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A correction resulting from two surface tension calculations

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Abstract

Hsin, *et al* derived the surface tension increment at depletion of solute in the interface:
 $\Delta \sigma = c k T \lambda$. Siow and Patterson used the Prigogine-Marechal theory to get $d\sigma / d\phi_2 = k T / r a$ in Jennings' paper. To relate these two expressions, one has to convert from c , concentration for Hsin, to c' , concentration for Jennings. We have $d c' / d c = MW_2 / N_o$, where MW_2 is molecular weight solute and N_o is Avogadro's number. At the limit of vanishing solute concentration, Hsin is $d\sigma / d c$

$= k T \lambda$. From dividing two of Jennings' equations, one gets $d c / d \phi_2 = \rho_2 N_o / MW_2$. The chain rule obtains $(d\sigma / d\phi_2)(d\phi_2 / d c) = k T \lambda$, so with algebra we eliminate $k T$ and r (ratio of molar volume of polymer to molar volume of solvent) to get $MW_1 = N_o \lambda a \rho_1$. Both theories work best at the limit of $c \rightarrow 0$ and they are general, so the author feels free to treat the solute in the same way for both. In Hsin, *et al*, they assume a value for λ , so this paper corrects that flaw. λ only depends on the solvent.

Keywords: Surface Tension, Solute, Polymer

1. Introduction

Hsin, *et al* used a statistical mechanical theory where there is a bulk phase of a solution of radius R with N solute molecules, so its concentration is $c = N / (4 \pi R^3 / 3)$. Then they have an interfacial shell outside of the bulk with thickness λ . Their flaw is that they assume that $\lambda = 0.213$ nm and my equation show a way of calculating λ , which only depends on the solvent, $MW_1 = N_o \lambda a \rho_1$, solving for λ . In the Results section I will show how to get $d c / d \phi_2$.

2. Results

Jennings, in 2012 (1) and 2020 (2), presented two equations for the limit of superheat of polymer solutions.

$$\lim_{\phi_2 \rightarrow 0} (dT/d\phi_2) = (3 k T^2) / (\sigma r a) \tag{1}$$

$$\lim_{c' \rightarrow 0} (dT/dc') = (3 k T^2 MW_1) / (\rho_1 \sigma a MW_2) \tag{2}$$

Then we need r , the molar volume of solute divided by the molar volume of solvent. The solute is interpreted to be polymer or electrolyte.

$$r = (MW_2 / \rho_2) / (MW_1 / \rho_1) \tag{3}$$

Dividing (1) by (2) and applying (3) we get.

$$\lim_{c' \rightarrow 0} (dc'/d\phi_2) = \rho_2 \tag{4}$$

As for units $[c]$ are molecules/cc and $[c']$ are gm/cc. Therefore, $d c' / d c = MW_2 / N_o$. So, $dc/d\phi_2 = \rho_2 N_o / MW_2$. Then, we have the chain rule.

$$(d\sigma / d\phi_2)(d\phi_2 / d c) = k T \lambda \tag{5}$$

Now $(d\sigma / d\phi_2) = k T / r a$ in Jennings' 2012 paper and $(d\phi_2 / d c) = MW_2 / \rho_2 N_o$.

Combining

$$(k T / r a) (MW2 / \rho2 No) = k T \lambda \quad (6)$$

Simplifying and using (3) we indeed have something that can be solved for λ .

$$MW1 = No \lambda a \rho1 \quad (7)$$

3. Discussion

In (7) notice that λ only depends on the solvent. Hsin, *et al* assumed a value for λ , the thickness of the monolayer in the statistical mechanical model, of 0.213 nm, but this formula gives an exact value based on Jennings' research in polymer solutions. The author maintains that these theories are both statistical mechanical and Siow-Patterson's goes back to the well-known Flory-Huggins theory of 1942 as built on by Prigogine-Marechal in 1952.

Jennings's polymer solution research began with a 1985 *Macromolecules* publication that has the data for bubble nucleation in polymer solutions.

4. Conclusion

While the author is not able to understand all of the math in the Hsin, *et al* article, he can only trust that The American Physical Society has competent reviewers to make sure their article is correct. Given that, Jennings found this flaw and was able to correct it.

Table 1: Nomenclature

1	a	Surface area of solvent molecule
2	c	Concentration of solute in molecules/cc
3	c'	Concentration of solute in gm/cc
4	k	Boltzmann constant
5	MW1	Molecular weight of solvent
6	MW2	Molecular weight of solute
7	N	Number of solute molecules
8	No	Avogadro's number
9	r	Ratio of molar volume of solute to molar volume of solvent
10	R	Radius of volume of bulk in statistical mechanical model
11	T	Temperature Kelvin
12	λ	Thickness of spherical shell in statistical mechanical model
13	$\rho1$	Density of solvent
14	$\rho2$	Density of solute
15	σ	Surface tension of solution
16	$\phi2$	Volume fraction of solute

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6. References

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