

## Infinite-dilution activity coefficients by comparative ebulliometry. Binary systems containing chloroform and diethylamine

João P. Coutinho and Eugénia A. Macedo \*

*Departamento de Engenharia Química, Faculdade de Engenharia, Rua dos Bragas, 4099 Porto Codex (Portugal)*

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### ABSTRACT

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New data were determined by comparative ebulliometry for infinite-dilution activity coefficients of the following systems: chloroform/methanol, chloroform/acetonitrile, chloroform/tetrahydrofuran, chloroform/methyl acetate, chloroform/diethylamine and diethylamine/*n*-hexane, at both the upper and lower concentration limits and at two different temperatures. The measured infinite-dilution activity coefficients were compared with the predicted values obtained with the MOSCED (Modified Separation of Cohesive Energy Density) and UNIFAC models. For the UNIFAC model the predictions were made using group-interactions from the VLE parameter Tables. The differences between experimental and calculated infinite-dilution activity coefficients show that both methods predict fairly well the majority of the experimental data. The data obtained were used to estimate UNIFAC interaction parameters for the groups  $\text{CCl}_3/\text{CH}_3\text{OH}$ ,  $\text{CCl}_3/\text{CCN}$ ,  $\text{CCl}_3/\text{CH}_2\text{O}$ ,  $\text{CCl}_3/\text{CCOO}$ ,  $\text{CCl}_3/\text{CNH}$  and  $\text{CH}_2/\text{CNH}$ , which are not available in the infinite-dilution specific Parameter Table. These parameters were used to predict VLE data for systems containing the same groups, and a comparison between experimental and predicted values is presented.

Keywords: experiments, data, method, infinite-dilution activity coefficients, group contribution, mixtures.

### INTRODUCTION

The infinite-dilution activity coefficient is a thermodynamic property which has a major role in chemical technology, allowing qualitative and

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\* Corresponding author.

quantitative analyses of separation processes as extractive and azeotropic distillations and liquid–liquid extractions. In addition, the infinite-dilution activity coefficient provides all the necessary information for a complete description of the phase equilibrium of a binary mixture and an accurate prediction of multicomponent vapor–liquid equilibria (Gautreaux and Coates, 1955; Schreiber and Eckert, 1971; Nicolaidis and Eckert, 1978; Bastos et al., 1988).

A UNIFAC parameter Table specially suited for the prediction of infinite-dilution activity coefficients was published by Bastos et al. (1988). This Table is exclusively based on experimental infinite-dilution activity coefficient data reported in the literature (Tiegs et al., 1986). Although the Table is very extensive, it contains many gaps corresponding to group–interaction parameters which were not estimated due to either the non-existence of experimental data or the scarcity of available data for the relevant systems.

A literature survey on infinite-dilution activity coefficients ( $\gamma^\infty$ ) for binary systems containing chloroform gives, among others, the following results: there are three data points for  $\gamma^\infty$  of methanol diluted in chloroform and one data point for  $\gamma^\infty$  of chloroform diluted in methanol (Thomas et al., 1982a; Landau et al., 1991); there are three data points for  $\gamma^\infty$  of acetonitrile in chloroform (Thomas et al., 1982a) and three data points for  $\gamma^\infty$  of chloroform in acetonitrile (Locke, 1968; Thomas et al., 1982b; Belfer and Locke, 1984); there are four data points for  $\gamma^\infty$  of chloroform in tetrahydrofuran and four data points for  $\gamma^\infty$  of tetrahydrofuran in chloroform (Thomas et al., 1982a; Paul, 1987); there are six data points for  $\gamma^\infty$  of chloroform in ethyl acetate (Thomas et al., 1982a; Trampe and Eckert, 1990). However, these data were not used to estimate the relevant UNIFAC parameters for the  $\gamma^\infty$  Parameter Table (Bastos et al., 1988), because the available data published until 1988 were considered to be limited.

In this work, infinite-dilution activity coefficients are given for mixtures of chloroform with acetonitrile, tetrahydrofuran, diethylamine, methanol and methyl acetate, and of diethylamine with *n*-hexane, at both the upper and lower concentration limit. They were measured at two different temperatures, using the technique of comparative ebulliometry.

The experimental data were compared with predictions obtained from the MOSCED method (Thomas and Eckert, 1984) and the UNIFAC group-contribution method with parameters based on VLE data (Gmehling et al., 1982; Macedo et al., 1983; Tiegs et al., 1987; Hansen et al., 1991).

The data obtained were used, together with the above-mentioned data already published in the literature, to estimate new group interaction parameters for the groups  $\text{CCl}_3/\text{CH}_3\text{OH}$ ,  $\text{CCl}_3/\text{CCN}$ ,  $\text{CCl}_3/\text{CH}_2\text{O}$ ,  $\text{CCl}_3/\text{CCOO}$ ,  $\text{CCl}_3/\text{CNH}$  and  $\text{CH}_2/\text{CNH}$ , previously not available in the infinite-dilution activity coefficient UNIFAC Parameter Table (Bastos et al., 1988).

## EXPERIMENTAL

### *Procedure*

The limiting activity coefficients were determined by comparative ebulliometry, i.e. by measuring isobaric changes in the boiling temperatures of a solvent which result when small, known amounts of solute are added. Measurements were made in a differential ebulliometer which consists of two glass, boiling chambers connected, through condensers, to a common manifold. The change in boiling point is measured as the difference between the boiling point of the pure solvent (in the reference chamber) and the boiling point of the solute plus solvent (in the measuring chamber). The measuring and the reference ebulliometers are both of the Swietoslawski type. This equipment has already been used in a previous work (Gonçalves and Macedo, 1993). The design of the ebulliometers and the experimental procedure are similar to those described in detail by Eckert et al. (1981).

The ebulliometers were first filled gravimetrically with about 100 ml of solvent. Usually, for each experiment, six injections of either pure solute or a mixture of solute and solvent, each of approximately 1 ml, were made. In order to obtain dilute concentrations, the mole fraction regions studied were always below 0.01.

A Fischer Vakuum-Konstanthalter VK1 instrument pressure gauge served as the sensor for the pressure control. In order to be able to measure the pressure with a higher accuracy, a mercury-filled U tube manometer (I.D. 20 mm) and a cathetometer were used. The accuracy of the measurements was within  $\pm 0.1$  mm Hg.

The boiling point elevation was measured with a 2801 A Hewlett-Packard quartz thermometer and two 2850 A sensing probes. The accuracy of the measurements was  $\pm 0.01$  K.

## MATERIALS

Acetonitrile (Merck; spectroscopy-grade, minimum purity 99.8%), chloroform, methanol and tetrahydrofuran (all from Merck; special for chromatography, minimum purity 99.8%), were used as supplied. *n*-Hexane (Merck; p.a., minimum purity 99%), was passed through silica gel and distilled. Diethylamine (Merck; for synthesis, minimum purity 99%) was distilled and dried with activated alumina before use. Methyl acetate (Merck; for synthesis, minimum purity 99%) was dried with magnesium sulphate and distilled. For all components, the purity assessed by gas–liquid chromatography was found to be greater than 99.8%.

The vapor pressures were determined for each pure component in the temperature range of interest. Fair agreement was obtained with the literature values, which provides an additional check of the purity of the materials used.

## RESULTS

The infinite-dilution activity coefficients of solute 1 in solvent 2 were evaluated from the measured limiting slopes  $(\partial T/\partial x_1)_P^\infty$  by means of the following equation first proposed by Gautreaux and Coates (1955) and improved by Null (1970), including the terms for vapor phase non-idealities (Bergmann and Eckert, 1991):

$$\gamma_1^\infty = \frac{\phi_1^{(P_2^s)} \left\{ P_2^s - \left[ 1 - \frac{P_2^s v_2}{RT} + \left( \frac{\partial \phi_2}{\partial P} \frac{P_2^s}{\phi_2^s} \right)_T \right] \left( \frac{\partial T}{\partial x_1} \right)_P^\infty \left( \frac{\partial P_2^s}{\partial T} \right) \right\}}{P_1^s \phi_1^s \exp\left( \frac{(P_2^s - P_1^s) v_1}{RT} \right)} \quad (1)$$

where  $\phi_i^P$  is the fugacity coefficient of component  $i$  at pressure  $P$ ;  $\phi_i^s$  is the fugacity coefficient of component  $i$  at its vapor pressure;  $\phi_i$  is the fugacity coefficient of component  $i$  in the vapor phase;  $v_i$  is the liquid molar volume of pure component  $i$ ;  $P_i^s$  is the vapor pressure of the component  $i$  at the equilibrium temperature;  $x_i$  is the equilibrium liquid mole fraction;  $T$  is the equilibrium temperature;  $R$  is the ideal gas constant.

The fugacity coefficients and their derivatives with respect to pressure were determined using the virial equation of state, with the second virial coefficients estimated according to the method described by Hayden and O'Connell (1975). The liquid molar volumes were calculated using the modified Rackett equation (Spencer and Danner, 1972). The pure component vapor pressures were calculated using the Antoine equation. The limiting composition derivative of the temperature,  $(\partial T/\partial x_1)_P^\infty$ , was obtained from the ebulliometric data. The enrichment of the vapor above the boiling mixture with the more volatile component and the holdup of liquid condensate have been taken into account to estimate the true equilibrium liquid-phase composition,  $x_1$ , from the gravimetrically determined composition of the mixture. This correction, usually less than 1%, was made by estimating the vapor and liquid condensate volumes, and solving the appropriate stoichiometric and thermodynamic relationships by an iterative method.

The slopes were determined by fitting the data to the following analytical equations:

$$\Delta T = ax_1 \quad (2)$$

$$\Delta T = ax_1 + bx_1^2 \quad (3)$$

$$\Delta T = ax_1 + b \ln(1 + x_1) \quad (4)$$

$$\Delta T = ax_1 + bx_1^2 + cx_1^3 \quad (5)$$

In each case, the best fit was chosen; expression of types (3) and (4) usually gave the lowest standard percentage deviation. Excluding the first equation (eqn. 2), hardly ever used, the slopes and the infinite-dilution activity coefficients obtained from the different equations differed by less than 2%.

Table 1 presents the limiting slopes  $(\partial T/\partial x_1)_P^\infty$  and the infinite-dilution activity coefficients calculated as described above for the studied systems. The absolute errors for  $\gamma^\infty$  given in Table 1 were estimated by calculating repeated  $\gamma^\infty$ , taking into account the maximum and minimum values in the limiting slopes due to fluctuations in the measured temperature, and the magnitude of the holdup corrections.

The infinite-dilution activity coefficients measured in this work for the systems chloroform/tetrahydrofuran and chloroform/acetonitrile are in good agreement with the values reported in the literature (Locke, 1968; Thomas et al., 1982a, b; Belfer and Locke, 1984). Regarding the  $\gamma^\infty$  of methanol diluted in chloroform, the values measured in this work are not in agreement with those given by Thomas et al. (1982a). While we obtained values between 9 and 10, Thomas et al. (1982 a) obtained values between 6 and 7. It is worth noting that the values presented in this work for  $\gamma^\infty$  of methanol in chloroform are the result of four experiments for each data point, and they were all reproducible. The solute concentration in our experiments was always kept below 0.01. Two other experiments were carried out at 40°C covering a concentration range for the solute up to 0.1 (mole fraction), and the  $\gamma^\infty$  values calculated from these experiments were around 6.5, which is closer to the value reported by Thomas et al. (1982a).

The experimental results were compared with predicted values obtained from UNIFAC with parameters based on VLE data (Gmehling et al., 1982; Macedo et al., 1983; Tiegs et al., 1987; Hansen et al., 1991) and MOSCED (Thomas and Eckert, 1984) methods. Table 1 also presents a comparison of the experimental and predicted infinite-dilution activity coefficients.

With the UNIFAC–VLE method it is only possible to predict 20  $\gamma^\infty$  values because there are no available interaction parameters for the groups  $\text{CCl}_3/\text{CNH}$ . The overall average error obtained is 13%, which is significantly smaller than the mean deviation reported by Bastos et al. (1988), 28.1%, for the prediction of more than 4800  $\gamma^\infty$  values, using the same UNIFAC–VLE parameters. It is worthwhile noting that there are only two data points with errors much higher than the average: they correspond to the  $\gamma^\infty$  values of tetrahydrofuran in chloroform. For most of the data the predictions are very satisfactory.

TABLE 1

Comparison of experimental and predicted values of  $\gamma^\infty$  using MOSCED and UNIFAC–VLE models

Solute	Solvent	$T$ (K)	$(\partial T/\partial x_1)^\infty_P$	$\gamma^\infty_{\text{exp}}$	Uncertainty	MOSCED		UNIFAC	
						$\gamma^\infty$	error (%)	$\gamma^\infty$	error (%)
Chloroform	Methanol	317.67	49.08	2.43	$\pm 0.04$	3.29	35	2.53	4
Chloroform	Methanol	328.22	45.86	2.39	$\pm 0.05$	3.18	33	2.56	7
Methanol	Chloroform	318.15	183.7	9.71	$\pm 0.10$	5.73	–41	7.71	–20
Methanol	Chloroform	328.15	205.5	9.24	$\pm 0.10$	5.02	–46	7.27	–21
Chloroform	Acetonitrile	318.05	45.09	1.32	$\pm 0.02$	1.60	21	1.39	6
Chloroform	Acetonitrile	328.34	46.18	1.31	$\pm 0.02$	1.57	20	1.38	5
Acetonitrile	Chloroform	318.28	–9.846	1.27	$\pm 0.01$	1.80	41	1.31	4
Acetonitrile	Chloroform	328.25	–9.700	1.29	$\pm 0.01$	1.77	37	1.30	1
Chloroform	Tetrahydrofuran	313.56	–15.38	0.35	$\pm 0.01$	0.26	–26	0.38	11
Chloroform	Tetrahydrofuran	323.27	–15.94	0.37	$\pm 0.01$	0.29	–22	0.40	7
Tetrahydrofuran	Chloroform	313.56	–21.78	0.23	$\pm 0.02$	0.24	4	0.37	62
Tetrahydrofuran	Chloroform	323.37	–22.62	0.26	$\pm 0.02$	0.27	4	0.38	45
Chloroform	Methyl acetate	312.85	–14.06	0.52	$\pm 0.01$	0.49	–6	0.50	–3
Chloroform	Methyl acetate	322.65	–14.30	0.56	$\pm 0.01$	0.52	–7	0.51	–9
Methyl acetate	Chloroform	313.41	–13.79	0.43	$\pm 0.01$	0.41	–5	0.38	–14
Methyl acetate	Chloroform	323.33	–12.86	0.49	$\pm 0.01$	0.44	–10	0.39	–20
Diethylamine	Hexane	313.65	31.25	1.41	$\pm 0.02$	1.48	5	1.38	–2
Diethylamine	Hexane	322.95	31.76	1.37	$\pm 0.02$	1.46	7	1.37	0
Hexane	Diethylamine	313.16	–4.525	1.26	$\pm 0.01$	1.37	9	1.42	12
Hexane	Diethylamine	323.24	–4.823	1.28	$\pm 0.01$	1.35	6	1.40	10
Chloroform	Diethylamine	313.19	–17.16	0.41	$\pm 0.01$	0.31	–24	n.a.	n.a.
Chloroform	Diethylamine	323.08	–19.88	0.38	$\pm 0.02$	0.35	–8	n.a.	n.a.
Diethylamine	Chloroform	313.39	–16.74	0.32	$\pm 0.01$	0.26	–19	n.a.	n.a.
Diethylamine	Chloroform	323.32	–17.42	0.34	$\pm 0.01$	0.30	–12	n.a.	n.a.

n.a.; not available; error (%) =  $100 (\gamma^{\text{calc}} - \gamma^{\text{exp}}/\gamma^{\text{exp}})$ .

The original MOSCED model proposed by Thomas and Eckert (1984) was used instead of the improved method presented by Howell et al. (1989). The reason for this choice is that for mixtures containing chloroform the performance of the original MOSCED is superior to that obtained with the modification (Howell, 1989).

In this method, which is an extension of the Regular Solution Theory, only parameters particular to pure components are required to perform the predictions, although to estimate them  $\gamma^\infty$  data were employed by Thomas and Eckert (1984). These parameters have been reported for all the components except diethylamine, whose parameters were calculated from the correlations given by Thomas and Eckert (1984). The value of the dispersive parameter  $\lambda$  was found to be too high and, as has already been done by other authors (Dohnal and Vrbka, 1990), a somewhat lower value of  $\lambda$  was adopted, which improves the predictions by a factor of two. The recommended values of the MOSCED parameters for diethylamine are as follows: dispersive  $\lambda = 6.45$ , polar  $\tau = 0.72$ , acidity  $\alpha = 0$ , basicity  $\beta = 5.24$ . When the MOSCED predictions are compared with the experimental  $\gamma^\infty$  data, the overall average error is 18.5%. If the experimental  $\gamma^\infty$  data for the systems chloroform/methanol and chloroform/acetonitrile are not considered in the calculations, the overall average error is reduced to 10.7%, which is comparable with the 9.1% obtained for more than 3000  $\gamma^\infty$  values by Thomas and Eckert (1984).

Using the experimental infinite-dilution activity coefficient values determined for the systems chloroform/methanol, chloroform/acetonitrile, chloroform/tetrahydrofuran, chloroform/methyl acetate, chloroform/diethylamine and diethylamine/*n*-hexane, new UNIFAC interaction parameters were estimated for the group pairs  $\text{CCl}_3/\text{CH}_3\text{OH}$ ,  $\text{CCl}_3/\text{CCN}$ ,  $\text{CCl}_3/\text{CH}_2\text{O}$ ,  $\text{CCl}_3/\text{CCOO}$ ,  $\text{CCl}_3/\text{CNH}$  and  $\text{CH}_2/\text{CNH}$ , previously not available in the  $\gamma^\infty$  specific Parameter Table (Bastos et al., 1988). For the interactions between the groups  $\text{CCl}_3/\text{CCN}$ , the experimental infinite-dilution activity coefficient data for the system chloroform/acetonitrile, given by Thomas et al. (1982a, b), Belfer and Locke (1984) and Locke (1968), were used together with the new data. For the interactions between the groups  $\text{CCl}_3/\text{CH}_2\text{O}$ , the experimental infinite-dilution activity coefficient values published by Thomas et al. (1982a) for the system chloroform/tetrahydrofuran were used in the parameter estimation. For the  $\text{CCl}_3/\text{CCOO}$  interactions, the experimental infinite-dilution activity coefficient values for chloroform diluted in ethyl acetate given by Thomas et al. (1982a) and Trampe and Eckert (1990) were also used in the parameter estimation. For the UNIFAC interactions between the groups  $\text{CCl}_3/\text{CH}_3\text{OH}$  we only used our experimental data with the data given by Landau et al. (1991). The reason for this is that the infinite-dilution activity coefficient data of methanol in chloroform published

TABLE 2

UNIFAC group interaction parameters (K)

Group <sub>i</sub>	Group <sub>j</sub>	T (K)	a <sub>ij</sub>	a <sub>ji</sub>
CCl <sub>3</sub>	CCN	318.05–328.34	133.6	–74.30
CCl <sub>3</sub>	CH <sub>3</sub> OH	317.67–328.22	750.2	–182.6
CCl <sub>3</sub>	CH <sub>2</sub> O	313.56–323.37	21.42	–266.9
CCl <sub>3</sub>	CCOO	312.85–323.33	–1.514	–77.35
CH <sub>2</sub>	CNH	313.16–323.24	452.1	–187.5
CCl <sub>3</sub>	CNH	313.19–323.32	54.67	–288.4

by Thomas et al. (1982a) are not in agreement with the data measured in this work, as already discussed. The objective function used was:

$$F_{\min} = \sum_i \sum_j \left[ \frac{\gamma_i(\text{calc}) - \gamma_i(\text{exp})}{\gamma_i(\text{exp})} \right]^2 \quad (6)$$

where exp and calc mean, respectively, experimental and calculated by the UNIFAC method. The summations were taken over all data points, *j*, and components, *i*. The estimated group-interaction UNIFAC parameters are given in Table 2. The modification of the Flory–Huggins term (Kikic et al., 1980) in the combinatorial term of the UNIFAC equations was used. This modification was also used by Bastos et al. (1988) in the estimation of the interaction parameters for the  $\gamma^\infty$  Parameter Table.

Naturally the reliability of the estimated parameters cannot be as high as that obtained when evaluating these parameters from extensive data bases. However, even though the calculated parameters are based on limited data, quite good predictions were achieved for the systems where experimental VLE data could be compared with the UNIFAC estimated values. This can be seen in Table 3, where the differences between experimental and calculated data are given for the systems chloroform/methanol at 25°C (Tamir et al., 1981), chloroform/acetonitrile at 55°C (Nagata and Kawamura, 1979), chloroform/methyl acetate at 40°C (Ohta et al., 1980) and diethylamine/hexane at 60°C (Humphrey and Van Winkle, 1967). For the same systems, a comparison between experimental and calculated activity coefficients is presented in Figs. 1–4. The errors obtained are quite small, indicating that this kind of extrapolation can be made with good accuracy.

## CONCLUSIONS

Infinite-dilution activity coefficients were determined for chloroform/methanol, chloroform/acetonitrile, chloroform/tetrahydrofuran, chloro-

TABLE 3

Comparison of the UNIFAC predictions with the experimental data

System	$T$ (K)	Number of data points	$\Delta P/P$ ( $\times 100$ )	$\Delta y$
Chloroform(1)/methanol(2) <sup>a</sup>	298.15	12	3.51	0.026
Chloroform(1)/acetonitrile(2) <sup>b</sup>	328.15	11	1.00	0.004
Methyl acetate(1)/chloroform(2) <sup>c</sup>	313.15	16	1.38	0.013
Diethylamine(1)/hexane(2) <sup>d</sup>	333.15	7	0.79	0.003

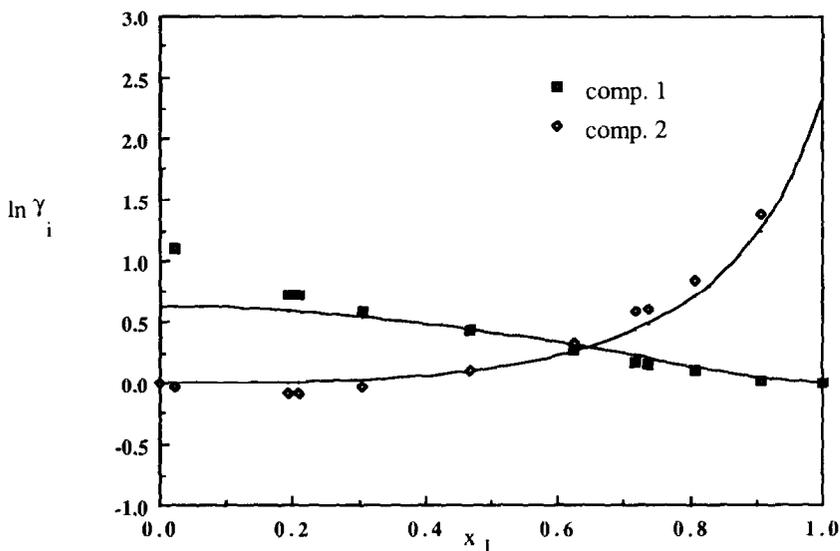
<sup>a</sup> Tamir et al. (1981).<sup>b</sup> Nagata and Kawamura (1979).<sup>c</sup> Ohta et al. (1980)<sup>d</sup> Humphrey and Van Winkle (1967).

Fig. 1. Comparison of the UNIFAC predictions with the experimental activity coefficients for chloroform(1)/methanol(2) at 25°C. Experimental data: Tamir et al. (1981).

form/methyl acetate, chloroform/diethylamine and diethylamine/*n*-hexane using the technique of comparative ebulliometry. New UNIFAC interaction parameters for the groups  $\text{CCl}_3/\text{CH}_3\text{OH}$ ,  $\text{CCl}_3/\text{CCN}$ ,  $\text{CCl}_3/\text{CH}_2\text{O}$ ,  $\text{CCl}_3/\text{CCOO}$ ,  $\text{CCl}_3/\text{CNH}$  and  $\text{CH}_2/\text{CNH}$ , estimated from the experimental infinite-dilution activity coefficients, were used to predict binary vapor–liquid equilibrium data and, from the values obtained for the deviations in

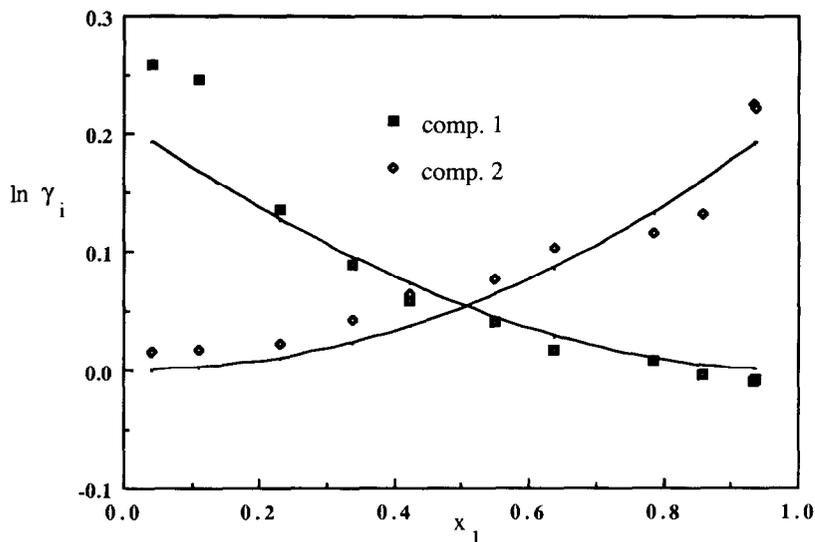


Fig. 2. Comparison of the UNIFAC predictions with the experimental activity coefficients for chloroform(1)/acetonitrile(2) at 55°C. Experimental data: Nagata and Kawamura (1979).

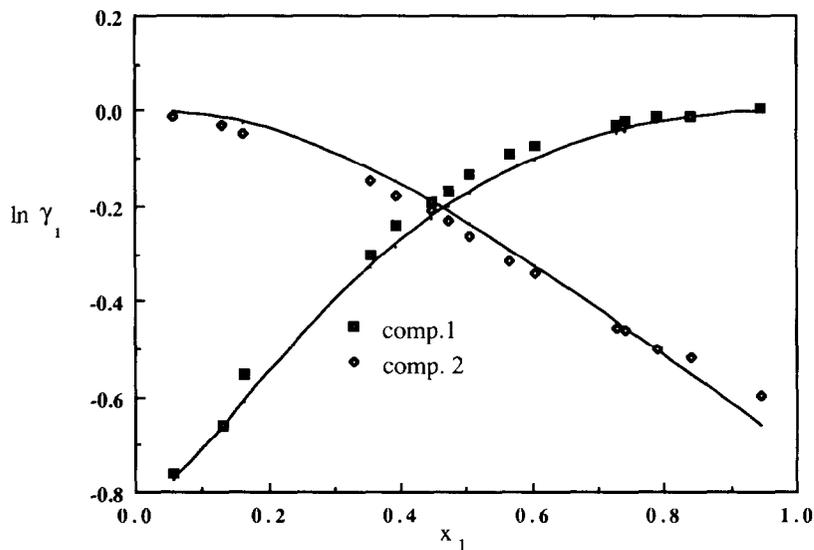


Fig. 3. Comparison of the UNIFAC predictions with the experimental activity coefficients for methyl acetate(1)/chloroform(2) at 40°C. Experimental data: Ohta et al. (1980).

pressure and vapor phase mole fractions, it was possible to conclude that the  $\gamma^\infty$  UNIFAC parameters are suitable for describing the vapor–liquid equilibrium behavior of the systems considered.

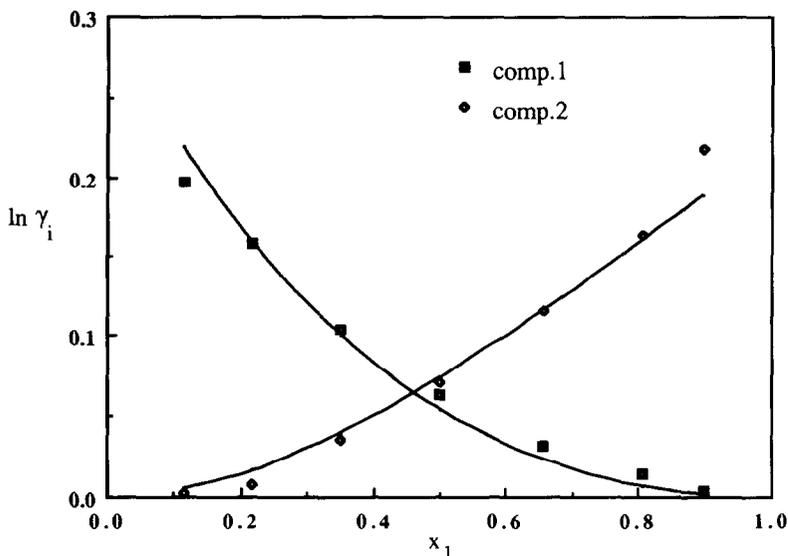


Fig. 4. Comparison of the UNIFAC predictions with the experimental activity coefficients for hexane(1)/diethylamine(2) at 60°C. Experimental data: Humphrey and van Winkle (1967).

The measured infinite-dilution activity coefficients were compared with the predicted values obtained with the MOSCED and UNIFAC–VLE models. The differences between experimental and calculated infinite-dilution activity coefficients show that both methods predicted reasonably well the majority of the experimental data.

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#### LIST OF SYMBOLS

- $a$  constant in eqns. (2)–(5); UNIFAC parameters
- $b$  constant in eqns. (3)–(5)
- $c$  constant in eqn. (5)
- $F_{\min}$  objective function
- $P$  pressure
- $P_i^s$  vapor pressure of component  $i$
- $R$  gas constant
- $t$  temperature
- $T$  absolute temperature

$v$	liquid molar volume
$x$	liquid phase mole fraction
$y$	vapor phase mole fraction

### Greek letters

$\alpha$	acidity parameter in MOSCED model
$\beta$	basicity parameter in MOSCED model
$\gamma_i$	activity coefficient of component $i$
$\lambda$	dispersion parameter in MOSCED model
$\tau$	polar parameter in MOSCED model
$\phi_i$	vapor phase fugacity coefficient of component $i$
$\phi_i^s$	fugacity coefficient of component $i$ at saturation pressure

### Subscripts

$i$	component $i$ ; group $i$
$j$	data point $j$ ; group $j$
1	component 1 (solute)
2	component 2 (solvent)

### Superscripts

calc	calculated
exp	experimental
s	saturation
$\infty$	infinite dilution

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