

Supporting Information

Estimation of Interfacial Tension between Organic Liquid Mixtures and Water

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Six pages of Supporting Information include a further description of the monolayer (ML) model, derivation of the linear mixing model based on mole fractions (LMMM) from the monolayer model, derivation of the linear mixing model based on volume fractions (LMMV), the method of interfacial tension measurements for one quinary system, and interfacial tension data for one quinary system (CT-DBBP-TBP-LO and water) in Table S1.

Model Derivations

Monolayer model: Based on Defay et al. (1) where the monolayer model was derived for a binary organic mixture and water system (i.e., ternary system), the monolayer (ML) model for ternary and higher order systems can be derived from the thermodynamic equation given by Butler (2):

$$\gamma = \gamma_i + \frac{RT}{a} \ln\left(\frac{\alpha_i^s x_i^s}{\alpha_i x_i}\right) \quad (\text{S1})$$

where γ is the interfacial tension of mixtures, γ_i is the interfacial tension of either pure organic component i, a is the surface area occupied by a molecule, α_i and x_i are the activity coefficient and mole fraction of component i, respectively, R is the ideal gas constant, T is the temperature, and superscript s stands for values at the interface. It is assumed in eq. (S1) that the chemical potentials of each i component in the interface region and bulk solution are the same and the surface areas occupied by molecules in the interface region are the same. If the interface is assumed ideal ($\alpha_i^s = 1$), eq. (S1) can be rearranged as

$$x_i^s = \alpha_i x_i \exp\left(a \frac{\gamma - \gamma_i}{RT}\right) = \alpha_i x_i \exp\left(\frac{\gamma a}{RT}\right) \exp\left(\frac{-\gamma_i a}{RT}\right) \quad (\text{S2})$$

Since the sum of mole fractions of all components at the interface is set equal to one ($\sum x_i^s = 1$), substituting eq. (S2) into the constraint ($\sum x_i^s = 1$) leads to the interfacial tension of mixtures as a function of the solution composition as

$$\exp\left(\frac{-\gamma a}{RT}\right) = \sum_i \alpha_i x_i \exp\left(\frac{-\gamma_i a}{RT}\right) \quad (\text{S3})$$

Rearranging eq. (S3) for the interfacial tension of organic mixtures, we obtain

$$\gamma = \gamma_i - RT\Gamma_m \ln\left[\alpha_i + \sum_{j \neq i} x_j \{q_{ij} \alpha_j - \alpha_i\}\right] \quad (\text{S4})$$

$$q_{ij} = \exp\left(\frac{\gamma_i - \gamma_j}{RT\Gamma_m}\right) \quad (\text{S5})$$

where Γ_m is the surface coverage at the interface ($= (a \times N_A)^{-1}$), N_A is Avogadro's number, and q_{ij} is the relative adsorption ratio of components i and j. Eq. (S4) was also derived by Yarranton and Masliyah (3) by employing the Gibbs and Langmuir adsorption isotherms. For an ideal monolayer model, all activity coefficients in eq. (S4) are unity.

Linear Mixing Model based on mole fractions: The linear mixing model based on mole fractions (LMMM) can be derived from the solution for the ideal ML model (eq. S4). If γ_i and γ_j in eq. (S5) are close, the exponential in eq. (S5) can be expanded as ($\exp(x) = 1 + x + x^2/2! + \dots$)

$$q_{ij} = \exp\left\{\frac{\gamma_j - \gamma_i}{RT\Gamma_m}\right\} = 1 + \frac{\gamma_j - \gamma_i}{RT\Gamma_m} \quad (\text{S6})$$

Eq. (S4) with eq. (S6) becomes

$$\gamma = \gamma_i - RT\Gamma_m \ln\left[1 + \sum_{j \neq i} x_j \frac{\gamma_j - \gamma_i}{RT\Gamma_m}\right] \quad (\text{S7})$$

Similarly, the logarithm can be expanded as ($\ln(1+x) = x - x^2/2! + \dots$)

$$\gamma = \gamma_i - RT\Gamma_m \left[\sum_{j \neq i} x_j \frac{\gamma_j - \gamma_i}{RT\Gamma_m} \right] \quad (\text{S8})$$

As in the ML model, the surface coverage is assumed to be constant for all components in the mixture. Eq. (S8) using the constraint ($\sum x_i = 1$) becomes

$$\gamma = \gamma_i - \sum_{j \neq i} x_j (\gamma_j - \gamma_i) = \sum_i x_i \gamma_i \quad (\text{S9})$$

Hence, the LMMM will work well only for mixtures with small difference of IFT values as shown in the manuscript.

Linear mixing model based on volume fractions: The linear mixing model based on volume fractions (LMMV) can be conceptually described for a quaternary system as

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline \end{array} \times \frac{V_2}{1 - V_1} + \begin{array}{|c|c|} \hline 1 & 3 \\ \hline \end{array} \times \frac{V_3}{1 - V_1} = \begin{array}{|c|c|c|} \hline 1 & 2 & 3 \\ \hline \end{array} \quad (\text{S10})$$

where the boxes on the left hand side of eq. (S10) represent ternary systems (two organic components and water), the box on the right hand side of eq. (S10) represents a quaternary system (three organic components and water), V_i is the volume fraction of component i in the quaternary system, component 1 is a common compound, and the interfacial tension of a ternary system containing organic components 1 and j is γ_{1j,V_1} . For quaternary system, both LMMV and LMMM can be expressed in similar forms as

$$\gamma = \gamma_{12,V_1} \frac{V_2}{1-V_1} + \gamma_{13,V_1} \frac{V_3}{1-V_1} \quad (\text{S11})$$

$$\begin{aligned} \gamma &= \gamma_1 x_1 + \gamma_2 x_2 + \gamma_3 x_3 = [\gamma_1 x_1 + \gamma_2 (1-x_1)] \frac{x_2}{1-x_1} + [\gamma_1 x_1 + \gamma_3 (1-x_1)] \frac{x_3}{1-x_1} \\ &= \gamma_{12,x_1} \frac{x_2}{1-x_1} + \gamma_{13,x_1} \frac{x_3}{1-x_1} \end{aligned} \quad (\text{S12})$$

where γ_{1j,x_1} is the interfacial tension of a ternary system containing components 1 and j.

The conceptual linear mixing model based on volume fractions can be expressed in a general form as

$$\gamma = \sum_{j \neq i} \gamma_{ij,V_i} \frac{V_j}{1-V_i} \quad (\text{S13})$$

The volume fraction in eq. (S13) can be computed from the mole fraction as follow:

$$V_1 = \frac{\frac{x_1 M_1}{\rho_1}}{\sum_i \frac{x_i M_i}{\rho_i}} \quad (\text{S14})$$

where ρ_i and M_i are the density and molar mass of organic component i.

Materials and Methods

Materials: IFT values of one quinary system (four organic components including the composite chemical lard oil) were measured in this study in order to test the newly developed LMMV. The organic chemical composition of this quinary system is representative of carbon tetrachloride mixtures discharged at the U.S. Department of Energy Hanford site in Washington State (4). The chemicals are carbon tetrachloride (99.9% purity, Sigma Aldrich), tributyl phosphate (99% purity, Sigma Aldrich), dibutyl butyl phosphonate (99% purity, Sigma Aldrich), and lard oil (Peacock Special Prime Burning Lard Oil, George Pfau's Sons Company, Jeffersonville, IN).

Methods: Each composition of NAPL mixtures was prepared separately and present in Table S1. The volume ratio of the NAPL mixture and water in the jar was 1:1. The jar was shaken by hand for several minutes and allowed to equilibrate for at least 24 hours. All interfacial tension measurements were performed using the pendant drop method with a CAM 200 goniometer (KSV Instruments, Helsinki, Finland). For this method, a drop of liquid was formed at the end of a needle, an image of the drop was taken, and then the shape of the drop was analyzed according to Axisymmetric Drop Shape Analysis (ADSA). A curved needle was used to create a water drop in a cuvette filled with the organic phase. For one composition without carbon tetrachloride which is lighter than water, a straight, flat tipped needle was used to create a liquid drop in a cuvette. Initial measurements were taken with a series of ten drops and repeated at least three times. The tension values of each drop changed over time. To obtain equilibrium tension values, each drop was imaged at twenty second intervals until at least 200 seconds elapsed when changes were no longer observable. The tension values from the last 200 seconds of each drop were averaged. This was repeated three times. The density is an important input parameter for determining interfacial tension using the ADSA. The density of each mixture was calculated from the mass of a set volume of sample. Five mass measurements were taken at a time, and then repeated again with a new volume sample. Interfacial tension and density values are presented in Table S1.

Table S1. Measured density and interfacial tension values for CT-DBBP-TBP-LO system.

Volume fraction of Carbon Tetrachloride	Density (g/mL)	Interfacial tension (mN/m)
0	0.949	7.05
0.2	1.041	6.25
0.4	1.140	7.34
0.6	1.331	12.78
0.736	1.421	17.02
0.8	1.467	18.25
0.9	1.532	20.80
0.95	1.549	23.85
0.975	1.573	25.75
1	1.594	41.41

DBBP, TBP, and LO stand for dibutyl butyl phosphonate, tributyl phosphate, and lard oil, respectively. Volume fractions of components as a function of CT (V_{CT}) are as following: $V_{DBBP} = (1-V_{CT}) \cdot 0.147/0.264$, $V_{TBP} = (1-V_{CT}) \cdot 0.088/0.264$, and $V_{LO} = (1-V_{CT}) \cdot 0.029/0.264$.

Literature Cited

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