Surface Tension by Molecular Weight Polystyrene at The Limit of Superheat of Cyclohexane

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ABSTRACT:- The author solved the problem of Bubble Nucleation in Polymer Solutions (Jennings, 2014) and a paper emanating from that is flawed. The precursor equation, $dlnA/dK = 1/6K$, led to the final formula, $\Delta T = 3kT^2wMW_1/\sigma a MW_2$ (Jennings, 2020), but the precursor equation is not true for all r as is purported (Jennings, CSIJ 2020). Here in this paper Jennings proves, with scant data, that the precursor is indeed true for $r \geq 2$. Fig. 2 has the surface tension of polystyrene in 2% decalin, so a linear fit gives $\sigma = 27.08 - 0.04977(T-20)$ erg/cm^2, where T is in degrees Centigrade and the other two data points are extrapolating surface tension at 20 degrees Centigrade, and (Wu, 1970) has $\sigma = 40.7 - 0.072(T-20)$. Then it makes sense to plot the three points to get σ versus $1/r$, so $\sigma_2 = -10.747(1/r) + 21.750$. We take the surface tension of Fig. 2 to be the surface tension of the polystyrene because it is 98% polymer. r is the degree of polymerization, in other words, r=1 is styrene monomer.

KEYWORDS:- nucleation polymer "surface tension" "limit of superheat" "molecular weight"

I. INTRODUCTION

In MACROMOLECULES, (Jennings and Middleman, 1985) published their data for Bubble Nucleation in Polystyrene-Cyclohexane Solutions and later (Jennings, 2020) proved his exact equation, $\Delta T = 3kT^2wMW_1/\sigma a.MW_2$, as the formula for the data. There is the precursor, $dlnA/dK = 1/6K$, and in this paper we show with scant data that the precursor is true for degrees of polymerization of $r \geq 2$. There are three data points in the linear regression of σ versus $1/r$, and the author will show it is appropriate to plot σ versus $1/r$ in RESULTS.

II. RESULTS

In (Siow and Patterson, 1973), there are two equations for surface tension in polymer solutions, here and they are worked up, so Eq. (1) is the first one. $\varphi_1 + \varphi_2 = 1$ and $\varphi_{1S} + \varphi_{2S} = 1$, where S denotes the surface volume fraction and the other is the bulk volume fraction.

$$(\sigma - \sigma_1) a / kT = \ln (\varphi_{1S} / \varphi_1) + ((r-1) / r) (\varphi_{2S} - \varphi_2) \qquad (1)$$

Taking $\lim \varphi_2 \to 0$ $\partial\sigma/\partial\varphi_2$ $(a/kT) = \lim \varphi_2 \to 0$ $(1/r)$ $(1 - \partial\varphi_{2S}/\partial\varphi_2)$ after simplification, see APPENDIX Part 1. If $\partial\varphi_{2S}/\partial\varphi_2 < 0.01$, say, then we have the 2012 result (Jennings, 2012), which is true for $r \geq 2$.

$$\partial\sigma/\partial\varphi_2 = kT/ra \qquad (2)$$

From (2), it is apparent that it makes sense to plot σ versus $1/r$ see APPENDIX, Part 2 in an effort to get the molecular weight dependence of the surface tension at limit of superheat of cyclohexane. The author was not able to find much data on the molecular weight dependence of the surface tension of polystyrene, but wanted to clarify under what conditions the precursor is valid.

For TABLE 1, the density of styrene monomer was estimated by using to following ratio: d1 (cyclohexane, 293.15K)/d1 (cyclohexane, 492.75K) $\approx$ d2 (styrene, 293.15K)/d2 (styrene, 492.75K) as we didn't have d2 (styrene, 492.75K), but had the other three. d1 and d2 at 293.15K were got from (CRC Handbook 1985-86) and d1 at 492.75K was got from (Jennings, 2012). Thus, we have est = 0.9060(0.5386/0.7785)=0.6268 g/cc. Both polymer densities are estimated from (Bernardo and Vesely, 2007) formula for Mn = 140,000 polystyrene above the glass transition of 94 degrees Centigrade

to be 0.9571 g/cc. Then r = ratio of molar volume of polystyrene/molar volume of cyclohexane=(MW2/d2)/(MW1/d1). See DISCUSSION for method to get σ_2.

TABLE 1. All values are at limit of superheat of cyclohexane = 492.75K; density of polymer $\approx$ 0.93 g/cc. and the sentence should end with a period.

Molecular Weight Polystyrene, MW$_2$	r	1/r	σ_2	d$_2$
104.16 (monomer)	1.0635	0.9403	11.6276	0.6268
44000	294.21	0.003399	26.33	0.9571
high polymer	∞	0	17.15	0.9571

The linear regression $\sigma_2 = m(1/r) + b$ yields $\sigma_2 = -10.747(1/r) + 21.750$, using monomer, 44,000 MW, and high polymer giving r(linearity) = - 0.78.

III. DISCUSSION

SURFACE TENSION OF POLYSTYRENE SOLUTIONS
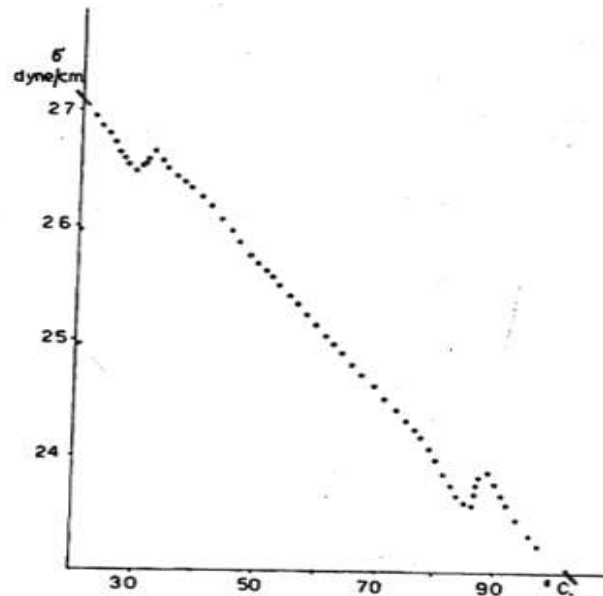
Fig. 2. Variation of the surface tension at equilibrium vs. temperature of a 2% solution in decalin, determined by the ring technique.

POLYMER LETTERS   VOL. 2, PP. 51-53 (1964)

E. Ferroni   G. Gabrielli

Fig. 2 is from (POLYMER LETTERS, 1964) as denoted. A line was formed from two (x, y) points:

(19.94ºC, 27.08erg/cm^2) and (102.52ºC, 22.97erg/cm^2) by measuring with a ruler and interpolating. This is for high polymer polystyrene in decalin. I can only assume the solution was 2% decalin, otherwise it is pointless. The formula for the line is $\sigma_2 = 27.08 - 0.04977(T-20)$ erg/cm^2, where T is in Centigrade. Putting in T = 219.6ºC gives a value for σ_2 of 17.15 erg/cm^2 and that was entered to TABLE 1. (Wu, 1970) has for molecular weight 44,000 polystyrene the formula

$\sigma_2 = 40.7-0.072(T-20)$ and that gives for T = 219.6ºC a value for σ_2 of 26.33 erg/cm^2 and that was entered into TABLE 1. To get σ_2 for the monomer, we used (Guggenheim, 1945) formula of corresponding states for surface tension, $\sigma_2 = \sigma_o (1-T/T_c)^{11/9}$, and got the value for the surface tension of polystyrene monomer (styrene) from (Jasper, 1972) of 32 erg/cm^2 at 20ºC or 293.15K. T_c for styrene is 647.55K (CRC Handbook 1985-86 page F-64) so plugging in gives σ_2 (492.75K) = 11.6276 erg/cm^2 and that was the third point used in the linear regression. σ_o only varies a little with temperature, so the author used Guggenheim's formula.

Now for the second equation from (Siow and Patterson, 1973) there is Eq. (3) here.

$$\ln[(\varphi_{2S} / \varphi_2)^{1/r} / (\varphi_{1S} / \varphi_1)] = (\sigma_1 - \sigma_2) \, a/kT \qquad (3)$$

Rearranging, and taking the limit as $\varphi_2 \to 0$, we have Eq. (4): as $\varphi_2 \to 0$ also $\varphi_{2S} \to 0$.

$$\varphi_{2S} = \varphi_2 \exp[r \, (\sigma_1 - \sigma_2) \, a/kT] \qquad (4)$$

So, we come to this expression for $\partial\varphi_{2S}/\partial\varphi_2$, viz, at $T_1 (\varphi_2 \to 0$ corresponds to pure cyclohexane).

$$\partial\varphi_{2S}/\partial\varphi_2 = \exp[r \, (\sigma_1 - \sigma_2) \, a/kT_1] \qquad (5)$$

In (Jennings, 2012) there is the value for σ_1 of 4.0904 erg/cm^2 and this is all at the limit of superheat of cyclohexane, because that is the limit as $\varphi_2 \to 0$. $T_1 = 492.75$K and $a = 196.73 \times 10^{-16}$ cm^2. k is Boltzmann constant, 1.3805×10^{-16} erg/K. Plugging these into (5) gives TABLE 2.

TABLE 2

The entry for $\partial\varphi_{2S}/\partial\varphi_2$ and r = 1 should be 0.135.

r	$\partial\varphi_{2S}/\partial\varphi_2$	σ_2 erg/cm^2
1	0.134	11.00
2	8.2×10^{-4}	16.376
5	1.8×10^{-10}	19.60

Thus, the precursor equation is true for the dimer and higher polymer, because $\partial\varphi_{2S}/\partial\varphi_2$ gets even smaller as r increases.

IV.   CONCLUSIONS

Essentially, what was proved here was that, using scant data, it is possible to prove that the precursor derived in (Jennings, 2012) is indeed true for polystyrene but not the monomer. These equations are general and not specific to polystyrene-cyclohexane, which has $\sigma_2 > \sigma_1$. A detailed treatment is found in (Siow and Patterson, 1973), which extends the work of (Prigogine and Marechal, 1952).

NOMENCLATURE
a   surface area of solvent molecule
A   prefactor in J = A exp K
b   intercept
d1   density of cyclohexane
d2   density of styrene monomer or polymer
k   Boltzmann constant
K   exponent in J = A exp K
m   slope
MW   molecular weight
MW_1 molecular weight of solvent
MW_2 molecular weight of polymer
r   ratio of molar volume of polystyrene/molar volume of cyclohexane
r   (linearity) coefficient of determination
T   degrees Kelvin in ΔT equation and Eqs. (1) & (2), otherwise in Centigrade
T_1 limit of superheat
ΔT rise in limit of superheat
w   weight fraction polymer
σ surface tension
σ_1 surface tension of cyclohexane
σ_2 surface tension of polystyrene
φ_1 volume fraction of solvent in bulk
φ_2 volume fraction of polymer in bulk
φ_{1S} volume fraction of solvent on surface

φ_{2S} volume fraction of polymer on surface

ACKNOWLEGMENTS

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APPENDIX

Part 1

The result of this calculus is what (1) simplifies to. Remember $\varphi 1 + \varphi 2 = 1$ and $\varphi 1S + \varphi 2S = 1$ and as $\varphi 2 \rightarrow 0$, $\varphi 2S \rightarrow 0$ also.

$(\sigma - \sigma 1) a/kT = \ln (\varphi 1S/\varphi 1) + ((r -1)/r)(\varphi 2S – \varphi 2)$ Eq. (1)

$\lim \varphi 2 \rightarrow 0 \ (\sigma - \sigma 1) a/kT = \lim \varphi 2 \rightarrow 0 \ ((\ln (\varphi 1S/\varphi 1) + ((r -1)/r)(\varphi 2S – \varphi 2))$

$\lim \varphi 2 \rightarrow 0 \ \partial(\sigma - \sigma 1) a/kT/\partial \varphi 2 = \lim \varphi 2 \rightarrow 0 \ (\partial(\ln \varphi 1S - \ln \varphi 1)/\partial \varphi 2 + (1-1/r)(\partial \varphi 2S /\partial \varphi 2– 1))$

$\lim \varphi 2 \rightarrow 0 \ \partial \sigma/\partial \varphi 2 \ (a/kT) = \lim \varphi 2 \rightarrow 0 \ ((1/\varphi 1S) \ \partial(1- \varphi 2S)/\partial \varphi 2 - (1/\varphi 1)(\partial \varphi 1/\partial \varphi 2) + \partial \varphi 2S/\partial \varphi 2 - 1 + (1/r)(1 - \partial \varphi 2S /\partial \varphi 2))$

$\lim \varphi 2 \rightarrow 0 \ \partial \sigma/\partial \varphi 2 \ (a/kT) = - \partial \varphi 2S/\partial \varphi 2 + 1 + \partial \varphi 2S/\partial \varphi 2 - 1 + (1/r)(1 - \partial \varphi 2S /\partial \varphi 2)$

So, we have $\lim \varphi 2 \rightarrow 0 \ \partial \sigma/\partial \varphi 2 \ (a/kT) = (1/r)(1 - \partial \varphi 2S /\partial \varphi 2)$, which is in the text.

Part 2 Here's the proof of plotting σ versus $1/r$.

$\partial \sigma/\partial \varphi 2 = kT/ra$ Eq. (2), $\varphi 2$ is polymer volume fraction and σ is surface tension

$d\sigma/d\varphi 2 = kT/ra$

$d\sigma = (kT/ra)d\varphi 2$ then integrate both sides, setting T=Tl
                        and integrate from $\varphi 2 = 0$ to $\varphi 2$ and σ from $\sigma 1$ to σ, so $\sigma 1$ = integration constant

$\sigma - \sigma 1 = (kTl/ra)\varphi 2$ $\sigma 1$ is surface tension of monomer

$\sigma = (kTl/ra)\varphi 2 + \sigma 1$ then set $\varphi 2 = 1$ for pure polymer

So $\sigma = (kTl/a) (1/r) + \sigma 1$ which has the form

$\sigma = m(1/r) + b$

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