

Evaluation of foam properties of saponin from *Ilex paraguariensis* A. St. Hil. (Aquifoliaceae) fruits

Gizele Scotti do Canto, Janine Treter, Samanta Yang, Gustavo Luís Borré, Maria Paula Garfo Peixoto, George González Ortega*

Faculdade de Farmácia, Universidade Federal do Rio Grande do Sul

Saponins are natural compounds able to form abundant foam, a desirable quality required in some chemical, foods, cosmetic and pharmaceutical processes. *Ilex paraguariensis* A. St. Hil. (Aquifoliaceae) known as mate, is a South American widely cultivated specie due to the preparation of a tea-like beverage from its leaves. Moreover, its green fruits are a rich source of non-toxic and very low haemolytic saponins. In this study, mate saponin fraction (MSF) was evaluated as a foam former, focusing on its foamability, foam lifetime, and film drainage in the presence of different electrolytes (ionic strength $I = 0.024$ M). Sodium dodecyl sulphate (SDS) and polysorbate 80 (Poly-80) were used as reference surfactants. The critical micelle concentration (CMC), the minimum attainable surface tension (γ_{CMC}), surface excess concentration (Γ) and cross-section molecular surface (A) values of MSF were comparable to those of Poly-80. The foamability of MSF and both reference surfactants was equivalent. The addition of $MgCl_2$ resulted in a negative effect on MSF foamability. The salts NaCl, KBr, and KNO_3 exhibited a negative influence on MSF foam lifetime. Similar behavior was observed for MSF film drainage (order of activity: $Na_2HPO_4 > MgCl_2 \approx NaCl \approx KNO_3 > KBr$), where a primary fast film drainage rate was followed by film thinning stabilization after around 5 min. The behavior described above seems to be uncorrelated to the solutions' zeta potential.

Uniterms: *Ilex paraguariensis*/Aquifoliaceae/Mate/saponins/Surfactants/foam/assay.

As saponinas são compostos naturais capazes de formar espuma abundante, qualidade desejável exigida em alguns processos químicos, alimentícios, cosméticos e farmacêuticos. *Ilex paraguariensis* A. St. Hil. (Aquifoliaceae), mais conhecida como mate, é uma espécie largamente cultivada devido ao consumo do chimarrão. Além disso, seus frutos verdes representam uma fonte rica de saponinas pouco tóxicas e pouco hemolíticas. Nesse trabalho avaliou-se a fração de saponinas de mate (MSF) como formadora de espuma, com ênfase na espumabilidade, permanência da espuma e drenagem do filme na presença de diferentes eletrólitos ($I = 0,024$ M). Dodecil sulfato de sódio (SDS) e polissorbato 80 (Poly-80) foram utilizados como tensoativos-referência. Os valores de concentração micelar crítica (CMC), tensão superficial na CMC (γ_{CMC}), concentração de excesso de superfície (Γ) e área do grupamento polar na interface (A) referente à MSF foram comparáveis ao Poly-80. A espumabilidade da MSF e de ambos os tensoativos-referência foram equivalentes. A adição de $MgCl_2$ resultou em um efeito negativo sobre a espumabilidade de MSF. Os sais NaCl, KBr e KNO_3 tiveram influência negativa sobre a estabilidade da espuma. Em relação à drenagem do filme de MSF, após 60 min. seguiu-se a ordem $Na_2HPO_4 > MgCl_2 \approx NaCl \approx KNO_3 > KBr$, caracterizando uma drenagem inicial acelerada seguida pelo equilíbrio hidrodinâmico do filme após 5 min. O comportamento observado parece não estar relacionado com o potencial zeta das soluções.

Unitermos: *Ilex paraguariensis*/Aquifoliaceae/Mate/saponinas/tensoativos/espuma/análise.

*Correspondence: G. G. Ortega. Faculdade de Farmácia, Universidade Federal do Rio Grande do Sul. Avenida Ipiranga, 2752 - 90610-000 - Porto Alegre - RS, Brazil. E-mail: ortega@farmacia.ufrgs.br

INTRODUCTION

Ilex paraguariensis A. St. Hil. (Aquifoliaceae), known as mate, is widely cultivated in Southern Brazil and other bordering countries for use in the preparation of tea-like beverages. The Brazilian crop of mate leaves attains approximately half a million tons per year (Mosele, 2002), not including mate fruits, which are discarded as a byproduct of the erva-mate production process. The stimulant action on the central nervous system of mate leaves is well established and is ascribed to their high methylxanthines content (Wichtl, 1989). In contrast, the highest saponin content occurs in the unripe mate fruits rather than in its leaves or other aerial parts (Pavei, 2004). Mate saponins are bidesmosidic and monodesmosidic compounds with a prevalence of non-ionic triterpenic derivatives of ursolic and oleanolic acids (Kraemer *et al.*, 1996; Taketa, 2001; Pavei, 2004).

As biodegradable natural surfactants, saponins are able to reduce the surface tension and improve foamability of aqueous solutions, even at low concentrations (Hostettmann, Marston, 1995; Sparg *et al.*, 2004). Moreover, saponins are also able to form intricate micelles showing a rather complex behavior as colloids (Vochten *et al.*, 1969; Mitra, Dungan, 1997, 2001).

Foams are metastable systems occurring at the liquid-air interface (Hunter, 1995) and have many applications in chemical, foods, cosmetic and pharmaceutical processes (Karakashev, Manev, 2001; Backleh *et al.*, 2004; Khristov *et al.*, 2004; Rouimi *et al.*, 2005). The main foam properties: foamability, foam lifetime, and film drainage are influenced by several internal or external factors such as surface tension, critical micelle concentration (CMC), surface excess concentration (Γ) and specific molecular features of the surfactant, as well as pressure, temperature, electrolytes, ionic strength and pH (Hunter, 1995; Hilgenfeldt *et al.*, 2001; Graner, 2002; Nguyen *et al.*, 2003; Pandey *et al.*, 2003; Tchoukov *et al.*, 2004; Harvey *et al.*, 2005; Neethling *et al.*, 2005; Tamura *et al.*, 2006). Similarly, the assay methods also play an important role on foamability and foam lifetime measurements, and results from different methods can differ (Backleh *et al.*, 2004; Potreck, 2004).

The present study aimed to evaluate the foam produced by an enriched mate saponin fraction, and to compare it to sodium dodecyl sulfate and polysorbate 80, chosen as ionic and non-ionic reference surfactants, respectively.

EXPERIMENTAL

Reagents and reference substances

Sodium dodecyl sulfate ($C_{12}H_{25}NaO_4S$, MW: 288.38) and polysorbate 80 ($C_{64}H_{124}O_{26}$, MW: 1310) (Merck), sodium chloride, potassium bromide and potassium nitrate (Synth), and magnesium chloride hexahydrate (Vetec) and monosodium phosphate (Nuclear) reagents used in this study were all of p.a. grade. Matesaponin-1, one of the main mate saponins, was kindly supplied by Prof. Dr. M.L. Athayde (UFMS, Brazil).

Electrolyte solutions

All aqueous solutions of each electrolyte (NaCl, KBr, KNO_3 , $MgCl_2$ and Na_2HPO_4) had an ionic strength of 0.024 M (Angarska *et al.*, 1998; Karakashev, Manev, 2001) and were utilized in the preparation of the working solutions of saponins and reference surfactants instead of water, as required.

Mate saponin fraction (MSF)

Unripe mate fruits (harvest in December 2006) were collected from an established cultivar of Ervateira Barão (Barão de Cotegipe, RS, Brazil). Fruits were dried for 72 h at 35 °C in a forced ventilation oven (Memmert, Germany), and milled using a cutter mill (Retsch SK1, Germany). The plant powder (0.85 μ m) was macerated with a 40% ethanol solution (10% w/v) for 40 min. and then extracted by turboextraction (IKA T-25, Germany) for 15 min. to avoid overheats. The extract was filtered and concentrated under vacuum (Rotovaporator Büchi B-480, USA) to one-half of its original volume and then freeze dried (Modulyo 4L Edwards, USA). The mate saponin fraction (MSF) was obtained from the freeze dried extract by solid phase extraction (Braz. Pat. PI 0501510-3 12/12/2006; Pavei, 2004). The product is free of pigment, chlorophyll, flavonoids, and polyphenols.

METHODS

Surface tension and Critical Micelle Concentration (CMC)

The surface tension was determined by the Le Comte DuNöuy method (model 8600, Krüss, Germany) at 20 ± 2 °C at a relative humidity of 55-65% (Digital Thermohygrometer TFA, Germany). Aqueous solutions ranging in concentration from 0.001 to 20.0 g/L were prepared using distilled water. The saponins molar concentration was expressed as matesaponin-1 (MW: 996.45). The CMC was calculated by plotting surface tension values against the natural logarithm of the concentration.

The surface excess concentration (Γ) was calculated by Gibbs surface adsorption equation 1, and the molecular cross-section area (A) was determined by equation 2 (Shaw, 1992). The results are expressed without further correction and each value corresponds to the mean of at least three measurements.

$$\Gamma = -(1/RT) (d\gamma/d \ln C) \quad (\text{Eq.1})$$

$$A = 1/(\Gamma N_{AV}) \quad (\text{Eq.2})$$

Where, Γ is the surface density (mmol/cm^2); R is $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is the thermodynamic temperature (K), γ is the surface tension (mNm^{-1}), C is the surfactant concentration (mmol L^{-1}), A is the molecular cross-section of the polar headgroup (\AA^2), and N_{AV} is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).

Foamability and foam lifetime assays

The instrument design was based on the Wieninger principle (Potreck, 2004). The concentrations of all saponin and surfactant solutions were established considering the inner volume of the device, namely, MSF 1.5 mmol L^{-1} (equivalent to 10 CMC), Poly-80 6 mmol L^{-1} (158 CMC); SDS 85 mmol L^{-1} (10 CMC). A 20 mL-aliquot of each surfactant solution was poured into a cylindrical borosilicate glass column (35.5 cm x 3.6 cm) equipped with a sintered glass septum (G4, 3.6 cm x 4 mm), fitted at the column bottom. Compressed dried air was supplied by a reciprocal pump (Inalar compact, Brazil) at a flow rate of 2 L/min for exactly 20 sec (Flowmeter Protec, Brazil). Pipes and air purge valve internal diameters were 2 mm. The temperature was $25 \pm 2 \text{ }^\circ\text{C}$ and the air outlet pressure $0.05 \pm 0.01 \text{ kgf cm}^{-2}$.

The foam column height (foamability) was recorded immediately after air supply suppression. The volume of liquid drained (LV) was measured after 0; 1; 5; 10; 30 and 60 min. using a graduated scale fixed outside the

glass column. The volume fraction of liquid retained in foam (LVF) was calculated using equation 3. Each result expresses the mean value of at least three replicates using fresh solutions.

$$\text{LVF} = 20 - \text{LV} \quad (\text{Eq. 3})$$

Zeta potential

Zeta potential measurements of MSF were performed on a Zeta potential Analyzer (Zeta Plus-BTC, Brookhaven, New York) at $25 \text{ }^\circ\text{C}$. Aqueous MSF solutions with and without electrolytes were prepared to have a concentration equivalent to 10-fold the CMC, calculated as matesaponin-1. Each result represents the mean of five replicates.

RESULTS AND DISCUSSION

The interface and micelle properties of sodium dodecyl sulfate (SDS) and polysorbate 80 (Poly-80) are well documented in the current literature and are therefore reliable reference substances to evaluate the MSF interface properties (Verlag, 2002). The surface tension isotherms and the respective values of surface tension at the CMC, surface excess concentration (Γ) and cross-section molecular surface (A) determined for SDS, Poly-80, and MSF are presented together in Table I.

The MSF values of CMC and γ_{CMC} were 0.15 mM (150 mg/L) and 52.8 mN m^{-1} , which are close to those of Poly-80. A similar CMC value of 123 mg/L was previously reported for saponin fraction from *Gypsophila struthium* roots and also derived from oleanolic acid (Vochten *et al.*, 1969). Conversely, the ionic SDS solution showed the lowest γ_{CMC} and highest Γ values of all.

The calculated MSF molecular cross-section (97.7 \AA^2) was comparable to the value reported for quilaja saponins (83 \AA^2), considered an unexpectedly high diameter given its hydrophilic sugar chains (Mitra, Dungan,

TABLE I - Critical micelle concentration (CMC), minimum attainable surface tension (γ_{CMC}), surface excess concentration (Γ) and molecular cross-section (A) determined for sodium dodecyl sulfate (SDS), polysorbate 80 (Poly-80) and mate saponin fraction (MSF) solutions

Solution	CMC (mM)	γ_{CMC} (mN m^{-1})	Γ (mmol m^{-2})	A (\AA^2)
SDS	8.58	37.0	2.87	57.87
Poly-80	0.038	46.0	1.84	90.27
MSF **	0.15	52.8	1.70	97.71

* CMC values: 8.3 mM for SDS (Gander *et al.*, 1985; Patist *et al.*, 2002) and 0.022 mM for Poly-80 (Decroos *et al.*, 2007)

** expressed as molar concentration of matesaponin-1 (MW: 996.45).

1997). Preliminary studies by dynamic, static light scattering showed that the size of MSF micelles can be even larger than those reported for quilaia (results not shown).

The highest molecular cross-section values are expected for Poly-80 and MSF, since Γ and γ_{CMC} are inversely related properties (Hunter, 1995; Tan *et al.*, 2005).

Influence of electrolytes on foamability

The set of salts chosen comprised 1:1 electrolytes (NaCl, KBr, and KNO_3), a 1:2 electrolyte (MgCl_2) and a polyelectrolyte (Na_2HPO_4). The pH of the MSF, SDS and Poly-80 solutions with and without electrolytes are showed in Table II.

Although the ionic strength of the five electrolyte working solutions was kept constant at $I = 0.024 \text{ M}$ (Angarska *et al.*, 1998), some unexpected pH-variations in the working solutions containing Na_2HPO_4 became evident.

TABLE II - Measured pH values for mate saponin fraction (MSF), sodium dodecyl sulfate (SDS), and polysorbate 80 (Poly-80) solutions with and without electrolytes ($I = 0.024 \text{ M}$) at $20 \pm 2^\circ \text{C}$

Electrolyte	Measured pH ($\bar{X} \pm s$)		
	MSF	SDS	Poly-80
None	6.20 ± 0.132	7.61 ± 0.05	7.55 ± 0.08
NaCl	6.37 ± 0.02	7.36 ± 0.02	6.83 ± 0.06
KBr	6.31 ± 0.01	7.79 ± 0.02	7.16 ± 0.06
KNO_3	6.70 ± 0.06	7.32 ± 0.01	7.23 ± 0.07
MgCl_2	6.28 ± 0.05	6.94 ± 0.14	6.55 ± 0.01
Na_2HPO_4	9.17 ± 0.07^a	10.53 ± 0.02	8.83 ± 0.01

An apparent pH displacement was observed in the pH of the Na_2HPO_4 after SDS addition, in contrast to previous reports under similar experimental conditions (Angarska *et al.*, 1998). Note that the concentration at 1.5 mM, 85.8 mM, and 0.60 mM, respectively, were theoretically unable to exceed the buffer capacity of a Na_2HPO_4 0.024 M solution.

The effect of the addition of electrolyte on foamability and foam lifetime (expressed as foam column height) is presented in Table III.

With the exception of MgCl_2 , the addition of electrolytes did not affect MSF foamability. On the other hand, the influence of the electrolytes was evident on MSF foam lifetime, but not on Poly-80 foam lifetime. However, the effect of KNO_3 and Na_2HPO_4 on Poly-80 foamability was positive, but negligible for MSF. Moreover, MSF foamability was decreased by Mg^{2+} , whereas Poly-80 was unchanged by Mg^{2+} . In theory, foamability changes induced

TABLE III - Results of addition of electrolytes ($I = 0.024 \text{ M}$) on foamability and foam column height (FCH) after 60 min for mate saponin fraction (MSF), sodium dodecyl sulfate (SDS), and polysorbate 80 (Poly-80) solutions

Electrolyte	Foamability (cm)		
	$(\bar{X} \pm s)$		
	MSF	SDS	Poly-80
None	16.7 ± 1.2	17.2 ± 0.1	14.5 ± 0.8
NaCl	16.6 ± 0.4	14.9 ± 0.7^a	15.0 ± 1.6
KBr	16.9 ± 0.2	16.7 ± 0.4	15.6 ± 0.6
KNO_3	16.7 ± 1.0	15.6 ± 0.6^a	16.8 ± 0.7^a
MgCl_2	14.2 ± 0.7^a	15.1 ± 2.1	15.0 ± 2.6
Na_2HPO_4	15.2 ± 0.8	17.0 ± 0.1	16.1 ± 0.1^a
Electrolyte	FCH after 60 min (cm)		
	$(\bar{X} \pm s)$		
	MSF	SDS	Poly-80
None	11.5 ± 0.4	15.0 ± 0.8	11.8 ± 0.8
NaCl	3.0 ± 0.0	10.4 ± 0.4	12.0 ± 1.4
KBr	2.7 ± 0.4	9.3 ± 1.8	12.6 ± 1.3
KNO_3	1.3 ± 0.2	11.7 ± 1.8	13.0 ± 1.1
MgCl_2	0.7 ± 0.1	12.0 ± 1.6	11.7 ± 2.4
Na_2HPO_4	0.6 ± 0.1	13.7 ± 0.4	12.1 ± 0.1

^a Indicates statistically significant different in value on direct comparison to confidence intervals of working solution without addition of electrolytes.

by electrolytes should be similar in non-ionic surfactants (Yamanaka *et al.*, 1975; Hunter, 1995; Schick, 1997). Therefore, the behavior difference observed between MSF and Poly-80 suggests the presence of partial ionized saponins in MSF.

Given that foamability and micelle relaxation time are inversely correlated phenomena, the negative effect caused by Mg^{2+} on MSF foamability likely involves a micelle stabilization mechanism (Patist *et al.*, 2002; Harvey *et al.*, 2005).

The results from the film drainage assay with and without electrolyte addition, expressed as volume of liquid retained in the foam are shown in Table IV.

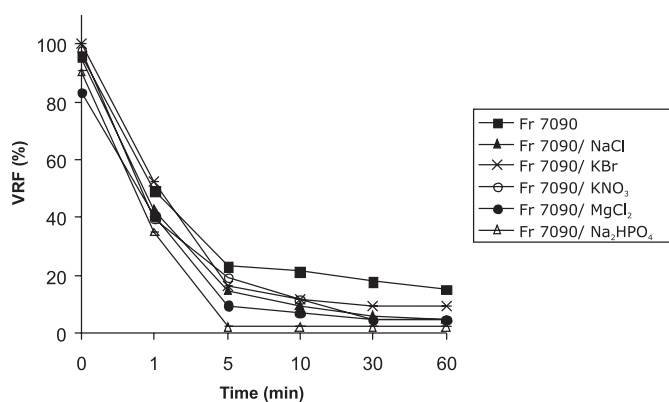
In general, but particularly in the case of MSF, addition of electrolytes accelerated liquid drainage (Figure 1).

All drainage curves reached hydrodynamic equilibrium after approximately 5 min. For MSF, the effect of each salt on liquid drainage rate can be ordered as follows: $\text{Na}_2\text{HPO}_4 > \text{MgCl}_2 \approx \text{NaCl} \approx \text{KNO}_3 > \text{KBr}$. The drainage rate of MSF was comparable but slower than those of SDS and Poly-80. The analysis of the data

TABLE IV - Percentage liquid retained in foam prepared with mate saponin fraction (MSF), sodium dodecyl sulfate (SDS) and polysorbate 80 (Poly-80) solutions, with and without electrolyte addition

Parameter	Electrolyte	MSF	SDS	Poly-80
LVF _{to} * (%) ($\bar{X} \pm s$)	None	96.2 ± 0.1	57.1 ± 0.6	57.1 ± 0.1
	NaCl	95.2 ± 0.0	63.3 ± 0.2	57.1 ± 0.2
	KBr	100.0 ± 0.0	76.2 ± 0.2	61.9 ± 0.6
	KNO ₃	97.6 ± 0.1	54.8 ± 0.2	66.7 ± 0.5
	MgCl ₂	83.3 ± 0.1	52.4 ± 0.1	54.3 ± 0.1
	Na ₂ HPO ₄	90.5 ± 0.3	95.2 ± 0.1	54.8 ± 0.6
LVF ₁₆₀ ** (%) ($\bar{X} \pm s$)	None	15.2 ± 0.2	7.1 ± 0.1	9.5 ± 0.0
	NaCl	4.8 ± 0.0	6.2 ± 0.0	7.1 ± 1.4
	KBr	9.5 ± 0.0	3.3 ± 0.1	9.5 ± 0.2
	KNO ₃	4.8 ± 0.0	4.8 ± 0.0	7.1 ± 0.0
	MgCl ₂	4.8 ± 0.0	6.2 ± 0.0	9.0 ± 0.1
	Na ₂ HPO ₄	2.4 ± 0.0	12.0 ± 0.0	6.2 ± 0.1

* LVF₁₀ = Volume of liquid retained in foam at time zero; ** LVF₁₆₀ = Volume of liquid retained after 60 min.

**FIGURE 1** - Influence of different electrolytes ($I = 0.024$ M) on liquid drainage rate of mate saponin fraction (MSF) foams.

presented in Tables III and IV indicates that foamability and drainage rate of MSF are uncorrelated. According to theory, the initial fast film drainage rate can be ascribed to a lowering of the surface shear viscosity and to interaction between adjacent surfactant molecules placed at the lamellar interface (Pandey *et al.*, 2003), while the film thinning stabilization observed after about 30 min. could be explained by positive surface elasticity or the

Gibbs-Marangoni effect (Shaw, 1992; Nierstrasz, Frens, 1999; Harvey *et al.*, 2005).

Influence of electrolytes on zeta potential of MSF solutions

The results from the zeta potential assay revealed that the MSF can be affected by electrolytes, in spite of its predominant non-ionic character (Table V).

The analysis of the data contained in Tables III, IV, and V revealed no apparent relationship between LVF values, foam stability or zeta potential after addition of NaCl, KBr, MgCl₂, and Na₂HPO₄, as expected (Schukin *et al.*, 1988). These first three electrolytes were able to significantly diminish the negative zeta potential of the MSF solution, although their effect on foam lifetime differed between the electrolytes. Moreover, Na₂HPO₄ increased the negative zeta potential of the MSF solution while its effect on MSF foam lifetime and LVF was, by contrast, clearly negative. The KNO₃ led to a different case in which none of the parameters studied was affected. This indicates that foamability, LVF and zeta potential were not significantly changed by its addition.

TABLE V - Effect of electrolyte addition ($I = 0.024$ M) on zeta potential zeta of mate saponin fraction (MSF) solution at 10-fold its critical micelle concentration (CMC)

	MSF	MSF/NaCl	MSF/KBr	MSF/KNO ₃	MSF/MgCl ₂	MSF/Na ₂ HPO ₄
Zeta potential (mV)	-22.3 ± 1.4	-3.17 ± 1.4	-2.0 ± 0.7	-23.6 ± 4.1	-6.2 ± 3.3	-34.8 ± 7.7

CONCLUSION

Studies on foam obtained from saponins are scarce, although this class of natural biodegradable product is emerging as a workable alternative to synthetic surfactants. The mate saponins, represented here by an enriched fraction, are able to form abundant and persistent foam. However, in contrast to foams produced from sodium dodecyl sulfate and polysorbate 80, the mate saponins foam appears to be especially sensitive to electrolytes. In fact, foamability, foam lifetime and film drainage were negatively affected by all electrolytes assayed in this study. Moreover, the potential zeta induced by electrolyte addition could not be associated to the negative effects on the MSF foam.

ACKNOWLEDGMENTS

The authors are grateful to the National Council for Research and Development (CNPq) for financial support and to Ervateira Barão (Barão de Cotegipe, RS) for the raw material.

REFERENCES

- ANGARSKA, J. K.; TACHEV, K. D.; KRALCHEVSKY, P. A.; MEXHRETEAB, A.; BROZES, G. Effects of counterions and co-ions on the drainage and stability of liquid films and foams. *J. Colloid Interface Sci.*, v.200, n.1, p.31-45, 1998.
- BACKLEH, M.; EKICI, P.; LEUPOLD, G.; COELHAN, M.; PARLAR, H. Enrichment of the glycoalkaloids α -solanine and α -chaconine from potato juice by adsorptive bubble separation using a pH gradient. *J. Sep. Sci.*, v.27, n.12, p.1042-1044, 2004.
- DECROOS, K.; VINCKEN, J. P.; VAN KONINGSVELD, G. A.; GRUPPEN, H.; VERSTRAETE, W. Preparative chromatographic purification and surfactant properties of individual soyasaponins from soy hypocotyls. *Food Chem.*, v.101, n.1, p.324-333, 2007.
- GANDER, B.; VENTOURAS, K.; GURNY, R.; DIELKER, E. In vitro dissolution medium with supramicellar surfactant concentration and its relevance for in vivo absorption. *Int. J. Pharm.*, v.27, n.1, p.117-124, 1985.
- GRANER, F. Two-dimensional fluid foams at equilibrium. In: MECKE, K.R., STOYAN, D. (Eds.). *Lecture notes in Physics*. Heidelberg: Springer Berlin, 2002. LNP 600. p.187-211.
- HARVEY, P. A.; NGUYEN, A. V.; JAMEXSON, G. J.; EVANS, G. M. Influence of sodium dodecyl sulphate and dowfroth frothers on froth stability. *Miner. Eng.*, v.18, n.3, p.311-315, 2005.
- HILGENFELDT, S.; KOEHLER, S. A.; STONE, H. A. Dynamics of coarsening foams: Accelerated and self-limiting drainage. *Phys. Rev. Lett.*, v.86, n.20, p.4704-4707, 2001.
- HOSTETTMANN, K.; MARSTON, A. *Saponins*. Cambridge: University Press, 1995. p.547.
- HUNTER, R. J. *Foundations of colloid science*. Oxford: Oxford University Press, 1995. v.1, 673 p.
- KARAKASHEV, S. I.; MANEV, E. D. Frothing behavior of nonionic surfactant solutions in the presence of organic and inorganic electrolytes. *J. Colloid Interface Sci.*, v.235, n.1, p.194-196, 2001.
- KHRISTOV, K. H.; EXEROWA, D.; CHRISTOV, L.; MAKIEVSKI, A. V.; MILLER, R. Foam analyzer: An instrument based on the foam pressure drop technique. *Rev. Sci. Instrum.*, v.75, n.11, p.4797-4803, 2004.
- KRAEMER, K. H.; TAKETA, A. T. C.; SCHENKEL, E. P.; GOSMANN, G.; GUILLAUME, D. Matesaponin 5, a Highly Polar Saponin from *Ilex Paraguariensis*. *Phytochemistry*, v.42, n.4, p.1119-1122, 1996.
- MITRA, S.; DUNGAN, S. Micellar properties of Quillaja saponin. 1. Effects of temperature, salt and pH on solution properties. *J. Agric. Food Chem.*, v.45, n.5, p.1587-1595, 1997.
- MITRA, S.; DUNGAN, S. Cholesterol solubilization in aqueous micellar solutions of quillaja saponin, bile salts, or nonionic surfactants. *J. Agric. Food Chem.*, v.49, n.1, p.384-394, 2001.
- MOSELE, S. H. *A governança na cadeia agro-industrial da erva-mate na região do Alto Uruguai Rio-grandense, sob a ótica da cadeia de suprimentos*. Porto Alegre, 2002. 231p. [Dissertação de Mestrado. Centro de Estudos e Pesquisa em Agronegócios. Programa de Pós-Graduação em Agronegócios. Universidade Federal do Rio Grande do Sul].
- NEETHLING, S. J.; LEE, H. T.; GRASSIA, P. The growth, drainage and breakdown of foams. *Colloid Surf. A.*, v.263, n.1-3, p.184-196, 2005.

- NGUYEN, A. V.; HARVEY, P. A.; JAMEXSON, G. J. Influence of gas flow rate and frothers on water recovery in a froth column. *Miner. Eng.*, v.16, n.11, p.1143-1147, 2003.
- NIERSTRASZ, V. A.; FRENS, G. Marginal regeneration and the Marangoni effect. *J Colloid Interface Sci.*, v.215, n.1, p.28-35, 1999.
- PANDEY, S.; BAGWE, P. R.; SHAH, O. D. Effect of counterions on surface and foaming properties of dodecyl sulfate. *J. Colloid Interface Sci.*, v.267, n.1, p.160-166, 2003.
- PATIST, A.; KANICKY, J.; SHUKLA, P. K.; SHAH, D. Importance of micellar kinetics in relation to technological processes. *J. Colloid Interface Sci.*, v.245, n.1, p.1-5, 2002.
- PAVEI, C. *Desenvolvimento de métodos analíticos e tecnológicos aplicados à fração saponosídica presente nos frutos de Ilex paraguariensis A. St. Hil.* Porto Alegre, 2004. 149p. [Dissertação de Mestrado. Faculdade de Farmácia. Universidade Federal do Rio Grande do Sul].
- POTRECK, M. *Optimierte Messung der Bierschaumstabilität in Abhängigkeit von Milieubedingungen und fluiddynamischen Kennwerten.* Berlin, 2004. 218p. [Genehmigte Dissertation. Fakultät III – Prozesswissenschaften, Universität Berlin].
- ROUIMI, S.; SCHORSCH, C.; VALENTINI C.; VASLIN, S. Foam stability and interfacial properties of milk protein–surfactant systems. *Food Hydrocolloids*, v.19, n.3, p.476-478, 2005
- SCHICK, M. *Nonionic surfactants physical chemistry.* New York: Marcel Dekker Inc., 1997. v.23, p.1123. (Surfactants Science Series).
- SHAW, D. J. *Introduction to colloid and surface chemistry.* 4.ed. London: Butterworth-Heinemann, 1992. 306 p.
- SCHUKIN, E. D.; PERTSOV, A. V.; AMÉLINA, E. A. *Química coloidal.* Moscou: Editora Mir, 1988. 301 p.
- SPARG, S. G.; LIGTH, M. E.; VAN STADEN, J. Biological activities and distribution of plant saponins. *J. Ethnopharmacol.*, v. 94, n.2-3, p.219-243, 2004.
- TAKETA, A. T. C. *Phytochemical investigation on the triterpenes and triterpenoids glycosides from the fruits and leaves of South American Ilex species.* Bonn, 2001. 211 p. [Ph.D. thesis, Rheinischen Friedrich-Wilhelms-Universität GER].
- TAMURA, T.; TAKEUCHI, Y.; KANEKO, Y. Influence of surfactant structure on the drainage of nonionic surfactant foam films. *J. Colloid Interface Sci.*, v.206, n.1, p.112-121, 2006.
- TAN, S. N.; FORNASIERO, D.; SEDEV, R.; RALSTON, J. The role of surfactant structure on foam behavior. *Colloid Surf. A*, v.263, n.1-3, p.233-238, 2005.
- TCHOUKOV, P.; MILEVA, E.; EXEROWA, D. Drainage time peculiarities of foam films from amphiphilic solutions. *Colloid Surf. A*, v.238, n.1-3, p.19-25, 2004.
- VERLAG, E. C. *Fiedler Encyclopedia of excipients for pharmaceuticals, cosmetics and related areas.* 5.ed. Aulendorf: Editio Cantor, 2002. v.2, 1737 p.
- VOCHTEN, R.; JOOS, P.; RUYSEN, R. Physico-chemical properties of saponin and their relation to the foam stability. *J. Pharm. Belg.*, v.24, n.5, p.213-226, 1969.
- WICHTL, M. *Teedrogen.* Ein Handbuch für die Praxis auf wissenschaftlicher Grundlage. 2 ed. Stuttgart: Wissenschaftliche Verlagsgesellschaft, 1989. 568 p.
- YAMANAKA, C.; YAMANAKA, T.; MIZUI, J. YAMAGUCHI, N. Self-phase modulation of laser light in a laser-produced plasma. *Phys. Rev. A.*, v.11, n.6, p.2138-2141, 1975.

Received for publication on 13th March 2009
Accepted for publication on 27th August 2009