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THERMODYNAMIC PROPERTIES OF AQUEOUS NON-ELECTROLYTE MIXTURES. II. EXCESS ENTHALPIES AND LIQUID–LIQUID EQUILIBRIUM OF 2-ALKANONE + WATER MIXTURES

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ABSTRACT

The liquid–liquid equilibrium and the excess enthalpies of 2-alkanone + water mixtures were determined experimentally. These results together with all the available literature data on liquid–vapor equilibria, liquid–liquid equilibria and excess enthalpies were taken into consideration and examined on the basis of the NRTL model. Using six parameters, the model provides a fairly consistent description of the properties of the mixtures as a function of composition, temperature and 2-alkanone chain length.

The discrepancies between theory and experiment are discussed.

INTRODUCTION

2-Alkanones are known to give non-ideal mixtures with aliphatic hydrocarbons [1–5]. This behavior may be ascribed to the influence of the dipole moment of the carbonyl group, CO, which becomes manifest in the form of strong carbonyl–carbonyl interactions.

The interactions are particularly strong when the ketones are mixed with substances which contain groups which are able to interact specifically with the carbonyl group, i.e. strongly polarizable groups (such as phenyl) [6] or proton donors, e.g. chloroform [7] or alcohols [8].

Our results on aldehydes [9], or cyclic ethers [10] + water mixtures have demonstrated that the number of alkyl groups located near the carbonyl, plays an important role in determining the extent of the molecular interactions involving the polar group (–CO– or –O–).

With the aim of establishing the occurrence of such effects when dealing with strongly polar solvents like water, we carried out a systematic investiga-

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tion of the thermodynamic properties of aqueous mixtures of alkanones of general formula $CH_3(CH_2)_{s-1}$–CO–$(CH_2)_{t-1}CH_3$ (with $s = 1, 2, 3$ and $t = 1$) ($K_{s,t}$). A search of the literature reveals that the thermodynamics of ketones + water mixtures have been exhaustively studied only for 2-propanone($K_{1,1}$): 2-butanone($K_{2,1}$) has been little investigated while data on 2-pentanone($K_{3,1}$) + water mixtures are rather scarce.

The liquid–vapor equilibrium (LVE) for the $K_{1,1}$ + water mixtures has been determined by several authors both by isobaric measurement ($T-x-y$) [11–16] and by isothermic measurement ($P-x-y$) [17,18] and the corresponding data correlated by means of Margules, UNIFAC and NRTL equations [19]. LVE data ($T-x-y$) of $K_{2,1}$ + water mixtures have also been reported [13,20–23] and correlated by means of the same equations [19] or the Van Laar equation [23], while the only available investigation on liquid–vapor equilibria for the $K_{3,1}$ + water system, due to Carlson et al. [24], regards the ternary system with ethanol.

$K_{1,1}$ is completely miscible with water [25] at all temperatures while an extended miscibility gap is observed with $K_{2,1}$ and $K_{3,1}$ in water [25] having an upper critical solution temperature (UCST) above 413.15 K [22]. 2-Butanone has a LCST ($\sim$ 263.15 K) in equilibrium with the saturated vapor at high pressures and would clearly have one at the vapor pressure if the system did not solidify first. Hunt and Lamb [26] have reported the liquid–liquid equilibrium (LLE) data at high pressure.

The excess enthalpy, H^E, for the $K_{1,1}$ + water mixtures has been determined by several authors [27–31] while for the $K_{2,1}$ + water mixtures, H^E data at 293.15, 308.15 and 313.15 K are reported by Belonsov and Sokolova [30] and at 298.15 K by Hanson and van Winkle [31]: for the $K_{3,1}$ + water mixtures, the only data reported are due to Dubois et al. [32].

The most extensive investigation of the enthalpy of solvation, at 298.15 K, as enthalpy of solution + enthalpy of vaporization, of the aliphatic ketones + water systems is due to Della Gatta [33].

Arnaud et al. [34], Kiyohara et al. [35] and Winnick and Kong [36] reported data on the heat capacities, C_p, and excess volumes, V^E, for 2-propanone + water mixtures.

All these data confirm the non-ideal behavior of the ketones + water systems, as pointed out by the fact that the activity coefficients differ from unity and show a precise trend in their values when changing the composition of the liquid phase. In the present work, the aqueous mixtures of 2-propanone ($K_{1,1}$), 2-butanone ($K_{2,1}$) and 2-pentanone($K_{3,1}$) were investigated by experimentally determining the excess enthalpy, H^E, at 298.15 K for $K_{1,1}$ + water, in the entire concentration range, while the $K_{2,1}$ + water and $K_{3,1}$ + water mixtures were investigated in the homogeneous region only: the liquid–liquid equilibrium (LLE) of the last two systems was studied by means of gas–liquid chromatography in the 273.15–338.15 K range. The NRTL (non-random two-liquid) six-parameter equation [37–40] was used for the simultaneous correlation of H^E, LVE and LLE data. The applicability limits of such a model in predicting the thermodynamic properties of hydroorganic mixtures are discussed.

EXPERIMENTAL AND RESULTS

Materials

The aliphatic ketones of pure reagent grade (Fluka AG, Switzerland) were first dried on a molecular sieve 3A. Purity was higher than 99.5% as determined by GLC using a chromosorb W 80–100 mesh column. Water was prepared by passing through a mixed bed ion-exchanging resin column and then distilled twice.

Calorimetric measurements

The excess enthalpies, H^E, were measured using a Tian Calvet ("CRMT") type calorimeter which was manually tilted. The principle of the apparatus and the experimental procedure are reported in literature [41,42]. The mixing cell was suitably modified in order to guarantee a perfect seal of the lower and upper compartments containing the two liquids and it was equipped with a heating resistance to carry out calibration directly on each mixture.

The performance of the calorimeter was regularly checked by determining the excess enthalpies for some test mixtures (tetrachloromethane + benzene and benzene + cyclohexane). The results obtained were in agreement within 1% with those of Stokes et al. [43]. All measurements were made at an average temperature of 298.15 K. The experimental H^E values are listed in Table 1 (see also Figs. 5–7).

Gas chromatographic measurements

The liquid–liquid equilibria for the mixtures 2-butanone + water and 2-pentanone + water have been investigated in the temperature range 273.15–338.15 K using a glass reactor (100 cm^3 volume) equipped with a thermostatic jacket and helicoidal stirring.

The stirring speed was measured by means of a stroboscope; the contact between the two fluids was started in nitrogen and a fine dispersion of the two fluids was reached only at a stirring speed of 1600 r.p.m.

After a contact time of about 10 min, the mixtures were allowed to decant so that the two phases could form; after drawing off an aliquot of each one, homogenization with known quantities of propanol and gas-chromatographic analysis then followed. The instrument used was a Hewlett-Packard 5700 A equipped with 3.5 m long column packed with Porapak Q.

TABLE 1

Experimental molar excess enthalpies, H^E, for 2-alkanones ($K_{s,t}$)(1)+water(2) mixtures at 298.15 K

$K_{s,t}$	2-Alkanone	x_1	H^E (J mole^{-1})
$K_{1,1}$	2-Propanone	0.0461	−341
		0.1017	−557
		0.1847	−628
		0.2400	−583
		0.2995	−495
		0.4143	−287
		0.4978	131
		0.6381	107
		0.7638	272
		0.7896	293
		0.8969	274
		0.9512	171
$K_{2,1}$	2-Butanone	0.0251	−200
		0.0515	−302
		0.0716	−385
		0.0875 [a]	−389
		0.2140 [a]	−300
		0.4085 [a]	76
		0.5916 [a]	380
		0.6602	484
		0.7155	540
		0.7612	551
		0.8057	534
		0.8744	445
		0.9500	223
$K_{3,1}$	2-Pentanone	0.0103	−75
		0.0311 [a]	−159
		0.3003 [a]	85
		0.4997 [a]	350
		0.6814 [a]	592
		0.7844 [a]	675
		0.8498 [a]	656
		0.8800	630
		0.9286	474
		0.9507	355

[a] Phase heterogeneity points.

Helium (20 mm^3 min^{-1}) was used as the carrier gas and the column temperature was 473.15 K.

Table 2 lists the LLE data for 2-butanone ($K_{2,1}$) and 2-pentanone ($K_{3,1}$) + water systems (see also Figs. 2 and 4).

TABLE 2

Data of liquid–liquid equilibria at various temperatures for the 2-alkanone ($K_{s,t}$)(1)+water(2) mixtures

x_{11} = molar fraction of 2-alkanone in the 2-alkanone-rich phase; x_{12} = molar fraction of 2-alkanone in the water-rich phase

$K_{s,t}$	2-Alkanone	T (K)	x_{11}	x_{12}
$K_{2,1}$	2-Butanone	273.15	0.6429	0.1679
		278.15	0.6631	0.1403
		283.15	0.6670	0.1158
		288.15	0.6608	0.1027
		293.15	0.6612	0.0930
		298.15	0.6571	0.0862
		308.15	0.6419	0.0718
		318.15	0.6214	0.0650
		328.15	0.6075	0.0542
		338.15	0.5890	0.0518
$K_{3,1}$	2-Pentanone	273.15	0.9214	0.0188
		278.15	0.9143	0.0150
		288.15	0.8993	0.0134
		298.15	0.8786	0.0116
		308.15	0.8500	0.0113
		318.15	0.8143	0.0106
		328.15	0.7786	0.0080
		338.15	0.7350	0.0075

ESTIMATION OF THE NRTL PARAMETERS

The NRTL equation (non-random, two liquids), described in detail by Renon et al. [37], provides a useful description of LVE and LLE of strongly non-ideal mixtures. The basic equation of the model for the molar excess Gibbs energies of binary liquid mixtures is

$$\frac{G^{\mathrm{E}}(x,T)}{RT} = x_1 x_2 \left[\frac{\tau_{21} \exp(-\alpha_{12}\tau_{21})}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} + \frac{\tau_{12} \exp(-\alpha_{12}\tau_{12})}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})} \right] \tag{1}$$

where $\tau_{12} = C_{12}/RT$ and $\tau_{21} = C_{21}/RT$, while $C_{12} = g_{12} - g_{22}$ and $C_{21} = g_{21} - g_{11}$ are the free energy parameters for the interactions between the pairs of constituents, 1–2.

The non-randomness parameter, α_{12}, can often be estimated with sufficient accuracy from the nature of components 1 and 2 [38] and for binary mixtures with partial miscibility it is possible to estimate the NRTL parameters C_{12} and C_{21} from mutual solubilities at the same temperature.

A more flexible model, which is also able to correlate the excess enthalpies simultaneously, can only be obtained by taking into account the temperature dependence of α_{12}, C_{12} and C_{21}, given by

$$\alpha_{12} = \alpha_{12}^{0} + \alpha_{12}^{T}(T - 273.15) \tag{2}$$

$$\mathrm{C}_{12} = \mathrm{C}_{12}^{0} + \mathrm{C}_{12}^{T}(T - 273.15) \tag{3}$$

$$\mathrm{C}_{21} = \mathrm{C}_{21}^{0} + \mathrm{C}_{21}^{T}(T - 273.15) \tag{4}$$

so that the excess enthalpy becomes

$$\begin{aligned} H^{\mathrm{E}} = {} & \frac{x_1 x_2 \exp(-\alpha_{12}\tau_{21})}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})}\left(1 - \frac{\alpha_{12}\tau_{21}x_1}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})}\right)\left(C_{21}^{0} - 273.15C_{21}^{T}\right) \\ & + \frac{x_1 x_2 \exp(-\alpha_{12}\tau_{12})}{x_1 + x_2 \exp(-\alpha_{12}\tau_{12})}\left(1 - \frac{\alpha_{12}\tau_{12}x_2}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})}\right)\left(C_{12}^{C} - 273.15C_{12}^{T}\right) \\ & + \alpha_{12}^{T}RT^2 x_1 x_2 \left\{\frac{\tau_{21}^2 x_1 \exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} + \frac{\tau_{12}^2 x_2 \exp(-\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2}\right\} \end{aligned} \tag{5}$$

COMPARISON WITH EXPERIMENT

The liquid–vapor (LVE) and liquid–liquid (LLE) curves, and the molar excess enthalpies (H^{E}) were calculated for all the 2-alkanone ($\mathrm{K}_{s,t}$) (1) + water (2) systems and the NRTL parameters were listed in Table 3.

Some calculated liquid–vapor phase diagrams, T vs. $x - y$, are shown in Figs. 1 and 2. A reasonably good agreement with the experimental values is observed.

A model-based prediction of G^{E} and μ_i^{E} for the 2-propanone(1) + water(2) system is shown in Fig. 3. The magnitude and shape of the curves are well reproduced by the NRTL model. The "experimental" molar excess Gibbs energy values, G^{E}, were calculated from the original isothermal P–$x - y$ data [18] with the 3-parameter Redlich–Kister equation. Vapor phase imperfection was accounted for a terms of the second virial coefficients estimated by the method of Hayden and O'Connell [44].

TABLE 3

Parameters in the NRTL equation calculated by the simultaneous correlation of LVE, LLE and H^{E} data for the 2-alkanone ($\mathrm{K}_{s,t}$)(1)+water(2) mixtures

$\mathrm{K}_{s,t}$	2-Alkanone	α_{12}	α_{12}^{T} (K^{-1})	C_{12} (J mole^{-1})	C_{12}^{T} (J mole^{-1} K^{-1})	C_{21} (J mole^{-1})	C_{21}^{T} (J mole^{-1} K^{-1})
$\mathrm{K}_{1,1}$	2-Propanone	0.2474	−0.0004	2525	−30	1831	57
$\mathrm{K}_{2,1}$	2-Butanone	0.3956	0.0003	3647	−3	4617	51
$\mathrm{K}_{3,1}$	2-Pentanone	0.3984	−0.0001	6444	−8	8737	56

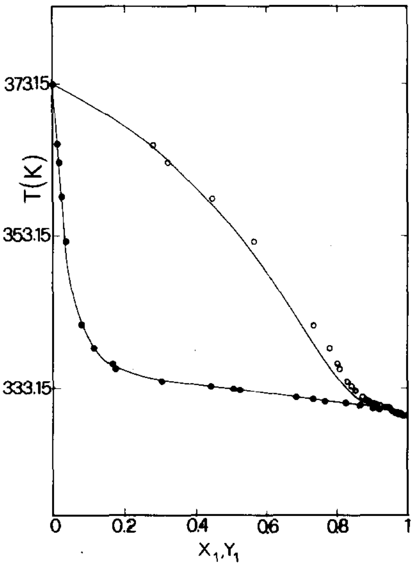

Fig. 1. Comparison of theory with experiment for the isobar liquid–vapor phase equilibrium diagram of 2-propanone ($K_{1,1}$)(1)+water(2) mixtures at $P = 760$ mm Hg. Equilibrium temperature, T, vs. x_1 or y_1, the mole fractions of component 1 in the liquid or vapor phase, respectively. ———, Predicted values; ●, ○, experimental results [19].

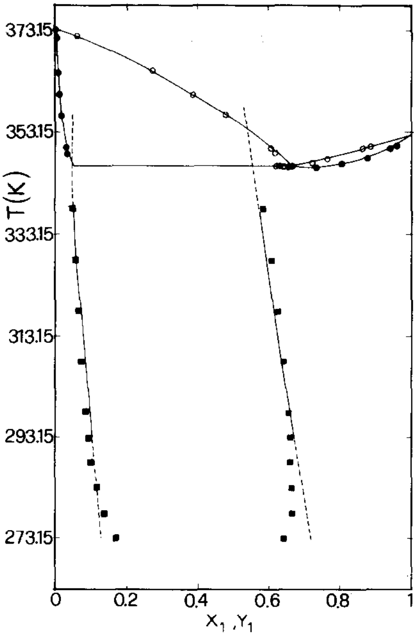

Fig. 2. Comparison of theory with experiment for the isobar liquid–vapor phase equilibrium and liquid–liquid phase equilibrium diagram of 2-butanone ($K_{2,1}$)(1)+water(2) mixtures at $P = 760$ mm Hg. Equilibrium temperature, T, vs. x_1 or y_1, the mole fractions of component 1 in the liquid or vapor phase, respectively. ———, Predicted values; ●, ○, liquid–vapor equilibrium [19], experimental results; ■, liquid–liquid equilibrium, experimental results from this paper.

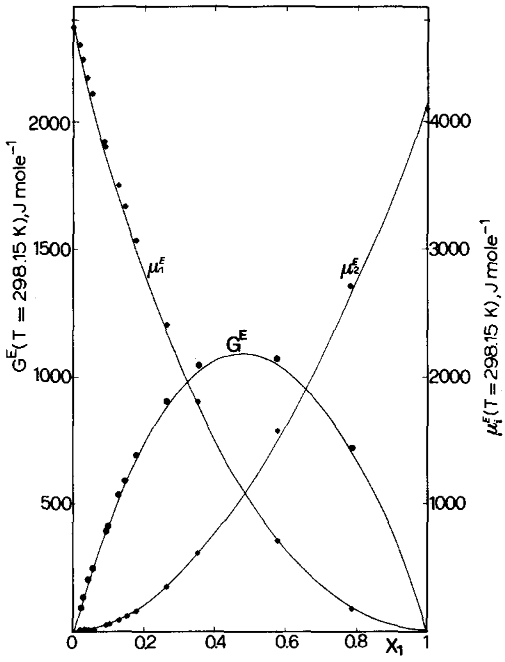

Fig. 3. Comparison of theory with experiment for the molar excess Gibbs energy, G^E, and partial molar excess Gibbs energies, μ_i^E, of 2-propanone $(K_{1,1})(1)$+water(2) mixtures at 298.15 K vs. x_1, the mole fraction of 2-propanone. ———, Predicted values; ●, *, smoothed values obtained by reduction of direct experimental $P - x$ values [18].

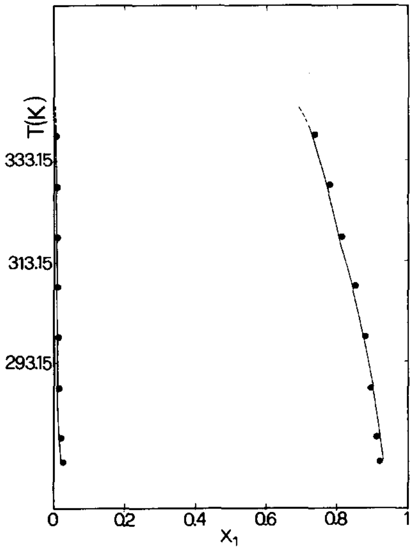

Fig. 4. Liquid–liquid phase diagram of 2-pentanone $(K_{3,1})(1)$+water(2) mixtures. ———, Predicted curve; ●, experimental results (this paper).

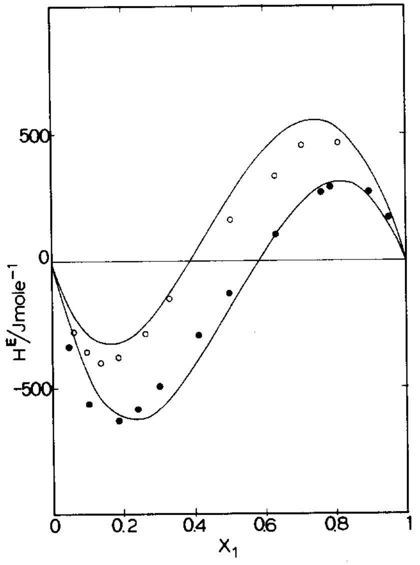

Fig. 5. Comparison of theory with experiment for the molar excess enthalpy, H^E, of 2-propanone ($K_{1,1}$)(1)+water(2) at 298.15 K and 323.15 K vs. x_1, the mole fraction of 2-propanone. ————, Predicted values; ●, experimental results from this paper ($T = 298.15$ K); ○, experimental results from ref. 30 ($T = 323.15$ K).

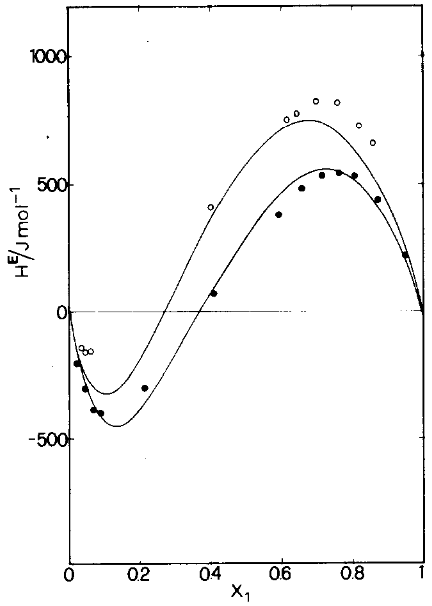

Fig. 6. Comparison of theory with experiment for the molar excess enthalpy, H^E, of 2-butanone ($K_{2,1}$)(1)+water(2) mixtures at 298.15 and 323.15 K vs. x_1, the mole fraction of 2-butanone. ————, Predicted values; ●, experimental results from this paper ($T = 298.15$ K); ○, experimental results from ref. 30 ($T = 323.15$ K).

The excess enthalpies of 2-alkanone(1) + water(2) systems do not agree, in general, with the prediction of the NRTL model with respect to both the magnitude and the symmetry of the H^E/x_1 curves (see Figs. 5–7). Furthermore, the model, using the value of 0.39 for the non-random coefficient α_{12}, correctly predicts phase splitting of 2-butanone and 2-pentanone in water. However, the calculated curves are different from the experimental ones in the vicinity of the lower critical temperature (Figs. 2 and 4). The shape of the calculated LLE curves agrees well with the experimental one at $T > 293.15$ K.

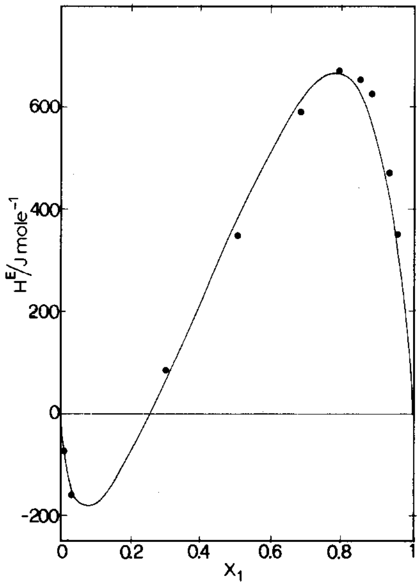

Fig. 7. Comparison of theory with experiment for the molar excess enthalpy, H^E, of 2-pentanone ($K_{3,1}$)(1)+water(2) mixtures at 298.15 K vs. x_1, the mole fraction of 2-pentanone. ———, Predicted values; ●, experimental results (this paper) ($T = 298.15$ K).

The difficulties in representing LLE are well-known. It is just for this purpose that UNIFAC has developed a new parameter table, different from the one used for LVE prediction [45].

DISCUSSION

The NRTL equation provides a useful description of the excess Gibbs energies of strongly non-ideal mixtures that may or may not be completely miscible. Parameters in the equation are estimated from limiting activity coefficients ($K_{1,1}$) and from mutual solubility ($K_{2,1}$ and $K_{3,1}$). The best agreement between calculated and experimental results is obtained when the non-randomness parameter, α_{12}, is determined from experimental data.

We find that α_{12} ranges from approximately 0.25 ($K_{1,1}$) to 0.40 ($K_{2,1}$ and $K_{3,1}$) accounting for the passage from a completely miscible system ($K_{1,1}$) to systems with a miscibility gap ($K_{2,1}$ and $K_{3,1}$).

A comparison of the NRTL equation with equations of the quasi-randomness parameter, α_{12}, shows that α_{12} is the inverse of the coordination number, z. We may therefore expect, on the basis of our α_{12} values, z values ranging from 4($K_{1,1}$) to 2.5($K_{2,1}$ and $K_{3,1}$); nevertheless, the z value reported in the literature for ketones is 10 [47,48], the value being constant for the entire class of 2-alkanones.

As a consequence, when the α_{12} value exceeds (approximately) 0.3 its physical significance becomes obscure, its apparent role being that of an empirical constant which allows the representation of associated (hydro-organic) mixtures for which the Guggenheim theory is not applicable. Anyway, it is our opinion that a physical significance can be given to the α_{12} parameter in order to correlate it with the coordination number, z, only if a way is found to keep it constant for each homologous series (alkanones, ethers, etc.) by simultaneously introducing in the NRTL equation geometric parameters (such as molecular volumes and surfaces) which are able to take account of differences in shape and dimensions of molecules within the same homologous series. As regards the symmetry of the excess enthalpy curves, it is seen that, in spite of the flexibility given to the model by the presence of six parameters, the agreement between the calculated and experimental values of the excess enthalpies is not satisfactory [on the average the standard deviations lie within 7%, for the systems investigated (see Table 4)] in the entire concentration range and the wide temperature range (293.15–363.15 K). Nevertheless, it is worth noting that although the three systems investigated are very complex the NRTL model reproduces the S-shaped enthalpy curves.

Anyway, the other prediction model for the activity coefficients (UNIFAC, ASOG) gives the same accuracy for the model based on the Guggenheim theory [46] or the NRTL model, but the temperature dependence of

TABLE 4

Standard deviation, $\sigma(X)$[a], for the experimental and calculated properties using the NRTL equation[b] for the 2-alkanone ($K_{s,t}$)(1)+water(2) mixtures

$K_{s,t}$	2-Alkanone	$\sigma(P)$	$\sigma(Y)$	$\sigma(H^E)$	$\sigma(S)$	$\sigma(\gamma_i^\infty)$
$K_{1,1}$	2-Propanone	2.6	2.0	11.5		1.8
$K_{2,1}$	2-Butanone	2.5	1.5	6.5	1.1	0.5
$K_{3,1}$	2-Pentanone			1.6	0.7	

[a] For the liquid–vapor equilibrium; P is the vapor pressure; Y is the molar fraction in the vapor phase); H^E is the excess enthalpy; S is the liquid–liquid equilibrium); γ_i^∞ represents the activity coefficients.

[b] $\sigma(X) = [\Sigma_i(X_C - X_{exp})^2/n(n-1)]^{1/2}$, where n = number of experimental points.

the activity coefficients, i.e. the enthalpy of mixing, is more difficult to predict.

Coming back to the physical significance of the parameters in the NRTL equation, it can be seen that asymmetric systems are those where C_{12} (or $\tau_{12} = C_{12}/RT$) is different from C_{21} (or $\tau_{21} = C_{21}/RT$), therefore we can say that the lack of symmetry of a system (or more precisely, the skewness of the Gibbs energy and excess enthalpy curves) is related to the difference between C_{12} and C_{21}, while the degree of non-ideality is related mainly to their sum.

The values of the parameters C_{12} and C_{21} found for the systems 2-alkanone ($K_{s,t}$) + water (see Table 3) thus suggest that the degree of non-ideality as well as the asymmetry, increase as the alkyl chain of the 2-alkanone increases in length; furthermore, in the short range (passing from 2-propanone to 2-butanone by adding a $-CH_2-$ group, $s = 2$) the degree effects of non-ideality predominate while in the long range [passing from 2-propanone to 2-pentanone by adding a $-(CH_2)_2-$ group, $s = 3$] the asymmetry effect prevails.

The excess enthalpies of the 2-alkanone(1) + water(2) mixtures shows the same evolution: exothermic in the water-rich region and endothermic in the 2-alkanone-rich region. This behavior can be qualitatively interpreted by referring to the "flickering cluster" model of liquid water proposed by Frank and Wen [49]. We have formerly applied this model to aqueous mixtures of aliphatic aldehydes [9] and cyclic ethers [10] whose behavior in water is very similar to that shown by the 2-alkanones.

The dependence of H^E on the number of alkyl groups (s,t) in the chain, according with the gradation of observed phase behavior, from solutes which are completely miscible (2-propanone), through solutes which exhibit an LCST (2-butanone), finally to solutes which exhibit a miscibility gap at all temperatures (2-pentanone) is the same as that observed by Della Gatta et al. [33] for the solvation enthalpies of homologous aliphatic ketones in water.

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