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The Equation for Rise in Superheat by Adding Electrolyte

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

For many liquids, the limit of superheat is 0.89 Tc, where Tc = temperature Kelvin at critical point. The rise in the limit of superheat by addition of polymer has a formula, B', derived by Jennings, and this paper makes use of a pattern to predict the formula for rise in superheat by adding electrolyte, B. The equations for boiling point elevation by addition of electrolyte, A, and polymer, A', are known, so we make use of a proportion and solve for the unknown, B, thus: B= (A/A') x B' to get the equation.

A, A' and B' all have the phase change temperature squared at 1 atmosphere pressure in the numerator times the ratio of the molecular weight solvent divided by the product of the density of solvent times molecular weight solute in the expression that equals lim c--->0 (dT/dc) giving the limiting slope of rise in temperature versus concentration solute. The van't Hoff factor is included. The proposed formula B for RISE IN SUPERHEAT BY ADDITION OF ELECTROLYTE is:

$$\lim_{c \to 0} (dT/dc)_{s,\ electrolyte} = (3\ k\ MW1\ Ts^{2}\ i) / (\rho 1\ \ \sigma 1\ a\ MW2(e)).$$

Keywords: *Homogeneous nucleation; boiling point elevation; limit of superheat; polymer solution; electrolyte solution.*

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NOMENCLATURES

a	*: Surface area of solvent molecule at Ts*
A	*: Equation for boiling point elevation by adding electrolyte*
A'	*: Equation for boiling point elevation by adding polymer*
B	*: Equation for rise in superheat by adding electrolyte*
B'	*: Equation for rise in superheat by adding polymer*
c	*: Concentration of solute = m2/V*
c--->0 (dT/dc)	*: limiting slope for infinite dilution*
I	*: Van't Hoff factor (equals Z+ + Z- for numbers of + or – ions)*
k	*: Boltzmann constant*
m	*: Molality*
mi	*: Mass: 1, solvent; 2, solute*
MW1	*: Molecular weight of solvent*
MW2(e)	*: Molecular weight of electrolyte*
MW2(p)	*: Molecular weight of polymer*
R	*: Universal gas constant*
T	*: Temperature Kelvin of solution*
Tc	*: Critical temperature of solvent Kelvin*
Ti	*: Temperature Kelvin, b = boiling, s = superheat*
V	*: Volume of a sample of solution*
w2	*: Weight fraction polymer*
ΔHvap	*: Heat of vaporization of solvent per mole*
Δ T	*: Incremental rise in boiling or superheat = T - Ti*
ρ1	*: Density of pure solvent at phase-change temperature = m1/V*
σ1	*: Surface tension of pure solvent at limit of superheat*

1. INTRODUCTION

The equation for boiling point elevation is arrived at by combining the Clausius-Clapeyron equation with Raoult's law at infinite dilution, where the molar heat of vaporization appears in the denominator for c--->0 (dT/dc) and it has been presented for electrolyte Wall [1] and Blackmore [2]. Jennings [3] derived the formula for infinite dilution for the limit of superheat by adding polymer. By taking the proportion A/A'=B/B' because of a pattern between the equations, we form B= (A/A') x B' for the desired equation. This appears to give a sensible answer. Work toward Jennings [3] began in 1980 with a project on Bubble Nucleation in Polymer Solutions, where the data was published by Jennings and Middleman [4].

2. THEORY

The formula for boiling point elevation by addition of electrolyte is presented (1) in Wall [1], page 363, and (2) is conversion of concentration to molality. In addition, the heat of vaporization, ΔHvap, is per mole.

$$\Delta T = (MW1\ R\ Tb^2\ m) / (1{,}000\ \Delta Hvap) \quad (1)$$

$$m = (1{,}000\ c) / (\rho 1\ MW2(e)) \quad (2)$$

Putting (2) into (1), we have, adding the van't Hoff factor, i = Z+ + Z- for ions.

$$\lim\ c \text{--->} 0\ \ (dT/dc)b,\ \text{electrolyte} = (R\ Tb^2\ MW1\ i) / (\ \rho 1\ \ \Delta Hvap\ MW2(e)) \quad (3)$$

Equation (3) is equation A in the ABSTRACT.

The formula for boiling point elevation by addition of polymer is presented in BLACKMORE [2].

$$\lim\ c \text{--->} 0\ \ (dT/dc)b,\ \text{polymer} = (R\ Tb^2\ MW1) / \ (\rho 1\ \ \Delta Hvap\ MW2(p)) \quad (4)$$

Equation (4) is equation A' in the ABSTRACT. Notice the MW2(p), where p is for polymer instead of e for electrolyte.

The formula for limit of superheat by addition of polymer was derived by Jennings [3] and is:

$$\lim\ w2 \text{--->} 0\ (dT/dw2)s,\ \text{polymer} = (3\ k\ Ts^2\ MW1) / (\sigma 1\ a\ MW2(p)) \quad (5)$$

Notice that σ is in the denominator instead of ΔHvap. We need to convert from w2, weight fraction at infinite dilution to concentration at infinite dilution.

$$w2 = m2 / (m1 + m2\} \quad (6)$$

$$\lim m2 \text{--->} 0 \ w2 = m2/m1 \quad (7)$$

$$(dT/dw2) = (dT/dc)\ (dc/dw2) \quad (8)$$

$$\rho 1 = m1/V \text{ independent of } \lim m2 \text{-->} 0 \ \ w2 \quad (9)$$

$$(dc/dw2) = (d\ (m2/V)/\ d\ ((m2/V)/(m1/V))) \quad (10)$$

$$(dc/dw2) = m1/V \quad (11)$$

Because c = m2/V, we have Jennings formula in terms of concentration.

$$\lim c \text{--->} 0 \ (dT/dc)s, \text{polymer} = (3\ k\ Ts^2\ MW1) / (\rho 1\ \ \sigma 1\ a\ MW2(p)) \quad (12)$$

Equation (12) is equation B' in ABSTRACT. B = (A/A') x B' to get proposed formula.

Proposed formula B for RISE IN SUPERHEAT BY ADDITION OF ELECTROLYTE is then:

$$\lim c \text{--->} 0 \ (dT/dc)s, \text{electrolyte} = (3\ k\ Ts^2\ MW1\ i) / \ (\rho 1\ \ \sigma 1\ a\ MW2(e)) \quad (13)$$

This is because a number of terms cancel out.

3. METHODOLOGY

In theory, we saw that the polymer MW2(p) cancels out, and it should be noted that Jennings [3] theory goes back to Prigogine/Marechal [5], which gives the surface tension for polymer solutions. The old theory for boiling point elevation for electrolyte is based on small molecules, but BLACKMORE [2] presents it for polymer. There is a kind of corresponding states between boiling point elevation and limit of superheat. All four equations have a similar form.

4. RESULTS AND DISCUSSION

One may ask, what is this all good for? A very accurate thermometer is required to measure boiling point elevation, but in Jennings [3] experiment, the effect was 10-15 degrees centigrade rather than millidegrees. Supposedly this is a better way to measure the molecular weight of a polymer, but an apparatus measuring the limit of superheat is rather complex.

5. CONCLUSION

Physical chemistry has a beauty and symmetry all its own. This paper completes the search for the missing formula – RISE IN SUPERHEAT BY ADDITION OF ELECTROLYTE. It takes more study to find a use for experiments above the limit of superheat of liquids.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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