

## Applications of the LFAS theory to VLE and volumetric properties in 1-alkanol+n-alkane mixtures

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**Abstract** - The present work is an extension of our previous work on the thermodynamics of associated solutions. Emphasis is given on vapor-liquid equilibrium calculations over an extended range of external conditions and calculations of excess volumes, excess volumes at infinite dilution and densities at moderately high pressures (our own experimental data) in 1-alkanol+n-alkane mixtures. The entropic correction term in the chemical potential is reconsidered and consistent expressions are, now, derived. The advantages and the limitations of our approach are discussed.

### INTRODUCTION

The overwhelming majority of theories of associated solutions, in common use, are theories of the liquid state their applicability being confined to a limited range of liquid density. Recently (ref. 1) we presented a new theoretical framework, the Lattice-Fluid theory of Associated Solutions (LFAS) which, in addition to other features, is applicable to both the liquid and the gaseous state. LFAS theory is particularly suited for studying vapor-liquid equilibria in associated mixtures over extended ranges of external temperature and pressure.

In ref. 1, emphasis was given on pure component properties, heats of mixing and volumes of mixing in 1-alkanol+n-alkane mixtures. The main purpose of the present work is to apply LFAS theory to calculations of vapor-liquid equilibria, mixture densities at high pressures and excess volumes at infinite dilution for the same class of systems. For this purpose all needed extensions of the formalism are presented. These applications are preceded by a short introduction to the essentials of LFAS theory.

### LFAS THEORY

Hydrogen bonding in alcoholic systems is usually treated as the consecutive formation of large linear polymeric complexes ( $A_1, A_2, \dots, A_i, \dots$ ) with one or more equilibrium constants for the association reaction:  $A_i + A_j = A_{i+j}$ . This treatment leads to expressions for the "chemical" or "association" contribution to the configurational properties of the system. To this "chemical" term is, then, added a "physical" term which accounts for the existence of non-negligible intermolecular interactions in the mixture (ref. 2). LFAS theory uses Flory's model for athermal polydisperse polymer solutions (ref. 3) for the chemical term and the Lattice-Fluid theory of fluid mixtures (ref. 4,5) for the physical term. The basic assumption of LFAS theory is that the association constant for the above association reaction is independent of  $i$  and  $j$  while the energy,  $E_H$ , the entropy,  $S_H$ , and the volume,  $V_H$ , of formation of a hydrogen bond are independent of temperature and degree of association and are the same for all 1-alkanols.

By combining, consistently, the Lattice-Fluid theory (ref. 4,5) and Flory's theory (ref. 3) the following expression is derived for the association constant:

$$K = \bar{v} r_1 \frac{\phi_{A_{i+j}}}{\phi_{A_i} \phi_{A_j}} \frac{ij}{i+j} = \frac{r_1}{\bar{\beta}} K_F = \exp \left[ - \frac{(E_H + PV_H - TS_H')}{RT} \right] \quad (1)$$

$\bar{v}$  and  $\bar{\beta}$  are the reduced volume and density ( $\bar{v}=1/\bar{\beta}$ ) of the system while  $r_1$  is the number of segments of the alkanol molecule. According to the Lattice-

Fluid theory each fluid is characterized, besides  $r$ , by two additional scaling constants: the close-packed volume,  $v^*$ , and the interaction energy,  $\epsilon$ , or the segmental lattice energy,  $\epsilon^* = \epsilon s/2$ ,  $s$  being the number of intermolecular contacts per segment - a measure of the "surface to volume" ratio (ref. 5). An alternative pair of additional scaling constants is the characteristic temperature  $T^* = \epsilon^*/R$  and the characteristic pressure,  $P^* = \epsilon^*/v^*$ .

If our mixture consists of  $N_1$  molecules of 1-alkanol and  $N_2$  molecules of  $n$ -alkane with  $N_{Ai}$   $i$ -mer alkanol complexes ( $i=1,2,\dots$ ), the segment fraction  $\phi_{Ai}$  of the  $i$ -mer is given by

$$\phi_{Ai} = \frac{ir_1 N_{Ai}}{\sum_{j=1}^{\infty} jr_1 N_{Aj} + r_2 N_2} = \frac{ir_1 N_{Ai}}{r_1 N_1 + r_2 N_2} = \frac{ir_1 N_{Ai}}{rN} \quad (2)$$

where  $N=N_1+N_2$  and  $r$  is the average number of segments per molecule. If  $\phi_1$  is the overall segment fraction of 1-alkanol in the mixture,  $\phi_{A1}$  for the free monomer is given by

$$\phi_{A1} = \frac{1+2K_F\phi_1 - (1+4K_F\phi_1)^{1/2}}{2\phi_1 K_F^2} \quad (3)$$

$\phi_{Ai}$  for the  $i$ -mer complex is then obtained by combining equations (1) and (3).

The scaling constants in our mixture are obtained by applying appropriate combining and mixing rules. Thus

$$v^* = \phi_1 v_1^* + \phi_2 v_2^* + 2\phi_1 \phi_2 v_{12}^* \quad (4)$$

where

$$v_{12}^* = \xi_{12} \left( \frac{v_1^{*1/3} + v_2^{*1/3}}{2} \right)^3 \quad (5)$$

and

$$\epsilon^* = \phi_1 \epsilon_1^* + \phi_2 \epsilon_2^* - \phi_1 \phi_2 X_{12}^{RT} \quad (6)$$

where  $\vartheta_2$  is the overall surface fraction of component 2 given by

$$\vartheta_2 = \frac{\phi_2 s_2 / s_1}{\phi_1 + \phi_2 s_2 / s_1} \quad (7)$$

and

$$X_{12} = \frac{\epsilon_1^* + s_1 / s_2 \epsilon_2^* - 2 \sqrt{s_1 / s_2} \epsilon_{12}^*}{RT} = \frac{s_1}{s_2} X_{21} \quad (8)$$

where

$$\epsilon_{12}^* = \zeta_{12} (\epsilon_1^* \epsilon_2^*)^{1/2} \quad (9)$$

$\zeta_{12}$  and  $\xi_{12}$  are the Lattice-Fluid binary parameters of the mixture. In direct analogy with the pure fluids, the scaling temperature and pressure for the mixture are defined by

$$T^* = \epsilon^*/R \quad \text{and} \quad P^* = \epsilon^*/v^* \quad (10)$$

while the reduced quantities in the mixture are

$$\tilde{T} = T/T^*, \quad \tilde{P} = P/P^*, \quad \tilde{v} = v/v^* \quad (11)$$

$v$  being the segmental volume.  $\beta$  (or  $\tilde{v}$ ) is obtained from the LFAS equation of state (ref. 1)

$$\beta^2 + \tilde{P} + \tilde{T} [\ln(1-\beta) + (1-1/r')\beta] = 0 \quad (12)$$

where

$$1/r' = 1/r - K_F \phi_{A1} \phi_1 / r_1 \quad (13)$$

The expressions for the chemical potential for the selfassociated and the inert component are

$$\begin{aligned} \frac{\mu_1}{RT} = -\frac{\mu_{A1}}{RT} = & \ln \phi_{A1} + K_F \phi_{A1} \phi_1 + \phi_2 (1-r_1/r_2) + r_1 \tilde{\rho} \phi_2^2 x_{12} + \ln(\tilde{\rho}/\omega_{A1}) \\ & + r_1 (\tilde{\nu}-1) \ln(1-\tilde{\rho}) + r_1 \tilde{P} \tilde{\nu} [2(\phi_2 v_{12}^* + \phi_1 v_1^*) / v^* - 1] / \tilde{T} - r_1 \tilde{\rho} / \tilde{T}_1 \end{aligned} \quad (14)$$

$$\begin{aligned} \frac{\mu_2}{RT} = & \ln \phi_2 + K_F \phi_{A1} \phi_1 r_2 / r_1 + \phi_1 (1-r_2/r_1) + r_2 \tilde{\rho} \phi_1^2 x_{21} + \ln(\tilde{\rho}/\omega_2) \\ & + r_2 (\tilde{\nu}-1) \ln(1-\tilde{\rho}) + r_2 \tilde{P} \tilde{\nu} [2(\phi_1 v_{12}^* + \phi_2 v_2^*) / v^* - 1] / \tilde{T} - r_2 \tilde{\rho} / \tilde{T}_2 \end{aligned} \quad (15)$$

$\omega_i$  is a constant characteristic of the molecular entity  $i$ . The corresponding expressions for pure liquids may easily be obtained from equations (14) and (15) ( $\phi_1=1$  and  $\phi_1=0$  respectively).

Volumes of mixing and heats of mixing are given by

$$V^E/N = r(\tilde{\nu} v^* - \phi_1 \tilde{\nu}_1 v_1^* - \phi_2 \tilde{\nu}_2 v_2^*) + x_1 V_H (K_F \phi_{A1} - K_F^O \phi_{A1}^O) \quad (16)$$

and

$$H^E/N = -r(\tilde{\rho} \epsilon^* - \phi_1 \tilde{\rho}_1 \epsilon_1^* - \phi_2 \tilde{\rho}_2 \epsilon_2^*) + x_1 E_H (K_F \phi_{A1} - K_F^O \phi_{A1}^O) + P V^E/N \quad (17)$$

where  $x_1$  is the mole fraction of 1-alkanol in the mixture. In the above equations superscript  $o$  refers to quantities of the pure fluid state.

## APPLICATIONS

### Vapor-liquid equilibrium

As mentioned earlier, in this Section we will, first, apply LFAS model to vapor-liquid equilibrium calculations. Besides equality of temperature and pressure, phase equilibrium requires equality of the chemical potential of all components in all coexisting phases. As pointed out in our previous work (ref. 1,5), equations (14) and (15) for the chemical potential are not entirely satisfactory when applied to highly non-ideal systems. Thus a Flory-type entropic correction was incorporated in these expressions which in the case of the associated component 1 was

$$-r_1 \phi_2^2 q_{12} \quad (18)$$

$q_{12}$  being the entropic correction binary parameter. As discussed previously (ref. 1,5), this expression is plausible for a theory of the liquid state such as Flory's theory (ref. 6). For a theory, however, valid for both the liquid and the vapor phase, such as the present Lattice-Fluid theory, the above expression must be reconsidered. Careful examination of the expression for the potential energy of the mixture and consistent application of Guggenheim's proposition (ref. 7) (replacement of interaction energy with interaction free energy) leads to the following modification of the expression(18):

$$-\tilde{\rho} r_1 \phi_2^2 q_{12} \quad (19)$$

Flory's proposition, expression (18), amounts to assuming that  $\tilde{\rho} q_{12} (=Q_{12})$  is a constant for a given liquid mixture. It is obvious that in vapor-liquid equilibrium calculations  $\tilde{\rho} q_{12}$  is orders of magnitude different in the vapor and in the liquid phase and Flory's assumption cannot be valid. Adoption of expression (19) implies, however, that the entropic parameter  $q_{12}$  influences not only the chemical potential but also the excess enthalpy through the equation of state. If one wishes to use the present model only for the liquid state, Flory's proposition - equation (18) - leads to some simplifications in the calculations.

We have applied the present model to vapor-liquid equilibria in a number of 1-alkanol+n-alkane mixtures using expression (19). The interaction binary parameter  $\zeta_{12}$  (or  $X_{12}$ ) was adjusted

Table 1 : Binary Parameters for 1-Alkanol(1) + n-Alkane(2) Mixtures

System	$\zeta_{12}$	$\epsilon_{12}$	$q_{12}$	$s_2/s_1$
Methanol-Hexane	1.039	1.000	-0.262	0.95
Ethanol-Hexane	1.019	0.9944	-0.145	0.97
Ethanol-Heptane	1.019	0.9960	-0.145	0.95
Ethanol-Octane	1.022	0.9975	-0.145	0.93
Decanol-Pentane	1.001	1.0082	-	1.00
Propanol-Hexane	0.9962	1.0023	-	1.00
Butanol-Hexane	0.9965	1.0018	-	1.00
Hexanol-Hexane	0.9982	1.0020	-	1.00
Octanol-Hexane	0.9990	1.0024	-	1.00
Decanol-Hexane	1.000	1.0032	-	1.00
Hexanol-Heptane	0.9950	1.0006	-	1.00
Octanol-Heptane	0.9994	1.0021	-	1.00
Decanol-Heptane	0.9994	1.0025	-	1.00
Dodecanol-Heptane	0.9994	1.0033	-	1.00
Decanol-Octane	1.0022	1.0024	-	1.00
Decanol-Decane	1.0013	1.0013	-	1.00

Table 2 : Average Absolute Per Cent Deviation (AAD) of Equilibrium Pressure and Mean Absolute Deviation (MAD) of Vapor Composition.

System	Temperature/K	$\Delta P$ AAD	$\Delta y$ MADx100
Methanol-Hexane	308.15-333.15	1.97	1.74
Ethanol-Hexane	303.15-328.38	2.37	2.56
Ethanol-Heptane	313.15-333.15	4.19	1.53
Ethanol-Octane	318.15-348.15	5.21	1.31

so that the excess enthalpy of the mixture (ref. 8) be correlated appropriately. The volume parameter  $\epsilon_{12}$  was adjusted so that the excess volume of the mixture (ref. 9) be correctly calculated. The entropic  $q_{12}$  parameter was determined, mainly, by the consistent vapor-liquid equilibrium data (ref. 10). It must be stressed that a single set of parameters was used in the complete range of the external conditions. Values of these parameters for some of the studied systems are given in Table 1. In Table 2 are reported the average absolute percent deviation of pressure and the mean absolute deviation of the vapor composition for some representative systems. Two typical examples of the performance of the model are given in Figs.1 and 2 showing vapor-liquid equi-

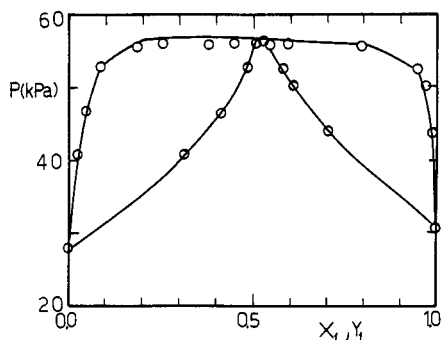


Fig. 1. Isothermal (308.15 K) vapor-liquid equilibria for the system n-hexane(1)-methanol(2). O: Experimental data (ref. 10); — Calculated by the present model.

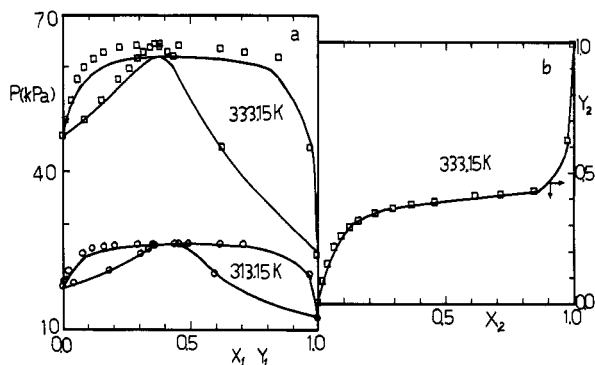


Fig. 2. Isothermal vapor-liquid equilibria for the system n-heptane(1)-ethanol(2). a: P-x,y diagrams at 313.15 K and 333.15 K. b: y-x diagram at 333.15 K. Symbols as in Fig. 1.

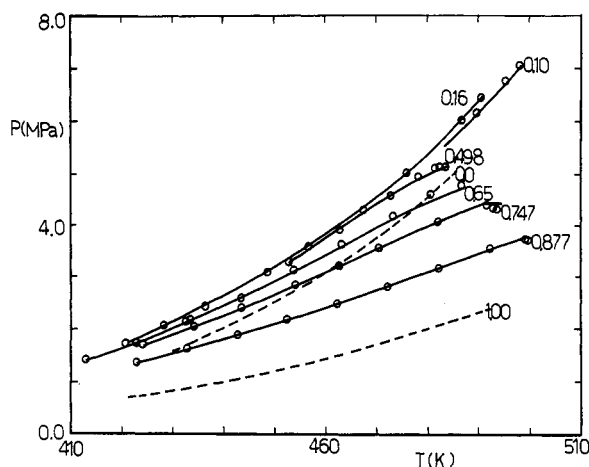


Fig. 3. Experimental (ref. 14) and calculated bubble pressures for the system n-hexane(1)-methanol(2) for various liquid mixture compositions.

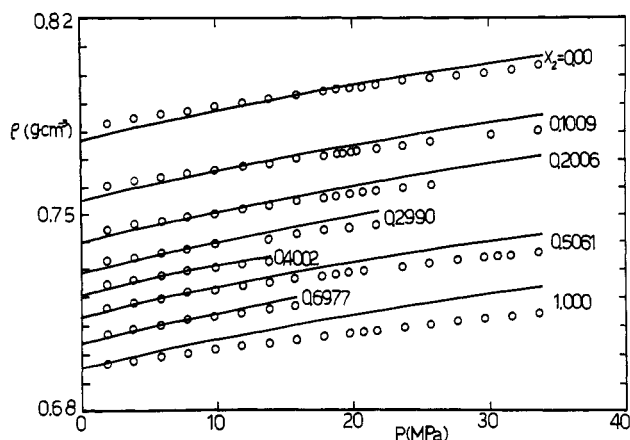


Fig. 4. Experimental (circles) and calculated (solid curves) densities of the system ethanol(1)+n-octane(2) at moderately high pressures for various mixture compositions.

librium calculations for the mixtures methanol(1)+n-hexane(2) and ethanol(1)+n-heptane(2) respectively. The performance of the model is comparable (ref. 11) with that of the biparametric PRSV equation of state (ref. 12) and Gibbons-Laughton equation of state (ref. 13) which were used only for the correlation of the vapor-liquid equilibrium data.

Using the same set of binary parameters for the system methanol+n-hexane reported in Table 1, we examined the predictions of the model for the vapor-liquid equilibria of the system at higher temperatures and pressures. In Fig. 3 are compared experimental (ref. 14) and predicted bubble pressures for the system up to the critical region. The agreement is quite satisfactory.

### High pressure densities

In a further application we compared experimental and predicted densities of ethanol(1)+n-octane(2) mixtures at moderately high pressures. The set of binary parameters used was the same with the set used in VLE calculations and reported in Table I. The experimental data were obtained in our Laboratory. The equipment used consisted of a high pressure density meter model DMA512 of Anton Paar, a home made compression cell equipped with a pressure transducer model PDCR610 of Druck and a dead-weight tester model MTU600 of Metronex. The compression cell consisted of an outer stainless-steel cylinder along the axis of which was located a thin-wall teflon tube containing the sample. Outside the teflon tube was the compression fluid—a commercial hydraulic fluid. The equipment was calibrated with highly accurate experimental high pressure densities of water (ref. 15) and methanol (ref. 16). The estimated experimental uncertainty is less than 0.02%. Experimental and calculated by the present model densities are compared in Fig. 4. As observed the agreement is only qualitative. This was expected since the original Lattice-Fluid model (ref. 17) can describe only qualitatively the pressure and temperature dependence of densities of pure compounds. This is clearly shown in Fig. 4 for the case of n-octane ( $x=1.000$ ).

### Excess volumes at infinite dilution

In a third application we extended the formalism of the model and derived expressions for the excess volumes at infinite dilution which are defined by

$$V_i^{E\infty} = \lim_{N_i \rightarrow 0} \left( \frac{\partial V^E}{\partial N_i} \right)_{T,P,N_j \neq i} \quad (20)$$

Combination of equations (20) and (16) leads to the following expressions for the excess volumes at infinite dilution;

$$V_1^{E\infty} = 2r_1 \bar{v}_2 (v_{12}^* - v_2^*/2) - r_1 \bar{v}_1 v_1^* - r_1 v_2^* \beta_2^* \tilde{T}_2 \psi_1^\infty - V_H K_F^O \phi_{A1}^O \quad (21)$$

$$V_2^{E\infty} = 2r_2 \bar{v}_1 (v_{12}^* - \frac{v_1^*}{2}) - r_2 \bar{v}_2 v_2^* + r_2 v_1^* \beta_1^* \tilde{T}_1 \psi_2^\infty + V_H \frac{r_2}{r_1} (1 + \delta_1 \beta_1^* \tilde{T}_1 \psi_2^\infty) A \quad (22)$$

where

$$A = K_F^O \phi_{A1}^O - 1 + 1 / \sqrt{1 + 4K_F^O} \quad (23)$$

$$\beta_1^* P_1^* = \bar{v}_1^2 / [T_1 \bar{v}_1 (\frac{1}{\bar{v}_1 - 1} + \frac{1}{r_1 \sqrt{1 + 4K_F^O}}) - 2] \quad (24)$$

$$\beta_2^* P_2^* = \bar{v}_2^2 / [\tilde{T}_2 \bar{v}_2 (-\frac{1}{\bar{v}_2 - 1} + \frac{1}{r_2}) - 2] \quad (25)$$

$$\psi_1^\infty = \bar{\rho}_2 (1/\tilde{T}_1 - 1/\tilde{T}_2 - X_{12}) + 2P\bar{v}_2 (v_{12}^* - v_2^*) / RT - 1/r_1 + 1/r_2 \quad (26)$$

$$\psi_2^\infty = \bar{\rho}_1 (1/\tilde{T}_1 - 1/\tilde{T}_2 + X_{21}) + 2P\bar{v}_1 (v_1^* - v_{12}^*) / RT + 1/r_2 - 1/r_1 \sqrt{1 + 4K_F^O} \quad (27)$$

The last term in equation (21) is the chemical contribution to  $V_1^{E\infty}$ .

In a preliminary application of the above formalism to 1-alkanol+n-alkane mixtures we observed that the calculated  $V_1^{E\infty}$  were systematically higher than the experimental ones the main cause being the relatively high value of  $V_H$  for the hydrogen bond formation. Careful examination of the related literature (ref. 18,19) revealed that the choice of  $V_H$  is indeed essential for the appropriate description of the excess volumes at infinite dilution. Seeking a comparison, on the same basis, with the successful ERAS model (ref. 20) we reevaluated the Lattice-Fluid scaling constants for 1-alkanols by setting

Table 3 : Scaling Constants for Pure 1-Alkanols ( $V_H = -5.6 \text{ cm}^3/\text{mol}$ )

Alkanol	$T^*/K$	$v^*/\text{cm}^3 \cdot \text{mol}^{-1}$	$r$
Methanol	496.34	13.10	3.11
Ethanol	463.57	11.76	4.74
Propanol	478.44	12.40	5.65
Butanol	494.25	12.85	6.68
Pentanol	512.55	13.62	7.48
Hexanol	533.74	14.73	8.00
Octanol	552.26	15.25	9.79
Decanol	566.24	15.65	11.74
Dodecanol	578.55	16.07	13.16

$V_H = -5.6 \text{ cm}^3/\text{mol}$  as suggested by Heintz (ref. 20) but leaving unchanged the other two parameters ( $E_H = -25.1 \text{ kJ/mol}$ ,  $S_H = -26.5 \text{ J/K mol}$ ) (ref. 1). The new scaling constants are reported in Table 3. The description of pure component properties with the new scaling constants is as good as with the previous scaling constants (ref. 1). In Table 4 are reported some experimental (ref. 18, 19, 21) and calculated excess volumes in typical 1-alkanol+n-alkane mixtures. In most cases the reported experimental excess volumes at infinite dilution are only approximate estimations obtained by extrapolations of empirical correlations for the excess volumes of not too dilute mixtures. In Table 5 is shown the chemical contribution to  $V_1^{E\infty}$  and its variation with temperature. The calculated mean chemical contribution is about  $5.10 \text{ cm}^3/\text{mol}$  as compared with the estimations of the ERAS model (about  $6.20 \text{ cm}^3/\text{mol}$ ) and those of Treszczanowicz and Benson (ref. 18) (about  $9.60 \text{ cm}^3/\text{mol}$ ).

Table 4 : Experimental and Calculated Excess Volumes at Infinite Dilution and at Equimolar Composition ( $V_{0.5}^E$ ) for some 1-Alkanol(1)+n-Alkane(2) Mixtures

T, K	Experimental			Calculated		
	$V_1^{E\infty}$	$V_{0.5}^E$	$V_2^{E\infty}$	$V_1^{E\infty}$	$V_{0.5}^E$	$V_2^{E\infty}$
			1-Propanol+n-Hexane <sup>a</sup>			
283.15	-	0.143	0.31	9.02	0.148	0.37
298.15	5.93	0.179	0.24	9.69	0.178	0.37
313.15	10.43	0.242	0.18	10.48	0.218	0.38
			1-Hexanol+n-Hexane <sup>a</sup>			
288.15	4.47	-0.204	-1.25	6.89	-0.192	-1.25
298.15	6.34	-0.223	-1.43	6.99	-0.224	-1.43
323.15	7.25	-0.282	-1.86	7.27	-0.325	-2.00
			1-Decanol+n-Hexane <sup>a</sup>			
283.15	-	-0.473	-1.62	5.27	-0.473	-1.49
298.15	3.63 <sup>b</sup>	-0.587	-2.08	4.95	-0.586	-1.84
313.15	2.12	-0.721	-2.51	4.49	-0.725	-2.27
			1-Hexanol+n-Heptane <sup>c</sup>			
283.15	-	-	-	7.23	-0.032	-0.38
298.15	4.60	-0.025	-0.70	7.55	-0.025	-0.43
313.15	-	-	-	7.90	-0.011	-0.49
			1-Dodecanol+n-Heptane <sup>c</sup>			
283.15	-	-	-	4.84	-0.387	-1.27
298.15	2.3	-0.449	-1.60	4.56	-0.449	-1.50
313.15	-	-	-	4.17	-0.536	-1.79
			1-Decanol+n-Octane <sup>c</sup>			
283.15	-	-	-	6.58	-0.159	-0.64
298.15	4.5	-0.190	-1.00	6.65	-0.189	-0.78
313.15	-	-	-	6.70	-0.223	-0.94

<sup>a</sup>. Experimental data from ref.21 assuming validity of the proposed correlation for  $V^E$  down to the infinitely dilute region.

<sup>b</sup>. Data from ref.19.

<sup>c</sup>. Data from ref.18.

Table 5 : Chemical Contribution to  $V_1^{E\infty}$  ( $\text{cm}^3/\text{mol}$ ) Calculated by the LFAS Model

T/K	283.15	298.15	313.15
Alkanol			
Ethanol	5.30	5.21	5.11
1-Propanol	5.27	5.18	5.07
1-Butanol	5.25	5.15	5.03
1-Hexanol	5.23	5.11	4.98
1-Decanol	5.16	5.02	4.87
1-Dodecanol	5.13	4.99	4.83

comparison of Tables 4 and 5 reveals that in mixtures of 1-alkanols with n-hexane and n-heptane the followings occur:

1.  $V_1^{E\infty}$  increases with decreasing 1-alkanol chain length.
2. The physical contribution to  $V_1^{E\infty}$  is large and positive at low 1-alkanol mixtures and decreases, becoming even negative, for higher 1-alkanols.
3.  $V_1^{E\infty}$  increases with temperature at low 1-alkanol mixtures mainly due to the corresponding increase of the physical term which offsets the decrease of the chemical contribution.

As observed in Table 4 the theoretical calculations are qualitatively correct.

Although not related directly with the thermodynamics of 1-alkanol+n-alkane mixtures it is worth pointing out that the present model has been extended to mixtures with one associated and one active component (formation of  $A_1B$  complexes) as well as to mixtures of two associated components (formation of  $A_1B_1$  complexes). The extended model is currently tested in our Laboratory against experimental data.

## CONCLUSIONS

The main advantage of the present model over similar associated solution theories is its validity to both the liquid and the gaseous state. This allows us to make VLE calculations at high pressures up to the critical point in mixtures of associated compounds. The model may also be used for a qualitative estimation of mixture densities at high pressures and for excess volumes at infinite dilution.

The present study has revealed that the set of the characteristic parameters for the hydrogen bond formation ( $E_H, S_H, V_H$ ) proposed in ref. 1 is by no means unique. Application of the model to data on excess volumes at infinite dilution has shown that a new value for  $V_H$  correlates better the experimental data. Application to other quantities at infinite dilution may suggest new optimal values for  $E_H$  and  $S_H$ . This possibility is currently explored in our Laboratory.

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