THE DISSOLUTION OF AN INTERFACE BETWEEN MISCIBLE LIQUIDS

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Abstract

The dissapearance of the surface tension of the interface of a binary mixture, measured using the dynamic surface light scattering technique, is slower for a binary mixture of higher density contrast. A comparison with a naive diffusion model, expected to provide a lower limit for the speed of dissolution in the absence of gravity shows that the the interfacial surface tension dissapears much slower than even by diffusion with the effect becoming much more pronounced when density contrast between the liquid phases is increased. Thus, the factor most likely to be responsible for this anomalously slow dissolution is gravity. A mechanism could be based on the competition between diffusive relaxation and sedimentation at the dissolving interface.

In a previous experiment[1] May and Maher studied the process of dissolution of liquid interfaces between miscible liquids by using dynamic surface light scattering. They observed that the interfacial surface tension decays anomalously slowly during the dissolution. They speculated that the process might be affected by gravity slowing down the dissolution. Computer simulations[2] of the process were not able to identify a significantly different rate of dissolution unless a strong restoring field was introduced into the simulations.

We have designed and performed experiments to explore the role of gravity in the interfacial dissolution process. We chose to study the well understood[3] cyclohexane and methanol (CM) binary mixture, since the densities of the components are naturally well matched. The strength of the coupling with gravity can be tuned by mixing in deuterated forms of the two components[4], which change the density contrast across the interface.

For CM the density contrast between the upper and lower phase at a temperature of 225 mK below T_c is $2 \cdot 10^{-3}$ g/cm^3. When a small amount of deuterated cyclohexane ia added, the density contrast can be considerably reduced[4]. We prepared a cyclohexane + deuterated cyclohexane + methanol mixture (CDCM) of deuterated fraction 1.65% which have a density contrast about 5 times smaller than the density contrast for CM. For such a small density difference the density contrast is obtained from the measurement of the cap-

illary length as in Ref. [5] since the rule of additivity of volumes fails[4]. To explore an even larger range of density contrast we prepared a cyclohexane and deuterated methanol d_4 (CDM) mixture, of density contrast about 8 times larger than CM.

At a temperature below the critical temperature the mixture is in a two phase state, and the upper and lower phases are separated by a sharp interface of the order of the correlation length. After the mixture's temperature is raised above T_c the interface starts dissolving while the system evolves toward the thermodynamic equilibrium one phase state.

The dissolution process can be studied by measuring the autocorrelation function of the light scattered by the capillary waves which naturally exist on the interface. For a binary mixture near the critical temperature the capillary waves are overdamped and the dispersion relation for interfacial capillary waves allows the reduction of the surface light scattering autocorrelation function to the form[6]:

$$G(t) \sim e^{-t/\tau} \tag{1}$$

with the relaxation time

$$\tau = \frac{2(\eta_1 + \eta_2)}{\sigma q} \tag{2}$$

where η_1 and η_2 are the viscosities of the two liquids, σ is the interfacial tension and q is the wavenumber of the scattered light. Thus, the interfacial surface tension can be extracted from the autocorrelation function of the scattered light.

Having an extremely small density contast, CDCM was unstable during heating. The flow of the mixture along the walls of the cell distroyed the integrity of the interface and we had to abandon our autocorrelation function measurements on this mixture. For the other two mixtures, CM and CDM the temperature gradients were brought under control by setting the heating time to a few minutes. About 30 minutes after raising the temperature, the mixture typically reached thermal equilibrium and the interface regained its flatness lost during the heating process. Our experiments showed that, after the temperature was raised, the relaxation time of the autocorrelation function for CDM is significantly smaller than that of CM indicating a smaller reduction in the effective interfacial tension and a corresponding slower progress to the interfacial dissolution. Since the main difference between the two mixtures is the density

contrast, which is higher for CDM, we attribute this difference in dissolution to the effect of gravity.

During the dissolution, the thermodynamic state of the system is far from equilibrium and the dynamics of the process is difficult to understand. However, in the absence of gravity we might expect that the mixing process should evolve at least as fast as diffusion. Since anything other than diffusion should speed up the mixing process, diffusion should set a lower limit for the speed of dissolution.

May and Maher compared the surface tension data obtained for an isobutyric acid and water binary mixture with a naive diffusion model and found that the interface dissolves even slower than diffusion. In a naive diffusion model of the interface, the smooth density gradient inside the interface can be taken as constant. A dissolving interface contains a significant amount of free energy due to the concentration gradients. As in the case of an equilibrium interface, an effective surface tension can be defined even for a dissolving interface[7],

$$\sigma \propto \int \left(\frac{dc}{dz} \right)^2 dz \qquad (3)$$

where c is the local composition and z is the direction normal to the interface.

This naive diffusion model predicts that the surface tension of the dissolving interface should be inverse proportional to the interface thickness

$$\sigma = \frac{F(T,t)}{[\xi_0 + (D_{eff}t)^{1/2}]} \qquad (4)$$

In agreement with May and Maher experiments, the results of our experiments found that the interfaces of both CM and CDM mixtures dissolve even slower than predicted by the naive diffusion model, expected to set a lower limit for the speed of dissolution. Together with the results that the interface of CDM dissloves even slower than the interface of CM, this strongly suggests that gravity is indeed slowing down the dissolution process.

In order to understand how gravity can affect the dissolution process, we propose a dimensional argument for a dissolving interface based on the competition between diffusion and sedimentation. Let us consider a domain of radius R, of the order of the interface thickness. The domain is dissolved diffusively in a time of the order of

$$\tau_d = \frac{R^2}{D}. \qquad (5)$$

where D is the diffusion constant. Gravity sediments the domain. A characteristic time for sedimentation can be

obtained as the time in which the fluctuation travels a distance equal to its own radius. Neglecting a multiplying numerical geometrical factor which depends on the shape of the domain, the sedimentation characteristic time should be

$$\tau_s = \frac{\eta}{R\Delta\rho g} \qquad (6)$$

where g is the gravitational acceleration and $\Delta\rho$ is the density difference between the liquids.

Immediately after the temperature of the mixture is raised and the interface starts dissolving, the interface thickness is small, the diffusion time is much smaller than the sedimentation time, and the dissolution process is dominated by diffusion. But as the interface thickness increases, the relative importance of the sedimentation increases. When the two characteristic times have the same order of magnitude, gravity might begin affecting the dissolution.

A length scale for the interface thickness, R^*, is selected by this competition. R^* is obtained by setting the two characteristic times equal.

$$R^{*3} = \frac{\eta D}{\Delta\rho g}. \qquad (7)$$

With reasonable numbers for the systems in the present experiment, the interface thickness reaches R^* in about 2-3 minutes for CM and about 30 sec for the CDM. This is a very large time for computer simulations of the dynamics of the dissolving interfaces and this could explain the failure of the simulations to observe a dissolution process different from diffusion.

Density fluctuations of size of the order of R^* could create a high density gradient inhomogeneous layer of thickness of the order of R^*. A recent experiment by Alberto Vailati and Marzio Giglio[8] showed that "giant

$Mixture$	$T_{final} - T_c$ (mK)	L ($10^{-4}cm$)	R^* ($10^{-4}cm$)
CM	35	9.0 ± 5.0	4.9
CM	52	6.2 ± 3.5	5.3
CM	95	7.2 ± 3.6	6.0
CM	173	5.2 ± 4.1	6.8
CDM	35	4.0 ± 1.6	2.5
CDM	61	1.5 ± 0.7	2.8
CDM	172	1.7 ± 0.7	3.5

Table 1: The interface thickness extracted from the results obtained in the surface light scattering experiments (L) vs R^*, the thickness selected by the diffusion/sedimentation competition across the interface.

fluctuations" at the interface in binary mixtures do exist under conditions similar to our system.

Our results from the surface light scattering experiments are consistent with the dimensional argument for competition between diffusion and sedimentation. Table 1 shows the magnitude of R^* and L, the thickness of the interface obtained from the experimental data. The magnitude of the thickness of the inhomogeneous region was extracted from the surface tension by using the simplifying assumption that the concentration difference between the upper and lower plane of the inhomogeneous region does not change in time.

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