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The prediction of Marangoni convection in binary liquid–liquid systems with added surfactants

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Abstract

The theoretically predicted stability of various binary liquid–liquid interfaces in the presence of a transferring surfactant is examined and compared against experimental observations. It is found that the accuracy of some of the current stability criteria in predicting interfacial stability under such conditions is poor. To improve this, a Marangoni coefficient is proposed, the magnitude of which predicts well the presence of surfactant induced Marangoni convection in the systems studied. Plots of the variation of the interfacial tension with concentrations of the various surfactants investigated are presented and changes in its value are related to the surfactant induced Marangoni convection observed. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

It has been known for several decades that the occurrence of Marangoni convection in a mass transfer system invariably leads to large increases in the mass transfer rates. However, so far, these effects have not been included in mass transfer models mostly because of the difficulty in their prediction. Furthermore, when systems are contaminated by surfactants, these may have an added effect, which will also need to be taken into account.

The hydrodynamic stability criteria of Sternling and Scriven [1] have been extensively used to predict interfacial stability in the presence of a transferring solute between two immiscible phases and has achieved some successes [2,3] as well as failures [4,5]. In all the experiments carried out to verify these criteria the transferring solute used was an organic solvent transferring into or out of an aqueous phase. Sternling and Scriven also suggested that the presence of a surfactant in the system

would eliminate the possibility of interfacial convection on account of the effect it has on surface viscosity. This belief appears to be consistent with some earlier, and subsequent studies [6–11] which showed that the presence of very small amounts of certain surfactants dampened interfacial convection and reduced interfacial mass transfer rates.

However, more recent experimental studies point to the fact that surfactants may play a key role in creating interfacial instabilities: Nakache and Raharimalala [12] observed the kicking and oscillation of drops of nitroethane contacted with solutions of dodecyl trimethyl ammonium bromide; Aunins et al. [13] reported instabilities during the transfer of methyl nicotinate across the planar *n*-heptane–water interface, when sodium dodecyl sulphate was present in the aqueous phase; Bennett et al. [14] have used electrochemical methods to create (temporarily) surfactant species which then induce interfacial tension gradients and Marangoni convection. Other studies include those by Liang and Slater [15] and Bekki et al. [16,17]. Alongside such experimental studies several theoretical studies have been undertaken which attempt to predict the conditions under which surfactants will cause Marangoni convection to occur. In many of these studies the definition of the term surfactant has been broadened to include any

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Nomenclature		Γ	surface excess (mol m ⁻²)
C	concentration of solute (mol m ⁻³)	μ	viscosity of liquid (kg m ⁻¹ s ⁻¹)
D	diffusion coefficient (m ² s ⁻¹)		
N_{Ma}	Marangoni coefficient (m ⁻²)		
<i>Greek symbols</i>		<i>Subscripts</i>	
γ	interfacial tension (mN m ⁻¹)	A	phase A
		B	phase B

transferring solute capable of altering (measurably) the interfacial tension. Hennenberg et al. [18–20] developed stability criteria for surfactant transfer across a liquid–liquid interface; Gouda and Joos [21], Sørensen [22], Sanfeld and Steinchen [23], Chu and Velarde [24] and Nakache and co-workers [12,25,26] also proposed criteria for transfer under such conditions. In all these studies the stability of a planar liquid–liquid interface to longitudinal disturbances was studied mathematically and conditions (including surfactant properties) that give rise to instabilities proposed.

There remains, however, inadequate experimental data to substantiate the validity of most of these criteria. Bekki et al. [17] checked predictions from the stability criteria by Sternling and Scriven, by Hennenberg et al. and by Sørensen against the instabilities observed when a nitroethane lens was placed in an aqueous solution of dodecyl trimethyl ammonium bromide. Unsatisfactory agreement was reported between the observed and predicted behaviour for all of those criteria. Later, Nakache et al. [25] investigated the kicking of drops at eight different interfaces and compared the observed results with predictions from stability criteria by Sternling and Scriven, by Sanfeld and Steinchen and by Sørensen. Only five out of the eight systems studied were in agreement with either Sanfeld and Steinchen's or Sørensen's criteria. This means that the criteria used were only correct in 60% of the cases tested. Apart from these efforts no other specific studies appear to have been undertaken to establish the validity of current stability criteria where surfactants are involved.

The main purpose of this paper is to present results from the application of existing stability to a wider range of experimental systems and to propose an empirical coefficient (N_{Ma}) for the prediction of interfacial convection in binary liquid–liquid systems with surfactants.

2. Experimentally observed interfacial instability

In a previous study by Agble and Mendes-Tatsis [27] the interfacial stability of 35 different liquid–liquid interfaces was determined experimentally. The experimental procedure involved visual observations of solvent drops immersed in various aqueous solutions using the Schlieren optical technique. These 35 interfaces had been formed with five binary organic–aqueous systems (aniline–water, 1-hexanol–water, isobutanol–water, ethyl acetate–water and ethyl acetoacetate–water), when the aqueous phase was either pure water (uncontaminated) or water contaminated with one of six different surfactants. The selection of surfactants used included both ionic [sodium dodecyl sulphate (SDS), lithium dodecyl sulphate (LDS) and dodecyltrimethyl ammonium bromide (DTAB)] and non-ionic [Softanol 30 (S30), Softanol 120 (S120) and Atlas G1300] surfactants, covering a range of molecule sizes (see Table 1).

In the uncontaminated cases mass transfer was allowed to occur from the organic into the aqueous phase only. When the aqueous phase was contaminated with one of the surfactants there was also the transfer of the surfactant species, due to partitioning, in the opposite direction of the transfer of organic species. Hence, the overall mass transfer situation involved the transfer of the organic solute into the aqueous phase, alongside potential transfer of the surfactant into the organic phase. For systems in which the aqueous phase was contaminated the possibility is thus raised of interfacial tension variations, which may lead to Marangoni convection, arising from the transfer of either or both species.

In fact, it has been observed [27] that in several of the systems investigated the presence of surfactant initiated Marangoni convection at the liquid–liquid interface. Furthermore, with some systems where there was already Marangoni convection present at the uncon-

Table 1
Relative molecular mass (RMM) of the surfactants selected

Surfactant	LDS	SDS	DTA B	Softanol 30	Softanol 120	ATLAS G1300
RMM (g mol ⁻¹)	273.3	288.3	308.3	330	726	~9500


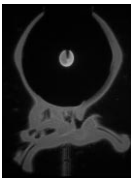
	Solvent Drop → Aqueous Phase ↓	aniline
Case (a)	water only	
Case (b)	water + SDS, 0.05g/100ml	

Fig. 1. Case (a) shows an example of a stable interface while Case (b) shows an example of an unstable interface.

taminated interface, the introduction of a surfactant to the aqueous phase increased the intensity of the convection. In a few systems, though, the presence of the surfactant caused interfacial convection to be dampened.

Experimental results obtained with similar interfaces were always repeatable, i.e., the interfaces were either consistently stable or consistently unstable. The assessment of whether an interface was either stable or unstable was based on the analysis of the Schlieren photos obtained for each type of system, as depicted in the examples shown in Cases (a) and (b) in Fig. 1. In Case (a) the aniline/water interface is seen to be well defined without any interfacial disturbances and is considered “stable”. In Case (b) the aniline/water + SDS interface shows interfacial motions and is considered “unstable”. Fig. 2, Case (a) shows an isobutanol/water interface which is also “unstable” while the isobutanol/water + Softanol 30 in Case (b) is shown to be “less unstable” than the corresponding pure system, conclusion which is even more obvious in the video films from where these images were obtained.

A summary of the experimental observations of the interfacial stability of the systems investigated is included in Table 2.

3. Application of existing stability criteria

In addition to the observed experimental stability of the systems, Table 2 also contains predictions of the interfacial stability of the systems investigated (when each surfactant was considered as the transferring species and had a concentration below the CMC) using the following stability criteria:

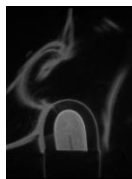

	Solvent Drop → Aqueous Phase ↓	isobutanol
Case (a)	water only	
Case (b)	water + Softanol 30 0.002g/100ml	

Fig. 2. A comparison between the intensity of motions at the interface in Case (a) and in Case (b) shows that Case (b) is “less unstable” than Case (a) (even more obvious in the video films).

1. the Sterling and Scriven criteria for ternary systems [1];
2. the Hennenberg et al. criteria for surfactant transfer by diffusion only (HBVAS-1) [18];
3. the Hennenberg et al. criteria which allows for surfactant transfer by adsorption–desorption (HBVAS-2) [19];
4. the semi-empirical criteria of Nakache et al. [25].

The first set of criteria of Hennenberg et al. is essentially equivalent to that of Sanfeld and Steinchen [23] or Sørensen [22]. All of these criteria attempt to predict the stability of a liquid–liquid interface when one solute only, in this case the surfactant, transfers from one phase to the other which is not exactly the situation in the cases studied here but the only way to do a prediction up to now. Application of these criteria to a given liquid–liquid system requires knowledge of certain physical properties of the liquids concerned, including viscosities, diffusion coefficients and the rate of change of interfacial tension with solute concentration. All the data values used for the relevant entities, and the methods used to obtain them, have been presented elsewhere [28]. For each of the stability criteria, it was therefore possible to obtain a predicted stability condition for every one of the thirty contaminated systems studied.

Assessment of each set of stability criteria was made based on whether or not the predicted condition was the same as the observed stability. However, the stability criteria predict interfacial behaviour assuming an initially *stable* system and therefore do not account for instabilities that may already have existed in the uncontaminated system. For example, Marangoni convection is observed during the transfer of isobutanol,

Table 2

Experimental observations and different theoretical predictions of the interfacial stability of the liquid–liquid systems investigated (S = stable; U = unstable; – not applicable; U♣ = less unstable than the pure system)

Liquid–liquid system	Interfacial stability				
	Observed	Predicted			
	Agble and Mendes-Tatsis [26]	Sternling and Scriven [1]	Henneberg et al. (HBVAS-1) [18]	Henneberg et al. (HBVAS-2) [19]	Nakache and co-workers [24]
Aniline–water	S	–	–	–	–
+SDS	U	S	U	S	U
+DTAB	U	S	U	S	U
+LDS	U	S	U	S	U
+S 30	S	S	U	S	S
+S 120	S	S	U	S	S
+Atlas	S	S	U	S	S
1-Hexanol–water	U	–	–	–	–
+SDS	U	S	U	S	U
+DTAB	U	S	U	S	S
+LDS	U	S	U	S	U
+S 30	S	S	U	S	S
+S 120	S	S	U	S	S
+Atlas	S	S	U	S	U
Isobutanol–water	U	–	–	–	–
+SDS	U	S	U	S	S
+DTAB	U	S	U	S	S
+LDS	U	S	U	S	S
+S 30	U♣	S	U	S	S
+S 120	S	S	U	S	S
+Atlas	S	S	U	S	S
Ethyl acetate–water	U	–	–	–	–
+SDS	U	U	U	U	U
+DTAB	U	U	U	U	U
+LDS	U	U	U	U	U
+S 30	S	U	U	U	S
+S 120	S	U	U	U	S
+Atlas	S	U	U	U	U
Ethyl acetoacetate–water	U	–	–	–	–
+SDS	U	S	U	U	U
+DTAB	U	S	U	U	S
+LDS	U♣	S	U	U	U
+S 30	U	S	U	U	S
+S 120	U	S	U	U	S
+Atlas	S	S	U	U	S

ethyl acetate or ethyl acetoacetate into uncontaminated water, even before any surfactants are introduced into the aqueous phase. Therefore, the stability of the uncontaminated system has also to be considered and this has been done in two ways.

(1) When the uncontaminated system was observed to be *unstable*, and in addition the contaminated system

displayed instabilities, then the fact that the stability criteria predict the contaminated system to be stable does not imply a disagreement between the predicted and the observed behaviour. For example, the criteria that predicted the systems ethyl acetoacetate–water + LDS, ethyl acetoacetate–water + Softanol 120 and ethyl acetoacetate–water + Softanol 30 to be *stable* are con-

sidered correct, since (given that the uncontaminated system is unstable) it is possible that the presence of the surfactant had no effect on the interfacial stability, particularly since the intensity of interfacial convection in these systems is very similar to that observed for the uncontaminated system. Only when the surfactant transfer was clearly seen to induce instabilities greater than existed in the uncontaminated system, was a contradiction between predicted and observed behaviour concluded. This was the case for the transfer of isobutanol into water with SDS, for example, where the presence of SDS induced much stronger interfacial convection than that observed during the transfer of isobutanol into pure water.

(2) However, when the instabilities observed were clearly weaker than those observed in the pure systems, as in the case of the systems isobutanol–water + Softanol 30 and ethyl acetoacetate–water + DTAB, stability criteria that predicted *stable* conditions (despite the fact that instabilities were observed) were considered correct, since the surfactant transfer obviously had a stabilising effect on the system.

4. Discussion of results

Following this procedure, the criteria of Nakache et al. appears to be the best, predicting correctly 23 out of 30 cases investigated. The criteria proposed by Sternling and Scriven correctly predicted 17 cases and the Hennenberg et al. criteria for diffusion controlled mechanisms (HBVAS-1) predicted correctly 16 cases, as did the Hennenberg et al. criteria for adsorption–desorption controlled mechanisms (HBVAS-2). If the HBVAS-2 criteria, instead of assuming adsorption–desorption controlled mechanisms for all surfactants, had assumed diffusion controlled mechanisms for ionic surfactants and adsorption–desorption controlled mechanisms for non-ionic surfactants, then the number of correct predictions increases to 25, compared with only seven correct if it had assumed adsorption–desorption controlled mechanisms for ionic surfactants and diffusion controlled mechanisms for non-ionic surfactants. However, adsorption–desorption controlled mechanisms are normally associated with ionic surfactants, due to molecular retardation by the electrical double layer at the interface, [29,30], so fewer rather than more correct predictions will result if this is taken into account.

One of the reasons that both of HBVAS-1's and HBVAS-2's criteria and Sternling and Scriven's criteria do not predict stability conditions very accurately is that they appear to predict either stable conditions only or unstable conditions only, for all the six different systems pertaining to a particular liquid–liquid pair (e.g., aniline–water), regardless of the type of surfactants involved. For example, Sternling and Scriven's criteria

predicts stable conditions for all six surfactants systems involving 1-hexanol–water, but unstable conditions only for all six surfactants systems involving ethyl acetate–water. Since not all the six systems involving 1-hexanol–water were observed to be stable, and not all the systems involving ethyl acetate–water were observed to be unstable, predictions from these criteria clearly do not account for the unique effect of each surfactant.

Nakache et al.'s criteria were the only criteria that predicted different stability conditions for each of the six different systems involved with a given liquid–liquid pair. For instance, a stable condition is predicted for the system aniline–water + ATLAS G1300, whereas an unstable condition is predicted for the aniline–water + SDS system. The other criteria appeared unable to predict such contrast and this explains the much better performance achieved by Nakache et al.'s criteria.

It seems, therefore, that for stability criteria to be robust it needs to discern different contaminated systems associated with a given organic–aqueous pair and to be able predict different stability conditions for a particular surfactant, depending on which organic–aqueous system it is involved with. Furthermore, for the establishment of good stability criteria the physical mechanisms underlying the phenomena need to be well understood. In the following section some surfactant properties which may explain some of those mechanisms are discussed.

4.1. Interfacial tension effects

Marangoni convection arises from variations in the interfacial tension, which may be induced by gradients in concentration, temperature or surface charge. Since surfactants are defined by their ability to alter interfacial tension through concentration gradients, a reasonable examination of why certain surfactants initiate Marangoni effects might consider the effect surfactants have on interfacial tension values. In fact, after observing kicking of certain drops during solvent extraction Haydon [31] first suggested that any solute capable of (noticeably) altering the interfacial tension will automatically produce Marangoni effects as it transfers through the liquid–liquid interface. During the mass transfer process surfactants adsorb at (and transfer through) the liquid–liquid interface, and in the process cause variations in the interfacial tension. The amount of surfactant present at the interface at any one instant is a function of the amount of surfactant in the (aqueous) bulk and various kinetic variables of the surfactant including its diffusion, adsorption and desorption coefficients. If the kinetic variables are neglected, the maximum permissible change in interfacial tension that a surfactant may cause is a function only of its bulk concentration. This bulk concentration will decrease as the surfactant mass transfer occurs. If these are accompanied by persistent changes in interfacial tension then

Marangoni convection may be generated. Hence, it is speculated that an indication of the likelihood of Marangoni convection may be obtained from plots of the equilibrium interfacial tension versus the bulk surfactant concentration.

In an effort to investigate this conjecture the variation of interfacial tension with surfactant concentration was measured for each of the 30 different contaminated systems. Measurements were carried out with a *Krus* *K10 Tensiometer*, using the de Nöuy ring method after contact times longer than 3 min. Equilibrium interfacial tension appeared to have been achieved after 3 min and generally later measurements showed no variation from the initial measurement. The results from this study are shown in Figs. 3–7 for the aniline–water, 1-hexanol–water, isobutanol–water, ethyl acetate–water and ethyl acetoacetate–water systems, using the six different surfactants listed in Table 1. In these figures each interfacial tension value is an average of five measured values, all carried out at 25°C.

As seen from Table 2, the ionic surfactants (SDS, LDS and DTAB) were the only surfactants that were observed to initiate Marangoni convection, when the pure system was unstable, or increase its intensity if the uncontaminated system was already unstable. Analysis of Figs. 3–7 shows that the ionic surfactants and the non-ionic ATLAS G1300 produce larger changes in the interfacial tension, while the other two non-ionics (Softanol 30 and Softanol 120) generally produce smaller changes in the value of the interfacial tension. Furthermore a closer examination of the plots involving ATLAS G1300 shows a subtle difference from those of the ionic surfactants. While the ionic surfactants show a high gradient over a wide concentration range, those

involving ATLAS G1300 show a very high initial gradient which rapidly flattens out. Hence during mass transfer, the former may represent circumstances that result in a sustained change in interfacial tension over the mass transfer process (conditions that will promote Marangoni effects) while the latter may represent a large initial change that is not sustained over the mass transfer process and therefore is unlikely to produce Marangoni convection.

One of the reasons for such behaviour may be related to the structure and size of the surfactant concerned. Longer chain (typically non-ionic) surfactants are generally more effective at reducing the interfacial tension, since they cause greater interaction between phase molecules at the interface (on account of their longer chains), and they also adsorb strongly at the interface (on account of their greater hydrophobic tendency). As a consequence, a very small amount of surfactant arriving at the interface will cause a large decrease in the interfacial tension, and further increases in the surfactant concentration at the interface will produce only small changes in the interfacial tension. Hence, a sustained significant variation of the interfacial tension with surfactant concentration is precluded, and therefore the possibility of Marangoni convection, which requires continual variations in the interfacial tension, is reduced. This is illustrated in Fig. 6, for instance, where the sustained slope of the SDS curve (which was associated with instabilities) can be contrasted with the plot for ATLAS G1300.

On the other hand, smaller surfactants (typically ionics) adsorb less readily at the interface – with ionic surfactants there is often electrical repulsion between the ionic heads of surfactant ions already at the interface

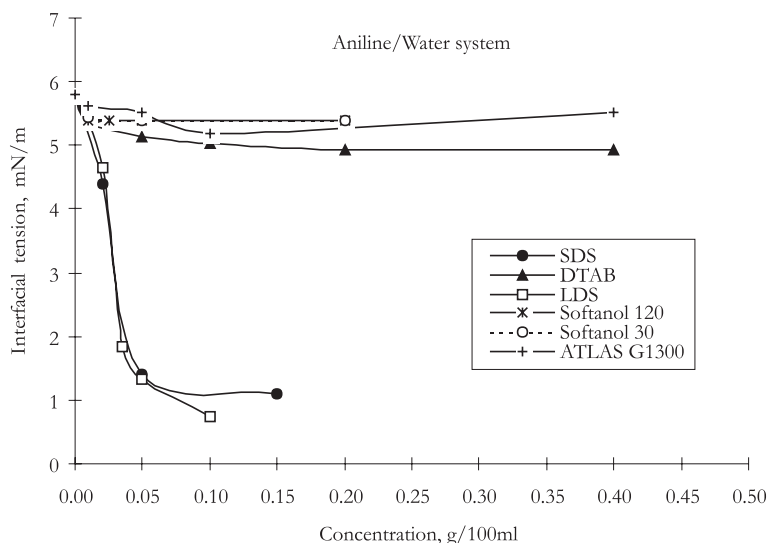


Fig. 3. Interfacial tension versus surfactant concentration for the aniline–water system.

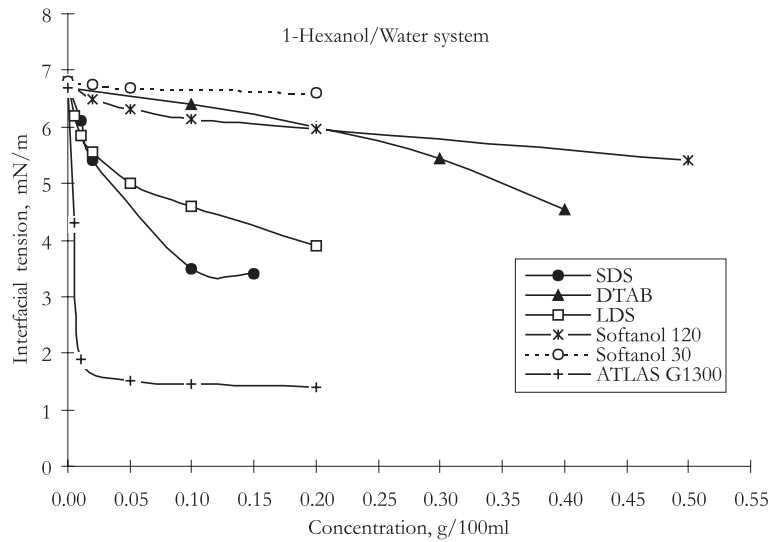


Fig. 4. Interfacial tension versus surfactant concentration for 1-hexanol–water system.

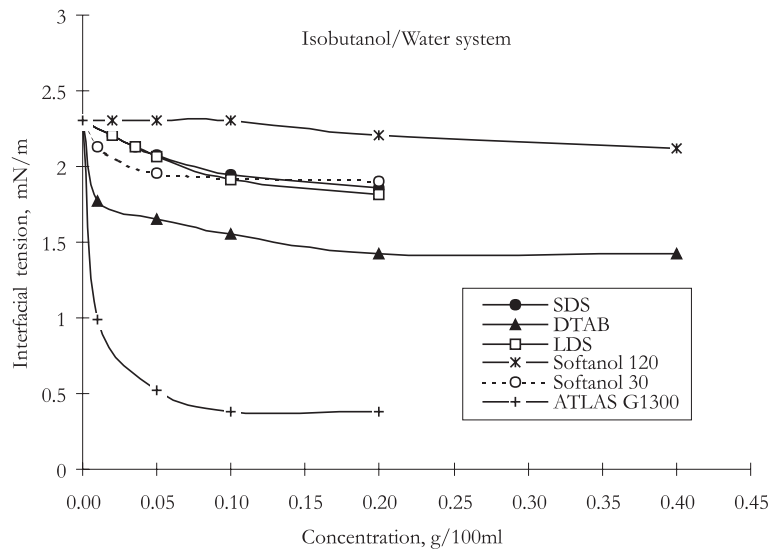


Fig. 5. Interfacial tension versus surfactant concentration for the isobutanol–water system.

and the similarly charged ions from the interior of the bulk. Therefore, a higher concentration of surfactant at the interface is required to effect changes in the interfacial tension and so significant changes in the interfacial tension occur over a much wider concentration range. As a consequence, a sustained significant change in the interfacial tension occurs as more and more surfactant continues to arrive at the interface, and this leads to conditions that promote Marangoni convection.

This finding is in good agreement with that reported by Lyford et al. [32]. During a study of Marangoni convection at the interface of oil drops in aqueous

solutions of various alcohols (which display surface activity) these authors have also reported that the greatest intensity of Marangoni convection was produced by the lower alcohols propanol and butanol in which the rate of change of interfacial tension with respect to concentration was high over a wide range of alcohol concentrations. For example, they say that the ability of the alcohol (equivalent to the surfactant in the present study) to produce a large change in the interfacial tension, which longer chain length favours, is in competition with the ability of the alcohol to lower the interfacial tension over a wide range of concentrations,

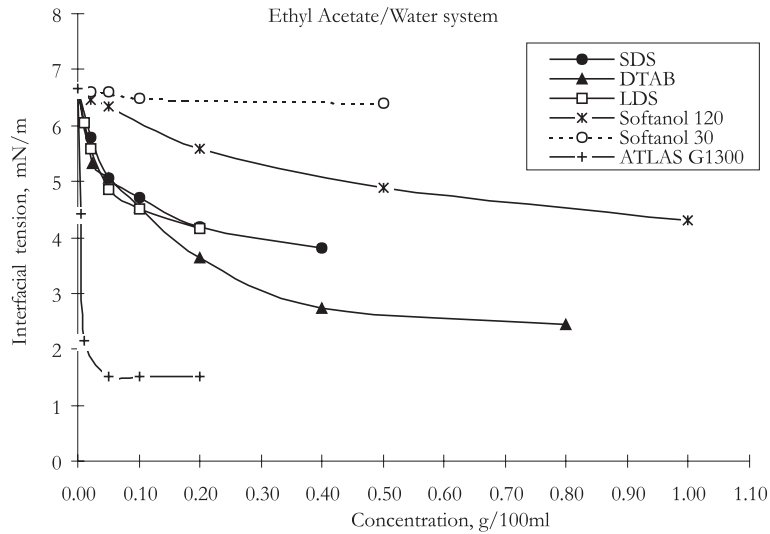


Fig. 6. Interfacial tension versus surfactant concentration for the ethyl acetate–water system.

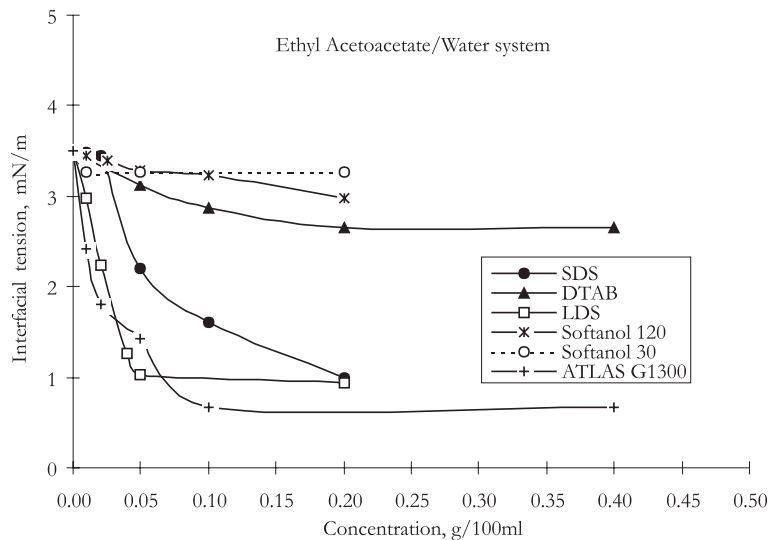


Fig. 7. Interfacial tension versus surfactant concentration for the ethyl acetoacetate–water system.

which shorter chain length favours, and propanol and butanol probably represent the optimum balance of these conflicting requirements for Marangoni convection.

In addition to this ability to promote Marangoni effects, surfactants have also been widely reported [6,9–11] to dampen interfacial convection. Surfactants adsorb at interfaces, and this leads to the formation of a surfactant monolayer, which renders the interface less flexible and results in the dampening of interfacial motion. The ability of a surfactant to do this is determined by its propensity to adsorb at the interface, and also the

size of the surfactant molecule, bigger surfactant molecules being more capable of dampening interfacial motions than smaller molecules [9,10]. Since non-ionic surfactants display a greater tendency to adsorb at interfaces [33] they will be more inclined to dampen interfacial motions than will ionic surfactants of similar size. This may explain why Softanol 30 consistently dampened interfacial convection (except for the ethyl acetoacetate system, see Table 2) while DTAB did not, despite their similar molecular size. The influence of the size of the surfactant molecule may also explain why ATLAS G1300, which adsorbs at an interface to a

similar extent as Softanol 30 and Softanol 120 is most effective at dampening instabilities. For instance, although ATLAS G1300, Softanol 30 and Softanol 120 all dampened the very weak instabilities present in the 1-hexanol–water system, Softanol 30 only partially dampened the moderate instabilities present in the isobutanol–water system and failed to dampen the strong instabilities in the ethyl acetoacetate–water system, whereas ATLAS G1300 dampened completely all the instabilities observed in these latter two binary systems. Consistent with this behaviour, Softanol 120 (with a molecule which is twice as large as Softanol 30, but less than one tenth the size of ATLAS G1300) was observed to dampen completely the moderate instabilities in the isobutanol–water system, but was unable to dampen the stronger instabilities in the ethyl acetoacetate–water system.

Therefore the addition of a surfactant to a liquid–liquid system may either promote Marangoni convection or dampen interfacial motions, depending on the size of the surfactant molecule and its tendency to adsorb at the interface. These two effects may compete with each other and the overall stability of a system will depend on which of these effects dominate. The question then arises as to whether these conflicting surfactant properties can be expressed in a unique manner through which Marangoni convection can be predicted.

4.2. Marangoni coefficient

A phenomenological approach is used for the prediction of Marangoni convection in systems which have surfactants by expressing all the relevant effects as a number or coefficient in such a manner that its magnitude reflects the propensity of a system to display Marangoni convection. In many complex phenomena where several effects compete, the ratio of positive contributors (which form the numerator) to detrimental contributors (which form the denominator) is often determined, and relevant values are made non-dimensional where necessary. This process usually involves a theoretical and semi-empirical analysis of the factors that affect the relevant phenomena, which in this case is the surfactant induced Marangoni convection. In this work a Marangoni coefficient, N_{Ma} , is defined for the case when surfactant transfers from an aqueous phase A into an organic phase B and such that high values of N_{Ma} are associated with conditions that promote Marangoni convection, while conditions that inhibit Marangoni convection reduce the value of N_{Ma} .

4.2.1. Factors that increase N_{Ma}

Large (maximum) changes in the value of the interfacial tension ($d\gamma$) due to the presence of surfactant, clearly promote Marangoni convection and consequently $N_{Ma} \propto d\gamma$. Furthermore, the relative change in

the interfacial tension that $d\gamma$ represents must be considered, since the effect of a given $d\gamma$ assumes greater significance if it occurs at an interface where the tension is low. Therefore, $N_{Ma} \propto d\gamma/\gamma$. Additionally, increasing the concentration driving force of solute (surfactant in this case) has been reported to produce an increase in the intensity of convection [34,35], and so it may be inferred that $N_{Ma} \propto C_{\text{surfactant}}$.

4.2.2. Factors that decrease N_{Ma}

Several factors combine to reduce the value of N_{Ma} as described earlier. For example, an increase in the amount of the surfactant adsorbed at the interface, Γ , the surface excess, results in an increase in the interfacial rigidity. This in turn restricts any surface movements or Marangoni convection, and therefore $N_{Ma} \propto 1/\Gamma$. Clearly, for a given surface excess the effect on the interfacial rigidity is greater the larger the size (RMM) of the surfactant molecule. Hence, $N_{Ma} \propto 1/\text{RMM}_{\text{surfactant}}$. Sternling and Scriven have shown that a high phase viscosity restricts the possibility of Marangoni convection by slowing down the motion of surface eddies, so $N_{Ma} \propto 1/\mu_B$. Finally, the diffusion coefficient of the surfactant must also be considered as it will affect the concentration difference (driving force) between the interface and the bulk; higher diffusion coefficients will favour a smaller concentration difference [36], reducing the driving force for Marangoni convection, so $N_{Ma} \propto 1/D_{AB}$.

4.2.3. Definition of N_{Ma}

Taking account of all the above considerations,

$$N_{Ma} \propto \frac{(d\gamma/\gamma)d\gamma}{\mu_B D_{AB} (\text{RMM}_{\text{surfactant}}/\text{RMM}_{\text{phase}})} \frac{C_{\text{surfactant}}}{\Gamma} \quad (1)$$

N_{Ma} as expressed above has units of m^{-2} , i.e., per unit surface area of interface. The dependence of N_{Ma} on the surfactant molecular mass, $\text{RMM}_{\text{surfactant}}$, has been made non-dimensional by dividing it by the relative molecular mass of the phase molecules, since it is the value of $\text{RMM}_{\text{surfactant}}$ relative to the RMM of the phase molecules that is significant in determining the surfactant effect on surface rigidity. $\text{RMM}_{\text{phase}}$ has been chosen to be the organic phase RMM , as it is larger than the aqueous phase RMM .

N_{Ma} as defined above, represents a ratio of the surface tension and associated effects, which produce surface motion, to the viscous and related effects that restrict surface movements.

4.2.4. Values for N_{Ma}

Having obtained a definition of N_{Ma} its value was calculated for each of the 30 contaminated systems studied: values of $d\gamma$ and γ were obtained from the plots of interfacial tension versus concentration for the

Table 3

Calculated values of the Marangoni coefficient for selected systems, $N_{Ma} \times 10^{-9} \text{ m}^{-2}$

Surfactant →	SDS	LDS	DTAB	Softanol 30	Softanol 120	ATLAS G1300
Liquid–liquid system ↓						
Aniline–water	311	757	141	0.289	0.0792	0.00683
1-Hexanol–water	204	274	14.3	0.0040	0.00756	0.0206
Isobutanol–water	63	56.7	555	0.0000845	0.000213	0.00591
Ethyl acetate–water	115	159	232	0.105	0.0798	0.0143
Ethyl acetoacetate–water	141	715	167	0.244	0.0512	0.00818

relevant systems (for example for the aniline/water system, $\gamma = 5.4 \text{ mN/m}$ and for the same system with SDS $d\gamma = 4.2 \text{ mN/m}$ as the addition of SDS to the water caused the interfacial tension to decrease as low as 1.2 mN/m); $C_{\text{surfactant}}$ corresponds to the aqueous surfactant concentration used when the observations of interfacial stability in Table 2 were made [27]; μ_B and D_{AB} were determined and presented elsewhere [28]; $RMM_{\text{surfactant}}$ values are given in Table 1 and values for RMM_{phase} are widely available in the literature; Γ was determined using the Gibbs formula. The values of N_{Ma} determined for the thirty systems studied are included in Table 3. A comparison of the N_{Ma} values of a system in Table 3 with its experimentally observed interfacial stability in Table 2, shows that all the systems associated with Marangoni convection have high N_{Ma} values (between 10^{10} and 10^{11} m^{-2}), while all the stable systems (except the DTAB ethyl acetoacetate–water system) have N_{Ma} values that are much lower (between 10^4 and 10^8 m^{-2}). In fact, if as a criterion for instability it is assumed that any system with an N_{Ma} value greater than 10^9 m^{-2} will be associated with Marangoni convection, then in 29 of the 30 systems studied the criterion is shown to predict the correct condition. This indicates that the factors that initiate or inhibit Marangoni convection have been properly accounted for in the determination of the Marangoni coefficient, N_{Ma} . The only case where there is disagreement between the prediction and the observed behaviour occurs with the ethyl acetoacetate–water + DTAB system, where instabilities are predicted, though some dampening of interfacial convection is observed to occur. However, results obtained with this particular system have been reported (28) not to be well understood.

5. Conclusions

It has been shown that certain physical properties, which appear to be significant in determining the onset of Marangoni convection in the 30 liquid–liquid systems studied have not been included in Sternling and Scriven's criteria or in either of Hennenberg et al.'s criteria, while some factors have been accounted for in the cri-

teria of Nakache et al., but not adequately. Analysis of the results lead to the development of an empirical Marangoni coefficient (N_{Ma}) and the suggestion for a limiting value for the existence of Marangoni convection. When the proposed N_{Ma} has a value greater than 10^9 m^{-2} (in 29 of the 30 systems studied) the criterion is shown to predict the observed stability condition. The success of the proposed Marangoni coefficient criterion has only been checked on the thirty systems discussed here and, as such, it does not represent an exhaustive assessment of the criterion. However, the authors believe that this new criterion is able to properly account for several factors that cause surfactants to initiate, increase or inhibit Marangoni convection. It is also easy to apply.

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