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A Test of the Equation for Bubble Nucleation in Polymer Solutions

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Abstract

Jennings/Middleman (1985) [1] got data for bubble nucleation in polymer solutions. Jennings (2012) [2] first derived the exact equation that agreed with that data and Jennings (2014) [3] expanded the (2012) equation. In this paper, Jennings presents mathematics that tests the (2014) equation, which is strictly true only for w2 → 0 or (n2 / no) → 0. The workup for (n2 / no) = 0, 0.01, 0.02 and 0.25 shows that the formula is only true for the limiting case mathematically, but the actual data gives straight lines for 2000 and 4000 daltons.

Keywords: Bubble Nucleation, Polymers, Molecular Weights

Introduction

Jennings/Middleman's (1985) [1] data is at the end of this document. This enabled Jennings to go from the (2012) [2] equation (1) to the (2014) [3] equation (2).

$$\lim_{w2 \to 0} (\partial T/\partial w2) = (MW1/MW2)\,(3kT_1^2/\sigma_1 a) \quad (1)$$

Then, the expanded form is.

$$T - To = (3\,k\,To^2\,w2\,MWo) / (\sigma o\,ao\,MW2) \quad (2)$$

Where

$$w2 = \text{polymer weight} / (\text{polymer weight} + \text{solvent weight}) \quad (3a)$$

Thus

$$w2 = n2\,MW2 / (no\,MWo + n2\,MW2) \quad (3b)$$

The n's are moles and MW's are the molecular weights. Eq. (1) is rigorously true, as proved in the (2012) treatment. w2 –> 0 means n2 –> 0 and MWo and MW2 are constants.

Results

Eq. (2) then becomes, for w2 –> 0.

$$T - To = (3\,k\,To^2 / \sigma o\,ao)\,(n2 / no) \quad (4)$$

This is quadratic in To.

$$(3\,k / \sigma o\,ao)\,(n2 / no)\,To^2 + To - T = 0 \quad (5)$$

Taking the positive root, we have.

$$To = (-1 + (1 + (12\,k\,T/ \sigma o\,ao)\,(n2 / no))^{1/2}) / ((6\,k / \sigma o\,ao)\,(n2 / no)) \quad (6)$$

Where

$$X = (12\ k\ T / \sigma o\ ao)\ (n2 / no) \quad (7)$$

For w2 small, n2 is small and X is small. This paper is to test whether w2 –> 0 is true and we present a table of results. According to the binomial expansion for $X^2 < 1$, there is the series up to X^3 that converges.

$$(1 + X)^{1/2} = 1 + (1/2)\ X - (1/8)\ X^2 + (1/16)\ X^3 \quad (8)$$

Another way to write (6) is.

$$To = (-\ 1 + (1 + X)^{1/2}) / (X / 2T) \quad (9)$$

(9) Simplifies to, using (8).

$$T - To = T\ (\ X/4 - X^2/8) \quad (10)$$

Another way to write (10) is.

$$T - To = (3\ k\ T^2/\ \sigma o\ ao)\ (n2/no) - (18\ k^2\ T^3\ n2^2)/(\sigma o\ ao\ no)^2 \quad (11)$$

Because

$$T - To = ((3\ k\ To^2) / (\sigma o\ ao))\ (n2 / no) \quad (12)$$

Plug (12) into (11) by eliminating T – To and simplify.

$$To^2 = T^2\ (1 - (6\ k\ T/\sigma o\ ao)\ (n2 / no)) \quad (13)$$

Then, eliminating T between (12) and (13) we get an expression with (n2/no) as the variable, which is a monstrosity, but allows a test of n2 –> 0.

$$To^2 = (To + 3\ k\ To^2\ n2/\sigma o\ ao\ no)^2 \text{ x } (\ 1 - (6\ k/\ \sigma o\ ao)\ (To + 3\ k\ To^2\ n2/\sigma o\ ao\ no)(n2/no)) \quad (14)$$

To check (2) we see if the left hand and right-hand sides of (14) agree. For the mole fractions of solvent o and polymer 2 we have (15) and (16). In the original (2012) experiment solvent = cyclohexane and polymer = polystyrene. All of the data is published in Jennings (2012) [2].

$$Xo = no /(no + n2) \quad (15)$$

$$X_2 = n2 / (no + n2) \quad (16)$$

To get σo, surface tension of the polymer solution, we assume the law for perfect solutions, according to Prigogine/Marechal (1952) [4], viz.

$$\sigma o = \sigma\ (\text{cyclohexane})\ Xo + \sigma\ (\text{polystyrene})\ X_2 \quad (17)$$

Discussion

These are the variables and since w2 –> 0 proves to be correct, the temperature is assumed to be 492.75 K = To.

σ (cyclohexane) = 4.0904 erg/cm^2

σ (polystyrene) = 26.329 erg/cm^2

k (Boltzmann constant) = 1.3805 x 10^{-16} erg/K

ao (surface area of cyclohexane at To) = 196.73 x 10^{-16} cm^2

We make a table by plugging in numbers into (14) Here we have for the left- and right-hand sides.

$$A = To^2 \quad (18)$$

$$B = (To + 3\ k\ To^2\ n2/\sigma o\ ao\ no)^2 \text{ x } (\ 1 - (6\ k/\ \sigma o\ ao)\ (To + 3\ k\ To^2\ n2/\sigma o\ ao\ no)(n2/no)) \quad (19)$$

Table of Results

n2/no	A	B	(A – B) / A	σo erg/cm^2
0	242802.6	242802.6	0	4.0904
0.01	242802.6	242089.4	0.3%	4.3403
0.02	242802.6	240109.3	1.1%	4.5265
0.25	242802.6	85849.23	0.65	8.5381

One can see that having n2/no = 0.25 is too much, as X has to be small for the binomial expansion to converge. However, the results bear out that w2 –> 0 and n2 –> 0 are correct for (1) and (4). The original Jennings (2012) [2] derivation was correct in the first place.

Conclusion

Jennings (2012) [2] gave the equation for the limit of superheat of polymer solutions. Here the author got (14) to test the validity of the original theory. Solving the quadratic equation and applying the binomial expansion to test w2 –> 0 proves that the equation is actually correct in the limiting case. However, because the 2000 and 4000 molecular weight data gave straight lines, in Jennings (2014) [3] the equation is expanded.

Acknowledgments

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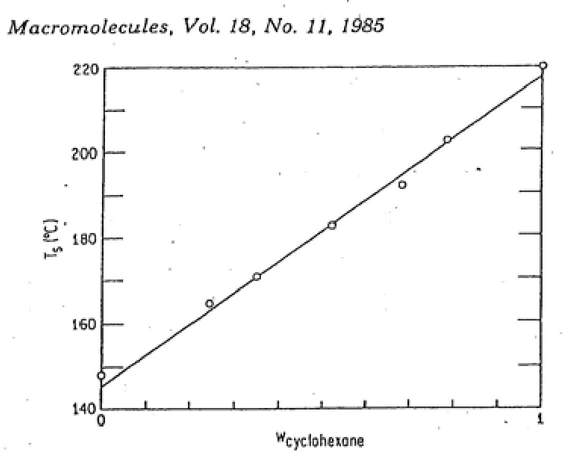

Fig 1: Data on limiting superheat for binary solutions of cyclohexane and pentane. Composition is mass fraction

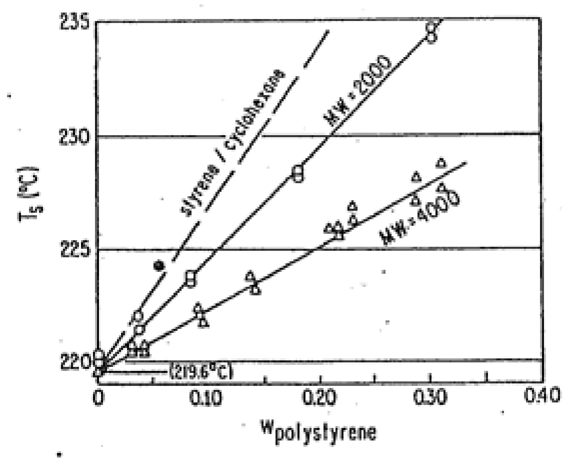

Fig 2: Data on limiting superheat for low molecular weight polystyrene in cyclohexane is taken as 219.6^0 C

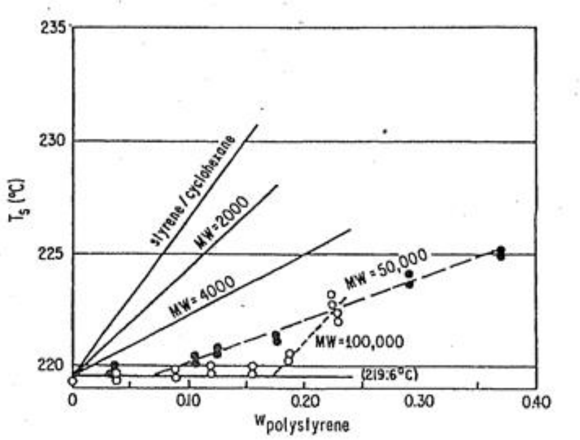

Fig 3: Data on limiting superheat for high molecular weight polystyrene in cyclohexane

References

1. Jennings JH, Middleman S. Homogeneous Nucleation of Vapor from Polymer Solutions. Macromolecules. 1985; 18:2274-2276.
2. Jennings JH. Limit of Superheat of Polystyrene-Cyclohexane Solutions: Theory. International Journal of Thermodynamics. 2012; 15(3):127-132.
3. Jennings JH. Homogeneous Nucleation from Polymer Solutions. Polymers Research. Journal. 2014; 8(4):311-319.
4. Prigogine I, Marechal J. The Influence of Differences in Molecular Size on the Surface Tensions of Solutions IV. Journal of Colloid Science. 1952; 7:122-127.