Liquid−Liquid Equilibrium Data, Viscosities, and Densities of Aqueous Mixtures of Poly(propylene glycol) with Tri-sodium Citrate at 298.15 K

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Phase diagrams of PPG425 + tri-sodium citrate + H_2O and PPG725 + tri-sodium citrate + H_2O systems at 298.15 K were determined. The densities and viscosities of these phase systems were also measured.

Introduction

Aqueous two-phase systems, which are useful for the separation of biological products from the complex mixtures in which they are produced,[1,2] can be made from aqueous solutions of two water-soluble polymers or a polymer and a salt. Poly(ethylene glycol) (PEG) is often used in this technique, and there are extensive data in the literature with this polymer.[3−9] Poly(propylene glycol) (PPG) is a polymer that is structurally closely related to PEG. Cheluget et al. and Zafarani et al. determined the LLE data for the systems PPG425 and PPG725 + NaCl + H_2O[10] and PPG425 + $MgSO_4$ + H_2O.[11] Some thermodynamics and transport properties of PPG425 + Na_2SO_4 + H_2O and PPG425 + $(NH_4)_2SO_4$ + H_2O systems at 298.15 K were measured by Salabat et al.[12,13] In this work, we observed that an aqueous PPG (with molecular weight 425 or 725) solution with tri-sodium citrate forms two liquid phases. Sodium citrate is one of the most important organic salts in biotechnology. In our previous work, the thermodynamics and transport properties of an aqueous system of this salt at 298.15 K were reported.[14] As far as we know, there is no report on the liquid−liquid equilibrium data for PPG425 + tri-sodium citrate + H_2O and PPG725 + tri-sodium citrate + H_2O systems. In this research work, phase compositions, densities, and viscosities of these systems were measured at 298.15 K.

Experimental Section

Poly(propylene glycol), of molecular weight 425, was obtained from Aldrich. The number-average molecular weight M_n of this polymer was determined by a cryoscopic osmometer (Osmomat model 030). For this purpose, freezing-point depression measurements on PPG + water were carried out at different concentrations, and a $\Delta T/K_sC$ versus C curve was plotted (ΔT, C and K_s are the freezing-point depression, concentration of samples, and cryoscopic constant, respectively). The intercept of this curve is $1/M_n$, from which M_n for this polymer was found to be 405 g·mol^{-1}. PPG, of molecular weight 725, was obtained from Merck. This polymer was in liquid form, and the polydispersity index of PPG725 reported by the manufacturer was 1.05. Tri-sodium citrate was obtained from Merck (GR, min 99%) and used without further purification.

Viscosity and density measurements were carried out for the concentrations corresponding to the tie lines, which were obtained from two-phase mixtures of PPG425 + tri-sodium citrate + H_2O and PPG725 + tri-sodium citrate + H_2O at different concentrations. The apparatus and procedure for the preparation of the two-phase system and the method of sampling have been described elsewhere.[7] In this work, a glass vessel (volume 50 cm^3) was used to carry out the phase-equilibrium determinations. Weighed amounts of poly(propylene glycol), salt, and water were loaded into the glass vessel. After mixing for 1 h, the solution was allowed to settle overnight for proper phase separation, as indicated by the absence of turbidity in each phase. Samples of the upper and lower phases were taken out carefully for analysis and density and viscosity measurements using syringes. The top phase was sampled first, with care being taken to leave a layer of material at least 0.5 cm thick above the interface. The bottom phase was withdrawn using a syringe with a long needle.

The concentration of PPG was determined from refractive index measurements performed at 298.15 K using a Mettler Toledo refractometer with temperature control (RE50). The precision of the refractive index determination was 0.00001 refractive index units. Because the refractive index of the phase samples depends on the PPG and salt concentrations, calibration plots of refractive index versus polymer concentration were prepared for different concentrations of salts. The average relative deviation of the weight percent of PPG by this method is about 0.4%. The concentration of tri-sodium citrate was measured with a flame photometer (Perkin-Elmer) with an average relative deviation of about 0.2%. The amount of water can be calculated by the mass balance method, but in this work, the amount of water in the top and bottom phases was determined by the Karl Fischer method using a Kyoto MKS-210 Karl Fischer titrator. The average relative deviation of the weight percent of water in the top phase by this method is about 0.4%, and in the bottom phase, it is about 0.9%. The mass balances for tie lines closed to within ~2%.

Density measurements were made with a Mettler Toledo densimeter (DE51). The precision of the instrument is ±1

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Table 1. Compositions and Physical Properties of the PPG425 (1) + Tri-sodium Citrate (2) + H_2O (3) Two-Phase System at 298.15 K

total system		top phase				bottom phase			
$100w_1$	$100w_2$	$100w_1$	$100w_2$	η/mPa·s	ρ/kg·m^{-3}	$100w_1$	$100w_2$	η/mPa·s	ρ/kg·m^{-3}
24.4	8.3	35.0	3.5	21.44	1033.50	5.1	16.0	2.20	1111.85
27.7	9.1	48.1	1.0	23.04	1033.48	2.1	19.1	2.18	1113.15
30.0	10.2	54.1	0.7	23.18	1033.06	2.1	21.0	2.05	1117.30
31.1	10.9	58.1	0.5	23.19	1032.52	1.5	22.0	2.03	1124.18
32.6	11.3	62.0	0.4	24.95	1032.43	0.8	23.0	1.99	1133.69
34.3	12.3	65.0	0.5	25.89	1032.24	1.0	24.5	1.99	1130.74
36.3	12.8	70.2	0.6	28.22	1031.75	0.7	25.7	1.95	1136.24
36.6	13.6	72.4	0.6	28.39	1030.86	0.6	27.2	1.94	1138.93
38.0	13.9	74.4	0.5	32.59	1024.04	0.5	28.1	2.00	1144.22

Table 2. Compositions and Physical Properties of PPG725 (1) + *Tri*-sodium Citrate (2) + H_2O (3) Two Phase System at 298.15 K

total system		top phase				bottom phase			
$100w_1$	$100w_2$	$100w_1$	$100w_2$	η/mPa·s	ρ/kg·m^{-3}	$100w_1$	$100w_2$	η/mPa·s	ρ/kg·m^{-3}
43.7	3.0	65.2	0.7	99.06	1019.18	11.9	6.9	0.00147	1042.92
44.0	3.7	69.1	0.6	127.05	1020.12	8.1	8.5	0.00162	1020.73
42.6	4.6	72.0	0.5	137.67	1019.88	3.0	10.1	0.00156	1035.54
44.6	5.0	76.0	0.5	141.36	1019.34	3.2	11.0	0.00152	1040.62
44.0	5.9	80.1	0.5	150.82	1018.69	2.5	12.1	0.00145	1044.38
43.7	7.0	85.1	0.4	154.49	1018.29	3.1	14.1	0.00144	1044.63
43.5	8.5	88.0	0.4	156.86	1017.08	1.0	16.8	0.00140	1072.16
41.0	11.0	93.1	0.3	163.86	1016.82	1.0	19.0	0.00135	1085.71

× 10^{-5} g·cm^{-3}. The temperature of the vibrating tube in the densimeter was controlled to within ±0.01 K. Viscosities were measured with an Ostwald-type viscometer. The viscometer was calibrated with water (0.8904 mPa·s) and toluene (0.5559 mPa·s) at 298.15 K. The volume of the solutions used in the viscometer was 7 cm^3 as measured with a pipet. It was assumed that the viscosity η was related to the time of flow (t) and density of solution (ρ) according to

$$\eta = A\rho t - \frac{B\rho}{t}$$

where A and B for the viscometer were found to be 0.0220 and −4.3960, respectively. The viscosity measurement was reproducible to within ±0.5%.

Results and Discussion

The experimental equilibrium compositions, viscosities, and densities of the aqueous two-phase systems PPG425 + tri-sodium citrate + H_2O and PPG725 + tri-sodium citrate + H_2O are presented in Tables 1 and 2. The top phases are rich in PPG and low in salt, whereas the bottom

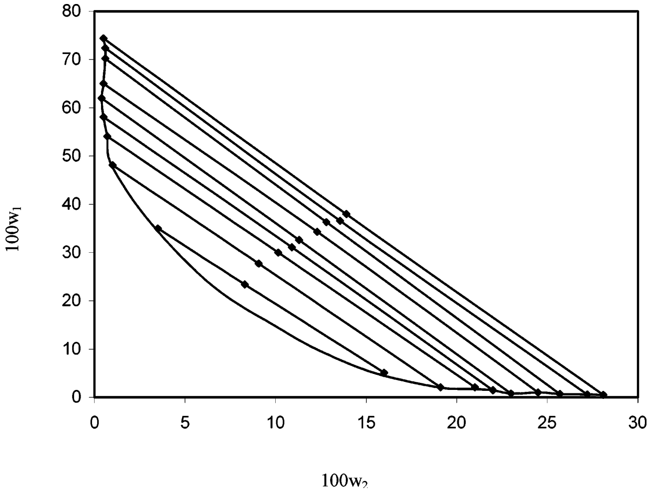

Figure 1. Binodal curve of PPG425 (1) + tri-sodium citrate (2) + H_2O (3) at 298.15 K.

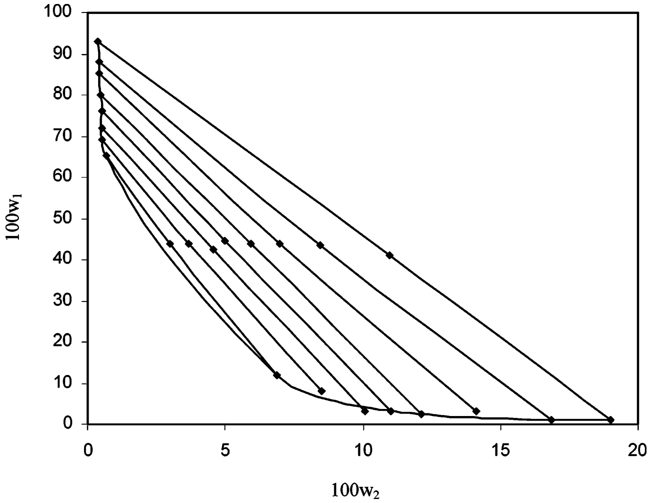

Figure 2. Binodal curve of PPG725 (1) + tri-sodium citrate (2) + H_2O (3) at 298.15 K.

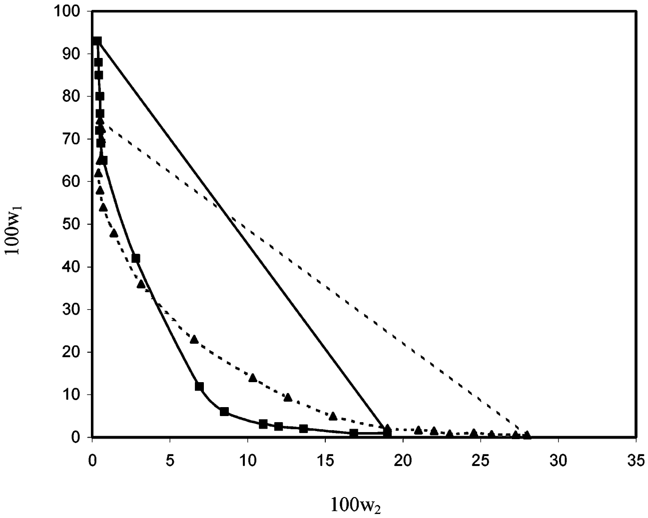

Figure 3. Effect of molecular weight on the bimodal curve of PPG (1) + tri-sodium citrate (2) + H_2O (3) at 298.15 K. PPG425 (dashed line); PPG725 (solid line).

phases contain most of the salt and little polymer. The top phases are viscous and have densities in the range of 1024.04−1033.50 kg·m^{-3} for PPG425 and 1016.82−1020.12 kg·m^{-3} for PPG725. The bottom phases were less viscous and have corresponding densities in the ranges of 1111.85−1144.22 kg·m^{-3} and 1020.73−1085.71 kg·m^{-3}. These equilibrium compositions are presented graphically in Figures 1 and 2. The tie lines are determined by connecting each corresponding set of total, bottom-, and top-phase points. The binodal curves were drawn through the top- and bottom-phase points and are estimated near the critical point on the basis of the locations and trends of the top- and bottom-phase compositions. The effect of increasing the molecular weight of the polymer, shown in Figure 3, is to increase the size of the two-phase region.

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