Thermodynamics of mixtures containing a very strongly polar compound: V - application of the extended real associated solution model to 1-Alkanol + Secondary Amide Mixtures

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THERMODYNAMICS OF MIXTURES CONTAINING A VERY STRONGLY POLAR COMPOUND: V – APPLICATION OF THE EXTENDED REAL ASSOCIATED SOLUTION MODEL TO 1-ALKANOL + SECONDARY AMIDE MIXTURES

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The extended real associated solution (ERAS) model is applied to 1-alkanol + secondary amide mixtures. The amides considered are: *N*-methylformamide (NMF), *N*-methylacetamide (NMA) and 2-pyrrolidone (2-PY). The ERAS parameters for pure amides and for the mixtures are reported. For pure amides, our enthalpy of association is constant $(-25 \, \text{kJ} \, \text{mol}^{-1})$ and is in good agreement with values obtained using different method, e.g., the optimized potentials for liquid simulations. For the mixtures, the ERAS parameters change regularly with molecular structure of the components. In general, ERAS describes quite well molar excess enthalpies and molar excess volumes. In contrast, the model cannot represent molar excess Gibbs energies. Discrepancies between experimental and calculated values are ascribed to: (a) large combinatorial entropies as in methanol + NMA, or + 2-PY systems; (b) association effects are less important than dipole–dipole interactions between amide molecules.

Keywords: Thermodynamics; Solutions; dipole moment

1. INTRODUCTION

We are engaged in a systematic investigation of the thermodynamic properties of solutions containing a compound with a very high dipolar moment in the gas phase (μ), such as, sulfolane ($\mu = 4.81 \, \text{D}$ [1]); dimethyl sulfoxide ($\mu = 4.06 \, \text{D}$ [1]); propylene carbonate ($\mu = 4.94 \, \text{D}$ [1]) or 1-methyl pyrrolidin-2-one (NMP; $\mu = 4.09 \, \text{D}$ [1]).

Amides, amino acids, peptides and their derivatives are of interest because they are simple models in biochemistry. *N*-Methylformamide (NMF) possesses the basic (–CO) and acidic (–NH) groups of the very common, in nature, peptide bond [2]. So, proteins are polymers of amino acids linked to each other by peptide bonds. Cyclic amides are also of importance as they are related to structural problems in biochemistry. Consequently, the understanding of liquid mixtures involving the amide functional group is necessary as a first step to a better knowledge of complex molecules of

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biological interest [3–5]. For example, the aqueous solution of *N,N*-dimethylformamide (DMF) is a model solvent representing the environment of the interior of proteins. Moreover, DMF and NMP are used as highly selective extractants for the recovery of aromatic and saturated hydrocarbons from petroleum feedstocks [6]. NMP, an excellent dissociating solvent [7,8] suitable for the use in electrochemistry [9] and organic synthesis requiring aprotic media [10], can replace with toxicological and environmental advantages solvents as chlorinated hydrocarbons [11].

From a theoretical point of view, amides are also a very interesting class of compounds. In pure liquid state, they present a significant local order [12,13] as their quite high heats of vaporization, ΔH_{vap}, indicate [14]. For example, at 298.15 K ΔH_{vap} (NMF) = 56.19 kJ mol^{-1}and ΔH_{vap} (DMF) = 46.88 kJ mol^{-1}. In the case of tertiary amides, this is due to the dominance of the general dipole–dipole interactions [13]. For primary and secondary amides, their self-association via H-bonds must be also taken into account [13,15–18]. On the other hand, mixtures containing a polar component of high polarity such as NMP and alkanes or benzene are located in the G^E–H^E diagram [19] in a range between hydrogen-bond associated and non-associated mixtures [20]. An important result is that it is not possible to describe both $G^E$and H^E of these systems by the Chemical Theory of Solutions [20]. This confirms the transitional character of mixtures containing a very polar component and makes difficult their theoretical treatment.

The extended real associated solution (ERAS) model [21], which combines the real association solution model [22–24] with the Flory equation of state [25], is typically applied to mixtures including one self-associated compound (1-alkanol [26], alkoxyethanol [27] + alkane), or to solutions with two self-associated components where strong solvation between them exist (e.g., 1-alkanol + linear amine systems [28–32]).

Regarding mixtures with amides, the ERAS model has been applied to NMP + aromatic compound [33], NMP or DMF + 1-alkyne [34], or NMP + 1-alkanol systems [35–37]. These theoretical treatments were developed under the assumption that NMP and DMF are self-associated compounds, which is not strictly justified [13]. In this work, we focus our attention on the ability of the ERAS model to represent the thermodynamic properties of 1-alkanol + secondary amide mixtures. The amides considered are: NMF, *N*-methylacetamide (NMA) and 2-pyrrolidone (2-PY). It should be mentioned that, previously, the Flory theory has been applied to 1-alkanol + 2-PY systems [38]. The symmetry of the H^E curves is not well described by this model [38]. Figure 1 shows the dependence on the composition of the energetic parameter,χ_{12}, of the Flory theory for some of the mentioned solutions. The observed variation points out the existence of orientational effects and suggests that the application of the ERAS model to the investigated mixtures may be pertinent.

In previous articles of this series, we have studied solutions formed by sulfolane [39], NMP [40] or DMSO [41] with different organic solvents (alkane, benzene, toluene, 1-alkanol) using DISQUAC [42].

2. ERAS MODEL

This model combines the real association solution model [22–24] with Flory equation of state [25]. The excess functions are written as:

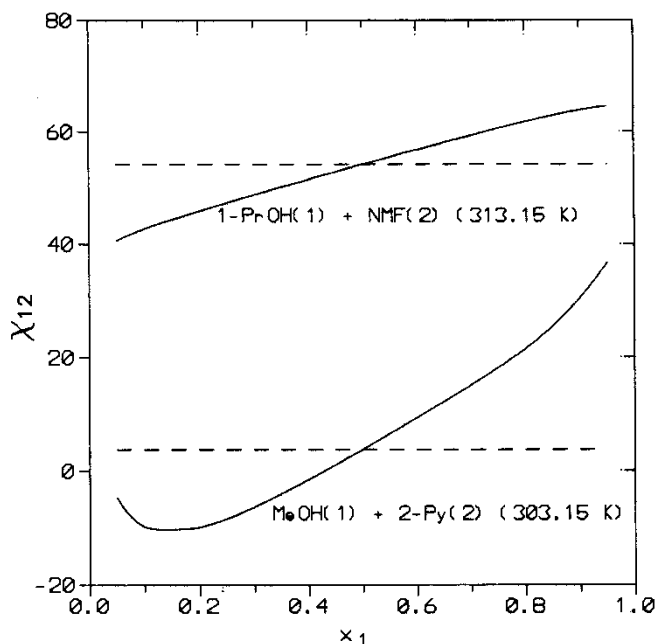$$X^E = X^E_{phys} + X^E_{chem} \tag{1}$$

FIGURE 1 Composition dependence of the interaction parameter of the Flory theory for 1-alkanol + secondary amide mixtures (solid lines). Dashed lines, values of the parameter calculated using H^E data at equimolar composition.

where $X^E = H^E$, V^E or excess Gibbs energy, G^E. In Eq. (1), X^E_{chem} is the chemical contribution, mainly due to the association reactions, and X^E_{phys} represents the physical contribution, which results from the physical interactions between molecules. The resulting expressions for H^E and V^E are given elsewhere [28].

The chemical contribution to the excess properties arises from chemical interactions between the molecules, in particular hydrogen bonding. It is assumed that there is a linear chain association equilibrium of the components A (alcohol) and B (secondary amide):

$$A_m + A \xleftrightarrow{K_A} A_{m+1} \tag{2}$$

$$B_n + B \xleftrightarrow{K_B} B_{n+1} \tag{3}$$

where m or n are the degree of self-association, ranging from 1 to ∞. The cross-association between A and B molecules is represented by:

$$A_m + B_n \xleftrightarrow{K_{AB}} A_m B_n \tag{4}$$

The association constants K_i ($i = A$, B, AB) are assumed to be independent of the chain length. Their temperature dependence is given by:

$$K_i = K_0 \exp\left[-\left(\frac{\Delta h_i^*}{R}\right) \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{5}$$

where K_0 is the equilibrium constant at the standard temperature T_0 (298.15 K), R is the gas constant and Δh_i^* is the enthalpy for the reactions given by Eqs. (2)–(4), which corresponds to the hydrogen bonding energy.

These reactions are also characterized by the volume change Δv_i^*, related to the formation of the linear chains.

X_{phys}^E is derived from Flory's equation of state [25], which is assumed to be valid not only for pure components but also for the mixture:

$$\frac{\tilde{P}_i \tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\left(\tilde{V}_i^{1/3} - 1\right)} - \frac{1}{\left(\tilde{V}_i \tilde{T}_i\right)} \tag{6}$$

where $i = A$, B, M (mixture). In Eq. (6), $\tilde{V}_i = V_i$ (molar volume of component i)$/V_i^*$; $\tilde{P}_i = P/P_i^*$; $\tilde{T}_i = T/T_i^*$ are the reduced volume, pressure and temperature, respectively. The pure components reduction parameters V_i^*, P_i^*, T_i^* are determined from P–V–T data (density, d, thermal expansion coefficient, α_P, and isothermal compressibility, κ_T) provided suitable association parameters, K_i, Δv_i^*, Δh_i^* are known. The method is explained elsewhere [43,44]. The reduction parameters for the mixture P_M^* and T_M^* are calculated from mixing rules [43,44].

3. ADJUSTEMENT OF ERAS PARAMETERS

For pure compounds, the values at T_o (298.15 K or 303.15 K) of d, α_P and κ_T used to calculate the reduction parameters V_i^*, P_i^* ($i = A$, B) are listed in Table I. In order to obtain V_i^*, P_i^* at $T \neq T_o$, the following expressions [45] were applied to determine d, α_p and γ ($= \alpha_p/\kappa_T$):

$$d = d_o \exp(-\alpha \Delta T) \tag{7}$$

$$\alpha = \alpha_o + \alpha_o^2(7 + 4\alpha_o T)\Delta T/3 \tag{8}$$

$$\gamma = \gamma_o - \gamma_o(1 + 2\alpha_o T)\Delta T/T \tag{9}$$

where d_o, α_o and γ_o are the values at T_o and $\Delta T = T - T_o$.

The parameters adjustable to the excess properties are K_A, K_B, K_{AB}, Δh_A^*, Δh_B^*, Δh_{AB}^*, Δv_A^*, Δv_B^*, Δv_{AB}^* and X_{AB}. X_{AB} is the energetic interaction parameter characterizing the difference of dispersive intermolecular interactions between molecules A and B in the

TABLE I   Physical properties of pure compounds at 298.15 K

Compound	$\alpha_P/10^{-4}\,\text{K}^{-1}$	$\kappa_T/10^{-10}\,\text{Pa}^{-1}$	$d/g\,\text{cm}^{-3}$
methanol (MeOH)	11.96[a]	12.48[a]	0.78637[a]
ethanol (EtOH)	10.96[a]	11.53[a]	0.78493[a]
1-propanol (1-PrOH)	10.04[a]	10.26[a]	0.79960[a]
1-butanol (1-BuOH)	9.48[a]	9.42[a]	0.80575[a]
1-pentanol (1-PeOH)	9.05[a]	8.84[a]	0.81080[a]
n-methylformamide (NMF)	8.69[a]	5.932[b]	0.9988[a]
n-methylacetamide (NMA)	8.69[c]	6.12[c]	0.950[d]
2-pyrrolidone (2-PY)	7.253[e]	4.21[e]	1.103[e]

[a][1]; [b][79]; [c][77]; [d][1] $T = 303.15$ K; [e][58] $T = 303.15$ K.

solution and in the pure components, and is the only adjustable parameter of the physical part of H^E and V^E [28,46].

K_A, Δh_A^* and Δv_A^* are known from H^E and V^E data for 1-alkanol + alkane mixtures [28,44]. The determination of K_B, Δh_B^* and Δv_B^* for secondary amides is somewhat difficult because these amides are not miscible with alkanes at room temperature (see below) and only a few H^E data at very high T are available [47–49]. The ERAS parameters for pure components are listed in Table II. The remaining parameters K_{AB}, Δh_{AB}^*, Δv_{AB}^* and X_{AB} (Table III) were adjusted using the avalilable data in the literature for H^E [38,50–52] and V^E [53–58] for the systems under study.

TABLE II ERAS parameters, at temperature T, for pure compunds

Compund	T/K	V_i/cm^3 mol^{-1}	V_i^*/cm^3 mol^{-1}	P_i^*/J cm^{-3}	K_i	Δh_i^*/kJ mol^{-1}	Δv_i^*/cm^3 mol^{-1}
MeOH	303.15	40.99	32.14	425.2	834	−25.1	−5.6
	313.15	41.48	32.17	421.4	607	−25.1	−5.6
	323.15	41.98	32.21	416.7	450.5	−25.1	−5.6
EtOH	303.15	59.02	47.16	397.5	268.2	−25.1	−5.6
	313.15	59.67	47.23	392.6	195.2	−25.1	−5.6
	333.15	60.99	47.37	382.4	109.4	−25.1	−5.6
1-PrOH	303.15	75.54	61.30	395.1	166.7	−25.1	−5.6
	313.15	76.30	61.39	390.7	121.3	−25.1	−5.6
	333.15	77.85	61.56	380.8	68	−25.1	−5.6
1-BuOH	303.15	92.43	75.57	404.6	148	−25.1	−5.6
	313.15	93.31	75.67	400.8	107.7	−25.1	−5.6
	333.15	95.09	75.84	391.6	60.4	−25.1	−5.6
1-PeOH	303.15	109.21	89.95	409.3	129.5	−25.1	−5.6
	333.15	112.22	90.16	396.7	52.8	−25.1	−5.6
NMF	298.15	59.14	49.67	528.7	64.8	−25.0	−3.6
	313.15	59.91	49.82	517.4	40.	−25.0	−3.6
NMA	313.15	77.61	64.33	534.1	35	−25.0	−3.6
	398.15	83.56	64.67	486.	4.5	−25.0	−3.6
2-Py	303.15	77.16	67.40	506.3	10.	−25.0	−3.6
	323.15	78.29	67.68	499.2	5.4	−25.0	−3.6
	333.15	78.87	67.81	492.5	4.1	−25.0	−3.6

TABLE III ERAS parameters, at temperature T, for the investigated mixtures

System	T/K	K_{AB}	Δh_{AB}^*/kJ mol^{-1}	Δv_{AB}^*/cm^3 mol^{-1}	X_{AB}/J cm^{-3}
MeOH + NMF	313.15	85	−38.4	−9.2	7
EtOH + NMF	313.15	50	−34.2	−6.3	7
1-PrOH + NMF	313.15	35	−34.2	−5.8	9.2
1-BuOH + NMF	313.15	35	−34.2	−5.8	9.2
MeOH + NMA	313.15	100	−43.0	−9.7	7
	398.15	2.9	−43.0	−9.7	8
EtOH + NMA	313.15	50	−40.1	−7.6	8
1-PrOH + NMA	313.15	40	−40.1	−7.6	9.5
1-BuOH + NMA	313.15	40	−40.1	−7.6	9.5
MeOH + 2-Py	303.15	85	−41.0	−9.7	5
	323.15	31.4	−41.0	−9.7	1.5
EtOH + 2-Py	303.15	50.	−35.9	−7.6	6.5
	333.15	14.2	−35.9	−7.6	1.5
1-PrOH + 2-Py	303.15	15	−34.2	−6.8	7.1
	333.15	4.2	−34.2	−6.8	2.5
1-BuOH + 2-Py	303.15	15	−34.2	−6.5	7.1
	333.15	4.2	−34.2	−6.5	2.5
1-PeOH + 2-Py	303.15	15	−34.2	−6.2	7.1
	333.15	4.2	−34.2	−6.2	2.5

It should be mentioned that the total relative molecular volumes and surfaces of the compounds present in these solutions were calculated from group volumes and surfaces as recommended by Bondi [59].

4. RESULTS AND DISCUSSION

4.1. ERAS Results

They are listed in Tables IV (H^E) and V (V^E). A graphical comparison between experimental data and theoretical results is presented in Figs. 2–7. In general, the model represents quite accurately H^E and V^E for the investigated mixtures. The H^E of systems where the endothermic and exothermic contributions to this magnitude are practically balanced (methanol + NMA, or + 2-PY) is described poorly (Table IV). In terms of ERAS, this means that $|H^E_{\text{chem}}|$ and $|H^E_{\text{phys}}|$ show low values which leads to the symmetry of the H^E curves is not well represented.

4.2. Secondary Amide + Alkane Mixtures

Secondary amides such as NMF, NMA, 2-PY or caprolactam are not miscible with alkanes at room temperature. The UCST (upper critical solution temperature) for the caprolactam + n-C$_8$ system is 361.25 [47]. The NMF + n-C$_6$ mixture shows a miscibility gap at 363.15 K in $0.012 < x_1 < 0.935$ [60] and the NMA + n-C$_{10}$ solution in $0.11 < x_1 < 0.82$ at 413.49 K [48]. These data reveal strong dipole–dipole interactions between amide molecules. Note that, e.g. NMF and NMA have large dipole moments, μ, in gas phase: 3.86 and 3.89 D, respectively [61]. The effective dipole moments [28,62], μ_{eff}, an useful quantity to examine the impact of polarity on bulk properties [28], are also large: $\mu_{\text{eff}}(\text{NMF}) = 1.93$ and $\mu_{\text{eff}}(\text{NMA}) = 1.70$. It is interesting to compare these results with the corresponding values for methanol: $\mu = 1.7$ D [63] and $\mu_{\text{eff}} = 1.02$ [28]. The UCSTs for the methanol + n-C$_6$ or + n-C$_8$ systems are 306.75 K [64] and

TABLE IV H^E, at equimolar composition and temperature T, for 1-alkanol(1) + secondary amide(2) mixtures

System	T/K	N	H^E ($x_1 = 0.5$)/J mol^{-1}		dev (H^E)[a]		Ref.
			Exp.	Calc.	Exp.	Calc.	
MeOH + NMF	313.15	17	258	258	0.008	0.029	[50]
EtOH + NMF	313.15	17	599	593	0.007	0.047	[50]
1-PrOH + NMF	313.15	17	730	722	0.009	0.044	[50]
1-BuOH + NMF	313.15	17	831	816	0.007	0.049	[52]
MeOH + NMA	313.15	20	−76	−49	−0.009	0.48	[51]
EtOH + NMA	313.15	20	195	190	0.008	0.073	[51]
1-PrOH + NMA	313.15	18	274	274	0.009	0.067	[51]
1-BuOH +NMA	313.15	21	314	320	0.011	0.092	[51]
MeOH + 2-Py	303.15	10	22	44	0.136	2.2	[38]
EtOH + 2-Py	303.15	11	495	494	0.005	0.11	[38]
1-PrOH + 2-Py	303.15	10	831	884	0.004	0.077	[38]
1-BuOH + 2-Py	303.15	11	953	993	0.002	0.067	[38]
1-PeOH + 2-Py	303.15	10	1060	1098	0.002	0.037	[38]

[a]$\text{dev}(H^E) = \left\{ \dfrac{1}{N} \sum \left[\dfrac{H^E_{\exp} - H^E_{\text{calc}}}{H^E_{\exp}(x_1 = 0.5)} \right]^2 \right\}^{1/2}$

TABLE V V^E, at equimolar composition and temperature T, for 1-alkanol(1) + secondary amide(2) mixtures

System	T/K	V^E ($x_1 = 0.5$)/cm^3 mol^{-1}		Ref.
		Exp.	*Calc.*	
MeOH + NMF	313.15	−0.338	−0.341	[54]
EtOH + NMF	313.15	−0.090	−0.089	[55]
MeOH + NMA	313.15	−0.426	−0.419	[56]
EtOH + NMA	313.15		−0.219	[57]
MeOH + 2-Py	303.15	−0.683	−0.641	[53]
		−0.648		[58]
	323.15	−0.796	−0.724	[53]
EtOH + 2-Py	303.15	−0.534	−0.529	[53]
		−0.532		[58]
	333.15	−0.704	−0.687	[53]
1-PrOH + 2-Py	303.15	−0.346	−0.337	[53]
		−0.327		[58]
	333.15	−0.458	−0.426	[53]
1-BuOH + 2-Py	303.15	−0.239	−0.249	[53]
		−0.255		[58]
	333.15	−0.329	−0.336	[53]
1-PeOH + 2-Py	303.15	−0.156	−0.157	[53]
		−0.152		[58]
	333.15	−0.240	−0.254	[53]
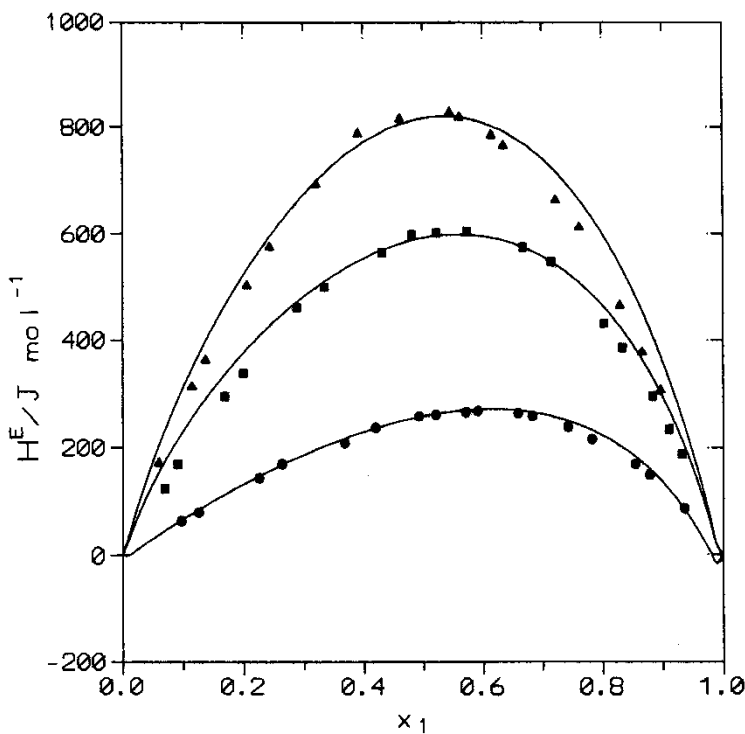
FIGURE 2 H^E at 313.15 K for 1-alkanol(1) + NMF(2) mixtures. Solid lines, ERAS calculations. Points, experimental values: (●), ethanol [50]; (■), 1-propanol [50]; (▲), 1-butanol [52].
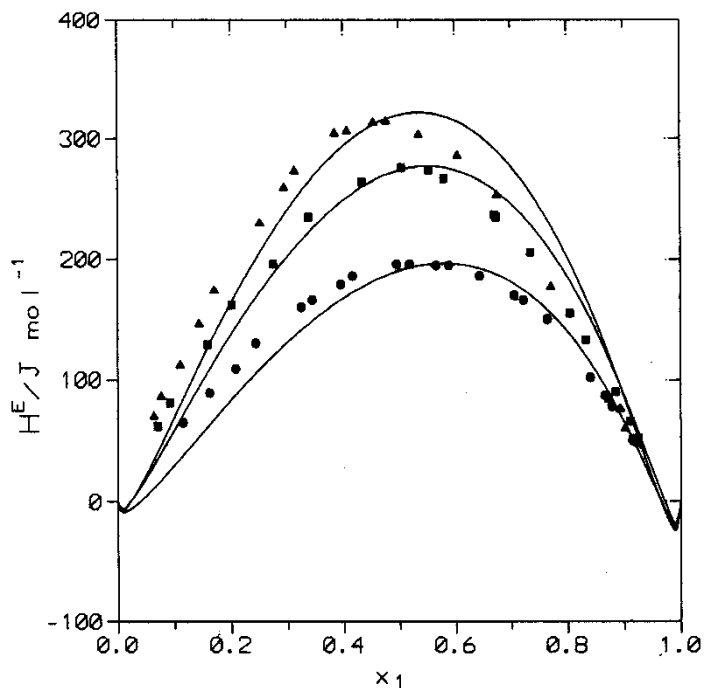
FIGURE 3 H^E at 313.15 K for 1-alkanol(1) + NMA(2) mixtures. Solid lines, ERAS calculations. Points, experimental values [51]: (●), ethanol; (■), 1-propanol; (▲), 1-butanol.
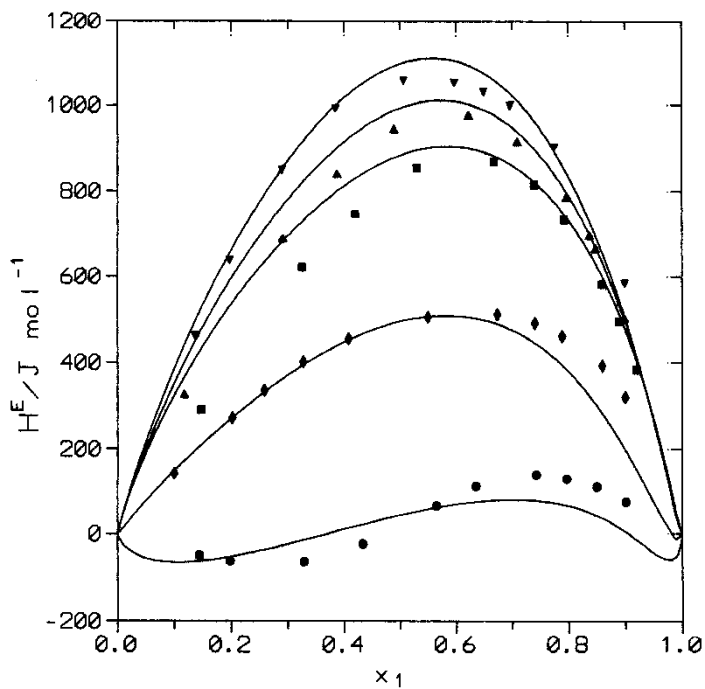

FIGURE 4 H^E at 303.15 K for 1-alkanol(1) + 2-Py(2) mixtures. Solid lines, ERAS calculations. Points, experimental values [38]: (●), methanol; (◆), ethanol); (■), 1-propanol; (▲), 1-butanol; (▼); 1-pentanol.
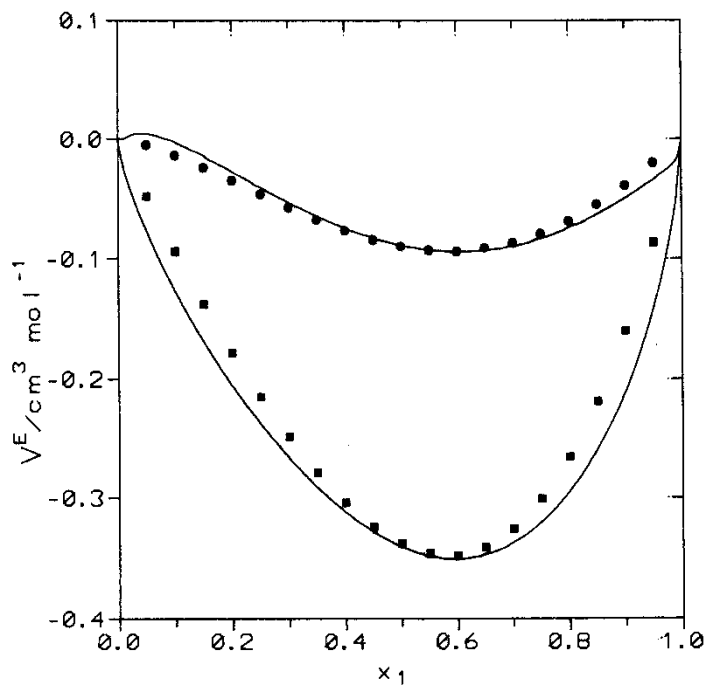
FIGURE 5 V^E at 313.15 K for 1-alkanol(1) + NMF(2) mixtures. Solid lines, ERAS calculations. Points, experimental values: (■), methanol [54]; (●), ethanol [55].
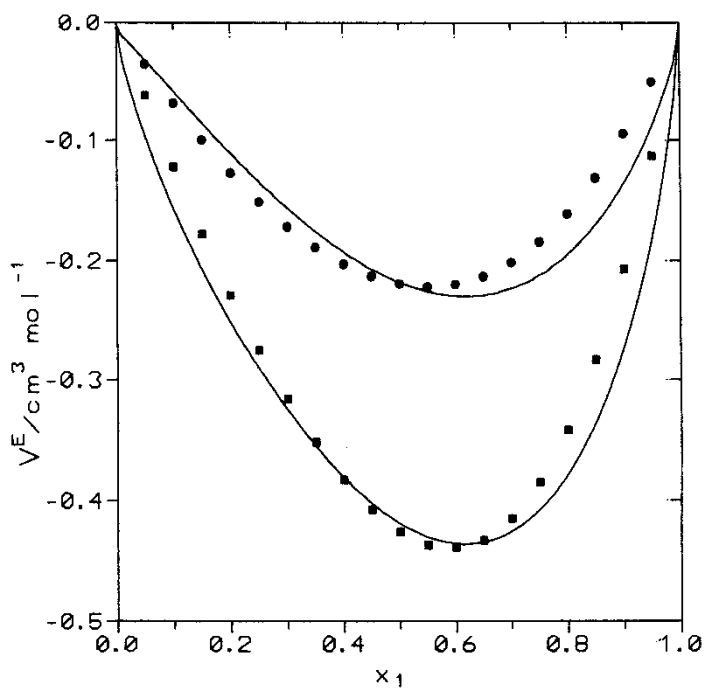

FIGURE 6 V^E at 313.15 K for 1-alkanol(1) + NMA(2) mixtures. Solid lines, ERAS calculations. Points, experimental values: (■), methanol [56]; (●), ethanol [57].
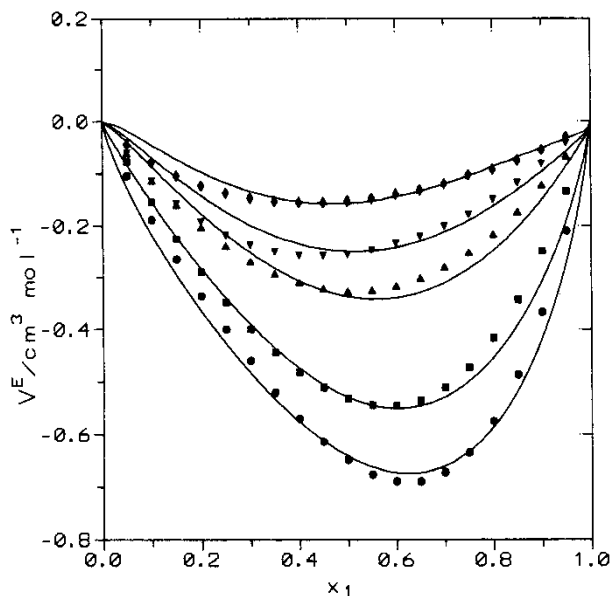
FIGURE 7 V^E at 303.15 K for 1-alkanol(1) + 2-Py(2) mixtures. Solid lines, ERAS calculations. Points, experimental values [58]: (●), methanol; (■), ethanol; (▲), 1-propanol; (▼), 1-butanol; (◆), 1-pentanol.

339.3 K [65], respectively. It is then possible to conclude that dipole–dipole interactions are stronger in solutions with amides and particularly in those containing NMF.

Our Δh_B^* value for secondary amides (-25 kJ mol^{-1}, Table II) agrees with those obtained using different methods. So, from *ab initio* calculations carried out at the uncorrelated, restricted Hartree–Fock level, the H-bond energy for NMF dimers is -25.53 kJ mol^{-1} [16] and for NMA dimers is -24.14 kJ mol^{-1} [17]. From calculations using the optimized potentials for liquid simulations (OPLS) functions [13], the dimerization energy for NMA is estimated to be -23.43 kJ mol^{-1} [13].

It is possible to predict the enthalpy of vaporization, ΔH_{vap}, of self-associated compounds using ERAS [66]. At 298.15 K, the experimental value for NMF is 56.19 kJ mol^{-1} [14], which is larger than our calculated value 46.62 kJ mol^{-1}. Such difference may be attributed to ERAS, which does not represent properly the dipole–dipole interactions between amide molecules. This is also clearly shown when H^E for secondary amide + alkane mixtures are considered. For example, at $x_1 = 0.0844$ and 398.15 K, H^E (NMA(1) + cyclooctane(2)) $= 779$ J mol^{-1} [49]. ERAS provides 948 J mol^{-1} with $H_{chem}^E = 926$ J mol^{-1}. That is, the model overestimates the chemical contribution to H^E. Calculations show that the ERAS results for H^E for systems including alkanes can be improved using $\Delta h_B^* = -18.5$ kJ mol^{-1}. However, then the calculated ΔH_{vap} of the amides decrease and the symmetry of the H^E curves for alcoholic solutions is not well described.

4.3. 1-Alkanol + secondary Amide Mixtures

4.3.1. Excess Enthalpies

For a given amide, $H^E(x_1 = 0.5)$ increases with the chain length of the 1-alkanol (Table IV), which may be due to: (a) interactions between unlike molecules become

weaker; (b) the increase of the aliphatic surface of the alcohol leads to a larger positive contribution to H^E from the disruption of the amide–amide interactions. This is supported by the fact that the maxima of the H^E curves are skewed to higher mole fractions of the amide when the length of the 1-alkanol increases (Figs. 2–4). A similar behaviour is encountered in 1-alkanol + tertiary amide [36,37,67,68], or + dimethyl-sulfoxide [68] mixtures and remarks the importance of the dipole–dipole interactions in the investigated solutions. In terms of ERAS, we note that $|\Delta h^*_{AB}|$ and K_{AB} only decrease when passing from methanol (or ethanol) to longer 1-alkanols (Table III). The quite different values of Δh^*_{AB}, Δv^*_{AB} and K_{AB} for solutions with methanol underline that alkanol–amide interactions are stronger for this class of systems. Mixtures of 1-alkanol with linear amine behave similarly [28–32].

It results in more difficulty to compare H^E for systems formed by a given amide and different 1-alkanols. From the experimental data, it seems that interactions between unlike molecules are stronger in solutions with NMA than in mixtures with NMF or 2-PY (Table IV). On the other hand, in systems involving methanol or ethanol, the mentioned interactions are stronger in solutions with 2-PY than in those with NMF. The opposite trend is observed for mixtures with the remainder alcohols.

The fact that, for a fixed 1-alkanol, H^E (NMA) < H^E (NMF) has been ascribed in great part to the larger proton accepting ability of NMA than of NMF [50,69]. However, the observed variation of H^E may be due the positive contribution to this magnitude from the disruption of dipole–dipole interactions between amide molecules is larger for NMF than for NMA (see above).

In accordance with the available measurements, the ERAS parameters $|\Delta h^*_{AB}|$ and K_{AB} are larger for systems with NMA (Table III). For mixtures containing methanol or ethanol, $|\Delta h^*_{AB}|$(2-PY) > $|\Delta h^*_{AB}|$(NMF). For the remainder alcohols, their different association with the amide (NMF or 2-PY) is characterized merely by different K_{AB} values (K_{AB}(2-PY) < K_{AB}(NMF)) (Table III). It is noteworthy that the quite good ERAS results for H^E are obtained using a few Δh^*_{AB} and K_{AB} parameters, which, on the other hand, change regularly with the molecular structure of the mixture components.

4.3.2. Excess Volumes

At $x_1 = 0.5$, V^E is usually negative (Table V). This may be due to: (a) specific interactions between unlike molecules; (b) free volume effects, as V^E curves shifted to low mole fractions of the larger component show (Figs. 5–7). For example, in the 1-alkanol + 2-PY series, the V^E curve is skewed towards the region rich in methanol for the solution containing this alcohol, and to the region rich in 2-PY for the 1-pentanol + 2-PY system (Fig. 7).

The increase of V^E when, for a given amide, the chain length of the alkanol increases may be explained in similar terms than that of H^E (see previous section). For longer 1-alkanols, V^E could become positive as in 1-alkanol + NMP mixtures [70].

It is very interesting to note that for 1-alkanol + 2-PY systems, V^E decreases with the increase of T (i.e., $dV^E/dT < 0$) (Table V). In 1-alkanol or linear monooxaalkane + n-alkane or 1-alkanol + linear polyether mixtures the negative values of V^E and dV^E/dT have been ascribed to the increasing predominance of the negative free volume contribution with rising temperature over the positive contributions (from

TABLE VI Values at equimolar composition and 313.15 K for some excess functions of 1-alkanol(1) + secondary amide(2) mixtures: G^E, molar excess Gibbs energy; $G^{E,\text{COMB}}$, combinatorial contribution to G^E; $G^{E,\text{int}}$, interactional contribution to G^E; H^E, molar excess enthalpy; $TS^E = H^E - G^E$ and $TS^{E,\text{int}} = H^E - G^{E,\text{int}}$

System	G^E /J mol^{-1}	$G^{E,\text{COMB}}$/J mol^{-1}	$G^{E,\text{int}}$/J mol^{-1}	H^E/J mol^{-1}	TS^E/J mol^{-1}	$TS^{E,\text{int}}$/J mol^{-1}
MeOH + NMF	99[a]	−90	189	258[b]	159	70
EtOH + NMF	195[c]	−7	202	599[b]	404	397
MeOH + NMA	−262[d]	−191	−71	−76[e]	186	−5
EtOH + NMA	−113[f]	−49	−64	195[e]	308	259
MeOH + 2-Py	−171[g]	−212	−41	22[h]	193	−19
EtOH + 2-Py	70[g]	−62	132	495[h]	425	363

[a][74]; [b][50]; [c][80]; [d][75]; [e][51]; [f][81]; [g][82]; [h][38]; $T = 303.15$ K.

the disruption of interactions between like molecules) [71]. Probably, the mixtures under study behave similarly.

In the framework of ERAS, $dV^E/dT < 0$ is represented (Table V) using $dX_{AB}/dT < 0$ (Table III). This leads to predicted H^E values which increase with T, in contradiction with the experimental data. At equimolar composition for the methanol + NMA mixture, H^E (313.15 K) = −76 J mol^{-1} [51] and H^E (398.15 K) = −260 J mol^{-1} [72]. In contrast H^E increases with the temperature for the water + NMA system [73].

4.3.3. Excess Gibbs Energies

Finally, it must be mentioned that ERAS fails when representing the symmetry of the G^E curves. For this type of calculations, a new parameter Q_{AB} is needed to characterize the entropic contribution to the difference of intermolecular interactions [46]. Q_{AB} is an adjustable parameter for the G^E_{phys} contribution. Assuming $Q_{AB} = 0$, at 313.15 K and equimolar composition, G^E_{chem} (methanol + NMF) = 1396 J mol^{-1} and G^E_{chem} (methanol + NMA) = 1380 J mol^{-1}. The experimental values for G^E are 99 [74] and −262 [75] J mol^{-1}, respectively. This means that the model overestimates the chemical contribution to G^E calculated as the difference of two large quantities which leads to poor results for G^E.

Table VI lists G^E, $TS^E (= H^E - G^E)$, and $TS^E_{\text{int}} (= H^E - G^E_{\text{int}}$; where $G^E = G^E_{\text{int}} + G^{E,\text{COMB}}$ with $G^{E,\text{COMB}}$ calculated using the Flory–Huggins equation [76]) for some of the mixtures under study. We note that TS^E and $TS^E_{\text{int}} > 0$. In the case of TS^E, this is due to some extent to size effects, particularly in systems with methanol. So, association, as a whole, does not play an important role. A similar conclusion has been stated when applying the Kirkwood–Buff theory to the present systems [77,78]. This might justify why it is not possible to describe simultaneously using ERAS H^E, V^E and G^E for the investigated mixtures. In a previous work, we have explained the poor ERAS results for H^E of 1-alkanol ($\neq$ methanol) + NMP systems by the large and positive TS^E_{int} values of such solutions attributed to strong dipole–dipole interactions between amide molecules [40].

5. CONCLUSIONS

1-Alkanol + secondary amide mixtures have been characterized in the framework of ERAS. The corresponding model parameters are reported. In general, ERAS describes

rather accurately H^E and V^E, but cannot represent G^E. The observed discrepancies between experimental and calculated results may be due to: (a) large and to combinatorial entropy, as in methanol + NMA, or + 2-PY systems; (b) association effects are less important than dipole–dipole interactions between amide molecules.

Acknowledgements

References

[1] J.A. Riddick, W.B. Bunger and T.K. Sakano (1986). *Organic Solvents. Physical Properties and Methods of Purification, Techniques of Chemistry*, Vol. II. John Wiley & Sons, N.Y.
[2] P. Bour, C.N. Tam, J. Sopková and F.R. Trouw (1998). *J. Phys. Chem.*, **108**, 351.
[3] H. Guo and M. Karplus (1992). *J. Phys. Chem.*, **96**, 7273.
[4] H. Guo and M. Karplus (1994). *J. Phys. Chem.*, **98**, 7104.
[5] E.S. Eberhart and R.T. Raines (1994). *J. Am. Chem. Soc.*, **116**, 2149.
[6] B. Blanco, M.T. Sanz, S. Beltrán, J.L Cabezas and J. Coca (2000). *Fluid Phase Equilib.*, **175**, 117.
[7] J.L. Wuepper and A.I. Popov (1969). *J. Am. Chem. Soc.*, **32**, 4352.
[8] J.D. Dyke, P.G. Sears and A.I. Popov (1967). *J. Phys. Chem.*, **71**, 4140.
[9] M. Breant (1971). *Bull. Soc. Chim. Fr.*, 725.
[10] A.F. Sowinski and G.M. Whitesides (1979). *J. Org. Chem.*, **44**, 2369.
[11] E. Muller and G. Hohfeld (1971). *Abstracts of the 8th World Petroleum Congress*, 213.
[12] O.D. Bonner and S.-J. Kim (1970). *J. Chem. Thermodyn.*, **2**, 63.
[13] W.L. Jorgensen and C.L. Swenson (1985). *J. Am. Chem. Soc.*, **107**, 569.
[14] V. Majer and V. Svoboda (1985). *Enthalpies of Vaporization of Organic Compounds*. Blackwell, Oxford.
[15] R. Ludwig (2000). *J. Molecular Liq.*, **84**, 65.
[16] R. Ludwig, F. Weinhold and T.C. Farrar (1997). *J. Chem. Phys.*, **197**, 499.
[17] R. Ludwig, F. Weinhold and T.C. Farrar (1997). *J. Phys. Chem. A*, **101**, 8861.
[18] J. Barthel, R. Buchner and B. Wurm (2002). *J. Molecular Liq.*, **98–99**, 51.
[19] F. Kohler and J. Gaube (1980). *Pol. J. Chem.*, **54**, 1987.
[20] R. Fuchs, L. Krenzer and J. Gaube (1984). *Ber. Bunsenges. Phys. Chem.*, **88**, 642.
[21] A. Heintz (1985). *Ber. Bunsenges. Phys. Chem.*, **89**, 172.
[22] C.B. Kretschmer and R. Wiebe (1954). *J. Chem. Phys.*, **22**, 1697.
[23] H. Renon and J.M. Prausnitz (1967). *Chem. Eng. Sci.*, **22**, 299.
[24] H.V. Kehiaian and A.J. Tresznanowicz (1968). *Bull. Acad. Pol. Sci.*, **16**, 171.
[25] P.J. Flory (1965). *J. Am. Chem. Soc.*, **87**, 1833; A. Abe and P.J. Flory (1965). *J. Am. Chem. Soc.*, **87**, 1838.
[26] M. Bender and A. Heintz (1993). *Fluid Phase Equilib.*, **89**, 197.
[27] J.A. González, S. Villa, N. Riesco, I. García de la Fuente and J.C. Cobos (2003). *Can. J. Chem.*, **81**, 319.
[28] J.A. González, I. García de la Fuente and J.C. Cobos (2000). *Fluid Phase Equilib.*, **168**, 31.
[29] J.A. González, I. García de la Fuente and J.C. Cobos (2000). *Can. J. Chem.*, **78**, 1272.
[30] S. Villa, N. Riesco, I. García de la Fuente, J.A. González and J.C. Cobos (2001). *Fluid Phase Equilib.*, **190**, 113.
[31] S. Villa, N. Riesco, I. García de la Fuente, J.A. González and J.C. Cobos. *Fluid Phase Equilib.*, **198**, 313.
[32] S. Villa, N. Riesco, I. García de la Fuente, J.A. González and J.C. Cobos (2003). *J. Solution Chem.*, **32**, 179.
[33] T.M. Letcher and P.K. Naicker (1999). *J. Chem. Thermodyn.*, **31**, 1585.
[34] T.M. Letcher and P.G. Whitehead (1999). *J. Chem. Thermodyn.*, **31**, 1537.
[35] T.M. Letcher, U. Domanska and E. Mwenesongole (1998). *Fluid Phase Equilib.*, **149**, 323.
[36] T.M. Letcher, J. Lachwa and U. Domanska (2001). *J. Chem. Thermodyn.*, **33**, 1169.
[37] T.M. Letcher, J. Lachwa and U. Domanska (2002). *J. Chem. Thermodyn.*, **34**, 1581.
[38] S.K. Mehta, R.K. Chauhan and A.D. Tripathi (1997). *J. Chem. Thermodyn.*, **29**, 353.

[39] J.A. González and U. Domanska (2001). *PCCP*, **3**, 1034; U. Domanska and J.A. González (2002). *Can. J. Chem.*, **80**, 476.

[40] J.A. González, U. Domanska and J. Lachwa (2003). *Can. J. Chem.*, **81**, 1.

[41] J.A. González, S. Villa, N. Riesco, I. García de la Fuente and J.C. Cobos (2003). *Phys. Chem. Liq.*, **41**, 583.

[42] H.V. Kehiaian (1983). *Fluid Phase Equilib.*, **13**, 243; (1985). *Pure Appl. Chem.*, **57**, 15.

[43] A. Heintz, P.K. Naicker, S.P. Verevkin and R. Pfestorf (1998). *Ber. Bunsenges. Phys. Chem.*, **102**, 953.

[44] A. Heintz and D. Papaioannou, (1998). *Thermochim. Acta*, **310**, 69.

[45] G. Allen, Z. Chai, C.L. Chong, J.S. Higgins and J. Tripathi (1984). *Polymer*, **25**, 239.

[46] H. Funke, M. Wetzel and A. Heintz (1989). *Pure Appl. Chem.*, **61**, 1429.

[47] J. Schmelzer and J. Pusch (1995). *Fluid Phase Equilib.*, **110**, 183.

[48] A. de Haan, K. Fischer, M. Haacke, O. Aufderhaar, M. Petri and J. Gmehling (1997). *J. Chem. Eng. Data*, **42**, 875.

[49] A. de Haan, A. Heine, K. Fischer and J. Gmehling (1995). *J. Chem. Eng. Data*, **40**, 1228.

[50] L. Pikkarainen (1991). *Thermochim. Acta*, **178**, 311.

[51] L. Pikkarainen (1987). *J. Solution Chem.*, **16**, 125.

[52] L. Pikkarainen (1991). *J. Chem. Thermodyn*, **23**, 877.

[53] B. García, C. Herrera and J.M. Leal (1991). *J. Chem. Eng. Data*, **36**, 269.

[54] J. Zielkiewicz (1995). *J. Chem. Thermodyn.*, **27**, 1275.

[55] J. Zielkiewicz (1996). *J. Chem. Thermodyn.*, **28**, 313.

[56] J. Zielkiewicz (1999). *J. Chem. Thermodyn.*, **31**, 1597.

[57] J. Zielkiewicz (2000). *J. Chem. Thermodyn.*, **32**, 789.

[58] S.K. Mehta, R.K. Chauhan and R.K. Dewan (1996). *J. Chem. Faraday Trans.*, **92**, 1167.

[59] A. Bondi (1968). *Physical Properties of Molecular Crystal, Liquids and Glasses.* John Wiley, N.Y.

[60] R.A. Harris, R. Wittig, J. Gmehling, T.M. Letcher, D. Ramjugernath and J.D. Raal (2003). *J. Chem. Eng. Data*, **48**, 341.

[61] A.L. McClellan (1974). *Tables of Experimental Dipole Moments.* Rahara Enterprises, El Cerrito, CA.

[62] J.S. Rowlinson and F.L. Swinton (1982). *Liquids and Liquid Mixtures*, 3th Edn. Butterworths, London.

[63] R.C. Reid, J.M. Prausnitz and B.E. Poling (1987). *The Properties of Gases and Liquids*, 4th Edn. McGraw Hill, N.Y.

[64] G. Hradetzky and H.-J. Bittrich (1986). *Int. DATA Ser., Sel Data Mixtures, Ser. A*, **3**, 216.

[65] J.B. Ott, I.F. Hölscher and G.M. Schneider (1986). *J. Chem. Thermodyn.*, **18**, 815.

[66] D. Kulikov, S.P. Verevkin and A. Heintz (2001). *Fluid Phase Equilib.*, **192**, 187.

[67] M. Oba, S. Murakami and R. Fujishiro (1977). *J. Chem. Thermodyn.*, **9**, 407.

[68] J.P. Chao, M. Dai and Y.X. Wang (1989). *J. Chem. Thermodyn.*, **21**, 1169.

[69] J.N. Spencer, S.K. Berger, C.R. Powell, B.D. Henning, G.S. Furman, W.M, Loffredo, E.M. Rydberg, R.A. Neubert, C.E. Shoop and D.N. Blauch. *J. Phys. Chem.*, **85**, 1236.

[70] B. García, R. Alcalde, S. Aparicio and J.M. Leal (2002). *PCCP*, **4**, 1170.

[71] S. Villa, N. Riesco, I. García de la Fuente, J.A. González and J.C. Cobos (2000). *Thermochim. Acta*, **362**, 169.

[72] A. de Haan, K. Fischer, M. Haacke and J. Gmehling (1997). *J. Chem. Eng. Data*, **42**, 597.

[73] A.B. de Haan and J. Gmehling (1996). *J. Chem. Eng. Data.*, **41**, 474.

[74] J. Zielkiewicz (1996). *J. Chem. Thermodyn.*, **28**, 887.

[75] J. Zielkiewicz (1999). *J. Chem. Thermodyn.*, **31**, 819.

[76] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova and A. Ait-Kaci (1995). *Fluid Phase Equilib.*, **112**, 63.

[77] J. Zielkiewicz (2000). *PCCP*, **2**, 2925.

[78] J. Zielkiewicz (1998). *J. Chem. Soc. Faraday Trans.*, **94**, 1713.

[79] Y. Uosaki, S. Kitaura, F. Iwama and T. Moriyoshi (1991). *J. Chem. Thermodyn.*, **23**, 1125.

[80] J. Zielkiewicz (1997). *J. Chem. Thermodyn.*, **29**, 229.

[81] J. Zielkiewicz (2000). *J. Chem. Thermodyn.*, **32**, 55.

[82] J. Zielkiewicz (2002). *J. Chem. Thermodyn.*, **34**, 1693.