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Thermodynamic and structure studies of Gibbs films at soft interfaces

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Abstract The thermodynamic and X-ray reflectivity studies were applied to the adsorbed films of 1-eicosanol, partially hydrogenated perfluorodecanol, and their mixtures at the hexane/water interface and clearly demonstrated the existence of domains. The thermodynamic and FTIR studies on ethyleneglycol monododecyl ether system and the thermodynamic and total reflection XAFS studies on dodecyltrimethylammonium bromide system at air/water interfaces confirmed that the inhomogeneous structure is rather generally observed in the adsorbed films. The knowledge from the thermodynamic and structure studies has been combined and further utilized in the mesoscopic thermodynamic formulation on the Gibbs films at soft interfaces.

Keywords Adsorbed films · Domain formation · Gibbs films · Phase transition · Soft interfaces · Thermodynamics

Introduction

Gibbs films of amphiphile molecules at soft interfaces have been widely studied from the viewpoints not only of fundamental surface sciences but also of nanotechnologies and biosciences. Here Gibbs films are referred to as adsorbed films from the upper or/and the lower bulk phases to the interface between them and soft interfaces to as fluid/fluid interfaces such as air/water and oil/water interfaces. There are various kinds of colloidal assemblies in solutions such as micelles, vesicles, bilayers, lyotropic liquid crystals, and so on [1]. The boundary between these assemblies and the surrounding media is the soft interfaces and thus shedding light on the phenomena at soft interfaces is also essentially required to understand the principles and processes of organization of individual molecules into such assemblies.

Although the Gibbs films do not exist for themselves without bulk phases and are variable in their thicknesses depending on molecular structure of amphiphiles, their states are categorized roughly and generally into three states of gaseous, expanded, and condensed ones [2] similarly to those of bulk phases. The changes among these states at interfaces are advanced sometimes gradually but often suddenly like the first order phase transition by changing thermodynamic variables such as temperature, pressure, and concentrations of surfactants [3–8]. In order to understand the adsorption at soft interfaces from molecular level, information on structure of soft interfaces is highly required. Although it is rather difficult to perform it with respect to soft interfaces compared to solid surfaces, several methods have been developed, e.g., Brewster Angle Microscope (BAM) [7], ellipsometry [9], Neutron scattering [10], X-ray reflectivity [11–14], and nonlinear spectroscopic method [15].

This paper reports the interfacial states and the phase transition of Gibbs films at water/air and oil/water interfaces studied by interfacial tension and structural methods such as X-ray reflectivity, FTIR, and total reflection XAFS.

Experimental

1-Icosanol (C20OH) and 1,1,2,2-tetrahydroheptadecafluorodecanol (FC10OH) were purified by recrystallization

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from hexane solution described in our previous papers [6, 16]. Dodecyltrimethylammonium bromide (DTAB) was purchased form Tokyo Chemical Industry Co. Ltd and purified from ethanol/acetone mixture [17]. Ethyleneglycol monododecyl ether (C12E1) was purchased from Nikko Chemicals Co. Ltd and since its purity was more than 99.9% by gas liquid chromatography, it was used without further purification [18]. The methods of purification and purity confirmation of water and hexane and the procedure of interfacial tension measurements were also reported previously [19]. The X-ray reflectivity, the total reflection XAFS, and the external reflection FTIR methods were described in our previous papers [17, 18, 20].

Results and discussion

For interfaces between oil and water phases with two amphiphiles, the interfacial tension γ is written as a function of temperature T, pressure p, and the molalities of the first and second amphiphile components m_1 and m_2 by

$$\begin{aligned} d\gamma &= -\Delta s dT + \Delta v dp - RT(\Gamma_1^{H}/m_1)dm_1 \\ &\quad - RT(\Gamma_2^{H}/m_2)dm_2 \end{aligned} \tag{1}$$

where Δs and Δv are the entropy and volume associated with the adsorption of amphiphiles, Γ_1^H and Γ_2^H are the interfacial densities of amphiphiles, respectively [21]. It is advantageous to rewrite Eq. 1 as a function of the total molality m and the mole fraction of the second component in the amphiphile mixtures X_2 by

$$\begin{aligned} d\gamma &= -\Delta s dT + \Delta v dp - RT(\Gamma^{H}/m)dm \\ &\quad - RT(\Gamma^{H}/X_1X_2)(X_2^{H} - X_2)dX_2 \end{aligned} \tag{2}$$

for examining the miscibility of two amphiphiles and drawing information on molecular interaction in the adsorbed films by constructing phase diagram of adsorption [22]. Here $m = m_1 + m_2$ and $X_2 = m_2/m$ and, the total interfacial density $\Gamma^H$and the mole fraction of the second in the adsorbed films X_2^H are defined by

$$\Gamma^{H} = \Gamma_1^{H} + \Gamma_2^{H} \tag{3}$$

and

$$X_2^{H} = \Gamma_2^{H}/\Gamma^{H}, \tag{4}$$

respectively. All the analysis of interfacial tension data are based on these equations.

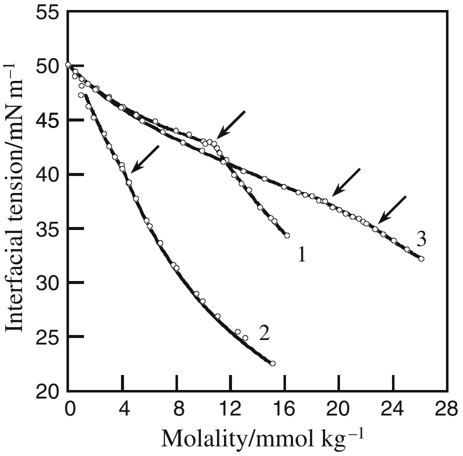

Fig. 1 Interfacial tension versus concentration curves; (1) C20OH, (2) FC10OH, (3) mixture at $X_2 = 0.280$

Figure 1 demonstrates the γ versus m curves of C20OH, TFC10OH, and their mixtures at $X_2 = 0.280$ at the interface between their hexane solutions and water at 298.15 K under atmospheric pressure. The γ value decreases and goes through a break point for C20OH, TFC10OH and two break points for the mixture, with increasing m. Since the interfacial tension is a kind of surface free energy, the presence of the break implies that a first order phase transition takes place in the interface. To examine the interfacial states below and above the transition points, first the interfacial densities Γ^H were evaluated using Eq. 2 and then converted into average area per one molecule $A = 1/\Gamma^{H}N_A$, where N_A is the Avogadro number. A is plotted against the interfacial pressure $\pi = \gamma^0 - \gamma$ in Fig. 2, where γ^0 is the interfacial tension of the pure hexane/water interface.

The value of A changes discontinuously at a certain π (denoted by π_1^{eq}) for C20OH and TFC10OH, while at two πs (denoted by π_1^{eq} and π_2^{eq}) for the mixture $X_2 = 0.280$, respectively. It should be noted that the π versus A curves have a totally different shape before and after the transition. For example, the π value of the C20OH system changes gradually with increasing A below the transition pressure π_1^{eq} but the π versus A curve above the π_1^{eq} is almost vertical. The latter means that the isothermal

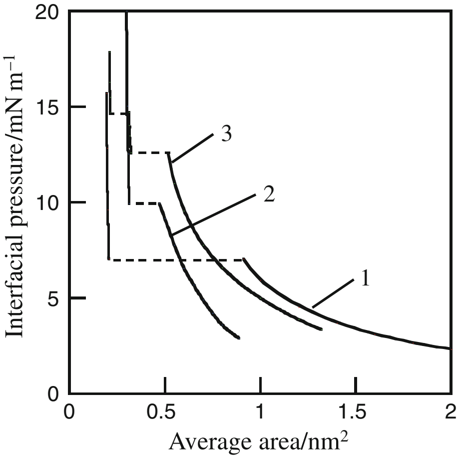

Fig. 2 Interfacial pressure versus mean area curves; (1) C20OH, (2) FC10OH, (3) mixture at $X_2 = 0.280$

compressibility defined by $\beta = -(1/A)(\partial A/\partial \pi)_{T,p,X_2^{\mathrm{H}}}$ is very close to zero and thus the film state is essentially similar to solid in its nature. The A value of about 0.2 nm^2 aboveπ_1^{eq} is a little larger but very close to the cross sectional area of all *trans* conformation of hydrocarbon chain and supports this view. The states below and above π_1^{eq} have been called the expanded and the condensed state, respectively. The similar situation is confirmed for the TFC10OH system, where the A value in the condensed state is about 0.3 nm^2, which is again similar to the cross sectional area of a fully extended fluorocarbon chain.

The more interesting is the π versus A curve of the mixture at $X_2 = 0.280$. The curve below the first transition pressure π_1^{eq} is locating in a position between the curves of the expanded states of both single amphiphile systems, which confirms that the film is also in the expanded state and two amphiphiles are miscible in it. The curve between π_1^{eq} and the second transition pressure π_2^{eq} coincides with that of the condensed state of the single FC10OH system and furthermore, the curve above π_2^{eq} does with that of the single C20OH system, respectively. This finding reveals that the adsorbed film of the mixture is transformed from the mixed expanded state to the condensed state of FC10OH and then to that of C20OH. Thus it is said that almost all C20OH molecules are squeezed out from the mixed expanded film and the condensed film of FC10OH is formed at π_1^{eq} and then all FC10OH molecules in the condensed film are replaced by C20OH molecules at π_2^{eq}. Why is the condensed film of FC10OH formed first and then that of C20OH followed? The answer for this was derived from a close examination of thermodynamic relations and is that FC10OH molecules have a larger cross sectional area than C20OH and interaction between FC10OH and C20OH molecules is weaker than that between same species [23].

The structure studies of Gibbs films at oil/water interfaces have been developed as described in “Introduction”. Uredat and Findenegg [7] have reported the BAM pictures of domain formation of 1-octadecanol (C18OH) and 1,1,2,2-tetrahydroperfluorododecanol (FC12OH), which are the homologues of C20OH and FC10OH at the hexane/water interface. The authors simultaneously monitored the BAM images and the interfacial tension, and clearly observed domains of condensed state and their morphological features. Since the characteristic features of their γ versus T curves at given concentrations, such as the existence of a break point and the magnitude of interfacial tension changes below and above the break point, are quite similar to those of the C20OH and FC10OH systems [20], it is expected to give similar BAM images also for the C20OH and FC10OH systems in the condensed state. Since the spatial resolution of BAM is at most the order of μm, however, we have employed the X-ray reflection method to obtain structural information on molecular level. The details of the results and discussion for the present systems have been reported in our previous paper [20] and briefly summarized in the followings.

The electron density of the hydrophobic layers of the condensed film of C20OH is 0.80 and almost equal to that of bulk liquid alkane and alkanols just above their freezing points. On the other hand, the electron density of the condensed film of FC10OH is in agreement with the value for the bulk solid fluoroalkane phases. The film thicknesses estimated from the electron density profiles were almost equal to those of fully extended alcohol molecules. Therefore, the X-ray reflection studies concluded that the C20OH condensed monolayer has a liquid ordering and the FC10OH condensed monolayer is a closely packed solid, which coincides almost completely with the thermodynamic conclusions. The striking contrast between C20OH and FC10OH appears in the mesoscopic structure of expanded films. The reflectivity data of the expanded states was tried to fit by two models. In the homogeneous layer model, amphiphile molecules are homogeneously dispersed in the film and in the inhomogeneous model, the domains of condensed monolayer are floating in the dilute gaseous monolayers but the average interfacial density has a similar magnitude to that in the expanded state. For the C20OH system, it was found that 7% of the interface is covered by domains having the same structure as the condensed monolayer, however, an alternative explanation that the expanded monolayer contains no condensed domains but C20OH molecules are homogeneously dispersed was also possible within the fitting error bars. For the FC10OH system, the reflectivity data could be well fit by only one parameter of the domain coverage and this success indicates that the monolayer consists of solid phase domains separated by the regions of gaseous monolayer. Furthermore, it was demonstrated that the coverage of condensed monolayer domain was about 50% at the phase transition point and still 30% domains remains well above it.

The X-ray reflection experiment was performed also for the mixture at $X_2 = 0.280$ and $m = 25.06$ mmol kg^{-1} as a function of temperature. The thermodynamic examination provided that the expanded film of C20OH and FC10OH mixture is transformed to the condensed film of FC10OH (CF) at T_1^{eq}(corresponding to π_1^{eq}) and the CF to the condensed film of C20OH (CH) at T_2^{eq}(corresponding to π_2^{eq}) as the temperature decreases as schematically shown in Fig. 3. With respect to the expanded state, the thermodynamic method could not show which one of a homogeneous one (EX) or an inhomogeneous one like (CF + GA) is real in it, where GA is a gaseous state with very low density like a gas. However, the X-ray method clearly demonstrated that the expanded state is the inhomogeneous

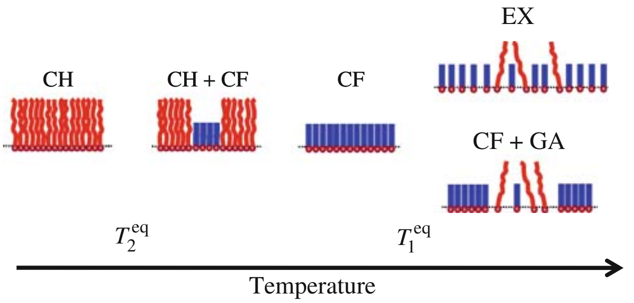

Fig. 3 Schematic illustration of adsorbed film of the mixture of C20OH and FC10OH at $X_2 = 0.280$; *CH* condensed film of C20OH, *CF* condensed film of FC10OH, *EX* expanded state, *GA* gaseous film

mixture (CF + GA), where domains of condensed monolayer of FC10OH (CF) are in the gaseous film of very low interfacial density of C20OH and FC10OH mixture (GA). Moreover, the new finding from the X-ray method is that the condensed film very near the transition temperature T_2^{eq} is an inhomogeneous mixture of CH and CF, although the thermodynamic method did not suggested such an intermediate situation between homogeneous CH and homogeneous CF.

Now the existence of domains in a gaseous film was clearly demonstrated for the so called expanded state. However, a few questions come up; whether such an inhomogeneous structure is generally observed or not in adsorbed films and how the existence of domains affects the interfacial tension values.

In regard to the former, we have already reported two examples of the adsorbed films of ethyleneglycol monododecyl ether (C12E1) [18] and cationic surfactants like dodecyltrimethylammonium bromide (DTAB) [24] at their aqueous solution/air surfaces. The surface tension measurements and the data analysis of the C12E1 system showed the phase transition from the expanded to the condensed state around the concentration of C12E1 $m = 12$–$16\ \mu\text{mol kg}^{-1}$. Furthermore the external reflection FTIR spectra from the adsorbed film indicated that the peak top of the C–H asymmetric stretching absorption band, ν_{a,CH_2}, shifts continuously from 2923 to 2918 cm^{-1} with increasing m as shown in Fig. 4, which suggested a gradual change of film state. However, the asynchronous spectra obtained from the two dimensional correlation analysis of the change of ν_{a,CH_2} with m revealed that the gradual changes in ν_{a,CH_2} is a superficial one and should be attributed to the linear combination of $\nu_{a,CH_2} = 2926\ \text{cm}^{-1}$ and $\nu_{a,CH_2} = 2915\ \text{cm}^{-1}$ and also that the time evolution of these two bands is in the opposite direction. These findings confirm an inhomogeneous structure of the film state in the transition region that the condensed film region is increased in the expanded film as m is increased between $m = 12$ and $16\ \mu\text{mol kg}^{-1}$.

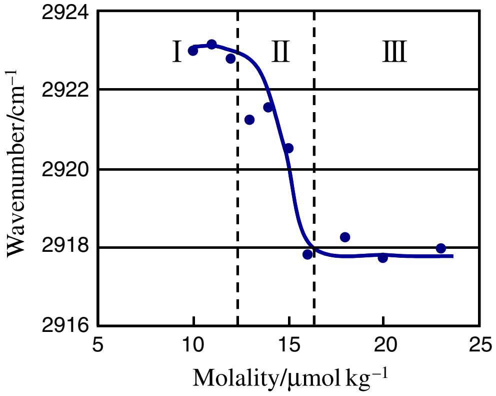

Fig. 4 Wave number of the peak top of absorption band of methylene asymmetric vibration vs concentration curves of the C12E1 adsorbed film

Another example is the expanded state of DTAB at the air/aqueous solution system as follows. The surface tension measurements and the data analysis of the DTAB system showed that the adsorbed film is in the expanded state at concentrations below the critical micelle concentration (cmc). The total reflection XAFS method was applied to the system and the EXAFS analysis revealed that their χ spectra has isosbestic points and thus the film is composed of two different states; the counter bromide ions are hydrated by six water molecules in the one state of them while they are hydrated by 3–4 water molecules and form ion pair with the cationic trimethylammonium head group in the other. Therefore, the expanded state definitely has an inhomogeous structure that surface aggregates (or domains) composed of ion pairs of surfactant cation-counter anion are existing in the gaseous film. Similar situation was also observed for other cationic surfactants including ionic surfactants [24].

To answer the second question, the mesoscopic thermodynamic formulation has performed recently [23] and provided that the relations among the interfacial tensions of the inside γ^{I} and outside γ^{O} of the domains and the measured one γ are given by

$$\gamma^{O} - \gamma^{I} = \tau/R \tag{5}$$

and

$$\gamma = (\tau/R)(1-\theta^{O}) + \gamma^{O} \tag{6}$$

$$= (\tau/R)(1+\theta^{I}) + \gamma^{I} \tag{7}$$

Here τ is the line tension at the boundary between the domains and the surroundings, R the radius of the domain, θ^{O} and θ^{I} the area fraction of the outside and inside of the domains, respectively. Equation 5 insists the higher interfacial tension of the outside compared to the inside irrespective of their film states and Eqs. 6 and 7 claims the domain formation raise the interfacial tension due to the positive line tension τ. When $R \sim 1\ \mu\mathrm{m}$ and $\tau \sim 10$ pN, the calculation gives $\gamma^{\mathrm{O}} - \gamma^{\mathrm{I}} \sim 10^{-2}\ \mathrm{mNm}^{-1}$ and $\gamma - \gamma^{\mathrm{O}} \sim 10^{-2}\ \mathrm{mNm}^{-1}$. Therefore, these differences in interfacial tensions are within the experimental error of even precise measurement ($\sim 10^{-1}\ \mathrm{mNm}^{-1}$) and thus the tensiometry practically does not discriminate whether the film state is in a homogenous or in an inhomogeneous one.

To our knowledge there have been only a few systematic studies in which the thermodynamic and structure studies are well and complementarily combined and its combination produces further advancement in the thermodynamic formulation. In this study, the thermodynamic studies on the adsorbed film of C20OH, FC10OH, and their mixtures at the hexane/water interface were combined with the X-ray reflectivity measurements and the domain formation in the expanded state and also even in the condensed state very near the phase transition region was clearly demonstrated. Furthermore the thermodynamic and FTIR studies on the C12E1 system and also the thermodynamic and total reflection XAFS studies on the DTAB system at air/water interfaces confirmed that the inhomogeneous structure is rather general in the phase transition region and in the so called expanded state. The knowledge obtained from the combination of thermodynamic and structure studies have been further utilized in the mesoscopic thermodynamic formulation on the Gibbs films at soft interfaces.

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References

1. Evans DF, Wennerström H. The colloidal domain, Chapter 1. New York: Wiley-VCH; 1999.
2. Adamson AW. Physical chemistry of interfaces, Chapter II. New York: John Wiley & Sons; 1976.
3. Matubayasi N, Motomura K, Aratono M, Matuura R. Thermodynamic study on the adsorption of 1-octadecanol at hexane/water interface. Bull Chem Soc Jpn. 1978;51:2800–3.
4. Lin M, Firpo JL, Mansoura P, Baret JF. A phase transition of the adsorbed layer: high pressure effect on fatty alcohol adsorption at an oil–water interface. J Chem Phys. 1979;71:2202–6.
5. Aratono M, Uryu S, Hayami Y, Motomura K, Matuura R. Phase transition in the adsorbed films at water/air interface. J Colloid Interface Sci. 1984;98:33–8.
6. Takiue T, Yanata N, Ikeda N, Motomura K, Aratono M. Thermodynamic study on phase transition in adsorbed film of fluoroalkanol at the hexane/water interface. 1. Pressure effect on the adsorption of 1,1,2,2-tetrahydroheptadecafluorodecanol. J Phys Chem. 1996;100:13743–6.
7. Uredat S, Findenegg GH. Domain formation in Gibbs monolayers at oil/water interfaces studied by Brewster angle microscopy. Langmuir. 1999;15:1108–14.
8. Fainerman VB, Miller R. Phase transition in adsorption layers at the water/hexane interface. J Phys Chem B. 2000;104:8471–6.
9. Lei Q, Bain CD. Surfactant-induced surface freezing at the alkane–water interface. Phys Rev Lett. 2004;92:176103–6.
10. Zarbakhsh A, Querol A, Bowers J, Yaseen M, Lu JR, Webster JRP. Neutron reflection from the liquid–liquid interface: adsorption of hexadecylphosphorylcholine to the hexadecane–aqueous solution interface. Langmuir. 2005;21:11704–9.
11. Sloutskin E, Sapir Z, Bain CD, Lei Q, Wilkinson KM, Tamam L, et al. Wetting, mixing, and phase transitions in Langmuir-Gibbs Films. Phys Rev Lett. 2007;99:136102–5.
12. Mitrinovic DM, Williams SM, Schlossman ML. X-ray study of oil–microemulsion and oil–water interfaces in ternary amphiphilic systems. Phys Rev E. 2001;63:021601–11.
13. Schlossman ML. Liquid–liquid interfaces: studied by X-ray and neutron scattering. Curr Opin Colloid Interface Sci. 2002;7:235–43.
14. Tikhnov AM, Pingali SV, Schlossman ML. Molecular ordering and phase transition in alkanol at the water–hexane interface. J Chem Phys. 2004;120:11822–38.
15. Knock MM, Bell GR, Hill EK, Turner JJ, Bain CD. Sum-frequency spectroscopy of surfactant monolayers at the oil–water interface. J Phys Chem B. 2003;107:10801–14.
16. Takiue T, Matsuo T, Ikeda N, Motomura K, Aratono M. Thermodynamic study on phase transition in adsorbed film of fluoroalkanol at the hexane/water interface. 4. Phase transition in the adsorbed film of the alkanol and fluoroalkanol mixture. J Phys Chem. 1998;102:4906–11.
17. Aratono M, Kashimoto K, Matsuda T, Muroi S, Takata Y, Ikeda N, et al. Selective determination of surface density of bromide ion through XAFS and its application to verification of a criterion of an ideal mixing of surfactant mixture. Langmuir. 2005;21:7398–404.
18. Azizian S, Shibata K, Matsuda T, Takiue T, Matsubara H, Aratono M. Surface phase transition of $C_{12}E_1$ at the air/water interface: a study by dynamic surface tension, external RA FT-IR, and 2D IR correlation methods. J Phys Chem B. 2006;110:17034–42.
19. Takiue T, Ikeda N, Toyomasu T, Matsubara H, Aratono M. Thermodynamic study on phase transition in adsorbed film of fluoroalkanol at the hexane/water interface. 7. Pressure effect on the miscibility in the adsorbed film of alkanol and fluoroalkanol mixture. J Phys Chem B. 2000;104:7096–101.
20. Pingali SV, Takiue T, Luo G, Tikhonov AM, Ikeda N, Aratono M, et al. X-ray reflectivity and interfacial tension study of the structure and phase behavior of the interface between water and mixed surfactant solutions of $CH_3(CH_2)_{19}$ and $CF_3(CF_2)_7(CH_2)_2OH$ in hexane. J Phys Chem B. 2005;109:1210–25.
21. Motomura K. Thermodynamic studies on adsorption at interfaces. 1. General formulation. J Colloid Interface Sci. 1978;64:348–55.
22. Aratono M, Villeneuve M, Takiue T, Ikeda N, Iyota H. Thermodynamic Consideration of mixtures of surfactants in adsorbed films and micelles. J Colloid Interface Sci. 1998;200:161–71.
23. Aratono M, Matsubara H, Murakami D, Takiue T. Phase transition and domain formation in the Gibbs adsorbed films of long-chain alcohols. J Phys Chem B. 2009;113:6347–52.
24. Aratono M, Shimamoto K, Onohara A, Murakami D, Tanida H, Watanabe I, et al. Adsorption of 1-decyl-3-methylimidazolium bromide and solvation structure of bromide at the air/water interface. Anal Sci. 2008;24:1279–83.