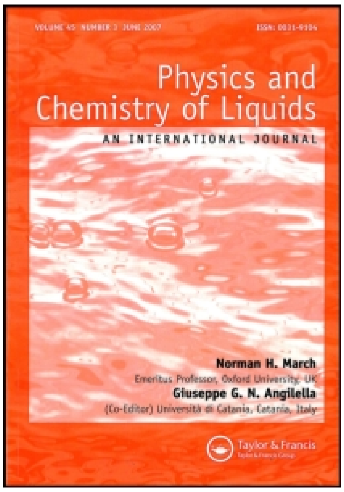

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PREDICTION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION BY USING THE WEIGHTED VOLATILITY FUNCTION

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A new method for calculating activity coefficients at infinite dilution is proposed, based on extrapolation of the weighted volatility function, $\omega = x_1 \ln(y_1/x_1) + x_2 \ln(y_2/x_2)$, to dilute compositions. The values of ω are calculated from vapor-liquid equilibria data smoothed by an appropriate G^E function. The ω function exhibits very good numerical sensitivity that improves the extrapolation capabilities of an activity coefficient model, when its parameters are adjusted to experimental VLE data instead of a bubble-point pressure fit technique. The results of the proposed method are compared with the results predicted by DECHMA and by MOSCED for 95 systems of known thermodynamic consistency and shown to be more accurate than those of DECHEMA and of equal or better accuracy to those of MOSCED. A mean deviation of 14% is achieved with respect to experiemental data on activity coefficients at infinite dilution.

KEY WORDS: Activity, gibbs energy, vapor-liquid equilibrium.

INTRODUCTION

Activity coefficients at infinite dilution are very useful for scientific and engineering applications, and their study constitute an active topic of experimental and theoretical investigation. Probably, they are the most important datum of phase equilibrium since, for a practical point of view, they can be directly related to the analysis of separation technologies, where the knowledge of the behaviour of the diluted solution is essential for evaluating the recovery or separability of the components. In liquid-liquid extraction, the limiting separation factor β_{12} can be approximated by[1]:

$$\beta_{12} \approx \frac{\gamma_1^\infty}{\gamma_2^\infty} \tag{1}$$

where γ_1^∞ and γ_2^∞ are the limiting activity coefficients of two miscible solutes in a solvent that induces LLE. It is a common practice to consider the magnitude of this ratio, also applicable to extractive distillation, as a preliminary step of solvent selection.

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The relative volatility α in the limit of pure solvent concentration, a dominant variable of high recovery distillation, is given by:

$$\alpha = \frac{y_1/x_1}{y_2/x_2} \underset{\text{low pressure}}{\approx} \frac{\gamma_1}{\gamma_2}\frac{P_1^{\text{sat}}}{P_2^{\text{sat}}} \tag{2}$$

When this variable is calculated for the impurities present in the distillate and bottom products, it will depend directly on activity coefficients at infinite dilution and will provide important qualitative information relative to the size of the equipment.

If activity coefficients are a monotonous function in the composition, azeotropy can be detected a priori when the following criteria are met[1]:

$$\gamma_2^{\infty} > \frac{P_1^{\text{sat}}}{P_2^{\text{sat}}} > \frac{1}{\gamma_1^{\infty}} \quad \text{or} \quad \gamma_2^{\infty} < \frac{P_1^{\text{sat}}}{P_2^{\text{sat}}} < \frac{1}{\gamma_1^{\infty}} \tag{3}$$

Furthermore, many empirical excess Gibbs energy models contaning only binary parameters, have been developed and they constitute the minimal information required to predict the phase equilibrium in intermediate concentration ranges, both for binary and multicomponent systems.

The scientific literature reports a considerable amount of full range experimental information for phase equilibrium, in comparison to data on activity coefficients at infinite dilution (γ^{∞}). For example, DECHEMA Chemistry Data Series dedicates eighteen parts of its first volume to VLE experimental data[2], but only four parts of its ninth volume to experimental γ^{∞} information[3]. This fact still motivates their estimation from existent experimental VLE data.

At low pressures and in intermediate concentration ranges, the phase compositions have been classically and satisfactorily interpolated by activity coefficients models (G^E), situation that would suggest the fit of the G^E model parameters to the experimental phase equilibrium data and its extrapolation to the infinite dilution ranges[1]. According to the analysis of Eckert *et al.*[4] and Paul and Knapp[5], there is a certain degree of incompatibility between the parameters of a G^E model obtained by fitting the experimental data in intermediate concentration ranges, and the parameters of the same model that can adjust γ^{∞} experimental values. Furthermore, it is a well known fact that different objective functions for VLE data correlation purposes produce different parameters[6].

Generally, reliable values of the activity coefficients at infinite dilution may be determined by experimental techniques, such as chromatography[7], gas stripping[8], headspace chromatography[9] and ebulliometry[10,11,12], but except for the redundant determination of the experimental values, there is no method that can determine the thermodynamic quality of the measured parameter[1]. In this context, it is important to study the trend of the available experimental VLE information in non-zero concentration vicinities.

Some predictive methods for γ^{∞} are already available, such as the UNIFAC model[13], with specific parameters obtained from experimental data[14], the MOSCED model (Modified Separation of Cohesive Energy Density), based on an extension of the regular solution theory[15] and developed by Thomas and Eckert[16], and the recent

SPACE model (solvatochromic Parameters for Activity Coefficient Estimation), developed by Hait *et al.*[17], and limited to 298.15 K and nonaqueous solutions. These predictive methods are fairly suitable for the prediction of γ^{∞} when the basic experimental VLE information is not available, but they are limited to a fixed number of compounds (or groups), and their genesis is independent of the experimental VLE data in intermediate concentration ranges, which is also necessary for the design and control of any separation process.

In addition, the scientific literature reports some graphical methods that are independent of an specific G^E empirical model and that allow calculation of the γ^{∞} values by extrapolation of VLE data. The most popular techniques is the calculation of the function $G^E/x_1 x_2$ in a certain experimental concentration range and the projection of its trend to the diluted range. More adequate and exact are the elegant techniques elaborated by Gautreaux and Coates[18] and by Ellis and Jonah (1962)[19], based on the graphical extrapolation of composition functionalities that involve measurable intensive variables of the phase equilibrium, such as pressure and temperature. When VLE data are used, the prediction capability of these graphical methods are overweighed by the data in the dilute range, that is, those data which accumulate the greatest experimental error. The ebulliometric technique, however, makes them suitable for the direct determination of γ^{∞}[4]. Wisniak and Apelblat[20] have used the fact that the function $G^E(x)$ has at least one extreme value in the central composition range (where the analytical accuracy is the best) to show that for 2-parameter models there is clear and definite mathematical relationship between the extreme value of G^E and the values of the activity coefficients at infinite dilution. In other words, if a particular 2-parameter model fits well the data and there are enough experimental points in the central composition range that allow a good estimation of the extreme value of G^E, then the mathematical relationship can be used to determine the values of γ^{∞} predicted by the model without extrapolation.

The objective of this work, is to present a new method for the estimation of γ^{∞} from full range VLE data, as a practical application of the weighted volatility function.

THEORETICAL BACKGROUND

The function ω, defined by Eqn. (4), was originally suggested by Malesinski[21] for the study of the azeotropic condition, and is also used in the recent test for thermodynamic consistency for VLE experimental data developed by Wisniak[22].

$$\omega = \sum_i x_i \ln\left(\frac{y_i}{x_i}\right) \tag{4}$$

If Eqn. (4) is applied to a binary system, we obtain:

$$\omega = x_1 \ln\left(\frac{y_1}{x_1}\right) + x_2 \ln\left(\frac{y_2}{x_2}\right) = x_1 \ln\alpha + \ln\left(\frac{y_2}{x_2}\right) \tag{5}$$

where x and y are the compositions of the two phases in equilibrium and α is the relative volatility between components 1 and 2.

In an equilibrium state, the isochemical potential condition can be written as[23]:

$$\mu_i^{\mathrm{l}} = \mu_i^{\mathrm{v}} \Rightarrow x_i \hat{\phi}_i^{\mathrm{l}} = y_i \hat{\phi}_i^{\mathrm{v}} \tag{6}$$

The fugacity coefficient $\hat{\phi}_i$ can be calculated from volumetric properties by using the following relations[23]:

$$\ln\phi = \int_0^p \frac{Z-1}{P} dP \bigg|_T \tag{7}$$

and

$$\ln\hat{\phi}_i = \left(\frac{\partial n \ln\phi}{\partial n_i}\right) = \int_0^p \frac{\bar{Z}-1}{P} dP \bigg|_T \tag{8}$$

Using Eqns. (6), (7) and (8), we can write Eqn. (4) as:

$$\omega = \sum_i x_i \ln\left(\frac{y_i}{x_i}\right) = \sum_i x_i \ln\left(\frac{\hat{\phi}_i^{\mathrm{l}}}{\hat{\phi}_i^{\mathrm{v}}}\right) = \sum_i x_i \int_0^p \frac{\bar{Z}_i^{\mathrm{l}} - Z_i^{\mathrm{v}}}{P} dP = \int_0^p \frac{Z^{\mathrm{l}} - \gtreqless_i x_i \bar{Z}_i^{\mathrm{v}}}{P} dP \tag{9}$$

Considering the magnitude of the compressibility factor for the liquid and the vapor phase, it can be deduced from Eqn. (9) that ω is negative.

For pure compounds and for azeotropy cases, i.e. $y_i = x_i$, and when the bubble point pressure is equivalent to the dew-point pressure, the last term of Eqn. (9) can be written as:

$$\omega = \sum_i x_i \ln\left(\frac{y_i}{x_i}\right) = 0 = \int_0^p \frac{Z^{\mathrm{l}} - Z^{\mathrm{v}}}{P} dP \tag{10}$$

The right-hand term in Eqn. (10) is equivalent to the well known Maxwell's area criterion:

$$RT \int_0^p \frac{Z^{\mathrm{l}} - Z^{\mathrm{v}}}{P} dP = P(v^{\mathrm{l}} - v^{\mathrm{v}}) - \int_{v^{\mathrm{v}}0}^{v^{\mathrm{l}}} P dv = 0 \tag{11}$$

Equations (9) and (10) prove that ω has a maximum zero value for the azeotropic point and for the pure compounds, and is negative in all other cases.

In this contribution, we have chosen as our objective function the following modification for ω, that retains its negative behaviour and non-zero limits for the pure compound, and is easily evaluated from experimental VLE data:

$$\Omega = \frac{\omega}{x_1 x_2} = \frac{1}{x_2} \ln\left(\frac{y_1}{x_1}\right) + \frac{1}{x_1} \ln\left(\frac{y_2}{x_2}\right) \tag{12}$$

Considering the γ-ϕ approach to the VLE, Eqn. (12) can be written as:

$$\Omega = \frac{1}{x_2}\ln\left(\frac{x_1\gamma_1 P_1^{\text{sat}}\phi_1^{\text{sat}}\vartheta_1/P\hat{\phi}_1^{v}}{x_1}\right) + \frac{1}{x_1}\ln\left(\frac{x_2\gamma_2 P_2^{\text{sat}}\phi_2^{\text{sat}}\vartheta_2/P\hat{\phi}_2^{v}}{x_2}\right) \tag{13}$$

where ϑ_i is the Polynting factor defined as:

$$\vartheta_i \cong \exp\left(\frac{v_i^{l}}{RT}(P - P_i^{\text{sat}})\right) \tag{14}$$

Equation 13, when applied to the low pressure VLE of non associated systems, can be simplified by assuming ideal behaviour for the vapor phase and a unitary Poynting factor, approximation which is also known as the modified Raoult's law[24]. An implicit equation in activity coefficients is then obtained:

$$\Omega = \frac{\omega}{x_1 x_2} = \frac{1}{x_2}\ln\left(\frac{P_1^{\text{sat}}\gamma_1}{P}\right) + \frac{1}{x_1}\ln\left(\frac{P_2^{\text{sat}}\gamma_2}{P}\right) \tag{15}$$

At infinite dilution, the limits for Eqn. (15) are given by:

$$\Omega_i^{\infty} = \lim_{x_i \to 0}\frac{\omega}{x_1 x_2} = \ln(\gamma_i^{\infty}\theta) - (\gamma_i^{\infty}\theta - 1) \quad \text{where } \theta = \begin{cases} P_1^{\text{sat}}/P_2^{\text{sat}} & \text{if } i = 1 \\ P_2^{\text{sat}}/P_1^{\text{sat}} & \text{if } i = 2 \end{cases} \tag{16}$$

Formally, Eqns. (15) and (16), define a graphical method that would permit evaluation of γ^{∞} by extrapolation in isothermal systems, if a complete set of experimental data (T, P, x, y) that evaluates Eqn. (4) is known. Figure 1 it shows the behavior of the $\Omega(x)$ curve for a system that exhibits positive deviations with respect to the Raoult's law, like ethanol–water at isobaric conditions[25], while Figure 2 describes the benzenehexafluorobenzene system at 303 K[26], the exhibits simultaneously positive and negative deviations from Raoult's law.

In general, the concavity of Ω will be negative, but as can be seen in Figure 3, there are ranges of saturation pressure ratios among the constituents that change the concavity for systems that deviate negatively from Raoult's law. From the analysis of the second derivative of Ω with respect to composition (see Appendix A), it is concluded that the sign of the concavity of Ω will will depend on the difference between the vapor pressures of the components and on the degree of deviation from ideality. For systems that exhibit large differences in vapor pressures and/or positive deviations with respect to the Raoult's law (see Fig. 4), negative concavities are dominant; and no system with positive concavity has been observed experimentally. Figures 3 and 4 were obtained from Eqn. 15, by using the symmetric model (regular solution):

$$G^E = Ax_1x_2 \tag{17}$$

with positive and negative A values for the simulation of positive and negative deviations from ideality. Boiling-point pressures were calculated from the modified

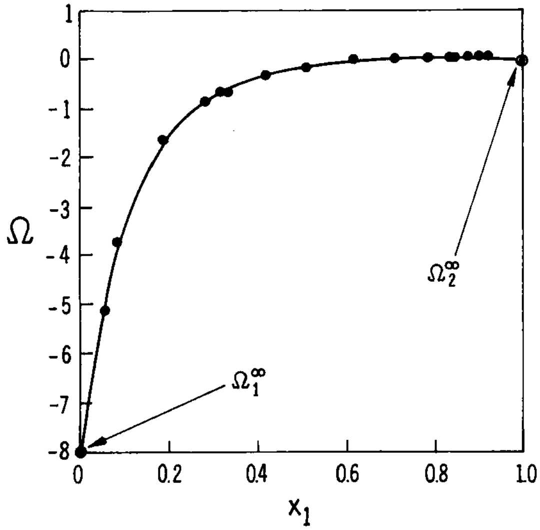

Figure 1 Ω function for the system ethanol (1) + water (2) at 101.3 kPa. Data of Kurihara *et al.* (1993).

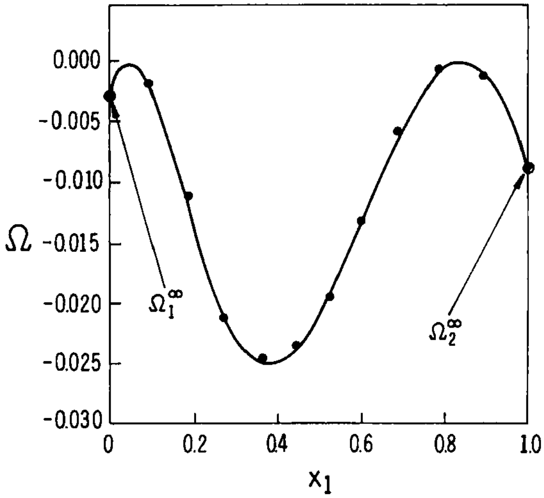

Figure 2 Ω function for the system benzene (1) + hexafluorobenzene (2) at 30.3 K. Data of Gaw and Swinton (1968).

Raoult's law, as indicated in Eqn. (19). In both figures the arrow indicates ratios $P_2^{\text{sat}}/P_1^{\text{sat}}$ increasing towards unit value.

In this work, we suggest a procedure for the numerical fit of Ω in the experimental composition range and its extrapolation to dilution ranges. Polynomial and rational functions were tested for extrapolation purposes, but they were found to be inadequate

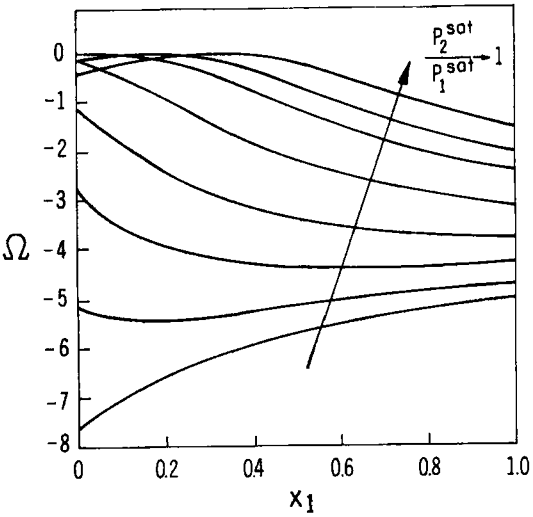

Figure 3 Ω function for a system with negative deviation from Raoult's Law. Arrow indicates values of P_1^{sat}/P_2^{sat} increasing towards unity.

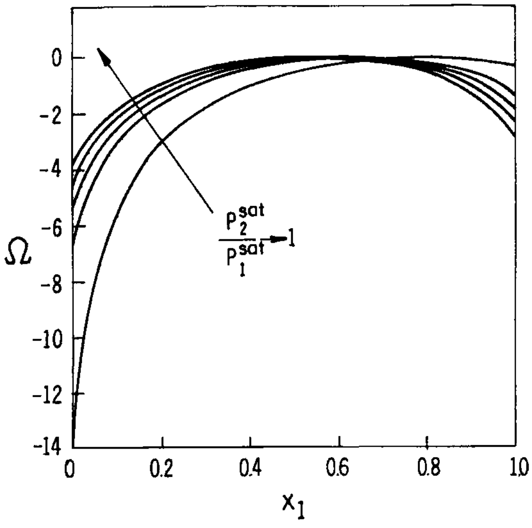

Figure 4 Ω function for a system with positive deviation from Raoult's Law. Arrow indicates values of P_1^{sat}/P_2^{sat} increasing towards unity.

due to wide oscillations in the extrapolation interval, and due to the prediction of positive values for the weighted volatity function.

The negative characteristic of Ω demands a negative interpolation function, and the presence of activity coefficients in Eqn. (15), suggests selecting a corrleation consistent with the Gibbs-Duhem equation, like a G^E model.

METHODOLOGY

Given an experimental $[T, P, x, y]$ VLE data set, the calculation method proceeds according to the following algorithm[1]:

(a) Evaluation of Ω using Eqn. (13) and the experimental liquid and vapor composition data.

(b) Search for the parameters of a G^E model, that will minimize the following objective function:

$$\Im = \min \sum_{k=1}^{N_d} \left| \Omega_{k,\mathrm{eqn}(12)} - \Omega_{k,\mathrm{eqn}(15)} \right| \times \left| 1 - \frac{y_{1,\mathrm{calc}}}{y_{1,\mathrm{exp}}} \right|_k \tag{18}$$

where $\Omega_{k,\mathrm{Eqn.}(15)}$ must be evaluated with experimental liquid compositions and the activity coefficients derived from the selected G^E model. The pressure needed in Eqn. (15) and the vapor phase compositions required in Eqn. (18), are calculated from the modified Raoult's law:

$$P_{\mathrm{calc}} = x_1 \gamma_1 P_1^{\mathrm{sat}} + x_2 \gamma_2 P_2^{\mathrm{sat}} \tag{19}$$

$$y_{1,\mathrm{calc}} = \frac{x_1 \gamma_1 P_1^{\mathrm{sat}}}{P} \tag{20}$$

Activity coeffecitents in Eqns. (19) and (20) are caculated from the selected G^E model.

It should be noted that Eqn. (15) does not depend on vapor phase compositions. To avoid this drawback, the mathematical form of the objective function (18) has been selected so as to produce a balanced adjustment of the vapor phase compositions and of the weighted volatility function.

The use of several G^E models is advisable, since as in the case of VLE fit, some of them adjust the experimental function, as calculated in (a), more satisfactorily than others. In this work, the Wilson[26], TK-Wilson[27] and NRTL[28] models for G^E have been selected to smooth the Ω function evaluated from experimental data, and the vapor pressures of the pure components have been estimated by using the Antoine parameters suggested by DECHEMA[2].

(c) Select the G^E model that minimizes the pressure deviation (i.e. the pressure obtained by Eqn. (19) with respect to the experimental pressure) in the range $0 < x_1 < 0.5$ to estimate γ_1^∞ and in the range $0.5 < x_1 <$ to estimate γ_2^∞.

(d) Extrapolate the G^E model selected in (c) to dilution ranges, by evaluating the model γ^∞'s expressions with their respective parameters, obtained in (b) (For more details, see Appendix B).

The minimization of the non-linear objective function in Eqn. (18) requires a numerical treatment. The second order BFGS optimization algorithm developed by Shanno[30] was used, assisted by a Levenberg-Marquardt routine[31], that protects the optimization against an ill-conditioned Hessian matrix.

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[1] A computer FORTRAN program is available from the authors.

RESULTS

The previously described methodology, has been applied to the determination of the values of γ^∞ for 95 VLE systems, with an experimental data base that includes multiple functional groups and aqueous systems. Experimental values for γ^∞ have been taken from the compilation of Tiegs *et al.*[3], except for the indicated cases.

Percentual deviations from the values obtained from G^E model parameters suggested by DECHEMA[2], the values predicted by this work and those calculated by MOSCED, are compared for each system, and are reported in Table 1. This Table shows that the most stable predictions are achieved by the MOSCED model, which is not affected by the consistency of the experimental VLE data. The weighted volatility method does not give, in general, a worse prediction than the fit recommended by DECHEMA, and in most of the cases it is observed that, in function of the consistency of the data, the suggested method achieves significant improvements. In Figure 5 a comparison is made between experimental γ^∞'s values and γ^∞'s predicted by the method proposed here and those given by DECHEMA. It is seen that the dispersion achieved by the ω method is well balanced in all the experimental range; in contrast, the dispersion of DECHEMA values tends to be larger when γ^∞ increases and many experimental points are under predicted in the range 10 to 100.

The large deviation observed in the data of Martin and George (1933) for the benzene-phenol system at 343 K, is due to the selection of the NRTL model, that predicts liquid phase immiscibility, not observed in the experimental data. If the Wilson model is selected, then $\gamma_1^\infty = 1.67$, which is comparable to the experimental value.

In the same manner, the acetic acid (1)-heptane (2) system at 313 K (data of Markuzin and Pavlova, 1971) could be well correlated by Eqn. (15), but extrapolation of the activity coefficient model to the dilute range will not represent a physically valid value, unless the acetic acid dimerization in the vapor phase is considered. For a dimerizing system, the function in Eqn. (12) can be evaluated in terms of apparent compositions, for liquid and vapor phases. From Eqns. (4) and (12), and by applying L'Hopital's rule, it can be deduced that:

$$\Omega_1^\infty = \lim_{x_1 \to 0} \Omega = \lim_{x_1 \to 0} \frac{\omega}{x_1 x_2} = \lim_{x_1 \to 0} \frac{d\omega/dx_1}{x_2 - x_1} = \left(\frac{d\omega}{dx_1}\right)_{x_1=0} \tag{21}$$

$$\Omega_2^\infty = -\left(\frac{d\omega}{dx_1}\right)_{x_1=1} \tag{22}$$

but

$$\Omega_1^\infty = -\left(\frac{d\omega}{dx_1}\right)_{x_1=0} = \ln\frac{y_1}{x_1} - \left(\frac{dy_1}{dx_1}\right)_{x_1=0} + 1 = \ln\frac{y_1}{x_1} - \frac{y_1}{x_1} + 1 \tag{23}$$

$$\Omega_2^\infty = -\left(\frac{d\omega}{dx_1}\right)_{x_1=1} = \ln\frac{y_2}{x_2} - \left(\frac{dy_2}{dx_2}\right)_{x_1=0} + 1 = \ln\frac{y_2}{x_2} - \frac{y_2}{x_2} + 1 \tag{24}$$

Table 1 Detailed prediction statistics of γ_{∞} by different methods.

System	*Consist* *p/i*	$\gamma_{1,\mathrm{exp.}}^{\infty}$	$\gamma_{2,\mathrm{exp.}}^{\infty}$	$\Delta\gamma_1^{\infty}$ *DECHEMA*	$\Delta\gamma_2^{\infty}$ *DECHEMA*	$\Delta\gamma_{1,\Omega}^{\infty}$	$\Delta\gamma_{2,\Omega}^{\infty}$	$\Delta\gamma_1^{\infty}$ *MOSCED*	$\Delta\gamma_2^{\infty}$ *MOSCED*
Acet ic acid-Heptane, 313 K Markuzin and Pavlova (1971)***	[+ +]	24.66	10.57	− 26.5	90.6	− 65.4	− 23.9	n.a.	n.a.
Acetone-Benzene, 303 K Kraus and Linek (1971)	[+ −]		1.59		− 7.5		0.8		− 11.5
Acetone-Hexane, 308 K Kudryavtseva and Susarev (1963)	[− +]	6.12 (c)	6.24 (c)	− 13.2	11.4	− 29.9	7.3	6.9	− 11.3
Acetone-Hexane, 328 K Kudryavtseva and Susarev (1963)	[− +]		4.95 (c)		5.1		8.2		− 5.9
Acetone-Octane, 313K Kolasinska *et al.* (1982)	n.a.		8.87* (c)		n.a.		− 33.5		− 19.7
Acetone-Toluene, 318 K Kraus and Linek (1971)	[+ +]		1.89 (c)		− 10.1		− 26.5		− 14.1
Acetone-Toluene, 308 K Kraus and Linek (1971)	[+ −]		2.03 (c)		− 17.7		− 25.3		− 18.2
Acetone-Toluene, 328 K Kraus and Linek (1971)	[+ −]		1.78 (c)		1.1		− 14.4		− 10.7
Acetonitrile-Benzene, 293 K Wemer and Schuberth (1966)	[+ +]	3.39	3.19	− 2.4	0.3	− 0.4	− 11.3	9.6	− 3.9
Acetonitrile-Benzene, 318 K Brown and Smith (1955)	[+ +]	3.08	2.95	− 7.8	− 7.1	− 2.4	− 8.3	0.3	− 11.8
Acetonitrile-Benzene, 318 K Palmer and Smith (1972)	[+ +]	3.08	2.95	− 2.3	− 7.1	5.0	− 16.8	0.3	− 11.8
Aniline-Cyclohexane, 308 K Abello *et al.* (1968)	[+ +]		11.3		− 41.3		40.4		− 17.1
Aniline-Cyclohexane, 323 K Abello *et al.* (1968)	[+ +]		10.7		− 25.9		− 3.7		− 24.9
Benzene-Cyclohexane, 313 K Kimura and Takagi (1978)	[+ +]		1.61		1.9		1.1		− 0.1
Benzene-Cyclohexane, 313 K Young *et al.* (1977)	[+ +]		1.61		1.2		2.6		− 0.1

System	*Consist* *p/i*	$\gamma^{\infty}_{1,\text{exp.}}$	$\gamma^{\infty}_{2,\text{exp.}}$	$\Delta\gamma^{\infty}_1$ *DECHEMA*	$\Delta\gamma^{\infty}_2$ *DECHEMA*	$\Delta\gamma^{\infty}_{1,\Omega}$	$\Delta\gamma^{\infty}_{2,\Omega}$	$\Delta\gamma^{\infty}_1$ *MOSCED*	$\Delta\gamma^{\infty}_2$ *MOSCED*
Benzene-Cyclohexane, 333 K Boublik (1963)	[++]	1.41	1.5/2	2.8	6.6	3.2	0.1	4	0.7
Benzene-Heptane, 318 K Palmer and Smith (1972)	[++]		1.92		15.1		2.9		−4.3
Benzene-Heptane, 353 K Letcher and Bayles (1971)	[++]		1.21		23.1		10.7		35.2
Benzene-Heptane, 333 K Letcher and Bayles (1971)	[−−]	1.37	1.24	−2.9	60.5	−5.4	13.5	4.6	40.4
Benzene-Phenol, 353 K Gmehling (1982)	[++]	2.56		−1.6		−12.3		−19.8	
Benzene-Phenol, 343 K Martin and George (1933)	[+−]	2.62		12960		7580		−20	
1-Butanol-Water, 343 K Kharin *et al.* (1969)	n.a.		3.27		n.a.		3.4		n.a.
1-Butanol-Water, 363 K Kharin *et al.* (1969)	n.a.		3.07		n.a		4.4		n.a.
1-Butanol-Water, 383 K Kharin *et al.* (1969)	n.a.		2.9		n.a.		−1.8		n.a.
1-Butanol-Cyclohexane, 101 kPa Rao and Rao (1963)	[++]	11.05 (c)		4.3		41.1		156.9	
1-Butanol-Cyclohexane, 318 K Smirnova and Kurtynina (1969)	[++]	24.5* (c)		71.4		62.4		−29.2	
1-Butanol-Cyclohexane, 323 K Vonka *et al.* (1971)	[++]	21.46 (c)		9.3		−8.2		−27.7	
1-Butanol-Cyclohexane, 343 K Vonka *et al.* (1971)	[−+]	13.31 (c)		−9.3		−5		−21.2	
1-Butanol-Cyclohexane, 353 K Ramalho and Delmas (1968)	[−−]	11.05 (c)		−44.1		−60.9		−19.6	
2-Butanone-Hexane, 333 K Hanson and Van Winkle (1967)	[++]	3.6		2.5		1.1		−3.8	

Table 1 (*Contd.*)

System	*Consist* *p/i*	$\gamma^{\infty}_{1,\text{exp}}$	$\gamma^{\infty}_{2,\text{exp}}$	$\Delta\gamma^{\infty}_{1}$ *DECHEMA*	$\Delta\gamma^{\infty}_{2}$ *DECHEMA*	$\Delta\gamma^{\infty}_{1,\Omega}$	$\Delta\gamma^{\infty}_{2,\Omega}$	$\Delta\gamma^{\infty}_{1}$ *MOSCED*	$\Delta\gamma^{\infty}_{2}$ *MOSCED*
2-Butanone-Water, 333 K Altsybeeva and Morachevskii (1964)	[− +]		7.2		− 18.2		− 18.2		n.a.
Carbon disulfide-Acetone, 308 K Zawidzki (1900)	[+ +]	4.09 (c)		− 7.6		− 1.2		1.1	
Carbon disulfide-Acetone, 302 K Hirshberg (1932)	[− +]	4.22 (c)		− 7.6		− 22		1.5	
Carbon disulfide-Ethanol, 303 K McKelgue and Gularl (1986)	n.a.		78.3 (c)		n.a.		− 25.8		− 38.7
1-Chlorobutane-Hexane, 300 K Gutsche and Knapp (1982)	[+ +]	1.52		6.6		8.8		5.9	
Chloroform-Acetic acid methyl ester, 313 K Ohta *et al.* (1980)	[+ +]	0.52 (b)	0.43 (b)	1.9	− 11.6	− 0.3	− 24.6	− 5.8	− 4.6
Chloroform-Acetic acid methyl ester, 323 K Nagata and Hayashida (1970)	[+ +]	0.56 (b)	0.49	− 1.8	− 14.3	− 3.4	− 21.6	− 7.2	− 9.6
Chloroform-Acetone, 308 K Kudryavtseva and Susarev (1963)	[+ +]	0.503 (c)		− 10.5		− 11.9		− 1.8	
Chloroform-Acetone, 313 K Roeck and Schroeder (1957)	[+ +]	0.51 (c)		− 3.9		− 1.8		0.2	
Chloroform-Acetone, 318 K Kudryavtseva and Susarev (1963)	[+ +]	0.509 (c)		− 5.7		− 7.9		3.6	
Chloroform-Acetone, 328 K Kudryavtseva and Susarev (1963)	[+ +]	0.53 (c)		− 5.7		− 5.4		5.3	
Chloroform-Acetone, 308 K Tamir *et al.* (1981)	n.a.	0.503 (c)		n.a.		− 8.4		− 1.6	
Chloroform-Acetonitrile, 328 K Nagata and Kawamura (1979)	n.a.	1.31 (b)	1.29 (b)	n.a.	n.a.	0.9	− 9.4	19.6	37.3
Chloroform-Ethyl acetate, 313 K Ohta *et al.* (1980)	[+ +]	0.431* (c)		− 7.2		− 4.8		7.9	
Chloroform-Ethyl acetate, 323 K Ohta *et al.* (1980)	[+ +]	0.459* (c)		0.2		0.7		7.5	
Chloroform-Hexane, 318 K Kudryavtseva and Susarev (1963)	[+ −]		1.79		3.9		− 3.4		9

System	*Consist* *p/i*	$\gamma^{\infty}_{1,\mathrm{exp.}}$	$\gamma^{\infty}_{2,\mathrm{exp.}}$	$\Delta\gamma^{\infty}_{1}$ *DECHEMA*	$\Delta\gamma^{\infty}_{2}$ *DECHEMA*	$\Delta\gamma^{\infty}_{1,\Omega}$	$\Delta\gamma^{\infty}_{2,\Omega}$	$\Delta\gamma^{\infty}_{1}$ *MOSCED*	$\Delta\gamma^{\infty}_{2}$ *MOSCED*
Chloroform-Methanol, 322 K Kireev and Sitnikov (1941)	[+ +]	2.41* (b)		−13.3		5.7		34.4	
Cyclohexane-Hexane, 343 K Susarev and Chen (1963)	[+ +]	1.054 (c)	1.07* (c)	−0.4	11.2	1.2	−2.2	−2	−2.7
Dimethylformamide-Benzene, 323 K Quitzsch (1965)	[+ +]	1.73	1.38	30.6	14.5	31.8	16.4	55.5	30.2
Ethanol-Acetone, 328 K Vinichenko and Susarev (1966)	[− −]	1.92 (c)		−17.7		−21.3		7.4	
Ethanol-Heptane, 363 K Ramalho and Delmas (1986)	[− +]	12.2		72.8		48.3		−27.9	
Ethanol-Cyclohexane, 323 K Scatchard and Satkiewicz (1964)	[+ +]	24.3 (c)		16.2		−9.2		−7.1	
Ethanol-Cyclohexane, 338 K Scatchard and Satkiewicz (1964)	[+ +]	17.0* (c)		34.3		15.2		−6.5	
Ethanol-Cyclohexane, 323 K Morachevskii and Zharov (1963)	[− +]	24.3 (c)		84.3		133.9		−7.1	
Ethanol-Cyclohexane, 323 K Zharov *et al.* (1968)	[− +]	24.3 (c)		38.7		12.9		−7.1	
Ethanol-Ethyl acetate, 313 K Mertl (1972)	[+ +]	3.29	2.77	−11.9	1.4	−11.7	1	10.9	−4.4
Ethanol-Heptane, 313 K Diaz Peña and Rodriguez Cheda (1970)	[+ +]	35.45	13	−24.3	9.2	−16.3	13.6	−25.2	−2.8
Ethanol-Heptane, 333 K Diaz Peña and Rodriguez Cheda (1970)	[+ +]	16	11	3.6	3.2	1.4	−8.4	−0.7	1.4
Ethanol-Heptane, 313 K Ratcliff and Chao (1969)	[− +]	35.45	13	−21.3	−13.2	−19.2	−29.7	−25.2	−2.8
Ethanol-Heptane, 343 K Ramalho and Delmas (1968)	[− +]	14.7	10.2	4.3	81.4	−20.8	63	−13	1.9
Ethanol-Heptane, 353 K Ramalho and Delmas (1968)	[− +]	13.3	9.8	69.7	140.5	3	89.5	−21	−1.6
Ethanol-Hexane, 323 K Diaz Peña and Rodriguez Cheda (1970)	[+ +]	23	10	−34.1	7.1	−36	5.7	−9.9	−2.2

Table 1 (*Contd.*)

System	*Consist* *p/i*	$\gamma^{\infty}_{1,\mathrm{exp.}}$	$\gamma^{\infty}_{2,\mathrm{exp.}}$	$\Delta\gamma^{\infty}_{1}$ *DECHEMA*	$\Delta\gamma^{\infty}_{2}$ *DECHEMA*	$\Delta\gamma^{\infty}_{1,\Omega}$	$\Delta\gamma^{\infty}_{2,\Omega}$	$\Delta\gamma^{\infty}_{1}$ *MOSCED*	$\Delta\gamma^{\infty}_{2}$ *MOSCED*
Ethanol-Octane, 318 K Boublikova and Lu (1969)	[+ +]		13.1		15.6		2.4		14.4
Ethanol-Toluene, 318 K Van Ness *et al.* (1967)	[+ +]		6.3		− 8.1		− 2.3		− 12.3
Ethyl acetate-Cyclohexane, 293 K Slavin and Abramzon (1977)	[+ +]		3.24		13.9		22.8		− 6.4
Ethyl acetate-Tolune, 333 K Linek *et al.* (1972)	[− +]		1.18		145.8		1.9		3.5
Ethyl acetate-Toluene, 343 K Linek *et al.* (1972)	[− −]	1.16		− 19		− 38.2		6.2	
Furfural-Cyclohexane, 101 kPa Thornton and Garner (1951)	[+ +]	13.9		20		1.9		n.a.	
Furfural-Heptane, 101 kPa Kolyuchkina *et al.* (1975)	n.a.	9.6		n.a.		11.9		n.a.	
Furfural-Toluene, 17 kPa Rivenq (1973)	n.a.		2.77		n.a.		− 26.1		n.a.
Heptane-Octane, 328 K Kudryavtseva *et al.* (1971)	[+ +]	1.06		− 1.9		− 0.8		− 5.9	
Methanol-1,4-Dioxane, 308 K Kortuem and Valent (1977)	[+ +]		3.23 (c)		− 2.2		− 7.7		− 24.6
Methanol-1,4-Dioxane, 323 K Kortuem and Valent (1977)	[+ +]		3.06* (c)		− 3.9		− 17.8		− 23.2
Methanol-1,4-Dioxane, 333 K Kortuem and Valent (1977)	[+ −]		2.93* (c)		− 4.4		− 17		− 21.9
Methanol-Cyclohexane, 318 K Marinichev and Susarev (1965)	[+ +]	54.2	17.4	− 47.6	− 2.1	− 13.5	− 0.9	− 38.5	4.8
Nitromethane-Benzene, 318 K Brown and Smith (1955)	[+ +]	3.48	3.86	− 7.5	− 12.7	− 8	− 13.9	− 1.6	− 30.6
Nitromethane-Benzene, 318 K Edwards (1969)	[+ +]	3.48	3.86	− 8.6	− 11.7	− 11.9	− 12.2	− 1.6	− 30.6

System	*Consist* *p/i*	$\gamma_{1,\text{exp.}}^{\infty}$	$\gamma_{2,\text{exp.}}^{\infty}$	$\Delta\gamma_1^{\infty}$ *DECHEMA*	$\Delta\gamma_2^{\infty}$ *DECHEMA*	$\Delta\gamma_{1,\Omega}^{\infty}$	$\Delta\gamma_{2,\Omega}^{\infty}$	$\Delta\gamma_1^{\infty}$ *MOSCED*	$\Delta\gamma_2^{\infty}$ *MOSCED*
Phenol-Octane, 383 K Gmehling (1982)	[+ +]		13.3**		−28.2		−36		−25.1
2-Propanol-Cyclohexane, 333 K Nagata (1973)	[+ +]		4.74 (c)		27.4		15.8		n.a.
2-Propanol-Cyclohexane, 313 K Storonkin and Morachevskii (1956)	[− +]		5.15 (c)		9.5		−2.3		n.a.
2-Propanol-Cyclohexane, 323 K Nagata *et al.* (1973)	[− +]		5.07 (c)		14.8		8.3		n.a.
2-Propanol-Cyclohexane, 342 K Storonkin and Morachevskii (1956)	[− +]		4.73 (c)		1.3		−4.6		n.a.
2-Propanol-Heptane, 331 K Barraza and Edwards (1981)	[+ +]		6.28 (c)		9.9		−29.2		n.a.
2-Propanol-Hexane, 328 K Berro *et al.* (1981)	[+ +]		5.58* (c)		8.2		0		n.a.
2-Propanol-Hexane, 331 K Barraza and Edwards (1981)	[+ +]		5.68 (c)		−16.4		−20.5		n.a.
2-Propanol-Hexane, 323 K Maciel and Francesconi (1988)	n.a.		5.68 (c)		n.a.		4		n.a.
2-Propanol-Hexane, 338 K Maciel and Francesconi (1988)	n.a.		5.35* (c)		n.a.		3		n.a.
2-Propanol-Hexane, 348 K Maciel and Francesconi (1988)	n.a.		5.18* (c)		n.a.		−0.7		n.a.
2-Propanol-Water, 353 K Wu *et al.* (1988)	n.a.		3.01		n.a.		20.7		n.a.
Pyridine-Water, 343 K Andon *et al.* (1957)	[+ +]		2.87		2.8		0.8		n.a.
Pyridine-Water, 363 K Andon *et al.* (1957)	[+ +]		2.8		7.9		5.7		n.a.
Tetrachloromethane-1-Propanol, 343 K Papousek *et al.* (1959)	[− +]	3.14 (c)	8.78 (c)	6.1	17.9	1	0.7	1.7	−7.5

Table 1 (*Contd.*)

System	*Consist* *p/i*	$\gamma^{\infty}_{1,\mathrm{exp.}}$	$\gamma^{\infty}_{2,\mathrm{exp.}}$	$\Delta\gamma^{\infty}_{1}$ *DECHEMA*	$\Delta\gamma^{\infty}_{2}$ *DECHEMA*	$\Delta\gamma^{\infty}_{1,\Omega}$	$\Delta\gamma^{\infty}_{2,\Omega}$	$\Delta\gamma^{\infty}_{1}$ *MOSCED*	$\Delta\gamma^{\infty}_{2}$ *MOSCED*
Tetrachloromethane-1-Propanol, 343 K Papousek *et al.* (1959)	[− +]	3.14 (c)	8.78 (c)	6.1	17.9	1	0.7	1.7	− 7.5
Tetrachloromethane-2-Propanol, 343 K Papousek *et al.* (1959)	[− +]	3.41 (c)		3.8		− 9.6		n.a.	
Tetrachloromethane-Acetone, 318 K Brown and Smith (1957)	[+ +]	2.07 (c)		− 1		− 5.5		0.5	
Tetrachloromethane-Dimethylformamide, 304 K Quitzsch (1966)	[+ +]		16.1		− 73.3		− 5.2		− 62.1

Where:

Consist *p/i*	point-to-point consistency (Fredenslund *et al.*, 1977) and integral Herington[35] consistency, respectively; as reported by DECHEMA.
$\Delta\gamma^{\infty}$	relative percent deviation, calculated as $\gamma^{\infty}_{\mathrm{calc}} - \gamma^{\infty}_{\mathrm{exp}}/\gamma^{\infty}_{\mathrm{exp}} \times 100$
DECHEMA	calculated using the G^E model and the parameters suggested by DECHEMA.
Ω	this work.
MOSCED	calculated using the MOSCED model.
n.a.	not available.
(b)	experimental values taken from Coutinho and Macedo (1994).
(c)	experimental values taken from Trampe and Eckert (1990).
*	interpolated from experimental data.
**	extrapolated from experimental data.
***	see references at the end of the table.

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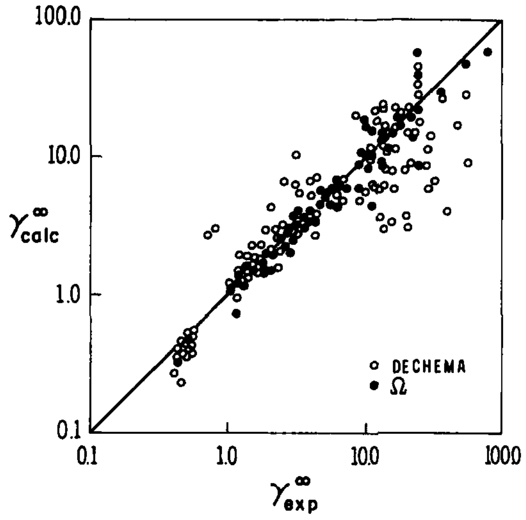
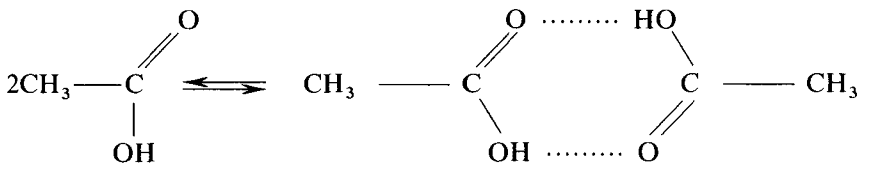


Figure 5 Graphical comparison of γ^{∞} give by DECHEMA and by Ω.

Equations (23) and (24) establish the limit of the apparent composition ratios for each phase in the dilution ranges. Let us now consider the following well-known dimerization reaction for acetic acid in the vapor phase:



the equilibrium constant for this dimerization, assuming that the mixture of heptane and the monomer and dimer of acetic acid behaves as an ideal gas, is given by:

$$K = \frac{Z_{\text{dimer}}}{Z^2_{\text{monomer}} P} \tag{25}$$

where Z represents the true compositions of species in the vapor phase, and can be calculated from a material balance by using apparent compositions (monomer of acetic acid and heptane) as:

$$Z_{\text{monomer}} = \frac{y_1 - 2\eta}{1 - \eta} \tag{26}$$

$$Z_{\text{dimer}} = \frac{\eta}{1-\eta} \tag{27}$$

$$Z_{\text{heptane}} = \frac{y_2}{1-\eta} \tag{28}$$

where η is the degree of advancement of the dimerzation reaction. Solving simultaneously Eqn. (25) and Eqns. (26–28), it can be deduced that:

$$\eta = \frac{1 + 4KPy_1 - \sqrt{1 + 8KPy_1 - 4KPy_1^2}}{2 + 8KP} \tag{29}$$

As pointed by Wisniak and Tamir[32], the equilibrium relations can be written in terms of apparent compostions for the liquid phase and true compositions for the vapor phase as:

$$x_i \gamma_i f_i^L = Z_i \hat{\phi}_i P \tag{30}$$

$$f_i^L = Z_i(y_i = 1)\phi_i^{\text{stat}} P_i^{\text{stat}} v_i \tag{31}$$

where γ_i is the apparent activity coefficent. When Eqns. (30–31) are applied to the low pressure VLE, then can be simplified to:

$$x_i \gamma_i f_i^L = Z_i P \tag{32}$$

$$f_i^L = Z_i(y_i = 1) P_i^{\text{stat}} \tag{33}$$

We can apply Eqs. (32) and (33) for the estimation of apparent activity coefficient at infinite dilution as:

$$\gamma_1^{\infty} = \frac{P_2^{\text{sat}}}{f_1^L} \lim_{x_1 \to 0} \frac{Z_{\text{monomer}}}{x_1} = \frac{P_2^{\text{sat}}}{f_1^L} \lim_{x_1 \to 0} \frac{y_1/x_1 - 2\eta/x_1}{1-\eta} \tag{34}$$

$$\gamma_2^{\infty} = \frac{P_1^{\text{sat}}}{f_2^L} \lim_{x_1 \to 2} \frac{Z_{\text{heptane}}}{x_2} = \frac{P_1^{\text{sat}}}{f_2^L} \lim_{x_2 \to 2} \frac{y_2/x_2}{1-\eta} \tag{35}$$

In Eqns. (34) and (35), the apparent composition ratios are be obtained by solving Eqns. (23) and (24), f_i^L and η are calculated from Eqn. (29) if the dimerization constant for acetic acid is known.

The two cases of dimerization described here have not been considered in the global deviation analysis included in Table 2.

From Table 2, it can be concluded that the most satisfactory predictions, for the data base of various consistency systems treated here, correspond to the MOSCED model and to the ω method proposed in this work, whose deviations are comparable. A reduction of 22% is observed in the average absolute prediction errors from experimental VLE data in comparison to the values calculated from the DECHEMA Collection, with an also significant reduction in the standard deviation. It can be

Table 2 Global Deviation Statistics.

Method	*number of systems*	*average absolute deviation (%)*	*standard dev. (%)*	*maximum error (%)*	*fraction of system with error > 20%*
VLE extrapolation (DECHEMA) parameters	80	18.2	25.9	145.8	27.5
This work	**93**	**14.4**	**18.9**	**133.9**	**29.0**
MOSCED	74	14.4	19.6	156.9	32.4

Table 3 Deviation Statistics over [+ +] and [+ −] Systems.

Method	*average absolute deviation (%)*	*standard dev.*	*maximum error (%)*
VLE extrapolation (DECHEMA parameters)	12.2	14.2	73.3
This work	**11.1**	**11.9**	**62.4**
MOSCED	14.6	21.8	156.9

concluded that the method proposed in this work is potentially attractive in the prediction of γ^{∞} from full range VLE data.

In Table 3 the prediction satistics for positive punctual consistency systems (61 VLE systems) are summarized. In this case, the weighted volatility function gives the smallest average deviation errors, and the trend observed in Table 2 is conserved.

CONCLUSIONS

According to results obtained in this work, the weighted volatility function shows an interesting and improvable potential for the rapid forecast of behavior at diluted concentrations, considering a standard parameter fit methodology for excess models on a new objective function. Accroding to Eqn. (13), it is possible to improve the *physical parameter fit soundness*, if the association effects for vapor and liquid phases, and the correction the vapor phase non-idealities by using equations of state are taken into consideration.

Nomenclature

A_{ij}	G^E model parameter in Eqns. (B.1) to (B.6).
G^E	excess Gibbs energy.
N_d	number of experimental data points.
P	Pressure.
P_i^{sa}	vapor pressure of component i.
R	gas constant.
Q	parameter defined in Eqn. (A.6).
T	temperature.

V	volume.
x	liquid phase composition.
y	vapor phase composition.
Z	compressibility factor.

Greek

α	relative volatility.
α_{12}	NRTL parameter in Eqn. (B.1)
β_{12}	approximate limiting separation factor in Eqn. (1).
γ	activity coefficient.
ϕ_i	fugacity coefficient for pure i.
$\phi_i^{\$}$	effective fugacity coefficient.
Λ_{ij}	Wilson and TK-Wilson parameters.
v	Poynting factor.
θ	saturation pressure ratio, defined in Eqn. (16)
τ_{ij}	NRTL parameter.
μ	chemical potential.
ω	weighted volatility function, defined in Eqn. (4)
Ω	modified weighted volatility function, defined in Eqn. (12)

Others:

$\Im$	objective function, defined in Eqn. (18)

Subscripts

calc.	calculated value.
exp.	experimental value.
i,j	pertaining to component i and j.

Superscripts

l	pertaining to liquid phase property.
v	pertaining to vapor phase property.
∞	infinite dilution.
sat	saturation.
NRTL	pertaining to NRTL G^E model.
W	pertaining to Wilson G^E model.
TKW	pertaining to TK-Wilson G^E model.

APPENDIX A: SOME MATHEMATICAL PROPERTIES OF EQN. 15.

The second derivative of the modified weighted volatility function at constant temperature is given by:

$$\frac{d^2\Omega}{dx_1^2} = \frac{2\omega}{x_1x_2}\left(\left(\frac{x_2-x_1}{x_1x_2}\right)^2 + \frac{1}{x_1x_2}\right) - \frac{2d\omega/dx_1}{(x_1x_2)^2}(x_2-x_1) + \frac{d^2\omega/dx_1^2}{x_1x_2} \qquad \text{(A.1)}$$

We can express Eqn. (A.1) in terms of the weighted volatility, as follows:

$$\omega = x_1 \ln\alpha + \ln\frac{y_2}{x_2} = x_1 \ln\alpha + \ln(\gamma_2 P_2^{\text{sat}}/P) \tag{A.2}$$

$$\omega = x_1 \ln\alpha + \ln\frac{y_2}{x_2} = x_1 \ln\alpha + \ln(\gamma_2 P_2^{\text{sat}}/P) \tag{A.3}$$

$$\frac{d^2\omega}{dx_1^2} = \frac{d\ln\alpha}{dx_1} - \frac{d^2 \ln(P/P_2^{\text{sat}})}{dx_1^2} \tag{A.4}$$

Equation (A.2) yields always a negative solution. For Eqns. (A.3) and (A.4), the sign will depend on the saturation pressure ratio and on the liquid phase deviation from ideality. A full composition range study for the concavity of Eqn. (A.1) is cumbersome, and it depends on additive contributions of higher activity coefficients derivatives.

If Eqn. (A.1) is analyzed in the diluted range, it can be concluded that:

$$\lim_{x_1\to 0} \frac{d^2\Omega}{dx_1^2} = -\frac{2}{3}Q^3 + Q^2\left[1 + \frac{2}{\gamma_1^\infty}\left(\frac{d\gamma_1}{dx_1}\right)_{x_1=0}\right] - Q\left[2 + \frac{1}{\gamma_1^\infty}\left(\left(\frac{d\gamma_1}{dx_1}\right)_{x_1=0} + \left(\frac{d^2\gamma_1}{dx_1^2}\right)_{x_1=0}\right)\right]$$
$$+ 2\ln(1+Q) + \frac{1}{3\gamma_1^\infty}\left(\left(\frac{d\gamma_1}{dx_1}\right)_{x_1=0}\right)^2 - \frac{4}{3\gamma_1^\infty}\left(\left(\frac{d\gamma_1}{dx_1}\right)_{x_1=0} + \left(\frac{d^2\gamma_1}{dx_1^2}\right)_{x_1=0}\right) \tag{A.5}$$

where

$$Q = \frac{P_1^{\text{sat}}}{P_2^{\text{sat}}}\gamma_1^\infty - 1 \tag{A.6}$$

When deviations from ideality are positive and index 1 represents the most volatile component, Q will be positive and constitute the dominant term in Eqn. (A.5), negative concavities in the extreme dilution range will then be favored. Q can be negative or not dominant in Eqn. (A.5) if deviations are negative, and depending on the saturation pressure ratio, positive concavities become more possible for Ω.

Eq. (A.5) is also applicable for the other limit when index 1 represents the less volatile component. Similar conclusions relative to the sign of the concavity are obtained.

APPENDIX B: G^E MODELS AND THEIR γ^∞ RELATIONS, AS USED IN THIS WORK

1 NRTL[29]

Activity coefficients at infinite dilution were calculated from:

$$\ln\gamma_1^\infty = \tau_{21} + \tau_{12}\exp(-\alpha_{12}\tau_{12}) \tag{B.1}$$

$$\ln\gamma_2^{\infty} = \tau_{12} + \tau_{21}\exp(-\alpha_{12}\tau_{21})$$

$$\tau_{21} = \frac{A_{21}^{\mathrm{NRTL}}}{RT};\ \tau_{12} = \frac{A_{12}^{\mathrm{NRTL}}}{RT} \tag{B.2}$$

the three parameters $\{A_{12}^{\mathrm{NRTL}}, A_{21}^{\mathrm{NRTL}}, \alpha_{12}\}$ were used to minize Eqn. (17)

2 WILSON[26]

Activity coefficients at infinite dilution were calculated from:

$$\ln\gamma_1^{\infty} = 1 - \ln\Lambda_{12} - \Lambda_{21} \tag{B.3}$$

$$\ln\gamma_2^{\infty} = 1 - \ln\Lambda_{21} - \Lambda_{12}$$

$$\Lambda_{12} = \frac{v_2^l}{v_1^l}\exp\left(-\frac{A_{12}^W}{RT}\right);\ \Lambda_{21} = \frac{v_1^l}{v_2^l}\exp\left(-\frac{A_{21}^W}{RT}\right) \tag{B.4}$$

where v_i^l is the molar volume of pure liquid component. In this work, volumes were estimated at 298.15 K by using Rackett's equation[33] for the Wilson and TK-Wilson models. Critical constants were taken from Reid, Sherwood and Prausnitz[34]. Two parameters $\{A_{12}^W, A_{21}^W\}$ were used to minimize Eqn. (17).

3 TK-WILSON[28]

Activity coefficients at infinite dilution were calculated from:

$$\ln\gamma_1^{\infty} = \ln\frac{v_2^l}{v_1^l\Lambda_{12}} + \frac{v_1^l}{v_2^l} - \Lambda_{21}$$

$$\ln\gamma_2^{\infty} = \ln\frac{v_1^l}{v_2^l\Lambda_{21}} + \frac{v_2^l}{v_1^l} - \Lambda_{12} \tag{B.5}$$

$$\Lambda_{12} = \frac{v_2^l}{v_1^l}\exp\left(-\frac{A_{12}^W}{RT}\right);\ \Lambda_{21} = \frac{v_1^l}{v_2^l}\exp\left(-\frac{A_{21}^W}{RT}\right) \tag{B.6}$$

The two parameters $\{A_{12}^{\mathrm{TKW}}, A_{21}^{\mathrm{TKW}}\}$ were used to minimize Eqn. (17).

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