

Effect of Melamine on the Foam Kinetics of Polyurethane Model System. I. Surface Properties in the Absence and Presence of Melamine Particles

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ABSTRACT: The dynamic and equilibrium surface tension of a polyurethane model system with and without melamine particles was investigated. It is concluded that the diffusion is the rate-determining factor in the adsorption process. Greater dynamic surface tension is found for the melamine-containing dispersion than for the corresponding solution in the absence of particles. A possible explanation is given by the presence of attractive interactions between the particles. The adsorption of the surfactant on the melamine surface, wetting properties of the particles by the investigated system, and the rheological behavior of the dispersions are discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1729–1738, 1998

Key words: surface tension; high viscous system; polyurethane model system; melamine; rheology

INTRODUCTION

Foams are important in many technologies (food industry, fire extinguishing, polymer foams). Liquid foams (gas-in-liquid dispersions) are thermodynamically unstable systems, but significant kinetic stability is observed in some cases. Rontelap et al. studied the rate-determining steps of disproportionation in relation to the surface rheological properties.^{1,2} The relation of stirred foam formation and foam stability was studied by Koczo and RácZ.³ Kinetic stability was studied mainly in aqueous solutions and the relationship between the foam stability and the equilibrium or dynamic surface tension and surface rheological properties was investigated.⁴ Szekrényesy et al.^{5,6}

discussed several foam models of differing complexity: The effects of surfactant type and concentration, salt content, temperature, bubble size, and foam complexity on the stability were presented. The antifoaming effect of poly(ethylene oxide)–poly(propylene oxide) block copolymers was investigated and the drainage rate is related to the mobility of the films.⁷

Solid foams are rigid or flexible gas-in-solid dispersions. Solid foams are produced via a gas/liquid (G/L) dispersion. Therefore, it is very important to study the stability of G/L dispersions. Polyurethane foam is one example of a solid foam. Solid foams can be produced in a variety of forms with different densities and properties. The production and mechanical properties of polyurethane foams were reviewed in refs. 8–10. The relationship between equilibrium or dynamic surface properties and foam properties was studied by Kendrick et al. in a polyurethane model sys-

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tem.^{11–13} It was concluded that a certain surface tension decrease is a necessary but not sufficient condition to have good foaming properties.^{11–14} The foaming properties of a polyurethane model system were studied by the present authors.¹⁵

The interfacial properties of surfactant solutions during foaming cannot be explained by the equilibrium surface tension and adsorption only; therefore, the diffusion, micellization, and orientation of the surfactant molecules are studied nowadays.¹⁶ The adsorption of surfactant molecules on liquid surfaces is very important in different technological processes involving dilating surfaces (foaming, wetting, emulsification). The surface area of the fluid increases in the period of foam formation. The surface tension differs from the static value when the surface is dilated or compressed. It is called dynamic surface tension. The increase of surface tension creates a force against the extension, which gives the elasticity of liquid films (Gibbs–Marangoni effect). The Gibbs–Marangoni effect is influenced by the rate of diffusion. Dynamic surface tension becomes especially important in the production of polyurethanes since the reaction is completed in a few minutes.

Melamine is used as a flame retardant in polyurethane foams. The effect of melamine particles on the interfacial properties of polyurethane model systems is not well known. It has been shown^{17–19} that solid particles can stabilize or destabilize foams according to their wetting parameters.

The effect of melamine on the dynamic and equilibrium surface tension of a high viscous, polyurethane model system was investigated in this work. The dynamic surface tension depends on the rate of diffusion and adsorption of the applied surfactant at the air/liquid interface. To reach a sufficient rate of diffusion and adsorption, a rather large surfactant concentration is necessary in the model system because of the high molecular mass of the materials. The optimal surfactant concentration can be predicted from the results of dynamic surface tension measurements.

EXPERIMENTAL

Materials

The following materials were used: *Voranol CP 3322* (poly(ether polyol), DOW): viscosity (298 K), 510 mPa s; surface tension, 32.8 mN/m; hy-

Table I Particle-Size Volume Distribution of Melamine Ultrafine Grade Measured by a Malvern Master Particle Sizer M6.10

Melamine Grade	d_{50} (μm) 50 vol % <	d_{90} (μm) 90% <	d_{10} (μm) 10% <
Ultrafine	10.2	17.4	4.9

droxyl number, 47.5 mg KOH/g; molecular weight, 3400 g/mol; water content, 0.027%; density, 1.0196 g/cm³. *Tegostab BF 2370* [organomodified poly(ether siloxane); TH. Goldschmidt]: density (298 K), 1.035 g/cm³; viscosity (298 K), 850 mPa s; solubility, soluble in polyols and in water; molecular weight, 10,000–12,000 g/mol (given by Goldschmidt). *Melamine* (2,4,6-triamino-1,3,5-triazine; DSM Melamine). The water content is max 0.1% and that of ash and iron, respectively, max 0.01% and max 1 mg/kg.

The results from a typical volume-averaged particle-size distribution is given in Table I. The particle-size distribution was measured in an aqueous solution saturated with melamine by a Malvern Master Particle Sizer M6.10.

The solutions and melamine suspensions were prepared by mixing first the surfactant and the polyol. After adding melamine, the components were mixed at a speed of 2500 rounds/min for 30–60 s to obtain a homogeneous suspension. The solutions were deaerated under a vacuum to remove the air bubbles formed during stirring.

In this article, the dispersion of *Tegostab BF 2370* and *Voranol CP 3322* will be called a *conventional system*. The load of melamine ultrafine is always 25 pphp in the melamine-filled systems. The concentration of surfactant and melamine is expressed as parts per hundred parts (by weight) polyol (pphp). By taking 10,000 g mol as the surfactant molecular weight, the concentration given in pphp must be multiplied by a factor of 1.0196 to express the concentration as mol/m³ polyol.

Methods

The surface tension of the investigated solutions was measured as a function of adsorption time as well as by the drop weight method and the Wilhelmy plate method.

Drop Weight Method

The drop volume or drop weight method is frequently used to determine the interfacial tension

of fluids. For solutions which achieve slowly the equilibrium surface tension, this method can be used to study the kinetics of surfactant adsorption at the air/liquid interface.²⁰ In this method, liquid drops are formed at a ground, circular tip of the stalagmometer (a pipette, calibrated and scaled for volume). The surface or interfacial tension can be calculated from the volume of a drop by²¹

$$\gamma = \frac{V_d \Delta \rho g}{r} f \left(\frac{r}{V_d^{1/3}} \right) \quad (1)$$

where V_d is the volume of drop; $\Delta \rho$, the density difference of the fluids; g , the acceleration due to gravity; r , the radius of the stalagmometer tip; and f , the Harkins factor, modified by Lando and Oakley.²²

The volume of the drop increases with a constant rate in time until the drop detaches from the tip; then, a dynamic surface tension can be calculated. The calculation of dilatation is rather complicated, because in the case of an ordinary stalagmometer, the rate of dilatation of the liquid surface is not steady. The dropping time (t_d) is longer than the time (t) needed for surfactant adsorption if the drops are formed continuously. For a suddenly formed drop, the adsorption time equals the dropping time (Thornberg method). According to Joos and Rillaerts,²⁰ the adsorption time can be calculated from the dropping time (time running between fall off of two drops) with the following equation:

$$t = 0.43t_d \quad (2)$$

Different adsorption times can be investigated by changing the dropping time.

The drop weight technique is used for solutions of large viscosity. In this case, during the formation of the drop, hydrodynamic effects are involved. A correction for gravitational and viscous forces was suggested by Jho and Carreras.²³ This correction was used by us.

An own-built stalagmometer²¹ was used to form the drops. It has four main parts: a thermostated stalagmometer, photodetector, stand, and electrolysis cell. The drops are formed at the tip of the stalagmometer with a constant rate by the effect of the pressure of gas generated in the electrolysis cell from the KOH solution. The falling drop interrupts the light beam, resulting in a changed signal in the phototransistor, which is amplified. The number of drops are counted in a

certain time interval. The weight of 5–15 drops was measured using a Scientech SA 210 analytical balance.

Before the start of an experiment, the tip of the stalagmometer is kept in KOH (10 wt %) for 0.5 h and rinsed subsequently with distilled water and acetone. The completely dry stalagmometer was filled with the solution to be studied. The drop rate was set by controlling the electrolysis cell.

Correction for hydrodynamic effects was made in some cases. This will be discussed further. However, most of our results are presented without correction.

Wilhelmy Plate Method

The dynamic surface tension of these high viscous, polymeric solutions can also be measured by the Wilhelmy plate method. The liquid is flown from a funnel into the measuring cell. Adsorption time is the time running from the initial creation of a new air/liquid surface. The first measured value can be taken at an adsorption time $t = 80$ s. The curves of different concentrations all give the same surface tension value of pure solvent after extrapolating to $t = 0$ s (Fig. 2). A Krüss K 12 Processor tensiometer was used. The equilibrium surface tension was determined by this method at 298 K after 24 h standing.

Contact-Angle Measurements

The contact angle of pure polyol and that of the 0.8 pphp conventional solution was determined on melamine pellets using an ERMA-G1 goniometer with an accuracy of 1° at ambient temperature. The contact angle of a given system was determined five times after waiting 20 min in each case. Melamine pellets were made by pressing a few grams of melamine standard grade for 1 min with a 15 kN force in a Zwick tensile tester (Type 1484).

Rheological Measurements

The viscosity of the materials and solutions was determined by a Contraves Rheomat 115 rotational viscometer and by a Haake RS 100 Rheoviscometer at 298 K.

RESULTS AND DISCUSSION

Polyol/Surfactant System

Equilibrium Surface Tension of Polyol/Surfactant System

The equilibrium surface tension of the polyol/surfactant system (the so-called conventional sys-

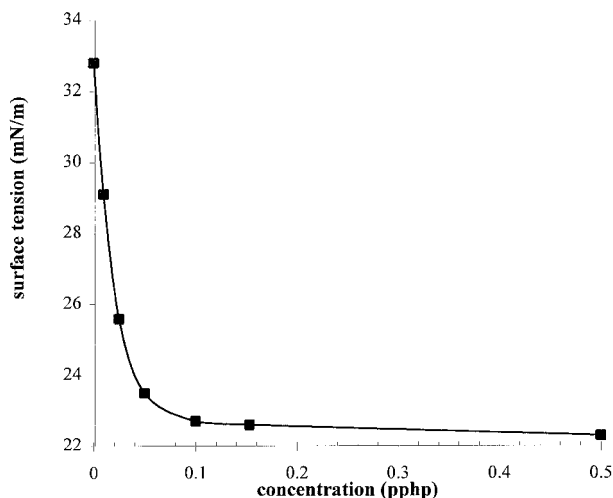


Figure 1 Equilibrium surface tension as a function of Tegostab BF 2370 concentration in Voranol CP 3322 at $T = 298$ K measured by the Wilhelmy plate method.

tem) was determined by the Wilhelmy plate method as a function of surfactant concentration. The results are shown in Figure 1. A break is observed in the surface tension versus surfactant concentration curve at about 0.06 pphp surfactant concentration. In analogy with aqueous systems, this can be the indication of micelle formation. By using SAXS, however, the existence of micelles could not be proven.

The saturation adsorption, Γ^∞ , was determined from the equilibrium surface tension versus log surfactant concentration graph by using the Gibbs equation and assuming that the activity equals the concentration. This calculation results in $\Gamma^\infty = 1.5 \cdot 10^{-6}$ mol/m².

The average area per molecule is $1.1 \cdot 10^{-18}$ m²/molecule. By comparing this result with the values (7.42 and $3.10 \cdot 10^{-18}$ m²/molecule) of Grabowski and Desiner,²⁴ we can see that this is in the same order. In our case, both the polyol and the surfactant are different, which can explain the differences.

Dynamic Surface Tension of Polyol/Surfactant System

The dynamic surface tension was determined using two methods: the drop weight and the Wilhelmy plate methods. The results for different surfactant concentrations are shown in Figure 2. The two methods complete each other since the drop weight method can be used in the time range of 0–100 s, while the Wilhelmy plate is suitable

for larger time ranges. The few first measurement points of the Wilhelmy plate method were left out, since in the first minute, there is a rapid change in surface tension due to the formation of a new surface (the meniscus created along the plate). After this correction, the points measured with the two methods give one continuous curve without a break.

In Figure 2, duplicate experiments are shown to give information about the reproducibility. The experimental error of the measurement is ± 0.2 mN/m. The γ - c curves at different times after surface formation were measured to investigate the effectiveness of the surfactant in stabilizing a dilating system. These curves are obtained from Figure 2 by reading the surface tensions at selected times of 5, 25, 200, and 400 s. The data are plotted in Figure 3. The γ - c curves belonging to short times are S-shaped showing that

- The surfactant is ineffective if its concentration is low,
- There is a concentration range (0.1–0.4 pphp) where the surface tension decreases steeply, and
- Above this concentration range, the surface tension decreases with concentration slowly again.

This graph makes it possible to calculate the minimal surfactant concentration needed for a technological process characterized by the time and surface pressure necessary for stabilizing the expanding surface.

Hydrodynamic Effect

The materials were used in their original form as they were manufactured for polyurethane production. The polyol and the surfactant are mixtures of isomeric and homologous compounds, so their dynamic surface properties show the characteristics of mixtures. Indeed, the surface tension of the “pure” polyol depends already on time (Fig. 2) and the decrease of the surface tension is surprisingly great (5 mN/m). We tried to correct the measured data for a hydrodynamic effect.²³

It is known that if the dropping time is short the weight of the drop developed on the tip of a stalagmometer depends on the surface tension of the liquid in the first line and it also depends on the viscosity of the liquid. The calculation is based on the following empirical function:

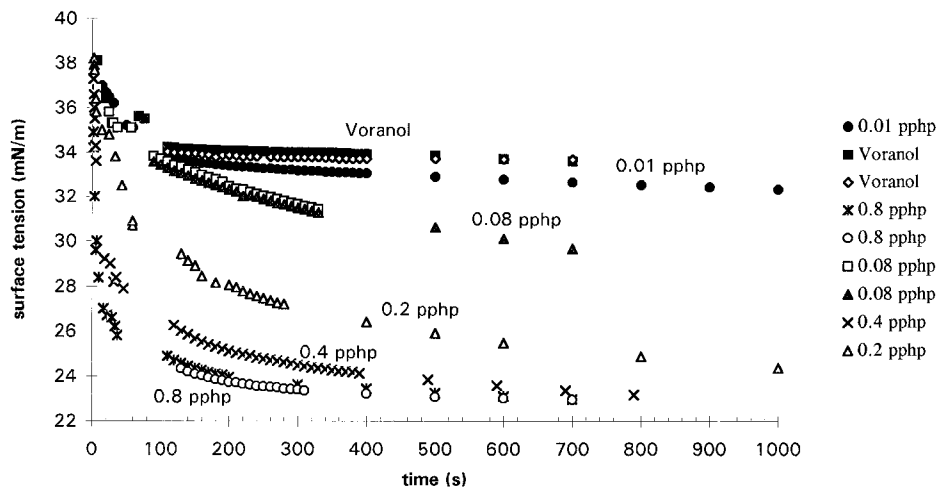


Figure 2 Modified graph of dynamic surface tension of solutions of different concentrations of Tegostab BF 2370/Voranol CP 3322 as a function of adsorption time at $T = 298$ K measured by the drop weight ($t < 100$ s) and Wilhelmy plate ($t > 100$ s) methods.

$$M(t) = M_e + St_d^{-3/4} \quad (3)$$

The drop mass [$M(t)$] is a linear function of the reciprocal of the three-fourths power of the drop time, t_d , for pure materials. Here, M_e is the corrected drop mass and S is the McGee slope. From the measured drop masses of liquids of low viscosity (below 10 mPa s), Jho and Carreras²³ concluded that S is related to M_e according to the following empirical equation:

$$M_e = 9.4S + 5.4 \text{ mg (below 10 mPa s)}$$

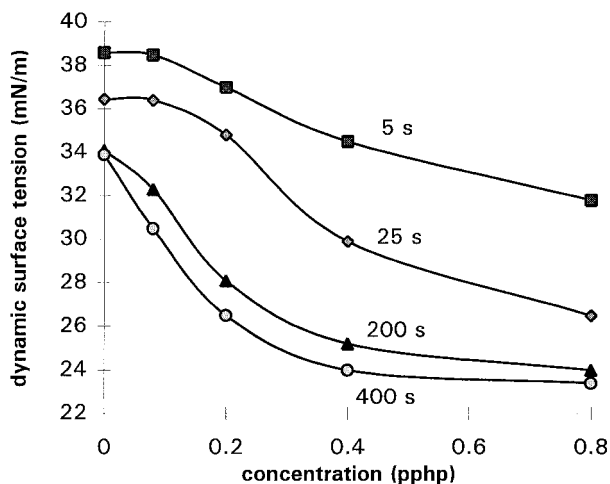


Figure 3 Dynamic surface tension as a function of surfactant concentration at different adsorption times.

They performed measurements also in the high-viscosity regime (up to 1 Pa s). They published two curves of the McGee slope as a function of viscosity characterized by constant M_e and linear interpolation between the two curves at constant viscosity was recommended. Jho and Carreras²³ used similar materials to ours. They experimentally found that the dynamic surface tension of silicone fluids was not seen if the correction was made, although these are polydisperse systems. This correction was used for pure polyol and for surfactant solutions.

The results for the polyol are shown in Table II and Figure 4 by comparing the dynamic surface tension versus time graphs with or without correction. A significant influence is seen if the adsorption time is in the range of 0–20 s. The dynamic surface tension was found for the conventional polyol, which is supported by the Wilhelmy plate measurements since a decrease in surface tension is seen for hundreds of seconds (Fig. 2). The equilibrium surface tension of the polyol is 32.8 mN/m, and by the drop weight method (after correction) at 70 s, the dynamic surface tension is still above 35 mN/m (Fig. 4). The surface tension measured by the drop weight method in the early stage is the combination of the aging (adsorption) of the surface and the hydrodynamic effect.

Jho and Carreras pointed out that the McGee equation forms the basis of the correction for the determination of the dynamic surface tension of the surfactant solution from the time-dependent

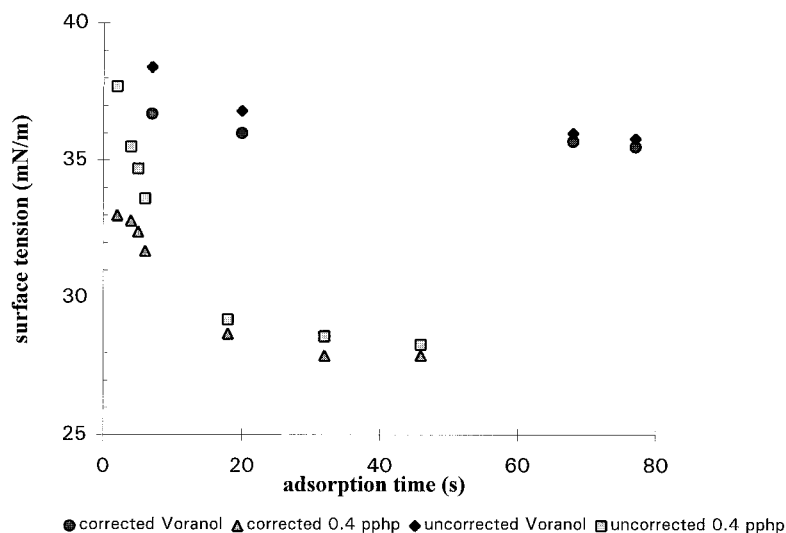
Table II Measured and Hydrodynamically Corrected Drop Mass and Surface Tension of the Polyol and of the 0.4 pphp Conventional System as a Function of Dropping Time

t (s)	Mass Measured (mg)	Mass Corrected (mg)	Surface Tension Measured (mN/m)	Surface Tension Corrected (mN/m)
Polyol $\eta = 510$ mPa s				
16.5	22.3	21.2	38.4	36.7
45.3	21.3	20.8	36.8	36.0
158.0	20.8	20.6	36.0	35.7
180.0	20.7	20.5	35.8	35.5
0.4 pphp conventional $\eta = 520$ mPa s				
4.7	21.8	18.9	37.7	33.0
9.3	20.5	18.8	35.5	32.8
11.6	20.0	18.6	34.7	32.4
14.0	19.3	18.1	33.6	31.7
41.9	16.8	16.3	29.2	28.7
74.4	16.2	15.8	28.6	27.9
107.0	16.1	15.8	28.3	27.9

drop mass. In their article,²³ experimental data measured for the surfactant systems were not published. We used their method given for pure liquids for the correction of the surface tension of the conventional solutions. In every case, the corrected surface tension is too low when the drop time was short. In Table II, only the surface tensions of the 0.4 pphp solution are included, as an example, because the effect can be well demonstrated in this case. So, the corrected value was practically constant in the first 5 s, and after this

time, it starts to decrease. This seems to be impossible, because the rate of diffusion is the largest at the beginning when the deviation from the equilibrium is the largest.

We can say that the surface pressure can be calculated from the uncorrected surface tension values since the parameters (viscosity, mass) involved in the hydrodynamic correction are very close to each other, and in this way, the difference is not influenced. Long-time surface tension is used for the determination of the diffusion coeffi-

**Figure 4** Effect of hydrodynamic correction.

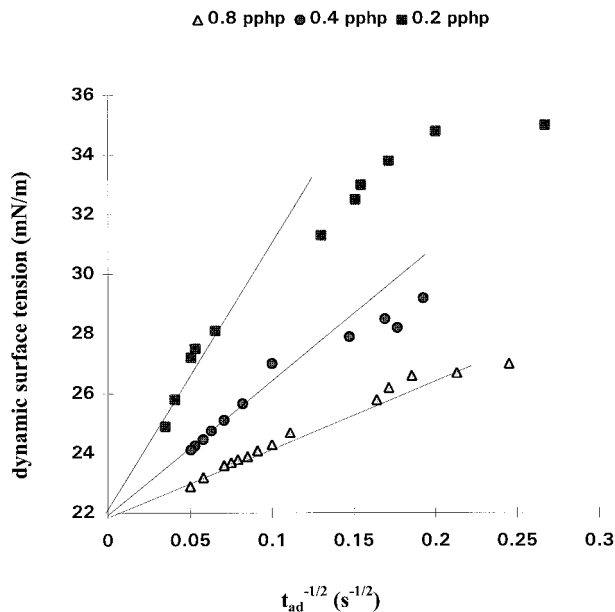


Figure 5 Dynamic surface tension of conventional solutions at different surfactant concentrations as a function of $t_{ad}^{-1/2}$ at $T = 298$ K measured by the drop weight and Wilhelmy plate methods.

cient where the effect of hydrodynamic correction can be neglected.

Mechanism of Adsorption

From practical point of view (polyurethane production conditions), the concentration region above the critical micelle concentration (cmc) is interesting for us. We will focus on that. The kinetics of developing the surface pressure was studied. Generally, the following steps are possible: disorganization of the micelles, diffusion of surfactant molecules to the surface, and activated adsorption taking into account the change of the molecular conformation in the surface layer.

According to Bleys and Joos,²⁵ the dynamic surface tension varies linearly with $t^{-1/2}$ if the adsorption is diffusion-controlled and the state of the surface is not far from equilibrium. The equilibrium surface tension should be read by extrapolating to $t^{-1/2} = 0$. Our measurements fulfill these conditions, so we can conclude that diffusion is the rate-determining step in our system (Fig. 5). The extrapolation gives 22.2 mN/m in the case of 0.8–0.2 pphp concentrations, which agrees with the measured equilibrium value (22.4 mN/m) within the limit of experimental error. At lower t (higher $t^{-1/2}$) values and at lower surfactant concentration (Fig. 5), there is a deviation from the

straight line because the dilated surface becomes similar to the surface of the pure solvent.

In micellar solutions, if diffusion is the rate-determining process, we may assume that the time of the measurement is long in comparison with the time needed to reach monomer–micelle equilibrium. Since we measured for seconds, we can assume a local equilibrium between micelles and monomers in the bulk and then the long-time approximation²⁶ can be used.

The long-time approximation for diffusion-controlled adsorption is given by

$$\gamma = \gamma_e + \frac{RT\Gamma_\infty^2}{cmc} \left(\frac{\pi}{4D_a t} \right)^{1/2} \quad (4)$$

where $Da = D(1 + \beta)(1 + \beta y^2)$, the apparent diffusion coefficient where

$$\beta = \frac{c - cmc}{cmc}, \quad y^2 = \frac{D}{D_m}$$

where t is the adsorption time; $\pi = 3.142$; D_m and D are the diffusion coefficients of micelles and monomers, respectively; γ_e , is the equilibrium surface tension; $\Gamma_\infty = 1.5 \cdot 10^{-6}$ mol/m², the equilibrium surface excess; and $cmc = 0.061$ mol/m³. The apparent diffusion coefficient can be calculated from eq. (4) and Figure 5. The results are summarized in Table III.

It can be seen from the results that the apparent diffusion coefficient is a linear function of $(1 + \beta)^2$. So, $y^2 = 1$, and the micellar diffusion coefficient is practically the same as that of the monomers. The most obvious explanation of this result is that there are no micelles present in the investigated solutions. The break in the surface tension versus surfactant concentration graph (Fig. 1) apparently does not correspond to the critical micelle concentration.

Table III Apparent Diffusion Coefficient Calculated from Eq. 4

Concentration (pphp)	$D_a \cdot 10^8$ (cm ² /s)	$1 + \beta$	$\frac{D = D_m}{(1 + \beta)^2} \cdot 10^{10}$ (cm ² /s)
0.2	1.0	3.3	9.4
0.4	4.1	6.6	9.4
0.8	16.4	13.3	9.3

Table IV Dynamic Surface Tension of the Polyol and that of the 0.8 pphp Conventional Solution with or without 25 pphp Melamine Ultrafine and the Calculated Surface Pressures, Π

Time (s)	γ_{polyol} (mN/m)	$\gamma_{0.8 \text{ pphp}}$ (mN/m)	$\Pi_{\text{without melamine}}$ (mN/m)	$\gamma_{\text{polyol/melamine}}$ (mN/m)	$\gamma_{0.8/\text{melamine}}$ (mN/m)	$\Pi_{\text{with melamine}}$ (mN/m)
5	35.3	27.2	8.1	40.0	30.2	9.8
10	34.2	24.7	9.5	38.1	27.5	10.6
15	33.9	23.6	10.3	36.8	26.4	10.4

The differences in surface tension between Table IV and Figure 2 is caused by the different surface tension of the polyol.

POLYOL/SURFACTANT/MELAMINE SYSTEM

Dynamic Surface Tension of Polyol/Surfactant/Melamine Dispersion

The surface tension of the solutions containing melamine is larger than that of the corresponding solutions without melamine at the same surfactant concentration (for short times, compare columns 2 and 5, or 3 and 6, in Table IV). This high surface tension value lasts for a long time. After centrifuging the melamine, the equilibrium surface tension of the corresponding polyol/surfactant was measured.

At longer times, we can compare the 0.8 pphp with and without melamine since the large viscosity does not influence the measurement of Wilhelmy plate method. The surface tension difference between the melamine-filled and melamine-free systems is 3.1 in the time range of 20–180 s.

We can see from the calculated surface tension differences (Table IV) that the surface pressure is high in the investigated time range, which is important from a technological point of view, and that the surfactant is effective in the solution containing melamine, resulting in an equally large surface pressure. From this fact, it can be said that the optimal surfactant concentration of the melamine dispersion can be the same as in the melamine-free system.

The dynamic and long-time surface tension of 25 pphp melamine ultrafine/polyol is also higher than that of pure polyol, which indicates again that the surface tension increase is caused by the presence of the solid particles. The larger dynamic surface tension of the suspension can be understood if the hydrodynamic correction becomes larger as a result of increased viscosity, but it cannot explain the difference in surface tension between the suspension and the corresponding solution after a long time.

Surfactant Adsorption on Melamine

Another effect of larger surface tension could be that the surfactant adsorbs on the surface of the particles. The possibility of surfactant adsorption on melamine was checked by surface tension measurements. Melamine ultrafine, 10 pphp, was mixed with a conventional system of a 0.01 pphp surfactant concentration ($\gamma_{\text{eq}} = 29.1 \pm 0.1$ mN/m), and after 2 days, it was centrifuged to separate the melamine. This surfactant concentration was chosen because in this concentration range a relatively large surface tension change can be expected with a small concentration decrease (Fig. 1). The equilibrium surface tension of the supernatant liquid was measured with the Wilhelmy plate method. We expected a 1 mN/m surface tension increase assuming that the surface-active agent adsorbs on the surface of melamine particles with 1 mg/m² coverage. The measured surface tension was $\gamma_{\text{eq}} = 28.9$ mN/m, which equals that of the solution without melamine at a 0.01 pphp concentration within the limits of experimental error.

To further prove this, the contact angle of pure polyol and of the 0.8 pphp conventional solution was determined on melamine pellets using a goniometer with an accuracy of 1°. The contact angle on melamine is 17° in both cases (pure polyol and surfactant solution) at ambient temperature. The contact angle is determined by the surface tensions of liquid/air, solid/air, and liquid/solid. Therefore, we expected a difference because the liquid/air surface tension of the two systems differs. We may conclude that, preferably, the polyol adsorbs on the melamine since the contact angle is not influenced by the presence of the surfactant.

Rheological Properties of Polyol/Surfactant/Melamine Dispersions

The viscosity of the materials and solutions was determined using a Contraves Rheomat 115 rota-

Table V Viscosity of Dispersions with Melamine Ultrafine Grade at 25 pphp Load

System	Viscosity (mPa s)
Polyol ^a	510
Polyol + melamine ^a	1550
0.8 pphp conventional ^b	550
0.8 pphp conventional + melamine ^b	1800

^a Measured by a Contraves Rheomat 115.

^b Measured by a Haake RS 100.

tional viscometer. The effect of melamine ultrafine in a 25 pphp load was studied. The viscosity is constant with an increasing shear rate in the range 1–100 1/s; the suspensions behave as Newtonian liquids. The viscosity values are summarized in Table V.

In conducting measurements below 1 Pa by a Haake RS 100 (Rheoviscosimeter), it appeared that the dispersion has a pseudoplastic feature, but the solution without melamine is still proved to be Newtonian (Fig. 6). So, we can conclude that 25 pphp melamine ultrafine in polyol or in surfactant/polyol mixtures makes the liquid pseudoplastic without a yield point and elasticity. In Figure 6, measurements are shown for the surfactant/polyol and surfactant/polyol/melamine systems, but all the tests were also done for polyol and polyol/melamine dispersions. The difference was not seen in the rheological behavior of the dispersions with and without the surfactant. We may assume that the dispersion has a certain structure which is destroyed by shear. Maybe this phenomenon can explain the larger surface tension of the polyol/surfactant/melamine dispersion as well. This will be further discussed.

The measured three phase contact angle shows that the presence of melamine particles in the air–liquid interface is thermodynamically possible. The effect of floating solids on fluid–fluid surfaces was theoretically studied by Lucassen.^{27,28} The possibility of attractive interaction between neighboring particles is shown. He concluded from calculations on model systems that particles with irregular wetting parameters can influence the surface smoothness even in the absence of gravity forces, resulting in a larger surface tension. We concluded from calculations made for our system that the large difference in surface tension between the suspension and the corresponding solutions cannot be explained by this effect.

As a matter of fact, in the melamine dispersion,

two subsystems exist. The rheological results show that in the stationary liquid there are forces between the melamine particles. These forces can be compared to the molecular forces between molecules in the liquid state. The two systems form the surface together because the particles can build in the surface layer. The classical explanation of surface tension is that the surface molecules have excess free energy because the number of the neighboring molecules are less at the surface than in the bulk, so a part of the bonds existing in the bulk have to break up, emerging into the surface. The same reasoning is valid for the subsystem of particles. If in the bulk there is a network of particles, being in an energy minimum, there must be an excess energy for the particles which are at the surface since they have neighbors only on the liquid side. We think that the excess surface tension is a consequence of the colloidal properties of this dispersion, and the viscoelastic properties and the excess surface tension have common roots: namely, the interaction between the melamine particles in the stationary liquid.

CONCLUSIONS

Diffusion-controlled adsorption is found for the conventional polyol/surfactant system. The mini-

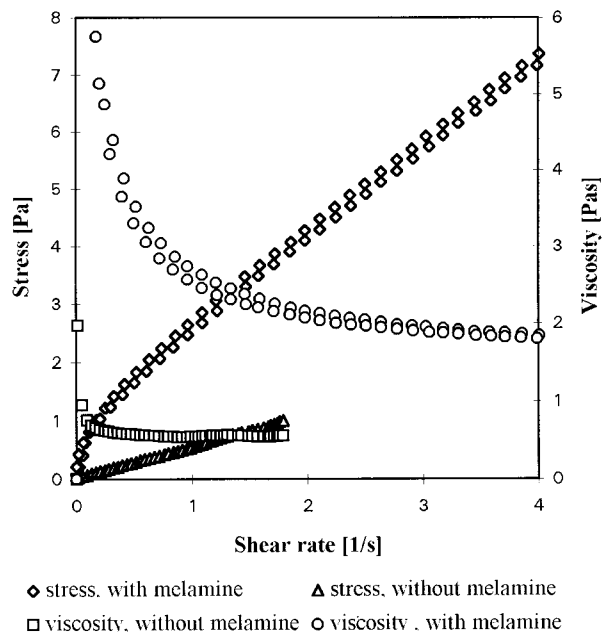


Figure 6 Flow curve of the 0.8 pphp conventional system with and without 25 pphp melamine ultrafine at 298 K.

mal surfactant concentration which is needed to stabilize the expanding surface can be calculated from the surface tension versus concentration curve at different times. The addition of melamine particles increases the surface tension. This may be explained by the energetically different state of particles in the surface layer than those in the bulk. The dynamic surface pressure and the aging of the surface is very important in polyurethane foam production since the expanding bubbles should be stabilized in the period of the foam rise. We have seen from the results that the aging process and the optimal surfactant concentration of polyurethane production is not influenced by melamine. The surfactant does not adsorb on the surface of the melamine. The wetting of the melamine by the conventional polyol and by the solution of 0.8 pphp is in both cases the same.

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