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### For Surface Tension of Polymer Solutions $\partial \sigma / \partial r = 0$ Implies That $r = \infty$

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#### Abstract

Jennings<sup>[1]</sup> used Blander and Katz<sup>[2]</sup> and Siow and Patterson<sup>[3]</sup> to get the formula for the limit of superheat for polymer solutions. Siow and Patterson is based on Prigogine and Marechal<sup>[4]</sup> who followed after Flory and Huggins treatment of polymer solutions. Siow and Patterson got the equations

for the surface tension of polymer solutions. Here we take their equations and get  $\partial \sigma / \partial r = 0$  and find that the answer dictates that  $r = \infty$ , which is borne out by Jennings<sup>[5]</sup> data and Jennings and Middleman<sup>[6]</sup>.

**Keywords:** Polymer Solution, Surface Tension, Flory and Huggins, Limit of Superheat

#### Introduction

Siow and Patterson get these two equations for the surface tension of polymer solutions. In Jennings (1) the final formula is for  $\phi_2 \rightarrow 0$  and we take that here for the two formulae.

$$(\sigma - \sigma_1) a / kT = \ln (\phi_{1S} / \phi_1) + ((r - 1) / r) (\phi_{2S} - \phi_2) \quad (1)$$

$$\ln [(\phi_{2S} / \phi_2)^{1/r} / (\phi_{1S} / \phi_1)] = (\sigma_1 - \sigma_2) a / kT \quad (2)$$

For (1) and (2) we have  $\phi_{1S} / \phi_1 = 1$  when  $\phi_2 \rightarrow 0$ . So, (1) and (2) simplify to (3) and (4).

$$(\sigma - \sigma_1) a / kT = (1 - 1/r) (\phi_{2S} - \phi_2) \quad (3)$$

$$\phi_{2S} = \phi_2 \exp [r (\sigma_1 - \sigma_2) a / kT] \quad (4)$$

#### Results

Now, we have to take the partial derivative of  $\sigma$ , the surface tension of the polymer solution at the surface by combining (3) and (4).

$$(\partial \sigma / \partial r) (a / kT) = \partial / \partial r [(1 - 1/r) \phi_2 (\phi_{2S} / \phi_2 - 1)] \quad (5)$$

Since  $\phi_{2S} / \phi_2 = \exp [r (\sigma_1 - \sigma_2) a / kT]$  from (4), we put that into (5) to get (6).

$$(\partial \sigma / \partial r) (a / kT) = \partial / \partial r [(1 - 1/r) \phi_2 (\exp [r (\sigma_1 - \sigma_2) a / kT] - 1)] \quad (6)$$

We set  $(\partial \sigma / \partial r) (a / kT) = 0$  and the  $\phi_2$  drops out to get (7).

$$0 = (1 / r^2) (\exp [r (\sigma_1 - \sigma_2) a / kT] - 1) + (1 - 1/r) \exp [r (\sigma_1 - \sigma_2) a / kT] (\sigma_1 - \sigma_2) a / kT \quad (7)$$

We simplify to (8).

$$0 = \exp [r (\sigma_1 - \sigma_2) a / kT] (1 / r^2 + (1 - 1/r) (\sigma_1 - \sigma_2) a / kT) - 1 / r^2 \quad (8)$$

For polystyrene solution in cyclohexane, we have from Jennings (1) that;

$\sigma_1 = 4.0904 \text{ erg/cm}^3$	cyclohexane surface tension
$\sigma_2 = 26.329 \text{ erg/cm}^3$	polystyrene surface tension
$a = 196.73 \times 10^{-16} \text{ cm}^2$	surface area of cyclohexane molecule
$k = 1.3805 \times 10^{-16} \text{ erg/deg}$	Boltzmann constant
$T = 492.75 \text{ Kelvin}$	limit of superheat of pure cyclohexane

So, putting these in we get  $(\sigma_1 - \sigma_2) a / kT = -6.4315$  for the system used by Jennings and Middleman. There then obtains:

$$0 = \exp [r (-6.4315)] (1/r^2 + (1 - 1/r) (-6.4315)) - 1/r^2 \quad (9)$$

The lowest molecular weight used was 2000 for polystyrene, which gives  $r = 13.4$  for the ratio of the molar volume of the polymer to that of the solvent. See Jennings (1) for details. The only way (9) is satisfied is for  $r = \infty$ .

### Discussion

What does it mean that the derivative of surface tension of the polymer solution has to be satisfied when  $r = \infty$ ? Notice in Figure 3 of the MACROMOLECULES data from Jennings and Middleman that the limit of superheat rise for high molecular weight polystyrene in cyclohexane drops to the level of pure cyclohexane. This is where the change in surface tension with  $r$  drops to zero.

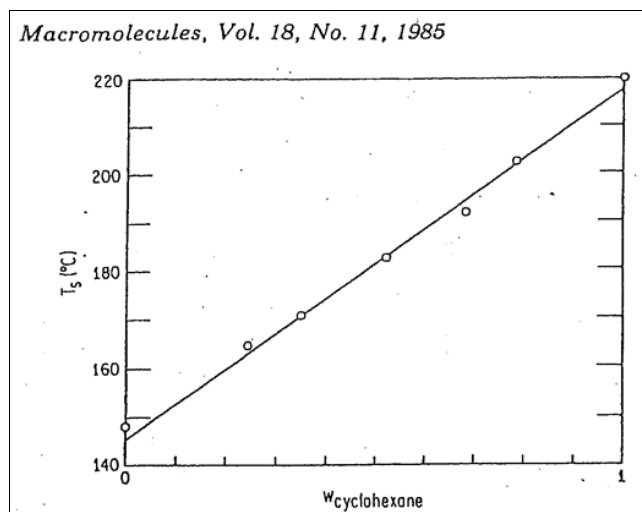


Fig 1: Data on limiting superheat for binary solutions of cyclohexane and pentane. Composition is mass fraction

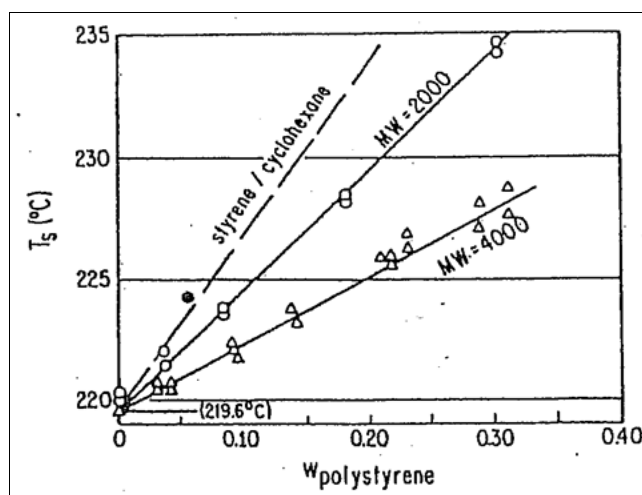


Fig 2: Data on limiting superheat for low molecular weight polystyrene in cyclohexane.  $T$  for pure cyclohexane is taken as  $219.6^\circ\text{C}$

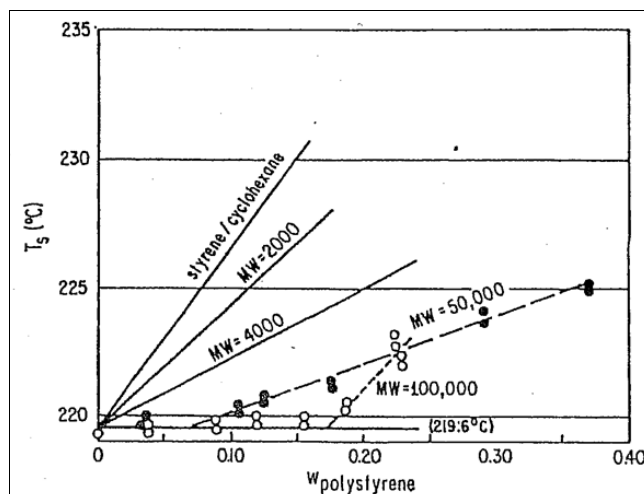


Fig 3: Data on limiting superheat for high molecular weight polystyrene in cyclohexane

### Conclusions

Adding polymer to solvent only affects the limit of superheat at low weight fraction polymer, if Jennings and Middleman's data is taken as a general result. There needs to be more study on these systems to ascertain if Jennings (1) has derived a general formula.

### Acknowledgments

The figures are taken from Jennings, J.H. and Middleman, S. "Homogeneous Nucleation of Vapor from Polymer Solutions" *MACROMOLECULES*. (1985) 18, 2274-2276 © 1985 American Chemical Society. We need to be aware of Pope Leo's words in his general audience on universal salvation. Who would be less deserving of salvation than Judas Iscariot? Pope Leo said, "at the Last Supper that one of his disciples will betray him. Despite the seeming harshness, Jesus' words are not meant to condemn or humiliate his betrayer." Pope Leo is sticking up for Jesus' intent to save the whole human race. (POPE LEO'S GENERAL AUDIENCE 13 AUG. 2025).

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