Dispersions of zirconia nanoparticles close to the phase boundary of surfactant-free ternary mixtures

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References
S1. UNIFAC model equations and UNIFAC-LLE parameters for the ternary mixture of water, 1,2-dichlorobenzene and ethanol

The mixtures leading to phase separations can give rise to two liquid phases, $\alpha$ and $\beta$, characterised by a $x^\alpha_i$ and $x^\beta_i$ composition, respectively, expressed via the molar fraction of the $i$-th component. These compositions represent the unknowns of the problem, thus leading to a total of $2NC$ unknowns, where $NC$ is the number of species in the system. In this case 3 species are present, namely DCB, water, and ethanol, thus the total number of unknowns is 6. Once equilibrium is reached at a given temperature, $T$, pressure, $P$, and composition $\mathbf{x}$ (expressed in vector terms), the same species in the two phases, $\alpha$ and $\beta$, must have the same fugacity, namely:

$$f_i^\alpha(T,P,\mathbf{x}^\alpha) = f_i^\beta(T,P,\mathbf{x}^\beta) \tag{S1}$$

The fugacity of the $i$-th component in a liquid mixture (phase $k$) can be expressed as:

$$f_i^k(T,P,\mathbf{x}^k) = \gamma_i^k(T,P,\mathbf{x}^k) \cdot f_i^k(T,P) \cdot x_i^k \tag{S2}$$

where $\gamma_i^k$ is the activity coefficient of the species in the mixture, and $f_i^k$ the fugacity of the pure species in liquid phase. Therefore, at equilibrium, it must be:

$$\gamma_i^\alpha(T,P,\mathbf{x}^\alpha) \cdot x_i^\alpha = \gamma_i^\beta(T,P,\mathbf{x}^\beta) \cdot x_i^\beta \tag{S3}$$

This will enforce a number of equations equal to 3. As a consequence of mass conservation, the stoichiometric relationships must hold true:
\[ \sum_{i} x_i^p = 1 \#(S4) \]

\[ \sum_{i} x_i^l = 1 \#(S5) \]

enforcing 2 additional equations. The total number of unknowns is 6, while 5 equations are available, thus there is still 1 degree of freedom for a ternary mixture. It is enough to set (arbitrarily) one of the molar fractions in one of the phases. By parametrically varying this degree of freedom one can obtain all the possible mixtures giving rise to phase separation in a ternary mixture.

To solve the set of Equations (S3), (S4), and (S5), equipped with the proper fixed molar fraction, a model is required to express the functional dependency of the activity coefficients on temperature, pressure, and composition of the phase considered. The UNIFAC-LLE model aims at doing so. Each activity coefficient expression is split into a combinatorial and a residual part:

\[ \ln \gamma_k^f(T, P, x^K) = \ln \gamma_f^c(x^K) + \ln \gamma_f^R(T, x^K) \#(S6) \]

The combinatorial part is the part of the activity coefficient described by the pure-species characteristics based on their chemical structure; the value is computed knowing which groups form each molecule in the mixture and the corresponding group-contributions are
combined by means of the molar fraction of each species. The residual part aims at
describing the interaction between the various groups by means of binary-interaction
parameters (no higher order parameters are necessary);\(^2\) furthermore, the residual part
describes the dependency of the activity coefficient on temperature. The pressure
dependency is not considered by this model. The equations describing the equilibrium by
means of the UNIFAC model are highly nonlinear, thus a numerical solution is needed.

In the following the explicit dependency of the variables on temperature, pressure, and
composition will be dropped for clarity purposes. The combinatorial part is expressed as:

\[
\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i^{NC}}{x_i} \sum_j x_i j \#(S7)
\]

where the parameters \(\phi_i\) and \(\theta_i\) are characteristics of the pure species considered and are
indications of area and volume fractions, respectively. \(l_i\) is an ensemble of pure-species
variables \(z\) is a characteristic constant equal to 10 for the UNIFAC model.

The aforementioned parameters can be expressed as:

\[
\phi_i = \frac{r_i x_i}{\sum_j^{NC} r_j x_j} \#(S8)
\]

\[
\theta_i = \frac{q_i x_i}{\sum_j^{NC} q_j x_j} \#(S9)
\]
\[ l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)\#(S10) \]

where \( r_i \) and \( q_i \) are representative of the molecule van der Waals volumes and surface areas, expressed by means of group contributions as:

\[ r_i = \sum_{k}^{NG_i} v_{ki}R_k\#(S11) \]

\[ q_i = \sum_{k}^{NG_i} v_{ki}Q_k\#(S12) \]

where \( NG_i \) is the number of different groups in molecule \( i \), \( v_{ki} \) the number of groups of type \( k \) in the \( i \)-th molecule, and \( R_k \) and \( Q_k \) represent the group contributions to molecular volume and area, respectively. It should be noted that only pure species parameters characterise the combinatorial part of the activity coefficient.

The residual part of the activity coefficient takes into account binary interactions between the molecules in the mixture. No further (ternary) parameter is necessary to take into account the interaction of three molecules together, even for systems with three or more components.\(^2\) The residual part is expressed as:

\[ \ln \gamma_i^R = \sum_{k}^{NG_i} v_{ki}(\ln \Gamma_k - \ln \Gamma_k(\beta))\#(S13) \]

where
\[ \ln \Gamma_k = Q_k \left[ 1 - \ln \left( \frac{\sum \Theta_m \Psi_{mk}}{\sum \sum \Theta_m \Psi_{km}} \right) \right] \] (S14)

\[ \Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \] (S15)

\[ \Psi_{mn} = \exp\left(-\frac{a_{mn}}{T}\right) \] (S16)

\( NG_{tot} \) is the total number of different group types in the mixture, \( X_m \) is the molar fraction of the \( m \)-th group in the mixture, and \( a_{mn} \) is the group-interaction parameter. The quantity \( \ln \Gamma_k^{(i)} \) (which can be seen as the interactions of the groups within the same molecule) is computed as from Equation (s8), but considering a fictitious solution made of molecules of species \( i \) only. Ultimately, the interaction between different groups is taken into account by \( a_{mn} \), while all other parameters are characteristic of the pure species.

The set of the parameters \( (a_{mn}, R_k, Q_k) \) is the one characteristic of UNIFAC-LLE. The equations defined here and in section 2.3.1 was numerically solved using the group-contribution parameters reported in Table S1 for the groups present in the ternary mixture of 1,2-dichlorobenzene, water, and ethanol. The groups constituting each molecule are reported in Table S2. For the sake of example, DCB is formed by 4 aromatic carbons with and hydrogen atom (CArH) and 4 aromatic carbons with a chlorine atom (CArCl).
Table S1. Group-contribution parameters for the ternary system DCB-water-ethanol.³

|       | ACH      | ACCl     | H₂O      | CH₃      | CH₂      | OH       | Rₘ       | Qₘ       |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|
| ACH   | 0        | 777.8    | 390.7    | -59.06   | -59.06   | 1989     | 1.1562   | 0.8440   |
| ACCl  | -878.1   | 0        | 859.4    | 156.5    | 156.5    | 703.9    | 0.5313   | 0.4000   |
| H₂O   | -97.27   | 372.8    | 0        | 342.4    | 342.4    | -122.4   | 0.9200   | 1.400    |
| CH₃   | 924.8    | -114.8   | 1300     | 0        | 0.000    | 644.6    | 0.9011   | 0.8480   |
| CH₂   | 924.8    | -114.8   | 1300     | 0.000    | 0        | 644.6    | 0.6744   | 0.5400   |
| OH    | -597.1   | -9.210   | 28.73    | 328.2    | 328.2    | 0        | 1.000    | 1.200    |
**Table S2.** Groups contained in each molecule: aromatic carbon and hydrogen atom (C<sub>A</sub>H), aromatic carbon and chlorine atom (C<sub>A</sub>Cl), water (H<sub>2</sub>O), carbon and three hydrogen atoms (CH<sub>3</sub>), carbon and two hydrogen atoms (CH<sub>2</sub>), hydroxyl group (OH).

|          | C<sub>A</sub>H | C<sub>A</sub>Cl | H<sub>2</sub>O | CH<sub>3</sub> | CH<sub>2</sub> | OH |
|----------|----------------|----------------|---------------|--------------|------------|-----|
| DCB      | 4              | 2              | 0             | 0            | 0          | 0   |
| Water    | 0              | 0              | 1             | 0            | 0          | 0   |
| EtOH     | 0              | 0              | 0             | 1            | 1          | 1   |
S2. Miscibility studies on ternary mixtures of water, 1,2-dichlorobenzene and ethanol.

UNIFAC-LLE model validation.

**Table S3.** Ternary solvents mixtures prepared for the validation of the UNIFAC model and observation concerning their miscibility. N = non miscible; Y = miscible.

| ω_{DCB} (%) | ω_{H2O} (%) | ω_{EtOH} (%) | Predicted miscibility | Observed miscibility |
|-------------|-------------|--------------|-----------------------|----------------------|
| 19.00       | 24.00       | 57.00        | N                     | N                    |
| 37.00       | 15.00       | 48.00        | N                     | N                    |
| 60.00       | 10.00       | 30.00        | N                     | N                    |
| 82.00       | 4.00        | 14.00        | N                     | N                    |
| 20.00       | 30.00       | 50.00        | N                     | N                    |
| 90.00       | 1.00        | 9.00         | N                     | Y                    |
| 50.00       | 12.00       | 38.00        | N                     | N                    |
| 70.00       | 9.00        | 21.00        | N                     | N                    |
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| 88.00 | 3.00 | 9.00 | N   | N   |
| 46.01 | 10.80 | 43.20 | N   | N   |
| 47.33 | 10.53 | 42.13 | N   | N   |
| 10.00 | 40.00 | 50.00 | N   | N   |
| 9.00  | 45.00 | 46.00 | N   | N   |
| 12.00 | 36.00 | 52.00 | N   | N   |
| 25.57 | 20.40 | 54.03 | N   | N   |
| 82.75 | 1.51  | 15.74 | Y   | Y   |
| 15.00 | 21.00 | 64.00 | Y   | Y   |
| 35.00 | 10.00 | 55.00 | Y   | Y   |
| 60.00 | 2.00  | 38.00 | Y   | Y   |
| 82.00 | 1.00  | 17.00 | Y   | Y   |
| 50.00 | 4.00  | 46.00 | Y   | Y   |
| 70.00 | 1.00  | 29.00 | Y   | Y   |
| 86.00 | 1.00  | 13.00 | Y   | Y   |
| 45.91 | 5.68  | 48.42 | Y   | Y   |
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| 44.95 | 7.66 | 47.40 | Y  | Y   |
| 46.43 | 7.45 | 46.12 | Y  | Y   |
| 45.50 | 9.30 | 45.20 | Y  | N   |
| 46.90 | 9.06 | 44.04 | Y  | N   |
| 4.00  | 40.00 | 56.00 | Y  | Y   |
| 2.00  | 41.00 | 57.00 | Y  | Y   |
| 10.00 | 30.00 | 60.00 | Y  | Y   |
| 65.00 | 3.00  | 32.00 | Y  | Y   |
| 24.82 | 18.92 | 56.27 | Y  | N   |
| 26.07 | 14.92 | 59.01 | Y  | Y   |
| 10.52 | 19.96 | 69.52 | Y  | Y   |
| 22.79 | 10.19 | 67.02 | Y  | Y   |
| 12.84 | 9.77  | 77.39 | Y  | Y   |
| 5.76  | 4.72  | 89.52 | Y  | Y   |
Figure S1. $^1$H-NMR of organic phase of entry 1.
Figure S2. $^1$H-NMR of aqueous phase of entry 1.
Figure S3. $^1$H-NMR of organic phase of entry 2.
Figure S4. $^1$H-NMR of aqueous phase of entry 2.

Figure S5. $^1$H-NMR of organic phase of entry 3.
Figure S6. $^1$H-NMR of aqueous phase of entry 3.
Figure S7. $^1$H-NMR of organic phase of entry 4.
Figure S8. $^1$H-NMR of aqueous phase of entry 4.
Figure S9. $^1$H-NMR of organic phase of entry 5.
Figure S10. $^1$H-NMR of aqueous phase of entry 5.

Figure S11. $^1$H-NMR of pure DMSO-d6 collected in order to evaluate the amount of water in the NMR solvent.
Figure S12. $^1$H-NMR of ethanol
Figure S13. Ternary miscibility diagram of H2O, ethanol and 1,2-dichlorobenzene mixtures as computed from UNIFAC-LLE model, expressed as molar fraction. Continuous blue and red lines represent the boundaries of the mixability region (phase separation below these lines). Circles and crosses represent the qualitative empirical validation test. Circles indicate the mixtures which do not lead to phase separation, while crosses indicate mixtures which show phase separation. Squares indicate the mixtures prepared to determine the tie lines (dashed lines) as from ¹H-NMR. (colour figure online). The three coloured circles (blue, red
and green) correspond to the composition of the three solvent mixtures discussed in Table 1, respectively TM1, TM2 and TM3.

**Table S4.** Ternary solvent mixtures prepared for the validation of the UNIFAC model by $^1$H-NMR characterization of each phase.

| Entry | Initial $\omega_{\text{DCB}}$ (%), $\omega_{\text{H}_2\text{O}}$ (%), $\omega_{\text{EtOH}}$ (%) | Measured $\omega$ of the obtained phases $\omega_{\text{DCB}}$ (%), $\omega_{\text{H}_2\text{O}}$ (%), $\omega_{\text{EtOH}}$ (%) | Predicted $\omega$ of the obtained phases $\omega_{\text{DCB}}$ (%), $\omega_{\text{H}_2\text{O}}$ (%), $\omega_{\text{EtOH}}$ (%) |
|-------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 1     | 30.53 40.17 29.30                                | 98.00 0.17 1.83                                 | 87.78 1.64 10.57                                |
|       |                                                 | 1.16 58.07 40.77                                 | 1.35 59.88 38.77                                |
| 2     | 31.36 25.13 43.52                                | 95.14 0.45 4.41                                 | 79.52 2.76 17.73                                |
|       |                                                 | 10.95 33.32 55.73                                | 7.34 36.23 56.43                                |
| 3     | 31.54 31.23 37.23                                | 96.71 0.25 3.05                                 | 83.76 2.17 14.07                                |
|       |                                                 | 4.28 43.65 52.07                                 | 3.60 46.71 49.69                                |
| 4     | 45.52 45.73 15.26                                | 94.18 0.36 5.46                                 | 75.51 3.33 21.16                                |
|       |                                                 | 19.19 22.98 57.83                                | 11.61 29.17 59.22                                |
| 5     | 50.56 10.00 39.44                                | 87.37 1.41 11.23                                | 66.97 4.65 28.38                                |
|       |                                                 | 37.01 13.98 49.01                                | 21.51 19.65 58.84                                |
S3. Characterization and dispersion in acidic aqueous solution of ZrO$_2$ nanoparticles.

Table S5. Crystalline properties of ZrO$_2$-NPs determined by XRD and Rietveld refinement.

| m-ZrO$_2$ fraction (wt%) | Crystallite size (nm) | t-ZrO$_2$ (nm) | $\chi^2$ | GOF |
|--------------------------|-----------------------|----------------|--------|-----|
| ZrO$_2$-NPs              | 69                    | 3.7            | 3.9    | 1.76| 1.33|

Figure S14. HR-TEM images of sample TM2.
S5. DLS tests of nanoparticle dispersibility in ternary mixtures: how to estimate the cluster sizes and concentration.

In the case of polydisperse samples, the field autocorrelation function \( g_1(\tau) \) is a sum of the exponential decays corresponding to each of the species in the population:

\[
g_1(\tau) = \sum_{i=1}^{n} w_i \exp \left( -\tau / \tau_i \right),
\]

where the weights \( w_i \) are proportional to the relative scattering from each species and the characteristic decay times \( \tau_i \) are proportional to the species size \( R_i \).

Exploiting the properties of the exponential, it is easy to demonstrate that the integral of the correlation function:

\[
\int_0^\infty d\tau g_1(\tau) = \sum_{i=1}^{n} w_i \tau_i = \tau_{AVG} #(S18)
\]

is equal to the intensity-averaged decay time \( \tau_{AVG} \).
Figure S15. Field correlation functions $g_1(\tau)$ of the zirconia dispersions in solvents TM2 (squares). Continuous grey line is an exponential curve with the characteristic decay time $\tau_p = 27.8 \mu s$. The black dot indicates the value of $g_1(\tau) = w_c$ where the correlation function deviates from the exponential decay expected for monodisperse particles.
To estimate the typical cluster size $R_c$ and concentration $c_c$ we make the simplifying assumption that in our samples are present only two populations, the particles and the clusters.

In this case Eq.S18 will become:

$$\int_0^\infty dτ g(τ) = w_p τ_p + w_c τ_c = τ_{AVG} #(S19)$$

Where the subscripts p and c refer to the particles and clusters respectively.

The $τ_p$ can be easily obtained by fitting the first part of the field correlation function for the nanoparticles in the original aqueous solvent ($H_2O + 0.1$ M NaCl). Our fit gives a value of $τ_p = 27.8 \mu s$, which corresponds to a typical particle radius $R_p = 4.66$ nm.

The weights $w_p$ and $w_c$ can be estimated by looking when the correlation function departs significatively from the single exponential behaviour expected for monodisperse particles (see figure S15). Once $τ_{AVG}$, $τ_p$, $w_p$ and $w_c$ are known, the value of $τ_c$ can be easily calculated by inverting Eq.2. To estimate the fraction of particles associated in clusters is useful to recall that:
\[ w_i \propto c_i (R_i)^3 \] \( (S20) \)

The fraction of particles associated in cluster is then:

\[ \frac{c_c}{c_p} = \frac{w_c (R_p)^3}{w_p (R_c)} \] \( (S21) \)

The results are reported in the Table S6.

**Table S6. DLS analysis: cluster sizes and concentration**

| Solvent               | \( w_p \) | \( w_c \) | \( \tau_{AVG} (\mu s) \) | \( \tau_c (\mu s) \) | \( R_c \) (nm) | \( c_c/c_p \) |
|----------------------|-----------|-----------|--------------------------|----------------------|----------------|----------------|
| Water+0.1M HCl       | 0.8       | 0.2       | 162.811                  | 703                  | 118            | 1.5 \( \times 10^{-5} \) |
| TM1                  | 0.2       | 0.8       | 1507                     | 1877                 | 314            | 1.3 \( \times 10^{-5} \) |
| TM2                  | 0.1       | 0.9       | 1664                     | 1846                 | 309            | 3 \( \times 10^{-5} \) |

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