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Limiting Activity Coefficients of Lower 1-Alkanols in *n*-Alkanes: Variation with Chain Length of Solvent Alkane and Temperature

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Limiting activity coefficients (γ_1^∞) of lower 1-alkanols (methanol, ethanol, 1-propanol, 1-butanol) in *n*-alkanes (hexane, heptane, octane, decane, dodecane, tetradecane, hexadecane) were systematically determined to obtain reliable information about their variation with the chain length of solvent alkane and temperature. Using the inert gas stripping technique, γ_1^∞ values were determined at 293.15 K and for methanol and ethanol in hexane, heptane, and octane at 5 K increments between 288 K and 323 K. The present data appear to be of higher accuracy than most previous measurements and are shown to be consistent with the solution-of-groups concept, the modified Flory−Huggins combinatorial of Kikic et al., and the calorimetric information on limiting partial molar excess enthalpies.

Introduction

The peculiar behavior of alcohol + hydrocarbon mixtures arising from the alcohol self-association has been traditionally attracting the interest of solution thermodynamicists. This evergreen subject not only presents a challenge for theory but also has lately become very important for oxygenate fuel formulations. In the past decade, the thermodynamic community targeted this theme by the IUPAC Project on Vapor−Liquid Equilibria in 1-Alkanol + *n*-Alkane Mixtures, under which several workshops were organized.[1−5] Our laboratory, which participated in this project, provided recommended values of limiting activity coefficients (γ_1^∞) for 1-alkanol (C_1-C_{10}) + *n*-alkane (C_5-C_{16}) systems, establishing the recommendation on the basis of a comprehensive critical compilation and our own extensive measurements.[6] The original γ_1^∞ data measured in our laboratory have not been released yet. The purpose of this paper is to present the first part of these data and give respective experimental details. Reported here are specifically the γ_1^∞ measurements (i) for lower 1-alkanol (C_1-C_4) solutes in *n*-alkane (C_6-C_{16}) solvents at ambient temperature and (ii) for methanol and ethanol in hexane, heptane, and octane at several temperatures between (288 and 323) K. These measurements allowed us to examine in a systematical way the effects of solute and solvent chain lengths as well as of temperature on the limiting activity coefficient of alkanol in alkane.

Experimental Section

Materials. Analar grade 1-alkanols were purchased from Lachema (Brno, Czech Rep.). To remove water, these materials were pretreated in different ways as follows: Methanol was refluxed with magnesium activated with iodine, ethanol was azeotropically distilled with benzene, and 1-propanol and 1-butanol were boiled with aluminum amalgam, each product being then fractionally distilled on a 1 m long packed column. Hexane (spectral grade), from Lachema, and heptane (puriss) and octane (puriss), both from Loba Chemie (Vienna, Austria), were distilled in the same manner. Decane, dodecane, tetradecane, and hexadecane, all obtained from Aldrich with stated purity greater than 99%, were subjected to a prolonged stripping by dry nitrogen to remove volatile impurities. Although the direct effect of the impurities on the limiting activity coefficient is, at the level of concentrations encountered, practically negligible, these impurities would otherwise greatly obscure the gas chromatographic monitoring of the solute contents in the equilibrium gas phase as carried out in the inert gas stripping measurement technique applied. The purities determined by gas chromatography were for all samples used for measurement better than 99.6%.

Apparatus and Procedure. The method of inert gas stripping (IGS) consists of measuring the rate of solute elution as an entraining inert gas is passed through a highly dilute solution ($x_1 < 10^{-3}$) in the equilibrium cell. We have applied the IGS technique to a number of systems, and the experimental setup and procedure used in the present work are similar to those we have described previously.[7,8]

Two inert gas stripping apparatuses were employed to measure limiting activity coefficients in this work. The first apparatus was designed around a Chrom-61 gas chromatograph (GC) (Laboratorní Přístroje, Praha). This dual-channel GC is equipped with a flame ionization detector and a manually operated six-port gas sampling valve (Chemoprojekt Satalice, Czech Republic) which is housed in a heated box placed around the column injection port and kept at (140 ± 1) °C. The second IGS apparatus was designed around a computer-interfaced Hewlett-Packard gas chromatograph, Model 5890 II, with a flame ionization detector. This chromatograph is equipped with a pneumatic six-port gas sampling valve which is housed in an independently heated zone of the GC and kept at 160 °C.

The equilibrium stripping cell is an all-glass jacketed device composed of the presaturator and the dilutor which were destined to hold the solvent and the dilute solution, respectively. The presaturator was filled only in the case of the volatile solvents (hexane, heptane, and octane), since in other cases solvent losses were negligible (<0.1%). Into

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the dilutor, the solvent was loaded gravimetrically, and the solute was added volumetrically by a chromatographic syringe. Then the contents were vigorously mixed with an efficient magnetic stirrer. The cell was thermostated by a water circulating bath to ±0.02 K. The temperature of the water bath was measured with a calibrated standard mercury thermometer (Karl Schneider, Wertheim, Germany) to ±0.01 K. Two equilibrium cells of similar design,[7] but of different capacities (17 cm^3 and 47 cm^3), were used in this work to cope well with the range of solute volatilities (Henry's law constants). The constant flow of stripping gas (N_2) was supplied by the second channel of the GC and introduced into the cell through a fine porosity glass tip which was found to disperse the stripping gas into bubbles of small diameter (1 mm). Before entering the cell, the stripping gas was dried by a silica gel column and brought to the temperature of the solution by passing through a thermostating coil immersed in the bath. The stripping gas flow rate was measured, before and after each experiment, with a thermostated soap-bubble flow meter. Typical flow rates used for the measurements of the systems studied in this work were from (8 to 24) $cm^3 \cdot min^{-1}$, which lead to small relative rates of the solute elution (approximately 0.01 min^{-1}). The flow rates showed a very good stability and could be determined to ±0.3%. The cell outlet is connected via Teflon glass-to-metal joints and a heated (140 °C) transfer line to the respective port of the gas sampling valve. The volume of the sampling loop used was either (500 or 250) μL. The process of the solute elution was monitored during (2.5 to 4) h, the sampling interval being from (5 to 18) min.

To separate the components, the following short glass or stainless steel packed GC columns were used depending on the alkane solvent: Porapak Q (0.35 m) for hexane and heptane, Chromosorb 101 (0.35 m) for octane and decane, Chromosorb 101 (0.10 m) for dodecane and tetradecane, and 5% Carbowax 20M on Inerton Super support (1 m) for hexadecane (not eluted). By optimizing oven temperatures and carrier gas flow rates individually for each mixture, peak tailing was suppressed and reasonably narrow solute peaks were obtained. For the Chrom-61 GC, detector responses were quantified by an electronic integrator (CI-100, Laboratorní Přístroje). The signal acquisition and integration for HP5890 GC were achieved by the interfaced personal computer using the HP ChemStation software.

Table 1. Experimental γ_1^∞ of 1-Alkanols (1) in *n*-Alkanes (2) at 293.15 K Determined in This Work and Their Comparison with Results from the Literature

		this work		literature		
solute (1)	solvent (2)	γ_1^∞	$\sigma(\gamma_1^\infty)$	γ_1^∞	method[a]	ref
methanol	hexane	104.0	3.0	109.5[b]	IGS	14
				134.5	IGS	15
	heptane	97.5	2.0	80	GLC	16
				115.3	IGS	15
	octane	95.1	1.9	80	GLC	16
				101.5	IGS	15
	decane	84.1	1.7	75.6	IGS	17
	dodecane	80.0	1.2			
	tetradecane	74.7	1.0	61.7	IGS	18
	hexadecane	69.9	1.0	72.3[b]	TENS	19
				58	IGS	18
ethanol	hexane	69.9	1.4	71.1[c]	IGS	20
				75.1	IGS	21
	heptane	67.9	1.3	51	GLC	16
				75.1	IGS	21
				72.7[b]	IGS	14
				48.6[d]	HSA	22
	octane	64.1	1.3	50.5	GLC	16
				67.8	IGS	21
	decane	58.4	1.2	49.2[b]	HSA	23
				60.3	IGS	21
	dodecane	55.9	0.8			
	tetradecane	53.4	0.8	51.9	IGS	18
	hexadecane	50.4	1.0	50.7[b]	TENS	24
				45.8	IGS	18
1-propanol	octane	48.0	0.8			
	decane	46.2	1.4			
	dodecane	44.4	1.3			
	tetradecane	38.9	1.2	40.2	IGS	18
	hexadecane	37.7	1.1	37.0[b]	HSA	25
				34.9	IGS	18
1-butanol	octane	42.2	1.3	34.2	HSA	26
	decane	39.6	0.8			
	dodecane	38.7	0.8			
	tetradecane	35.7	0.7	30.7	IGS	18
	hexadecane	34.5	0.7	32.5[b]	HSA	25
				23.5	IGS	18

[a] IGS, inert gas stripping; GLC, retention time gas−liquid chromatography; TENS, tensimetry; HSA, headspace analysis. [b] Converted to 293.15 K from the original measurement at 298.15 K using $\bar{H}_1^{E,\infty} = 23$ kJ·mol^{-1}. [c] Converted to 293.15 K from the original measurement at 297.15 K using $\bar{H}_1^{E,\infty} = 23$ kJ·mol^{-1}. [d] Converted to 293.15 K from the original measurement at 293.45 K using $\bar{H}_1^{E,\infty} = 23$ kJ·mol^{-1}.

Results and Discussion

The limiting activity coefficients were determined from the IGS measurements using the second-order approximation formula[7,9]

$$\gamma_1^\infty = n_2^\circ RT(P_1^s D)^{-1}(-\mathrm{d}\ln A_1/\mathrm{d}t)\beta\prod_{i=1}^{4} k_i \qquad (1)$$

where n_2° is the molar amount of the alkane solvent loaded into the stripping cell, D is the flow rate of pure stripping gas at temperature T and pressure P of the cell, P_i^s are the pure component vapor pressures, d ln A_1/dt is the slope of the semilogarithmic plot of solute peak area A_1 against time t, and $\beta = 1 - P_2^s/P$ (stripping gas presaturated with solvent vapor) or $\beta = 1$ (no presaturation). The last term in eq 1, which is close to unity (for systems studied in this work, $0.98 < \prod_{i=1}^{4} k_i < 1.05$), comprises correction factors k_i accounting for the following four effects: (1) change of the stripping gas flow rate due to the saturation in the cell, (2) removal of the solvent from the dilution cell due to its volatility, (3) amount of the solute in the vapor space, and (4) vapor-phase nonideality. The correction factors were calculated as described elsewhere.[7,9] For our calculations, vapor pressures (except for 1-propanol and 1-butanol)[10] and the molar volumes of pure liquids were taken from the CDATA database,[11] and the virial coefficients were obtained from Hayden−O'Connell correlation[12] with parameters from Prausnitz et al.[13] and the CDATA database. For the present systems, the individual correction factors k_i were in the following ranges: $0.98 < k_1 < 1.0$; $0.9996 < k_2 < 1$; $1.01 < k_3 < 1.05$; $0.98 < k_4 < 1.02$.

The limiting activity coefficients determined at 293.15 K for the four lower 1-alkanols (C_1-C_4) in a series of *n*-alkanes (C_6-C_{16}) are given in Table 1, and those for methanol and ethanol in hexane, heptane, and octane determined additionally at 5 K increments between the temperatures 288.15 K and 323.15 K are given in Table 2. 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. For comparison, listed in Table 1 are also available data from the literature. Note that far less information is at our

Table 2. Temperature Dependence of γ_1^∞ for Methanol and Ethanol in Hexane, Heptane, and Octane

T/K	γ_1^∞	$\sigma(\gamma_1^\infty)$	γ_1^∞	$\sigma(\gamma_1^\infty)$	γ_1^∞	$\sigma(\gamma_1^\infty)$
			Methanol (1) +			
	Hexane (2)		Heptane (2)		Octane (2)	
288.15	125.5	3.0	115.8	3.0	112.9	3.0
293.15	104.0	3.0	97.5	2.0	95.1	1.9
298.15	90.5	2.0	81.8	2.5	84.0	2.5
303.15	78.2	1.7	71.4	2.0	72.3	2.0
308.15	67.8	1.7	60.7	1.5	60.0	1.5
313.15	58.3	1.5	53.8	1.3	54.0	1.5
318.15	50.7	1.3	46.5	1.0	46.8	1.0
323.15			40.8	1.0	40.7	0.9
$\bar{H}_1^{E,\infty}$/kJ·mol^{-1}	22.7 ± 0.3		22.9 ± 0.2		22.5 ± 0.4	
			Ethanol (1) +			
	Hexane (2)		Heptane (2)		Octane (2)	
288.15	83.7	2.0	83.4	2.0	77.8	2.0
293.15	69.9	1.4	67.9	1.3	64.1	1.3
298.15	60.1	1.5	58.8	1.5	55.4	1.4
303.15	51.5	1.5	49.7	1.2	47.6	1.2
308.15	43.8	1.1	42.2	1.1	41.1	1.0
313.15	38.3	1.0	37.6	1.0	35.9	0.9
318.15	33.9	0.8	32.0	0.8	31.1	0.8
323.15			28.1	0.8	27.4	0.7
$\bar{H}_1^{E,\infty}$/kJ·mol^{-1}	23.0 ± 0.3		23.7 ± 0.4		22.8 ± 0.2	

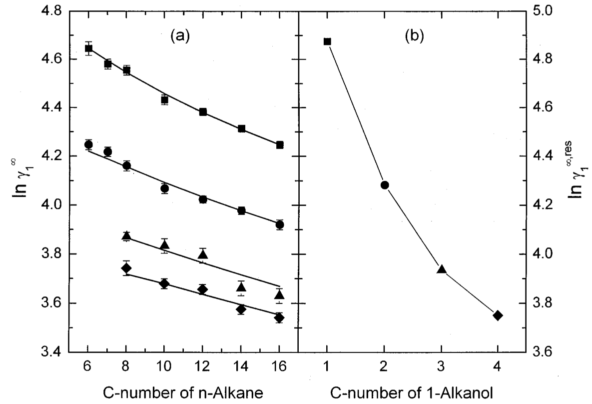

Figure 1. Limiting activity coefficients of 1-alkanols (1) in n-alkanes (2) at 293.15 K: (a) γ_1^∞ as a function of carbon number of n-alkane; (b) $\gamma_1^{\infty,\mathrm{res}}$ as a function of carbon number of 1-alkanol. Points are data from this work: ■, methanol; ●, ethanol; ▲, 1-propanol; ◆, 1-butanol. Lines in part a are fits by eq 2, and those in part b just aid visualization.

disposal for 1-propanol and 1-butanol systems than for methanol and ethanol ones and that dodecane systems have not been previously studied. Literature data are considerably scattered, this fact being reflected by rather large disparities observed between the present data and some literature values. On the other hand, a very good agreement of our results with the highly accurate tensimetric measurements of Tucker and Christian[19,24] and with the reliable headspace analysis measurements of Dallas and Carr[25] provides strong support for considering the present results to be more accurate than most information from the literature.

In Figure 1a our values of ln γ_1^∞ for 1-alkanols in alkanes at 293.15 K are plotted as a function of the solvent alkane chain length. The lines shown are fits of the data by the equation

$$\ln \gamma_1^\infty = L_1 + 1 - (r_1/r_2)^{2/3} + \ln(r_1/r_2)^{2/3} \tag{2}$$

where r_1 and r_2 are the UNIQUAC size parameters of the respective 1-alkanol and n-alkane and L_1 is an adjustable parameter specific for each solute. This equation stems from the solution-of-groups concept[27] and employs the modified Flory−Huggins combinatorial proposed by Kikic et al.[28] As seen, eq 2 describes the effect posed by the solvent alkane chain length on γ_1^∞ very well, giving a perfect fit of our data. The calculated values of parameter L_1, which represents the residual part of the limiting activity coefficient (ln $\gamma_1^{\infty,\mathrm{res}}$), are plotted as a function of alkyl chain length of 1-alkanol in Figure 1b. While the effect of the solvent alkane chain length on γ_1^∞ is entirely combinatorial, that of alkyl chain length of 1-alkanol on ln $\gamma_1^{\infty,\mathrm{res}}$, following an exponential decay pattern, originates from the dilution of the hydroxy group by aliphatic groups. Smooth regular variations of ln γ_1^∞ with carbon numbers of both the solute alkanol and the solvent alkane give an additional proof of the quality of the present data.

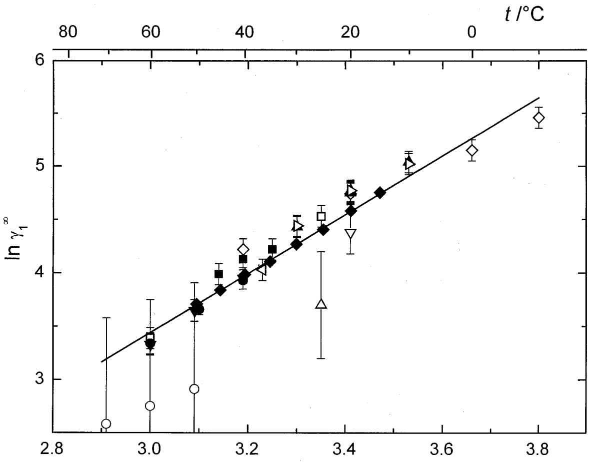

Figure 2. Temperature dependence of limiting activity coefficient of methanol (1) in heptane (2): □, Pierotti et al. (1959);[30] ○, Tochigi and Kojima (1976);[31] △, Rytting et al. (1978);[32] ▽, Thomas et al. (1982);[16] ◇, Warsow (1987);[17] triangle pointing left, Shen et al. (1988);[33] triangle pointing right, Wobst (1988);[21] ■, Bao et al. (1990);[14] ●, Hauschild and Knapp (1991);[34] ▲, Wobst et al. (1992);[15] ▼, Dallinga et al. (1993);[35] ◆, this work; —, fit of data from this work.

Pronounced drops of γ_1^∞ with increasing temperature, seen in Table 2, arise from breaking hydrogen bonds of the self-associated alkanol upon its infinite dilution in the alkane. Straight line fits in the van't Hoff coordinates

$$\ln \gamma_1^\infty = A + B/T \tag{3}$$

adequately represent the results, yielding reliable values for the limiting partial molar excess enthalpy. The values of $\bar{H}_1^{E,\infty}$ together with their standard deviations as derived from the fits using the Gibbs−Helmholtz equation

$$\bar{H}_1^{E,\infty} = -RT^2(\mathrm{d} \ln \gamma_1^\infty/\mathrm{d}T) = RB \tag{4}$$

are listed also in Table 2. Ranging from 22.5 kJ·mol^{-1} to 23.7 kJ·mol^{-1}, the $\bar{H}_1^{E,\infty}$ values can be considered to be approximately uniform for all six systems studied, being about 23 kJ·mol^{-1} on average. This result is in excellent agreement with the highly accurate calorimetric measurements of Stokes and Burfitt,[29] who reported for $\bar{H}_1^{E,\infty}$ of ethanol in hexane 23.6 kJ·mol^{-1}, 23.2 kJ·mol^{-1}, and 22.2 kJ·mol^{-1} at 283.15 K, 298.15 K, and 318.15 K, respectively.

Figures 2−4 illustrate the temperature dependences of γ_1^∞ of 1-alkanols in n-alkanes for three of the systems studied. Our present data are plotted here together with

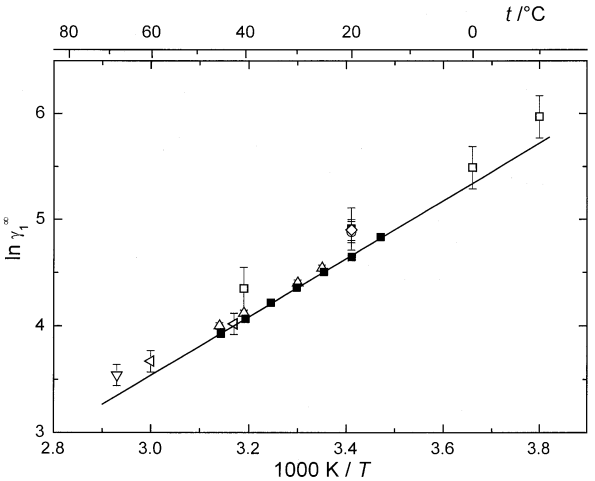

Figure 3. Temperature dependence of limiting activity coefficient of methanol (1) in hexane (2): □, Warsow (1987);[17] ○, Wobst (1988);[21] △, Bao et al. (1990);[14] ▽, Trampe and Eckert (1990);[36] ◇, Wobst et al. (1992);[15] triangle pointing left, Dallinga et al. (1993);[35] ■, this work; —, fit of data from this work.

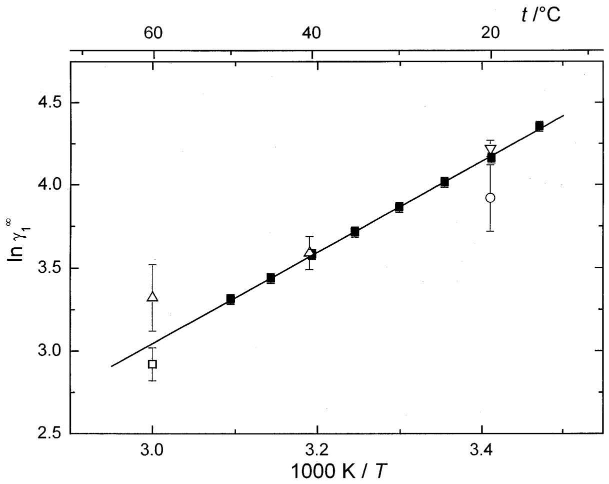

Figure 4. Temperature dependence of limiting activity coefficient of ethanol (1) in octane (2): □, Belfer (1972);[37] ○, Thomas et al. (1982);[16] △, Belfer and Locke (1984);[38] ▽, Wobst (1988);[21] ■, this work; —, fit of data from this work.

their fits and available literature values which were extracted from the Prague Limiting Activity Coefficients Inquiry Database (PLACID),[39] a continuously updated database representing a comprehensive collection of experimental values of limiting activity coefficients (currently containing more than 40 000 γ_1^∞ values). The uncertainties of the literature data are standard errors as assigned in the process of their critical evaluation[6] and provided by PLACID. Methanol (1) + heptane (2) in Figure 2 is an example of a system where ample literature information is at our disposal. The mutual agreement of all data appears to be reasonably good, the only exceptions being the data of Tochigi and Kojima[31] and Rytting et al.,[32] which are considered as clear outliers and labeled with considerably enhanced uncertainties. An analogous situation is seen in Figure 3 for methanol (1) + hexane (2) except that there are no apparent outliers. Nevertheless, it is to be noted that the data of Warsow,[17] Wobst,[21] and Wobst et al.,[15] which follow approximately the same temperature trend as that of our data and the data of Bao et al.[14] (but the γ_1^∞ values[15,17,21] are about 20% higher), all have the same origin from the former TH Merseburg laboratory. For octane systems, as exemplified in Figure 4 for ethanol (1) + octane (2), there exist only fragmentary data in the literature, and thus the present data greatly enhance our knowledge.

In conclusion, it is to be stated that the present measurements of γ_1^∞ of 1-alkanols in *n*-alkanes are believed to be reliable and of higher accuracy than most measurements reported previously in the literature. As demonstrated, our measurements are internally consistent, following smoothly plausible homologous trend patterns and temperature variations. 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.[6]

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