

LETTER TO THE EDITOR

Forces between Mica Surfaces in PEO/Water and PEO/Toluene Solutions

In a recent paper (1) Marra and Hair present results on force-distance profiles between mica surfaces in polyethylene oxide (PEO)/toluene solutions. Briefly summarized, their results (which were broadly similar to those reported much earlier by Israelachvili *et al.* (2) for interaction between mica sheets in a PEO/water solution) indicated that the PEO was aggregating from the solution and that adsorption of different sized aggregates occurred randomly across the mica surfaces. The consequent surface interactions varied considerably from experiment to experiment, but were characteristic of polymer aggregates being squeezed and extruded from between the surfaces. These results are in marked contrast to our earlier studies (3, 4) of forces between mica surfaces in both PEO/toluene and PEO/water solutions, where equilibrium force profiles were attained, and no evidence of behavior was observed which could be attributed to phase separation or aggregation in the PEO solutions. The range of the repulsive forces in our studies was of the order of 5 unperturbed radii of gyration of the polymer chains; and the forces were interpreted in terms of the interaction between two surfaces bearing adsorbed polymer layers in a good solvent medium. The discrepancy between the Marra/Hair data and our results has been a cause of some puzzlement.

A very recent letter in *Nature* (5) sheds considerable light on the source of this discrepancy. In a series of careful dynamic light scattering measurements, Devenand and Selser have shown unambiguously that PEO solutions (both in water and in a nonaqueous solvent, methyl alcohol) that have *not* been filtered are very prone to phase-separate and aggregate from solution. In their words, they find "that even an extremely low concentration of organic impurities ("dust") in PEO solutions results in aggregation. It seems that the presence of very minute amounts of such impurities can readily shift the thermodynamic coordinates of such a solution so as to approach polymer association and phase separation." Devenand and Selser find that filtering of the PEO solutions, on the other hand, results in their behaving as true, molecularly dispersed polymer solutions, presumably because the filtering removes the dust. We recall that a crucial difference between our studies and those of Marra and Hair (and also those of Israelachvili *et al.* (2), was indeed that we filtered our solutions, while they did not. It is noteworthy that in all three studies

(Marra and Hair, Devenand and Selser, and ours) the PEO used was from the identical source (Toyo Soda), and that in the latter two studies identical filters were used (Millipore/Fluoropore 0.22 μm). This strongly suggests that the rather different results obtained by Marra and Hair and by ourselves are due to the presence of minute traces of organic impurities (dust) in the unfiltered Marra/Hair solutions; this resulted in the phase separation exhibited by their system, and in the consequent presence of large aggregates. In contrast, our (filtered) PEO solutions (both in water and in toluene) behave as molecularly dispersed solutions (in agreement with the Devenand/Selser study (5), and result in a force-distance behavior representative of the interaction between mica sheets, each bearing a layer of PEO chains adsorbed from the solution.

REFERENCES

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