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Limiting Activity Coefficients by Comparative Tensimetry: 1-Propanol and 1-Butanol in Heptane and in Octane

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Limiting activity coefficients (γ_1^∞) of 1-propanol and 1-butanol in heptane and octane were determined at 10-K increments between 303 K and 343 K using a differential static cell equilibrium apparatus. The comparative tensimetric technique was employed because it is well suited for the systems and conditions examined. The new measurements supplement and extend previously released γ_1^∞ data for some lower 1-alkanol in *n*-alkanes we determined by the inert gas stripping. The sets of data obtained by the two different experimental techniques show good mutual consistency. The present γ_1^∞ data compare favorably also with other literature information, and their temperature trends are reasonably consistent with calorimetric data on limiting partial molar excess enthalpies.

Introduction

Theoretical as well as practical aspects of the behavior of alcohol + hydrocarbon mixtures have been attracting the interest of the thermodynamic community for a number of decades. In the past decade, the theme was addressed by the IUPAC Project on Vapor−Liquid Equilibria in 1-Alkanol + *n*-Alkane Mixtures[1] under which we established recommended values of limiting activity coefficients (γ_1^∞) for these systems.[2] The recommendation was based on a comprehensive critical compilation of the values from the literature and our own systematic measurements. The original γ_1^∞ data we measured were not reported. Quite recently, we have begun to release these data and the respective experimental details. Following the first release,[3] which reported γ_1^∞ values for some lower 1-alkanols in *n*-alkanes measured by the inert gas stripping method, in this paper, we continue releasing our original experimental data by reporting γ_1^∞ for 1-propanol and 1-butanol in heptane and octane measured by the comparative tensimetry. When determining γ_1^∞, the selection of an appropriate experimental technique is the key for obtaining accurate results and the comparative tensimetric technique, newly employed here, is well suited for the present systems and the temperature range examined where the solute limiting relative volatilities (α_{12}^∞) reach moderately enhanced values ($4 < \alpha_{12}^\infty < 55$).

Comparative Tensimetry

The principle of the tensimetric determination of limiting activity coefficients consists of measuring the equilibrium pressure at constant temperature as a function of gravimetrically or volumetrically determined compositions of dilute solutions. As shown in the literature,[4,5] the value of the limiting activity coefficient can be obtained from these measurements without employing a concrete liquid-phase nonideality model, just extrapolating the equilibrium equations to infinite dilution

$$\gamma_1^\infty = \frac{\epsilon_1^\infty P_2^s}{P_1^s}\left[1 + \beta\left(\frac{\partial P}{\partial x_1}\right)_T^\infty\right] \tag{1}$$

where

$$\epsilon_1^\infty = \exp\left[\frac{(B_{11} - v_1^L)(P_2^s - P_1^s) + (2B_{12} - B_{11} - B_{22})P_2^s}{RT}\right] \tag{2}$$

and

$$\beta = \frac{1}{P_2^s} + \frac{B_{22} - v_2^L}{RT} \tag{3}$$

Here, P_i^s and v_i^L are the pure-component vapor pressures and liquid molar volumes, respectively, and B_{ii} and B_{ij} are the second virial coefficients. The quantity to be yielded by the tensimetric experiment is $(\partial P/\partial x_1)_T^\infty$, the limiting derivative of the equilibrium pressure P with respect to the solute liquid-phase mole fraction x_1 at constant temperature. This limiting slope can be evaluated from an analytical smoothing equation fitted to the measured dilute-range $P-x_1$ data.

For practical applications, however, it is important to consider that the gravimetrically (or volumetrically) determined global composition x_1^0 of the material loaded into the equilibrium cell differs, due to the presence of a vapor space in the cell, from the composition of the equilibrium liquid phase x_1. Although iterative equilibrium calculations have been applied to provide the respective correction, an explicit analytical formula for γ_1^∞ taking into account this correction can be obtained in an analogous manner to that

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elaborated[6] for the ebulliometric determination of limiting activity coefficients. The resulting equation takes the following form

$$\gamma_1^\infty = \frac{\epsilon_1^\infty P_2^{\mathrm{s}}}{P_1^{\mathrm{s}}}\left[1 + \frac{\beta(\partial P/\partial x_1^0)_{\mathrm{T}}^\infty}{1 - \beta(\partial P/\partial x_1^0)_{\mathrm{T}}^\infty N_{\mathrm{V}}^\infty}\right] \tag{4}$$

where $(\partial P/\partial x_1^0)_{\mathrm{T}}^\infty$ is the infinite dilution slope of the equilibrium pressure vs the gravimetrically determined *global* mole fraction of the solute and N_{V}^∞ stands for the limiting relative amount of the vapor phase. With regard to the state of infinite dilution, the latter quantity corresponds to the neat solvent and can be calculated as follows

$$N_{\mathrm{V}}^\infty = \frac{n_{2\mathrm{V}}^\infty}{n_2} = \left(\frac{V_{\mathrm{T}} M_2}{m_2 v_2^{\mathrm{L}}} - 1\right)\frac{v_2^{\mathrm{L}}}{RT/P_2^{\mathrm{s}} + B_{22} - v_2^{\mathrm{L}}} \tag{5}$$

where $n_{2\mathrm{V}}^\infty$ and n_2 are the amounts of the solvent in the vapor phase and in the entire equilibrium cell, respectively, V_{T} is the total volume of the equilibrium cell and m_2 and M_2 are the mass of the solvent charged into the cell and the molar mass of the solvent, respectively. The vapor-space correction affects calculated values of γ_1^∞ in the positive direction, and its magnitude depends on the limiting relative volatility α_{12}^∞ of the system studied; for a moderate departure of α_{12}^∞ from unity, this correction is usually quite small ($\leq 1\%$ for $0.1 < \alpha_{12}^\infty < 10$), but for limiting relative volatilities greatly departing from unity ($\alpha_{12}^\infty \leq 0.002$ or $\alpha_{12}^\infty \geq 1000$), it may become prohibitively large (100%).

To a great advantage, the tensimetric measurements in the dilute range are usually performed in the comparative arrangement,[7,8] i.e., measuring the differential pressure between two isothermally operated static cells, the measuring cell containing the dilute mixture and the reference cell containing the neat solvent, rather than measuring the absolute pressure. By use of the comparative technique, the measurement process is efficiently stabilized and the precision of the measurement increased. In general, correct tensimetric measurements require absolute tightness of the static apparatus and careful degassing of liquids used for experiment. In terms of its applicability, the comparative tensimetry can be considered as a suitable complementary technique to more frequently applied methods of comparative ebulliometry and the inert gas stripping.

Experimental Section

Materials. Analar-grade 1-propanol and 1-butanol were purchased from Lachema (Brno, Czech Rep.). To remove water, these materials were boiled with aluminum amalgam, each product being then fractionally distilled on a 1 m long packed column. Heptane (Merck, “zur Synthese”) and octane (Fluka, puriss) were distilled in the same manner. All purified samples were stored with Merck 0.4-nm molecular sieves. The residual water content, as determined by a Karl Fischer titration, was lower than 0.002 mass % and 0.01 mass % for *n*-alkanes and 1-alkanols, respectively. The purity of all samples was checked by gas chromatography and by comparison of determined densities and refractive indices with literature data (Table 1).

Table 1. Purity of the Components and Comparison of Their Density ρ and Refractive Index n_{D} at 293.15 K with Literature Data

		ρ/g·cm^{-3}		n_{D}	
component	% GC[a]	exp[b]	lit[c]	exp	lit[d]
1-propanol	99.96	0.80355	0.80348	1.3855	1.38556
1-butanol	99.80	0.80968	0.80959	1.3992	1.39929
heptane	99.97	0.68379	0.68373	1.3876	1.38764
octane	99.85	0.70276	0.70268	1.3973	1.39743

[a] Gas chromatography (GC) column HP-1, 10 m, 0.53 mm i.d., carrier gas helium 7 mL·min^{-1}, detected by a flame ionization detector. [b] Vibrating-tube densitometry. [c] Reference 9. [d] Reference 10.

Apparatus and Procedure. The differential static cell apparatus used in this work was designed at TU Berlin[11] as a modification stemming from the previous setup described by Kassmann and Knapp.[7] Basically the same apparatus was employed also by Sandler and co-workers.[12,13] Good performance of this apparatus was verified in a number of applications involving various aqueous[13,14] and nonaqueous[12,15] systems.

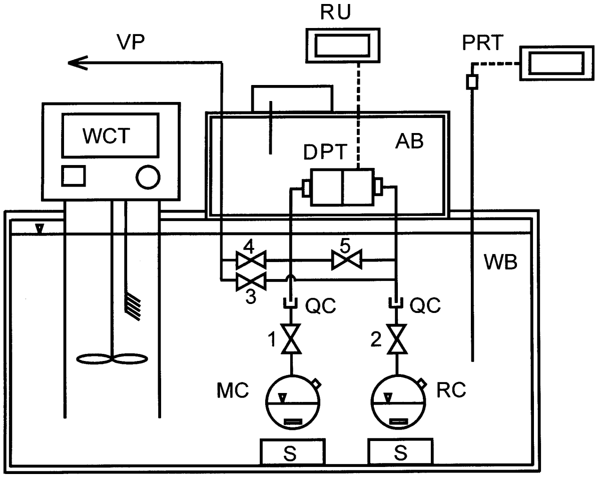

Figure 1. Schematic diagram of the differential static cell apparatus: DPT, differential pressure transducer; RU, pressure readout unit; MC, measuring cell; RC, reference cell; PRT platinum-resistance thermometer; 1−5, valves; QC, quick connection gadgets; WCT, water-circulating thermostating unit; WB, constant temperature water bath; AB, constant temperature air bath; S, magnetic stirrers; VP, connection to vacuum pump.

A schematic diagram of the experimental setup is shown in Figure 1. The apparatus consists of twin magnetically stirred 50-mL glass cells, connected through a valved stainless steel manifold system to the differential pressure gage. Each cell can be isolated by a valve (Whitey SS-OKM2) and removed or replaced through a Leybold quick connection gadget. A Swagelok union with Teflon ferrules provides the glass−stainless steel connection. Liquid substances can be added into the cells through ports sealed with Teflon-coated septa. The pressure gage is a Baratron MKS differential pressure transducer, model 221A, with a 13.3-kPa range and an accuracy of 0.05%, which is connected to an MKS PDR-D-1 readout unit. The transducer is housed in an insulated stainless steel box maintained at a constant temperature (383 ± 1) K to prevent condensation and to eliminate the temperature effect on the output signal of the transducer. The calibration over the range of pressure readings was done with an accuracy of ±3 Pa using a water U-manometer and a cathetometer. The transducer is connected to the valved (Whitey SS-OKM2) manifold system using Cajon Ultratorr fittings. A 60-L water bath with a Haake E8 control unit maintains constant temperature of static cells within 0.01 K. By lifting the pressure transducer box the cells are raised from the bath to make them accessible. A calibrated platinum-resistance thermometer Pt 100 (Conatex) connected to a multimeter Prema 6000 is used to measure the water bath temperature with an accuracy of ±0.02 K. To evacuate the equipment and to degas the liquid samples, a Leybold Heraeus oil vacuum pump is employed. A separate manifold equipped with an auxiliary pressure gage, and the Leybold quick fittings is used to attach the cells with samples for degassing.

Before an experiment, the cells were cleaned and dried and the apparatus was thoroughly evacuated. Both cells were loaded with the solvent, after the measuring cell (the one destined to solute additions) had been weighed while empty. The cells were then attached to the degassing apparatus where vacuum and ultrasonic bath were alternately applied to one cell at a time. This degassing cycle was repeated until the pressure in the cell decreased to the known value of saturated vapor pressure of the pure substance. Complete degassing was also verified by the "click test" as suggested by Van Ness and Abbott.[16] The solute was degassed in the same manner by using an extra cell which is identical to those used for differential pressure measurements.

After degassing, the cells were removed from the degassing manifold, the measuring cell was reweighed to determine the exact mass of the solvent, and then the cells with the solvent were connected to the differential tensimetric apparatus. With valves 1 and 2 closed and valves 3, 4, and 5 open, the vacuum was applied to the system for about 1 h. The zero point of the transducer was then adjusted. Next, valves 3, 4, and 5 were closed and valves 1 and 2 were opened. The apparatus was immersed in the thermostatic water bath so that the water level of the bath was just above valves 4 and 5. The cell contents were stirred, and the differential pressure, which was small in all cases, was recorded to determine the zero offset. After this initial pressure difference measurement, the apparatus was raised above the water bath and valves 1 and 2 were closed. A small amount of the degassed solute was injected into the measuring cell using a gastight syringe (Hamilton, Model 1725). The exact amount of the added solute was determined by weighing the syringe before and after the addition. Then valves 1 and 2 were opened and the apparatus was re-immersed in the water bath. The pressure difference was then recorded until a stable value was obtained in (20 to 30) min. Usually, six additions of the solute were carried out which resulted in a range of about 2 mol % concentration.

Results and Discussion

As illustrated in Figure 2, the measured dependence of ΔP on x_1^0 was usually nearly linear. Thus, it was well fitted by either of the equations

$$\Delta P = \sum_{i=1}^{p} A_i (x_1^0)^i \qquad p = 1,2 \tag{6}$$

which yielded the desired limiting slope $(\partial P/\partial x_1^0)_T^\infty = (\partial \Delta P/\partial x_1^0)_T^\infty = A_1$. The parameters in eq 6 were determined by the least-squares method. To select the appropriate representation, we considered both the standard deviation of fit (F-test) as well as the distribution of residuals. The limiting activity coefficients were determined from the experimental value of $(\partial P/\partial x_1^0)_T^\infty$ using eq 4. The auxiliary data for this calculation were obtained as follows. The molar volumes were taken from the CDATA database,[9] and the virial coefficients were obtained from the Hayden−O'Connell correlation[17] with parameters from Prausnitz et al.[18] or CDATA. The vapor pressures of pure components were calculated from the Antoine equation as given in Table 2.

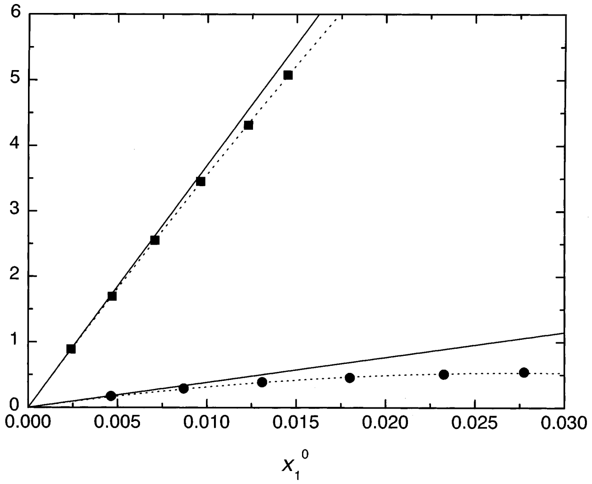

Figure 2. Typical plots of the differential pressure vs the global mole fraction of solute. ■, 1-propanol (1) in heptane (2), 343.15 K; ●, 1-butanol (1) in octane (2), 303.15 K. Dotted lines are smoothing polynomial fits (eq 6), and full lines are the limiting tangents at infinite dilution.

Table 2. Parameters A_A, B_A, and C_A of the Antoine Equation[a] for Pure Substances

substance	temp range/K	A_A	B_A	C_A	ref
1-propanol	333−378[b]	6.87065	1438.587	−74.598	19
1-butanol	296−391	6.76666	1460.309	−83.939	19
heptane	297−375	6.02633	1268.583	−56.054	20
octane	297−400	6.04231	1351.497	−64.014	20

[a] $\log P^S$ (kPa) $= A_A - B_A/(T(\mathrm{K})+C_A)$. [b] For temperatures lower than 333 K, the Wagner equation from ref 21 was used: $\ln(P^S/P_C) = (-8.53706\theta + 1.9621\theta^{1.5} - 7.6918\theta^{2.5} + 2.945\theta^5)T_C/T$, where $\theta = 1 - T/T_C$, $P_C = 5168$ kPa, and $T_C = 536.78$ K.

Table 3. Experimental Values of γ_1^∞ Determined in This Work Together with Their Estimated Uncertainties

solute (1)	solvent (2)	T/K	γ_1^∞	$\sigma(\gamma_1^\infty)$
1-propanol	heptane	303.15	36.2	0.5
		313.15	27.2	0.3
		323.15	21.2	0.5
		333.15	15.8	0.2
		343.15	12.5	0.1
1-propanol	octane	303.15	34.2	0.9
		313.15	26.5	0.7
		323.15	20.5	0.2
		333.15	16.2	0.1
		343.15	12.9	0.1
1-butanol	heptane	303.15	31.3	1.5
		313.15	24.5	0.5
		323.15	19.3	0.5
		333.15	14.6	0.4
		343.15	11.6	0.2
1-butanol	octane	303.15	32.1	0.8
		313.15	23.9	0.4
		323.15	18.4	0.2
		333.15	14.5	0.2
		343.15	11.2	0.4

The limiting activity coefficients of 1-propanol and 1-butanol in heptane and in octane determined at 10-K increments between the temperatures 303.15 K and 343.15 K are listed in Table 3. Each reported value of γ_1^∞ is an average of at least two independent measurements, and the given uncertainty (standard error) comprises both the propagation of random errors and the effect of possible systematic errors. As seen from Table 3, the limiting

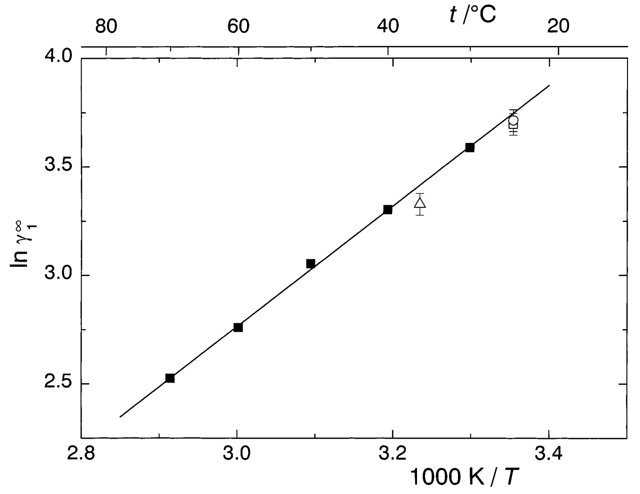

Figure 3. Temperature dependence of limiting activity coefficient of 1-propanol (1) in heptane (2): □, Rytting et al. (1978);[22] ○, Smirnova et al. (1987);[23] △, Shen et al. (1988);[24] ■, this work; solid line, fit of data from this work.

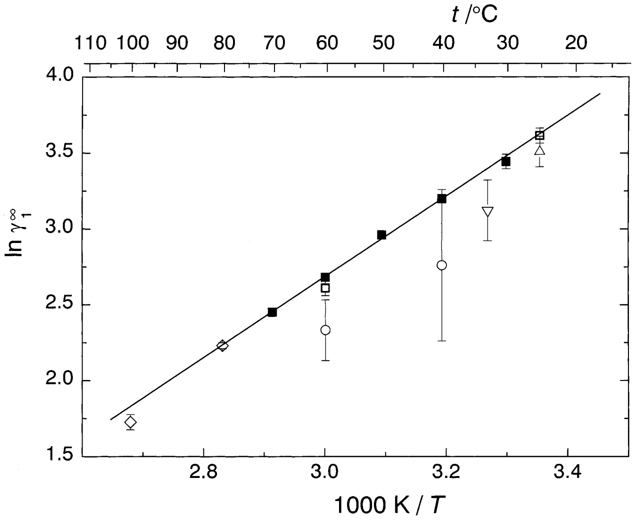

Figure 4. Temperature dependence of limiting activity coefficient of 1-butanol (1) in heptane (2): □, Pierotti et al. (1959);[25] ○, Hofstee et al. (1960);[26] △, Rytting et al. (1978);[22] ▽, Shen et al. (1988);[24] ◇, Pividal and Sandler (1990);[27] ■, this work; solid line, fit of data from this work.

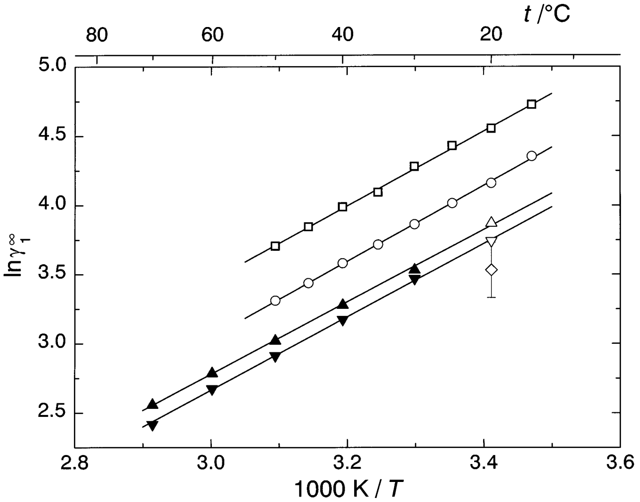

Figure 5. Temperature dependence of limiting activity coefficient of 1-alkanols (1) in octane (2). Our measurements by (i) the inert gas stripping method:[3] □, methanol; ○, ethanol; △, 1-propanol; ▽, 1-butanol; and (ii) by comparative tensimetry (this work): ▲, 1-propanol; ▼, 1-butanol. The headspace analysis measurement by Sagert and Lau:[28] ◇, 1-butanol. Lines are fits of our data.

Table 4. Values of $\bar{H}_1^{E\infty}$ Derived from Temperature Dependence of γ_1^∞ As Measured by Differential Tensimetry in This Work and Their Comparison with Published Calorimetrically Determined Values[a]

solute (1)	solvent (2)	this work	literature		
		$\bar{H}_1^{E\infty}$/kJ·mol^{-1}	$\bar{H}_1^{E\infty}$/kJ·mol^{-1}	T/K	ref
1-propanol	heptane	23.1 ± 0.3	24.2 ± 0.4	303.15	30
	octane	21.3 ± 0.1	-		
1-butanol	heptane	22.2 ± 0.5	24.5 ± 0.3	303.15	31
	octane	22.2 ± 0.3	23.9 ± 0.4	298.15	32

[a] Uncertainties given correspond to standard deviations.

activity coefficients were determined with a good accuracy (1−3) %. The correction for the vapor space of the cell, which is incorporated in eq 4, ranged from the negligible 0.2% (1-propanol systems at 303.15 K) to about 5% (1-butanol systems at 343.15 K).

Figures 3−5 show the temperature dependences of γ_1^∞ in the van't Hoff coordinates for the systems studied. Pronounced drops of γ_1^∞ with increasing temperature, seen in these figures, arise from breaking hydrogen bonds of the self-associated alkanol upon its infinite dilution in the inert alkane. Our data are plotted in the figures together with their straight-line fits which adequately represent the results. In addition, available literature values extracted from the Prague Limiting Activity Coefficients Inquiry Database (PLACID)[29] are involved in these plots for comparison. The uncertainties of literature data shown are standard errors as assigned in the process of their critical evaluation[2] and provided by PLACID. In Figure 3 for 1-propanol (1) + heptane (2), one can see that the fragmentary data which are at disposal from literature and the present measurements are in a reasonably good agreement. For 1-butanol (1) + heptane (2) in Figure 4, for which the literature information is little more extensive, the mutual agreement appears to be also quite good except for data of Hofstee et al.[26] and Shen et al.,[24] which are too low. These gas−liquid chromatography retention-time measurements are considered as clear outliers and labeled with considerably enhanced uncertainties. In Figure 5 for octane solvent systems displayed are our present tensimetric data together with those we measured by the inert gas stripping technique and reported in a previous communication.[3] The only experimental value from other researchers to compare with the present tensimetric data is that by Sagert and Lau[28] for 1-butanol at 293.15 K. While this value appears to be significantly lower than our measurements, both sets of our data obtained by the two different techniques match well, showing consistent temperature trends. For solutes from methanol to 1-butanol these trends are approximately parallel in the van't Hoff coordinates, the inferred values of partial molar excess enthalpies $\bar{H}_1^{E,\infty}$, and their standard deviations being (22.5 ± 0.4, 22.8 ± 0.2, 21.7 ± 0.3, and 22.0 ± 0.3) kJ·mol^{-1} for methanol, ethanol, 1-propanol, and 1-butanol, respectively. As seen from Table 4, the values of $\bar{H}_1^{E,\infty}$ derived from the fits of our tensimetric measurements of γ_1^∞ for 1-propanol (1) in heptane (2) and 1-butanol (1) in heptane (2) fall within the same range (22−23 kJ·mol^{-1}). Calorimetric measurements available in the literature for the systems studied in this work seem to be clustered slightly higher, the level of their consistency with our $\gamma_1^\infty(T)$ determinations being nevertheless quite fair.

In conclusion, it is to be stated that for the systematic study of limiting activity coefficients in a class of mixtures the application of different experimental techniques is indispensable in order to respect the suitability of the techniques for each particular case. If consistency of results measured by different methods is achieved, strong support is obtained for the reliability of the results. In this respect, the present measurements are believed to be reliable and improving our knowledge of γ_1^∞ in 1-alkanol + n-alkane mixtures. In fact, the experimental data released in this paper have been considered for the generation of recommended values of limiting activity coefficients for 1-alkanol + n-alkane systems and for the performance evaluation of methods for their correlation and prediction.[2]

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