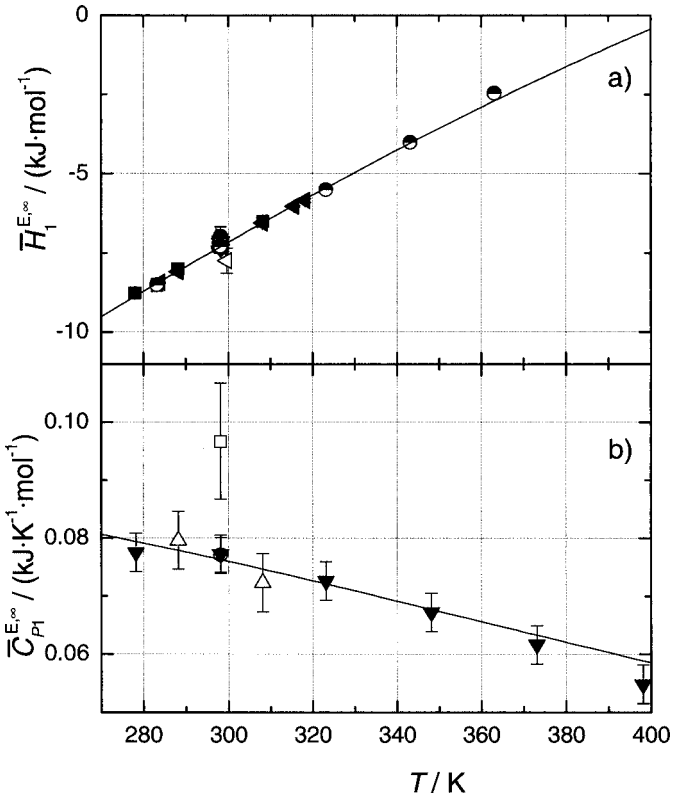

FIG. 6. Limiting partial molar excess enthalpy $\overline{H}_1^{E,\infty}$ (a) and heat capacity $\overline{C}_{p,1}^{E,\infty}$ (b) of methanol(1) in water(2) as a function of temperature. Experimental $\overline{H}_1^{E,\infty}$ values are from Table 2a: □, Aveyard and Lawrence;[57] ○, Lama and Lu;[58] △, Arnett and McKelvey;[59] ◇, Bertrand *et al.*;[60] ▽, Reid *et al.*;[62] ◁, Brower *et al.*;[63] ▷, Krishnan and Friedman;[64] ■, Alexander and Hill;[65] ●, Murakami *et al.*;[66] ▲, Rouw and Somsen;[67] ▼, Nilsson and Wadsö;[68] ◆, Korolev *et al.*;[69] ◀, Hallén *et al.*;[70] ▶, Trampe and Eckert;[71] ⬒, Dohnal *et al.*;[72] ◓, Pfeffer *et al.*[73] Experimental $\overline{C}_{p,1}^{E,\infty}$ values are from Table 3a: □, Arnett *et al.*;[61] ○, Jolicoeur and Lacroix;[87] △, Benson and D'Arcy;[88] ▼, Makhatadze and Privalov.[89] The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\overline{H}_1^{E,\infty}$, and $\overline{C}_{p,1}^{E,\infty}$ data by Eq. (13).

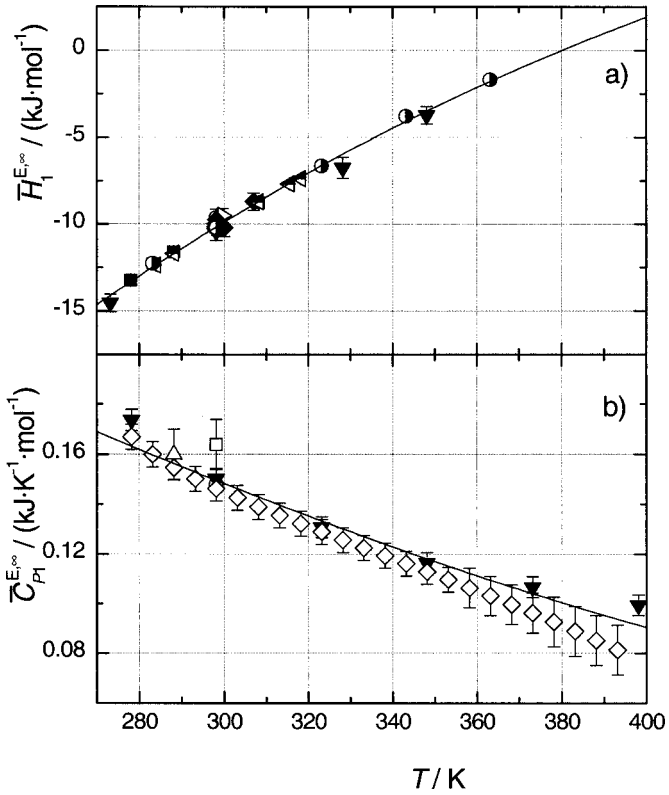

FIG. 7. Limiting partial molar excess enthalpy $\overline{H}_1^{E,\infty}$ (a) and heat capacity $\overline{C}_{p,1}^{E,\infty}$ (b) of ethanol(1) in water(2) as a function of temperature. Experimental $\overline{H}_1^{E,\infty}$ values are from Table 2b: □, Aveyard and Lawrence;[57] ○, Lama and Lu;[58] △, Bertrand *et al.*;[60] ▽, Arnett and McKelvey;[59] ◇, Aveyard and Mitchell;[74] ◁, Franks and Watson;[75] ▷, Brower *et al.*;[63] ■, Alexander and Hill;[65] ●, Krishnan and Friedman;[64] ▲, Reid *et al.*;[62] ▼, Belousov and Makarova;[76] ◆, Pannell;[77] ◀, Landgren and McEachern;[78] ▶, Costigan *et al.*;[79] ⬒, Rouw and Somsen;[67] ◓, Nilsson and Wadsö;[68] ◆, Korolev *et al.*;[69] ◀, Hallén *et al.*;[70] ▶, Trampe and Eckert;[71] ◨, Dohnal *et al.*;[72] ◑, Pfeffer *et al.*[73] Experimental $\overline{C}_{p,1}^{E,\infty}$ values are from Table 3b: □, Arnett *et al.*;[61] ○, Jolicoeur and Lacroix;[87] △, Benson and D'Arcy;[88] ▼, Makhatadze and Privalov;[93] ◇, Origlia-Luster and Woolley.[94] The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\overline{H}_1^{E,\infty}$, and $\overline{C}_{p,1}^{E,\infty}$ data by Eq. (13).

retention-time gas-liquid chromatography (GLC) measurements,[4,8,12] environmental screening of air–water partitioning by the wetted-wall column technique,[32] and a curious patented method using molecular beams[16] produced results that belong typically to those grossly deviating. The ebulliometric measurements lead also to a number of outliers, viz. data of Bergmann and Eckert[23] for methanol, Lobien and Prausnitz[49] and Ochi and Kojima[22] for 1-butanol; note however that for the present systems, whose limiting relative volatilities significantly depart from unity, the ebulliometry is not a reliable method owing to a great uncertainty in the involved evaporation-ratio and gas-phase holdup corrections.[101] Largely deviating data are further encountered for the inert gas stripping (IGS) measurements on low (C_1-C_3) 1-alkanols,[19,20] reflecting the fact that the inherent applicability domain of the IGS method is for systems with more enhanced solute volatilities. It is noteworthy that also for the most recent IGS measurements[35,43] performed as a function of temperature, the indicated temperature trends of γ_1^∞ are often in rather poor agreement with those inferred from calorimetry. As for the tensimetry, a technique which is better suited for the present systems and used in the largest number of determinations, gross deviations from the fit are exhibited only by some of the older data of Pierotti *et al.*[5] for ethanol, 1-propanol and 1-butanol and by a few isolated data points of more recent measurements of Pividal *et al.*[25] (283 and 293 K) and Rarey and Gmehling[41] (318 K) for ethanol. Measurements on circulation stills, except for those of Ikari *et al.*[45] for 1-propanol which are the only ones substantially off, appear to be very reliable, too. Of the numerous headspace analysis determinations, the systematically deviating data are those of Kolb *et al.*[51], other outliers being isolated data points of Friant and Suffet,[48] Whitehead and Sandler[53] (308 K) for 1-butanol, Rohrschneider[37] for ethanol, and Merk and Riederer[29] for 1-pentanol. The air–water partitioning measurements of Gupta *et al.*[33] using a modified phase ratio variation method do not mostly lead to deviations exceeding 0.2 in $\ln \gamma_1^\infty$, positive curvatures of van't Hoff plots of the limiting activity coefficients ($\ln \gamma_1^\infty$ vs $1/T$) obtained

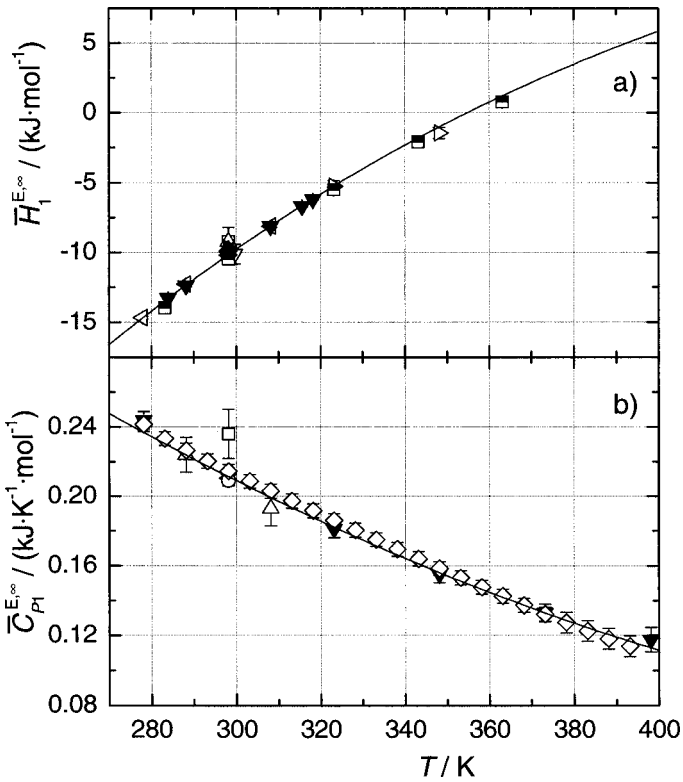

FIG. 8. Limiting partial molar excess enthalpy $\overline{H}_1^{E,\infty}$ (a) and heat capacity $\overline{C}_{p,1}^{E,\infty}$ (b) of 1-propanol(1) in water(2) as a function of temperature. Experimental $\overline{H}_1^{E,\infty}$ values are from Table 2c: □, Aveyard and Lawrence;[57] ○, Arnett and McKelvey;[59] △, Aveyard and Mitchell;[74] ▽, Brower *et al.*;[63] ◇, Krishnan and Friedman;[64] ◁, Alexander and Hill;[65] ▷, Belousov *et al.*;[80] ■, Rouw and Somsen;[67] ●, Nilsson and Wadsö;[68] ▲, Korolev *et al.*;[69] ▼, Hallén *et al.*;[70] ◆, Denda *et al.*;[81] ◀, Trampe and Eckert;[71] ▶, Dohnal *et al.*;[72] ⬒, Pfeffer *et al.*[73] Experimental $\overline{C}_{p,1}^{E,\infty}$ values are from Table 3c: □, Arnett *et al.*;[61] ○, Jolicoeur and Lacroix;[87] △, Benson and D'Arcy;[88] ▼, Makhatadze and Privalov;[93] ◇, Origlia-Luster and E. M. Woolley;[94] ◁, Fenclová *et al.*[95] The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\overline{H}_1^{E,\infty}$, and $\overline{C}_{p,1}^{E,\infty}$ data by Eq. (13).

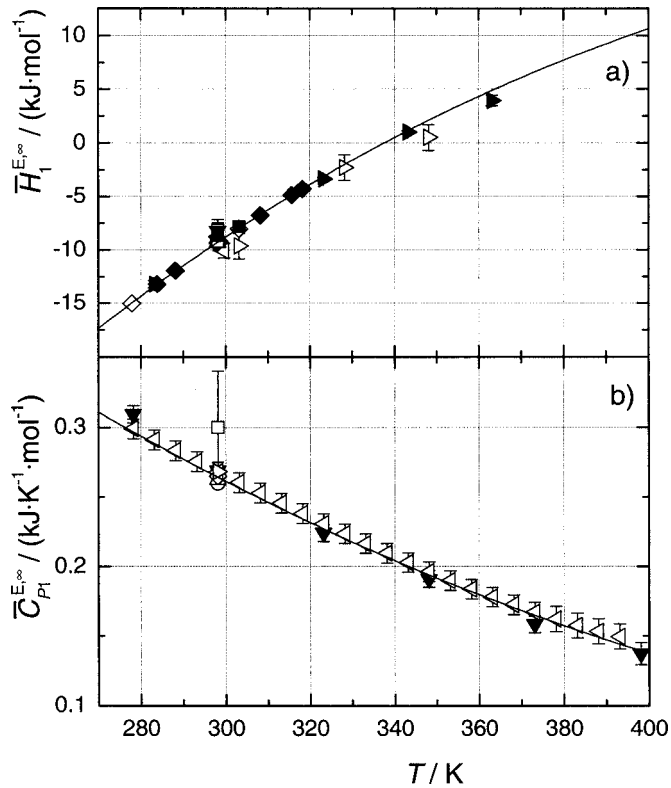

FIG. 9. Limiting partial molar excess enthalpy $\overline{H}_1^{E,\infty}$ (a) and heat capacity $\overline{C}_{p,1}^{E,\infty}$ (b) of 1-butanol(1) in water(2) as a function of temperature. Experimental $\overline{H}_1^{E,\infty}$ values are from Table 2d: □, Aveyard and Lawrence;[57] ○, Arnett and McKelvey;[59] △, Aveyard and Mitchell;[74] ▽, Krishnan and Friedman;[64] ◇, Alexander and Hill;[65] ◁, Brower *et al.*;[63] ▷, Belousov and Ponner;[83] ■, Goodwin and Newsham;[84] ●, Rouw and Somsen;[67] ▲, Nilsson and Wadsö;[68] ▼, Bury and Treiner;[85] ◆, Hallén *et al.*;[70] ◀, Trampe and Eckert;[71] ▶, Pfeffer *et al.*;[73] ⬒, Hovorka *et al.*[86] Experimental $\overline{C}_{p,1}^{E,\infty}$ values are from Table 3d: □, Arnett *et al.*;[61] ○, Jolicoeur and Lacroix;[87] △, Roux-Desgranges *et al.*;[96] ▼, Makhatadze and Privalov;[93] ◇, Hovorka *et al.*;[97] ◁, Origlia-Luster and Woolley;[98] ▷, Fenclová *et al.*[95] The line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\overline{H}_1^{E,\infty}$, and $\overline{C}_{p,1}^{E,\infty}$ data by Eq. (13).

from their measurements however contradict to large positive values of limiting partial molar excess heat capacities as obtained calorimetrically.

Even with the outliers mentioned, many other data are in a fairly reasonable agreement 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 especially those of Tucker *et al.*[17,39] (tensimetry), Pemberton *et al.*[13,15] (GLC), Rytting *et al.*[14] and Li and Carr[26] (headspace analysis), Christensen[30] (circulation still), and those measured in this laboratory[2] (applicability optimized use of various techniques).

Compared to the measurements of dilute-range vapor–liquid equilibria, the calorimetric determinations of dilute-range thermal properties appear to be considerably less scattered, as seen from Figs. 5–10. The observed outliers correspond usually to the earliest measurements that were carried out in the 1960s and are generally regarded as less accurate. At room temperature, notably off are the dissolution enthalpies for 1-propanol, 1-butanol, and 1-pentanol reported by Aveyard *et al.*[57,74] (less exothermic) and those for methanol and 1-butanol by Brower *et al.*[63] (more exothermic). Somewhat newer measurements of $\overline{H}_1^{E,\infty}$ (298.15 K) for 1-butanol and 1-pentanol by Bury and Treiner[85] also deviate markedly (being less exothermic) from the values of most other investigators. The early measurements of $\overline{H}_1^{E,\infty}$ of 1-alkanols in water as a function of temperature performed (except for 1-pentanol) by Alexander and Hill[65] and (except for methanol and 1-pentanol) by Belousov *et al.*[76,80,83] match quite well the accurate more recent determinations by Hallén *et al.*[70] and Pfeffer *et al.*,[73] but the data of Belousov *et al.* are apparently more scattered and thus considered here as significantly less accurate.

Regarding $\overline{C}_{p,1}^{E,\infty}$, the only data clearly in error are those resulting from the earliest determinations by Arnett *et al.*[61]; their $\overline{C}_{p,1}^{E,\infty}$ values are too high for all the five alkanols studied. The comparison of systematic determinations of $\overline{C}_{p,1}^{E,\infty}(T)$ by Makhatadze and Privalov[93] with those by Origlia and Woolley[94,98] indicate their good mutual agreement except for ethanol at higher temperatures (>353 K) where the $\overline{C}_{p,1}^{E,\infty}$

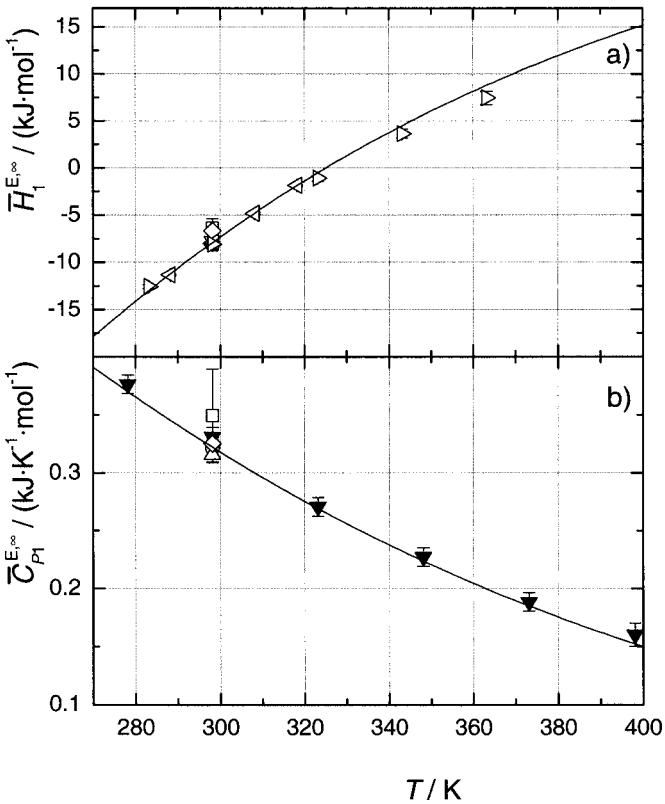

FIG. 10. Limiting partial molar excess enthalpy $\bar{H}_1^{E,\infty}$ (a) and heat capacity $\bar{C}_{p,1}^{E,\infty}$ (b) of 1-pentanol(1) in water(2) as a function of temperature. Experimental $\bar{H}_1^{E,\infty}$ values are from Table 2e: □, Aveyard and Lawrence[57]; ○, Aveyard and Mitchell[74]; △, Krishnan and Friedman[64]; ▽, Rouw and Somsen[67]; ◇, Bury and Treiner[85]; ◁, Hallén *et al.*[70]; ▷, Pfeffer *et al.*[73] Experimental $\bar{C}_{p,1}^{E,\infty}$ values are from Table 3e: □, Arnett *et al.*[61]; ○, Sköld *et al.*[99]; △, Jolicoeur and Lacroix[87]; ▼, Makhatadze and Privalov[93]; and ◇, Fenclová *et al.*[95] 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. (13).

data from the two laboratories start to deviate significantly, each exhibiting an inconsistency with existing $\bar{H}_1^{E,\infty}(T)$ data, but in different directions. To cope with this issue we labeled the $\bar{C}_{p,1}^{E,\infty}$ data in question with some higher compromising values of uncertainties. A slight inconsistency between $\bar{H}_1^{E,\infty}(T)$ and $\bar{C}_{p,1}^{E,\infty}$ data was found at higher temperatures also for other 1-alkanols; we accounted for it by assigning larger uncertainties to the both $\bar{H}_1^{E,\infty}$ and $\bar{C}_{p,1}^{E,\infty}$ data involved.

5.3. Recommended $\gamma_1^\infty(T)$ and $K_H(T)$ Data

Equation (13) with parameters from Table 4 yields for available data a thermodynamically consistent description of superior quality and we consider it to establish the recommended temperature dependences of γ_1^∞, as well as 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 probable uncertainty (68% confidence level) of the recommended values, as inferred by the error propagation from the parameter variance-covariance matrix, does not exceed 1%–2% for γ_1^∞ and 2%–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 5. The recommended temperature dependences of γ_1^∞ are believed to be reliable even in a moderate extrapolation towards higher temperatures: e.g., at 400 K the probable uncertainty of the calculated γ_1^∞ values is estimated to approximately 3%.

To obtain the recommendation for the temperature dependences of the Henry's law constants and the related hydration properties, the dependences $\gamma_1^\infty(T)$ were combined with reliable data on respective pure solute properties according to Eqs. (5), (6), (10), and (11). The vapor pressures of 1-alkanols were calculated from the Wagner equation with parameters given by Ambrose and Walton,[102] their fugacity coefficients were calculated from truncated virial equation of state with the second virial coefficients estimated by the Hayden and O'Connell correlation,[103] and the liquid densities were obtained from CDATA.[104] The standard vaporization enthalpies were obtained from the temperature dependences of standard vaporization internal energies (cohesive energies) given by Majer and Svoboda.[105]

Although the selected data on the pure 1-alkanols may be considered to be the best of those presently available, they were noted to exhibit a considerable uncertainty and/or lack of mutual consistency in some cases. Extrapolations necessary to cover the temperature range of interest are at least partially responsible for these problems. At subambient temperatures, the vapor pressures of 1-butanol and especially of 1-pentanol are quite low and their values calculated from the Wagner equation[102] lack any support by experimental data in this temperature region. The disparity of results we obtained by various other extrapolations from available data at higher temperatures indicate that uncertainties in p_1^s (273.15 K) may be as high as 5% and 10%, for 1-butanol and

TABLE 5. Recommended values of excess thermodynamic functions at infinite dilution[a] for 1-alkanols in water at 298.15 K.

Alkanol	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})
Methanol	1.64±0.01	1.23±0.01	−7.30±0.01	76±1
Ethanol	3.91±0.02	3.38±0.01	−10.16±0.01	150±1
1-Propanol	14.2±0.1	6.57±0.01	−10.16±0.01	211±1
1-Butanol	51.3±0.3	9.76±0.01	−9.28±0.01	264±1
1-Pentanol	195±1	13.07±0.03	−7.90±0.04	322±2

[a]Calculated from Eq. (13) with parameters from Table 4.

TABLE 6. Parameters of Eq. (16)[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]
Methanol	35.2636	−31.9283	−13.6130	−0.0177	0.007
Ethanol	48.4419	−50.3880	−34.4862	5.3681	0.009
1-Propanol	59.5372	−67.7465	−56.3580	11.8908	0.008
1-Butanol	69.1201	−82.5385	−74.7421	17.2409	0.009
1-Pentanol	78.7049	−99.5059	−97.8025	24.8176	0.015

[a]Recommended temperature dependence for Henry's law constant.
[b]$s_{rel}=[S_{min}/(n-4)]^{1/2}$
$S=\Sigma_{i=1}^{n_G}[K_{H,i}(\text{calc})/K_{H,i}(\text{exp})-1]^2+\Sigma_{i=1}^{n_H}[\Delta_{hyd}H_{1,i}^\infty(\text{calc})/\Delta_{hyd}H_{1,i}^\infty(\text{exp})-1]^2+\Sigma_{i=1}^{n_C}[\Delta_{hyd}C_{p,1,i}^\infty(\text{calc})/\Delta_{hyd}C_{p,1,i}^\infty(\text{exp})-1]^2$, $n_G=n_H=n_C=21$.

1-pentanol, respectively. In addition, differences in the values of vaporization enthalpy inferred from the Wagner equation[102] and those recommended from calorimetric measurements[105] reach for 1-butanol and 1-pentanol at subambient temperatures a level of 1 kJ mol^{-1} A similar inconsistency was found also for ethanol and methanol at temperatures approaching 373 K; here the vapor phase nonideality corrections exceed 5% and their uncertainty may well contribute to the problem. In some cases, a lack of consistency was also encountered between $\Delta_{vap}H^0(T)$ and $(C_{p,1}^{L,\bullet}-C_{p,1}^{G,0})$ data. It is obvious, that all these inconsistencies in pure solute property data are translated into the calculated values of hydration properties.

In order to establish recommended temperature dependences 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:

$$\ln K_H = A + B/\tau + C \ln \tau + D\tau. \quad (16)$$

Equation (16) was used instead of an analogous form of Eq. (13), because for hydration properties the latter equation was found to perform significantly worse than the former. Yet, Eq. (16) is a compromise to fit rather nonlinear $\Delta_{hyd}C_{p,1}^\infty(T)$ dependences encountered for higher 1-alkanols. 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. (16), along with the corresponding relative standard deviations of fit s_{rel}, are listed for the 1-alkanols studied in Table 6. It is seen that Eq. (16) fits the hydration data quite well, the relative standard deviation being within 1%, except for 1-pentanol where s_{rel} is 1.5%. The values of s_{rel} may suggest the probable level of uncertainty for the recommended hydration properties calculated from Eq. (16), except for the following cases where one should expect a somewhat higher uncertainty. For the Henry's law constants of 1-butanol and 1-pentanol uncertainties as high as 3% and 5%, respectively, are probable at subambient temperatures close to 273 K. An increased uncertainty (1.5%) is also probable for $\Delta_{hyd}H_1^\infty$ of methanol and ethanol at higher temperatures close to 373 K. These cases reflect the above-mentioned problems with pure 1-alkanol properties which, thanks to the simultaneous thermodynamically consistent treatment applied, are now rather attenuated. Further, uncertainties of 2%–3% should be also expected in $\Delta_{hyd}C_{p,1}^\infty$ at the ends of the temperature interval (273 K, 373 K), mainly due to the compromised linear fit of $\Delta_{hyd}C_{p,1}^\infty$ provided by Eq. (16). Nevertheless, for estimation of the Henry's law constants, moderate extrapolations by Eq. (16) 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 approximately 5%. The values of thermody-

TABLE 7. Recommended values of hydration thermodynamic functions[a] for 1-alkanols in water at 298.15 K and their comparison with those given by Plyasunov and Shock[1] (in parentheses).[b]

Alkanol	K_H (kPa)	$\Delta_{hyd}G_1^\infty$ (kJ mol^{-1})	$\Delta_{hyd}H_1^\infty$ (kJ mol^{-1})	$\Delta_{hyd}C_{p,1}^\infty$ (J K^{-1} mol^{-1})
Methanol	27.6	−3.19	−45.36	114
	(26.9±2.2)	(−3.25±0.20)	(−45.13±0.20)	(114±5)
Ethanol	30.6	−2.93	−52.73	198
	(29.3±2.0)	(−3.04±0.17)	(−52.59±0.15)	(199±5)
1-Propanol	39.7	−2.29	−57.71	271
	(37.6±4.9)	(−2.42±0.32)	(−57.65±0.20)	(268±6)
1-Butanol	45.7	−1.94	−62.07	335
	(46.0±4.5)	(−1.92±0.24)	(−61.72±0.20)	(335±10)
1-Pentanol	55.5	−1.46	−65.74	401
	(62.3±6.5)	(−1.17±0.26)	(−65.0±0.3)	(402±10)

[a]Calculated from Eq. (16) with parameters from Table 6.
[b]Converted from the molality scale used in Plyasunov and Shock (Ref. 1) to the mole fraction scale used in the present work.

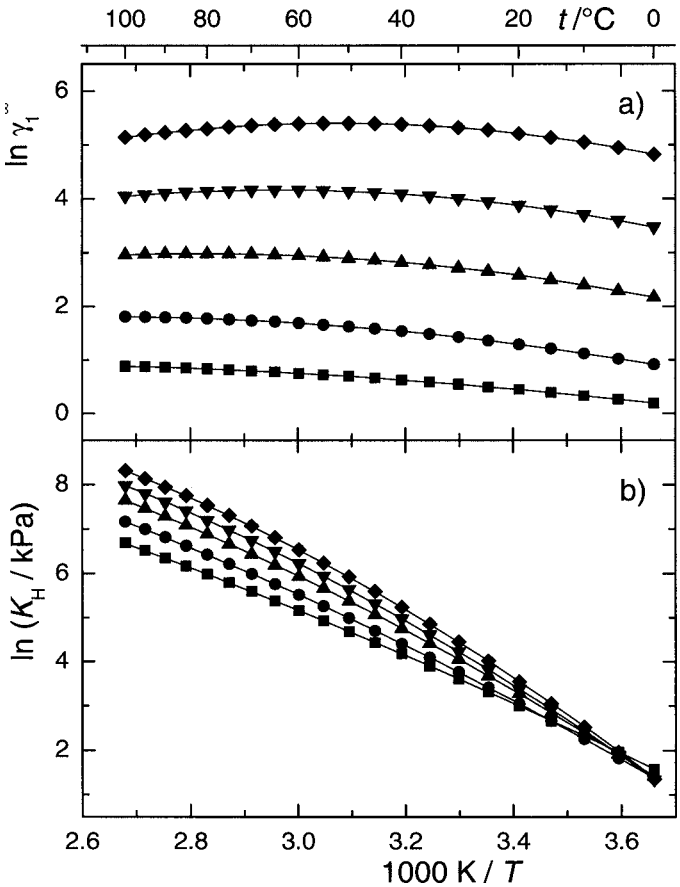

FIG. 11. Recommended temperature dependences for (a) limiting activity coefficients γ_1^∞ and (b) Henry's law constants K_H of lower 1-alkanols(1) in water(2): –■–, methanol; –●–, ethanol; –▲–, 1-propanol; –▼–, 1-butanol; and –◆–, 1-pentanol.

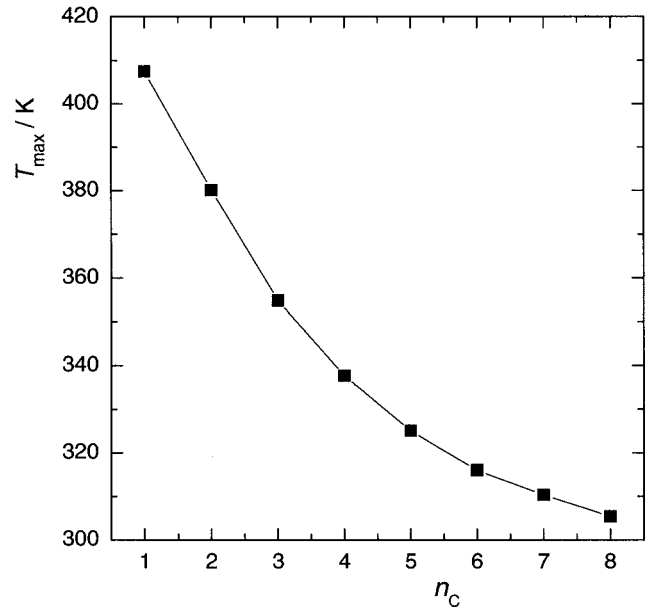

FIG. 12. Temperature T_{max} at which γ_1^∞ of 1-alkanol(1) in water(2) is maximum vs the number of carbon atoms of 1-alkanol. For C_1-C_5 1-alkanols the values of T_{max} are from Table 4 [recommended fits by Eq. (13)] and for C_6–C_8 1-alkanols they were obtained from calorimetric $\bar{H}_1^{E,\infty}(T)$ measurements of Hallén *et al.*[70]

namic functions of hydration at 298.15 K calculated from Eq. (16) are compared with recent recommendations by Plyasunov and Shock[1] in Table 7. In general, a very good agreement is observed for all the 1-alkanols and properties studied. The present values, especially of K_H ($\Delta_{hyd}G_1^\infty$), should be preferred however as they are significantly more accurate.

5.4. Evolution of Properties with Temperature and Homologous Series

The recommended temperature dependences established in this work for various infinite dilution properties of the aqueous lower 1-alkanols compose a very accurate general picture of thermodynamic behavior of these systems. A detailed theoretical analysis of this behavior is desirable but out of the scope of this article. The present discussion is therefore confined only to commenting on essential features of the behavior and its evolution with temperature and homologous sequence.

In Fig. 11 the recommended $\gamma_1^\infty(T)$ and $K_H(T)$ for all the lower 1-alkanols studied are plotted in the van't Hoff coordinates. In Fig. 11(a), going from 273 K the values of ln γ_1^∞ are seen to rise with temperature, following concave courses which at a higher T display a maximum. For methanol and ethanol, the maximum appears above the normal boiling temperature of water, the temperature corresponding to the maximum, T_{max} (see Table 4), decreases as the carbon number n_C of 1-alkanol increases. Plotting T_{max} vs n_C, as shown in Fig. 12, results in a smooth trend which proves the mutual consistency of the recommended data obtained for each individual member of the homologous series. At a constant T, γ_1^∞ increases monotonously in the homologous sequence, the increase from methanol to 1-pentanol amounting to two orders of magnitude.

The Henry's law constants [Fig. 11(b)] also exhibit a concave rise with temperature, but in contrast to γ_1^∞, the K_H curves for the individual 1-alkanols are far from being parallel. Although at the normal boiling temperature of water the K_H values for the five lower 1-alkanols span a factor of 5, at the melting point temperature of water they are remarkably about the same. Note that it is only at temperatures close to ambient and higher where, in agreement with a traditional expectation of the homologous trend, K_H of 1-alkanols distinctly increases with the prolongation of the aliphatic chain.

Figs. 13 and 14 give a graphical overview of the evolution of thermodynamic functions of dissolution and hydration with temperature and homologous sequence. As a whole, the homologous behavior seen is quite coherent; methanol however exhibits some obvious differences, which is typical for the first member of any homologous series. The pattern of thermodynamic behavior resembles in many respects that of aqueous hydrophobic solutes which is increasingly approached going from methanol to 1-pentanol. Large negative

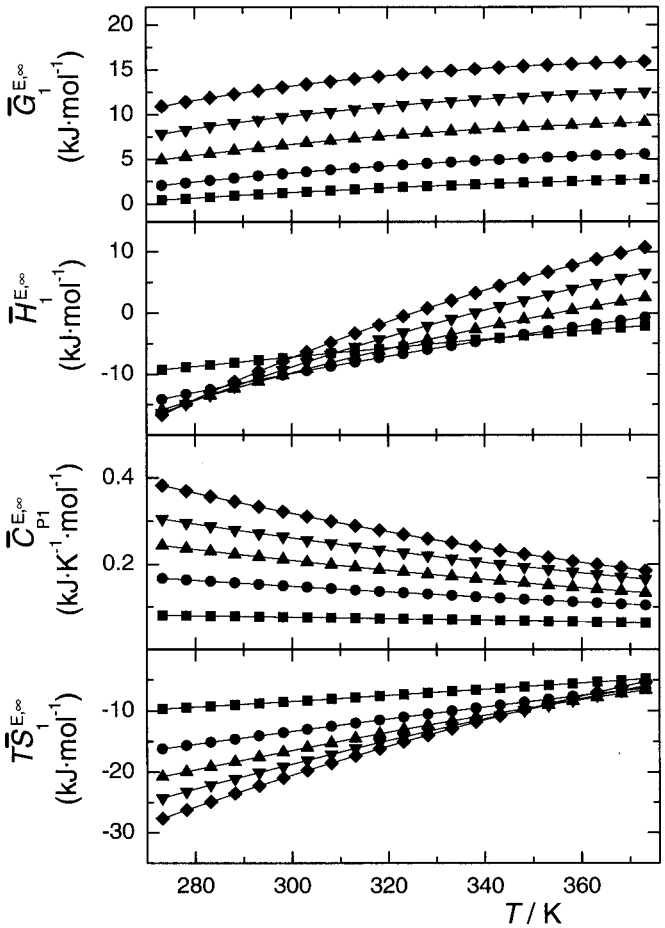

FIG. 13. Evolution of limiting partial molar excess functions $\bar{Y}_1^{E,\infty}$ ($Y = G, H, C_p, TS$) of lower 1-alkanols(1) in water(2) with temperature and homologous sequence: –■–, methanol; –●–, ethanol; –▲–, 1-propanol; –▼–, 1-butanol; and –◆–, 1-pentanol.

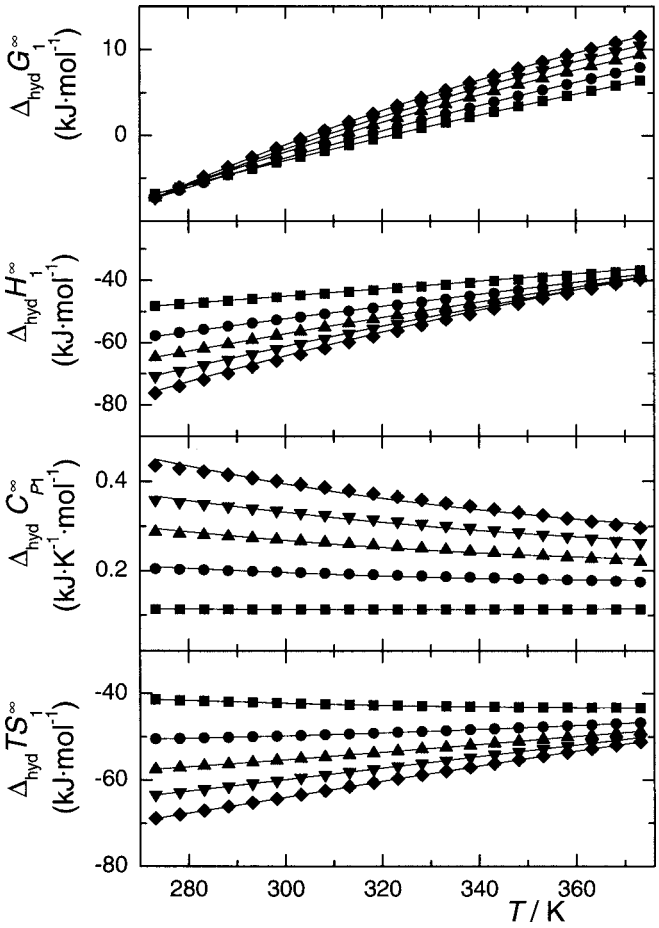

FIG. 14. Evolution of thermodynamic functions of hydration $\Delta_{hyd}Y_1^{\infty}$ ($Y = G, H, C_p, TS$) of lower 1-alkanols(1) with temperature and homologous sequence: –■–, methanol; –●–, ethanol; –▲–, 1-propanol; –▼–, 1-butanol; and –◆–, 1-pentanol.

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 the reorganization of water molecules around the solute.[106] 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 still remain positive and large at 373 K and hence, in the temperature range considered, the respective enthalpies and entropies are rapidly increasing functions of T. The values of $\Delta_{sol}C_{p,1}^{\infty}$ and $\Delta_{hyd}C_{p,1}^{\infty}$ of 1-alkanols monotonously ascend in the homologous sequence, so do the temperature coefficients of the dissolution and hydration entropies and enthalpies, which implies that in each of the plots $T\Delta_{sol}S_1^{\infty}(T)$, $\Delta_{sol}H_1^{\infty}(T)$, $T\Delta_{hyd}S_1^{\infty}(T)$, and $\Delta_{hyd}H_1^{\infty}(T)$ the curves for the individual alkanols should cross. For $T\Delta_{sol}S_1^{\infty}(T)$ and $\Delta_{sol}H_1^{\infty}(T)$ the crossings are seen to occur between the melting point and the normal boiling point of water, whereas for their hydration counterparts these crossings appear at more or less higher temperatures. It is noteworthy, that for the three higher 1-alkanols (C_3–C_5) the crossings occur at essentially the same points. The respective crossover temperatures are approximately 353 K ($\Delta_{sol}S_1^{\infty}$), 283 K ($\Delta_{sol}H_1^{\infty}$), 423 K ($\Delta_{hyd}S_1^{\infty}$), and 383 K ($\Delta_{hyd}H_1^{\infty}$). Isoentropic and isoenthalpic temperatures have been reported in the literature also for various nonpolar solutes, the hydration entropy convergence being of particular attention due to its possible link to protein unfolding.[107–111]

As a result of a rather delicate balance of the large enthalpic and entropic contributions, $\Delta_{sol}G_1^{\infty}$ and $\Delta_{hyd}G_1^{\infty}$ of 1-alkanols in the given temperature range exhibit monotonously increasing temperature dependences. The entropy and enthalpy contributions largely compensate for each other, and it is only for $\Delta_{sol}G_1^{\infty}$ at temperatures higher than T_{max} where both act in the positive direction. As expected, in the homologous sequence the Gibbs energies of dissolution and hydration rise, $\Delta_{hyd}G_1^{\infty}$ at temperatures near the melting point of water is however an exception [cf. $K_H(T)$]. The closely similar $\Delta_{hyd}G_1^{\infty}$ values found here for all the 1-alkanols stud-

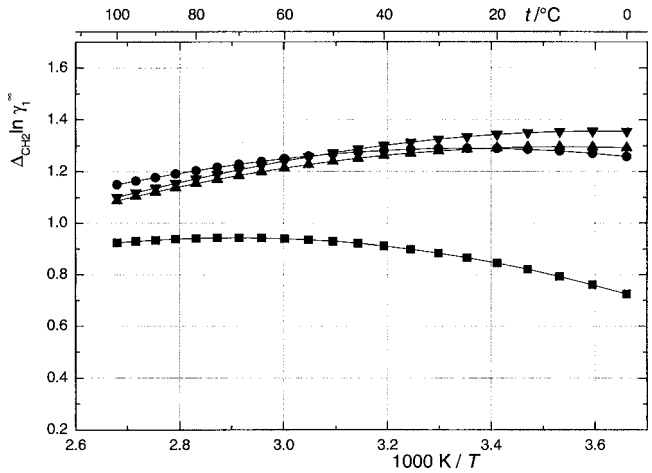

FIG. 15. Methylene increment to the limiting activity coefficient $\Delta_{CH_2}\ln\gamma_1^\infty$ in the homologous sequence of 1-alkanols(1) in water(2) as a function of temperature: –■–, ethanol-methanol; –●–,, 1-propanol-ethanol; –▲–, 1-butanol-1-propanol; and –▼–, 1-pentanol-1-butanol.

ied indicate that in the vicinity of melting point of water the enthalpy-entropy compensation in the hydration process of 1-alkanols is virtually independent of their chain length.

The traditional analysis of the homologous sequence variation of dissolution and hydration properties by means of incremental group contributions shows that the respective methylene increments are substantially dependent on temperature, sometimes even changing their signs (cf. crossover points). Going from methanol to 1-pentanol at a given temperature the methylene increments to most properties vary substantially and systematically, too. It appears that the incremental group contribution approach is for lower 1-alkanols well obeyed only for $\ln\gamma_1^\infty$ or $\Delta_{sol}G_1^\infty$, provided methanol is excluded (see Fig. 15).

6. Conclusion

Based on a comprehensive critical compilation of relevant equilibrium and calorimetric data and their simultaneous correlation, recommended temperature dependences of limiting activity coefficients, Henry's law constants, and other related infinite dilution thermodynamic properties of lower 1-alkanols in water have been established in this work. These thermodynamically consistent, truly reliable recommendations of superior accuracy are valid in the range from the melting point to the normal boiling point of water, but for limiting activity coefficient and Henry's law constant reasonable accuracy can be expected even in moderate extrapolations towards higher temperatures (<400 K). The treatment presented improves our knowledge of thermodynamic behavior of highly dilute solutions of 1-alkanols in water, opening new possibilities for its detailed theoretical analysis and generalization. In addition, these results contribute to establishment of a data base on hydration properties of organic nonelectrolytes within an international project[112] (2005–2007) conducted under the auspices of IUPAC and IAPWS.

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