Effect of Additives on Phase Transition of NIPA Gels

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Phase curves for mixing transitions



Gibbs free energy

A thermodynamic potential that measures the "usefulness" or process initiating work obtainable from a thermodynamic system at a constant temperature and pressure (isothermal, isobaric).



Gibbs energy (also referred to as ΔG) is also the chemical potential that is minimized when a system reaches equilibrium at constant pressure and temperature. Its derivative with respect to the reaction coordinate of the system vanishes at the equilibrium point. As such, it is a convenient criterion of spontaneity for processes with constant pressure and temperature.

http://hyperphysics.phy-astr.gsu.edu/, wikipedia

The Gibbs free energy (unmixed):

 $G = (1 - x)G_A^o + xG_B^o$

The entropy of mixing:

$$\Delta S_{mixing} = -R[x \ln x + (1-x)\ln(1-x)]$$



The Gibbs free energy (ideal mixture):

 $G_{ideal} = (1-x)G_A^o + xG_B^o + RT[x\ln x + (1-x)\ln(1-x)]$



$$U_{AB} = U_{AA} = U_{BB}$$



Energy does not depend on temperature

Mixing A and B can often increase the energy of the system

Daniel V. Schroeder, An Introduction to Thermal Physics

If we sum up

$$G = G_{ideal} + \Delta U_{mixing}$$



Decreasing the temperature of this system widens the solubility gap, while increasing the temperature narrows the gap until it disappears when G is everywhere concave up.



- Evaluation of curves shows that there is instability region
- But at some temperature that instability disappears





Done by Mathcad

Thermoswelling and thermoshrinking

Thermoswelling

Thermoshrinking













NIPA gel and PNIPA

- T_{sol-gel}(NIPA) = 19°
 T_{cloud point}(PNIPA) = 21°



N-Isopropylacrylamide

Difference in temperature is because of the surface effects



Poly(*N***-isopropylacrylamide**)

Otake et al., Macromolecules, Vol. 23, No. I, 1990

Effect of additives on phase transition

If we add additives, we can manipulate with the energy because of hydrophobic interaction

Effect of Additives on Phase Transition of N-Isopropylacrylamide Gels

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Effects of salts on volume phase transition of N-isopropylacrylamide gels and cloud points of poly-(N-isopropylacrylamide) solution were measured. The experiments were performed with inorganic salts and tetraalkylammonium salts. The transition temperature for inorganic salts was dependent on anions rather than cations, and the change in transition temperature was linearly correlated with the viscosity B coefficient of anions. On the other hand, the transition temperature for tetraalkylammonium bromides strongly depended on alkyl chain length, which was suspected to result from an adsorption of the salts to the polymer segments.

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Hydrophobic interaction



No Interactions ΔH = Negative ΔS = Negative ΔG = Positive



Hydrophobic Interaction ΔH = Positive

 $\Delta S = Positive$ $\Delta G = Negative$



http://chemwiki.ucdavis.edu

Additives

- Two types of electrolytes
- inorganic salts: NaCI, KCl, NaBr, KBr, NaI, KI, KNO₃, KCl0₃, and KBr0₃
- 2. organic salts: six kinds of tetraalkylammonium bromide of different chain lengths (NH_4Br to $N(C_5H_{11})_4Br$).

Results



Figure 4. Relationship between viscosity *B* coefficients of anions and ΔT , change in transition temperature of NIPA gel by an addition of potassium salt. ΔT is defined by the following equation and salt concentration 1×10^{-4} mol/g of solution: ΔT = $(T_t \text{ in pure water}) - (T_t \text{ in salt solution})$, where T_t is transition temperature.



| Table II. | Viscosity | B Coefficients of | Ion |
|-----------|-----------|--------------------------|-----|
|-----------|-----------|--------------------------|-----|

| B^{a}_{mol} | ion | B,ªL/mol | | |
|---------------|---|---|--|--|
| 0.086 | I- | -0.069 | | |
| -0.007 | NO ₃ - | -0.046 | | |
| -0.007 | ClO ₃ - | -0.024 | | |
| -0.042 | BrO ₃ - | 0.006 | | |
| | B,°L/mol 0.086 -0.007 -0.007 -0.042 | B,*L/mol ion 0.086 I ⁻ -0.007 NO3 ⁻ -0.007 ClO3 ⁻ -0.042 BrO3 ⁻ | | |

"Value in water at 25 °C.

The transition temperature for inorganic salts was dependent on anionic species rather than the cationic species, and a linear relationship was obtained between the viscosity B coefficient of anions and the degree of the change in the transition temperature of the gel. These results were explained from the structure making or breaking character of the inorganic ions.

Velocity B coefficient

By physical intuition B should consist of two parts:

$$B = B_{Coul} + B_{hyd},$$

which follows from the highest approximations of the Coulomb theory of interaction and from the effect of the hydration of ions, respectively.

Conclusion

- The thermoshrinking-type volume phase transition of NIPA
- The hydrophobic interaction
- The transition temperature for inorganic salts depends on anions