Physical Chemistry of Polymer Solutions

Theoretical Background

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To our families

Preface

Numerous physical properties of polymer solutions are known to be significantly different from those of low molecular weight solutions. The most probable explanation of this obvious discrepancy is the large molar volume ratio of solute to solvent together with the large number of consecutive segments that constitute each single molecule of the polymer chains present as solute. Thorough understanding of the physical chemistry of polymer solutions requires some prior mathematical background in its students. In the original literature, detailed mathematical derivations of the equations are universally omitted for the sake of space-saving and simplicity, which physicists hold in high regard. However, students learning about the physical chemistry of polymer solutions are predominantly chemists, whose physical and mathematical skills are not necessarily high. In textbooks of polymer science only extremely rough schemes of the theories and then the final equations are shown. As a consequence, the student cannot unaided learn the details of the theory in which he or she is interested from the existing textbooks. Without a full understanding of the theory, one cannot analyze actual experimental data to obtain more basic and realistic physical quantities. In particular, if one intends to apply the theories in industry, accurate understanding and ability to modify the theory as one wishes are essential.

This book is mainly concerned with building a narrow but secure ladder which polymer chemists or engineers can climb from the primary level to an advanced level without great difficulty (but by no means easily, either). The need for a book of this kind has been widely recognized for many years among polymer scientists, including ourselves, but as far as we know, no such book has yet been published. We believe that this book is, in that sense, unique and unparalleled. The Japanese manuscript was originally written by Kamide and nearly completed in the 1970s and 1980s, but was not published. Based on these Japanese manuscripts, Kamide gave a series of intensive lecture courses to students at universities of Kanazawa, Hokkaido, Okayama, Osaka City, Essex, Bristol and Bradford. The manuscripts, thanks to this valuable experience, have been repeatedly revised and improved. The English edition was originally planned for the beginning of the 1990s and the Japanese manuscript was drastically reduced to fit the size requested by the publishers and transformed in part into an English version for this book. Although this attempt was interrupted by Kamide's illness, the book has now materialized through the enthusiastic cooperation of Professor Dobashi.

This book describes some fundamentally important topics, carefully chosen, covering subjects from thermodynamics to molecular weight and its distribution effects. For help in self-education the book adopts a "Questions and Answers" format. The mathematical derivation of each equation is shown in detail. For further reading, some original references are also given. The contents of the book frankly belong to the realm of classical physical chemistry, because it does not treat areas newly developed during the 1980s and 1990s, such as scaling theory and spectroscopic theory (e.g., NMR). To add chapters about these areas is beyond both our ability and the planned size of the book. The reader should not, however, consider that all the theories covered by the book have already been firmly established. Any topic, although apparently mature and fully grown, may start to develop quickly again due to the advent of a new motive force, hitherto unknown, and so may present important new unsolved problems. We experienced this in the study of phase separation and critical phenomena of multicomponent polymer solutions during the 1970s and 1980s (see, for example, K. Kamide, "Thermodynamics of Polymer Solutions : Phase Separation and Critical Phenomena", Elsevier, 1990). Throwing out "old" and jumping after "new" techniques seems an inevitable fashion intrinsic as inherent to polymer science as to other disciplines of applied science, but is not always unconditionally reasonable.

The authors will be very gratified if this book proves a help not only to students at universities and to industrial researchers, who may be studying the physical chemistry of polymer solutions and dissatisfied with existing books, but also, as a reference book, to technologists intending to apply the physical chemistry of polymer solutions to industrial practice (but not as a simple quality control method, like a fully automated analytical instrument!) and to educators teaching this or related subjects. We should like to thank Professor J. Eric McIntyre of University of Leeds, UK for his meticulous reading of the manuscript, and for important suggestions. The authors would like to offer thanks to Dr Masatoshi Saito, Dr Shigenobu Matsuda, Dr Hironobu Shirataki, Dr Kunio Hisatani, Professor Yukio Miyazaki, Mr Kazuishi Sato, Mr Yuji Ito and Mr Katsunari Yasuda of the Fundamental Research Laboratory of Fibers and Fiber-Forming Polymers, Asahi Chemical Industry Company, Ltd., Takatsuki, Osaka, Japan, who cooperated in the downsizing of the Japanese manuscript and in re-examination of the mathematical derivations in the text although the authors are, of course, responsible for any possible errors and mistakes in the book.

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Glossary

A: Area
A_i : *i* th virial coefficient
a_i : activity of *i* th component
B: enthalpy per contact area
b: bond length
b_m : *m* th cluster integral
C: weight concentration
c_p : specific heat under constant pressure
c_v : specific heat under constant volume
c: velocity of light in vacuum
D: diffusion coefficient
D: electric displacement
d: diameter
d′Q: differential heat
d′W: differential work
E: energy
E: electric field
E: unit tensor
e: strain
e: strain tensor
F: Helmholtz free energy
F_N: N -body partition function
F: force
f_D: friction coefficient for translational motion
f_s: friction coefficient for sedimentation
$f_n(n)dn$: number fraction of the polymer with the degree of polymerization n
$f_w(n)dn$: weight fraction of the polymer with the degree of polymerization n
G: Gibbs free energy
$\overline{G}$: mean molar Gibbs free energy
G_{ij} : differential of Gibbs free energy with respect to the mole fractions of *i* th component and *j* th component
g: velocity gradient
g: Huggins' free energy correction factor
$g_n(M)$: number distribution of molecular weight

$g_w(M)$: weight distribution of molecular weight
H: enthalpy
H_i : partial molar enthalpy of *i* th component
h: Planck constant
h: inhomogeneity parameter for molecular weight distribution
I_0: incident light intensity
I_s: scattered light intensity
I_t: transmitted light intensity
$\mathbf{I}$: inertia moment
J: extensive thermodynamic variable
$\mathbf{j}$: flow by diffusion
K: tension
K: Flory constant
K: optical constant
k: Boltzmann constant
k: degree of connectivity
k: reaction constant
k': Huggins' constant
L: camera length
L_0: molar heat of vaporization
l: segment length
$\mathbf{l}$: position vector of segment
M: molecular weight
M_n: number-average molecular weight
M_w: weight-average molecular weight
M_z: z-average molecular weight
M_v: viscosity-average molecular weight
M_{SD}: sedimentation-diffusion-average molecular weight
m_0: molecular weight of segment
N: number of moles of molecule
N: number of molecules
N_A: Avogadro's number
n: association number
n: segment number or chain length
n: number density
n_m: medium for the degree of polymerization

n_n: number-average degree of polymerization
n_w: weight-average degree of polymerization
n_z: z-average degree of polymerization
n_v: viscosity-average degree of polymerization
n_r: refractive index of solution
n_r^0: refractive index of solvent
P: pressure
P: polarization
P: stress tensor
P_i : vapor pressure of *i* th component
P_i^0 : vapor pressure of *i* th component before mixing
P(q): particle scattering factor
p: probability that condensation reaction occurs
p_i : coefficient for concentration dependence of χ
Q: heat
q_1: molecular partition function
$q_{w,z}$: correction factor for molecular weight distribution
q: wave vector
R: gas constant
R: phase volume ratio
R: Reynolds number
R: end-to-end distance
R: vector connecting one end to another end of polymer
R_e: radius of hydrodynamically identical sphere
R_θ: Rayleigh ratio
R_θ' : reduced scattered light intensity
$\langle R^2 \rangle$: mean square end-to-end distance
$\langle R^2 \rangle_0$: mean square end-to-end distance of unperturbed chain
r: radius
S: entropy
S: radius of gyration
S^0: entropy before mixing
S_i: partial molar entropy of *i* th component
$\langle S^2 \rangle$: mean square radius of gyration
s: scattering vector
s_0 : sedimentation coefficient at infinite dilution

T: absolute temperature
T: matrix for rotational mapping
T_c: critical solution temperature
t: time
U: internal energy
u: potential energy
V: volume
V': volume of dilute phase
V'': volume of concentrated phase
V_i : partial molar volume of *i* th component
V_0: molar volume
V_0^0: molar volume of solvent
V^0: molar volume before mixing
v_0 : volume of molecule
$\bar{v}$: partial specific volume
v: velocity
W: work
w: interchange energy
w: mean force potential between solute molecules
w_i : weight fraction of *i* th component
X: parameter for free draining
x: distance from rotational axis to surface
x_i : mole fraction of *i* th component
x_c : critical mole fraction
Y: increment of refractive index
Z: partition function for canonical ensemble
Z: excluded volume parameter
z: coordination number

α: expansion factor
α: polarizability
α: volumetric thermal expansion coefficient at constant pressure
α_R: end distance expansion factor
α_S : radius expansion factor
α_η : viscosity expansion factor

β : effective two-body excluded volume per segment pair or two-body cluster integral
γ : shear modulus
γ_i : activity coefficient of *i* th component
ΔG_{mix}: Gibbs free energy of mixing
ΔG_v: Gibbs free energy of mixing per unit volume
ΔH_{mix}: enthalpy of mixing
ΔQ_{mix}: heat of mixing
ΔS_{mix}: entropy of mixing
ΔV_{mix}: mixing volume
$\Delta \mu_i$: chemical potential of mixing of *i* th component
(superscripts id and E denote the quantities for ideal solution and excess quantities)
δC: fluctuation of concentration
ε : dielectric constant
ε : interaction energy
ζ : friction coefficient between fluid and small particle
η: viscosity coefficient
η_0:viscosity coefficient of solvent
η_r: relative viscosity
η_{sp}: specific viscosity
$[\eta]$: intrinsic viscosity or limiting viscosity number
η_v : volumetric viscosity
Ξ : partition function for grand canonical ensemble
ξ : partition function for semi-grand canonical ensemble
θ: Flory temperature
θ: bond angle
κ : isothermal compressibility
κ : enthalpy parameter
κ : elastic modulus
κ_0 : Flory enthalpy parameter at infinite dilution
λ: Lamè constant
λ : absolute activity
λ_0 : wave length of incident light
μ : permeability
μ : Lamè constant

μ : moment for molecular weight distribution
μ_i : chemical potential of *i* th component
μ_i': chemical potential of *i* th component in vapor phase
μ^0 : chemical potential before mixing
$\mu_0{}^0$: chemical potential of solvent
μ_{ij} : differential of chemical potential with respect to mole fractions of *i* th component and *j* th component
Π: osmotic pressure
ρ: density
ρ_s: weight fraction of polymer partitioned in dilute phase
ρ_p : weight fraction of polymer partitioned in concentrated phase
σ : partition coefficient
σ: stress
σ: steric hindrance factor
σ: standard deviation
τ: turbidity
τ:delay time
Φ: Flory-Fox viscosity coefficient
ϕ_0:volume fraction of solvent
ϕ_1:volume fraction of solute
ϕ_n: volume fraction of polymer with the degree of polymerization n
χ: thermodynamic interaction parameter
Ψ : penetrating function
ψ: entropy parameter
ψ_0: Flory entropy parameter at infinite dilution
Ω: partition function for microcanonical ensemble
ω: vibration number
ω: angular velocity of molecular chain

Contents

Contents