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Fluid Phase Equilibria 218 (2004) 141–148

FLUID PHASE EQUILIBRIA

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Water + esters + methanol: experimental data, correlation and prediction of surface and interfacial tensions at 303.15 K and atmospheric pressure

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Received 12 September 2003; accepted 5 December 2003

Abstract

For the ternary system water + ethyl propionate + methanol, and the constituent binaries, the surface tension at 303.15 K and atmospheric pressure was measured over the whole miscible composition range. The liquid interfacial tension was determined in the liquid–liquid equilibrium range at the same conditions of temperature and pressure. Correlation of the excess surface tension of the above mentioned binary and ternary systems as well as for the ternary water + ethyl butyrate + methanol and constituent binaries, was performed with empirical and thermodynamic-based models. The interfacial tension was correlated with the equation of Fu et al.

The prediction of the surface tension of the binary and ternary systems was made using the model of Sprow and Prausnitz. The models of Fu et al. and Li et al. were also applied to predict the surface tension in the ternary systems.

The liquid interfacial tension of the ternary systems was correlated and predicted using the relations proposed by Li and Fu and Fu et al., respectively, with satisfactory results.

Keywords: Surface tension; Interfacial tension; Correlation; Prediction; Water; Methanol; Esters

1. Introduction

The efficiency of many important unit operations in industry, which involve mass transfer across gas–liquid or liquid–liquid interfaces depends strongly on the values of surface and liquid interfacial tensions of fluids. In the last years information about surface tension have been published for many binary systems, but this information is still scarce for ternary mixtures. For the interfacial tension detailed data are available only for about 30 systems [1]. The ternary systems water + esters + methanol show large liquid–liquid immiscibility gaps and, have also appreciable homogeneous liquid domains. This makes these systems suitable for the study of both the surface and interfacial tension.

Recently, in our laboratory a systematic study has been made on the experimental determination of surface and liquid interfacial tensions and also on the prediction and correlation methods for these properties [2,3]. This research effort is also justified from the practical point of view since the recovery of the alcohol from the binary aqueous mixtures can be made using esters.

A few equations are available for correlation of surface tension data, some of them were recently proposed and are well founded on a thermodynamic basis. Recently, Li et al. [4] proposed a two-parameter model for liquid mixtures which is based on the Wilson equation for the excess Gibbs energy. The experimental data of a large number of binary systems including the aqueous systems are very well correlated with this model. Another two-parameter equation was developed by Fu et al. [5] some years ago which uses the local composition concept due to Wilson [6]. This equation was able to correlate the data of 251 binary systems with an overall percent deviation of 0.5. Both models can be applied for the prediction of the surface tension of multicomponent liquid mixtures provided that binary parameters are known. Some important thermodynamic-based equations were developed from the Butler equation [7], which has been used extensively in different forms, for example the Sonawane

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doi:10.1016/j.fluid.2003.12.003

and Kumar equation [8] and the Sprow and Prausnitz model [9]. The former is commonly used to correlate the surface tension of binary liquid mixtures when the pure components have comparable surface tension values and the later is used to predict the surface tension of binary and multicomponent liquid mixtures when suitable models for the excess Gibbs energy are used to calculate the activity coefficients of the individual components at surface and in the bulk liquid conditions. The predictive UNIFAC model is widely used in this context. Recently, we have developed a generic expression from the Butler equation to correlate the surface tension of binary mixtures [2]. This simple model proved to give a good description of the data for highly asymmetric systems with large values of the excess surface tension.

Some empirical equations have been largely used to correlate excess thermodynamic properties. The Redlich–Kister [10] and the Marsh [11] equations are good examples. The Marsh model shows a high flexibility to describe complex analytical behaviour of the excess properties since it embodies rational functions. This model is so general that it can generate a significant number of equations including the Redlich–Kister equations, if some simple assumptions are made.

For the correlation of the interfacial tension with the composition of the conjugate liquid phases, a few models can be found in the literature. Among them the method due to Fleming et al. [12–14] and the equation developed by Li and Fu [15] seem the most appropriate for this purpose. Both methods are based on thermodynamics: the former uses the scaling theory of critical phenomena and the later is based on a diffuse interface model. Concerning the prediction of the liquid interfacial tensions some methods are available in the literature [16–19], but most of them have a limited range of applicability. The testing and the improvement of correlations requires a lot of experimental data. Therefore, for practical use it is very important that the interfacial tension of multicomponent systems can be predicted from the composition of the conjugate phases and some predictable physical parameters without any adjustable parameters. Fu et al. [5] developed a method which satisfies this aim and is easy to apply: the prediction of the interfacial tensions of multicomponent mixtures can be made from the composition of the conjugate phases and from the knowledge of easily predictable structural parameters of the components.

In this paper we report experimental data for water + ethyl propionate + methanol at 303.15 K. The data for water+butyl acetate+methanol and water+n-pentyl acetate+methanol has been presented in a recent paper [2] where we have tested the prediction and correlation methods mentioned above. In this work the same is done for the ternary system under study and also for the system water + ethyl butyrate + methanol for which experimental data were already published [3]. Both systems were also used to test the prediction of interfacial tensions in ternary systems using the method proposed by Fu et al. [5].

2. Experimental

2.1. Materials

Pure water (water G Chromasolv) was supplied by Riedel de Häen. Methanol (Panreac) was supplied with a purity >99.8 mass%, while the ethyl propionate (Riedel de Häen and Acros) was supplied with a purity >99%. Table 1 lists the measured surface tensions of the pure components together with the values found in the literature. Since the agreement is very good, all the compounds were used without further purification. Mixtures were prepared by mass using a Mettler AT 200 balance with an uncertainty of $\pm 10^{-5}$ g. The uncertainty of the mole fraction is estimated to be of the order $\pm 10^{-3}$.

2.2. Measurements

Surface and interfacial tensions were measured using a PC controlled KSV Sigma 70 tension balance which employs the Du Noüy ring-detachment method. The platinum ring was thoroughly cleaned by immersion in a concentrated solution of nitric acid during several hours. Then it was rinsed with distilled water, carefully flamed in a Bunsen burner, washed again with distilled water and dried. The measurements were automatically corrected to the actual values by means of the Huh and Mason compensation for interface distortion. To apply this correction the density was calculated using the experimental data taken from a previous paper [22]. The temperature inside the surface tension measurement vessel was maintained and controlled at 303.15 ± 0.10 K using a Julabo FP50 bath.

For the liquid interfacial tension measurements, the mixture with a known global composition was kept at 303.15 K in a thermostated vessel and shaken several times during a period of at least 24 h to reach the equilibrium. The surface tension of each liquid phase was also measured separately.

The precision of the surface tension is indicated by the instruction manual of the tension balance to be of the order of ± 0.01 mN m^{-1}. Each experimental point results from a set of about 20 measurements. After the first few measurements there is a tendency to the repeatability of the measurements and a practically constant value is obtained.

Table 1
Surface tensions of the pure components at 303.15 K and atmospheric pressure

Component	σ (mN m^{-1})	
	Experimental	Literature
Water	71.40	71.40 [20]
Ethyl propionate	24.15	24.22 [21]
Methanol	21.68	21.71 [20]

3. Equations for the surface and the interfacial tensions

The composition dependence of the surface tension of mixtures can be represented in terms of the excess surface tension, σ^{E}, defined as

$$\sigma^{\mathrm{E}} = \sigma - \sum x_i \sigma_i{}^*, \tag{1}$$

where σ is the surface tension of the mixture, and σ_i the surface tension of the ith component of mole fraction x_i.

The analytical expressions of the methods used to correlate and predict the surface and interfacial tensions were already mentioned in detail in a previous paper [2].

For the surface tension correlation we used the following models: the Redlich–Kister (RK) polynomial equation [10]; a more flexible rational expression proposed by Marsh (MM) [11]; a thermodynamic-based equation, developed from the Butler equation [7], proposed by Sonawane and Kumar (BSK) [8]; the Fu et al. (FLW) equation [5], based on the modified Hildebrand–Scott equation [23] for ideal binary systems with the local composition model proposed by Wilson [6]; the Li et al. [4] model also derived from the Wilson equation (LWW) and a simple equation introduced in our previous paper [2] (SFF).

Prediction of the surface tension with the method of Sprow and Prausnitz [9] (SP) was applied to the binary and ternary systems. With the parameters obtained from regression of binary surface tension data, the prediction of this property in multicomponent systems can be performed with the FLW and LWW models.

The relevant equations for all the models for surface tension calculation, in this section, are summarised in Table 2.

In this work we use the Li and Fu (LF) model [15] to correlate the liquid interfacial tension

$$\sigma' = \sigma'_0 \left(\frac{X}{X_0}\right)^k \tag{2}$$

where

$$X = -\ln[x_1^{\alpha} + x_2^{\beta} + x_{3\mathrm{p}}] \tag{3}$$

σ' is the interfacial tension between the two immiscible liquid phases α and β in the ternary system and σ'_0 the interfacial tension of the partially miscible binary pair which corresponds to $x_3 = 0$ and $X = X_0$ in Eq. (3). x_1^{α} is the mole fraction of component 1 in the liquid phase α richer in component 2, x_2^{β} the mole fraction of component 2 in the phase richer in component 1 and $x_{3\mathrm{p}}$ the mole fraction of component 3 in the phase poor in it. Li and Fu considered the parameter k as an adjustable parameter in Eq. (2) and they used a more general form, $k = k_1 + k_2 X$.

Fu et al. [5] developed a thermodynamic-based model to predict the liquid interfacial tension of ternary systems from the mutual solubility. The equation is

$$\sigma' = K\Sigma \tag{4}$$

where

$$\Sigma = \frac{RTX}{A_{\mathrm{w0}} \exp(X)(x_1^{\alpha} q_1 + x_2^{\beta} q_2 + x_{3\mathrm{r}} q_3)} \tag{5}$$

and K is an adjustable parameter found from binary data. In Eq. (5)

$$X = -\ln[x_1^{\alpha} + x_2^{\beta} + x_{3\mathrm{r}}] \tag{6}$$

Table 2
Models for σ and σ^{E} used in this work

Author	Expression for σ (or σ^{E})	Parameters	Application
Santos et al.	$\frac{\sigma^{\mathrm{E}}}{x_i x_j} = A + B(1 - z_{ij})^C,\ z_{ij} = x_i - x_j$	A, B and C	Correlation of binary σ^{E}
Sonawane and Kumar	$\frac{\sigma^{\mathrm{E}}}{RT} = x_i x_j \left(\frac{1}{A_i^*} - \frac{1}{A_j^*}\right)(\delta_{\mathrm{p}} + \delta_{\mathrm{m}} x_j)$	δ_{p} and δ_{m}	Correlation of binary σ^{E}
Fu et al.	$\sigma = \sum_{i=1}^{N_{\mathrm{c}}} \frac{x_i \sigma_i^*}{\sum_{j=1}^{N_{\mathrm{c}}} x_j f_{ij}} - \sum_{i=1}^{N_{\mathrm{c}}} \sum_{j=1}^{N_{\mathrm{c}}} \frac{x_i x_j \lvert\sigma_i^* - \sigma_j^*\rvert}{\sum_{q=1}^{N_{\mathrm{c}}} x_q f_{iq} \sum_{r=1}^{N_{\mathrm{c}}} x_{\mathrm{r}} f_{j\mathrm{r}}}$	f_{ij}, f_{ji} for each binary	Correlation of binary and prediction of multicomponent σ (or σ^{E})
Li et al.	$\sigma^{\mathrm{E}} = -RT \sum_{i=1}^{N_{\mathrm{c}}} \left[\frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j^{N_{\mathrm{c}}} x_j \left(\frac{\partial \Lambda_{ij}}{\partial A}\right)_{T,P,x}\right]$	Λ_{ij}, $\left(\frac{\partial \Lambda_{ij}}{\partial A}\right)_{T,P,x}$	Correlation of binary and prediction of multicomponent σ (or σ^{E})
Sprow and Prausnitz	$\sigma = \sigma_i^* + \frac{RT}{A_i^*} \ln\left(\frac{\gamma_{i,\mathrm{s}} x_{i,\mathrm{s}}}{\gamma_i x_i}\right) \quad (i = 1, 2, \ldots, N_{\mathrm{c}})$		Correlation and prediction of multicomponent σ (or σ^{E})
Redlich–Kister	$\sigma^{\mathrm{E}} = x_i x_j \sum_{k=0}^{p} B_k z_{ij}^k$	B_k	Correlation of binary σ^{E}
Malanovsky–Marsh	$\sigma^{\mathrm{E}} = x_i x_j \frac{\sum_{k=0}^{p} B_k z_{ij}^k}{1 + \sum_{l=1}^{m} C_l z_{ij}^l}$	B_k and C_l	Correlation of binary σ^{E}

x_1^{α} and x_2^{β} have the same meaning has before, in Eq. (3), x_{3r} is the mole fraction of component 3 in the bulk phase richer in component 3, T the temperature, A_{w0} the van der Waals area of a standard segment ($A_{w0} = 2.5 \times 10^9\,\mathrm{cm^2\,mol^{-1}}$ [5]) and q_i ($= A_{wi}/A_{w0}$) the pure component area parameter of molecule i. When $x_3 = 0$, Eq. (5) takes the form corresponding to binary systems.

4. Results and discussion

4.1. Surface tension

The measured surface tension and the corresponding excess surface tension as a function of the composition for the ternary system water + ethyl propionate + methanol at 303.15 K and atmospheric pressure are shown in Table 3. Results for the constituent binaries ethyl propionate + methanol and water + ethyl propionate are also included, while results for the binary water + methanol were presented in a previous paper [2]. In Fig. 1 the measured σ^{E} values and the curves obtained with the SFF model are presented as a function of composition of the ester for the binary systems ethyl propionate (2) + methanol (3) and ethyl butyrate (2) + methanol (3) [3]. As can be seen from Fig. 1 the agreement between the experimental data and the results from the correlation is good.

The excess surface tension for the ternary mixtures, $\sigma_{123}^{\mathrm{E}}$, have been fitted to the equation

$$\sigma_{123}^{\mathrm{E}} = \sigma_{12}^{\mathrm{E}} + \sigma_{13}^{\mathrm{E}} + \sigma_{23}^{\mathrm{E}} + \sigma_{\mathrm{T}}^{\mathrm{E}} \tag{7}$$

where the ternary term, $\sigma_{\mathrm{T}}^{\mathrm{E}}$, is given by

$$\sigma_{\mathrm{T}}^{\mathrm{E}} = x_1 x_2 x_3 \frac{D_1 + D_2(x_1 - x_2) + D_3(x_2 - x_3)}{1 + D_4(x_1 - x_2)} \tag{8}$$

and σ_{ij}^{E} represents the excess surface tension for the binaries which is given by SFF equation,

$$\frac{\sigma_{ij}{}^{\mathrm{E}}}{x_i x_j} = A + B[1 - (x_i - x_j)]^C \tag{9}$$

For the water + ester binary, only one parameter was considered in σ_{12}^{E} since the components are practically immiscible. The coefficients A, B, C in the SFF model, D_i from Eq. (8) and the standard deviations, S, calculated using a

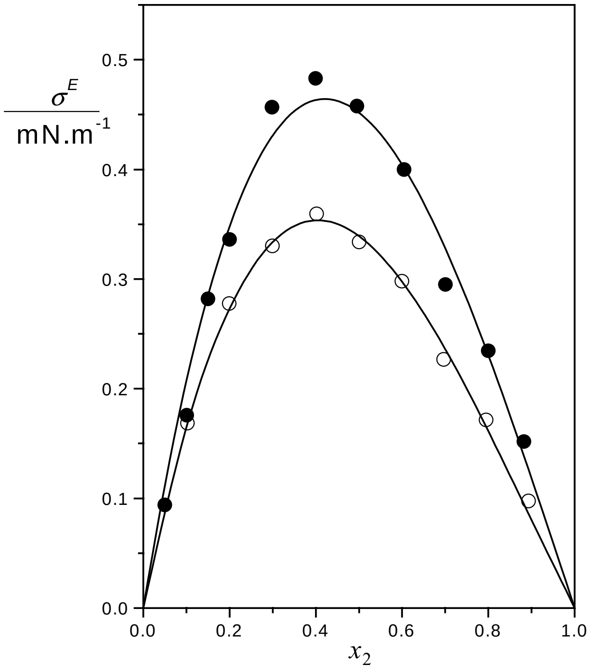

Fig. 1. Excess surface tension, σ^{E}, for the binary systems ester + methanol, at 303.15 K, as a function of the composition of the ester. The symbols correspond to the experimental data: (○) ethyl propionate; (●) ethyl butyrate [3]. Curves represent SFF model.

Table 3
Experimental surface tension, σ, and excess surface tension, σ^{E}, for the system water (1) + ethyl propionate (2) + methanol (3) at 303.15 K and atmospheric pressure

x_1	x_2	σ (mN m^{-1})	σ^{E} (mN m^{-1})
0	0.103	22.00	0.17
0	0.199	22.25	0.28
0	0.299	22.45	0.33
0	0.402	22.63	0.36
0	0.501	22.75	0.33
0	0.600	22.86	0.30
0	0.696	22.93	0.23
0	0.795	23.02	0.17
0	0.893	23.09	0.10
0.056	0.944	23.34	−2.51
0.042	0.958	23.30	−1.88
0.019	0.981	23.18	−0.91
0.100	0.050	23.06	−3.66
0.091	0.150	23.10	−3.33
0.079	0.251	23.05	−2.93
0.071	0.350	23.15	−2.57
0.061	0.450	23.20	−2.18
0.051	0.550	23.28	−1.77
0.042	0.649	23.24	−1.46
0.030	0.750	23.18	−1.08
0.021	0.848	23.24	−0.73
0.191	0.050	24.24	−7.01
0.172	0.150	24.09	−6.35
0.151	0.250	23.85	−5.71
0.129	0.350	23.66	−4.97
0.110	0.450	23.54	−4.28
0.092	0.546	23.49	−3.55
0.069	0.650	23.23	−2.86
0.050	0.750	23.23	−2.04
0.280	0.050	25.26	−10.41
0.249	0.150	24.47	−9.83
0.221	0.250	24.07	−8.96
0.192	0.349	23.71	−8.05
0.160	0.450	23.56	−6.75
0.132	0.549	23.51	−5.54
0.102	0.649	23.45	−4.23
0.379	0.052	25.87	−14.72
0.340	0.150	24.59	−14.25
0.300	0.250	24.09	−12.86
0.480	0.050	26.65	−19.01
0.450	0.100	25.46	−18.76

Table 4
Fitted coefficients to the excess surface tension, σ^E (mN m^{-1}), Eqs. (9) and (7) for the binary and ternary systems. The standard deviation of the fitting, *S*, is defined by Eq. (10)

System	D_1	D_2	D_3	D_4	S (mN m^{-1})
Water + ethyl propionate + methanol	−38.487	−172.065	−81.625	−1.298	0.12
	A	B	C	S (mN m^{-1})	
Water + ethyl propionate	−46.874	0	0	0.02	
Ethyl propionate + methanol	0.773	0.583	1.000	0.01	

Levenberg–Marquardt fit method, are given in Table 4. The standard deviation of the fitting is defined as

$$S = \left[\sum_{i=1}^{M} \frac{(\sigma^E_{\text{exp}} - \sigma^E_{\text{calc}})^2_i}{M - N}\right]^{1/2} \qquad (10)$$

where σ^E_{exp} and σ^E_{calc} are the experimental and calculated excess surface tension, M the number of data points and N the number of adjustable parameters. As can be seen from Table 4 the standard deviations are low, and are of the order of magnitude of those obtained in previous works [2,3].

The experimental determinations of the surface tension for the ternary system were made following lines of constant ratio z $(= x_1/x_3)$. In Fig. 2 we have represented experimental σ^E values and fitted lines of constant (x_1/x_3) obtained using Eqs. (7) and (8).

The models given in Section 3 and Table 2 were applied to the correlation of the surface tension of the binary systems. In Table 5 the fitted coefficients of the equations used to correlate all binary data are listed as well as their respective standard deviations and the average absolute deviation of the surface tension. Similar data for the binary system water + methanol have been presented by Santos et al. [2].

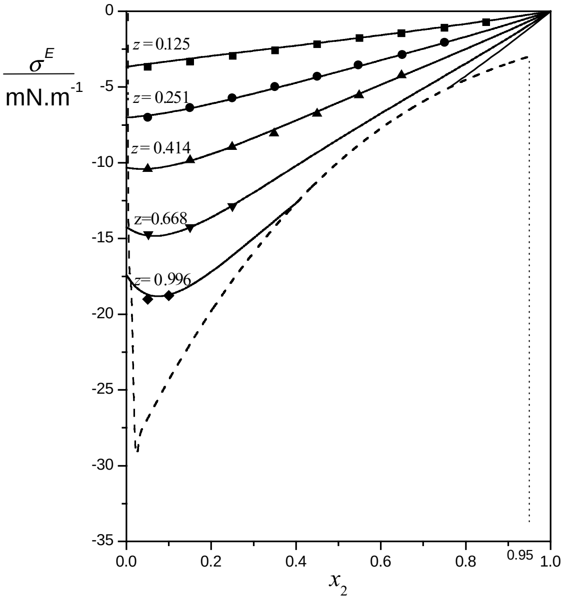

Fig. 2. Excess surface tension, σ^E, for the ternary system water (1) + ethyl propionate (2) + methanol (3), at 303.15 K and atmospheric pressure, along the curves of constant ratio $z = x_1/x_3$ as a function of the ester composition, x_2. Symbols represent the experimental points. Solid curves calculated with Eq. (7). The dashed line is the binodal curve [24].

The average absolute deviations, AAD (%) for M data points is given by

$$\text{AAD}\,(\%) = 100\left[\sum_{i=1}^{M} \frac{|(\sigma_{\text{exp}} - \sigma_{\text{calc}})/\sigma_{\text{exp}}|}{M}\right] \qquad (11)$$

As can be seen from the statistical parameters shown in Table 5 the empirical models (RK-3 and MM-2) have a similar performance as the thermodynamic models with the same number of adjustable parameters.

The surface tension of the ternary systems was predicted using the methods of Li et al. [4] and Fu et al. [5]. The binary coefficients needed for the calculations are listed in Table 5. The predictive method of Sprow and Prausnitz was applied to the binary and ternary systems. The results of the predictions with the SP and FLW models are given in Table 6. Results obtained with the SP and FLW models are very good, as can be seen from the low AAD values. The LWW model gives high values of AAD for both systems (about 32%), which is expectable taking into account the results obtained in our previous work [2]. In that work we observed some significantly different behaviour when the LWW model was applied to the water + n-butyl acetate + methanol and water + n-pentyl acetate + methanol systems. The values of the AAD obtained were 11.5 and 2.9%, respectively. This difference is due to the short liquid miscibility range of the water + n-butyl acetate system when compared with that of the water + n-pentyl acetate binary. This fact makes difficult the determination of the model parameters. As can be seen in Table 7, the water + ethyl propionate system shows a very short homogeneous liquid range and the same happens for the water + ethyl butyrate binary [3].

4.2. Interfacial tension

The experimental liquid interfacial tension and the values of the surface tension of the aqueous and organic phases of the systems water + ethyl propionate + methanol are listed in Table 7. The interfacial tension was fitted with Eq. (2) using the interfacial tension of the binary system water + ethyl propionate, σ'_0, as an input value.

The parameter k has been calculated considering that $k = k_1$ and that $k = k_1 + k_2X$. The results of the fittings

Table 5
Coefficients, standard deviation, *S*, and absolute average deviation, AAD (%) of the models used to correlate surface tension with the composition for the binary systems

System	Model	*A*	*B*	*C*	*S* (mN m^{-1})	AAD (%)
Water + ethyl butyrate	This work	−46.805	–	–	0.03	0.1
	LWW[a]	0.542	-2.153×10^{-5}	–	0.02	0.0
	LWW[b]	−185.68	−1204.21	–	0.02	0.0
	FLW[c]	0.568	1.474	–	0.01	0.0
Ethyl butyrate + methanol	This work	1.195	0.613	1.000	0.02	0.1
	BSK[d]	−0.157	−0.161	–	0.02	0.1
	LWW[a]	1.835	-2.205×10^{-6}	–	0.02	0.1
	LWW[b]	184.02	−36.43	–	0.02	0.1
	FLW[c]	0.6466	1.3515	–	0.02	0.1
	RK-3[e]	1.8433	−0.6300	−0.2197	0.02	0.1
	MM-2[f]	1.7844	0.2946	–	0.02	0.1
Water + ethyl propionate	This work	−46.874	–	–	0.02	0.1
	LWW[a]	0.784	-6.665×10^{-5}	–	0.02	0.1
	LWW[b]	−73.77	−2577.16	–	0.02	0.1
	FLW[c]	0.849	1.075	–	0.02	0.1
Ethyl propionate + methanol	This work	0.7732	0.5834	1.0000	0.01	0.0
	BSK[d]	−0.1129	−0.1704	–	0.01	0.0
	LWW[a]	2.3326	-1.5343×10^{-6}	–	0.01	0.0
	LWW[b]	256.76	−19.94	–	0.01	0.0
	FLW[c]	0.5158	1.7709	–	0.01	0.0
	RK-3[e]	1.3418	−0.5830	0.1039	0.01	0.0
	MM-2[f]	1.3256	0.3980	–	0.01	0.0

[a] The coefficients *A* and *B* correspond to Λ_{21} and $(\partial\Lambda_{21}/\partial A)_{T,P,x}$, respectively.
[b] The values given corresponds to $U_{12} - U_{11}/R$ (in K) and $10^5 \times [\partial(U_{12} - U_{11})/\partial A]_{P,T,x}/R$ (in K mol^{-1} m^{-2}), respectively.
[c] The coefficients correspond to f_{12} and f_{21}, respectively.
[d] The coefficients *A* and *B* correspond to δ_p and δ_m, respectively.
[e] The coefficients *A*, *B* and *C* correspond to B_0, B_1 and B_2.
[f] The coefficients *A* and *B* correspond to B_0 and C_0, respectively.

are listed in Table 8. In Fig. 3 we represent the liquid interfacial tension, σ' as a function of *X* for the water + ethyl propionate + methanol and water + ethyl butyrate + methanol systems. From this figure we see that the liquid interfacial tension of the system water + ethyl butyrate + methanol is represented adequately by any of the models with very small values of standard deviations, while for the water + ethyl propionate + methanol system better results were obtained taking into account the dependence of *k* on the composition.

For the calculations with Eq. (4) we have used the binary liquid interfacial tension data, σ'_0 reported by Fu et al. [5] for which σ'_0 is less than 20 mN m^{-1} since higher values show a different dependence on the parameter Σ. It is important to note that our ternary data have values in the range 2–16 mN m^{-1}.

In our previous paper [2] we present the following relation between σ'_0 and Σ:

$$\sigma'_0 = (0.717 \pm 0.034)\,\Sigma \tag{12}$$

Table 6
Average absolute deviation, AAD (%) obtained for the models used to predict surface tension

System	Model	AAD (%)
Ethyl butyrate + methanol	SP	0.6
Ethyl propionate + methanol	SP	0.5
Water + ethyl butyrate + methanol	SP, FLW	2.8, 3.1
Water + ethyl propionate + methanol	SP, FLW	2.2, 2.8

Table 7
Experimental liquid interfacial tension, σ', for the ternary system water (1) + ethyl propionate (2) + methanol (3) at 303.15 K and atmospheric pressure. The surface tension, σ, and the compositions of the liquid phases at equilibrium are also listed

Overall composition		Water layer			Organic layer			σ' (mN m^{-1})
x_1	x_3	x_1	x_3	σ (mN m^{-1})	x_1	x_3	σ (mN m^{-1})	
0.850	0	0.996	0	–	0.054	0.000	–	12.2
0.811	0.046	0.948	0.048	56.33	0.087	0.035	23.44	9.2
0.772	0.092	0.899	0.096	51.26	0.094	0.067	23.46	7.3
0.733	0.137	0.852	0.140	46.22	0.112	0.121	23.64	5.2
0.693	0.185	0.800	0.187	41.81	0.136	0.170	23.77	3.6

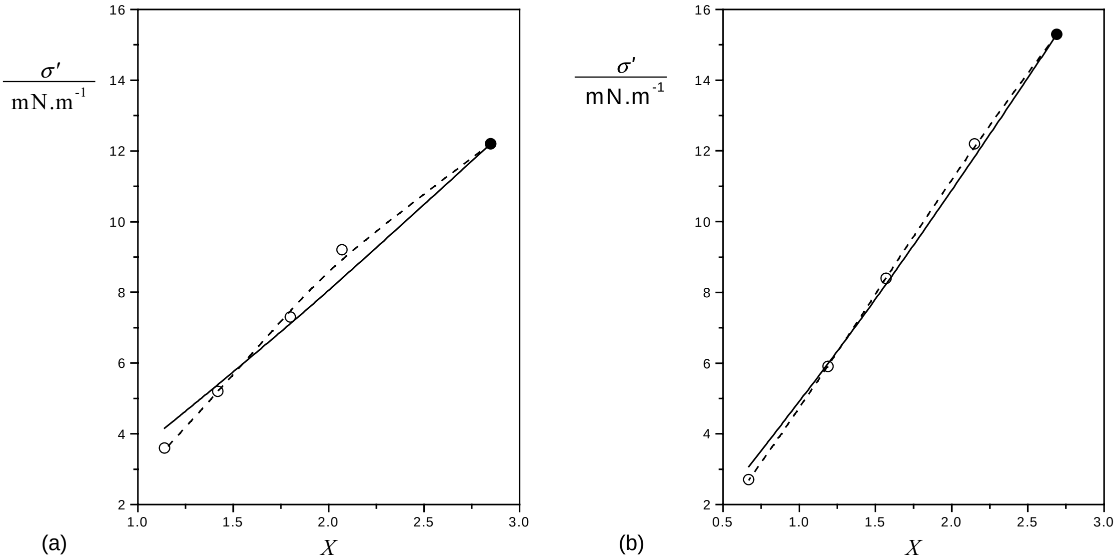

Fig. 3. Liquid interfacial tension, σ', as a function of X for the ternary systems: (a) water + ethyl propionate + methanol; (b) and water + ethyl butyrate + methanol. The symbols (●) and (○) represent the experimental data of the binary and ternary systems, respectively, and the lines the curves fitted with the Li and Fu model (Eq. (2)): (—) k = constant and (- - -) $k = k_1 + k_2X$.

Table 8
Coefficients of Eq. (2) fitted to the liquid interfacial tension, σ' (mN m^{-1}), for the ternary system water (1) + ethyl propionate (2) + methanol (3)

X_0	σ'_0 (mN m^{-1})	k_1	k_2	S (mN m^{-1})
2.847	12.2	1.174	0	0.51
		1.851	−0.440	0.15

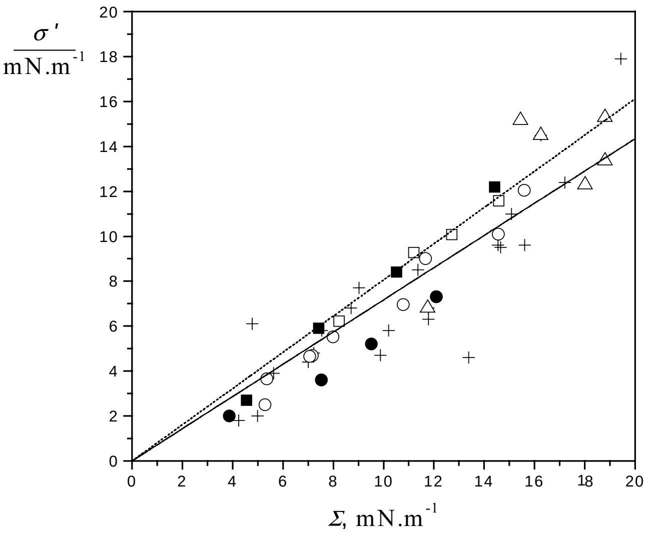

Fig. 4. Liquid interfacial tension, σ', as a function of Σ: (+) data of binary systems given by Fu et al. [5] including some binary systems water + ester (Δ); (—) Eq. (4) with $K = 0.717$; (- - -) Eq. (4) with $K = 0.806$. Ternary data: (○) water + n-butyl acetate + methanol [2]; (□) water + n-pentyl acetate + methanol [2], and ternary data represent in this paper (●) water + ethyl propionate + methanol and (■) water + ethyl butyrate + methanol.

and using only the values of σ'_0 for the binary systems of the type water + ester the result obtained was

$$\sigma'_0 = (0.806 \pm 0.081)\,\Sigma \tag{13}$$

The liquid interfacial tension data of the binary and ternary systems presented in this work and in a previous paper [2] as a function of the parameter Σ are represented in Fig. 4. The predictions with Eqs. (12) and (13) are plotted in the same figure. Both correlations can describe in a satisfactory way the different sets of experimental ternary data. As can be seen Eq. (13) can predict the ternary liquid interfacial tension for the system water + ethyl butyrate + methanol very well, while for the water + ethyl propionate + methanol system the experimental values are lower than the predicted ones. Indeed, Fig. 4 stresses that Eq. (13) can accurately predict the data of three ternary systems. It is important to stress that the prediction of the ternary liquid interfacial tension was made using only binary data.

5. Conclusions

The systems water + ethyl propionate + methanol measured at 303.15 K and atmospheric pressure and water + ethyl butyrate + methanol have similar behaviour, showing negative excess surface tensions in the whole composition range—the binaries (ester + methanol) have low positive excess surface tensions values. The surface tension in the homogeneous region of both ternary systems lies in the range 21–27 mN m^{-1}.

The performance of the surface tension correlations for the binaries, either thermodynamic or empirical, is similar;

the mean of the standard deviations obtained are of the same magnitude of the instrument precision.

The ternary surface tension data were well correlated using pair additivity and a rational function as the ternary term.

The prediction of the surface tension of the ternary systems with the models of Sprow and Prausnitz and of Fu et al. gives satisfactory results in spite of the large immiscibility gap found in both systems (the AAD is less than 3%).

The liquid interfacial tension data were well correlated with the Li and Fu model (the standard deviation of the fitting is less than 1 mN m^{-1}). The prediction of this property with the method of Fu et al. gives good results for the system water + ethyl butyrate + methanol.

List of symbols

A	adjustable parameter of SFF model
AAD	average absolute deviation
A_i^*	molar surface area of pure component i
B	adjustable parameter of SFF model
B_k	adjustable parameter of RK and MM models
C	adjustable parameter of SFF model
C_l	adjustable parameter of MM model
f_{ij}	adjustable parameter of FLW model
M	number of experimental points
N	number of adjustable parameters
N_c	number of components
q_i	area parameter of molecule i
R	universal gas constant
S	standard deviation
T	temperature
U	interaction energy
x_i	liquid mole fraction of the ith component
X	defined by Eqs. (3) and (6)

Greek letters

γ	activity coefficient
δ_p, δ_m	adjustable parameters of BSK model
Λ_{ij}	Wilson binary parameter
σ	surface tension
σ'	liquid interfacial tension
Σ	defined by Eq. (5)

Superscripts

E	excess property
$*$	pure component

Subscripts

calc	calculated
exp	experimental
i, j	components
T	ternary

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