Int. j. adv. multidisc. res. stud. 2025; 5(5):294-296

Received: 21-07-2025
Accepted: 01-09-2025

International Journal of Advanced Multidisciplinary Research and Studies

ISSN: 2583-049X

Polymer Solution Limit of Superheat T Falls to that of Solvent To as r –> ∞

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Abstract

Jennings and Middleman [1] measured the limit of superheat of polystyrene in cyclohexane and Jennings [2] derived the following equation for the effect, found in Jennings [3].

$$T - To = (3\ k\ To^2\ w_2\ MW_o) / (\sigma o\ ao\ MW_2)$$

Looking at the data in [1] one can see that the rise in superheat is falling to that of the cyclohexane as the molecular weight of the polystyrene rises. In this paper, the author takes the partial derivative of T, solution limit of superheat, and shows that $\partial T / \partial \ln MW_2 \rightarrow 0$ as $r \rightarrow \infty$. r is the ratio of molar volume of polymer to that of solvent. An image of the apparatus used to measure the temperature of the superheated solution is presented from Holden and Katz [4]. Figures 1, 2 and 3 of the 1985 Jennings and Middleman data are here. In a previous paper, Jennings [5], Jennings proved that, $\partial \sigma / \partial r = 0$ comes from $r = \infty$. I take the above equation to:

$$\partial T / \partial \ln MW_2 = -\ (3\ k\ T_o^2\ \rho_o\ w_2) / (\sigma_o\ a_o\ r\ \rho_2).$$

Notice that the left side goes to zero as r goes to infinity. This is the tendency in the Jennings and Middleman data.

Keywords: Limit of Superheat, Polymer Solution, Infinite Molecular Weight Polymer, Surface Tension, Classical Nucleation Theory, Flory-Huggins Theory

Introduction

Classical nucleation theory has its origin in W. Thomson (Lord Kelvin) (1870) and Josiah Willard Gibbs (1877), both mentioned in the Max Plank Institute website [6]. Others contributed, including Max Volmer (1925), and L. Farkas (1927) getting the pre-exponential factor, both in [6]. Jennings [7, 3] eliminated the pre-exponential factor, taking the Blander and Katz [8] formula here as (1) to J = f(K) exp (K).

$$J = A \exp (K) \tag{1}$$

In Jennings [3] the author used data for ten polar and non-polar solvents to get K = - 64.5605 and equation (2).

$$\ln J = (1/12) \ln K^2 + 75.379 + K \tag{2}$$

Jennings and Middleman got data for the limit of superheat of polystyrene in cyclohexane using polystyrene of molecular weight 2000, 4000, 50,000 and 100,000 as shown in Figures 1, 2 and 3 with a device similar to that of Holden and Katz pictured in the figure here.

In their article, Prud'homme *et al* [9], show their data for the limit of superheat of polystyrene in benzene using a similar device to Jennings and Middleman and they had molecular weights of polystyrene of 17500, 100,000, 600,000 and 20 million.

Results

In a previous paper, Jennings [5] calculated that $\partial \sigma / \partial r = 0$ as $r = \infty$. Here, we start with Jennings' formula in ABSTRACT and derive the equation for $\partial T / \partial \ln MW_2$.

$$T - To = (3\ k\ To^2\ w_2\ MW_o) / (\sigma o\ ao\ MW_2) \tag{3}$$

First we take the partial derivative of (3) with respect to MW_2.
We get.

$$\partial T / \partial MW_2 = - (3\ k\ To^2\ w_2\ MW_o) / (\sigma o\ ao\ MW_2^2) \quad (4)$$

Then, we note, from the definition of r, the ratio of the molar volume of polymer to that of solvent, we can substitute for MW_o / MW_2 in (4) where 2 is polymer, o is solvent, MW molecular weight and ρ is density.

$$r = (MW_2 / \rho_2) / (MW_o / \rho o) \quad (5)$$

Solving (5) for MW_o / MW_2 we have.

$$MW_o / MW_2 = \rho o / (r\ \rho_2) \quad (5a)$$

Eliminating (5a) from (4) we have.

$$\partial T / \partial MW_2 = - (3\ k\ T_o^2\ \rho_o\ w_2) / (\sigma_o\ a_o\ r\ \rho_2\ MW_2) \quad (6)$$

Then we have the desired equation in ABSTRACT, forming the logarithm.

$$\partial T / \partial \ln MW_2 = - (3\ k\ T_o^2\ \rho_o\ w_2) / (\sigma_o\ a_o\ r\ \rho_2) \quad (7)$$

Prud'homme *et al* measured the limit of superheat up to 20 million daltons polystyrene and Jennings and Middleman only to 100,000. We can easily see in (7) that $\partial T / \partial \ln MW_2 \rightarrow 0$ as $r \rightarrow \infty$. In (7) for polystyrene in cyclohexane we have the following numbers from Jennings [10].
To = 492.8 Kelvin MWo = 84.2 daltons MW_2 = 2000 – 100,000 daltons σ_o = 4.09 dyne/cm
$a_o = 196.7 \times 10^{-16}$ cm^2 ρ_o = 0.5386 gram / cm^3 ρ_2 = 0.9571 gram / cm^3 $k = 1.38 \times 10^{-16}$ erg / deg
To is limit of superheat of cyclohexane and k is Boltzmann constant. $0 \leq w_2 \leq 1$ is weight fraction polystyrene.

Discussion

The Jennings and Middleman data seem to indicate that $\partial T / \partial \ln MW_2 \rightarrow 0$ as $r \rightarrow \infty$ but Prud'homme *et al* report that the limit of superheat for polystyrene/benzene falls off below the limit for pure benezene. Jennings and Middleman had to turn to cyclohexane because in using benzene the benzene dissolved into the glycerol column fluid. This author feels that the choice of cyclohexane was correct but with Dr. Middleman we did not test the limit of superheat for above molecular weight 100,000. The test of Equation (7) would be to use 600,000 and 20 million molecular weight polystyrene in cyclohexane. Eq. (7) predicts that the limit of superheat for very high molecular weight polymer would be that of the solvent. This could be useful in the polymer industry.
The derivation of Eq. (3) by Jennings, essentially accomplished in Jennings [10], comes from mathematics of Lord Kelvin, Josiah Willard Gibbs and what came from Flory [11], Huggins [12] and Prigogine [13]. Prigogine (1952) got their method for the surface tension of polymer solutions from Flory-Huggins (1942) theory. Siow and Patterson (1973) [14] developed Prigogine's surface tension theory. From what I know, these two trains of thought united in Jennings [10]. The polymer industry is very huge.

Conclusion

To test the validity of equation (3) it would be necessary to do experiments with different polymers and solvents. Knowing that an equation is a general rule would be very useful in polymer science. Jennings [15] published a paper showing how equation (3) can be used to inexpensively measure polymer molecular weight for low molecular weight polymer.

Acknowledgements

The figures 1, 2 and 3 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. The image of the experimental apparatus is taken from Holden, BS and Katz, JL "The Homogeneous Nucleation of Bubbles in Superheated Binary Liquid Mixtures" AIChE Journal (1978) 24(2): 260-267.
Let me mention the Pastor of NEWMAN HALL, Berkeley, Father Xavier Lavagetto, where the author attends Mass. Father Xavier helps us understand the Catholic faith well and cares about me in particular. At a NEWMAN Mass a Priest said, "The Second Coming is Overdue."

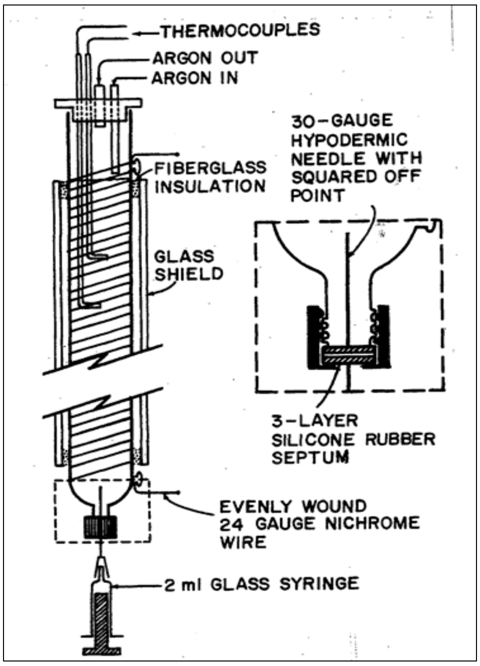

Fig 1: Low gradient rising droplet column and detail

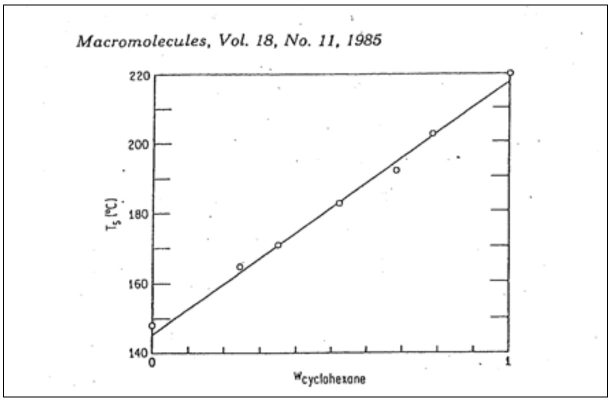

Fig 1: Data on limiting superheat for binary solutions of cyclohexane and pentane. Composition is mass fraction

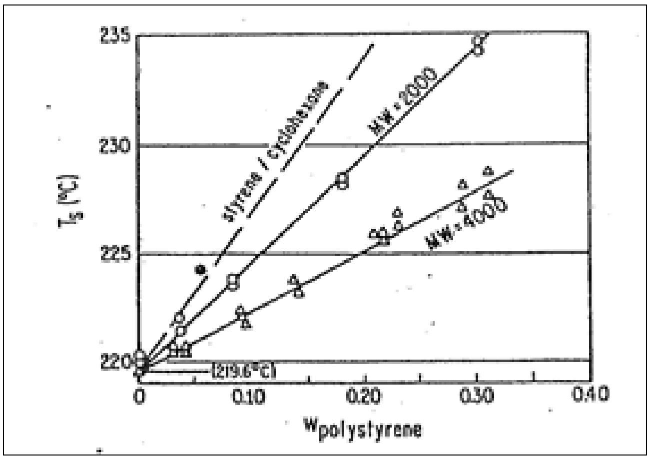

Fig 2: Data on limiting superheat for low molecular weight polystyrene in cyclohexane. T_s for pure cyclohexane is taken as 219.6 ^{0} C.

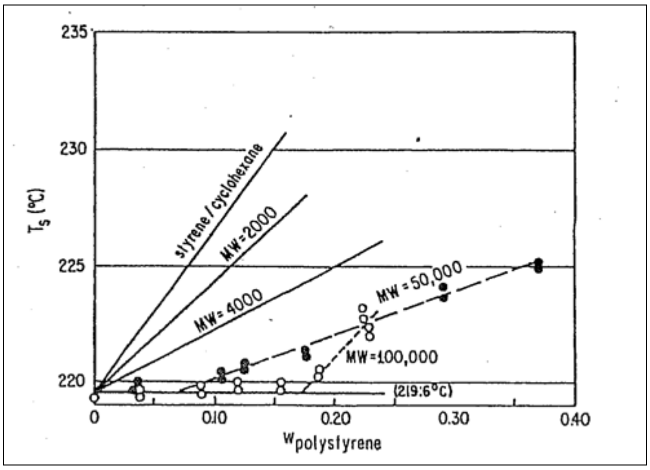

Fig 3: Data on limiting superheat for high molecular weight polystyrene in cyclohexane

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