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Collapse in two good solvents, swelling in two poor solvents: defying the laws of polymer solubility?

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Collapse in two good solvents, swelling in two poor solvents: defying the laws of polymer solubility?

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Abstract

In this work we discuss two mirror but distinct phenomena of polymer paradoxical properties in mixed solvents: co-non-solvency and co-solvency. When a polymer collapses in a mixture of two miscible good solvents the phenomenon is known as co-non-solvency, while co-solvency is a phenomenon that is associated with the swelling of a polymer in poor solvent mixtures. A typical example of co-non-solvency is provided by poly(N-isopropylacrylamide) in aqueous alcohol, while poly(methyl methacrylate) in aqueous alcohol shows co-solvency. We discuss these two phenomena to compare their microscopic origins and show that both can be understood within generic universal concepts. A broad range of polymers is therefore expected to exhibit these phenomena where specific chemical details play a lesser role than the appropriate combination of interactions between the trio of molecular components.

Keywords: coil-globule transition, mixed solvents, smart responsive polymers

(Some figures may appear in colour only in the online journal)

1. Introduction

Smart responsive polymers are becoming increasingly important as high-performance multifunctional soft materials [1–4]. A polymer is considered to be smart responsive when a small change in external stimuli can drastically alter its structure, function and stability [5–17]. Because of this fast responsiveness to external stimuli, these systems serve as suitable candidates to tune polymer properties for desired applications [1, 2]. In this context, polymer conformations in solutions are often characterized by their solvent qualities. Starting from a good solvent chain, where single chain static structure factor $S(q)$ follows the scaling law $q^{-5/3}$, increased attraction between monomers first brings a chain in a $\Theta-$configuration with $S(q) \sim q^{-2}$ and further increase of monomer-monomer attraction collapses a chain where the collapsed globule follows a scaling law $S(q) \sim q^{-4}$ [18, 19]. Here the monomer excluded volume $\mathcal{V} = 2\pi \int \left[1 - e^{-v(r)/k_B T} \right] r^2 dr$, with $v(r)$ being the interaction potential between monomers and $k_B T$ is

the thermal energy, follows: $\mathcal{V} > 0$ for good solvent, $\mathcal{V} = 0$ for $\Theta-$solvent and for poor solvent $\mathcal{V} < 0$. Furthermore, the $\Theta-$point is a critical point that is dictated by large diverging fluctuations. When a polymer goes from coil-to-globule transition via standard $\Theta-$collapse, it is a second order phase transition [18, 19]. Moreover, in some cases, the coil-to-globule transition is coupled with strong hysteresis between the heating and the cooling cycles [20–22], indicating a first order phase transition where the conformational behavior is given by the two state process [23].

In a broad sense, polymers are usually generalized into two distinct categories, i.e. the upper critical solution temperature (UCST) behavior and the lower critical solution temperature (LCST) behavior, as shown in figure 1. When a polymer goes from a globule-to-coil transition upon heating, with a transition temperature T_u, it is known as UCST and is an energy driven process. On the other hand when a polymer collapses upon heating it is known as a LCST transition. During LCST, when $T > T_\ell$, solvent-monomer interaction breaks down

as a result the expelled solvent molecules gain translational entropy that is larger than the conformational entropy loss upon collapse, making LCST an entropy driven process. T_u or T_ℓ can be tuned for instance by introducing hydrophobic or hydrophilic comonomer units along a polymer backbone [24–28]. While the behavior of these polymers in single component solvents is interesting, they often exhibit unexpected and puzzling behavior when they are dissolved in a mixture of two solvents. For example, when cosolvent molecules are added to the polymer-solvent mixtures, the transition points can again be tuned with changing the compositions of cosolvents in the solution [5, 6]. Two of the most intriguing phenomena of polymer solvency are co-non-solvency [2, 5–17] and co-solvency [29–34]. A generic schematic representation of both these phenomena is shown in figure 2, where the representative change in polymer gyration radius with cosolvent molar ratio is illustrated.

In this short comparative review, we discuss generic concepts of these two phenomena and also compare their distinct molecular origins. The remainder of the paper is organized as follows: in section 2 we revisit the discussion related to the phenomenon of co-non-solvency, in section 3 we discuss co-solvency and finally we draw a comparative summary in section 4.

2. Co-non-solvency revisited

Co-non-solvency is the generic designation of polymer collapse in a mixture of two well miscible and individually good solvents. For example, when a polymer is well soluble in a solvent and a small amount of cosolvent is added in the same binary solution, the polymer undergoes a coil-globule transition. While the recent literature generally associates co-non-solvency with the LCST polymers [5–15, 17], the term co-non-solvency was first coined for a UCST system of polystyrene solvation in a mixture of cyclohexane and *N*,*N*-dimethylformamide (DMF) [35]. There are a wide range of polymers, both LCST and UCST, that show the phenomenon of co-non-solvency when they are disolved in appropriate mixtures of solvent and cosolvent. In particular, the addition of cosolvents into a LCST system reduces T_ℓ and, therefore, causes the collapse of a polymer [5, 6]. On the other hand, addition of cosolvents into a polymer solution of UCST nature, increases its T_u [35]. A list of polymers showing co-non-solvency is presented in table 1. It can be seen from the table that there is a broad range of polymers showing co-non-solvency. An interesting observation can be made when looking into the change in the window of collapse $\triangle x_c$ with change in solvent-cosolvent mixtures. In order to highlight the large number of polymer-solvent-cosolvent combinations displaying co-non-solvency, and to present a unified picture of $\triangle x_c$ for three different polymers with changing temperatures and aqueous cosolvent mixtures we have shown figure 3. Note that here we only concentrate on the aqueous solutions.

Interestingly, the standard solvent-cosolvent mixtures that are suitable to observe co-non-solvency are aqueous alcohol mixtures. For example, a closer look into the behavior of
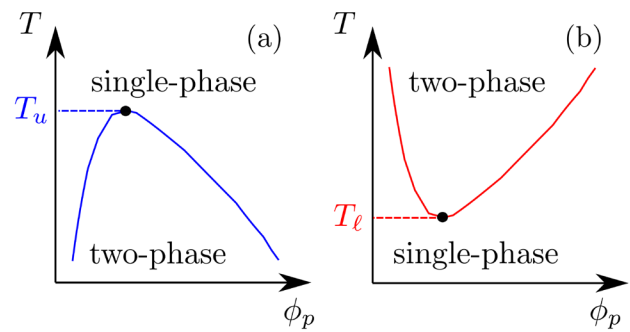

Figure 1. Schematic representation of polymer phase diagram of polymer solution for system exhibiting upper critical solution temperature (UCST) part (a) and lower critical solution temperature (LCST) part (b). Here ϕ_p is the polymer volume fraction, T_u is the UCST and T_ℓ is the LCST.

PNIPAm [5–7, 10, 11] and PAPOMe [37] in aqueous alcohol mixtures shows that $\triangle x_c$ decreases with increasing size of the alcohol, see figure 4. Note that $T_\ell \simeq 32\,°C$ for PNIPAm [20] and $T_\ell \simeq 14\,°C$ for PAPOMe [37] in pure water. In figure 4 data for three different alcohols and for available temperatures T is shown. It can be appreciated from figure 4 that change in $\triangle x_c$ is maximum with increasing alcohol size when T is closest to T_ℓ (see black ∘ curve in figure 4). The larger the difference $T_\ell - T$ the smaller the change in this effect, see green ⋄ curve in figure 4. This observation is not surprising given that for larger alcohols the phenomenon of co-non-solvency should disappear because of the strong hydrophobic-hydrophobic attractions.

The microscopic origin of the puzzling phenomenon of co-non-solvency is a matter of intense debate in the current literature, where a number of explanations have been provided based on the Flory–Huggins (FH) type mean field theory [5], cooperativity effect [9], preferential polymer-cosolvent interaction [2, 12, 13, 17], and solvent-cosolvent interaction parameter [43]. In our earlier works, combining a multi-scale model, a generic model, experiments and analytical theory [2, 13, 44], we have presented a possible mechanism of co-non-solvency that is based on preferential binding of methanol with PNIPAm and have shown that this concept can be applied to describe a broad range of polymers within a unified generic concept [2, 13]. It was discussed that when a small amount of better cosolvent, methanol in the case of aqueous PNIPAm solution, is added to the polymer-solvent solution, preferential binding of cosolvent drives these molecules towards the polymer. Since the amount of cosolvent is rather small, they try to bind to more than one monomer at a time to reduce the binding free energy, thus initiating the collapse process. On the other hand, when a large amount of cosolvent molecules is added, the system can overcome translational solvent entropy and opens up by the complete decoration of the polymer with cosolvent. Note that this preferentiability is about $4k_BT$ per monomer to observe co-non-solvency and below this contrast co-non-solvency usually disappears [45]. We also would like to highlight that this phenomenon is not strictly dependent on the sensitivity of the polymer to temperature in each of the solvents and that specific chemical details do not play any role in describing the phenomenon.
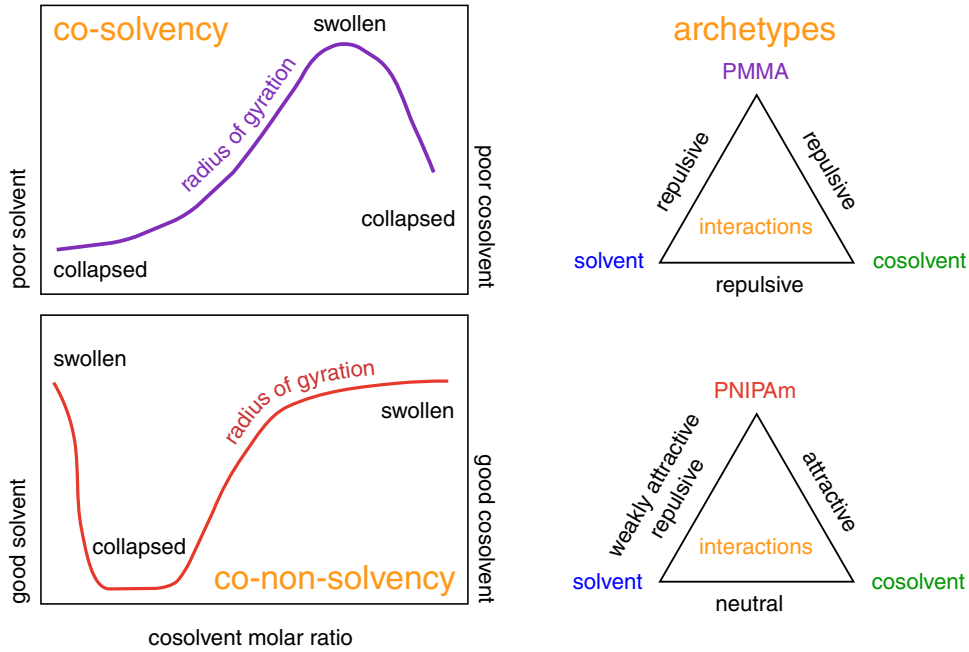
Figure 2. Schematic representation of co-solvency (top panel) and co-non-solvency (bottom panel) for a polymer chain. We also show schematic of the underlying interaction details. Note that neutral interaction between solvent and cosolvent means that neither has a clear preference, i.e. the solvents are very well miscible.

Table 1. A table listing various polymer systems that show co-non-solvency effect when solvated in their respective mixture of solvents.

Polymer (p)	Solvent (s)	Cosolvent (c)
Poly(N-isopropylacrylamide) (PNIPAm) [5–8, 10, 11, 36]	Water	Methanol (MeOH), ethanol(EtOH), iso-propanol (iPrOH), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), 1,4-dioxane, or acetone (Ac)
Poly(acryloyl-L-proline methyl ester) (PAPOMe) [37]	Water	MeOH, EtOH, or iPrOH
Poly(ethylene oxide) (PEO) [38]	Water	N,N-dimethylformamide (DMF)
Polystyrene [35]	Cyclohexane	DMF
Poly(vinyl alcohol) [39]	Water	Dimethyl sulfoxide
Poly(2-(methacryloyloxy)ethylphosphorylcholine) (PMPC) [40, 41]	Water	MeOH, EtOH, or iPrOH
Poly(N,N-diethylacrylamide) (PDEA) [42]	Water	EtOH

Because the cosolvent driven coil-to-globule transition is dictated by preferential binding, the standard FH type mean-field theory may not be suitable to explain the phenomenon [46, 47]. For example, when adding a polymer of length N_l at fraction ϕ_p in a mixture of solvent s and cosolvent c, respectively, the FH free energy $\mathcal{F}_{\mathrm{FH}}$ can be written as [18, 19],

$$\frac{\mathcal{F}_{\mathrm{FH}}}{\kappa_{\mathrm{B}} T} = \frac{\phi_p}{N_l} \ln \phi_p + x_c (1-\phi_p) \ln \left[x_c (1-\phi_p) \right]$$
$$+ (1-x_c)(1-\phi_p) \ln \left[(1-x_c)(1-\phi_p) \right]$$
$$+ \chi_{ps} \phi_p (1-x_c)(1-\phi_p)$$
$$+ \chi_{pc} \phi_p x_c (1-\phi_p)$$
$$+ \chi_{sc} x_c (1-x_c)(1-\phi_p)^2. \qquad (1)$$

Here, the first three terms represent the entropy of mixing and the last three terms deal with interactions between different solvent components. The monomer excluded volume $\mathcal{V}$ can be directly calculated from the second order expansion of equation (1) that gives,

$$\mathcal{V} = 1 - 2(1-x_c)\chi_{ps} - 2x_c \chi_{pc} + 2x_c(1-x_c)\chi_{sc}, \qquad (2)$$

where χ_{ps} and χ_{pc} are FH interaction parameters between $p-s$ and $p-c$, respectively. The factor χ_{sc} is the parameter that deals with solvent-cosolvent interaction. Here the first two terms of equation (2) only give a linear variation of $\mathcal{V}$ with x_c (i.e. placing $\chi = 0$ in equation (2)). When $\chi < 0$, $\mathcal{V}$ becomes negative and thus opens the possibility of the coil-to-globule-to-coil conformational transition. However, it has been earlier recognized that in common solvent mixtures where co-non-solvency is observed, χ remains positive and close to zero [5]. Therefore, a particle based theory related to adsorption competitive displacement was devised to explain the phenomenon [2, 46].

While detailed theoretical analysis was presented in our earlier works [2, 46], we only sketch some key ingredients here. For this purpose, we consider a polymer to be an adsorbing substrate where the solvent and the cosolvent molecules compete for adsorption. Additionally, because of the
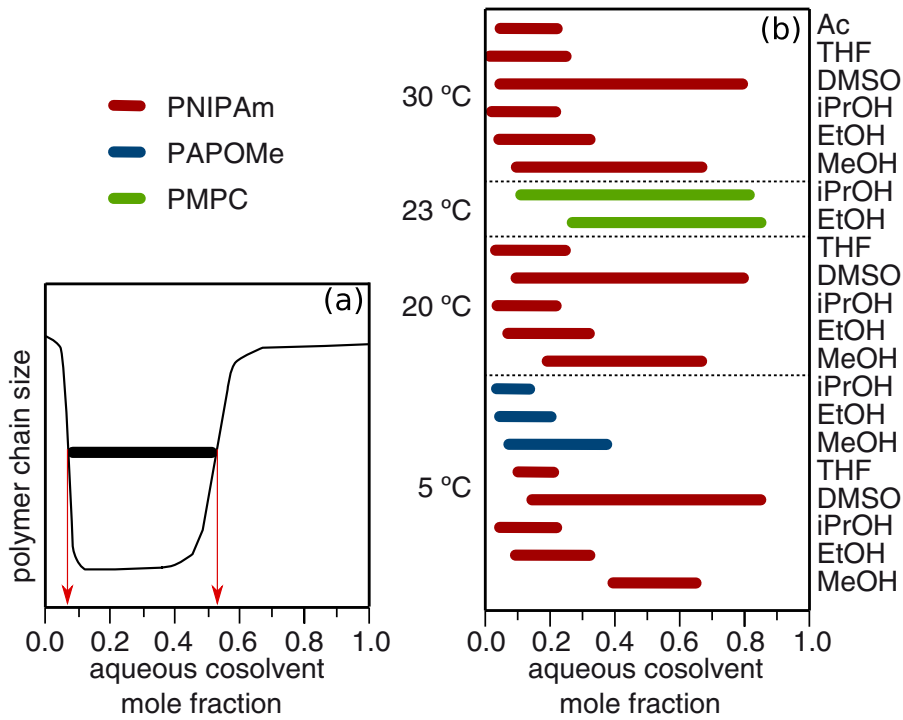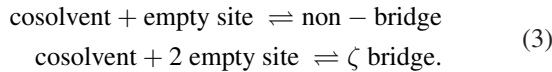
Figure 3. Part (a) shows the scheme to calculate the window of co-non-solvency collapse $\triangle x_c$ and part (b) presents a unified plot showing the window of collapse (represented by horizontal bars) in the units of cosolvent mole fraction for three different polymers with changing temperatures and for different aqueous cosolvent mixtures. $\triangle x_c$ data is extracted from the experimental literature in [5–8, 10, 11, 36, 37, 40, 41].

molecular flexibility of a polymer chain, polymer segments may form short segmental loops. Polymer collapse under co-non-solvency is thus explained by the preferential attraction of cosolvent molecules to the monomers, forming cosolvent bridges between two monomers [2]. This picture can be treated equivalently as two pseudo chemical reactions,

$$\text{cosolvent} + \text{empty site} \rightleftharpoons \text{non} - \text{bridge}$$
$$\text{cosolvent} + 2 \text{ empty site} \rightleftharpoons \zeta \text{ bridge.}$$
(3)

Consider a polymer as a substrate with $\mathcal{N}$ sites exposed to the bulk solution, with $\mathcal{N}^s$, $\mathcal{N}^c$, and $2\mathcal{N}_B^c$ sites occupied by solvents, cosolvents and bridging cosolvents, respectively. This makes $\mathcal{N} = \mathcal{N}^s + \mathcal{N}^c + 2\mathcal{N}_B^c$. Therefore, $\phi = \mathcal{N}^c/\mathcal{N}$ represents the fraction of cosolvents that are attached to a single monomer and $\phi_B = \mathcal{N}_B^c/\mathcal{N}$ is the fraction of cosolvent bridges. This picture based on competitive adsorption can equivalently be written in terms of free energy density of adsorption for non-bridges and bridges,

$$\frac{\Psi}{\kappa_B T} = \phi \ln(\phi) + \zeta \phi_B \ln(2\phi_B)$$
$$+ (1 - \phi - 2\phi_B) \ln(1 - \phi - 2\phi_B)$$
$$- \mathcal{E}\phi - \mathcal{E}_B \phi_B - \frac{\mu}{\kappa_B T}(\phi + \phi_B),$$
(4)

with $\mu = \kappa_B T \ln(x_c)$ being the chemical potential of the bulk cosolvent in the bulk solvent mixture and $\mathcal{E}$ measures single site cosolvent adsorption energy and $\mathcal{E}_B$ gives bridging cosolvents energy. The first three terms represent translational entropic contributions, the factor 2 in the mixing entropy accounts for the fact that a bridge occupies two sites on the polymer backbone. The unusual pre-factor
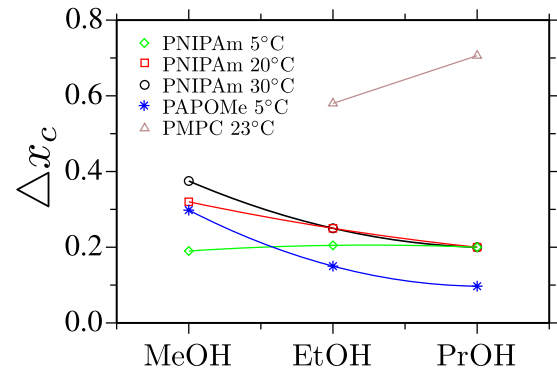

Figure 4. Window of co-non-solvency collapse $\triangle x_c$ for different aqueous alcohol mixtures. Here MeOH, EtOH, and iPrOH stands for aqueous methanol, ethanol and propanol solutions, respectively. $\triangle x_c$ data is extracted from the experimental literature in [5–8, 10, 11, 36, 37, 40, 41].

$\zeta = 2 - m$ and the critical exponent m can be estimated within a simple scaling argument. For example, if we consider a partition function of vanishing end-to-end distance $R_e \to 0$ [19],

$$Z_{N_l}(R_e \to 0) \propto q^{N_l} N_l^{\alpha - 2},$$
(5)

and the partition function at finite R_e is given by,

$$Z_{N_l}(R_e) \propto q^{N_l} N_l^{\gamma - 1}.$$
(6)

Here $1/q$ is the critical fugacity and the universal exponents $\alpha \cong 0.2$ and $\gamma \cong 1.15$ [19]. From these two cases one can estimate the free energy barrier to form a loop of length ℓ as $\triangle \mathcal{F}(\ell) = m \kappa_B T \ln(\ell)$, with $m = \gamma - \alpha + 1 \cong 1.95$.
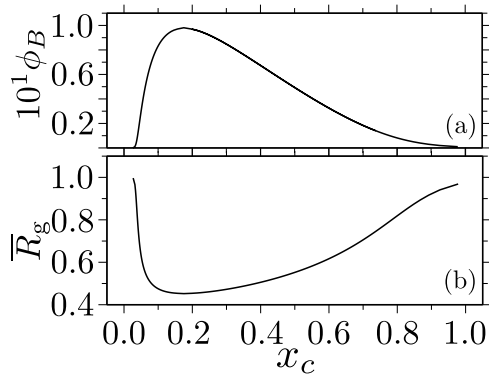
Figure 5. Part (a) shows a solution of equation (7) for fraction of briding cosolvents ϕ_B and part (b) represents the corresponding normalized gyration radius $\overline{R}_g = R_g(x_c)/R_g(x_c = 0)$ as a function of cosolvent mole fraction x_c. The data for these curves is extracted from [46].

Minimization of equation (4) with respect to ϕ_B and ϕ leads to the implicit equation for the bridge density $\phi_B(x_c)$,

$$16\phi_B{}^\zeta x_c = x_c^* \left\{ \left(\frac{x_c^*}{x_c^{**}} \right)^{1/2} (1 - 2\phi_B) \right.$$
$$\left. \pm \sqrt{\left(\frac{x_c^*}{x_c^{**}} \right) (1 - 2\phi_B)^2 - 16\phi_B{}^\zeta} \right\}^2 \quad (7)$$

with $x_c^* = \exp(-\mathcal{E})$ and $x_c^{**} = \exp(-\mathcal{E}_B + 2\ln 2e - \zeta)$. This expression explains well the variation of ϕ_B within the collapsed region of a polymer under co-non-solvency [46], see figure 5(a). As shown in figure 5(b) ϕ_B can be translated into polymer R_g using [46]

$$\left[\frac{R_g}{R_g(x_c = 0)} \right]^{-3} - 1 = \mathcal{V}. \quad (8)$$

The magnitude of the negative excluded volume $-|\mathcal{V}|$ can then be estimated from ϕ_B by using the relation $\mathcal{V} \simeq N_l \phi_B(x_c)$. Including ϕ_B from equations (7) in (8), describes well the variation of R_g with x_c. Note that the theory presented in equation (4) deals with only single chain. Furthermore, this theory can be extended to concentrated polymer system, where bridging scenario should be considered not only within the chain, rather also between different chains in the solution. For example, when the polymer concentration is high, the system can be classified as consisting of two domains: (1) the polymer rich domain with encapsulated cosolvents forming bridges between monomer of different chains and (2) polymer poor phase with solvent molecules. Here a closer inspection of the polymer rich phase reveals that it behaves as a good solvent chunk of cosolvent rich system, where single chain structure factor within this chunk can be well described by $S(q) \sim q^{-5/3}$. Along this line an extension of our theory was proposed, which can describe co-non-solvency of polymer brushes [48].

Another key observation is that the polymer collapses when the solvent quality remains good or even gets increasingly better by the addition of the better cosolvent. This puzzling phenomenon, where the solvent quality is completely decoupled from the polymer conformation, is driven by (co) solvent-monomer attraction making the mean field description unsuitable to describe this behavior. Furthermore, because a polymer collapses in good solvent, the depletion (or repulsive) forces, that are responsible for standard poor solvent collapse, do not play any role in describing co-non-solvency. Conversely, depletion forces do play a significant role when a polymer swells in a mixture of two competing poor solvents, also known as co-solvency, which is described in the next section.

3. Co-solvency revisited

Co-solvency is a mirror effect to that of co-non-solvency that occurs when two poor solvents for a polymer are mixed together, such that the polymer swells within the intermediate mixing ratios of the two solvents [29–34]. Typical examples include PMMA in aqueous alcohol mixtures. While pure water and pure alcohol are individually poor solvents for PMMA, when PMMA is dissolved in a mixture of water and alcohol it shows improved solubility. Traditionally PMMA is a standard system that was associated with the phenomenon of co-solvency, recent experiments also showed that systems such as corn starch [33] and poly(*N*-(6-acetamidopyridin-2-yl)acrylamide) [34] have similar swelling within intermediate mixing ratios of aqueous alcohol, see table 2. Moreover, it is also important to notice that—while co-solvency is predominantly observed in water-alcohol mixtures, other solvent mixtures also show similar phenomenon [49]. Furthermore, unlike co-non-solvency where the phenomenon becomes weaker with increasing alcohol sizes, co-solvency becomes stronger with increasing size of alcohol, i.e. swelling ratio in aqueous propanol > aqueous ethanol > aqueous methanol [30–32]. This poses two important questions: (1) why does a polymer swell at all in poor solvent mixtures and (2) what is so special about aqueous alcohol mixtures.

In this context, it is known that a polymer collapses in a solution when the solvent-monomer repulsion is larger than the monomer-monomer repulsion, thus induces an effective attraction between monomers reducing $\mathcal{V}$, also known as depletion induced attraction known from colloidal science [50]. Therefore, the effect is dictated by the number density of depletants, in this case solvent particles consisting of water and alcohol, within the solvation volume [51]. This argument holds in pure water and in pure alcohol. However, when a polymer swells up within the intermediate mixing ratios of water and alcohol, the number of depletants is reduced. This can be seen by looking into the total number density ρ_{total} of bulk solution as a function of mixing ratios of two solvents [51]. In figure 6 it can be be seen for aqueous alcohol mixtures ρ_{total} reduces from its mean-field value (linear extrapolation between pure solvent $x_c = 0.0$ and pure cosolvent $x_c = 1.0$) with a maximum deviation observed for the 50–50 mixing ratio [52]. The larger the alcohol the larger the deviation from the mean-field value. This deviation is a key factor that reduces the number of depletants within the solvation volume and thus reduces the depletion attractive forces, reducing the magnitude of the negative excluded volume $\mathcal{V}$. Therefore, the

Table 2. A table listing various polymer systems that show co-solvency effect when solvated in their respective mixture of solvents.

Polymer (*p*)	Solvent (*s*)	Cosolvent (*c*)
Poly(methyl methacrylate) (PMMA) [30–32]	Water	MeOH, EtOH, or iPrOH
Corn starch [33]	Water	MeOH, EtOH, or iPrOH
Poly(*N*-(6-acetamidopyridin-2-yl)acrylamide) [34]	Water	MeOH, EtOH, or iPrOH
PMMA [49]	2-Butanol	1-chlorobutane

Table 3. A table listing similarities and differences between co-non-solvency and co-solvency phenomena observed in binary aqueous solutions.

| Co-non-solvency	Co-solvency
Polymer collapse in miscible good solvents	Polymer swelling in miscible poor solvents
Dictated by preferential attractive binding	Dictated by depletion (repulsive) effects
Bulk solution property plays negligible effect	Bulk solution density drives the transition and the phenomenon emerges at constant pressure only
Mean field theory does not describe the effect	Can be explained within the FH mean field picture
Interstitial sticky contacts mediated by cosolvents	Dictated by 2nd order depletion effects
A broad range of systems show this phenomenon	Predominantly observed in aqueous alcohol solution
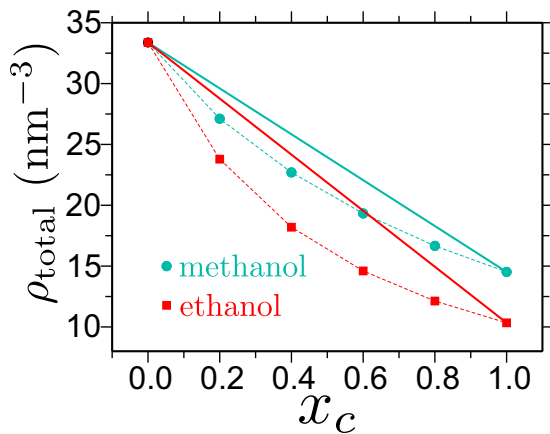
Figure 6. Total number density ρ_{total} of the bulk solution as a function of cosolvent mole fraction x_c for aqueous methanol and aqueous ethanol solutions under ambient conditions. Solid lines are linear interpolation between the data points of $x_c = 0.0$ and $x_c = 1.0$.

polymer swelling in a mixture of two poor solvents can be viewed as a second order effect. For example, the solvent molecules deplete monomers giving rise to the poor solvent condition for a polymer. However, when cosolvent molecules are added into the system, cosolvents not only deplete monomers but also solvent molecules leading to a second order depletion effect.

Unlike co-non-solvency, the phenomenon of co-solvency can be explained within an FH mean-field picture. However, because the phenomenon naturally emerges at constant pressure, such that a density dip is observed in the bulk solution, it is necessary to devise a theory that can take account of the density dip. In a recent work [51], it was shown that the co-solvency can be explained within a unified picture combining the knowledge known from polymer physics [18, 19] and colloid science [50]. While a detailed theoretical analysis was presented in [51], here we only sketch a few key ingredients. We are studying single chain property, i.e. under infinite

dilution $\phi_p \to 0$, and the majority of the system volume is occupied by solvent-cosolvent mixture. Therefore, the system can be treated within a simplified limit of a binary mixture. Additionally, solvent-solvent and cosolvent-cosolvent interactions were considered to be identical, but that solvent-cosolvent interactions are distinct. The total free energy is the given as,

$$\frac{\mathcal{F}v}{\kappa_B T} = \frac{v\mathcal{F}_s(v)}{\kappa_B T} + x_c \ln(x_c) + (1 - x_c)\ln(1 - x_c) + \chi_{sc}(v)x_c(1 - x_c), \tag{9}$$

where $\mathcal{F}_s(v)$ is the volume-dependent free-energy of the pure solvent systems [51]. The Flory–Huggins interaction parameter between solvent and cosolvent χ_{sc} also depends on the system volume or solvent-cosolvent composition. For a given pressure P, the molar volume v is thus controlled by,

$$P = P_s(v) - \kappa_B T x_c(1 - x_c)\frac{\partial \chi_{sc}(v)}{\partial v} \tag{10}$$

with $P_s(v) = -\partial v \mathcal{F}_s / \partial v$ being the pressure of the reference system. For a small variation of the molar volume of the solvent-cosolvent mixture with respect to that of the reference system, one gets $v = v_o [1 + \zeta x_c(1 - x_c)]$ where

$$\zeta = \frac{\kappa_B T}{v}\frac{\partial \chi_{sc}(v)}{\partial v}\left[\frac{\partial P_s(v)}{\partial v}\right]^{-1} \tag{11}$$

measures the relative interaction parameter and the reference P for a given v. Furthermore, the change in χ_{sc} between constant density and constant pressure ensembles can be estimated from,

$$\chi_{sc}(v) = \chi_{sc}(v_o) + v\frac{\partial \chi_{sc}(v)}{\partial v}\bigg|_{x_c \to 0}\zeta x_c(1 - x_c). \tag{12}$$

For $x_c = 0.5$, the above equation will lead to a $\sim 11\%$ variation in χ_{sc} values with respect to the standard values calculated when ρ_{total} is kept constant [51]. Therefore, in this system the

χ_{sc} parameter relevant to the FH analysis keeps consistent values throughout the range of compositions.

4. Summary: co-non-solvency versus co-solvency

In this short article we have compared two puzzling phenomena of polymer properties in mixed good and mixed poor solvent mixtures, namely co-non-solvency and co-solvency. We discuss that each of these phenomena can be classified within unified generic concepts and therefore a broad range of systems exhibit these phenomena. To make a comprehensive comparison highlighting the differences between these two effects, we present in table 3 an overview of these systems.

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References

[1] Cohen-Stuart M A *et al* 2010 *Nat. Mater.* **9** 101
[2] Mukherji D, Marques C M and Kremer K 2014 *Nat. Commun.* **5** 4882
[3] Zhang Q and Hoogenboom R 2015 *Prog. Pol. Sci.* **48** 122
[4] de Beer S, Kutnyanszky E, Schön P M, Vancso G J and Müser M H 2014 *Nat. Commun.* **5** 3781
[5] Schild H G, Muthukumar M and Tirrell D A 1991 *Macromolecules* **24** 948
[6] Winnik F M, Ringsdorf H and Venzmer J 1990 *Macromolecules* **23** 2415
[7] Zhang G and Wu C 2001 *Phys. Rev. Lett.* **86** 822
[8] Costa R O R and Freitas R F S 2002 *Polymer* **43** 5879
[9] Tanaka F, Koga T and Winnik F M 2008 *Phys. Rev. Lett.* **101** 028302
[10] Kojima H, Tanaka F, Scherzinger C and Richtering W 2012 *J. Pol. Sci.* B **51** 1100
[11] Walter J, Sehrt J, Vrabec J and Hasse H 2012 *J. Phys. Chem.* B **116** 5251
[12] Heyda J, Muzdalo A and Dzubiella J 2013 *Macromolecules* **46** 1231
[13] Mukherji D and Kremer K 2013 *Macromolecules* **46** 9158
[14] Richter M, Hunnenmörder M and von Klitzing R 2014 *Colloid Polym. Sci.* **292** 2439
[15] Kyriakos K *et al* 2016 *Macromol. Rapid Commun.* **37** 420
[16] Kyriakos K, Philipp M, Silvi L, Lohstroh W, Petry W, Müller-Buschbaum P and Papadakis C M 2016 *J. Phys. Chem.* B **120** 4679
[17] Backes S, Krause P, Tabaka W, Witt M U, Mukherji D, Kremer K and von Klitzing R 2017 *ACS Macro Lett.* **6** 1042
[18] de Gennes P-G 1979 *Scaling Concepts in Polymer Physics* (London: Cornell University Press)
[19] Des Cloizeaux J and Jannink G 1990 *Polymers in Solution: their Modelling and Structure* (Oxford: Clarendon)
[20] Wang X, Qiu X and Wu C 1998 *Macromolecules* **31** 2972–6
[21] Ray B, Okamoto Y, Kamigaito M, Sawamoto M, Seno K, Kanaoka S and Aoshima S 2005 *Polym. J.* **37** 234–7
[22] Hirano T, Okumura Y, Kitajima H, Seno M and Sato T 2006 *J. Polym. Sci.* A **44** 4450–60
[23] Jeppesen C and Kremer K 1996 *Eur. Phys. Lett.* **34** 563
[24] Hoffman A S *et al* 2000 *J. Biomed. Mat. Res.* **52** 577
[25] Shen Z, Terao K, Maki Y, Dobashi T, Ma G and Yamamoto T 2006 *Colloid Polym. Sci.* **284** 1001
[26] Samanta S, Bogdanowicz D R, Lu H H and Koberstein J T 2016 *Macromolecules* **49** 1858
[27] de Oliveira T E, Mukherji D, Kremer K and Netz P A 2017 *J. Chem. Phys.* **146** 034904
[28] De Silva C C, Leophairatana P, Ohkuma T, Koberstein J T, Kremer K and Mukherji D 2017 *J. Chem. Phys.* **147** 064904
[29] Masegosa R M, Prolongo M G, Hernandez-Feures I and Horta A 1984 *Macromolecules* **17** 1181
[30] Hoogenboom R, Remzi Becer C, Guerrero-Sanchez C, Hoeppener S and Schubert U S 2010 *Aust. J. Chem.* **63** 1173
[31] Lee S M and Bae Y C 2014 *Polymer* **55** 4684
[32] Yu Y, Kieviet B D, Kutnyanszky E, Vancso G J and de Beer S 2015 *ACS Macro Lett.* **4** 75
[33] Galvez L O, de Beer S, van der Meer D and Pons A 2017 *Phys. Rev.* E **95** 030602
[34] Asadujjaman A, Ahmadi V, Yalcin M, ten Brummelhuis N and Bertin A 2017 *Pol. Chem.* **8** 3140
[35] Wolf B A and Willms M M 1978 *Makromol. Chem.* **179** 2265
[36] Yamauchi H and Maeda Y 2007 *J. Phys. Chem.* B **111** 12964
[37] Hiroki A, Maekawa Y, Yoshida M, Kubota K and Katakai R 2001 *Polymer* **42** 1863
[38] Lund R, Willner L, Stellbrink J, Radulescu A and Richter D 2004 *Macromolecules* **37** 9984
[39] Ohkura M, Kanaya T and Kaji K 1992 *Polymer* **33** 3686
[40] Kiritoshi Y and Ishihara K 2002 *J. Biomater. Sci. Polym. Ed.* **13** 213
[41] Kiritoshi Y and Ishihara K 2003 *Sci. Technol. Adv. Mater.* **4** 93
[42] Jia D, Zuo T, Rogers S, Cheng H, Hammouda B and Han C C 2016 *Macromolecules* **49** 5152
[43] Dudowicz J, Freed K F and Douglas J F 2015 *J. Chem. Phys.* **143** 131101
[44] Mukherji D, Wagner M, Watson M D, Winzen S, de Oliveira T, Marques C M and Kremer K 2016 *Soft Matter* **12** 7995
[45] de Oliveira T E, Netz P A, Mukherji D and Kremer K 2015 *Soft Matter* **11** 8599
[46] Mukherji D, Marques C M, Stuehn T and Kremer K 2015 *J. Chem. Phys.* **142** 114903
[47] Mukherji D and Kremer K 2017 *Pol. Sci. Ser.* C **59** 119
[48] Sommer J-U 2017 *Macromolecules* **50** 2219
[49] Wolf B A and Blaum G J 1975 *J. Polym. Sci. Polym. Phys. Ed.* **13** 1115
[50] Lekkerkerker H N W and Tuinier R 1990 *Colloids and the Depletion Interaction* (Oxford: Clarendon)
[51] Mukherji D, Marques C M, Stuehn T and Kremer K 2017 *Nat. Commun.* **8** 1374
[52] Perera A, Sokolic F, Almasy L and Koga Y 2006 *J. Chem. Phys.* **124** 124515