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Ordered structures in poly(allylamine hydrochloride) gel and sodium dodecylbenzenesulfonate surfactant complexes

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Abstract

We investigated the structure of poly(allylamine hydrochloride) (PAAMHCl) gel-sodium dodecylbenzenesulfonate (SDBS) surfactant complexes using small-angle X-ray scattering. PAAMHCl gels were prepared by using *N*,*N*′-methylenebisacrylamide as a cross-linking agent. These gels were complexed with SDBS below a critical micelle concentration of the surfactant. The gel–surfactant complexes (GSC) exhibited lamellar structures with an interlayer spacing of 35 Å which is less than twice the length of the stretched SDBS molecule. The effect of ionic strength on the formation and the structure of GSC were investigated. The complexes were found to be highly stable in presence of salt solutions.

Keywords: Gel–Surfactant complexes; Ionic strength; Small-angle X-ray scattering

1. Introduction

Polyelectrolyte gels are an emerging topic due to their wide applications in a variety of areas viz., responsive systems, superabsorbents, controlled delivery systems, etc. [1–4]. These gels exhibit discrete volume transitions with small variations in temperature, pH, and solvent compositions and also with oppositely charged hydrotopes [5–9]. This interesting property has been exploited in the above-mentioned applications. Polyelectrolyte gels also undergo drastic volume collapse when they interact with oppositely charged surfactants. These gel–surfactant complexes (GSC) have attracted many researchers due to their interesting structural properties [10–13]. These complexes exhibit supramolecular ordering. The physical reason for the formation of ordered structures in statistically disordered gels was not known. This has led to a series of studies on GSC by Chu's and Khokhlov's research groups and they demonstrated that the highly ordered structures in GSC depend on the chemical properties of the gel, nature and size of the surfactant molecules [10,14–21].

Interesting results were reported for the influence of ionic strength on GSC [20,22,23]. The mole ratio (γ) of surfactant to the number of charges on the polymer chain employed for the preparation of GSC decides the stability of the complexes. If $\gamma < 1$, the addition of salt decreases the stability of GSC obeying ion-exchange equilibrium between the polyelectrolyte and surfactant. The addition of salt increases the stability of the GSC if $\gamma > 1$, and was explained due to the formation of non-stoichiometric complexes. Such phenomenon was reported for strong polyelectrolytes [20]. Osada et al. reported that the formation of non-stoichiometric complexes between polyelectrolyte and surfactant was favored as the distance between the charges on the polymer backbone became larger and as the surfactant became more hydrophobic (surfactants with longer alkyl chains) [24]. The structure and the formation process of GSCs are expected to depend on the nature of the polyelectrolyte and the factors influencing the stability of the complexes are not clearly understood. To understand the stability and the structure of GSC in salt solution, we have chosen a different gel system, namely poly(allylamine hydrochloride) (PAAMHCl). In this communication, the effects of salt concentration on the formation and structure of the complexes between PAAMHCl gel-sodium dodecylbenzenesulfonate (SDBS) surfactant are studied. It is worth mentioning that our results and interpretation for PAAMHCl are different from those reported before, for example, by Mironov et al. for poly(diallyldimethylammonium chloride) (PDADMACl) [20]. The results show that the complexes are stable in presence of salt solution.

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2. Experiments

PAAMHCl samples (PAA-HCl-10S) supplied by Nitto Boseki Co. Ltd, Japan, were purified by ultrafiltration using Amicon membranes of PM10. The solutions thus obtained were freeze-dried and the resultant powders were used for the preparation of the gels. The weight average molecular weights of these polymers were estimated from GPC measurements, calibrated using light scattering and found to be in the order of 10^6. Cross-linking agent *N*,*N*′-methylenebisacrylamide (MBA) and SDBS from Wako Chemicals, Japan, were used without further purification. SDBS was characterized by ^{1}H NMR spectroscopy and identified as a para isomer with negligible amounts of other isomers. Milli-Q reagent grade water was used for all the experiments.

The degree of neutralization of the polymer was determined by Mohr titration using standard 0.1N $AgNO_3$ solution. Potassium chromate was used as an indicator. The degree of neutralization was found to be 0.96, in other words, polymer was almost completely in the protonated form with Cl^-. PAAMHCl gels were prepared by using cross-linking agent MBA. A suitable amount of polymer (monomer concentration 1.75 M) was dissolved in water and MBA was added under stirring and the reaction mixture was further stirred at 80°C. A transparent gel was obtained within few minutes. The gels were washed with a large amount of water for 2–3 weeks by intermittently changing the water. The resultant highly swollen gels (130–150 times of their dried gel) were used for further studies.

The critical micelle concentration (CMC) of SDBS was found to be 1.6 mM from conductivity measurements using Horiba Conductivity Meter DS-14 at 25°C (±0.2). The molar ratio of the surfactant to the monomer units was maintained at 2.0. Gels were equilibrated with a surfactant solution of 0.3 mM concentration for 3–4 weeks. Consumption of the surfactant by the gels was monitored at regular intervals of time by measuring the absorbance at 261 nm by a Shimadzu UV-2200 spectrophotometer. The amount of the SDBS consumed was normalized with the monomers of polymer present in the gel. To investigate the complexes under salt conditions, the swollen gels were first equilibrated with NaCl solutions of various concentrations from 1.5 mM to 1.0 M. The volume of the gels was decreased and the shrunken gels were then equilibrated with SDBS solution of 0.3 mM concentration in the presence of salt solution. Swelling was estimated by measuring the area of the gel pieces when equilibrated with the surfactant solution using laser scanning microscope (LSM) Model No. 410, Carl Zeiss, Germany. The swelling ratio is defined as the ratio of area of the gel in surfactant solution to that of fully swollen gel in water.

Gel-surfactant complexes were characterized by small-angle X-ray scattering (SAXS) using a Rigaku apparatus. A 14 kW rotating anode generator (Rotaflex RU-300, target: Cu, the wavelength of the X-ray: 1.54 Å) was used. The X-ray beam was collimated by the Kratky U-slit camera and hit on the gel in a quartz capillary. The scattered X-ray was detected by a position-sensitive-proportional counter. The entrance slit width of 70 μm was used. Quartz capillaries of 2 mm diameter from W. Müller, Germany, were used for the present measurements. Temperature of the measurement was maintained at 25°C. Blank runs were obtained with surfactant solutions which were in equilibrium with GSCs. GSC pieces (which were immersed in SDBS solution for 2–3 weeks) were introduced into the capillary together with the surfactant for SAXS studies. The transmittances of the blank solution and samples were taken into account in correction and the scattering intensity of the blank was subtracted from that of the sample. Gel pieces were not uniformly packed in the capillary and hence desmearing was not carried out for the scattering data.

3. Results and discussion

The mechanism of gelation of PAAMHCl with MBA was studied by using IR, ^{1}H and ^{13}C NMR spectroscopic techniques [25]. It was proposed that the cross-linking is taking place by the reaction of amine group of the polymer with the terminal carbon of MBA. Fig. 1 shows the swelling curves of PAAMHCl gel in salt free SDBS solution (0.3 mM). The swollen PAAMHCl gels were collapsed to around 20% (in area) of the swollen sample within 24 h after being immersed in surfactant solutions. The surfactant molecules were strongly absorbed by the charges on the gels and when the concentration of the surfactant in the gel network exceeded its critical aggregation concentration (cac), the micelle-like aggregates were presumably formed in the gel phase probably due to hydrophobic interaction between the surfactant chains. The aggregation of the surfactants in the gel network changed the osmotic pressure inside the gel and resulted in gel collapse [20,26]. The gels turned opaque after its collapse. We note here that the volume change is slow because the diffusion of the surfactant ions into the gel

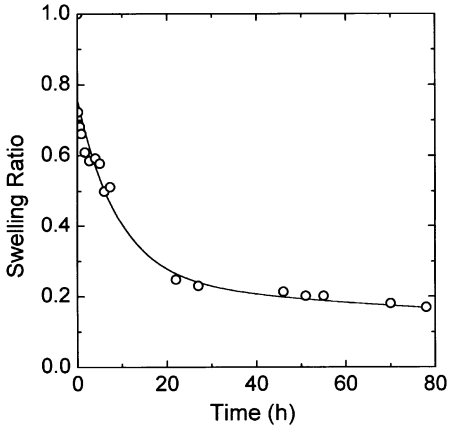

Fig. 1. Swelling profile of PAAMHCl gel as a function of time in salt free SDBS solution (0.3 mM).

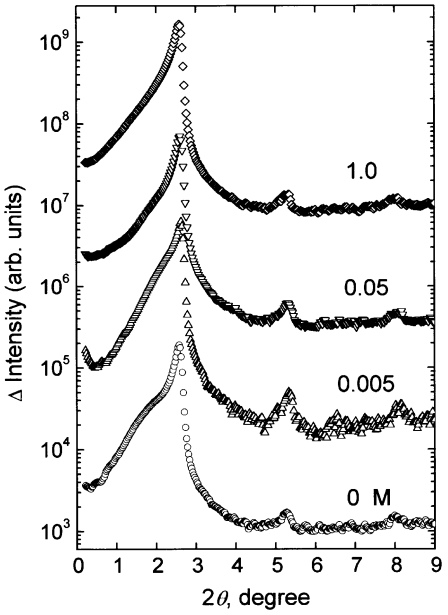

Fig. 2. Smeared SAXS intensity against apparent scattering angle 2θ, which is the angle between central lines of the incident beam and the scattered X ray beam detected, from gel-surfactant complexes prepared at various concentrations (moles/liter) of NaCl, salt free (○), 0.005 (△), 0.05(▽), and 1.0 (◇). A slight shoulder was observed at $2\theta = 2°$ and may be due to less ordered structure coexistent in the inhomogeneous GSC, which was also observed by Mironov et al. (Ref. [20])..

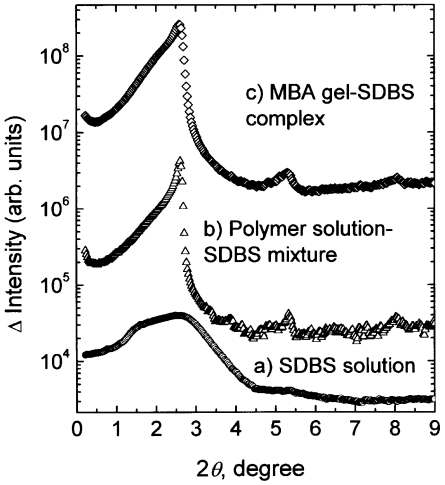

Fig. 3. SAXS profiles: (a) sodium dodecyl benzene sulfonate solution 30 wt.% (○); (b) PAAMHCl- SDBS mixture (△); (c) MBA gel-SDBS complex (◇) monomer concentration in (b) and (c): 14 wt.%.

network is hindered or slowed down by cross-linking of the polymer. This is supported by the fact that the consumption of the surfactant by the gel obtained from UV absorption spectroscopy is slower with increasing cross-linking density (data not shown).

Fig. 2 shows the SAXS patterns of MBA gel-surfactant complexes in salt solutions. For the sake of clarity, scattering curves were shifted vertically from each other. The existence of sharp peaks suggests the formation of highly ordered structures in GSCs. The structure was identified as a lamellar type with appearance of the peaks at the relative positions of 1:2:3. The interlayer distance was found to be 35 Å and was less than twice the length of the fully stretched surfactant chain (the length of fully stretched surfactant was calculated to be 22 Å assuming a para isomer, according to the model proposed by Saito et al [27]). Mironov et al. [20] reported the formation of the lamellar structures in PDADMACl gel-SDBS complexes and the interlayer distance was reported to be 35 Å, which corroborates well with the present results. From the observed value of inter-lamellar distance, the lamellar structure may be an alternate multilayer of two regions (polyallylamine chain and surfactant) with different electron density.

For the formation of supramolecular structures, surfactants may need the oppositely charged gel as a bed. To confirm this, SAXS measurements were carried out on solutions of SDBS (30 wt.%) without polymer (Fig. 3). The appearance of sharp peaks in the polymer solution-surfactant mixture and the relative position of the peaks indicate the presence of ordered lamellar structures. These results show that structures of the surfactants in the polymer solution-surfactant mixture and GSC are similarly ordered and are different from that in surfactant solution even though the peak position is similar in these cases. In other words, the medium of the oppositely charged polymer favors the ordering of the surfactant.

From Fig. 2, the lamellar structure seems to be retained and the interlayer distance was unchanged in the presence of salt. The formation of the complex is basically an ion-exchange process

$$PAAMH^+Cl^- + SDBS^-Na^+ \rightleftharpoons PAAMH^+SDBS^- + Na^+ + Cl^- \quad (1)$$

Then, the GSC should be unstable and dissociate into polymer in the presence of salt. It was reported by Khokhlov et al. that the complexes formed between cetylpyridinium bromide and partly neutralized polymethacrylic acid or copolymers of sodium methacrylate with acrylamide were stable at and below 0.01 M sodium bromide solution even without the surfactant and dissociated at higher salt concentrations [22]. In the present study of PAAMHCl and SDBS complexes, SAXS results showed that GSC structures were stable and ordered in 1 M NaCl solution with the 0.3 mM surfactant. The interlayer distance (33–35 Å) was not altered with salt concentration. Different behavior was reported for PDADMACl and SDBS system by Mironov et al. [20], in which a somewhat higher period of packing was observed for GSC complexes in 1 M NaCl solution compared to that in 0.3 M NaCl solution. It was inferred that the increase in the lamellar spacing was due to increase in swelling ratio with increasing salt concentration from 0.3 to 1 M [20].

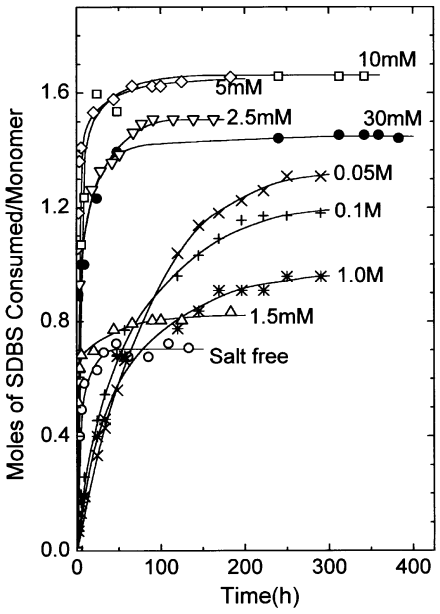

Fig. 4. The uptake of the surfactant by the gels immersed in 0.3 mM SDBS solution (the molar ratio of the surfactant to the monomer units being maintained at 2.0) at various concentrations of NaCl, salt free (○), 0.0015 (△), 0.0025 (▽), 0.005 (◇), 0.01 (□), 0.03 (●), 0.05 (×), 0.1 (+), and 1.0 M (✳).

The consumption of the surfactant by the gel obtained from UV absorption spectroscopy was presented in Fig. 4. The uptake was rapid up to a salt concentration of 0.03 M and decreased on further increase of salt concentration and the consumption was more than the stoichiometric ratio in the salt concentration range 0.0025–0.1 M. The data indicate the formation of non-stoichiometric complexes up to salt concentration of 0.1 M. The diffusion of the surfactant ions into the gel network was hindered at salt concentration higher than 0.03 M. Mironov et al. observed a similar non-stoichiometric behavior and found that the PDADMACl gel-SDBS complexes are stable in salt solutions [20]. They invoked a steric fitting model, in which they attributed the stability of complexes to the formation of non-stoichiometric GSCs which were formed due to the large distance between the alternating ionic groups on PDADMACl chain (7 Å), allowing extra surfactant molecules to be included. They observed an increase in the degree of order (peak intensity and sharp SAXS peaks) with increasing salt concentration, which was also explained by the model.

In the present case, the distance between the alternating charges in PAAMHCl is around 5 Å [28] and is very close to that obtained for the surfactant component from packing considerations (4 Å) [20] and hence steric fitting model proposed by Mironov et al. is not applicable. This is also supported by the fact that the SAXS peak intensity shown in Fig. 2 was independent of the salt concentration contrary to Mironov et al.'s results.

Osada et al. dealt extensively the role of ionic strength on the formation of GSC [23,29–31]. They reported that presence of cross-linkage of polymer enhances the uptake of the surfactant but decreases the cooperativity. It was explained that the high osmotic pressure created by the mobile counter-ions promotes an expansion of the network in competition with the shrinkage due to surfactant binding. The gel binding becomes cooperative on addition of neutral salt to suppress the network expansion. They evaluated the stability constants of GSCs both in salt and salt free environments and reported that stability constant of GSCs decreases in presence of salt. Even though the stability constant decreases due to presence of salt, the degree of binding of surfactant to the polymer network is comparable to the salt free system. Since the data about the γ (the ratio of number of moles of surfactant to the number of moles of monomer present in the polymer) employed for their system was not available, if the starting moles of surfactant are much in excess of monomer charges, the non-stoichiometric complexes might have also formed in these cases. However, the scattering data was not reported for their GSCs.

The complexation of PAAMHCl with SDBS is also highly favored as in the case for other GSC systems reported before. The electrostatic interactions play a predominant role for the initiation step of the binding. In the presence of salt, the charge repulsion between the surfactants was decreased. Since SDBS is highly hydrophobic surfactant, the aggregation of SDBS in the gel network might have taken place thus leading to non-stoichiometric complexes. In the presence of salt, the hydrophobic interactions between free surfactants and the bound surfactants in GSC might be dominating resulting higher consumption of the surfactant. The increase in the uptake of the surfactant by the gels in the presence of salt ($c_s < 10$ mM) may also be due to increase in its aggregation number. The presence of the salt generally decreases the CMC of the SDBS [32] and hence surfactant aggregation might have been enhanced in the gels. At higher concentrations of salt, the competition between the formation of non-stoichiometric complexes and dissociation of GSCs according to Eq. (1) might occur, resulting in lower uptakes of the surfactant.

From the observed uptake behavior and the corresponding discussion above, it may be proposed that the resultant whole non-stoichiometric GSC is composed of stoichiometric complex strongly combined by ion pair and an aggregation of additional SDBS which was adsorbed on the stoichiometric complex by hydrophobic interaction. Results of elemental analysis experiments for the GSC prepared in 0.005 and 0.05 M NaCl solutions indicated that the GSCs after washing by water were entirely stoichiometric complexes without extra SDBS. Since the gels had been equilibrated with excess amount of surfactant in solution (the molar ratio of the surfactant to the monomer units being maintained at 2.0), the amount of the surfactant in the strongly complexed GSC is determined to be stoichiometric in the present spontaneous complex formation. This result tells that the additional SDBS, which could be easily washed away, is much more weakly complexed in the GSC

than the SDBS in the stoichiometric GSC. The micelle structure of SDBS is very much affected by the salt concentration as is observed for concentrated SDBS in salt solution without polyelectrolyte [20]. On the other hand, the highly ordered structures (sharp peaks in SAXS profiles) of stoichiometric GSCs is not directly affected by the salt concentration because the polyelectrolyte is strong enough to form ion pairs with oppositely charged surfactant.

Next, we discuss the stability or the rigidity of the highly ordered structures. By comparing the results for GSCs of PAAMHCl and PDADMACl [20], it can be inferred that the PAAMHCl complex is more rigid than PDADMACl complex, because it was reported that the highly ordered structure of non-stoichiometric complex of PDADMACl gel and SDBS was appreciably affected by the concentration of salts, but that is not the case for GSCs of PAAMHCl-SDBS. The lamellar spacing and the degree of order for PDADMACl complex were dependent on salt concentration, where the effect of salt was not direct but was through the swelling of the gel and also through the special aggregation as is explained by 'steric fitting model' [20].

It is unexpected that the structure of GSCs of PAAMHCl is less affected by the salt concentration than that of PDADMACl. The chemical structures of these two polyelectrolytes indicate that PDADMACl (quaternary ammonium salt) is a stronger electrolyte than PAAMHCl, and then it should be expected that the GSC of PAAMHCl is more affected by external conditions. The observed behavior is opposite. It is worth mentioning that the ionization conditions with various pH (4.5–10.5) of PAAMHCl did not appreciably affect the highly ordered structures of GSCs formed with SDBS.[2] Furthermore, SAXS results showed that the network structure of the gel, such as cross-linking density and the type of cross-linking agent, did not affect the lamellar structure either.[2] These results indicate that the stability of the GSC cannot be simply explained by the strength of the polyelectrolytes or by network structure, but other structural conditions such as configuration of the polyelectrolyte chain or steric hindrance near the charge etc. may play a decisive role.

4. Conclusions

Ordered lamellar structures were formed in PAAMHCl-SDBS complexes with interlayer spacing of 35 Å which is less than twice the length of the stretched surfactant chain. The supramolecular structures were stable in solutions of salt concentrations up to 1 M. The formation of non-stoichiometric complexes in the presence of salt solution may be due to increased hydrophobic interactions among the surfactant groups. The highly ordered structure of the GSC is mainly determined by the stoichiometric part of the GSC and the additional SDBS absorbed on GSC did not influence the degree of order and lamella spacing.

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References

[1] Langer R. Nature 1998;392(suppl.):5.
[2] Osada Y, Okuzaki H, Hori H. Nature 1992;355:242.
[3] Hu Z, Zhang X, Li Y. Science 1995;269:525.
[4] Tanaka T, Wang C, Pande V, Grosberg AY, English A, Masamune S, Gold H, Levy R, King K. Faraday Discuss 1995;101:201.
[5] Tanaka T. Phys Rev Lett 1978;40:820.
[6] Tanaka T, Fillmore D, Sun ST, Nishio I, Swislow G, Shah A. Phys Rev Lett 1980;45:1636.
[7] Ohmine I, Tanaka TJ. Chem Phys 1982;77:5725.
[8] Siegel RS, Firestone BA. Macromolecules 1988;21:3254.
[9] Rama Rao GV, Konishi T, Ise N. Macromolecules 1999;32:7582.
[10] Zhou S, Chu B. Adv Mater 2000;12:545.
[11] Khandurina YV, Dembo AT, Rogacheva VB, Zezin AB, Kabanov VA. Polym Sci 1994;36:189.
[12] Khandurina YV, Alexeev VL, Evmenenko GA, Dembo AT, Rogacheva VB, Zezin AB. J Phys II 1995;5:337.
[13] Okuzaki H, Osada Y. Macromolecules 1995;28:380.
[14] Chu B, Yeh F, Sokolov EL, Starodoubtsev SG, Khokhlov AR. Macromolecules 1995;28:8447.
[15] Yeh F, Sokolov EL, Khokhlov AR, Chu B. J Am Chem Soc 1996;118:6615.
[16] Sokolov EL, Yeh F, Khokhlov AR, Chu B. Langmuir 1996;12:6229.
[17] Yeh F, Sokolov EL, Walter T, Chu B. Langmuir 1998;14:4350.
[18] Dembo AT, Yakunin AN, Zaitsev VS, Mironov AV, Starodoubtsev SG, Khokhlov AR, Chu B. J Polym Sci, Part B: Polym Phys 1996;34:2893.
[19] Zhou S, Burger C, Yeh F, Chu B. Macromolecules 1998;31:8157.
[20] Mironov AV, Starodoubtsev SG, Khokhlov AR, Dembo AT, Yakunin AN. Macromolecules 1998;31:7698.
[21] Zhou S, Yeh F, Burger C, Chu B. J Phys Chem 1999;103:2107.
[22] Khokhlov AR, Kramarenko EY, Makhaeva EE, Starodubtzev SG. Macromolecules 1992;25:4779.
[23] Narita T, Gong JP, Osada Y. J Phys Chem B 1998;102:4566.
[24] Chen L, Yu S, Kagami Y, Gong JP, Osada Y. Macromolecules 1998;31:787.
[25] Rama Rao GV, Konishi T, Ise N. 2001 (in press).
[26] Khokhlov AR, Kramarenko EY, Makhaeva EE, Starodubtzev SG. Makromol Chem, Theory Simul 1992;1:105.
[27] Saito M, Morioi Y, Matuura R. In: Mittal KL, Lindman B, editors. Surfactants in solutions, vol. 2. New York: Plenum Press, 1982. p. 771.
[28] Sumaru K, Mastuoka H, Yamaoka H. J Phys Chem 1996;100:790.
[29] Okuzaki H, Osada Y. Macromolecules 1994;27:502.
[30] Okuzaki H, Osada Y. Macromolecules 1995;28:4554.
[31] Isogai N, Gong JP, Osada Y. Macromolecules 1996;29:6803.
[32] Rosen MJ. Surfactants and interfacial phenomena. New York: Wiley, 1978. p. 104.

[2] Unpublished results.