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Calculations of quaternary liquid–liquid equilibria by use of a new local composition model

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Abstract

A new local composition model with two adjustable parameters per binary can represent binary vapour–liquid equilibria with good accuracy. For a ternary mixture the model includes six binary parameters and three additional ternary parameters in order to fit the model to ternary liquid–liquid equilibria. An extended form of the model for a quaternary mixture is proposed to involve further four quaternary parameters. Calculated liquid–liquid equilibrium results for 12 quaternary systems apparently show the good performance of the new model.

LIST OF SYMBOLS

a_{ij}	binary interaction parameter related to Δu_{ij} and τ_{ij}
a^{E}	excess molar Helmholtz energy
F	objective function as defined by eqn. (23)
g^{E}	excess molar Gibbs energy
n_i	number of moles of component i
n_{T}	total number of moles
p	exponent
R	universal gas contant
r_i	molecular structural size parameter of component i
T	absolute temperature
Δu_{ij}	binary interaction parameter for i–j pair
u^{E}	excess molar energy of mixing
x_i	liquid-phase mole fraction of component i
y_i	vapour-phase mole fraction of component i

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Greek letters

γ_i	activity coefficient of component i
δ_{jki}, δ_{jkli}	ternary and quaternary coefficients
τ_{ij}	binary parameter as defined by $\exp(-\Delta u_{ij}/RT) = \exp(-a_{ij}/T)$
τ_{jki}, τ_{jkli}	ternary and quaternary parameters
ϕ_i	segment fraction of component i
ϕ_{ij}, ϕ_{jki}, ϕ_{jkli}	local segment fractions

Subscripts

calc	calculated
com	combinatorial
exp	experimental
res	residual
i, j, k	components

INTRODUCTION

The workability of a newly proposed local composition model has been extensively studied to represent binary coexistence curves over a wide temperature range for mixtures of small molecules [1] as well as aqueous polymer mixtures [2] and further to predict ternary vapour–liquid and to correlate ternary liquid–liquid equilibria (LLE) for many liquid mixtures [3]. This paper presents an extended form of the new local composition model for quaternary LLE calculations.

SOLUTION MODEL

A new local composition model, called extended Wilson, has two contributions of the excess Gibbs free energy g^E, a combinatorial term expressed by the modified Flory–Huggins equation and a residual term.

Binary systems

$$g^E = g^E_{\text{com}} + g^E_{\text{res}} \tag{1}$$

$$\frac{g^E_{\text{com}}}{RT} = x_1 \ln\frac{\psi_1}{x_1} + x_2 \ln\frac{\psi_2}{x_2} \tag{2}$$

$$\frac{g^E_{\text{res}}}{RT} = -x_1 \ln(\phi_1 + \phi_2\tau_{21}) - x_2 \ln(\phi_2 + \phi_1\tau_{12}) \tag{3}$$

where the modified segment fraction ψ, the segment fraction ϕ and the binary parameter τ are defined by

$$\psi_1 = x_1 r_1^p/(x_1 r_1^p + x_2 r_2^p) \qquad \psi_2 = x_2 r_2^p/(x_1 r_1^p + x_2 r_2^p) \tag{4}$$

$$\phi_1 = x_1 r_1/(x_1 r_1 + x_2 r_2) \qquad \phi_2 = x_2 r_2/(x_1 r_1 + x_2 r_2) \tag{5}$$

$$\tau_{21} = \exp(-a_{21}/T) \qquad \tau_{12} = \exp(-a_{12}/T) \tag{6}$$

a_{21} and a_{12} are the binary energy parameters and the exponent p is taken as 2/3 [4].

The activity coefficient of any component i is derived from

$$\ln \gamma_i = \frac{1}{RT}\left(\frac{\partial n_T g^E}{\partial n_i}\right)_{P,T,n_j \neq i} \tag{7}$$

Substituting eqns. (2) and (3) into eqn. (7) gives

$$\begin{aligned}\ln \gamma_1 = {} & \ln \frac{\psi_1}{x_1} + 1 - \frac{\psi_1}{x_1} - \ln(\phi_1 + \phi_2\tau_{21}) - \left(1 - \frac{\phi_1}{x_1}\right) \\ & + \phi_2\left[\frac{\tau_{21}}{\phi_1 + \phi_2\tau_{21}} - \frac{r_1}{r_2}\left(\frac{\tau_{12}}{\phi_2 + \phi_1\tau_{12}}\right)\right]\end{aligned} \tag{8}$$

$$\begin{aligned}\ln \gamma_2 = {} & \ln \frac{\psi_2}{x_2} + 1 - \frac{\psi_2}{x_2} - \ln(\phi_2 + \phi_1\tau_{12}) - \left(1 - \frac{\phi_2}{x_2}\right) \\ & + \phi_1\left[\frac{\tau_{12}}{\phi_2 + \phi_1\tau_{12}} - \frac{r_2}{r_1}\left(\frac{\tau_{21}}{\phi_1 + \phi_2\tau_{21}}\right)\right]\end{aligned} \tag{9}$$

Ternary systems

The ternary expression of g^E includes unlike three-body interaction terms.

$$\begin{aligned}\frac{g^E}{RT} = \sum_i x_1 \ln \frac{\psi_i}{x_i} & - x_1 \ln(\phi_1\tau_{11} + \phi_2\tau_{21} + \phi_3\tau_{31} + \phi_2\phi_3\tau_{231}) \\ & - x_2 \ln(\phi_1\tau_{12} + \phi_2\tau_{22} + \phi_3\tau_{32} + \phi_1\phi_3\tau_{132}) \\ & - x_3 \ln(\phi_1\tau_{13} + \phi_2\tau_{23} + \phi_3\tau_{33} + \phi_1\phi_2\tau_{123})\end{aligned} \tag{10}$$

where $\tau_{ii} = 1$. The conventional local composition models include only binary interaction terms and are not useful in the correlation of ternary LLE data using binary parameters obtained from binary phase equilibrium data. Equation (10) involves the three adjustable ternary parameters, τ_{231}, τ_{132} and τ_{123}, which are evaluated in fitting the model to ternary phase equilibrium data.

The activity coefficient of component 1 in a ternary mixture is given by

$$\begin{aligned}\ln \gamma_1 = {} & \ln \frac{\psi_1}{x_1} + 1 - \frac{\psi_1}{x_1} - \ln\left(\sum_j \phi_j\tau_{j1} + \phi_2\phi_3\tau_{231}\right) \\ & - \Bigg[\phi_1 \frac{\tau_{11} - \sum_j \phi_j\tau_{j1} - 2\phi_2\phi_3\tau_{231}}{\sum_j \phi_j\tau_{j1} + \phi_2\phi_3\tau_{231}}\end{aligned}$$

$$+\frac{r_1}{r_2}\phi_2\frac{\tau_{12}-\sum_j\phi_j\tau_{j2}+(1-2\phi_1)\phi_3\tau_{132}}{\sum_j\phi_j\tau_{j2}+\phi_1\phi_3\tau_{132}}$$

$$\left.+\frac{r_1}{r_3}\phi_3\frac{\tau_{13}-\sum_j\phi_j\tau_{j3}+(1-2\phi_1)\phi_2\tau_{123}}{\sum_j\phi_j\tau_{j3}+\phi_1\phi_2\tau_{123}}\right] \qquad (11)$$

Quaternary systems

An extended expression of the ternary g^{E} to a quaternary system can be given by

$$\frac{g^{\mathrm{E}}}{RT}=\sum_i x_1\ln\frac{\psi_i}{x_i}-\sum_i x_i\ln\left(\sum_j\phi_j\tau_{ji}+\frac{1}{2}\sum_{j\neq k\neq i}\sum\phi_j\phi_k\tau_{jki}+\frac{1}{6}\sum\sum_{j\neq k\neq l\neq i}\sum\phi_j\phi_k\phi_l\tau_{jkli}\right) \qquad (12)$$

where $\tau_{jki}=\tau_{kji}\neq 0$, and $\tau_{jji}=\tau_{jij}=\tau_{jii}=0$, $\tau_{jkli}=\tau_{jlki}=\tau_{kjli}=\tau_{klji}=\tau_{ljki}=\tau_{lkji}\neq 0$ and $\tau_{jjji}=\tau_{kkji}=\tau_{kjki}=0$. The expanded form of $g^{\mathrm{E}}_{\mathrm{res}}$ is

$$\begin{aligned}\frac{g^{\mathrm{E}}_{\mathrm{res}}}{RT}=&-x_1\ln(\phi_1+\phi_2\tau_{21}+\phi_3\tau_{31}+\phi_4\tau_{41}+\phi_2\phi_3\tau_{231}+\phi_2\phi_4\tau_{241}+\phi_3\phi_4\tau_{341}\\&+\phi_2\phi_3\phi_4\tau_{2341})-x_2\ln(\phi_1\tau_{12}+\phi_2+\phi_3\tau_{32}+\phi_4\tau_{42}+\phi_1\phi_3\tau_{132}\\&+\phi_1\phi_4\tau_{142}+\phi_3\phi_4\tau_{342}+\phi_1\phi_3\phi_4\tau_{1342})-x_3\ln(\phi_1\tau_{13}+\phi_2\tau_{23}+\phi_3\\&+\phi_4\tau_{43}+\phi_1\phi_2\tau_{123}+\phi_1\phi_4\tau_{143}+\phi_2\phi_4\tau_{243}+\phi_1\phi_2\phi_4\tau_{1243})\\&-x_4\ln(\phi_1\tau_{14}+\phi_2\tau_{24}+\phi_3\tau_{34}+\phi_4+\phi_1\phi_2\tau_{124}+\phi_1\phi_3\tau_{134}\\&+\phi_2\phi_3\tau_{234}+\phi_1\phi_2\phi_3\tau_{1234})\end{aligned} \qquad (13)$$

Equation (13) is derived in the following way. The excess energy of mixing u^{E} for a quaternary mixture may be given by

$$\begin{aligned}u^{\mathrm{E}}=&\sum_{j\neq i}\sum x_i\phi_{ji}\Delta u_{ji}+\frac{1}{2}\sum\sum_{j\neq k\neq i}\sum x_i\phi_{jki}(\Delta u_{ji}+\Delta u_{ki})\\&+\frac{1}{6}\sum\sum_{j\neq k\neq l\neq i}\sum\sum x_i\phi_{jkli}(\Delta u_{ji}+\Delta u_{ki}+\Delta u_{li})\end{aligned} \qquad (14)$$

where the local segment fractions, ϕ_{ji}, ϕ_{jki} and ϕ_{jkli}, are defined by

$$\phi_{ji}=\frac{\phi_j\tau_{ji}}{\sum_k\phi_k\tau_{ki}+\frac{1}{2}\sum_{j\neq k\neq i}\sum\delta_{jki}\phi_j\phi_k\tau_{ji}\tau_{ki}+\frac{1}{6}\sum\sum_{j\neq k\neq l\neq i}\sum\delta_{jkli}\phi_j\phi_k\phi_l\tau_{ji}\tau_{ki}\tau_{li}} \qquad (15)$$

$$\phi_{jkl}=\frac{\frac{1}{2}\sum_{j\neq k\neq i}\sum\delta_{jki}\phi_j\phi_k\tau_{ji}\tau_{ki}}{\sum_k\phi_k\tau_{ki}+\frac{1}{2}\sum_{j\neq k\neq i}\sum\delta_{jki}\phi_j\phi_k\tau_{ji}\tau_{ki}+\frac{1}{6}\sum\sum_{j\neq k\neq l\neq i}\sum\delta_{jkli}\phi_j\phi_k\phi_l\tau_{ji}\tau_{ki}\tau_{li}} \qquad (16)$$

$$\phi_{jkli} = \frac{\frac{1}{6}\sum_{j\neq k\neq l\neq i}\sum\sum \phi_j\phi_k\phi_l\tau_{jl}\tau_{kl}\tau_{li}}{\sum_k \phi_k\tau_{ki} + \frac{1}{2}\sum_{j\neq k\neq i}\sum \delta_{jki}\phi_j\phi_k\tau_{ji}\tau_{ki} + \frac{1}{6}\sum_{j\neq k\neq l\neq i}\sum\sum \delta_{jkli}\phi_j\phi_k\phi_l\tau_{ji}\tau_{ki}\tau_{li}} \tag{17}$$

where δ_{jki} and δ_{jkl} are ternary and quaternary coefficients.

An expression for the excess molar Helmholtz energy a^{E} is derived from the relation

$$\frac{\mathrm{d}(a^{\mathrm{E}}/T)}{\mathrm{d}(1/T)} = u^{\mathrm{E}} \tag{18}$$

Integration of eqn. (18) from $1/T_0$ to $1/T$ yields

$$\frac{a^{\mathrm{E}}}{T} = \int_{1/T_0}^{1/T} u^{\mathrm{E}}\,\mathrm{d}\left(\frac{1}{T}\right) + \text{constant of integration} \tag{19}$$

As $1/T_0 \to 0$, we adopt the modified Flory–Huggins equation as a boundary condition of eqn. (19). At low pressures we can take it that $a^{\mathrm{E}} \approx g^{\mathrm{E}}$ [5]. Then we can obtain eqn. (12) by taking $\tau_{jki} = \delta_{jki}\tau_{ji}\tau_{ki}$ and $\tau_{jkli} = \delta_{jkli}\tau_{ji}\tau_{ki}\tau_{li}$.

Substituting eqn. (12) into eqn. (7) yields the activity coefficient of component 1.

$$\begin{aligned}
\ln\gamma_1 = {} & \ln\frac{\psi_1}{x_1} + 1 - \frac{\psi_1}{x_1} - \ln\left(\sum_j \phi_j\tau_{j1} + \phi_2\phi_3\tau_{231} + \phi_2\phi_4\tau_{241} + \phi_3\phi_4\tau_{341} + \phi_2\phi_3\phi_4\tau_{2341}\right) \\
& - r_1\left\{\frac{\phi_1}{r_1}\,\frac{1 - \sum_j \phi_j\tau_{jl} - 2(\phi_2\phi_3\tau_{231} + \phi_2\phi_4\tau_{241} + \phi_3\phi_4\tau_{341}) - 3\phi_2\phi_3\phi_4\tau_{2341}}{\sum_j \phi_j\tau_{j1} + \phi_2\phi_3\tau_{231} + \phi_2\phi_4\tau_{241} + \phi_3\phi_4\tau_{341} + \phi_2\phi_3\phi_4\tau_{2341}}\right. \\
& + \frac{\phi_2}{r_2}\,\frac{\tau_{12} - \sum_j \phi_j\tau_{j2} - (2\phi_1 - 1)\phi_3\tau_{132} - (2\phi_1 - 1)\phi_4\tau_{142} - 2\phi_3\phi_4\tau_{342} - (3\phi_1 - 1)\phi_3\phi_4\tau_{1342}}{\sum_j \phi_j\tau_{j2} + \phi_1\phi_3\tau_{132} + \phi_1\phi_4\tau_{142} + \phi_3\phi_4\tau_{342} + \phi_1\phi_3\phi_4\tau_{1342}} \\
& + \frac{\phi_3}{r_3}\,\frac{\tau_{13} - \sum_j \phi_j\tau_{j3} - (2\phi_1 - 1)\phi_2\tau_{123} - (2\phi_1 - 1)\phi_4\tau_{143} - 2\phi_2\phi_4\tau_{243} - (3\phi_1 - 1)\phi_2\phi_4\tau_{1243}}{\sum_j \phi_j\tau_{j3} + \phi_1\phi_2\tau_{123} + \phi_1\phi_4\tau_{143} + \phi_2\phi_4\tau_{243} + \phi_1\phi_2\phi_4\tau_{1243}} \\
& \left. + \frac{\phi_4}{r_4}\,\frac{\tau_{14} - \sum_j \phi_j\tau_{j4} - (2\phi_1 - 1)\phi_2\tau_{124} - (2\phi_1 - 1)\phi_3\tau_{134} - 2\phi_2\phi_3\tau_{234} - (3\phi_1 - 1)\phi_2\phi_3\tau_{1234}}{\sum_j \phi_j\tau_{j4} + \phi_1\phi_2\tau_{124} + \phi_1\phi_3\tau_{134} + \phi_2\phi_3\tau_{234} + \phi_1\phi_2\phi_3\tau_{1234}}\right\}
\end{aligned} \tag{20}$$

The expression of $\ln\gamma_2$ is given by changing the subscripts as follows: 1 → 2, 2 → 3, 3 → 4 and 4 → 1. Analogously the expressions for $\ln\gamma_3$ and $\ln\gamma_4$ are obtained by cyclic advancement of the subscripts.

CALCULATED RESULTS

Binary systems

Vapour–liquid equilibrium data for binary systems constituting quaternary systems were reduced using a computer program based on the maxi-

TABLE 1

Values of molecular structural size parameters for pure compounds

Compound	*r*	Compound	*r*
Acetone	2.5739	Ethanol	2.1055
Acetonitrile	1.8701	*n*-Heptane	5.1742
Acetic acid	2.2024	Methanol	1.4311
Benzene	3.1878	*n*-Octane	5.8486
1-Butanol	3.4543	1-Propanol	2.7791
2-Butanone	3.2479	2-Propanol	2.7791
n-Butyl acetate	4.8274	Toluene	3.9228
Chloroform	2.8700	Water	0.9200
Cyclohexane	4.0464		

mum likelihood principle. The fugacity coefficients were usually calculated using the truncated volume-explicit virial equation and those for acetic acid containing mixtures were estimated using a chemical theory of vapour imperfections; the Poynting correction was also taken into account [6]. The energy parameters for partially miscible systems were obtained by solving the equations of isoactivity for the components (eqn. (21)) and eqn. (22) in equilibrated phases.

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{21}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \quad \text{and} \quad \sum_i x_i^{\mathrm{II}} = 1 \tag{22}$$

where the superscripts I and II indicate two liquid phases.

Table 1 shows the values of pure-component molecular size parameters *r* and Table 2 gives the values of the energy parameters obtained from binary phase equilibrium data reduction. All values of *r* were taken from Gmehling et al. [7-9, 11-13, 17-23].

Ternary systems

The three ternary parameters for each of the tie-lines were sought by minimizing the following objective function

$$F = 100\left[\sum_k \min \sum_j \sum_j (x_{ijk,\mathrm{exp}} - x_{ijk,\mathrm{calc}})^2/6M\right]^{0.5} \tag{23}$$

where $i = 1, 2, 3$ (components), $j = 1, 2$ (phases), $k = 1, 2, \ldots M$ (tie-lines) and min indicates minimum values. Table 3 denotes the values of ternary parameters and the root-mean-squared deviation between experimental and calculated tie-line values for 27 systems. Figures 1-5 illustrate the calculated and experimental results for ternary systems making up five quaternary systems, showing that the present model can correlate many ternary LLE satisfactorily.

TABLE 2

Calculated results of binary phase equilibrium data reduction

No.	System (1 + 2)	Temp./°C	Number of data points	Energy parameters		Root-mean-squared deviations				Ref.
				a_{12}/K	a_{21}/K	δP/mmHg	δT/K	$\delta x/10^3$	$\delta y/10^3$	
1	Acetic acid + 1-butanol	115.7–120.3	18	402.21	−160.73	1.08	0.07	1.1	10.2	7
2	Acetic acid + *n*-butyl acetate	117.7–125.2	15	−368.88	620.44	3.24	0.18	2.1	20.1	8
3	Acetone + acetic acid	35.0	12	168.01	−166.67	0.99	0.00	0.0	5.4	9
4	Acetone + 1-butanol	58.1–115.0	15	78.71	172.03	2.34	0.16	1.7	19.7	7
5	Acetone + 2-butanone	56.9–78.5	16	288.68	−140.38	2.84	0.18	2.1	11.4	9
6	Acetone + chloroform	35.0	9	−254.20	21.51	1.66	0.00	0.6	3.9	9
7	Acetone + 1-propanol	62.9–86.6	6	89.38	116.77	1.76	0.11	1.6	3.5	10
8	Acetone + water	25.0	13	636.54	−28.35	1.14	0.00	1.9	10.0	11
9	Acetonitrile + benzene	20.0	45	17.89	330.11	0.73	0.01	0.6	4.1	12
10	Acetonitrile + ethanol	20.0	13	147.50	359.62	0.51	0.01	0.0		13
11	Acetonitrile + methanol	55.0	13	234.15	117.98	1.78	0.00	0.4	2.8	14
12	Acetonitrile + 1-propanol	45.0	9	74.80	461.67	1.50	0.00	0.5	4.7	15
13	Acetonitrile + 2-propanol	50.0	15	63.43	388.46	0.92	0.00	0.5	3.2	16
14	Benzene + cyclohexane	25.0	11	42.69	103.70	0.91	0.00	0.1	0.9	17
15	Benzene + *n*-octane	65.0	26	204.22	11.76	1.47	0.04	0.6	4.4	18
16	1-Butanol + *n*-butyl acetate	116.8–121.2	9	132.94	65.01	0.76	0.05	0.9	8.5	7
17	2-Butanone + 1-butanol	80.7–111.2	14	53.66	129.51	1.70	0.10	1.3’	3.5	19
18	2-Butanone + 1-propanol	79.9–94.8	15	108.05	110.53	1.59	0.10	1.4	8.0	13
19	Chloroform + acetic acid	25.0	8	171.77	−53.48	5.49	0.06	2.0	18.0	8
20	Cyclohexane + *n*-heptane	25.0	30	77.59	−31.46	0.04	0.00	0.1	0.7	20
21	Cyclohexane + *n*-octane	25.0	26	118.58	−54.28	0.04	0.00	0.1	0.4	20
22	Cyclohexane + 1-propanol	25.0	27	846.93	177.51	1.18	0.00	0.2		13
23	Cyclohexane + 2-propanol	50.0	9	831.00	106.01	1.49	0.05	0.7	6.6	7

TABLE 2 (continued)

No.	System (1 + 2)	Temp./°C	Number of data points	Energy parameters		Root-mean-squared deviations				Ref.
				a_{12}/K	a_{21}/K	δP/mmHg	δT/K	$\delta x/10^3$	$\delta y/10^3$	
24	Cyclohexane + toluene	25.0	10	92.59	58.18	0.12	0.00	0.0		17
25	Ethanol + 1-butanol	80.0–115.0	12	226.99	−83.81	0.52	0.04	0.7	5.1	21
26	Ethanol + 2-butanone	55.0	14	25.19	253.39	1.77	0.06	0.8	7.5	21
27	Ethanol + cyclohexane	20.0	7	148.31	1061.81	0.31	0.00	0.0		13
28	*n*-Heptane + toluene	25.0	27	94.84	51.36	0.17	0.00	0.4	2.6	18
29	Methanol + benzene	35.0	9	11.93	911.43	0.70	0.02	1.0	4.2	21
30	Methanol + ethanol	25.0	11	270.85	−118.18	0.57	0.01	0.3	3.0	13
31	Methanol + 1-propanol	30.0	9	285.60	−37.46	0.37	0.01	0.0		21
32	Methanol + 2-propanol	55.0	20	−125.79	119.60	1.79	0.07	0.9	3.9	21
33	Methanol + toluene	45.0	11	−44.01	945.68	1.94	0.00	0.9	3.5	13
34	1-Propanol + 1-butanol	40.0	13	−76.35	83.90	0.07	0.00	0.0		22
35	1-Propanol + water	30.0	13	455.43	340.83	1.14	0.00	2.2	8.9	11
36	Toluene + *n*-octane	110.9–124.1	16	−38.38	131.07	1.62	0.09	0.6	4.1	18
37	Water + acetic acid	100.3–115.2	11	−107.51	330.17	0.82	0.05	0.8	5.3	23
38	Water + ethanol	25.0	10	65.54	327.07	0.75	0.00	1.2	6.0	23
39	Acetonitrile + cyclohexane	25.0	MS[a]	611.26	1320.1					24
40	Methanol + cyclohexane	25.0	MS	157.62	1141.5					16
41	Methanol + *n*-heptane	25.0	MS	67.37	1049.1					25
42	Methanol + *n*-octane	25.0	MS	51.15	1096.6					25
43	Water + 1-butanol	25.0	MS	600.15	455.22					26
44	Water + 1-butanol	25.0	MS	605.20	444.85					27
45	Water + 2-butanone	25.0	MS	195.42	700.96					27
46	Water + *n*-butyl acetate	25.0	MS	837.00	1224.9					26
47	Water + chloroform	25.0	MS	1398.0	1901.7					28

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[a] MS, mutual solubility.

TABLE 3

Calculated results of ternary liquid–liquid equilibria at 25°C

No.	System (1 + 2 + 3)	Number of tie-lines	Ternary parameters	Root-mean squared deviations/mol%		Ref.
				I^a	II^b	
1	Acetonitrile + benzene + cyclohexane	6	$\tau_{231} = -0.2230$ $\tau_{132} = 0.1971$ $\tau_{123} = -0.3483$	3.47	0.42	29
2	Acetonitrile + ethanol + cyclohexane	13	$\tau_{231} = 0.0700$ $\tau_{132} = -0.1781$ $\tau_{123} = -0.3244$	2.80	0.96	30
3	Acetonitrile + methanol + cyclohexane	7	$\tau_{231} = -0.1882$ $\tau_{132} = -0.1468$ $\tau_{123} = 0.7452$	2.52	0.63	31
4	Acetonitrile + 1-propanol + cyclohexane	7	$\tau_{231} = 0.1804$ $\tau_{132} = -0.3347$ $\tau_{123} = -0.0198$	1.93	0.47	15
5	Acetonitrile + 2-propanol + cyclohexane	8	$\tau_{231} = 0.1221$ $\tau_{132} = -0.4110$ $\tau_{123} = -0.0131$	1.10	0.39	32
6	Methanol + benzene + cyclohexane	6	$\tau_{231} = -0.0326$ $\tau_{132} = 1.8312$ $\tau_{123} = -1.1439$	2.92	0.19	29
7	Methanol + benzene + *n*-octane	6	$\tau_{231} = 0.1029$ $\tau_{132} = 0.5299$ $\tau_{123} = 0.9193$	6.66	0.68	25
8	Methanol + cyclohexane + *n*-heptane	11	$\tau_{231} = 0.0033$ $\tau_{132} = 0.0640$ $\tau_{123} = 0.1258$	1.08	0.21	33
9	Methanol + cyclohexane + *n*-octane	9	$\tau_{231} = 0.0188$ $\tau_{132} = 1.2158$ $\tau_{123} = -1.2607$	0.97	0.28	34
10	Methanol + ethanol + cyclohexane	7	$\tau_{231} = -0.1638$ $\tau_{132} = 0.2032$ $\tau_{123} = -0.9081$	4.93	0.16	29
11	Methanol + 1-propanol + cyclohexane	4	$\tau_{231} = -0.6076$ $\tau_{132} = 2.3300$ $\tau_{123} = -1.8886$	1.81	0.39	35
12	Methanol + 2-propanol + cyclohexane	7	$\tau_{231} = -0.1014$ $\tau_{132} = 0.6728$ $\tau_{123} = -0.8117$	2.82	0.52	29
13	Methanol + toluene + cyclohexane	7	$\tau_{231} = 0.0329$ $\tau_{132} = 1.4390$ $\tau_{123} = -0.4582$	3.37	0.16	29
14	Methanol + toluene + *n*-heptane	7	$\tau_{231} = -0.0222$ $\tau_{132} = 1.6601$ $\tau_{123} = -0.4383$	3.45	0.43	25

TABLE 3 (continued)

No.	System (1 + 2 + 3)	Number of tie-lines	Ternary parameters	Root-mean squared deviations/mol%		Ref.
				I [a]	II [b]	
15	Methanol +	7	$\tau_{231} = 0.0038$	2.85	0.38	25
	touene +		$\tau_{132} = 0.5362$			
	n-octane		$\tau_{123} = 0.6636$			
16	Water +	5	$\tau_{231} = 0.4667$	2.60	0.35	29
	acetic acid +		$\tau_{132} = 0.2333$			
	1-butanol		$\tau_{123} = 0.1733$			
17	Water +	15	$\tau_{231} = 0.4116$	2.95	0.46	29
	acetic acid +		$\tau_{132} = -1.1518$			
	n-butyl acetate		$\tau_{123} = -3.0218$			
18	Water +	8	$\tau_{231} = -0.3273$	6.20	1.35	29
	acetic acid +		$\tau_{132} = -0.8205$			
	chloroform		$\tau_{123} = -0.4460$			
19	Water +	5	$\tau_{231} = 0.6659$	3.83	0.49	29
	acetone +		$\tau_{132} = -0.0206$			
	1-butanol		$\tau_{123} = 0.4098$			
20	Water +	7	$\tau_{231} = 0.1169$	3.40	0.30	29
	acetone +		$\tau_{123} = 0.5530$			
	2-butanone		$\tau_{123} = 0.7439$			
21	Water +	8	$\tau_{231} = -0.0924$	7.18	0.51	29
	acetone +		$\tau_{132} = -0.8576$			
	chloroform		$\tau_{123} = -2.6484$			
22	Water +	4	$\tau_{231} = 0.0284$	2.15	0.35	36
	1-butanol +		$\tau_{132} = 0.3491$			
	n-butyl acetate		$\tau_{123} = 0.6098$			
23	Water +	4	$\tau_{231} = -0.0343$	7.43	0.07	29
	2-butanone +		$\tau_{132} = 2.9113$			
	1-butanol		$\tau_{123} = -0.6413$			
24	Water +	10	$\tau_{231} = -0.1376$	2.54	0.26	36
	ethanol +		$\tau_{132} = 4.5339$			
	1-butanol		$\tau_{123} = -1.1491$			
25	Water +	3	$\tau_{231} = 0.3667$	2.66	0.15	36
	ethanol +		$\tau_{132} = 2.1111$			
	2-butanone		$\tau_{123} = 0.0956$			
26	Water +	9	$\tau_{231} = 0.0045$	2.11	0.48	29
	1-propanol +		$\tau_{132} = 1.5244$			
	1-butanol		$\tau_{123} = -0.8945$			
27	Water +	3	$\tau_{231} = 0.3434$	4.15	0.11	29
	1-propanol +		$\tau_{132} = 1.8925$			
	2-butanone		$\tau_{123} = 0.7244$			

[a] I, Predicted results based on binary parameters. [b] II, Correlated results based on binary and ternary parameters.

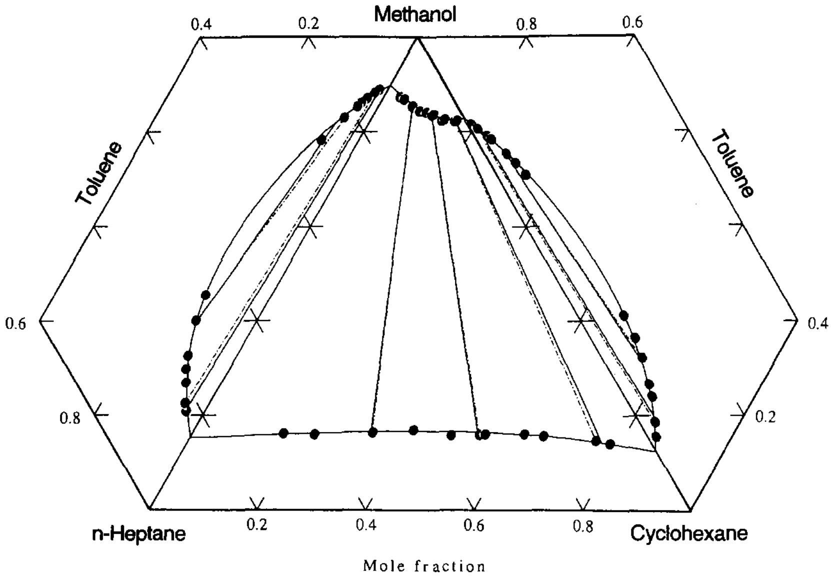

Fig. 1. Representation of ternary liquid–liquid equilibria using the extended Wilson model as obtained by incorporating ternary parameters. ● – · – ●, Experimental: methanol + tolune + cyclohexane [29]; methanol + toluene + n-heptane [25]; methanol + cyclohexane + n-heptane [33]. ——, Calculated.

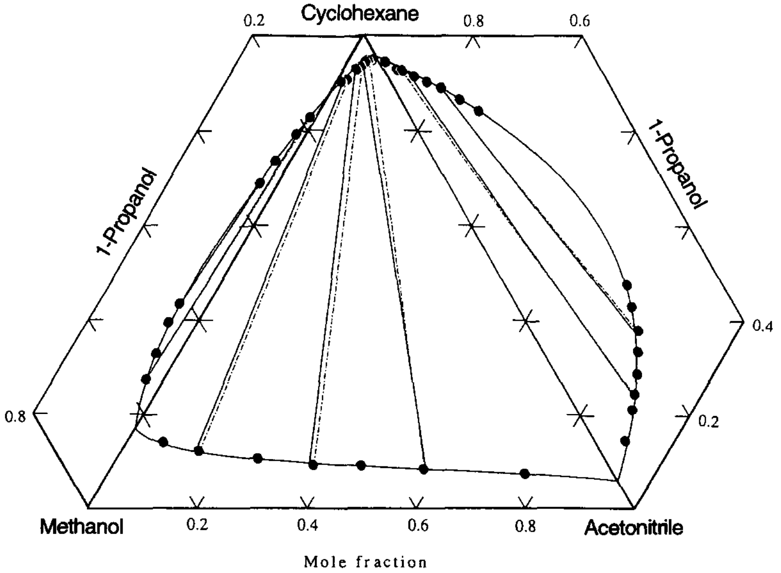

Fig. 2. Representation of ternary liquid–liquid equilibria using the extended Wilson model as obtained by incorporating ternary parameters. ● – · – ●, Experimental: cyclohexane + 1-propanol + acetonitrile [15]; cyclohexane + 1-propanol + methanol [35]; cyclohexane + acetonitrile + methanol [31]. ——, Calculated.

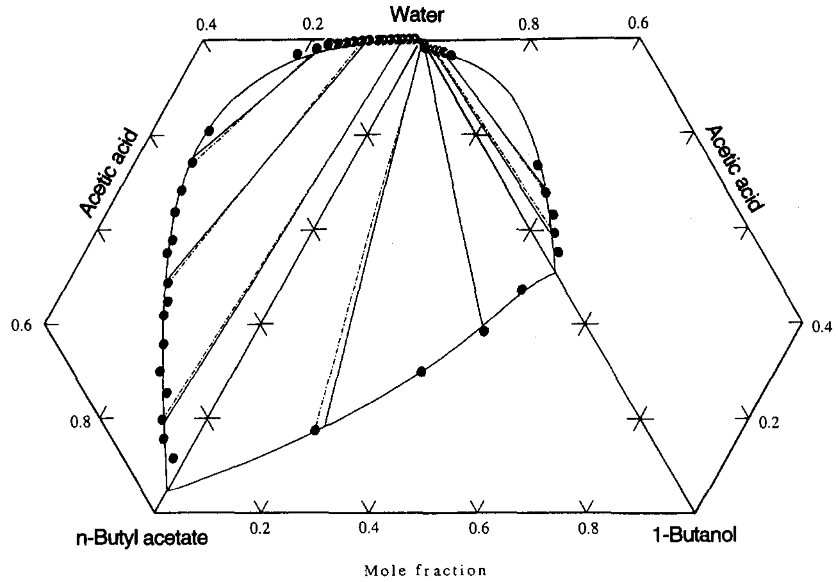

Fig. 3. Representation of ternary liquid–liquid equilibria using the extended Wilson model as obtained by incorporating ternary parameters. ●– · –●, Experimental: water + acetic acid + 1-butanol [29]; water + acetic acid + n-butyl acetate [29]; water + 1-butanol + n-butyl acetate [29]. ——, Calculated.

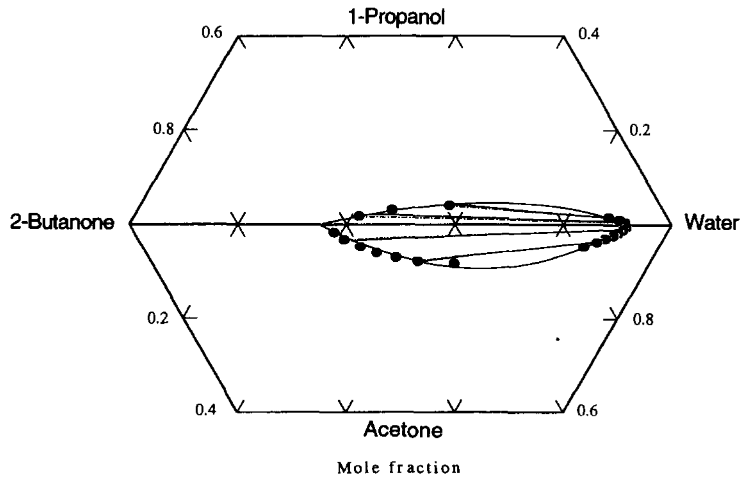

Fig. 4. Representation of ternary liquid–liquid equilibria using the extended Wilson model as obtained by incorporating ternary parameters. ●– · –●, Experimental: 2-butanone + 1-propanol + water [29]; water + acetone + 2-butanone [29]. ——, Calculated.

TABLE 4

Calculated results of Quarternary liquid–liquid equilibria at 25°C

No.	System (1 + 2 + 3 + 4)	Number of tie-lines	Ternary parameters	Root-mean squared deviations/mol%		Ref.
				I[a]	II[b]	
1	Cyclohexane +	13	τ_{2341} = 0.7290	1.35	0.63	32
	benzene +		τ_{1342} = −4.9561			
	acetonitrile +		τ_{1243} = −0.4246			
	methanol		τ_{1234} = 1.5906			
2	Cyclohexane +	15	τ_{2341} = −2.3805	1.18	0.70	32
	ethanol +		τ_{1342} = −3.2021			
	acetonitrile +		τ_{1243} = −0.0193			
	methanol		τ_{1234} = 4.7852			
3	Cyclohexane +	16	τ_{2341} = 1.0322	1.03	0.63	32
	1-propanol +		τ_{1342} = 0.7249			
	acetonitrile +		τ_{1243} = 0.7410			
	methanol		τ_{1234} = −0.2943			
4	Cyclohexane +	14	τ_{2341} = −1.6528	0.71	0.63	32
	2-propanol +		τ_{1342} = −4.5771			
	acetonitrile +		τ_{1243} = 0.4362			
	methanol		τ_{1234} = 1.6517			
5	Methanol +	23	τ_{2341} = −0.1246	3.55	1.28	34
	benzene +	19[c]	τ_{1342} = 0.1343	0.78[c]		
	cyclohexane +		τ_{1243} = 0.8600			
	n-octane		τ_{1234} = −0.8062			
6	Methanol +	24	τ_{2341} = 0.0120	2.59	0.75	34
	toluene +	22[c]	τ_{1342} = 2.1378			
	cyclohexane +		τ_{1243} = −3.2889			
	n-octane		τ_{1234} = −0.2477			
7	Methanol +	21	τ_{2341} = 0.1578	3.30	0.66	33
	toluene +	16[c]	τ_{1342} = 0.0779	0.84[c]		
	cyclohexane +		τ_{1243} = −0.7104			
	n-heptane		τ_{1234} = −0.0980			
8	Water +	40	τ_{2341} = −0.6230	0.81	0.73	26
	acetic acid +		τ_{1342} = 1.0451			
	1-butanol +		τ_{1243} = 0.9510			
	n-butyl acetate		τ_{1234} = −0.3086			
9	Water +	32	τ_{2341} = −0.1030	1.31	0.60	29
	acetone +		τ_{1342} = −1.6472			
	acetic acid +		τ_{1243} = 10.5587			
	chloroform		τ_{1234} = −3.3536			
10	Water +	26	τ_{2341} = 1.3781	0.66	0.66	36
	acetone +		τ_{1342} = −7.2218			
	1-propanol +		τ_{1243} = 2.0552			
	1-butanol		τ_{1234} = 0.3746			
11	Water +	19	τ_{2341} = 1.5054	2.12	0.76	29
	acetone +	16[c]	τ_{1342} = 0.3085	0.42[c]		
	1-propanol +		τ_{1243} = −0.1478			
	2-butanone		τ_{1234} = 1.5508			
12	Water +	11	τ_{2341} = −0.9054	1.44	0.39	36
	ethanol +	10[c]	τ_{1342} = 0.6989	0.46[c]		
	2-butanone +		τ_{1243} = 0.6998			
	1-butanol		τ_{1234} = 0.2198			

[a] I, Predicted results based on binary and ternary parameters alone. [b] II, Correlated results based on binary, ternary and quaternary parameters. [c] Rejected tie-lines for which the calculations did not show phase separation.

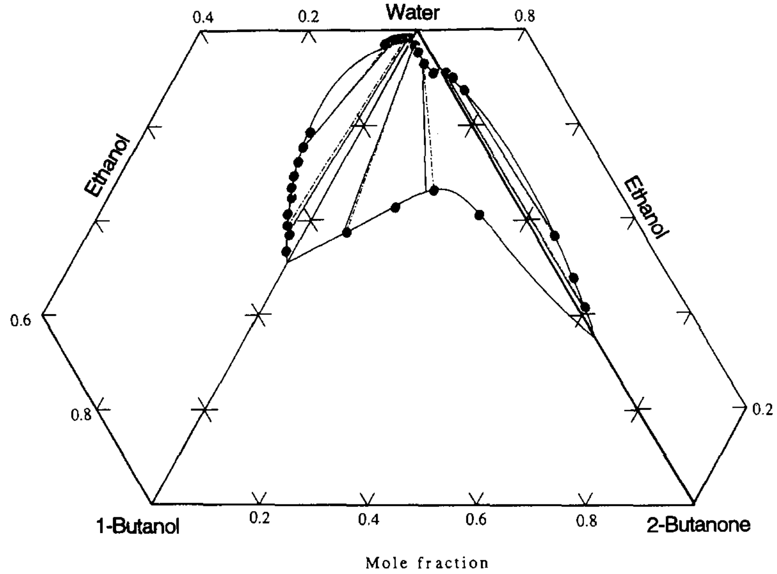

Fig. 5. Representation of ternary liquid–liquid equilibria using the extended Wilson model as obtained by incorporating ternary parameters. ● – · – ●, Experimental: water + ethanol + 2-butanone [36]; water + ethanol + 1-butanol [29]; water + 2-butanone + 1-butanol [36]. ——, Calculated.

Quaternary systems

Table 4 gives the quaternary calculated results. These results indicate that the model with binary and ternary parameters was unable to reproduce phase separation for some experimental tie-lines as shown in systems no. 5–7, 11 and 12; by introducing additional quaternary parameters the model can represent all the tie-lines of 12 quaternary systems studied here with good accuracy.

CONCLUSION

The proposed model can correlate accurately the experimental tie-line data of the 12 quaternary systems studied.

REFERENCES

1 I. Nagata, M. Rogalski and K. Miyamoto, Thermochim. Acta, 224 (1993) 59–69.
2 I. Nagata and K. Miyamoto, Thermochim. Acta, in press.
3 I. Nagata and M. Notoh, Thermochim. Acta, in press.
4 I. Kikic, P. Alessi, P. Rasmussen and A. Fredenslund, Can. J. Chem. Eng., 58 (1980) 253–258.
5 J.H. Hildebrand and R.L. Scott, The Solubility of Nonelectrolytes, 3rd edn., Reinhold, New York, 1950.

6 J. M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice-Hall, Englewood Cliffs, NJ, 1980.

7 J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols, DECHEMA Chemistry Data Ser., Vol. I, Part 2b, DECHEMA, Frankfurt am Main, Germany, 1978.

8 J. Gmehling, U. Onken and P. Grenzheuser, Vapor–Liquid Equilibrium Data Collection, Carboxylic Acids, Anhydrides, Esters, DECHEMA Chemistry Data Ser., Vol. I, Part 5, DECHEMA, Frankfurt am Main, Germany, 1982.

9 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aldehydes, Ketones, Ethers, DECHEMA Chemistry Data Ser., Vol. I, Parts 3 and 4, DECHEMA, Frankfurt am Main, Germany, 1979.

10 N. Gültekin, J. Chem. Eng. Data, 34 (1989) 168–171.

11 J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Aqueous Organic Systems, DECHEMA Chemistry Data Ser., Vol. I, Part 1, DECHEMA, Frankfurt am Main, Germany, 1977.

12 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aromatic Hydrocarbons, DECHEMA Chemistry Data Ser., Vol. I, Part 7, DECHEMA, Frankfurt am Main, Germany, 1980.

13 J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Suppl. 1), DECHEMA Chemistry Data Ser., Vol. I, Part 2c, DECHEMA, Frankfurt am Main, Germany, 1982.

14 I. Nagata, K. Katoh and J. Koyabu, Thermochim. Acta, 47 (1981) 225–233.

15 I. Nagata, Thermochim. Acta, 119 (1987) 357–368.

16 I. Nagata and K. Katoh, Thermochim. Acta, 39 (1980) 45–62.

17 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons C_4–C_6, DECHEMA Chemistry Data Ser., Vol. I, Part 6a, DECHEMA, Frankfurt am Main, Germany, 1980.

18 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons C_7–C_{18}, DECHEMA Chemistry Data Ser., Vol. I, Part 6b, DECHEMA, Frankfurt am Main, Germany, 1980.

19 J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols (Suppl. 2), DECHEMA Chemistry Data Ser., Vol. I, Part 2d, DECHEMA, Frankfurt am Main, Germany, 1982.

20 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons (Suppl. 1), DECHEMA Chemistry Data Ser., Vol. I, Part 6c, DECHEMA, Frankfurt am Main, Germany, 1983.

21 J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols, DECHEMA Chemistry Data Ser., Vol. I, Part 2a, DECHEMA, Frankfurt am Main, Germany, 1977.

22 J. Gmehling, U. Onken and J. R. Rarey-Nies, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Suppl. 3), DECHEMA Chemistry Data Ser., Vol. I, Part 2e, DECHEMA, Frankfurt am Main, Germany, 1988.

23 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aqueous Systems (Suppl. 1), DECHEMA Chemistry Data Ser., Vol. I, Part 1a, DECHEMA, Frankfurt am Mian, Germany, 1981.

24 I. Nagata and T. Ohta, J. Chem. Eng. Data, 28 (1983) 256–259.

25 H. Higashiuchi, Y. Sakurai, Y. Iwai, Y. Arai and M. Nagatani, Fluid Phase Equilibria, 35 (1987) 35–47.

26 F. Ruiz, D. Prats, V. Gomis and P. Varo, Fluid Phase Equilibria, 18 (1984) 171–183.

27 F. Ruiz and D. Prats, Fluid Phase Equilibria, 10 (1983) 95–114.

28 F. Ruiz and D. Prats, Fluid Phase Equilibria, 10 (1983) 77–93.

29 E. A. Macedo and P. Rasmussen, Liquid–Liquid Equilibrium Data Collection, Suppl. 1, DECHEMA Chemistry Data Ser., Vol. V, Part 4, DECHEMA, Frankfurt am Main, Germany, 1987.
30 I. Nagata, Fluid Phase Equilibria, 26 (1986) 59–68.
31 I. Nagata, Thermochim. Acta, 114 (1987) 227–238.
32 I. Nagata, Thermochim. Acta, 232 (1994) 285–295.
33 I. Nagata, Thermochim. Acta, 208 (1992) 61–71.
34 I. Nagata, Thermochim. Acta, 210 (1992) 281–292.
35 I. Nagata, Thermochim. Acta, 127 (1988) 337–346.
36 F. Ruiz, D. Prats and V. Gomis, An. Quim., 82 (1986) 393–398.