Supporting Information
Equilibrium swelling of thermo-responsive gels in mixtures of solvents

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S-1 Preparation procedures and experimental conditions for PNIPAAm gels

Figure 1

Fluorescently labeled PNIPAAm gel was synthesized [1] by free-radical cross-linking polymerization (several days at room temperature) of a solution of NIPAAm monomers (0.7 M) in water/DMF mixture (3:2 v/v) by using N, N'-methylenebisacrylamide (BIS, 8.6 mM) as a cross-linker, ammonium persulfate (APS, 0.88 mM) as an initiator, N, N, N', N'-tetramethylenethylenediamine (TEMED, 2.7 mM) as an accelerator, and Dansyl ethylacrylamide (DaEAM, 4 mM) as fluorescent labels.

Equilibrium swelling tests were conducted at temperature $T = 20$ °C in water/methanol mixtures on disk-shaped specimens with the initial diameter $d_* = 8$ mm. The duration of each test was 2 weeks. The diameter d of a sample in the equilibrium state was measured by the vernier micrometer. The equilibrium degree of swelling Q is determined from the equation

$$\frac{1+Q}{1+Q_*} = \Big(\frac{d}{d_*}\Big)^3, \tag{S-1}$$

where $Q_* = 12.6$ stands for the degree of swelling of the as-prepared gel.

Figure 2

PNIPAAm gel was prepared [2] by free-radical cross-linking polymerization (20 h at temperature 4 °C) of an aqueous solution of NIPAAm monomers (0.66 M) by using BIS (1.33 g/L) as a cross-linker, APS as an initiator and TEMED as an accelerator (concentrations were not provided).

Equilibrium swelling tests in water/methanol mixtures were conducted at temperatures $T = 14.4$, 26.1 and 35.3 °C on dried cylindrical samples. The duration of tests was not provided. The equilibrium degree of swelling Q was determined from Eq. (S-1) with $Q_* = 12.3$.

Figure 3A

PNIPAAm gel was synthesized [3] by free-radical cross-linking polymerization (24 h at temperature 5 °C) of an aqueous solution on NIPAAm monomers (693 mM) by using BIS (7 mM) as a cross-linker, APS (400 mg/L) as an initiator, and TEMED (2.4 mL/L) as an accelerator.

Equilibrium swelling tests in water were conducted in the interval of temperatures between 10 and 50 °C on cylindrical specimens with diameter $d_* = 0.141$ mm. The diameter d of a

sample in the equilibrium state was measured under the microscope. The equilibrium degree of swelling Q is determined from Eq. (S-1) with $Q_* = 12.6$.

Figures 3B and 4

PNIPAAm microgel was prepared [4] by emulsion polymerization (6 h at temperature 70 °C) of an aqueous solution of NIPAAm monomers (140 mM) by using BIS (1.94 mM) as a cross-linker, sodium dodecyl sulfate (SDS, concentration 0.3 g/L) as a surfactant, and potassium persulfate (KPS, 0.6 g/L) as an initiator. After cooling to room temperature, microgel particles were purified.

Experiments were conducted in pure water in the interval of temperatures between 10 and 40 °C and in water/methanol and water/ethanol mixtures at temperature $T = 12.5$ °C. The hydrodynamic radius of microgel particles R_h was measured by the dynamic light scattering (DLS) method. The equilibrium degree of swelling $Q(T)$ at temperature T in pure water was determined from the equation

$$\frac{1+Q(T)}{1+Q(T_*)} = \Big(\frac{R_\mathrm{h}(T)}{R_\mathrm{h}(T_*)}\Big)^3, \tag{S-2}$$

where T_* is the maximum temperature in the tests (that exceeds strongly T_c) and $Q(T_*) = \frac{1}{2}$. The equilibrium degree of swelling in water/alcohol mixtures was calculated from Eq. (S-2), where T_* is replaced with ϕ_c.

Figures 3C and 5

PNIPAAm microgels were prepared [5] by free-radical cross-linking polymerization (6 h at 70 °C under stirring with the speed 300 rpm) of an aqueous solution of NIPAAm monomers (15 g/L) by using BIS (molar ratio with respect to monomers 0.034) as a cross-linker, SDS (0.16 g/L) as a surfactant, and KPS (concentration was not provided) as initiator.

The hydrodynamic radius R_h of microgel particles was measured by the DLS method. Experiments were performed in pure water in the interval of temperatures between 0 and 60 °C and in water/DMF mixtures at temperatures $T = 5$, 20 and 40 °C. The equilibrium degree of swelling Q is calculated from Eq. (S-2).

Figure 6

PNIPAAm gel was synthesized [6] by free-radical cross-linking polymerization (24 h at room temperature) of an aqueous solution of NIPAAm monomers (mass fraction 0.08) by using BIS (molar ratio with respect to monomers 0.02) as a cross-linker, APS as an initiator and sodium disulfite as an accelerator (total mass ratio with respect to monomers $4.2 \cdot 10^{-4}$).

Swelling tests in water/methanol mixtures were conducted at temperatures $T = -5$, 25 and 40 °C on dried samples. The duration of each test was 2 weeks. Masses of specimens were measured with a precision microbalance. The equilibrium degree of swelling Q was determined by the formula

$$Q = \frac{m_\mathrm{s} - m_\mathrm{d}}{m_\mathrm{d}}, \tag{S-3}$$

where m_d and m_s are masses of dry and swollen samples.

Figure 7

PNIPAAm gel [7] was prepared by free-radical cross-linking polymerization (several hours at room temperature) of an aqueous solution of NIPAAm monomers (1 M) by using BIS (0.02 M) as a cross-linker, APS as an initiator and TEMED as an accelerator (concentrations were not provided).

Equilibrium swelling tests were conducted in water/dioxane mixtures on dry samples (mass 0.2 g) at temperatures $T = 22$ and 34 °C. The duration of each test was 2 days. Masses of specimens are measured by the gravimetric method. The equilibrium degree of swelling Q is calculated from Eq. (S-3).

Figure 8A

PNIPAAm gel was synthesized [8] by free-radical cross-linking polymerization (1 day at 70 °C) of a solution of NIPAAm monomers (1 g/mL) in 1,4-dioxane by using ethylene glycol dimethacrylate (EGDMA, 1 mol.% with respect to monomers) as a cross-linker and 2,2′-azobis(isobutyronitrile) (AIBN, $4.12 \cdot 10^{-4}$ mol/L) as an initiator. Before tests, disk-shaped samples (with masses of 30 mg) were soaked in ethyl acetate, methanol and deionized water and, finally, dried.

Equilibrium swelling tests were conducted in water/dioxane mixtures at temperature $T = 25$ °C. The duration of each test was 1 week. Masses of specimens are measured by the gravimetric

method. The equilibrium degree of swelling Q was determined by Eq. (S-3).

Figures 8B and 8C

PNIPAAm gels were prepared [9, 10] by free-radical cross-linking polymerization (1 day at 0 °C) of an aqueous solution of NIPAAm monomers (0.6 M) by using BIS (6.0 mM) as a cross-linker, APS (3.2 mM) as an initiator and TEMED (0.8 mM) as an accelerator.

Equilibrium swelling tests were conducted at temperature $T = 25$ °C in water/DMSO mixtures [9] and aqueous solutions of poly(ethylene glycol) chains with mass-average molecular weight $M_{\mathrm{w}} = 200$ g/mol (PEG-200) [10]. Experiments were performed on cylindrical samples with length 5 mm and diamater $d_* = 0.85$ mm. The diameter d of each specimen the swollen state was measured under a calibrated microscope. The duration of each test was 2 h for water/DMSO mixtures and 3 days for aqueous solutions of PEG-200. The equilibrium degree of swelling Q is determined from Eq. (S-1) with $Q_* = 14.72$.

References

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S-2 Supplementary tables

Table S1: Material parameters for PNIPAAm gel in water/methanol mixture at temperature $T = 20$ °C (Fig. 1).

$\chi_0^{(1)}$	$\chi_1^{(1)}$	$\chi_0^{(2)}$	$\chi_1^{(2)}$	g_1	Q_0
−0.1356	2.7716	0.0081	1.1832	0.006	12.0

Table S2: Material parameters for PNIPAAm gel in water/methanol mixture at various temperatures T (Fig. 2).

T °C	$\chi_0^{(1)}$	$\chi_1^{(1)}$	$\chi_0^{(2)}$	$\chi_1^{(2)}$	$\chi_{\max}^{(1)}$	$\chi_{\max}^{(2)}$	g_1	Q_0	$\bar{g}_2$	$\beta^{(1)}$	$\beta^{(2)}$
14.4	−0.3548	3.4366	0.3788	0.6234			0.018	12.0			
26.1	0.3782	0.6969	0.3439	0.7466	0.48	0.74	0.018	12.0	3.2	2.0	0.3
35.3			0.3258	0.8026		0.74	0.018	12.0	3.2		0.3

Table S3: Material parameters for PNIPAAm gels and microgels in water (Fig. 3).

Fig.	χ_{T0}	χ_{T1}	$\chi_{\max}$	g_1	Q_0	$\bar{g}_2$	β	T_{c} °C
3A	−2.0980	0.7908	0.53	0.040	7.2	1.4	3.0	33.2
3B	−2.0980	0.7908	0.39	0.090	1.7	2.0	3.0	31.4
3C	−2.0980	0.7908	0.42	0.007	0.2	1.0	3.0	31.8

Table S4: Material parameters for PNIPAAm microgel in water/methanol and water/ethanol mixtures at temperature $T = 12.5$ °C (Fig. 4).

Cosolvent	$\chi_0^{(1)}$	$\chi_1^{(1)}$	$\chi_0^{(2)}$	$\chi_1^{(2)}$	g_1	Q_0
Methanol	−1.3536	6.0287	−0.4189	2.0784	0.09	1.7
Ethanol	−1.3895	7.4900	−0.4659	2.3093	0.09	1.7

Table S5: Material parameters for PNIPAAm microgel in water/DMF mixture at various temperatures T (Fig. 5).

Fig.	T °C	$\chi_0^{(1)}$	$\chi_1^{(1)}$	$\chi_0^{(2)}$	$\chi_1^{(2)}$	$\chi_{\max}^{(2)}$	g_1	Q_0	$\bar{g}_2$	$\beta^{(2)}$
5A	5	−2.4749	4.7421	−0.4133	2.8981		0.009	0.1		
5B	20	−0.7725	2.2825	−0.1112	1.8771		0.009	0.1		
5C	40			0.0255	1.5632	0.70	0.009	0.1	1.0	0.8

Table S6: Material parameters for PNIPAAm gel in water/methanol mixture at various temperatures T (Fig. 6).

Fig.	T °C	$\chi_0^{(1)}$	$\chi_1^{(1)}$	$\chi_0^{(2)}$	$\chi_1^{(2)}$	$\chi_{\max}^{(2)}$	g_1	Q_0	$\bar{g}_2$	$\beta^{(2)}$
6A	−5	−0.6547	2.5384	0.2076	0.8921		0.02	11.6		
6B	25	0.2500	1.5292	0.2300	1.0234		0.02	11.6		
6C	40			0.2610	0.8346	0.585	0.02	11.6	0.8	2.0

Table S7: Material parameters for PNIPAAm gel in water/dioxane mixture at various temperatures T (Fig. 7).

Fig.	T °C	$\chi_0^{(1)}$	$\chi_1^{(1)}$	$\chi_0^{(2)}$	$\chi_1^{(2)}$	$\chi_{\max}^{(1)}$	$\chi_{\max}^{(2)}$	g_1	Q_0	$\bar{g}_2$	$\beta^{(1)}$	$\beta^{(2)}$
7A	22	0.4785	0.4957	0.1588	0.8354			0.04	9.0			
7B	34			0.2402	0.7703		0.78	0.04	9.0	2.5		0.8

Table S8: Material parameters for PNIPAAm gels in water/dioxane mixture (Fig. 8A), water/DMSO mixture (Fig. 8B) and aqueous solution of PEG-200 (Fig. 8C) at temperature $T = 25$ °C.

Fig.	$\chi_0^{(1)}$	$\chi_1^{(1)}$	$\chi_0^{(2)}$	$\chi_1^{(2)}$	$\chi_{\max}^{(1)}$	$\chi_{\max}^{(2)}$	g_1	Q_0	$\bar{g}_2$	$\beta^{(1)}$	$\beta^{(2)}$
8A	0.3688	0.6248	0.3207	4.0109	0.53	0.70	0.02	5.0	7.0	1.2	0.10
8B	−1.9798	18.450	−1.6123	10.154	0.54	0.54	0.02	12.0	0.4	0.2	0.16
8C	0.4071	0.3838	0.4530	1.1698	0.55	0.69	0.02	12.0	3.5	1.0	0.50

Supplementary figures

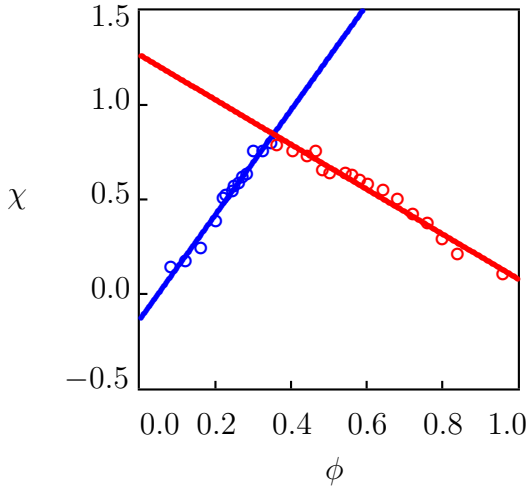


Figure S1: Parameter χ versus volume fraction of methanol ϕ in water/methanol mixture. Circles: treatment of experimental data [1] on PNIPAAm gel at temperature $T = 20$ °C. Solid lines: results of numerical analysis.

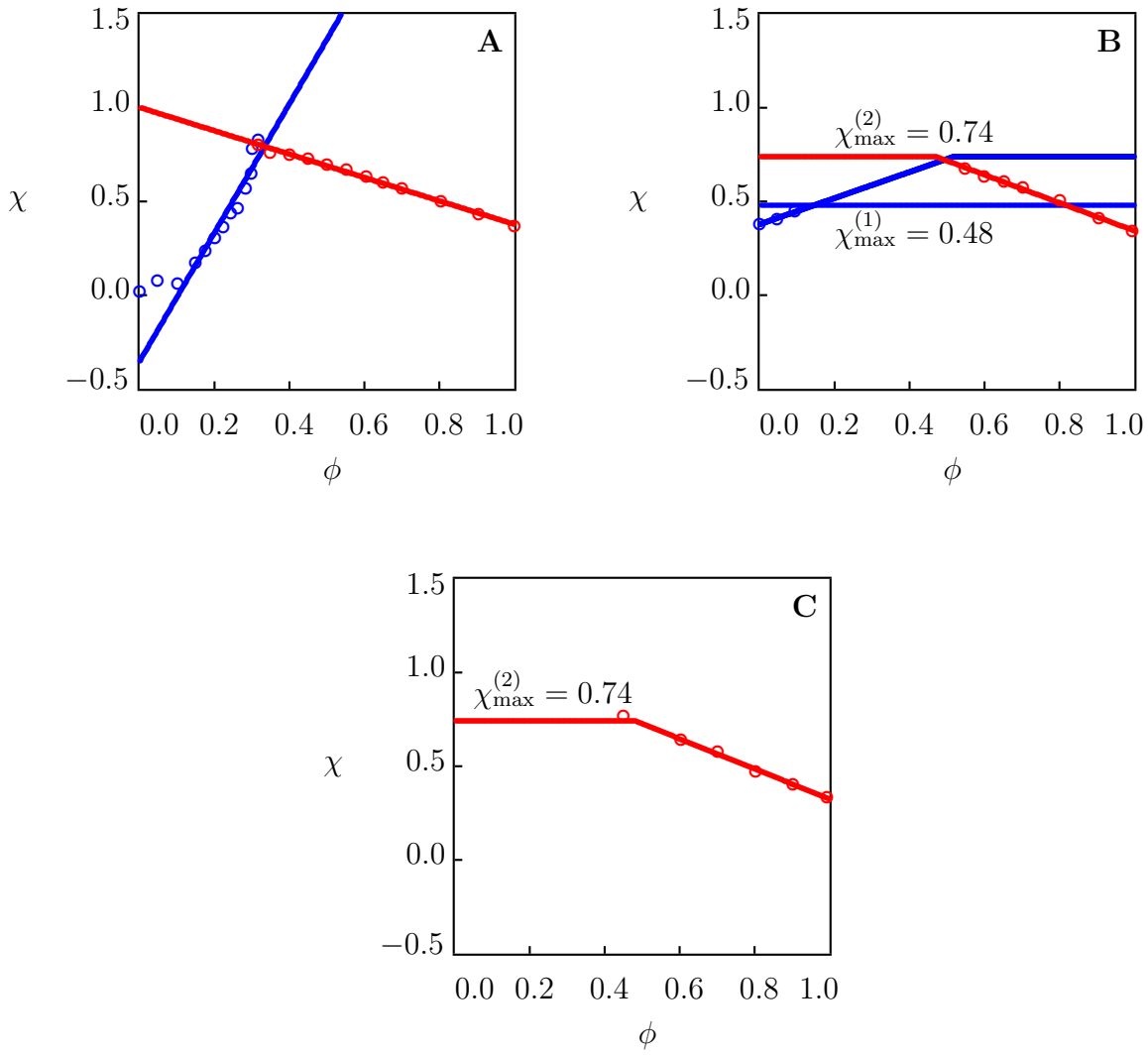


Figure S2: Parameter χ versus volume fraction of methanol ϕ in water/methanol mixture. Circles: treatment of experimental data [2] on PNIPAAm gel at temperatures $T = 14.4$ (A), $T = 26.1$ (B) and $T = 35.3$ (C) °C. Solid lines: results of numerical analysis.

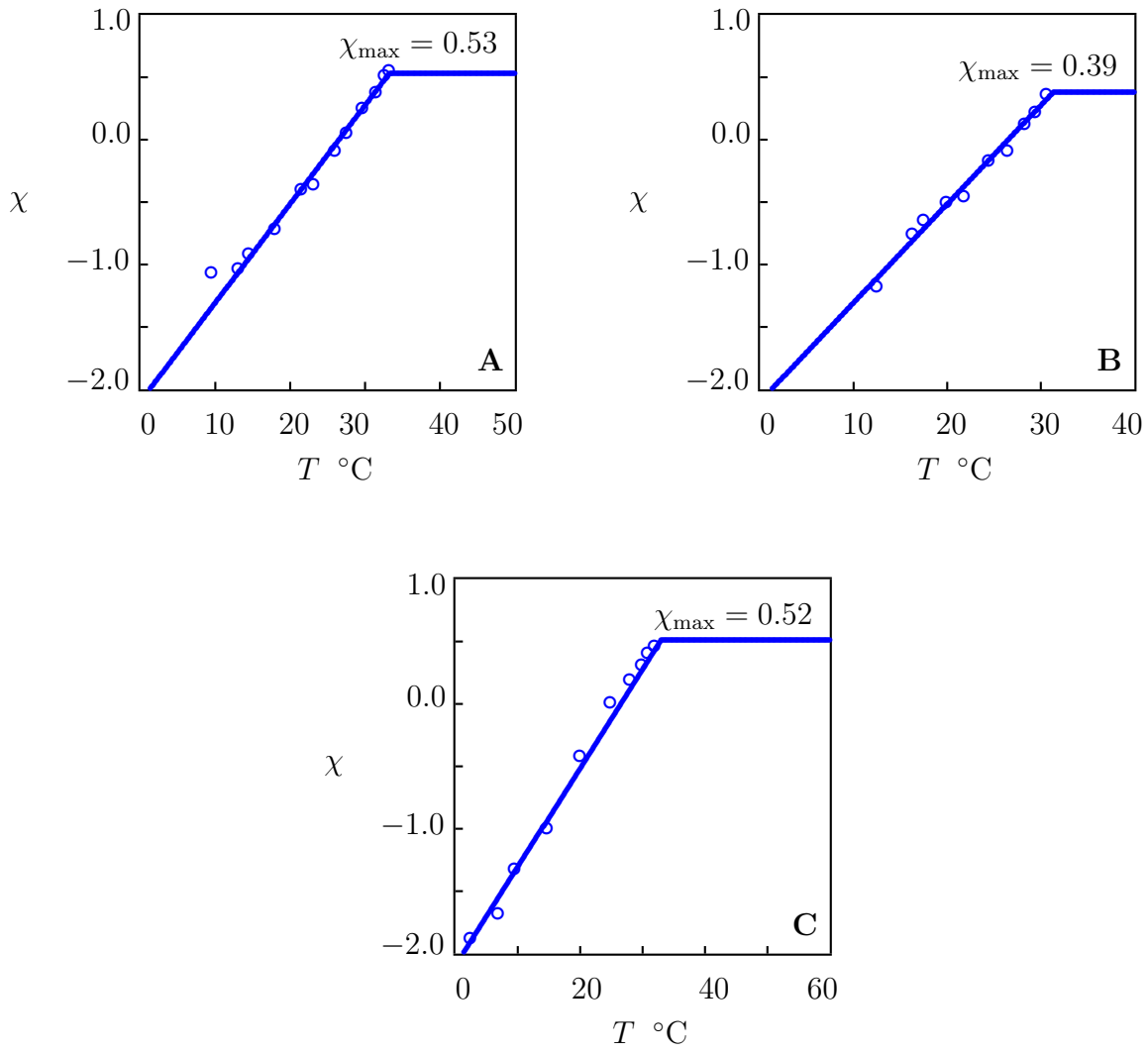


Figure S3: Parameter χ versus temperature T. Circles: treatment of experimental data on PNIPAAm gels (A – [3]) and microgels (B – [4], C – [5]) in water. Solid lines: results of numerical analysis.

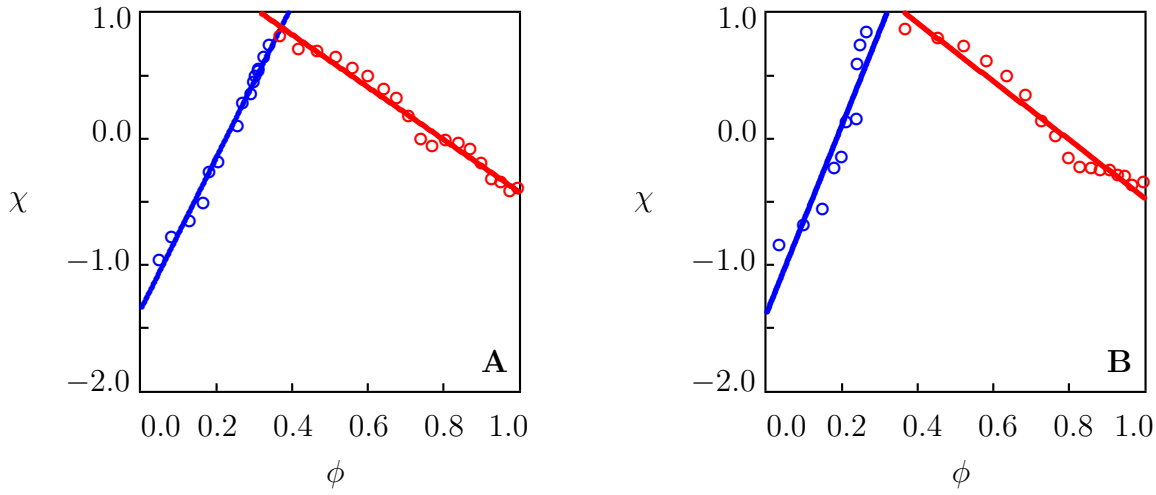


Figure S4: Parameter χ versus volume fraction ϕ of methanol (A) and ethanol (B). Circles: treatment of experimental data [4] on PNIPAAm microgel in water/alcohol mixtures at temperature $T = 12.5$ °C. Solid lines: results of numerical analysis.

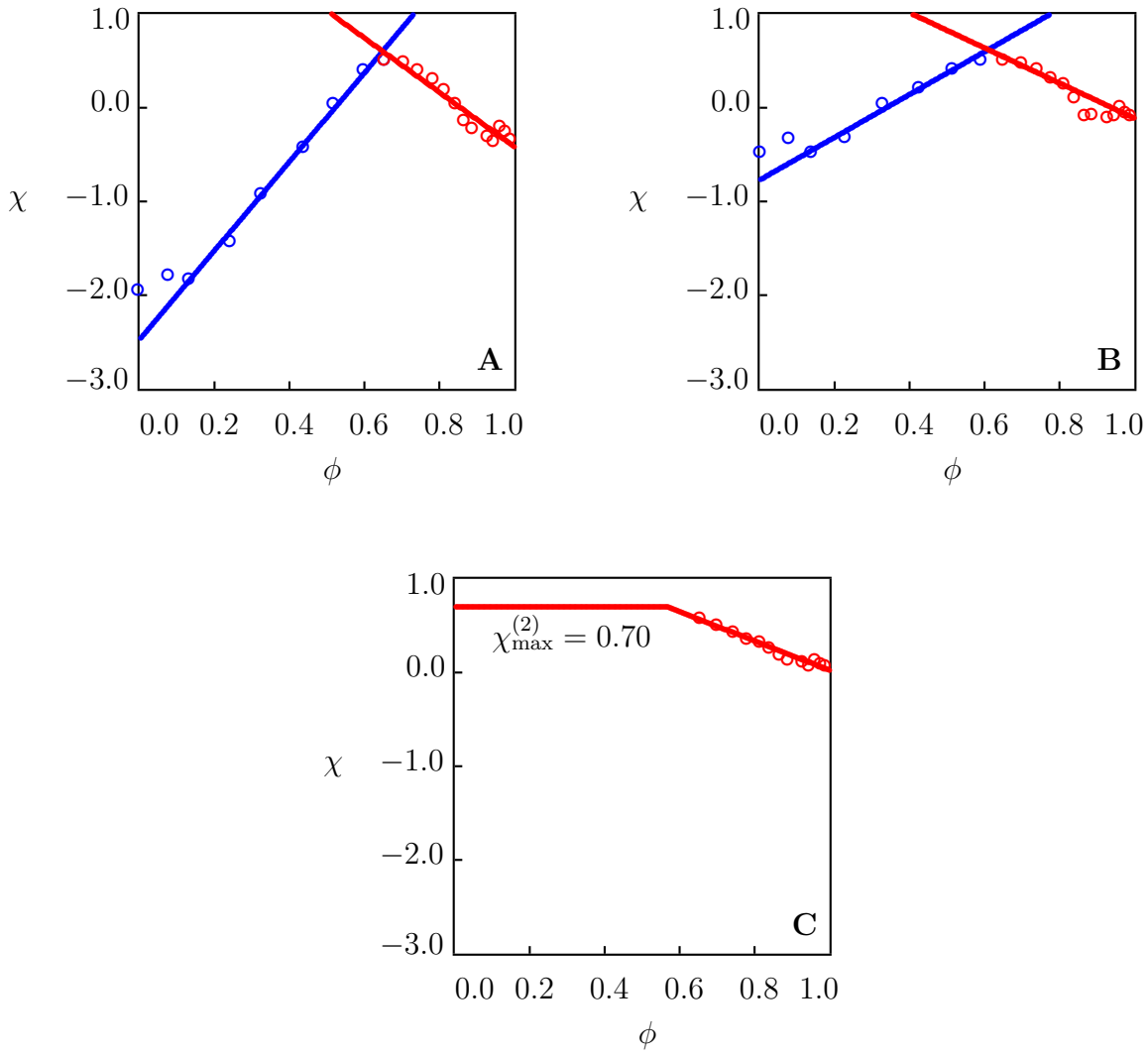


Figure S5: Parameter χ versus volume fraction of DMF ϕ in water/DMF mixture. Circles: treatment of experimental data [5] on PNIPAAm microgel at temperatures $T = 5$ (A), $T = 20$ (B) and $T = 40$ (C) °C. Solid lines: results of numerical analysis.

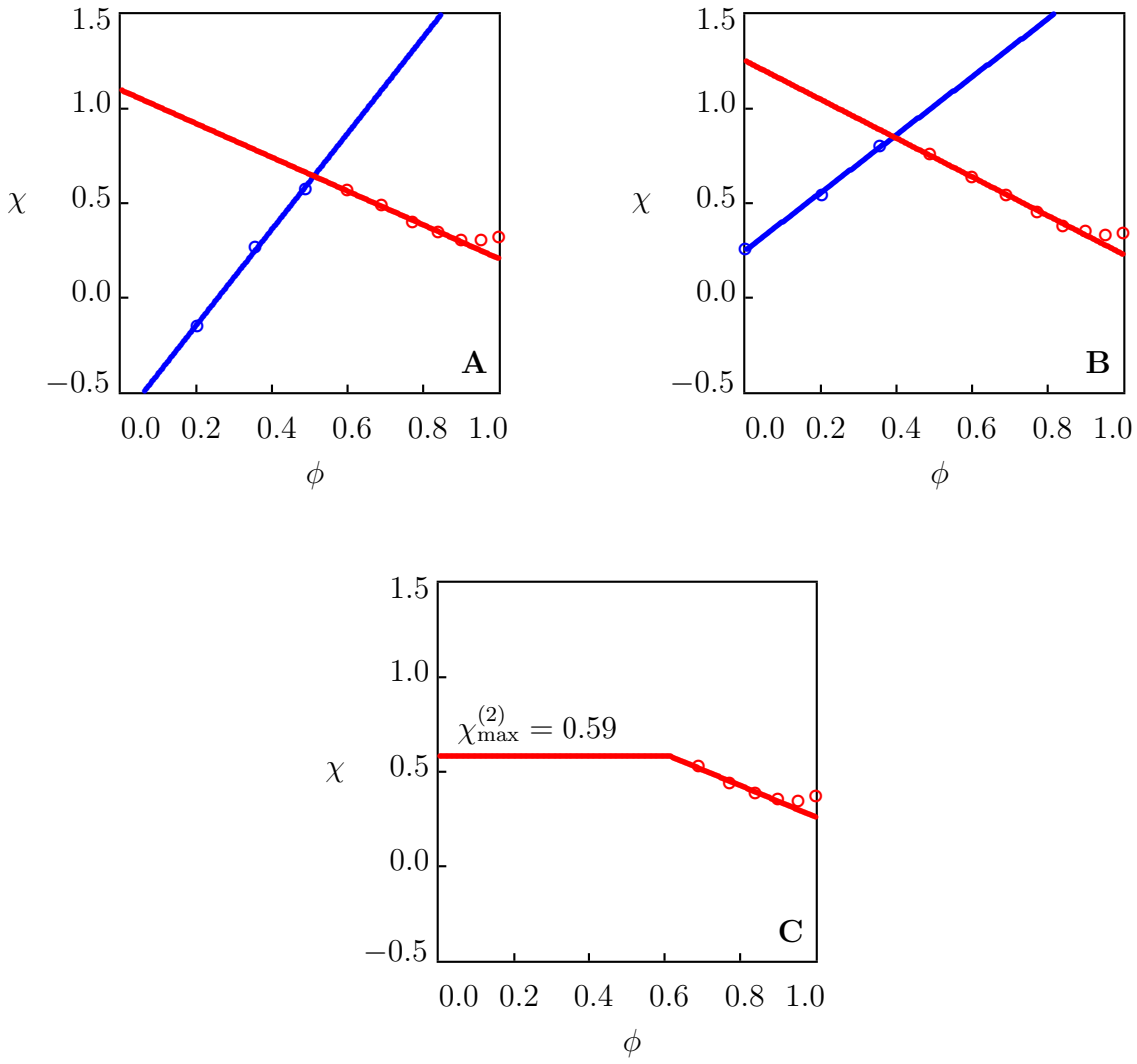


Figure S6: Parameter χ versus volume fraction of methanol ϕ in water/methanol mixture. Circles: treatment of experimental data [6] on PNIPAAm gel at $T = -5$ (A), $T = 25$ (B) and $T = 40$ (C) °C. Solid lines: results of simulation.

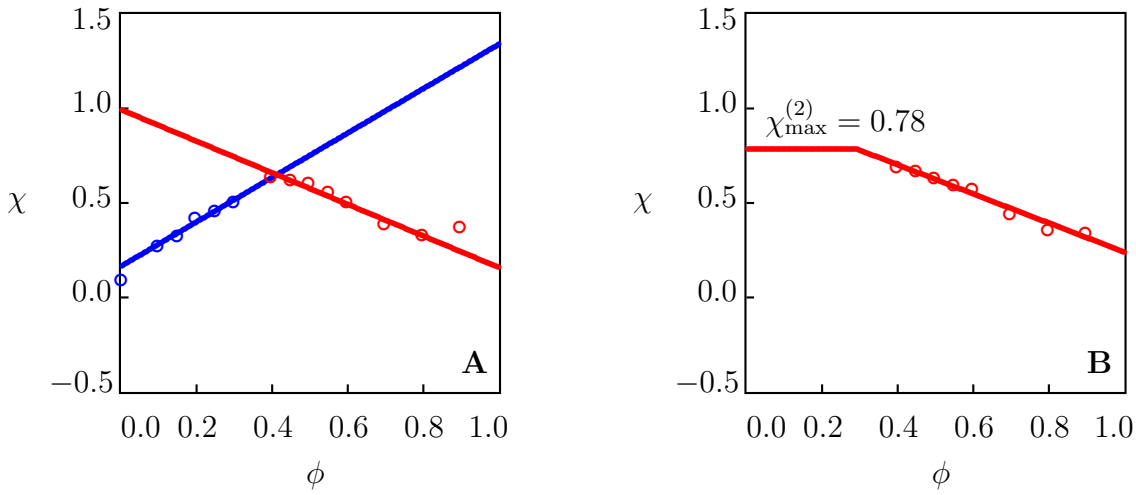


Figure S7: Parameter χ versus volume fraction of dioxane ϕ in water/dioxane mixture. Circles: treatment of experimental data [7] on PNIPAAm gel at temperatures $T = 22$ (A) and $T = 34$ (B) °C. Solid lines: results of numerical analysis.

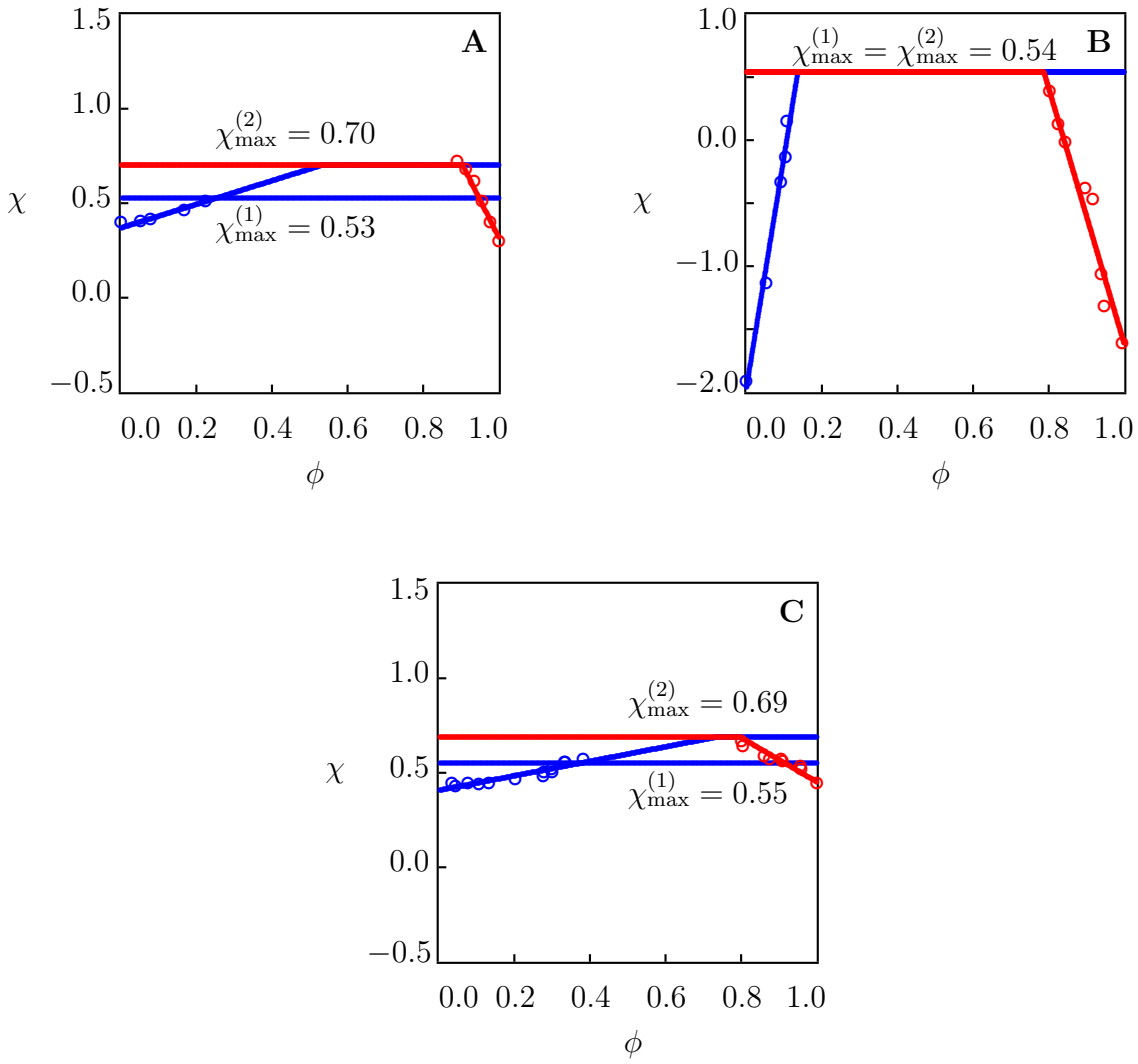


Figure S8: Parameter χ versus volume fraction of cosolvent ϕ in binary mixtures. Circles: treatment of experimental data at temperature $T = 25$ °C. Solid lines: results of numerical analysis. A – PNIPAAm gel in water/dioxane mixture [8]. B – PNIPAAm gel in water/DMSO mixture [9]. C – PNIPAAm gel in aqueous solution of PEG-200 [10].