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Mass Transfer in the Dissolution of a Multi-Component Liquid Droplet in an Immiscible Liquid Environment

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Abstract

The Epstein Plesset equation has recently been shown to accurately predict the dissolution of a pure liquid microdroplet into a second immiscible solvent, such as oil into water. Here, we present a series of new experiments and a modification to this equation to model the dissolution of a two-component oil-mixture microdroplet into a second immiscible solvent, in which the two materials of the droplet have different solubilities. The model is based upon a reduced surface area approximation and the assumption of ideal homogenous mixing:

$$\text{Mass flux} \frac{dm_i}{dt} = A \text{frac}_i D_i (c_i - c_s) \left\{ \frac{1}{R} + \frac{1}{\sqrt{\pi D_i t}} \right\},$$

where $A \text{frac}_i$ is the area fraction of component i ; c_i and c_s are the initial and saturation concentrations of the droplet material in the surrounding medium; R is the radius of the droplet; t is time; and D_i is the coefficient of diffusion of component i in the surrounding medium. This new model has been tested by use of a two-chamber micropipette-based method, which measured the dissolution of single individual microdroplets of mutually-miscible liquid mixtures (ethyl acetate/butyl acetate, and butyl acetate/amyl acetate) into water. We additionally measured the diffusion coefficient of the pure materials: ethyl acetate, butyl acetate, and amyl acetate, in water at 22 deg C. Diffusion coefficients for the pure acetates in water were: 8.65×10^{-6} , 7.61×10^{-6} , and $9.14 \times 10^{-6} \text{ cm}^2/\text{s}$ respectively. This model accurately predicts the dissolution of microdroplets for the ethyl acetate/butyl acetate and butyl acetate/amyl acetate systems given the solubility and diffusion coefficients of each of the individual components in water as well as the initial droplet radius. The average mean squared error was 8.96%. The dissolution of a spherical ideally mixed multi-component droplet closely follows the modified Epstein Plesset model presented here.

INTRODUCTION

Following the early work of Epstein and Plesset for gas microbubbles, the Needham lab has developed new experimental and theoretical models for the dissolution of single component (gas [1] and oil [2]) and multi-component (protein solution[3]) liquid droplets in a liquid environment. These models have been experimentally verified using a micropipette

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Author Contributions

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Supporting Information Available: The full experimental vs. theoretical prediction data for this model are available as supporting information. The data series are: Ethyl Acetate/Butyl Acetate droplets in ratios of 3:1, 1:1, and 1:3, and Butyl Acetate/Amyl Acetate droplets in ratios of 3:1, 1:1, and 1:3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

technique capable of forming and manipulating single microdroplets of one immiscible liquid in a second dissolving solvent. These single microdroplets have volumes on the order of tens of picoliters, and are formed and manipulated in a .8 mL glass cuvette. They can therefore be considered to be in infinite dilution and well below their solubility limit. In this paper, we present a new model based on the Epstein Plesset equation for mass transfer of single component and two component mixtures of mutually -miscible liquids (ethyl acetate, butyl acetate and amyl acetate) from single liquid microdroplets diffusively dissolving into a second immiscible solvent (water), as well as experimental verification for this model. Additionally, we report three new values for diffusion coefficients of ethyl acetate, butyl acetate, and amyl acetate in water. These single microdroplet studies and accompanying models can now inform our knowledge of multi-component mixing and mass transfer for multi droplet suspensions on the bulk scale.

In those earlier papers, we used the classic diffusion-based droplet dissolution model of Epstein and Plessett[4] to model the dissolution of air microbubbles in water [1] and then both aniline droplets in water and water droplets in aniline[2]. Su *et al*[5] used the dissolution of water droplets in *n*-alkanes (*n*-pentane to *n*-hexadecane) and *n*-alcohols (*n*-butanol to *n*-octanol) to measure the diffusion coefficients of water in these homologous series, finding that the diffusion coefficients of water in alcohols was some 25 times slower than in the same viscosity alkane. By using a microdroplet of protein solution in *n*-decanol, Rickard *et al*[3] was able to show how, as water is lost, the protein solution concentrates to reduce the water of solution, and even the water of hydration of a protein like lysozyme to a density of 1100mg/ml [3]). This process of “microglassification” is now forming the basis for new protein preservation and formulation studies.

The micropipette system, mounted on an inverted microscope, allows us to study any liquid-liquid system as long as it is immiscible; that is, as long as the droplet material forms an interface with the surrounding medium. Ethyl acetate, butyl acetate, and amyl acetate were chosen as a model homologous series because they are all soluble in water (Table 1), are expected to mix ideally in their own liquid solution, and each of these chemicals is immiscible with water (Table 1, Figure 4), as can be seen from their positive interfacial tension with water, and the ability to form a microdroplet in an aqueous phase. As shown schematically in Fig. 1, ethyl, butyl, and amyl acetate are all molecules with the same polar acetate group and a carbon chain. Ethyl, butyl, and amyl acetate differ only in the length of the carbon chain, with ethyl, butyl, and amyl acetates having two, four, and five carbon chains, respectively. In the model it is assumed that, because these molecules all have the same polar acetate group, each molecule should have similar adsorption to the droplet interface with water, and hence the same area per molecule normal to the interface. The longer carbon chain results in a lowered solubility in water as shown in Table 1). Because of this lowered solubility, we expect a longer carbon chain will correspond to a slower rate of mass transfer from the micro-droplets into the surrounding aqueous medium.

Mass transfer in a system of many droplets is a common occurrence in liquid-liquid extraction processes. Liquid-liquid extraction processes have been used in analytical chemistry since 1892, when Rothe[6] described an extraction method based on the differing solubilities of ferric chloride (soluble) and manganous, nickelous, chromic, and aluminum chlorides (insoluble) in ether in the presence of hydrochloric acid. Since then, liquid-liquid extraction processes have been widely used for a large number of purposes, including the formation of polymer microspheres through solvent evaporation[7–13], in uranium production[14] and, in new innovation from our lab, the formation of dehydrated, glassified protein microspheres[3]. Mass transfer in these systems, however, is difficult to model *en masse* for multi-particle systems. Understanding the mass transfer in a single droplet system can improve models of more thermodynamically and kinetically complex, multi-particle

systems. Nauman[15], for example, proposed a simple model for micromixing based on the idea that the mixing of one liquid into another can be modeled by the dissolution of a large number of uniform spherical droplets diffusing into a liquid with a suitable average concentration. Rys[16] proposed a simple mixing-reaction model based on the idea that a liquid mixed into another can be thought of as forming spherical constant-radius liquid elements.

Previous studies of the dissolution of two component droplets in another liquid has been primarily focused on interfacial turbulence which can rapidly increase mass transfer[17]. Because of the greater interest in the literature in this spontaneous interfacial turbulence (which does not occur in our static system), the purely diffusive dissolution of droplets of a liquid mixture in another liquid remains relatively unexplored, and is one motivation for addressing it in the current paper. In principle, single particle studies could also explore the interfacial turbulence, which will be addressed in future studies.

We present a new model, based upon a modification to the Epstein Plesset equation, for diffusive single particle dissolution of a multi component droplet. This model approximates this amount by assuming ideal homogenous mixing both in the internal volume of the microdroplet and at its interface. Our model has been tested for single microdroplets of short chain alkyl acetate liquid mixtures by using our signature micropipette-based method. As this model assumes diffusive dissolution and ideal mixing, it cannot be applied for systems where core-shell structures may form at the microdroplet boundary, or micelles in the bathing medium are involved in diffusive transport. These phenomena are also currently under study, and are accessible, one particle at a time, using the micropipet technique.

MODEL DEVELOPMENT: DROPLETS COMPRISED OF A MIXTURE OF TWO MUTUALLY-MISCIBLE LIQUIDS DISSOLVING IN A SECOND IMMISCIBLE SOLVENT

The Epstein-Plesset equation [4] was originally derived by Epstein and Plesset to describe the dissolution of a gas bubble due to diffusive mass transfer into an undersaturated liquid-gas solution, as well as the rate of growth of a bubble in an oversaturated liquid-gas solution. Duncan and Needham[1] tested this equation for dissolution of single air microbubbles. While the EP model had remained difficult to test on mm-sized bubbles because of their relatively long dissolution time, the micropipet technique allowed them to form single microbubbles. That is, by taking advantage of scaling ($x^2 = 2Dt$) into the micrometer range, dissolution could occur and be measured accurately in a laboratory time frame of just a few seconds. They could therefore show that the EP model was indeed a very good model for gas microbubble dissolution. Since air is relatively hydrophobic, they then hypothesized that this model might also predict the dissolution of organic liquids into water. They then applied this equation to the dissolution of a liquid droplet (aniline or water) in another liquid (water or aniline) [2] where mutual diffusion coefficients and solubilities of aniline and water were already known from the literature, and showed, again that the Epstein-Plesset model predicted liquid-in-liquid dissolution.

Based upon the concentration gradient at the edge of the droplet and the diffusion coefficient of the droplet material in the surrounding medium, an expression can be derived for the mass flow out of the droplet, which can then be related to the change in the dimensions of the droplet via its density.

The detailed derivation of the Epstein-Plesset equation is available in the original paper by Epstein and Plesset[4]. The mass transfer expression obtained from the Epstein-Plesset equation is:

$$\frac{dm}{dt} = D(c_0 - c_s) \left\{ \frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right\} \quad (1)$$

where D is the diffusion coefficient of the droplet material in the surrounding medium, R is the radius of the droplet, t is the time, c_0 is the initial concentration of the droplet material in the surrounding medium, and c_s is the saturation concentration of the droplet material in the surrounding medium. Since what is measured in the single microdroplet micropipette experiment [1, 2, 5] is the diameter of the microdroplet over time, this expression can be turned into the equivalent expression for the change in radius R over time, including fractional saturation, through the definition of density as mass per volume:

$$\frac{dR}{dt} = \frac{D c_s (1-f)}{\rho} \left\{ \frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right\} \quad (2)$$

where f is the ratio of the initial concentration of the droplet material in the surrounding medium c_0 over the saturation concentration of the droplet material in the surrounding material c_s , (i.e., c_0/c_s) and ρ is density of the dissolving liquid. This is the Epstein-Plesset equation as used by Duncan and Needham [2] for single component droplets, (e.g., either aniline droplet dissolving in water or a water droplet dissolving in aniline, and by Su *et al* [5], for water droplets dissolving in alkanes and alcohols).

In order to accommodate a mixture of liquids in the droplet, it is now assumed that two miscible liquids in a droplet mix ideally and are homogeneously distributed throughout the droplet, including at its interface, i.e., the area per molecule at the interface (and indeed, at any radial circumference throughout the droplet) reflects the ideal mixing of the two components. According to the Epstein Plesset equation, mass transfer due to diffusion from of a pure droplet is related to the concentration gradient at the boundary and the surface area through which mass is transferred. It can therefore be assumed that the surface area available to each component of the droplet is in proportion to the volume fraction that each component occupies in the droplet.

The total mass flux into the surrounding area, J_{total} , will be equal to $J_{\text{total}} = J_{\text{liquid 1}} + J_{\text{liquid 2}}$ where $J_{\text{liquid 1}}$ and $J_{\text{liquid 2}}$ are the mass flux of each component of the droplet. From the Epstein Plesset derivation, the concentration gradient at the edge of the droplet is given by:

$$\left(\frac{\partial c}{\partial r} \right)_R = (c_i - c_s) \left\{ \frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right\} \quad (3)$$

where c_i and c_s are the initial and saturation concentrations of the droplet material in the surrounding medium, respectively.

Furthermore, from Fick's first law, the mass flux from the droplet is proportional to the concentration gradient via the diffusion coefficient. The mass transferred by this mass flux is, in turn, proportional to the surface area through which the flux occurs, which is assumed to be proportional to the volume fraction of the components. Hence, the mass flux of each component i is

$$\frac{dm_i}{dt} = A_{\text{frac}_i} D_i (c_i - c_s) \left\{ \frac{1}{R} + \frac{1}{\sqrt{\pi D_i t}} \right\} \quad (4)$$

where, A_{frac_i} is the area fraction of component i and D_i is the coefficient of diffusion of component i in the surrounding medium. These mass fluxes can be related to volume

changes via the density of each component, which can, in turn, be related to the radius of a spherical droplet, which is what we measure (diameter) in the single microdroplet dissolution experiment. Naturally, for the case for which a single liquid comprises the entirety of the droplet, this collapses back to the original Epstein-Plesset equation. Thus, this equation effectively tests for ideality of mixing in the droplet and importantly, ideality of adsorption (surface excess concentrations) at the interface. It is this equation that is now compared to the experimental data for dissolution of single droplet mixtures.

DIFFUSION COEFFICIENT MEASUREMENT

In order to use this model, diffusion coefficients of pure ethyl, butyl, and amyl acetate in water were first measured using the technique of Su *et al*[5]. This technique is based on measuring the radius vs time profile of a dissolving pure spherical droplet of solvent into water. Since solubility of these acetates is known from the literature (Table 1), diffusion coefficient can be obtained from a curve-fit of the Epstein Plesset equation (Equation 2) to the experimental data. The results are summarized in Table 2.

MATERIALS AND METHODS

Materials

Butyl acetate (CAS No: 123-86-4, 99.5% pure) was obtained from Sigma Aldrich (St. Louis, Missouri). Ethyl acetate (CAS No: 141-78-6, 99.9% pure) and amyl acetate (628-63-7, 99.5% pure) were purchased from Mallinckrodt (St. Louis, Missouri). Deionized water was purified through a Branstead Nanopure Life Sciences (UV/UF) ultrapure water system.

Method

The two-chamber technique (Fig 2), previously described in Su *et al.* [5], was used for these experiments. This technique uses two .8 mL cuvettes that are mounted side by side on a microscope slide, as shown in Figure 2. Briefly, two chambers were employed. One chamber contained the liquid that will make the droplets. The other chamber contained both the surrounding liquid that the droplets will be formed in and a small amount of a relatively inert plug material (Figure 3) (water saturated with the respective solvents) that separates the droplet material from the rest of the pipet volume. By inserting the micropipette into the cuvettes in the correct order, an amount (~10 pico liters) of plug material was drawn into the micropipette, followed by 20–30 pico liters of droplet material. This plug material prevented evaporation of the droplet material out of the rear of the (air-filled) micropipette. After moving this front-filled micropipet to the adjacent cuvette, the droplet material was then gently blown into the cuvette containing the surrounding medium, retained on the end of the pipet, and the dissolution of this droplet was observed through the microscope. Droplet diameter vs time was measured on a recording of the experiment using calibrated video calipers. An image of a micro-droplet formed and isolated on the end of a micropipette is shown in Figure 4.

The concentration of the droplet material is clearly constant for pure liquid droplets containing a single component. The same is not true, however, for droplets that contain more than one component. In this case, all mass transfer processes occurring throughout the experiment must be carefully accounted for, including experimental errors due to evaporation of droplet and surrounding media (and therefore change of concentration of the solutions) during all phases of the experiment, including any time a bottled sample of organic mixture is not stoppered. While this is not a problem for pure systems, or for liquids that are not particularly volatile, problems arise when studying systems that are more

volatile and will evaporate into the surrounding air environment, such as is the case for solution mixtures containing the ethyl acetate.

In order to eliminate this source of error in both the chamber and the pipet, the non-volatile plug of water saturated with the respective solvents is placed at the entrance to the cuvette that contains the droplet material, as shown in Fig 3. This aqueous plug is saturated with the droplet material. This greatly slows the transfer of mass from the cuvette to the surrounding environment and for all intents and purposes eliminates it as an experimental variable. While some plug material may diffuse into the cuvette, on a case-by-case basis, selection of the appropriate material should ensure that this quantity is minimal, as shown in Fig 3a.

RESULTS AND DISCUSSION

Formation and Dissolution of a Single Droplet

The two-chamber technique allows droplets to be created, by expelling the already drawn-in liquid from the micropipet tip, in 0.1 – 0.5 s. The time taken to form a micro-droplet is relatively short in comparison with the overall lifetime of the droplet during its dissolution phase, which in these experiments ranges anywhere from ~100s to ~400s. However, appreciable mass transfer can still occur during this droplet creation, or ‘blowing out’ phase, especially when one component is extremely soluble in the surrounding medium (such as ethyl acetate in water).

We therefore estimated the quantity of mass transfer into the aqueous phase that occurs during this 0.1 – 0.5 s ‘droplet formation (“blowing out”)’ process. The quantity of lost material is estimated by applying the multicomponent droplet model developed in this paper. This involves obtaining a value for mass lost at each time point by measuring the radius of the droplet during the ‘blowing out’ process every 0.1 seconds, finding the total surface area available, and applying Equation 4. The amount of the correction will be highly dependent on both the composition of the system and the size of the droplet. As an example, a droplet formed in .27 seconds containing 3 parts ethyl acetate to 1 part butyl acetate may, in fact, be estimated to contain 2.97 parts ethyl acetate to 1 part butyl acetate once the droplet is completely formed, having lost this 0.03 parts of ethyl acetate even during the .27 seconds of droplet formation.

Figures 5 and 6 include the droplet radius measurements made during this initial droplet formation process. This process is completed within 0.1 – 0.5 seconds, in comparison to the tens to hundreds of seconds of our droplet lifetime. This difference in timescales may cause these data points to appear to fall upon the y (radius) axis.

Droplet Mixtures

Droplets consisting of mixtures of either ethyl acetate/butyl acetate or butyl acetate/ethyl acetate were formed from the micropipette into water. Ethyl acetate, butyl acetate, and ethyl acetate are soluble in water with solubilities between 8 to $0.2 \times 10^{-2} \text{ g/cm}^3$ (see Table 1) [19].

Theoretical comparisons to the experimental data (EtAc – ButAc, and But Ac – AmylAc at mol %s of 100:0, 75:25, 50:50, 25:75, 0:100) are shown in Figs. 5 and 6. Because the droplets are perfectly spherical, measurements of droplet diameter are simply converted to radius and plotted versus time. Our plots show the time rate of change of droplet size due to loss of material into the surrounding water, and the characteristically increasing droplet dissolution rate predicted by the modified Epstein Plesset model. As shown in Fig 5, microdroplets of about the same size (40 – 43 microns radius), dissolved increasingly more slowly as droplet composition was changed from pure ethyl acetate to pure butyl acetate.

Similarly, for the series from butyl to amyl (Fig. 6), microdroplets (40 – 45 microns radius) dissolved increasingly more slowly with increasing fraction of amyl acetate. Comparison of the data to the modified Epstein-Plesset model shows that both components of the droplet begin to diffuse from the droplet as soon as the droplet is formed in the second solvent medium.

We have included in our supporting information theoretical comparisons to the experimental data, where the model matches the single microdroplet experimental observations. As expected, droplets containing a mixture of ethyl acetate and butyl acetate (Fig 6.) dissolve more slowly than a droplet of pure ethyl acetate, and more quickly than a droplet of pure butyl acetate (Fig 5.) Similarly, droplets containing a mixture of butyl acetate and amyl acetate dissolve more slowly than a droplet of pure butyl acetate, and more quickly than a droplet of pure amyl acetate (Fig 6.) Interestingly the individual “S”-shaped dissolution curve (most prominent in the ethyl acetate-butyl acetate mixture) is well represented by the model as the more soluble smaller component leaves first and the less soluble component concentrates and leaves last.

In order to evaluate the closeness of fit (solubilities were known and diffusion coefficients were fitted), we calculated the mean squared error (MSE) for our theoretical model prediction versus experimental results for each of our droplets. In order to give a feel for the size of this difference between our theoretical values and our results, we calculated mean squared error as a percentage of initial droplet diameter. As can be seen in Table 3, the average mean squared error for the droplets ranged from 3.40% (25 % Ethyl Acetate, 75% Butyl Acetate), to 15.56% (75% Butyl Acetate, 25% Amyl Acetate). Overall, our model had an average mean squared error of 8.96% for all systems evaluated, which shows that our model is a good fit for the data.

Figure 7 shows the time for dissolution of 45 um radius microdroplets dissolving in water versus the whole range of droplet composition. It is clear that dissolution time is a function of the composition of the droplet. For a given droplet size, the droplet mixtures have a dissolution time between the dissolution time of the pure fastest dissolving droplet and the pure slowest dissolving droplet. For example, a droplet containing a mixture of ethyl and butyl acetates has a dissolution time between that of pure ethyl acetate and pure butyl acetate. The more butyl acetate a droplet contains, the more similar its dissolution time to the pure butyl acetate; similarly, the more ethyl acetate a droplet contains, the faster its dissolution time.

The underlying assumption of this model is that each component of the droplet leaves in accordance to its proportion of the droplet surface area that the homogeneously mixed component occupies. Because this model successfully reflects our experimental findings, the droplet components must indeed mix homogeneously. Deviation from this model may, in the future, be used as an indicator of inhomogeneous mixing, surface accumulation, and even shell formation.

The micropipette technique allows the measurement of the dissolution of a single spherical microdroplet of pure and mixed compositions. The developed theoretical model and single microdroplet experiments represent, to the best of our knowledge, the first model and experimental verification for the diffusive dissolution of a multicomponent spherical droplet containing two ideally mixed components. The model is particularly relevant to our understanding of liquid-liquid extraction processes, in which one, more soluble, component is extracted from a mixture. By understanding how this process proceeds in this idealized purely diffusive spherical dissolution system, a solid foundation can be established which can contribute to the understanding of more complicated systems, such as is the case for

bulk suspension systems of many particles, or when mixing and stirring occur. Understanding the dissolution of a microdroplet on a single particle scale can also guide the scale-up of these processes.

CONCLUSION

A modification to the Epstein Plesset equation based upon a reduced surface area approximation has been presented and evaluated experimentally. This modified equation models the dissolution of a liquid droplet mixture in a liquid environment in which both components of the droplet are soluble in the aqueous phase. With fast diffusive equilibration within the microdroplet, it assumes that their fractional volume in the microdroplet solution mixture represents the fractional surface coverage by each component at any moment in time during the dissolution process. Additionally, a modification to the two-chamber method, as previously laid out in Su *et al*[5] is presented which allows for the study of multi-component droplets, that overcomes the challenge of working with relatively more volatile materials.

This model has been shown to accurately predict the dissolution of microdroplets for the ethyl acetate/butyl acetate and butyl acetate/ethyl acetate systems given the solubility and diffusion coefficients of each of the pure components in water as well as the initial droplet radius. Care should be taken, however, in applying the model to systems where the assumptions of homogenous mixing does not hold true. In the case where there exists a surface excess of one component of the droplet, this model is expected to fail since the occupied fractional surface would not match the volume fraction due to surface excess concentrations that arise because of for example surface activity. In such cases, interest shifts to the time taken to form shells, and their relative stability at droplet interfaces. Similarly, in any case where slow diffusion causes concentration gradients within the droplet, deviation from the model is expected, such as for large macromolecules. In this instance, it might be expected that they also could form insoluble shells.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Chemical structures of (a) Ethyl Acetate (b) Butyl Acetate (c) Amyl Acetate

Figure 2. Illustration of the two-chamber method. The pipette is inserted into the chamber containing the test liquid, A. Liquid is drawn into the pipette, which is then withdrawn from the micro-chamber and placed into liquid B. A droplet of liquid A may then be blown into the micro-chamber containing liquid B the test solvent for A dissolution.

Figure 3.

Two cuvettes, side by side, illustrating the use of immiscible solvent plugs. Since the droplet liquid must be kept at a constant concentration, and the droplet liquid may be volatile, a saturated solvent plug (in this case, water saturated with the respective solvents) is first drawn into the micropipet followed by the desired droplet liquid to avoid evaporation. The loaded pipet is then simply transferred from chamber 1 to chamber 2 and the droplet is blown out into the desired surrounding immiscible liquid. The same immiscible solvent plug is also used in the entrance to the microchamber to prevent any loss into the lab air environment.

Figure 4. Ethyl Acetate droplet in water (Diameter = 42 micrometers) formed and isolated on the end of a micropipet. Despite its relatively high solubility in water of $8 \times 10^{-2} \text{ g/cm}^3$, ethyl acetate has a positive surface tension (as do butyl and amyl acetates), is immiscible with water and so forms a clear and measurable interface. Diameter was measured using video calipers.

Figure 5.

For microdroplets all about the same size (40 – 43 microns radius), here are the experimental Ethyl Acetate/Butyl Acetate droplet dissolution compared with model predictions in order of increasing amount of butyl acetate. Experimental data points (from left to right): Pure ethyl acetate droplet (diamonds), 3:1 ethyl acetate/butyl acetate (triangles), 1:1 ethyl acetate/butyl acetate (*), 1:3 ethyl acetate/butyl acetate (+), and pure butyl acetate (-).

Figure 6.

For microdroplets all about the same size (40 – 45 microns radius), here are the experimental Butyl Acetate/Amyl Acetate droplet dissolution compared with model predictions in order of increasing amount of amyl acetate. Experimental data points (from left to right): Pure butyl acetate droplet (diamonds), 3:1 butyl acetate/amyl acetate (triangles), 1:1 butyl acetate/amyl acetate (x), 1:3 butyl acetate/amyl acetate (+), and pure amyl acetate (-).

Figure 7.

Time for dissolution of ($R=45$ μm) droplets dissolving in water for each droplet composition. From left to right: Pure ethyl acetate, 3:1 ethyl acetate/butyl acetate, 1:1 ethyl acetate/butyl acetate, 1:3 ethyl acetate/butyl acetate, pure butyl acetate, 3:1 butyl acetate/amyl acetate.

Table 1

Solubility values for ethyl acetate from[18]. Solubility of Butyl acetate from[19]. Solubility of Amyl Acetate from[20]. Density values from[21].

Chemical	Density (g/cm ³)	Solubility in Water (g/cm ³)	Interfacial Tension with Water (dynes/cm)
Ethyl Acetate	0.895	8×10^{-2}	6.8
Butyl Acetate	0.879	7.8×10^{-3}	14.5
Amyl Acetate	0.859	2.2×10^{-3}	15.2

Table 2

Diffusion coefficients as measured using the method of Su *et al* [5].

Chemical	D in Water (cm ² /s)
Ethyl Acetate	$8.65 \times 10^{-6} (\pm 9 \times 10^{-7})$
Butyl Acetate	$7.61 \times 10^{-6} (\pm 4 \times 10^{-7})$
Amyl Acetate	$9.14 \times 10^{-6} (\pm 6 \times 10^{-7})$

Table 3

Mean Standard Error of the model compared to the experimental measurements for each system. Average mean standard error for the droplets ranged from 3.40% (25% Ethyl Acetate, 75 % Butyl Acetate) to 15.56% (75% parts Butyl Acetate, 25% Amyl Acetate). Overall, the average mean standard error was 8.96% for all systems evaluated.

Percent Ethyl Acetate	Percent Butyl Acetate	Average Mean Standard Error
75%	25%	8.01%
50%	50%	8.11%
25%	75%	3.40%
Percent Butyl Acetate	Percent Amyl Acetate	
75%	25%	15.56%
50%	50%	7.90%
25%	75%	10.08%
Overall Average Mean Standard Error		8.96%