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Liquid–liquid equilibrium correlation of aqueous two-phase systems composed of polyethylene glycol and nonionic surfactant

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ABSTRACT

Phase diagrams of aqueous two-phase systems (ATPS) composed of polyethylene glycol 20000 (PEG 20000) + polyoxyethylene octyl phenyl ether (Triton X-100) or polyoxyethylene sorbitan monooleate (Tween 80) + water are determined at 273.15, 293.15 and 313.15 K, respectively. The liquid–liquid equilibrium (LLE) experimental data are correlated using the Flory–Huggins model derived from the lattice theories, and new interaction parameters (λ_{12}, λ_{13} and λ_{23}) between any two compositions (the polymer(1) and the nonionic surfactant(2), the solvent(3)) in the ATPS are estimated at various temperature. Two kinds of fitting results are obtained when the surfactant molecules are regarded as single molecules or micellar molecules, respectively. It indicates that the interaction parameters (λ_{12}) between PEG and nonionic surfactant including Triton X-100 and Tween 80 decrease 52.3% and 105% as single molecules, while decrease 421% and 403% as micellar molecules by raising temperature, respectively. Moreover, the slightly better fitting effect can be observed if the surfactant molecules are regarded as the micellar molecules. The standard deviation between prediction values and experimental data of the components weight fraction is lower than 0.1% using the surfactant micellar parameters, showing the good descriptive quality and applicability of the Flory–Huggins model.

1. Introduction

Recently, the polymer/surfactant aqueous two-phase system (ATPS) [1–3] has been studied in the separation of biological materials, such as proteins, enzymes, and nucleic acids due to the extensive use of polymer and surfactant in pharmaceutical industry [4]. In this kind of ATPS, nonionic surfactant and polyethylene glycol (PEG) as a hydrophilic polymer are usually used to form the two-phase system. The surfactant molecules in the solution can self-organize and aggregate spontaneously to form the micelles with hydrophilic head-groups facing outwards and hydrophobic chains pointing inwards. The micelles and the PEG molecules in the solution can impel two phases formation due to the steric hindrance effect. The two compositions are concentrated in each phase, respectively, and the surfactant micelles can be regarded as the second phase composition [5–7]. In the polymer/nonionic surfactant ATPS, biomolecules partitioning depends largely on the hydrophobic interaction and excluded volume interaction due to the micelles structure existing. Thus, the polymer/nonionic surfactant ATPS has an advantage of the hydrophobic biomolecules separation such as membrane proteins [8–10]. However, liquid–liquid equilibrium (LLE) data of the polymer/nonionic surfactant aqueous systems are relatively scarce, which would limit partly the universal application of this kind of ATPS.

Previous studies on ATPSs show that the system temperature is usually important for the LLE of ATPS [11–13]. In polymer/nonionic surfactant ATPS, the micelles comprised by the nonionic surfactant molecules greatly care about the system's temperature. The form and the amount of the micelles both in the surfactant-rich phase and in the polymer-rich phase vary with the system's temperature [14–17], so the LLE of the polymer/nonionic surfactant ATPS would depend greatly on the system's temperature. Moreover, the type of the nonionic surfactant molecule determines the micelles aggregation structure and number in ATPS, and then influences the LLE of the polymer/nonionic surfactant ATPS. In this paper, polyoxyethylene alkyl phenol (Triton X-100) and polyoxyethylene sorbitan monooleate (Tween 80) are selected to investigate the effect of the nonionic micelles type on the LLE of the polymer/nonionic surfactant ATPS. Using the Flory–Huggins model derived from the lattice theories, the temperature dependency of the interaction parameters is discussed when the surfactant molecules are

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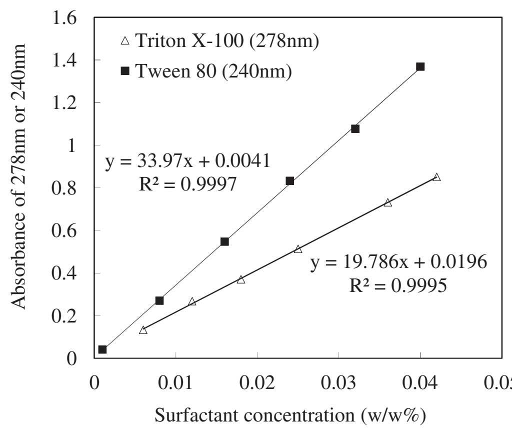

Fig. 1. The standard curves and fitting linear equations of Triton X-100 (278 nm) and Tween 80 (240 nm) aqueous solutions by spectrometer measurement, respectively.

regarded as single molecules or micellar molecules, respectively. The effect of temperature on the LLE of the polymer/nonionic surfactant ATPS has been studied further.

2. Experimental

2.1. Materials

PEG 20000 (GR, ≥95% mass purity) was purchased from Merck (Shanghai, China). The non-ionic surfactant, Triton X-100 (polyoxyethylene octyl phenyl ether, GR, ≥95% mass purity) and Tween 80 (polyoxyethylene sorbitan monooleate, GR, ≥95% mass purity) were purchased from Amresco (Shanghai, China). The polymer and surfactants were used without further purification. Aqueous solutions were prepared with deionized and doubly distilled water.

2.2. Methods

2.2.1. Determination of the binodal curve

Aqueous solutions of PEG 20000 and Triton X-100 (or Tween 80) with known concentrations were prepared beforehand and mixed in definite proportions, in such a way that the total mass of the system was around 10 g; masses were measured to within ±0.1 mg. The three components solutions were well mixed by a turbine mixer in a capped plastic tube designed for centrifugation. The tubes were centrifuged at 2800 × g for 20 min using a centrifuge of Universal 320R Hettich (Germany), and then were left undisturbed for at least 24 h at 273.15, 293.15 and 313.15 K, respectively, in a thermostatic bath controlled within ±0.05 K. The binodal curves represent the borderline between the one-phase and two-phase regions, which were determined by cloud-point measurements in the thermostatic bath with different temperature of 273.15 ± 0.05, 293.15 ± 0.05 and 313.15 ± 0.05 K, respectively. Samples of 25% (w/w) PEG 20000 solution were prepared and carefully added drop-wise into 40% (w/w) Triton X-100 (or Tween 80) solution until the two-phase region was reached (turbid samples). Then water was added drop-wise until the one phase region was reached (transparent samples). The compositions where the change from a two-phase to a one phase system occurs lie on the binodal. A sample was regarded as monophasic when it

Table 1
The refractive index (N) of the mixed aqueous solution including PEG 20000 and surfactant with various concentrations at T = 293.15 K and pressure p = 0.1 MPa.[a]

N	Concentration (%, w/w)		N	Concentration (%, w/w)	
	PEG 20000	Triton X-100		PEG 20000	Tween 80
1.3330	–	–	1.3330	–	–
1.3342	0	1.0	1.3345	1.0	1.0
1.3358	1.0	1.0	1.3361	2.0	1.0
1.3370	2.0	1.0	1.3375	3.0	1.0
1.3384	3.0	1.0	1.3388	4.0	1.0
1.3398	4.0	1.0	1.3402	5.0	1.0
1.3411	5.0	1.0	1.3415	1.0	1.0
1.3350	0	1.5	1.3353	1.0	1.5
1.3363	1.0	1.5	1.3367	2.0	1.5
1.3377	2.0	1.5	1.3380	3.0	1.5
1.3390	3.0	1.5	1.3396	4.0	1.5
1.3404	4.0	1.5	1.3407	5.0	1.5
1.3416	5.0	1.5	1.3421	1.0	1.5
1.3355	1.0	2.0	1.3359	1.0	2.0
1.3371	2.0	2.0	1.3373	2.0	2.0
1.3385	3.0	2.0	1.3386	3.0	2.0
1.3398	4.0	2.0	1.3400	4.0	2.0
1.3411	5.0	2.0	1.3415	5.0	2.0
1.3425	1.0	2.0	1.3427	1.0	2.0
1.3371	0	2.5	1.3366	1.0	2.5
1.3380	1.0	2.5	1.3382	2.0	2.5
1.3398	2.0	2.5	1.3396	3.0	2.5
1.3411	3.0	2.5	1.3411	4.0	2.5
1.3426	4.0	2.5	1.3424	5.0	2.5
1.3440	5.0	2.5	1.3439	1.0	2.5
1.3380	1.0	3.0	1.3374	1.0	3.0
1.3392	2.0	3.0	1.3388	2.0	3.0
1.3406	3.0	3.0	1.3402	3.0	3.0
1.3420	4.0	3.0	1.3416	4.0	3.0
1.3435	5.0	3.0	1.3430	5.0	3.0
1.3447	1.0	3.0	1.3444	1.0	3.0

[a] Standard uncertainties u are $u(T)$ = 0.05 K, $u(w)$ = 0.001, and $u(p)$ = 10 kPa.

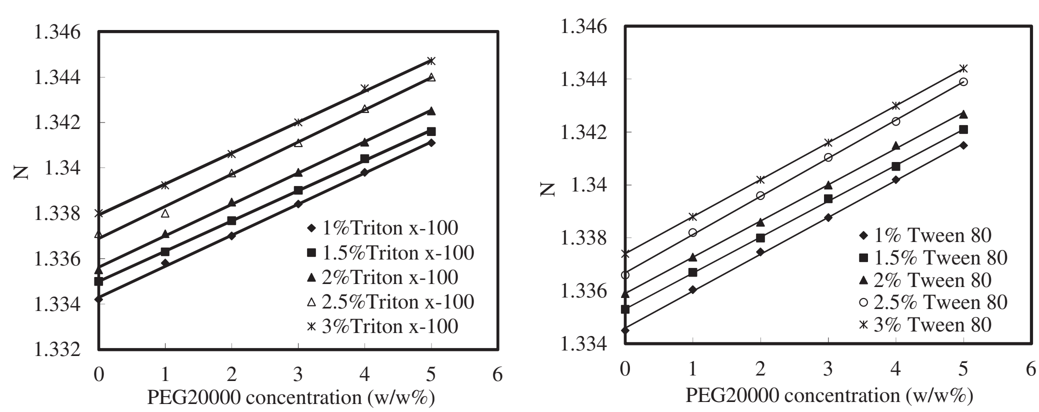

Fig. 2. The refractive index (N) of the mixed aqueous solution including PEG 20000 and surfactant with various concentrations. Left figure expresses PEG 20000 and Triton X-100 solution, and right figure expresses PEG 20000 and Tween 80 solution.