Diffusion across the Interface of an Liquid-Liquid System

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In chemical engineering extraction plays a crucial role for the purification of products ranging from bulk products to biopharmaceuticals. For the extraction the mass transfer of the target product across the interface is essential as it determines the residence time and so the dimensions of the extraction unit. The nature of the interface between two fluids has been the subject of science since Young, Laplace and Gauss in the 1800. All three have the assumption of an interface between two fluids as a surface of zero thickness. On this surface there would be unsteadiness in all physical properties. Later Poisson, Maxwell and Gibbs recognized that the interface actually represented a rapid but smooth transition of physical quantities between the bulk fluid values. The idea of an interface with a non-zero thickness was developed in detail by Lord Rayleigh and van der Waals proposing gradient theories for the interface based on thermodynamic principles [1]. Based on the ideas of the gradient theory by Van der Waals, Cahn and Hilliard developed the spinodal decomposition [2]. In contrast to other mass transfer models, the thermodynamics can be directly considered by the inclusion of the Helmholtz free energy in the Cahn-Hilliard theory. Up to now, relative simple thermodynamic models were used which cannot represent experimental data.

The aim of this work is to close this gap in the modelling of mass transfer across the interface using the Cahn Hilliard theory. For this reason, different systems will be investigated. These systems contain polymer blend or polymer solutions. In the scope of this work is the impact of different functional groups of polymers and the structure of polymers on the mass transfer. For this investigation two phenomena will be regarded: On the one hand the dissolution of drops and the demixing of liquids.

One Example is the calculation of the interfacial properties of PDMS/PDMSE. Figure 1 (left) shows the liquid-liquid equilibrium (LLE), which can be calculated in good accordance with experimental data by the Koningsveld-Kleintjens approach. By combination of this approach with density gradient theory the interfacial tension can be calculated Figure 1 (right).

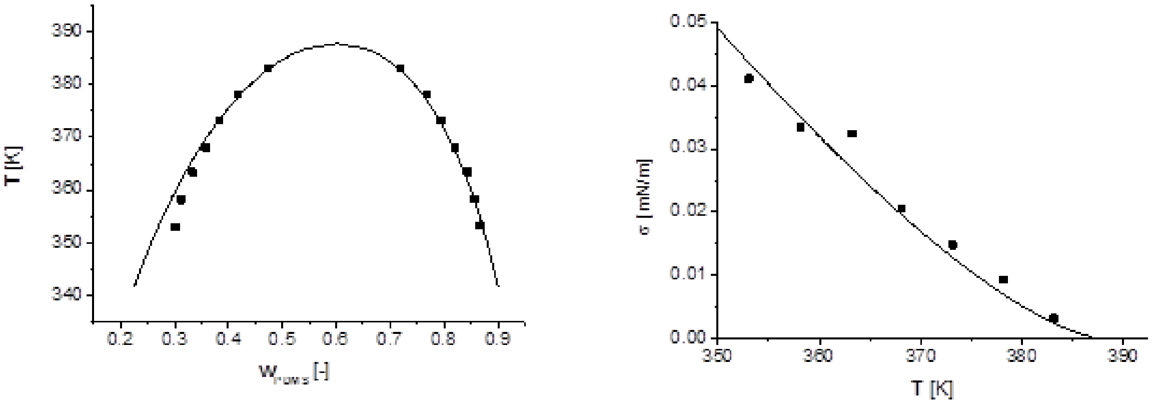

Figure 1: Left: Liquid-liquid equilirbium of PDMS and PDMSE calculated by Koningsveld-Kleintjens approach and compared to experimental data. Right: Interfacial Tension of PDMS/PDMSE calculated by Koningsveld-Kleintjens in combination with Density Gradient Theory.

Based on the determined influence parameter, the concentration profile for different periods of time can be calculated. Figure 2 (left) shows the concentration as profile at different periods of time and the equilibrium concentration profile. As initial profile a line was used superposed by a sinus function with very small amplitude to get perturbation for the demixing. By comparing the profiles at equilibrium and a long period of time, it can be stated, that the equilibrium is reached.

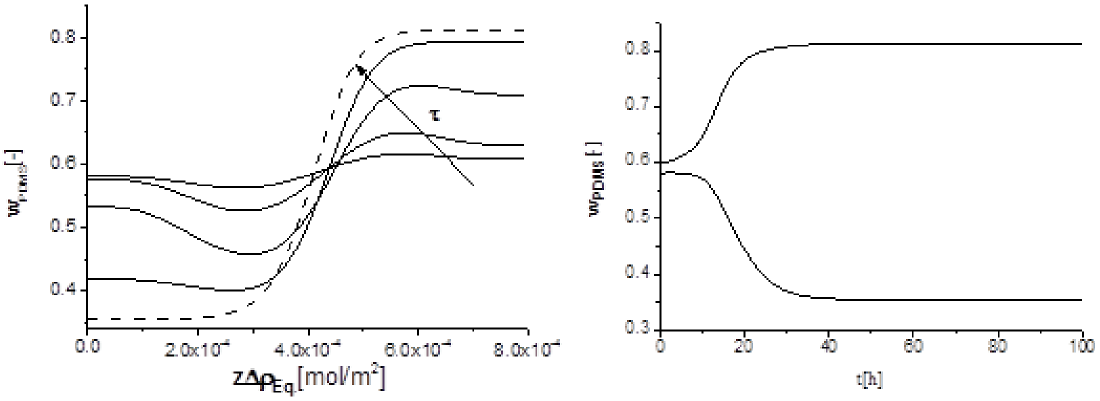

Figure 2: Demixing of the system PDMS-PDMSE (Left) at 369 K: Broken line is the profile in equilibrium and the straight lines are the concentration profiles at different times. Development of the concentration in the bulkphase with time (right) at 369 K.

Moreover, it can be seen that in contrast to sharp interface models, the interface is changing during the whole demixing process, as the steepness of the concentration profile and the width of the interfacial region is changed. On the right hand side of Figure 2, the weight fraction of PDMS in the bulk phase is shown and it an asymmetric demixing behavior was calculated because of the used thermodynamic model. Furthermore, the bulk phases reached after 40 hours the equilibrium.

In contrast to other works [3], this contribution investigates the interfacial mass transfer of real liquid-liquid system offering the possibility to develop new transport models.

References

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