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An analytical solution to calculate bulk mole fractions for any number of components in aerosol droplets after considering partitioning to a surface layer

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Abstract

Calculating the equilibrium composition of atmospheric aerosol particles, using all variations of Köhler theory, has largely assumed that the total solute concentrations define both the water activity and surface tension. Recently however, bulk to surface phase partitioning has been postulated as a process which significantly alters the predicted point of activation. In this paper, an analytical solution to calculate the removal of material from a bulk to a surface layer in aerosol particles has been derived using a well established and validated surface tension framework. The applicability to an unlimited number of components is possible via reliance on data from each binary system. Whilst assumptions regarding behaviour at the surface layer have been made to facilitate derivation, it is proposed that the framework presented can capture the overall impact of bulk-surface partitioning. Predictions made by the model across a range of surface active properties should be tested against measurements. The computational efficiency of using the solution presented in this paper is roughly a factor of 20 less than a similar iterative approach, a comparison with highly coupled approaches not available beyond a 3 component system.

1 Introduction and rationale

The process by which aerosol particles indirectly scatter radiation via activation to cloud droplets remains one of the largest uncertainties of climate change (Halquist et al., 2009). The relationship between equilibrium size, chemical composition and ambient conditions is given by the Köhler equation.

$$\frac{RH}{100} = a_w \exp\left(\frac{2v_w \sigma_{ws}}{RT r_{\text{drop}}}\right) \quad (1)$$

where RH in the ambient relative humidity, a_w is the water activity (dimensionless), v_w the partial molar volume of water ($\text{m}^{-3} \text{mol}^{-1}$), σ_{ws} the solution surface tension (N m^{-1}),

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R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and r_{drop} the radius of the droplet (m). As discussed by Topping et al. (2007), calculating the equilibrium composition using all variations of Köhler theory has largely assumed that the total solute concentrations define both the water activity and surface tension. Recently however, bulk to surface phase partitioning has been postulated as a process which significantly alters the predicted point of activation (e.g. Sorjamaa et al., 2004; Laaksonen et al., 1999; Kokkola et al., 2006). Briefly, accounting for this process is based on the fact that an alteration of the surface tension is caused by changing concentration gradients approaching the surface. However, in Gibbs surface thermodynamics this surface phase between the homogeneous liquid and vapour phase is taken to be infinitely thin, allowing an exact definition of the droplet radius (Sorjamaa et al., 2004). Any extra material which is related to the change in surface tension is described using surface excess quantities which can be positive or negative:

$$n_i^{\dagger} = n_i^{\text{b}} + n_i^{\text{s}} \quad (2)$$

Where n_i^{\dagger} is the total amount of component i , and the bulk and surface phase concentrations respectively (mol). In order to solve these quantities, a solution to the Gibbs adsorption equation must be found. This relates the change in surface energy to changes in thermodynamic variables and excess quantities:

$$\sum_i n_i^{\text{s}} d\mu_i + A_{\text{drop}} d\sigma_{\text{ws}} = 0 \quad (3)$$

where μ_i is the chemical potential of component i (J mol^{-1}), A_{drop} the surface area of the droplet (m^2) and σ_{ws} the surface tension (N m^{-1}). The size of the droplet is important since as the surface to volume ratio increases then depletion of material from the bulk becomes important for thermodynamic properties. There have been methods presented to solve Eq. (3), thus Eq. (2), for up to 3 component systems two solutes and water (Sorjamaa et al., 2004). In essence, one has to derive relationships such that the system is no longer represented with a set of indeterminate equations. Sorjamaa and

Laaksonen (2006) and Kokkola et al. (2006) devised a numerical technique for binary organic systems in water and ternary mixed inorganic/organic systems in water using relationships for activity coefficients and surface tension isotherms. To increase the number of components would require an, as yet, undetermined set of additional relationships or unjustified assumptions. In this study we present a methodology for such an extension relying on accurate and well established surface tension models, validated using bulk empirical data. These validated models enable an elegant analytical solution to Eq. (3) for any number of components to be derived. Using this approach, it is possible to use data derived from binary systems to describe a complex mixture.

2 Derivation

There are a number of surface tension models capable of treating multi-component systems as reviewed by Topping et al. (2007). Briefly, for multi-component systems, three groups of calculation have been presented in the literature (Hu and Lee, 2004). These include simple additive methods and conventional methods based on the Gibbs adsorption equation (Topping et al., 2005). A common approach consists combining thermodynamic relations together with an adsorption model, thus accounting for transfer of material between the bulk and a surface phase, leading to changes in the molecular forces and the subsequent surface tension. To calculate the surface tension in the model presented by Li and Lu (2001), the authors combined the Gibbs dividing surface, the Langmuir adsorption equation and an appropriate model for calculating activity coefficients in mixed solutions to arrive at two different schemes. The Langmuir adsorption isotherm is a relationship which describes the number of adsorbed molecules on a surface to the concentration above that surface. The surface tension in binary systems is given by:

$$\sigma_{ws} = \sigma_w + RT \Gamma_i^{wo} \ln \left(\frac{1}{1 + K_i a_i} \right) \quad (4)$$

where σ_{ws} is the surface tension of the mixture (mN m^{-1}), σ_w is the surface tension of

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pure water (mN m^{-1}), Γ_i^{wo} is the saturated surface excess of solute i (mmol m^{-2}), K_i the adsorption equilibrium constant for solute i (dimensionless – tabulated) and a_i the activity of component i (dimensionless). The reader is reminded that activity represents an effective concentration which relies on calculations of activity coefficients. Activity coefficients are related to the molecular forces taking place in a solution. The thermodynamics of a solution mixture however depend on the intermolecular forces that operate between molecules and are dependent on the nature of the solvent(s) and solutes. For more information the reader is referred to Topping et al. (2005b) and references therein. As stated by Li and Lu (2001), the quantity Γ_i^{wo} is defined as the excess of i in a unit cross sectional area of the surface region over the moles which would be present in the bulk liquid phase containing the same number of moles of water as does the section of surface region. The superscript wo indicates that the dividing surface is chosen so that $\Gamma_w=0$, or $n_w^S=0$. Re-expressing this in relation to the Gibbs adsorption Eq. (2) and choosing $\Gamma_w=0$, Eq. (4) reduces to Eq. (5):

$$-d\sigma_{\text{ws}} = \Gamma_i^{\text{wo}} RT d \ln(a_i) \quad (5)$$

For a binary system, It is then possible to solve the set of equations for a given dry and wet particle size (thus volume), pure component properties and surface tension parameters as described by Sjørjamaa et al. (2004).

For multi-component systems, Li and Lu (2001) proposed two surface tension methods. These semi-empirical methods have been reviewed by Topping et al. (2007) and found to reproduce experimental data more accurately than entirely predictive methods. Thus we use the empirical validation of these methods against bulk data as a driving force for their use. This ultimately enables us to arrive at a simple solution for bulk/surface partitioning. The first method was to propose that the adsorption behaviour of solute i still followed the Langmuir gas-solid adsorption model, applied previously, in a mixed solution. It assumes that there is no interaction, nor competing adsorption, from the other solutes. In other words, it assumes that the relationship defining the surface excess used in a binary system still holds in a mixture. The expression

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for the multi-component surface tension is given as Eq. (6):

$$\sigma_{ws} = \sigma_w + RT \sum_{i=1}^k \Gamma_i^{wo} \ln \left(\frac{1}{1 + K_i a_i} \right) \quad (6)$$

As discussed by Fainerman et al. (2002), most authors have proposed procedures or models to predict the adsorption behaviour for a surfactant mixture from the known surface characteristics of the single compound. This naturally requires detailed experimental studies of surface tensions of individual solutions, and often, additional parameters that account for the mutual influence of solutes. This imposes certain restrictions on the capability of such approaches (Fainerman et al., 2002). Whilst theoretical predictive frameworks exist, the ability to capture the varying surface tension is hindered by a neglect of important processes or parameters which can define the behaviour of a mixed surfactant system (Fainerman et al., 2001b). However, following this, Fainerman et al. (2002) derived a general but simple approximate expression for the surface tension of a surfactant mixture that allows estimation of the characteristics of a mixed solution, without any detailed analysis of the behaviour of the individual solutions and/or any account for specific interactions between the mixed species. It has been shown that it is possible to predict the surface tension of a mixed solution of two (or even n) surfactants of different natures from the surface tensions for the individual solutions using this scheme. Considering an ideal mixture of homologues, the generalised Szyskowski equation was derived (Fainerman et al., 2002). This was then further generalised to a system of n components to give the following equation of state, hereafter referred to as the FM mixing rule:

$$\exp \Pi_{sol} = \sum_{i=1}^n \exp \Pi_i + 1 - n \quad (7)$$

where Π_{sol} and Π_i are surface pressures of the solution and component i (the difference between the multi-component solution/binary system i surface tension and that

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of the solvent; mN m^{-1}). Fainerman et al. (2001) compared the above formulation with experimental data and found it to be valid for several different surfactant systems, even those containing components with large differences in molar surface areas and other adsorption parameters. Fainerman et al. (2001) state this validity is ascribed to the fact that many particular features of adsorption process in mixed components (surface layer non-ideality, capability to reorient at the surface layer etc) are accounted for automatically because the surface tensions of the individual solutions are used. Solving the Gibbs adsorption equation for each binary system relies on the same assumption employed by Li et al. (1998) who defined the dividing surface as the equimolar surface with respect to water. Whilst this is different to the approach used by Laaksonen et al. (1999), it is unlikely that there will be any recognisable differences at droplet sizes larger than 10 nm (Sorjamaa et al., 2004). When Eq. (2) is used to describe the surface tension of binary systems in the FM mixing rule then predictions for multicomponent organic aqueous systems are identical to the full LiLu thermodynamic model. This is discussed in detail by Topping et al. (2007). Note that the Gibbs adsorption isotherm can now be used to describe the behaviour of each component as it would in a binary system. With an expression for the multicomponent surface tension we can now proceed to derive a general expression for altered mole fractions in the solution due to partitioning. Re-expressing the logarithm in Eq. (6) we get the following:

$$\sigma_{\text{ws}} = \sigma_{\text{w}} - RT \sum_{i=1}^k \Gamma_i^{\text{wo}} \ln(1 + K_i a_i) \quad (8)$$

To derive the generalised expression, we now need to convert the Gibbs adsorption isotherm into a complete differential (Eq. 5). Assume chemical equilibrium between bulk and surface layer:

$$n_{\text{is}} d(RT \ln(x_{\text{iB}} \gamma_{\text{iB}})) + A d \sigma_{\text{ws}} = 0 \quad (9)$$

$$n_{\text{is}} d \ln(x_{\text{iB}} \gamma_{\text{iB}}) + A \frac{d\sigma}{R} T = 0 \quad (10)$$

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$$n_{is} \frac{d \ln(x_{iB} \gamma_{iB})}{dx_{iB}} + \frac{A}{R} T \frac{d\sigma}{dx_{iB}} = 0 \quad (11)$$

Note that since we assume the surface excess of water to be zero and chemical equilibrium to exist, the activity of component i is written to be the same as that of the bulk fraction. Since we are also relying on behaviour within each binary system to describe the mixture then this parameter can be assumed to be implicitly included in derived surface tension parameters as discussed shortly. Firstly, converting the binary surface tension equation into a differential assuming that the activity a_i is represented by the solute mole fraction x_i (Eq. 8):

$$\frac{d\sigma}{dx_{iB}} = -RT\Gamma_i^{\text{wo}} \left(\frac{K_i}{1 + K_i x_{iB}} \right) \quad (12)$$

Substituting back into the Gibbs differential (Eq. 5):

$$n_{is} \frac{d \ln(x_{iB} \gamma_{iB})}{dx_{iB}} + \frac{A}{R} T \left(-RT\Gamma_i^{\text{wo}} \left(\frac{K_i}{1 + K_i x_{iB}} \right) \right) = 0 \quad (13)$$

Now re-expressing the derivative of $\ln(x_{iB} \gamma_{iB})$:

$$\frac{d \ln(x_{iB} \gamma_{iB})}{dx_{iB}} = \frac{d \ln(x_{iB} \gamma_{iB})}{d(x_{iB} \gamma_{iB})} \frac{d(x_{iB} \gamma_{iB})}{dx_{iB}} \quad (14)$$

$$\frac{d \ln(x_{iB} \gamma_{iB})}{dx_{iB}} = \frac{1}{x_{iB} \gamma_{iB}} \left[\gamma_{iB} + x_{iB} \frac{d\gamma_{iB}}{dx_{iB}} \right] \quad (15)$$

$$\frac{d \ln(x_{iB} \gamma_{iB})}{dx_{iB}} = \left[\frac{1}{x_{iB}} + \frac{1}{\gamma_{iB}} \frac{d\gamma_{iB}}{dx_{iB}} \right] \quad (16)$$

In line with the assumption that the activity a_i is represented by the solute mole fraction x_i , it is possible to neglect the derivative of activity coefficients since the use of empirical surface tension parameters enables this variation to be included implicitly

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within the derived values of Γ_i^{wo} and K_i . From this point onward we therefore refer to these variables as $\Gamma_i^{\text{wo}'}$ and K_i' . Using this approach, the equation now reduces to:

$$\frac{d\ln(x_{iB}Y_{iB})}{dx_{iB}} = \frac{1}{x_{iB}} \quad (17)$$

We can now substitute this equation into Eq. (16).

$$n_{is} \frac{1}{x_{iB}} + \frac{A}{R} T \left(-RT \Gamma_i^{\text{wo}} \left(\frac{K_i}{1 + K_i x_{iB}} \right) \right) = 0 \quad (18)$$

$$n_{is} \frac{1}{x_{iB}} = -\frac{A}{R} T \left(-RT \Gamma_i^{\text{wo}} \left(\frac{K_i}{1 + K_i x_{iB}} \right) \right) \quad (19)$$

$$n_{is} \frac{1}{x_{iB}} = -A \Gamma_i^{\text{wo}'} \left(\frac{K_i'}{1 + K_i' x_{iB}} \right) \quad (20)$$

We can easily derive an expression for n_{is} in terms of x_{iB} by relying on the fact that we are working with each binary system to describe the mixture as manifest in the expression for σ_{ws} .

$$n_{is} = n_{iT} - n_{iB} \quad (21)$$

Assuming that the surface excess of water is zero in the binary mixture, we can then write:

$$n_{is} = n_{iT} - \frac{x_{iB}}{1 - x_{iB}} n_{\text{wT}} \quad (22)$$

Substituting this expression into Eq. (20):

$$\left[n_{iT} - \frac{x_{iB}}{1 - x_{iB}} n_{\text{wT}} \right] \frac{1}{x_{iB}} = A \Gamma_i^{\text{wo}'} \left(\frac{K_i'}{1 + K_i' x_{iB}} \right) \quad (23)$$

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$$\left[n_{iT} - \frac{x_{iB}}{1-x_{iB}} n_{WT} \right] = x_{iB} A \Gamma_i^{\text{wo}'} \left(\frac{K_i'}{1+K_i' x_{iB}} \right) \quad (24)$$

$$n_{iT} - \frac{x_{iB}}{1-x_{iB}} n_{WT} = \left(\frac{x_{iB} A \Gamma_i^{\text{wo}'} K_i'}{1+K_i' x_{iB}} \right) \quad (25)$$

Now deriving an expression for x_{iB} :

$$n_{iT}(1-x_{iB}) - x_{iB} n_{WT} = \left(\frac{x_{iB} A \Gamma_i^{\text{wo}'} K_i'}{1+K_i' x_{iB}} \right) (1-x_{iB})$$

$$n_{iT} (1+K_i' x_{iB}) - x_{iB} n_{WT} (1+K_i' x_{iB}) = x_{iB} A \Gamma_i^{\text{wo}'} K_i' (1-x_{iB})$$

$$n_{iT} (1+K_i' x_{iB} - x_{iB} - K_i' x_{iB}^2) - x_{iB} n_{WT} - n_{WT} K_i' x_{iB}^2 = x_{iB} A \Gamma_i^{\text{wo}'} K_i' - x_{iB}^2 A \Gamma_i^{\text{wo}'} K_i'$$

$$n_{iT} + n_{iT} K_i' x_{iB} - n_{iT} x_{iB} - n_{iT} K_i' x_{iB}^2 - x_{iB} n_{WT} - n_{WT} K_i' x_{iB}^2 = x_{iB} A \Gamma_i^{\text{wo}'} K_i' - x_{iB}^2 A \Gamma_i^{\text{wo}'} K_i'$$

$$x_{iB}^2 (A \Gamma_i^{\text{wo}'} K_i' - n_{WT} K_i' - n_{iT} K_i') + x_{iB} (n_{iT} K_i' - n_{iT} - n_{WT} - A \Gamma_i^{\text{wo}'} K_i') + n_{iT} = 0$$

Thus we have a quadratic expression for x_{iB} . A solution to a basic quadratic equation written as:

$$x_{iB}^2 a + x_{iB} b + c = 0 \quad (26)$$

is simply given as:

$$x_{iB} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (27)$$

where the negative root must be used to obtain mole fractions between 0 and 1.

To solve the above we need to calculate concentrations n_{iT} and n_{wT} . The total wet volume (m^3) is given as:

$$V_{\text{drop}} = V_w + V_i = n_{wT}V_w + n_{iT}V_i \quad (28)$$

where:

$$V_w = 1.8^{-53} \text{ mol}^{-1} \quad (29)$$

$$V_i = \frac{M_i}{\rho_i} \quad (30)$$

$$n_{iT} = \frac{V_{\text{dry}}\rho_i}{M_i} \quad (31)$$

and therefore:

$$n_{wT} = \frac{(V_{\text{drop}} - n_{iT}V_i)}{V_w} \quad (32)$$

3 Application

It is useful to perform an example of a binary system using the above formulation. Take a hypothetical compound for which the parameters K_i and Γ_i were chosen arbitrarily to be 400 and 0.005, respectively. Take a 10 nm dry radius aerosol at a wet size of 100 nm. We can prescribe the following parameters $M_i=200 \text{ g mol}^{-1}$; $\rho_i=1500 \text{ kg mol}^{-1}$ such that we get the following values: $v_i=1.33^{-4} \text{ m}^3 \text{ mol}^{-1}$; $n_{iT}=3.1416^{-20} \text{ mol}$; $n_{wT}=2.3248^{-16} \text{ mol}$; $A=1.2566^{-13} \text{ m}^2$. Then we can calculate values for the original bulk mole fraction x_{iB}^0 and that after accounting for bulk to surface partitioning, x_{iB} , as 1.3512^{-4} and 1.3368^{-4} . Thus, only 50% of material remains in the bulk phase after partitioning. If we change the wet size to

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50, 200 and 500 nm the amount of material remaining in the bulk changes to: 35, 65 and 82%. Thus, as the surface to volume ratio decreases, the amount of material partitioned to a surface layer, relative to the original bulk value, decreases. This is to be expected. Similarly, the effect is expected to reduce with increasing dry size. If we increase the dry size to 100 nm and use the same wet/dry ratios as the latter example, the percentage of material remaining in the bulk after partitioning is predicted to be: 86, 95 and 98 accordingly. These values are greater than the 10 nm example, suggesting bulk/surface partitioning reduces. Unfortunately, an extensive database of empirically determined values of K_i and Γ_i does not exist. However, we can initially prescribe values according to observed surface tension isotherms, such as those presented by Topping et al. (2007) and Booth et al. (2009). In Fig. 1a, a collection of isotherms informed from pendant drop measurements, as reported by Topping et al. (2007) and Booth et al. (2009) are given. Figure (1b) plots the ratio of bulk concentrations after consideration of partitioning to those without, for a broad range of surface tension parameters. In this example the dry and wet sizes were arbitrarily chosen to be 10 nm and 200 nm. Placed on the same graph are points highlighting the same compounds presented in Fig. 1a. For example, the removal of material from the bulk to surface layer is much more pronounced for cis-pinonic acid relative to malonic acid. One would expect this by simple analysis of the isotherm presented in Fig. 1a. It must be noted that the same values $M_i=200$ g/mol; $\rho_i=1500$ kg/mol as stated in the previous example have been used for purely illustrative purposes.

The equations presented in the previous section can be applied to mixtures of any number of components as dictated by the surface tension model employed. It must be pointed out that this approach neglects phenomena postulated to occur at a bulk/surface interface. For example, the surface tension framework described in the previous section can be modified to account for competing adsorption (Li and Lu, 2001). This will form the focus of another publication. However, comparison with bulk data by Topping et al. (2007) and more recently, Booth et al. (2009), could not conclusively determine whether this increased level of complexity is necessary. It should

be pointed out that detailed frameworks presented by Sorjamaa et al. (2004) and Kokkola (2006) are likely more apt at diagnosing specific phenomena occurring at bulk/surface interfaces in simple mixtures. However, we believe the overall effect of partitioning in mixtures of any number of components can be captured by the framework presented in this report such that the altered critical saturation ratio should be measurable by conventional CCN instruments. This, of course, requires testing.

3.1 Computational performance

It is useful to briefly compare the computational cost of using the analytical expression with regards to an iterative method. For any given set of surface tension parameters only 23 floating point operations, or FLOPS, are required. The number of corresponding FLOPS required in the iterative method depends on the efficiency of root finding scheme. For example, applying a newton-raphson search with root bracketing on the cis-pinonic acid example presented in Fig. 1 requires 498 FLOPS. Similarly, the malonic acid example requires 423 FLOPS. These values represent binary systems using the same assumptions employed in the analytical method. Using the coupled method presented by Sorjamaa et al. (2004), accounting for activity coefficient variation with 5th order polynomials (including the derivative), requires 933 FLOPS. These values were simply derived by assuming a root finding tolerance of <0.1% change in the bulk concentration. For multi-component systems the cost of the analytical expression can be extrapolated linearly. For example, for a 10 component testcase, the analytical solution requires 230 FLOPS, whereas the iterative search employing the same assumptions may take 4230–4980 FLOPS for similar compounds. The coupled approach would require a considerable amount more, though it is difficult to quantify since it is presently not possible to account for more than 3 compounds.

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4 Conclusions and future work

An analytical solution to calculate the removal of material from a bulk to a surface layer has been derived using a well established and validated surface tension model. The potential applicability to multi-component mixtures requires only surface tension parameters from binary systems. Whilst assumptions regarding behaviour at the surface layer have been made to facilitate derivation, we feel the framework presented can capture the overall impact of bulk-surface partitioning. This requires validating against measured CCN data of known composition from laboratory studies. However, it is also important to apply the framework to ensemble mixtures from smog chamber and ambient studies where possible. The computational efficiency of using the solution presented in this paper is roughly a factor of 20 less than a similar iterative approach.

We will revisit the derivation using surface tension models that account for competing adsorption at the surface layer as described by Topping et al. (2007). Perhaps more importantly, we also intend to derive a generalised predictive framework in which the surface tension parameters K_i and Γ_j can be linked to broad functional groups and characteristics of the individual organic compounds. This requires compilation of an extensive database of binary systems. This will form the focus of a future publication and will allow sensitivity studies to be carried out along the lines of those presented by McFiggans et al. (2010).

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**An analytical solution
to bulk/surface
partitioning**

D. Topping

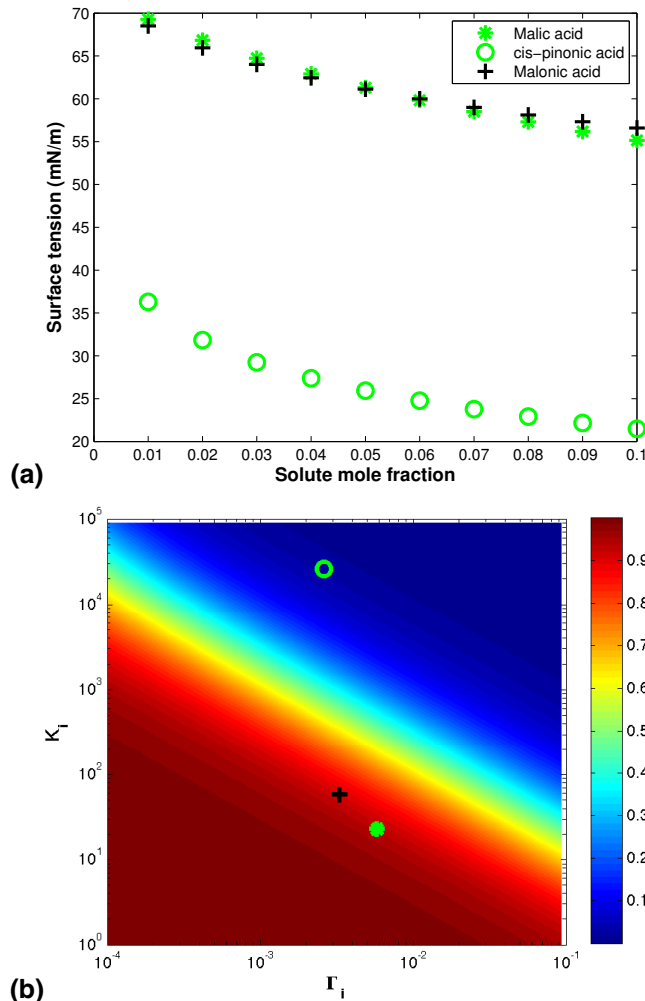
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Fig. 1. (a) Surface tension isotherms. (b) Ratio of bulk concentrations after partitioning to those without.