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Surface Tension of Surfactant Solutions

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The true surface tension value of a solvent or a solution, being an intensive thermodynamic quantity, should not depend on extensive parameters such as the diameter of a container or the filling height of the liquid. However, here we describe how a so far unknown phenomenon, that of drastically decreasing the surface tension of surfactant solutions by lowering the solution's level in nonwetting containers, can be achieved. This effect can be explained by removal of the adsorbed surfactant material from the solid/liquid interface and spreading at the air/liquid interface. The surfactant adsorption at the solid/solution interface can be estimated from the accompanying changes of the solution's surface tension. It depends on the structure, concentration, and purity of the surfactant as well as on the properties of the nonwetting surface. Generally, surfactant adsorption at the solid/liquid interface is smaller than that at the air/liquid interface. The procedure described allows compression of adsorption layers of soluble surfactants at the air/water interface without applying a movable barrier.

Surface tension represents an intensive parameter of surface thermodynamics. Hence, the surface tension value (σ) of a liquid or a liquid solution is a well-defined quantity, provided that temperature (T), pressure (p), and concentration (c), in the case of a solution, are given. This quantity must not depend on extensive parameters such as liquid volume, surface area, or the depth of the fluid in a container.[1,2] Thus,

$$\sigma = \sigma(p,T,c) \qquad (1)$$

However, when we measured the surface tension of various surfactant solutions in nonwetting containers, we detected an intriguing effect that seems to contradict the above-given fundamental thermodynamic assumptions.

Figure 1. Schematic illustration of the apparatus used for measuring surface tension of a surfactant solution at different heights of the solution in a container consisting of nonwetting poly(tetrafluoroethylene) (PTFE).
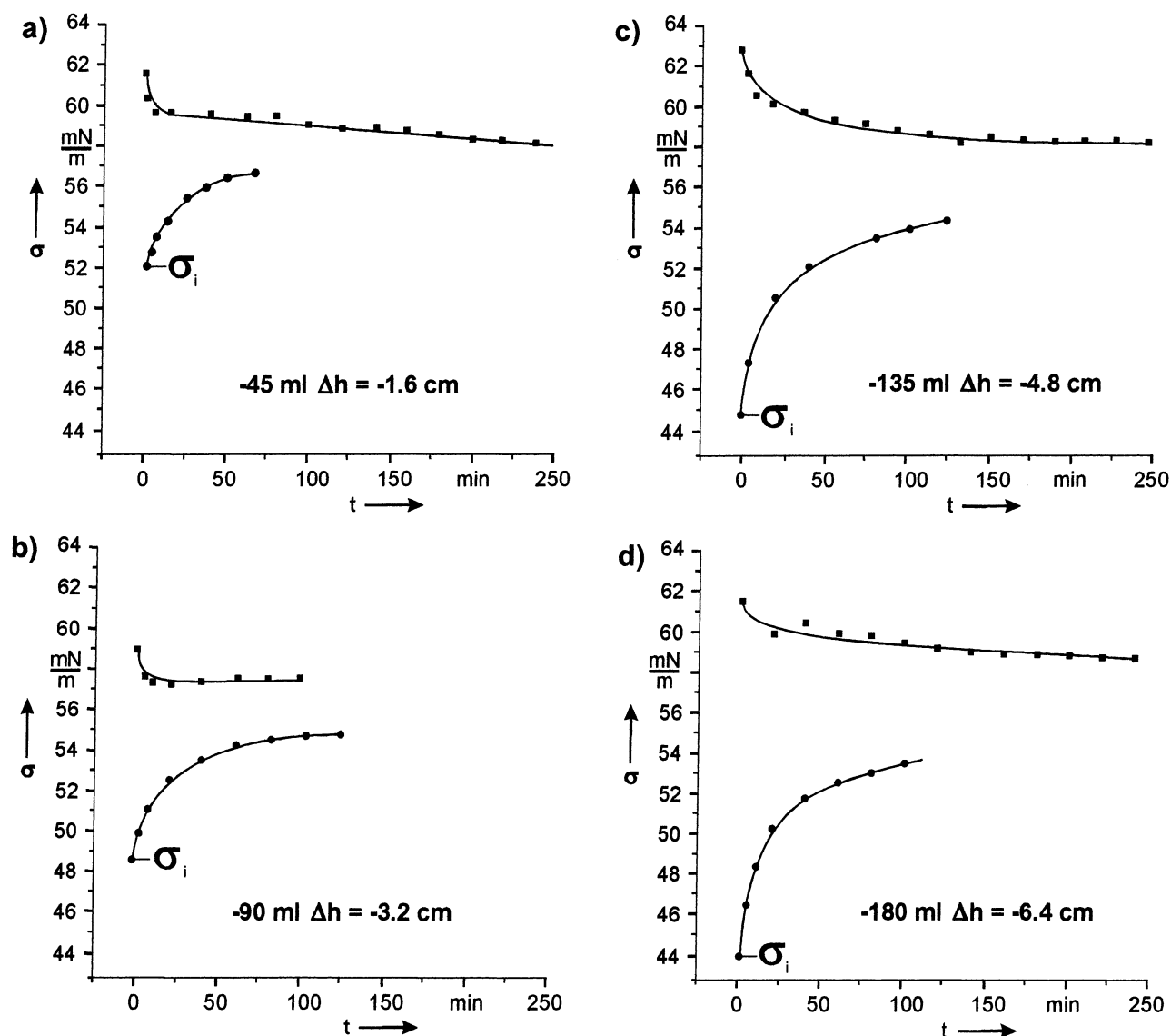
An aqueous 1×10^{-3} M solution of sodium dodecylsulfate (Merck, as received) was measured in a container made of poly(tetrafluoroethylene) (PTFE). The inner diameter of this container was 6.0 cm, and its inner height was 10.0 cm. The container was equipped with an outlet and a stopcock at its base (Figure 1). It was filled with the solution up to its maximum height (h_{max}). Following a general rule of surface chemistry,

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Figure 2. Course of the dynamic surface tension of an aqueous 1×10^{-3} M sodium dodecyl sulfate solution measured in a PTFE container at various solution levels h. The lowering of the level by removing part of the solution via the stopcock was performed after the apparent equilibrium surface tension value σ_e had approximately been reached. The various σ_i values refer to the surface tension values measured immediately after having removed the solution. Runs: (a) 45 mL removed, $\Delta h_1 = -1.6$ cm, $\sigma_{i,1} = 52.6$ mN/m; (b) 90 mL removed, $\Delta h_2 = -3.2$ cm, $\sigma_{i,2} = 48.5$ mN/m; (c) 135 mL removed, $\Delta h_3 = -4.8$ cm, $\sigma_{i,3} = 44.5$ mN/m; (d) 180 mL removed, $\Delta h_4 = -6.4$ cm, $\sigma_{i,4} = 43.9$ mN/m.

the solution surface was aspirated carefully by a fine capillary, and the dynamic surface tension was measured until an almost constant surface tension value ($\bar{\sigma}_e$) was reached. The surface tension was measured with a Wilhelmy plate. When the constant surface tension value $\bar{\sigma}_e$ was reached, part of the solution was removed via the outlet down to the level h_1. Measuring surface tension again at this level immediately after having finished the outflow resulted in a surface tension value $\sigma_{i,1}$ which was considerably lower than the value $\bar{\sigma}_e$ measured at the maximum level h_{max}. Surprisingly, the surface tension value $\sigma_{i,1}$ increased again with time until another apparently constant surface tension value was reached, which we denote as the apparent equilibrium surface tension value, $\bar{\sigma}_e(h_1)$. Remarkably, $\bar{\sigma}_e(h_1)$ is still considerably lower than $\bar{\sigma}_e(h_{max})$.

We repeated this experiment, starting again with the solution at maximum height and its apparent equilibrium surface tension value, $\bar{\sigma}_e$. We then removed a 2-fold amount of solution via the outlet to the final solution level h_2. The corresponding surface tension was considerably reduced again. The dynamic surface tension behavior at level h_2 resembles very much that

at level h_1, but with lower surface tension values of the corresponding states. Again we repeated these experiments under the same conditions, removing a 3-fold and a 4-fold amount of solution to the lower levels h_3 and h_4, respectively. In these cases, the corresponding surface tension values were even lower. Thus, summarizing,

$$h_1 > h_2 > h_3 > h_4 = h_{min} \qquad (2a)$$

$$\bar{\sigma}_e(h_{max}) > \bar{\sigma}_e(h_1) > \bar{\sigma}_e(h_2) > \bar{\sigma}_e(h_3) > \bar{\sigma}_e(h_4) \qquad (2b)$$

$$\sigma_{i,1} > \sigma_{i,2} > \sigma_{i,3} > \sigma_{i,4} \qquad (2c)$$

The results of these runs are shown in Figure 2.

There is a distinct dependence of the corresponding (apparent) equilibrium surface tension values on the level of the surfactant solution, with a clear trend for the dynamic surface tension behavior. To understand the mechanism, we first would like to point out that the accuracy of measuring surface tension amounts to ± 0.2 mN/m. This is more than 1 order of magnitude smaller than the observed differences of the surface tension values at

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TABLE 1: Surfactant Adsorption at Solid/Liquid Interfaces Calculated from Changes of Surface Tension after Successive Removal of Solution[a]

surfactant solution	Δh (cm)	$\bar{\sigma}_e$ (mN/m)	σ_i (mN/m)	solid	Γ_∞ (10^{-10} mol/cm²)	Γ (10^{-10} mol/cm²)	Γ_{SL}/Γ (%)
5×10^{-5} M decanoic acid in 0.005 M HCl	-3.2	56.9	51.9	PTFE	6.68	$0.61\Gamma_\infty$	5.1
	-6.4	56.0	47.1	PTFE	6.68	$0.61\Gamma_\infty$	3.9
1×10^{-3} M sodium dodecyl sulfate	-3.2	57.8 a	48.6 a	PTFE	6.17	$0.59\Gamma_\infty$ a	13.8 a
		66.1 b	60.3 b			$0.32\Gamma_\infty$ b	10.4 b
	-6.4	58.8 a	44.0 a	PTFE	6.17	$0.59\Gamma_\infty$ a	10.8 a
		65.5 b	54.0 b			$0.32\Gamma_\infty$ b	8.7 b
5×10^{-5} M decanoic acid in 0.005 M HCl	-3.2	56.4	49.4	paraffin	6.68	$0.61\Gamma_\infty$	6.6
1×10^{-3} M sodium dodecyl sulfate	-1.6	62.2 b	54.5 b	paraffin	6.17	$0.32\Gamma_\infty$ b	20.2 b
	-3.2	64.4 b	48.0 b	paraffin	6.17	$0.32\Gamma_\infty$ b	19.5 b
1×10^{-4} M sodium perfluoro-decanoate	-3.0	52.0	40.0	paraffin	5.24	$0.80\Gamma_\infty$	6.2

[a] Container diameter, 6.0 cm; Δh, change of filling height of solution; $\bar{\sigma}_e$, apparent equilibrium surface tension value of surfactant solution in the case of adsorption; σ_i, surface tension value measured immediately after having finished the removal of solution; Γ, surface concentration (surface excess) at the air/solution interface; Γ_∞, saturation value of Γ; Γ_{SL}, surface concentration at the solid/solution interface. The indices "a" and "b" for sodium dodecyl sulfate indicate two products of rather different grades of purity.

the various levels h. Before looking for an explanation of this phenomenon, we noted that a similar behavior was also observed for other surfactant solutions. The results are presented in Table 1.

This phenomenon cannot, therefore, be caused by some other peculiar property of the surfactant but is presumably due to the property of the polymer surface. Surface-active impurities originating from the PTFE surface are excluded because the surface tension of pure water was always exactly identical to 72.4 mN/m at 295 K, irrespective of the water level in the container.

The described phenomenon is reminiscent of the compression of soluble adsorption layers in a Langmuir trough when surface tension is measured separately in the compartment of the compressed adsorbed layer.[3-5] When the adsorption kinetics of a surfactant solution is measured in a Langmuir trough, surface tension decreases until an apparently constant surface tension value ($\bar{\sigma}_e^A$) is reached. If the surface area is then reduced by means of a floating barrier, surface tension in the compressed part of the surface will be considerably lower. The initial surface tension value measured after compression is analogously called $(\sigma_i)_{trough}$. It increases with time until again another apparently constant surface tension value $(\bar{\sigma}_e^D)_{trough}$ is reached, analogous to the experiment in the PTFE cylinder,

$$(\sigma_i)_{trough} < (\bar{\sigma}_e^D)_{trough} \qquad (3a)$$

However, generally the relation (3b), set out below, holds,

$$(\bar{\sigma}_e^A)_{noncompressed\ surface} > (\bar{\sigma}_e^D)_{compressed\ surface} \qquad (3b)$$

as given by eq 2b. The superscripts A and D denote conditions of adsorption and desorption, respectively. Consequently, the described phenomenon of different surface tension values at different solution heights in the container has to be related to the surfactant adsorption at the solid/liquid interface. To prove this assumption, we performed two similar experiments with an identical aqueous solution of 1×10^{-3} M sodium dodecyl sulfate. In one case we compressed the adsorption layer of the solution in a Langmuir trough by 50% of its original surface area, as described above. In the other case we lowered the solution level to such a height h that the released area between the liquid and the solid (A_{SL}) was equal to the area of the air/
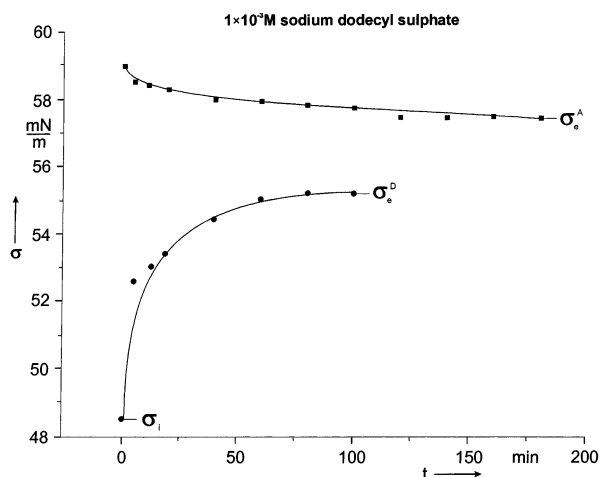
Figure 3. Course of dynamic surface tension of an aqueous 1×10^{-3} M solution of sodium dodecyl sulfate before and after compression of the adsorption layer by 50% in a Langmuir trough. The compression was performed after the (apparent) equilibrium surface tension value σ_e^A had been reached. (Superscripts A and D denote conditions of adsorption and desorption, respectively; σ_i refers to the initial surface tension value measured immediately after compression of adsorption layer.)

liquid interface (A). The latter case corresponds to the conditions given in the experiment shown in Figure 2a. The results of these experiments are shown in Figures 2a and 3.

Comparing the results of the two experiments, it is seen that the corresponding dynamic surface tension behaviors are indeed similar.

Although we do not know the underlying mechanism, the removal of the adsorbed surfactant layer from the solid/liquid interface could qualitatively be understood as the stripping off of a film adhering on a solid support.

If this were true, we could estimate the surface concentration of the surfactant adsorbed at the solid/liquid interface from the surface tension of the surfactant solution by applying an adsorption equation. This is to be demonstrated by the equations of Langmuir/Szyszkowski describing "ideal surface behavior".[6]

The most important adsorption equations are those of Szyszkowski,

$$\sigma_w - \sigma_e = RT\Gamma_\infty \ln(1 + c/a_L) \qquad (4)$$

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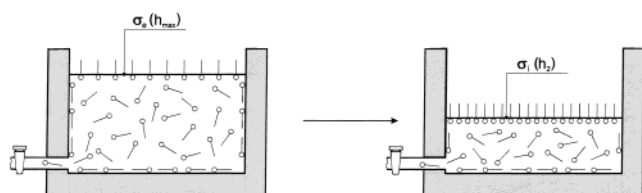
Figure 4. Schematic illustration of the mechanism of collecting surfactant adsorbed at the solid/liquid interface in the air/liquid surface during lowering of the level of the surfactant solution (see text).

and of Langmuir,

$$\Gamma = \Gamma_\infty c/(a_L + c) \qquad (5)$$

Equation 4 provides us with the adsorption parameters of concentration of half-saturation (a_L) and saturation adsorption (Γ_∞) by evaluating the experimental dependence of the equilibrium surface tension (σ_e) on bulk concentration (c). σ_w is the surface tension of water. The surface concentration (surface excess, Γ) is calculated by using eq 5.

Now, if we assume that the surfactant adsorbed at the released solid/solution interface (ΔA_{SL}) is completely transported into the air/liquid interface, then the surface tension value σ_i, measured immediately after the removal of the solution, corresponds to the overall amount of adsorbed material belonging to the two interfacial areas ($A + \Delta A_{SL}$). For a cylindrical container of inner radius r, the area of the air/solution interface is given by $A = \pi r^2$, and the released area of the solid/liquid interface is given by $\Delta A_{SL} = 2\pi r\Delta h$. h is the solution height in the container. The surface tension value σ_i was then used as the new equilibrium surface tension value ($\sigma_e^* \equiv \sigma_i$) and the corresponding Γ_i calculated likewise. Subtracting Γ from Γ_i and taking into consideration the geometrical conditions, we arrive at the simple relation

$$\Gamma_{SL} = r/2\Delta h(\Gamma_i - \Gamma), \qquad (6)$$

by means of which the adsorption at the solid/liquid interface (Γ_{SL}) is calculated.

These calculations assume that desorption of surfactant from the compressed adsorption layer during the outflow process can be neglected and that the solid/liquid interface is not rough. Compared with the long time dependence of the dynamic surface tension, the former assumption will hold. The latter assumption, however, is not fulfilled, since solid surfaces possess a certain roughness.[7,8] This would decrease the adsorption value Γ_{SL} by a certain amount, according to the roughness factor. However, roughness will not change the behavior decisively. The values of Γ_{SL}, which are calculated by the procedure outlined above, should give reasonable estimates of the surfactant adsorption at the solid/liquid interface, provided that the surfactant solution does not wet the solid container's surface.

Table 1 compiles the results of experiments performed with various surfactant solutions. These experiments were carried out not only with surfaces of the polymer PTFE but also with surfaces of paraffin-coated glass. The paraffin surfaces were prepared by wetting the glass surfaces with molten paraffin.

The last column of Table 1 contains the adsorption at the solid/liquid interface, Γ_{SL}, in relation to the adsorption at the liquid surface, Γ. As can be seen from Table 1, not only does the extent of the surfactant adsorption at the solid/liquid interface depend on the structure of the surfactant, but above all, it depends on the surface property of the solid. Thus, for sodium dodecyl sulfate, the adsorption Γ_{SL} is stronger at the paraffin than at the PTFE surface, whereas Γ_{SL} of decanoic acid is only

slightly increased on the paraffin surface. This trend is reasonable, because the interaction of a surfactant with *n*-alkanes is stronger than its interaction with perfluoroalkanes.[8,9] In addition, Γ_{SL} depends also on the grade of purity of the surfactant used. This is illustrated by the example of the 1 mM sodium dodecyl sulfate solutions. We have used two different samples of SDS. One sample had been synthesized in the laboratory, and the other one was purchased from Merck (ar) and applied without further purification. As a matter of fact, the two samples' grade of purity was extremely different. The first product was already rather pure (sample b). It almost sufficed the grade of surface chemical purity indicated by the comparatively high apparent equilibrium surface tension values, $\bar{\sigma}_e$. The second sample was heavily contaminated, as is usually met with as-received SDS products, indicated by comparatively low $\bar{\sigma}_e$ values and a long-lasting dynamic surface tension (sample a). Analogous to the observation at the air/water interface, adsorption at the S/L interface from the stronger contaminated SDS solution is also increased up to 33% at maximum. However, the influence of the surface-active impurity is not so strong that the order of magnitude of adsorption is changed.

To compare the adsorption behavior of the various surfactant structures, the results obtained with the SDS sample b, possessing better purity, should be used because the other surfactant's purity was rather good.

Summarizing, we can conclude that the surfactant adsorption at the S/L interface of the discussed surfactants at submicellar concentrations is noticeably lower than that at the corresponding air/water interface.

To prove whether this result is correct, we looked for comparable data in the literature. By using a quite different approach, the adsorption at the solid/liquid interface can be calculated from contact angle (θ) and surface tension (σ_L) measurements by combining Young's and Gibbs's adsorption equations.[10] This results in

$$(\Gamma_S - \Gamma_{SL})/\Gamma_L = d(\sigma_L \cos \theta)/d\sigma_L \qquad (7)$$

If the adhesion tension, $\sigma_L \cos \theta$, is known as a function of surface tension (surfactant concentration), the ratio Γ_{SL}/Γ_L can easily be calculated as $\Gamma_S = 0$. Γ_L and Γ_S denote adsorption at the air/water interface and the solid/air interface, respectively. Zisman has measured the adhesion tension for sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) on polyethylene substrates.[11] We have taken his data and calculated the adsorption of the two surfactants and from it the ratio Γ_{SL}/Γ_L. For CTAB, $\Gamma_{SL}/\Gamma_L \approx 1\%$ within the surface tension interval between 40 and 70 mN/m, and 6% between 30 and 40 mN/m. For SDS, the ratio Γ_{SL}/Γ_L amounts to $\approx 1\%$ between 50 and 70 mN/m, to $\approx 1.9\%$ between 40 and 50 mN/m, and to $\approx 7.4\%$ between 35 and 40 mN/m.

These ratios well correspond to the data we have calculated for paraffin in our investigation which are derived from a quite different experiment. (With respect to surface properties, paraffin and polyethylene are chemically related.) The same conclusion, namely "negligible adsorption of the surfactant at the solid/liquid interface", was reported by Bose[10] in evaluating Zisman's data on these systems.[11]

Gau and Zografi have estimated the ratios of Γ_{SL} to Γ_L from investigations on wetting for the nonionic surfactants petaoxyethylene dodecylmonoether (C$_{12}$E$_5$) and petaoxyethylene decylmonoether (C$_{10}$E$_5$) on PMMA, PS, and paraffin.[12] Their conclusion is that for PMMA, in both cases, the ratios remain quite low until the surface tension has been reduced to below

about 40 mN/m. This effect was also seen with $C_{12}E_5$ and PS, but to a less extent.

The results obtained with the two different samples of sodium dodecyl sulfate give grounds for a concluding remark. Although the phenomenon described may reasonably be explained by a stripping-off mechanism of the adsorbed layer, and although the inherent procedure opens up a new possibility to determine surfactant adsorption at the solid/liquid interface, the results obtained so far should be considered as estimates only. That is why we always use the term "estimates" in this work. However, it is well possible to retrieve reliable, quantitative data from such experiments. To do so, it is necessary to take into consideration first the required grade of surface-chemical purity. Furthermore, calculating adsorption requires applying an appropriate surface-equation of state. This is especially important for ionic surfactants. Thus, for example, for calculating exactly the adsorption of surface-chemically pure ionic 1:1 surfactants, like SDS, a factor of 2 should be used in eq 4, resulting in 50% lower adsorption values.[13,14] In addition, ion exclusion effects need to be taken into account as well.[15] Finally, as the experiment with the two different samples of SDS has shown, it is highly probable that part of the effect of lowering the surface tension by reducing the level of the solution is brought about by the nonionic impurity dodecanol.

We are preparing a subsequent paper in which the strict requirements on surfactant purity are obeyed and the adsorption is calculated quantitatively. These results will prove that the conclusions drawn in this paper are correct.

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