Concentration fluctuations and surface adsorption in non-ideal binary mixtures. A light-scattering and surface tension study

Ramón G. Rubio,* Ana Díez-Pascual, Baudilio Coto,† A. Crespo-Colín and A. Compostizo

Departamento Química Física I, Facultad de Química, Universidad Complutense, 28040, Madrid, Spain. E-mail: rgrubio@quim.ucm.es

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The concentration fluctuations and the surface tension of binary mixtures of non-electrolytes have been measured at 298.15 K, using light scattering and plate tensiometry. The results show that all the mixtures are highly non-ideal, and present an important tendency to homocoordination. All the mixtures studied present negative values of the excess surface tension. The combination of the results of both techniques allows one to calculate the excess surface adsorption \( \Gamma_{12} \) of one of the components.

The experimental results have been compared with the predictions of several solution models that have been recently used for predicting \( \Gamma_{12} \) from surface tension data. It has been found that, in spite of being used in many recent papers, the UNIFAC model leads to rather poor predictions. The experimental results have also been compared with the predictions of a lattice-fluid model, the agreement is not satisfactory.

**Introduction**

The composition dependence of the surface tension \( \Gamma \) of liquid mixtures is often required for rational chemical process design, and it is of great relevance for biological processes.1 When the components have rather different values of \( \Gamma \) there usually is a tendency to preferential adsorption of the component with the lowest surface tension at the air/liquid interface. An extreme case of these behaviour is found in aqueous solutions, where many organic molecules containing polar and nonpolar groups segregate to the surface of water, often forming compact hydrocarbon films that impede gas transport through the interface.2–4 The composition and structure of the surface films may differ significantly depending on the type of molecular interactions that exist between the molecules of the mixture.4–6

For a fluid mixture at constant temperature and pressure, the relationship between \( \Gamma \) and the surface composition \( \Gamma \) is given by

\[
d\Gamma = -RT \sum_i \Gamma_i \, d \ln a_i
\]  

where the sum is done over all the components of the mixture, and \( a_i \) is the activity of component \( i \). For binary mixtures, when the dividing surface is defined so that the surface excess of the solvent (component 1) is zero, eqn. (1) is reduced to

\[
d\Gamma = -RT \Gamma_{12} \, d \ln a_2
\]  

\( \Gamma_{12} \) being the relative surface adsorption of component 2.1 Eqn. (2) can be easily rearranged to lead to

\[
\Gamma_{12} = \frac{\partial \Gamma_1 / \partial x_2}{\partial \mu_2 / \partial x_2} T_P
\]

where \( \partial \mu_2 / \partial x_2 \) is the osmotic compressibility, and \( \mu_2 \) is the chemical potential of component 2. Therefore, \( \Gamma_{12} \) can be calculated if the composition dependence of \( \gamma \) and of \( \mu_2 \) is known.

In the case of aqueous surfactant concentration, and for concentrations below the critical micelle concentration (c.m.c.), it has been rather frequent to assume that the solutions show ideal behaviour, i.e. \( \partial \mu_2 / \partial x_2 = RT/x_2 \). Strey et al.7 have shown that such an approach may be inadequate even for dilute water + alcohol mixtures. In refs. 4, 5 and 7, the activity of the solute \( a_2 \) has been estimated from vapour pressure data. In order to do so, it is necessary to carry out a double derivative of the Gibbs energy with respect to \( x_2 \), which might introduce a noticeable uncertainty in \( \partial \mu_2 / \partial x_2 \) unless the vapour pressure data are highly precise. Moreover, in a recent paper using small angle neutron scattering, Almasy et al.8 have shown that small inaccuracies in the \( G^b \) results may lead to large errors in the osmotic compressibility. More recently,9,10 the activity coefficients, needed to calculate \( \mu_2 \) at each \( x_2 \), have been evaluated using approximate liquid solution models, such as UNIFAC, NRTL, etc.14 In spite that such models are convenient because the parameters needed for calculating \( \mu_2 \) are available for many mixtures, their ability to predict the Gibbs energy of the mixtures is, in many cases, poor.12 As a consequence, the values of \( \partial \mu_2 / \partial x_2 \) obtained may be in great error, thus leading to poor \( \Gamma_{12} \) predictions.

It is well known that the light scattering technique is well suited for obtaining the osmotic compressibility of binary mixtures.13 Therefore, the combination of light scattering and surface tension data for binary mixtures is adequate for obtaining reasonably precise surface adsorption data in mixtures. These can be used to test the reliability of some of the abovementioned liquid mixture models for calculating \( \Gamma_{12} \) from surface tension data. Furthermore, as we have shown before,14,15 the osmotic compressibility is directly related to the nonrandomness of the distribution of the mixture components of the mixture. Again, this local composition problem has been recently discussed in terms of approximate mixture models for some binary mixtures.15,16 Light scattering experiments may also shed light on this problem.

The purpose of this paper is to report precise surface adsorption data for a set of eight binary organic mixtures which are highly non-ideal, and which show a broad range of differences between the surface tension of the pure components. The results will be compared with the predictions of some approximate liquid mixture models.
**Experimental**

The light scattering experiments were performed at 298.15 K using a Malvern 4700 instrument and a Coherent Ar+ laser working at 632.8 nm. The refractive index was measured with a Carl Zeiss refractometer at six wavelengths between 404.7 and 656.3 nm. The values at 623.8 nm were calculated from the Cauchy equation. The densities were measured using an Anton-Paar DMA 620 vibrating-tube densimeter. Rayleigh ratios were computed from the intensity of the scattered light at 90° using benzene as the reference. The depolarisation ratios were calculated from the ratio of the intensities of the light scattered at 35° and at 145°. The method for obtaining the osmotic compressibility from the raw data has been described in detail in a previous work, and it is summarized in the Appendix. The precision of the osmotic compressibility is estimated to be better than 6%. The surface tension experiments were carried out using a Krüss K-10 ST tensiometer using the plate method. The measurement cell was modified in order to minimize evaporation of the sample. Each experimental data is the average of five readings taken in 10 min intervals. The reproducibility of the results was better than ±0.03 mN m⁻¹. The mixtures were prepared by weight in an external bath, and was controlled within ±0.005 K.

Cyanomethane (AcN), Cl₄C, n-heptane (n-C₇), propanone (Ac), and n-dodecane (n-C₁₂) were purchased to Carlo Erba (Italy), and were of RPE quality. Nitrobenzene (NBz), 1-propanol (POH), 1-butanol (BuOH), pentylenethanole (PAc), and 1-chloronaphthalene (CIN) were from Fluka, of the highest purity available. 1,2-Dibromoethane (DBE) was purchased to Aldrich and has a stated purity higher than 99 mol%. The purity available. 1,2-Dibromoethane (DBE) was purchased to Aldrich and has a stated purity higher than 99 mol%. The values of AcN, Cl₄C, n-heptane (n-C₇), propanone (Ac), and n-dodecane (n-C₁₂) were purchased to Carlo Erba (Italy), and were of RPE quality. Nitrobenzene (NBz), 1-propanol (POH), 1-butanol (BuOH), pentylenethanole (PAc), and 1-chloronaphthalene (CIN) were from Fluka, of the highest purity available. 1,2-Dibromoethane (DBE) was purchased to Aldrich and has a stated purity higher than 99 mol%. The densities and surface tensions of the pure components at 298.15 K agreed well with values published in the literature.

**Results**

Concentration fluctuations and non-randomness in binary mixtures can be described in terms of the concentration-concentration correlation function $S_{cc}$ (i.e. the structure factor at zero wavevector), which is directly related to the osmotic compressibility:

$$S_{cc} = 1 \frac{1}{x_1x_2} \left| \frac{\partial \mu_j}{\partial x_j} \right| \frac{RT}{\Omega \ln x_2}$$

In ideal mixtures, with a random distribution of molecules, $S_{cc} = x_2(1 - x_2)$, i.e. $S_{cc}$ is a symmetric parabola when plotted against $x_2$, with a maximum at $S_{cc} = 0.25$ at $x_2 = 0.5$. Fig. 1 shows the $S_{cc}$ curves obtained for the present systems from the light scattering data. In all the systems studied the maximum of the $S_{cc}$ curves is much higher than 0.25, which indicates that the molecules have a clear tendency to homo-coordination, i.e. the local value of $x_2$ in the immediate vicinity of one molecule of type 2 is higher than the overall value of $x_2$ in the mixture. This behaviour of $S_{cc}$ is characteristic of highly non-ideal mixtures, for which $S_{cc}$ tends to infinity at the liquid–liquid critical point. In terms of surface adsorption, the divergence of $S_{cc}$ leads to that of $I_{12}$ (see eqns. (4) and (5)) at phase separation. The second point that is clearly visible in Fig. 1 is that the $S_{cc}$ curves are non-symmetric with respect to $x_2$. We have fitted the experimental data to the following Padé approximant

$$S_{cc} = x_2(1 - x_2) \sum_{i} A_i(1 - 2x_2)^{i-1} \frac{1}{1 + \sum_j B_j(1 - 2x_2)^j}$$

**Table 1** contains the values of $A_i$ and $B_j$ constants that give the best fit of the data.

A more familiar way of pointing out the non-ideality of mixtures is to show the excess Gibbs energy $G^E$. We have calculated them by integration of the osmotic susceptibility results (see the Appendix), and the results are shown in Fig. 2. The systems studied have maximum values of $G^E$ within a broad range (600–1300 J mol⁻¹), thus being adequate for testing the ability of theoretical models to predict the osmotic compressibility of mixtures. Table 2 gives the parameters of the Padé approximant, eqn. (6), corresponding to the best fits of the $G^E$ vs. $x_2$ curves. It can be observed, the $G^E$ curves are not as skewed as the $S_{cc}$ ones, thus no $B_j$ parameters are necessary.

**Fig. 3(a)** shows the surface tension $\gamma$ of the mixtures. The excess surface tension $\gamma^E$ gives a rough idea of the non-ideality of the surface behaviour. There is no clear consensus about the definition of $\gamma^E$ in terms of $\gamma$ and the surface tension of the pure components. In the present work $\gamma^E$ will be used for obtaining a correlation equation from which $\partial \gamma / \partial x_j$ can be calculated. Therefore, the following simple equation will be used as an operational definition of $\gamma^E$

$$\gamma^E = \gamma - (1 - x_2)\gamma_1 - x_2\gamma_2$$

and the results are shown in Fig. 3(b). It can be observed that $\gamma^E$ is negative for all the present systems, which is the most frequent situation for highly non-ideal mixtures. Table 3 gives the parameters of the Padé approximant, eqn. (6), that best fit the $\gamma^E$ vs. $x_2$ curves. The residuals of the fits, i.e. the differences between experimental and fitted results are randomly distributed when potted vs. $x_2$, which is important since the fits are used in order to obtain the values of $\partial \gamma / \partial x_j$, which are needed for calculating $I_{12}$.

The relative adsorption of component 2, $\Gamma_{12}$ has been calculated from the $S_{cc}$ and the $I$ vs. $x_2$ curves according to eqn. (3), and the results are shown in Fig. 4. A comparison between Figs. 1, 3 and 4 points out that the systems with the largest $\partial \gamma / \partial x_j$ also have the highest values of $I_{12}$. No clear correlation between the values of $S_{cc}$ and of those of $I_{12}$ has been found.

In the next section the $I_{12}$ results will be compared with those calculated from the osmotic compressibility calculated from selected theoretical models of mixtures.
Table 1 Coefficients of the best fit of the Sec experimental data to eqn. (6); $\chi^2$ is the variance of the fit \(^a\)

<table>
<thead>
<tr>
<th>System</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$B_3$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2DBE + nC7</td>
<td>3.4129</td>
<td>–0.2722</td>
<td>0.1899</td>
<td>δ–0.3455</td>
<td>–1.7792</td>
<td>3.0455</td>
<td>–</td>
<td>1.1</td>
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<tr>
<td>1CN + nC16</td>
<td>1.6386</td>
<td>0.5972</td>
<td>–0.4254</td>
<td>–0.769</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.9</td>
</tr>
<tr>
<td>AcN + POH</td>
<td>2.6270</td>
<td>–2.2834</td>
<td>2.7361</td>
<td>1.0456</td>
<td>–2.8110</td>
<td>5.6807</td>
<td>–</td>
<td>0.8</td>
</tr>
<tr>
<td>AcN + PenAc</td>
<td>1.6985</td>
<td>0.0598</td>
<td>–0.0928</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.2</td>
</tr>
<tr>
<td>AcN + ClC</td>
<td>6.8300</td>
<td>1.6457</td>
<td>0.3381</td>
<td>–2.3263</td>
<td>2.7618</td>
<td>4.3151</td>
<td>–</td>
<td>1.1</td>
</tr>
<tr>
<td>AcN + BuOH</td>
<td>3.2958</td>
<td>0.3340</td>
<td>–0.6602</td>
<td>–0.4931</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.9</td>
</tr>
<tr>
<td>Ac+ nC12</td>
<td>5.6605</td>
<td>0.0873</td>
<td>0.2183</td>
<td>–2.6687</td>
<td>2.4688</td>
<td>0.8</td>
<td>–</td>
<td>–</td>
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<tr>
<td>NBz + nC7</td>
<td>62.600</td>
<td>–1.5138</td>
<td>–0.4497</td>
<td>1.0964</td>
<td>–0.0490</td>
<td>17.564</td>
<td>–11.460</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^a\) The parameters have been obtained minimizing the sum of the weighted squared differences between the experimental and the calculated values.

Discussion

Although several molecular models have been proposed to predict G\(_{12}\) and reasonable results have been obtained for pure components, the estimation of G\(_{12}\) for real complex mixtures using rigorous Statistical Mechanical theories is not satisfactory yet. Therefore, in this section, we will focus on the predictions of (\(\partial G_{12}/\partial x_2\)). To this end it is possible to use any theory suitable for the prediction of the bulk thermodynamic properties of the mixtures. This is due to the fact that equilibrium conditions impose that the chemical potential of any component at the interface has to be the same that in any of the coexistent bulk phases. In this work we have test two different mixture models.

One of the most popular mixture models over the last thirty years has been the UNIFAC.\(^{23,24}\) As already mentioned in the introduction, the UNIFAC group-contribution model\(^{25}\) has been used in some recent papers in order to estimate the osmotic compressibility of mixtures, including aqueous solutions. In spite that this model is based on a rigid lattice theory, it is a functional group. More sophisticated liquid models that take into account the free volume concept have been used for the predictions of the lattice-fluid model for S\(_{cc}\) with the composition dependence of the surface tension allows one to obtain accurate values of the relative surface adsorption G\(_{12}\) of one of the components of the mixture. The results have been compared with the predictions of an approximate solution model (UNIFAC) that has been used frequently in the last years to predict G\(_{12}\). It has been found that this model leads to rather poor predictions for the binary mixtures.

The comparison of the experimental values of S\(_{cc}\) with the predictions of the UNIFAC model point out noticeable discrepancies, e.g., while the experimental maxima of the S\(_{cc}\) curves for the AcN + ClC and for Ac + nC\(_{12}\) systems are of the order of two, the predicted values are almost four. Also, the mole fraction at which the maxima are predicted are not in agreement with the experimental values. The disagreement between experiment and theory will be directly reflected on the predicted values of G\(_{12}\) because the experimental values of (\(\partial G_{12}/\partial x_2\)) have been used in the calculations. Fig. 5 shows the ratio of the relative adsorption calculated from the experimental S\(_{cc}\) and from the predictions of UNIFAC. It becomes obvious that the error of the predictions may be rather large depending on the system and on the composition.

The G\(_{cc}\) curves have been used to obtain the binary interaction parameters of the Sanchez–Lacombe model for the different systems.\(^{26}\) Although the model was able to give the right order of magnitude of G\(_{cc}\), it predicts curves which are more skewed than the experimental ones. This mismatch of the shape has important consequences in the prediction of the osmotic compressibility, which is overestimated (the values of S\(_{cc}\) are smaller than the experimental ones). As a consequence, the model leads to values of G\(_{12}\) lower than the experimental ones. It is somewhat surprising that, overall, the predictions of the lattice-fluid model for G\(_{12}\) are worse than those of the UNIFAC model.

Conclusions

Light scattering is a precise technique for measuring the osmotic compressibility of binary mixtures, from which the concentration fluctuations can be calculated as the concentration-concentration correlation function S\(_{cc}\). The combination of S\(_{cc}\) with the composition dependence of the surface tension allows one to obtain accurate values of the relative surface adsorption G\(_{12}\) of one of the components of the mixture. The results have been compared with the predictions of an approximate solution model (UNIFAC) that has been used frequently in the last years to predict G\(_{12}\). It has been found that this model leads to rather poor predictions for the binary mixtures.

Fig. 2 Excess Gibbs energies G\(_{cc}\) for the different binary mixtures obtained from the integration of the osmotic compressibility data. The curves with symbols shown are the fits to eqn. (6) with the coefficients of Table 2. The abbreviations of the systems are the same than in Fig. 1.
studied in this work. The predictions of a lattice-fluid model for \( \frac{\partial m}{\partial \ln x} \) overestimate the experimental ones, thus leading to important disagreements with the experimental values of \( G_{12} \).

Appendix

The osmotic compressibility has been calculated from the light scattering data according to the following procedure. The Rayleigh ratio, \( R \), has been computed from the intensity of the light scattered by the sample at 90\(^\circ\), \( I \), and the intensity of the light scattered by a sample of benzene, \( I_B \), for which the Rayleigh ratio, \( R_B \), is known: 
\[
R = R_B \frac{I}{I_B}
\]

The isotropic contribution to the Rayleigh ratio, \( R_i \), has been calculated from \( R \) and the depolarisation factor, \( \rho \), obtained as the ratio of the intensities of the light scattered at 35\(^\circ\) and 145\(^\circ\). According to Wakker et al.\(^{27} \), \( R_i \) can be written as
\[
R_i = R_d + R_c + R^*\]

where \( R_d \) arises from concentration fluctuations, \( R_c \) from density fluctuations, and \( R^* \) is the coupling term between both types of fluctuations. These contributions can be written as:
\[
R_d = \frac{2}{2\varepsilon} k_B T \left\{ \rho \left( \frac{\partial \rho}{\partial p} \right)_T \right\}^2
\]
\[
R_c = \frac{2}{2\varepsilon} k_B T V x_1 \left( \frac{\partial \rho}{\partial x} \right)_T \left( \frac{\partial \rho}{\partial \varepsilon} \right)_T
\]
\[
R^* = \frac{2}{2\varepsilon} k_B T \rho \left( \frac{\partial \rho}{\partial p} \right)_T x_1 x_2 \left( \frac{\partial \rho}{\partial \varepsilon} \right)_T
\]

with \( \varepsilon \approx n^2 \); and
\[
\rho \left( \frac{\partial \rho}{\partial p} \right)_T = \frac{2m(n^2 - 1)(n + 0.4)}{n^2 + 1 + 0.8n}
\]

Table 3  Coefficients that give the best fit of the excess surface tension data \( \gamma^* \) to eqn. (6); \( \chi^2 \) is the variance of the fit calculated as in Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>(-A_1)</th>
<th>(-A_2)</th>
<th>(-A_3)</th>
<th>(-A_4)</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12DBE + nC7</td>
<td>16.7</td>
<td>-9.4</td>
<td>18.2</td>
<td>-18.8</td>
<td>1.3</td>
</tr>
<tr>
<td>CIN + nC16</td>
<td>11.9</td>
<td>2.96</td>
<td>10.6</td>
<td>14.4</td>
<td>1.2</td>
</tr>
<tr>
<td>AcN + POH</td>
<td>1.56</td>
<td>0.59</td>
<td>1.175</td>
<td>1.01</td>
<td>0.9</td>
</tr>
<tr>
<td>AcN + Pac</td>
<td>1.57</td>
<td>0.146</td>
<td>0.912</td>
<td>0.961</td>
<td>0.9</td>
</tr>
<tr>
<td>AcN + ClC</td>
<td>2.29</td>
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<td>0.90</td>
<td>0.21</td>
<td>1.1</td>
</tr>
<tr>
<td>AcN + BuOH</td>
<td>3.54</td>
<td>0.576</td>
<td>0.218</td>
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<td>1.1</td>
</tr>
<tr>
<td>Ac + nC12</td>
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<td>-0.0031</td>
<td>0.0111</td>
<td>-0.0014</td>
<td>1.2</td>
</tr>
<tr>
<td>NBz + nC7</td>
<td>26.7</td>
<td>-23.3</td>
<td>13.32</td>
<td>-4.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Fig. 4  Relative surface adsorption \( \Gamma_{12} \) for the different mixtures studied in this work. The abbreviations of the systems are the same than in Fig. 1.

Fig. 5  Ratio of the experimental values of the relative surface adsorption to the value calculated with UNIFAC. The abbreviations of the systems are the same than in Fig. 1.
Here $\lambda_0$ is the wavelength of incident light in vacuum, $\kappa_T$ the isothermal compressibility, $\rho$ the density, $V$ the molar volume of the mixture, $\varepsilon$ the high-frequency permittivity and $n$ the refractive index. In this work, the isothermal compressibility of the mixtures has been calculated as $\kappa_T = \phi_1 \kappa_{T,1} + \phi_2 \kappa_{T,2}$, where $\phi_1$ is the volume fraction of component 1, and the $\kappa_{T,i}$ are the isothermal compressibilities of the pure components, which were taken from the literature.

$S_{cc}$ can be calculated from the experimental data through

$$S_{cc} = x_1 x_2 \frac{R}{R_0}$$

and is related to $(\partial \mu_2 / \partial x_2)_T$ through eqn. (4). The Gibbs-Duhem equation allows one to calculate $(\partial \mu_i / \partial x_i)_T$ from $(\partial \mu_2 / \partial x_2)_T$. Subsequent integration leads to values for the activity coefficients

$$\ln \gamma_i = \int_0^{x_i} \left( \frac{1 - R_d}{R_c} \right) x_i \, dx_i$$

from which the excess Gibbs energy can be calculated. In the above equations $R_d$ is the value of $R_c$ for an ideal mixture, for which $(\partial \mu_2 / \partial x_2)_{T,p} = \frac{RT}{x_2}$.

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**References**