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Densities and Viscosities of Polyethylene Glycol 2000 + Salt + Water Systems from (298.15 to 318.15) K

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Densities and viscosities of aqueous solutions of poly(ethylene glycol) 2000 (mass fraction from (5 to 50) %) have been measured at 298.15, 303.15, 308.15, 313.15, and 318.15 K. The density data show a linear variation with mass fraction of the polymer for all temperatures. The viscosity data of PEG 2000 solutions were correlated as a function of mass fraction, using a nonlinear equation, for the five different temperatures covered in the present work. Densities and viscosities of poly(ethylene glycol)−sodium citrate two-phase systems have been measured and are correlated with composition. The tie line lengths (TLL) of the aqueous two-phase systems have also been estimated.

Introduction

Poly(ethylene glycol) (PEG) plays a vital role in the formation of aqueous two-phase systems (ATPS), which provide a powerful technique for the separation and purification of biological materials such as proteins, enzymes, plant cells and animal cells, viruses, chloroplasts, and nucleic acids.[1] Because of their high water content and nontoxicity, the poly(ethylene glycol)-based aqueous two-phase system provides an environmentally safe process for the purification of biological materials and at the same time does not affect their activity. PEG finds a wide range of applications in the automotive, petroleum, textile, and food industries. Despite the success of the ATPS separation techniques, data on the physical properties of PEG at various concentrations and temperatures are necessary for a fundamental understanding of the phase-forming ability and also for the development of theoretical models for the prediction of the partitioning behavior of the two-phase system. In the present work, densities and viscosities of aqueous PEG 2000 solutions with mass fractions of PEG 2000 from (5 to 50) % and PEG 2000 with varying sodium citrate compositions, in both the single- and two-phase systems, have been measured, and the temperature effects were also studied.

Experimental Section

Materials. Poly(ethylene glycol) with an average molecular mass of 2000 (cat. no. 8.21037.1000) and sodium citrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) (analytical grade, (Merck)) (cat. no. 61770905001046) were used. Distilled, deionized water was used in this study.

Apparatus and Procedures. The aqueous solutions were prepared by mass, using an analytical balance (OHAUS-Essae-Teraoka Ltd, Japan, model AR2140) with an accuracy of ±0.1 mg. Solutions for the formation of aqueous two-phase systems were prepared in a 50 cm^3 centrifuge tube and brought into a Schott-Gerate CT 52 (Germany) thermostatic bath to maintain the appropriate temperature with an uncertainty of 0.05 K. The systems were stirred and well mixed and allowed to settle to ensure the proper phase separation at the desired temperature, as indicated by the absence of turbidity in each phase.[2] Samples of the top phase were taken using a pipet and samples of the bottom phase were also taken through the top phase using a pipet by maintaining a small positive pressure to avoid contamination, and then the densities and viscosities of both the phases were measured.[3] The density measurements were carried out at (298.15, 303.15, 308.15, 313.15, and 318.15) K using a 5 cm^3 glass pycnometer.[4] The pycnometer was filled with the solution and immersed in the water bath. After thermal equilibrium was achieved, the pycnometer was removed from the water bath and then cleaned and dried quickly. Densities were determined from the measurements of the mass of the samples and the pycnometer. The volume of the pycnometer was calibrated as a function of temperature using deionized water. The density of water was taken from Perry's Chemical Engineers' Handbook.[5] The uncertainty of the density measurements was estimated to be $\pm 0.0001\ g{\cdot}cm^{-3}$

Viscosities of the aqueous PEG 2000 solutions and that of the top phase of the aqueous two-phase systems were determined using an Ostwald viscometer at (298.15, 303.15, 308.15, 313.15, and 318.15) K in a water bath.[4] The uncertainty of the measurements was ±0.002 mPa·s. The viscosities of the bottom phase of the aqueous two-phase system were nearly the same as that of water, and hence they were not measured. For the determination of tie line compositions, the concentrations of sodium citrate in the top and bottom phases were determined using flame photometry.[6] The concentrations of PEG 2000 in both phases were determined by refractive index measurements. The relation between the refractive index, n, and the mass fraction of polymer, w_p and that of salt, w_s is given by

$$n = a_o + a_1 w_p + a_2 w_s \qquad (1)$$

The values of coefficients a_0, a_1, and a_2 for the present systems were obtained as 1.3332, 0.1411, and 0.1478, respectively. The uncertainty of the mass fraction of PEG was ±0.002.

Results and Discussion

The densities and viscosities of aqueous solutions of PEG 2000 and the densities of PEG 2000 + sodium citrate +

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Table 1. Densities and Viscosities of the PEG 2000 (p) + Water System at Various Temperatures

w_p	ρ/g·cm^{-3}	$100(\rho - \rho_{calcd})/\rho$	μ/mPa·s	$100(\mu - \mu_{calcd})/\mu$	w_p	ρ/g·cm^{-3}	$100(\rho - \rho_{calcd})/\rho$	μ/mPa·s	$100(\mu - \mu_{calcd})/\mu$
T = 298.15 K									
0.00	0.99700	0.00	0.894	0.00	0.30	1.04924	−0.01	9.170	2.42
0.05	1.00487	−0.09	1.689	−1.03	0.35	1.05854	0.04	13.640	1.90
0.10	1.01327	−0.12	2.271	−0.56	0.40	1.06756	0.07	19.378	−1.11
0.15	1.02219	−0.10	2.921	−1.36	0.45	1.07612	0.05	27.431	−1.77
0.20	1.03160	−0.03	4.161	2.12	0.50	1.08394	−0.03	39.297	1.54
0.25	1.04037	−0.03	6.120	2.66					
T = 303.15 K									
0.00	0.99560	0.00	0.768	0.00	0.30	1.04754	−0.01	7.076	0.42
0.05	1.00314	−0.11	1.661	1.20	0.35	1.05638	0.00	10.721	1.31
0.10	1.01168	−0.13	2.166	0.46	0.40	1.06562	0.05	15.882	1.26
0.15	1.02082	−0.08	2.653	0.75	0.45	1.07446	0.07	22.992	1.39
0.20	1.02976	−0.05	3.399	0.18	0.50	1.08250	0.01	32.599	2.24
0.25	1.03830	−0.07	4.857	2.06					
T = 308.15 K									
0.00	0.99400	0.00	0.723	0.00	0.30	1.04412	−0.03	5.638	1.84
0.05	1.00135	−0.10	1.560	0.44	0.35	1.05284	0.00	8.254	−0.83
0.10	1.00939	−0.14	1.991	0.29	0.40	1.06209	0.08	12.186	−2.17
0.15	1.01787	−0.13	2.325	0.62	0.45	1.07097	0.13	17.849	−2.01
0.20	1.02673	−0.09	2.879	2.11	0.50	1.07789	−0.01	26.414	2.01
0.25	1.03501	−0.10	3.869	1.90					
T = 313.15 K									
0.00	0.99220	0.00	0.594	0.00	0.30	1.04056	−0.06	4.344	1.61
0.05	0.99926	−0.11	1.290	0.78	0.35	1.04962	0.03	6.593	1.82
0.10	1.00732	−0.12	1.646	1.82	0.40	1.05868	0.11	9.899	1.31
0.15	1.01488	−0.18	1.862	1.07	0.45	1.06674	0.10	14.433	0.21
0.20	1.02344	−0.14	2.230	1.37	0.50	1.07380	0.00	20.866	1.20
0.25	1.03250	−0.05	2.940	0.34					
T = 318.15 K									
0.00	0.99020	0.00	0.599	0.00	0.30	1.03766	−0.02	3.524	2.16
0.05	0.99728	−0.09	1.021	−1.53	0.35	1.04640	0.06	5.257	0.92
0.10	1.00466	−0.14	1.262	0.66	0.40	1.05431	0.05	7.749	−0.76
0.15	1.01190	−0.21	1.412	−1.05	0.45	1.06248	0.07	11.219	−1.80
0.20	1.02025	−0.17	1.756	1.32	0.50	1.07048	0.08	16.482	1.57
0.25	1.02882	−0.11	2.393	1.89					

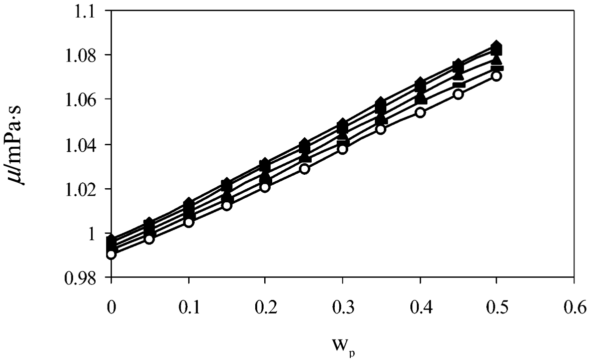

Figure 1. Relationship between the densities and mass fraction, w_p, for PEG 2000 + water: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; −, 313.15 K; ○, 318.15 K.

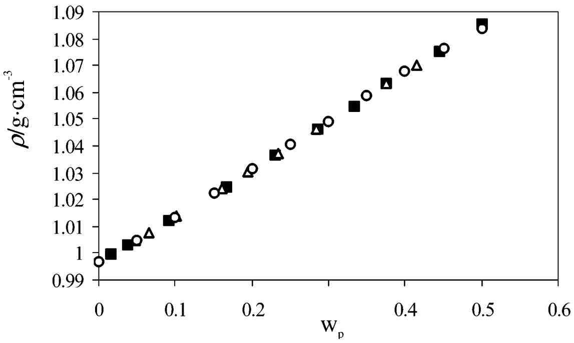

Figure 2. Comparison of present experimental data with literature data on density: ○, experimental; ■, Stanislava Kirincic and Cveto Klofutar; △, Sheau Ping Teng and Tjoon Tow Teng.

water solutions at various temperatures are given in Tables 1 and 2. The density data presented in Table 1 are plotted in Figure 1.The densities are found to increase with an increase in PEG 2000 concentration and decrease with an increase in temperature. The densities of aqueous PEG 2000 solutions could be correlated by using the following equation

$$\rho/\mathrm{g{\cdot}cm^{-3}} = \rho_o/\mathrm{g{\cdot}cm^{-3}} + Aw_p \qquad (2)$$

at 298.15 K, $A = 0.1746$ and $\rho_0 = 0.9970$

at 303.15 K. $A = 0.1736$ and $\rho_0 = 0.9956$

at 308.15 K, $A = 0.1680$ and $\rho_0 = 0.9940$

at 313.15 K, $A = 0.1633$ and $\rho_0 = 0.9922$

at 318.15 K, $A = 0.1589$ and $\rho_0 = 0.9902$

where ρ is the density of the solution, ρ_0 is the density of pure water at the corresponding temperature, and w_p is the mass fraction of PEG 2000.The average relative deviation is less than 1%. Very close agreement was found between the densities measured in the present work and those reported by Teng et al.[7] and Kirincic et al.,[8] which are shown in Figure 2.

The densities of the PEG 2000 + sodium citrate + water systems could be correlated as follows:

$$\rho/\mathrm{g{\cdot}cm^{-3}} = Aw_p + Bw_s + \rho_0/\mathrm{g{\cdot}cm^{-3}} \qquad (3)$$

at 298.15 K, $A = 0.1799$, $B = 0.6317$, and $\rho_0 = 0.9970$

at 308.15 K, $A = 0.1801$, $B = 0.6419$, and $\rho_0 = 0.9940$

at 318.15 K, $A = 0.1698$, $B = 0.6493$, and $\rho_0 = 0.9902$

where w_p and w_s are the mass fractions of polymer and salt, respectively. Constants A and B are dependent on the

Table 2. Densities of the PEG2000 (p) + Sodium Citrate (s) + Water System at Various Temperatures

		$T = 298.15$ K		$T = 308.15$ K		$T = 318.15$ K	
w_p	w_s	ρ/g·cm^{-3}	$100(\rho - \rho_{calcd})/\rho$	ρ/g·cm^{-3}	$100(\rho - \rho_{calcd})/\rho$	ρ/g·cm^{-3}	$100(\rho - \rho_{calcd})/\rho$
0.40	0.02	1.08221	0.14	1.07840	0.15	1.06857	−0.07
0.35	0.02	1.07330	0.15	1.06950	0.16	1.06134	0.05
0.30	0.02	1.06371	0.10	1.06135	0.24	1.05358	0.12
0.25	0.02	1.05506	0.13	1.05190	0.20	1.04600	0.20
0.20	0.02	1.04665	0.19	1.04200	0.12	1.03800	0.25
0.15	0.02	1.03650	0.08	1.03330	0.15	1.02890	0.20
0.10	0.02	1.02712	0.04	1.02370	0.09	1.01944	0.10
0.05	0.02	1.01810	0.04	1.01435	0.06	1.01083	0.09
0.00	0.02	1.01060	0.19	1.00479	0.01	1.00089	−0.05
0.35	0.04	1.08400	−0.03	1.08110	0.05	1.07202	−0.17
0.30	0.04	1.07445	−0.08	1.07160	0.00	1.06560	0.02
0.25	0.04	1.06524	−0.10	1.06300	0.04	1.05803	0.11
0.20	0.04	1.05644	−0.08	1.05304	−0.05	1.04930	0.09
0.15	0.04	1.04720	−0.11	1.04418	−0.04	1.04110	0.12
0.10	0.04	1.03800	−0.13	1.03498	−0.06	1.03189	0.05
0.05	0.04	1.02903	−0.12	1.02650	−0.01	1.02292	0.00
0.00	0.04	1.02141	0.01	1.01657	−0.10	1.01330	−0.11
0.25	0.06	1.07904	0.01	1.07570	0.02	1.07100	0.11
0.20	0.06	1.06960	−0.03	1.06650	0.01	1.06222	0.08
0.15	0.06	1.06004	−0.08	1.05801	0.05	1.05363	0.07
0.10	0.06	1.05148	−0.04	1.04800	−0.04	1.04365	−0.07
0.05	0.06	1.04186	−0.10	1.03940	0.00	1.03436	−0.15
0.00	0.06	1.03314	−0.08	1.02970	−0.07	1.02523	−0.21
0.20	0.08	1.08219	−0.03	1.07910	−0.02	1.07510	0.07
0.15	0.08	1.07365	0.01	1.06950	−0.07	1.06647	0.06
0.10	0.08	1.06436	−0.02	1.06060	−0.06	1.05660	−0.07
0.05	0.08	1.05549	−0.01	1.05196	−0.03	1.04720	−0.16
0.00	0.08	1.04682	0.02	1.04201	−0.12	1.03840	−0.19
0.15	0.10	1.08621	0.00	1.08266	−0.04	1.07923	0.04
0.10	0.10	1.07755	0.03	1.07364	−0.04	1.07059	0.02
0.05	0.10	1.06912	0.09	1.06548	0.04	1.06216	0.03
0.00	0.10	1.06070	0.14	1.05769	0.15	1.05356	0.02
0.40	0.00	1.06756	−0.04	1.06209	−0.17	1.05431	−0.19
0.35	0.00	1.05854	−0.04	1.05284	−0.20	1.04640	−0.14
0.30	0.00	1.04924	−0.07	1.04412	−0.17	1.03766	−0.16
0.25	0.00	1.04037	−0.06	1.03501	−0.18	1.02960	−0.12
0.20	0.00	1.03160	−0.04	1.02673	−0.12	1.02140	−0.10
0.15	0.00	1.02219	−0.08	1.01787	−0.10	1.01330	−0.06
0.10	0.00	1.01327	−0.08	1.00939	−0.05	1.00466	−0.08
0.05	0.00	1.00487	−0.02	1.00135	0.04	0.99728	0.03
0.00	0.00	0.99700	0.10	0.99400	0.21	0.99020	0.18

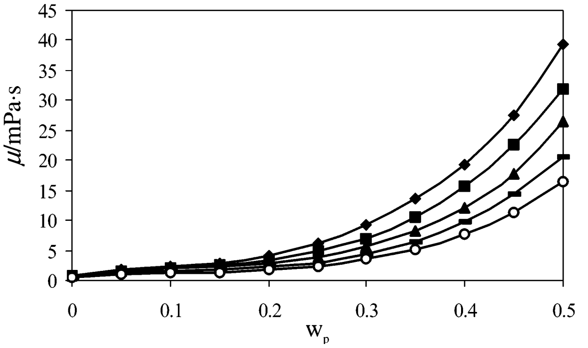

Figure 3. Relationship between the viscosities and mass fraction, w_p, for PEG 2000 + water: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; −, 313.15 K; ○, 318.15 K.

temperature. The viscosity data presented in Table 1 are plotted in Figure 3. It is observed that the viscosities increase with an increase in PEG 2000 concentration and decrease with an increase in temperature. Kirincic et al.[9] have successfully used a third-order polynomial to represent their viscosity data with respect to the mass fraction of PEG 2000 and the nonelectrolyte system. Hence, in the present work a polynomial of the following form is used to represent the present viscosity data on the PEG 2000−sodium citrate−water system

$$\mu/\text{mPa·s} = Aw_p^3 + Bw_p^2 + Cw_p + \mu_o/\text{mPa·s} \qquad (4)$$

where μ is the absolute viscosity of the solution and μ_0 is the viscosity of water at the corresponding temperature. Constants A, B, and C are the coefficients of the polynomial and are determined by regression analysis. These values along with the average absolute relative deviation (AARD) are given in Table 3. Figure 4 shows close agreement between the present and literature data (Kirincic et al.[9]) on viscosity. The viscosities of the top phase and densities

Table 3. Coefficients of Equation 4

T/K	A	B	C	AARD
298.15	447.5	−114.25	20.847	0.014978
303.15	427.89	−135.94	23.201	0.01025
308.15	385.95	−137.35	22.508	0.012923
313.15	321.68	−118.46	18.854	0.010482
318.15	235.08	−79.289	12.125	0.012411

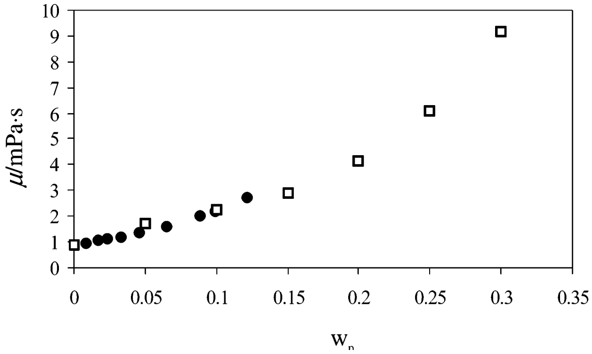

Figure 4. Comparison of present experimental data with literature data on viscosity: □, experimental; ●, Stanislava Kirincic and Cveto Klofutar.

Table 4. Densities and Viscosities of the PEG 2000 (p) + Sodium Citrate (s) + Water Aqueous Two-Phase System at Various Temperatures

total system			ρ			
w_p	w_s	TLL	ρ_T/g·cm^{-3}	ρ_B/g·cm^{-3}	$\Delta\rho$/g·cm^{-3}	μ_T/mPa·s
			$T = 298.15$ K			
0.150	0.125	0.264	1.0863	1.1321	0.0457	7.4858
0.175	0.125	0.328	1.0865	1.1472	0.0607	11.6874
0.200	0.125	0.378	1.0882	1.1583	0.0701	13.9607
0.225	0.125	0.437	1.0888	1.1755	0.0867	17.0189
			$T = 308.15$ K			
0.125	0.125	0.204	1.0779	1.1044	0.0265	
0.150	0.125	0.302	1.0778	1.1224	0.0447	6.3789
0.175	0.125	0.353	1.0797	1.1321	0.0524	9.0251
0.200	0.125	0.408	1.0797	1.1454	0.0657	10.5383
0.225	0.125	0.459	1.0814	1.1601	0.0787	13.0251
			$T = 318.15$ K			
0.125	0.125	0.277	1.0648	1.0977	0.0329	
0.150	0.125	0.348	1.0666	1.1106	0.0440	5.4079
0.175	0.125	0.401	1.0672	1.1187	0.0515	6.7018
0.200	0.125	0.434	1.0693	1.1263	0.0570	7.6599
0.225	0.125	0.471	1.0705	1.1385	0.0680	9.6606

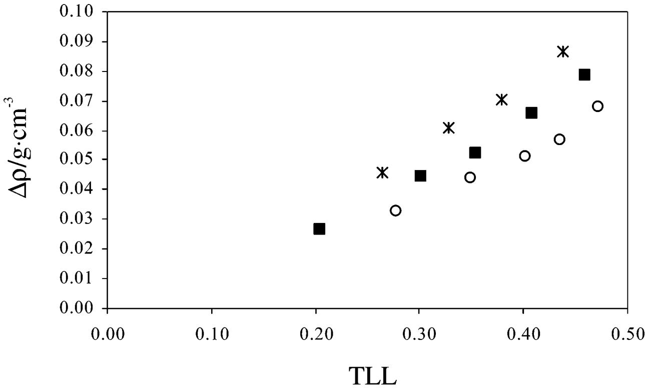

Figure 5. Relationship between density difference *(*$\Delta\rho$*)* and tie line length (TLL) for PEG 2000 + sodium citrate + water two-phase system: *, 298.15 K; ■, 308.15 K; ○, 318.15 K.

of the top and bottom phases for PEG 2000 + sodium citrate + water two-phase systems are given in Table 4, along with tie line compositions and tie line lengths (TLL). The tie line lengths are estimated using the following relationship[4]

$$\mathrm{TLL} = [(w_{p(T)} - w_{p(B)})^2 + (w_{s(T)} - w_{s(B)})^2]^{1/2} \qquad (5)$$

It is observed that the TLL increase with increasing temperature and PEG composition, in good agreement with the observations of Voros et al.[10] and Zafarani-Moattar and Sadeghi.[11] The density difference between the phases ($\Delta\rho$) and the viscosities of the top phases (μ_T) are also given in Table 4. The density difference between the phases and the viscosities of the top phases increase with an increase in the tie line length and decrease with an increase in temperature. From Figures 5 and 6, it is observed that the density differences between the phases and the viscosities of the top phase show a linear relationship with the TLL.

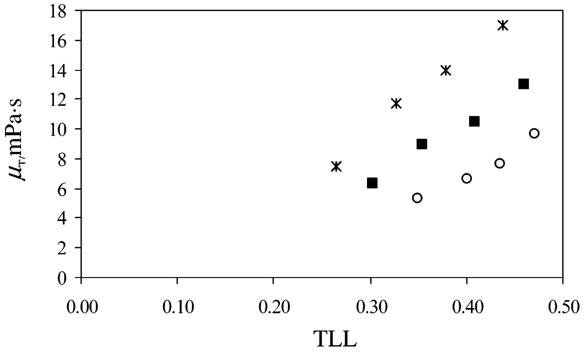

Figure 6. Relationship between viscosity of top phase (μ_T) and tie line length (TLL) for PEG 2000 + sodium citrate + water two-phase system: *, 298.15 K; ■, 308.15 K; ○, 318.15 K.

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