Interfacial Tension and Viscosity for Poly(ethylene glycol) + Maltodextrin Aqueous Two-Phase Systems

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This study presents interfacial tension and viscosity experimental data, at 30 °C, for aqueous two-phase systems (ATPS) composed of poly(ethylene glycol) (PEG) with different molar mass (4000, 6000, and 8000) g·mol^{-1} and maltodextrin (MD), with molar mass of 2800 g·mol^{-1}. Interfacial tension and viscosity were measured by using a spinning drop tensiometer and a rolling ball viscosimeter, respectively. An increase on the PEG molar mass resulted in an increase of interfacial tension and viscosity. The interfacial tension varied from (0.038 to 0.121) mN·m^{-1} for the systems formed by PEG 4000 ($w = 0.08$) + MD ($w = 0.35$) + water ($w = 0.57$) and PEG 8000 ($w = 0.10$) + MD ($w = 0.30$) + water ($w = 0.60$), respectively. Viscosity values varied from (7.9×10^{-3} to 2.17×10^{-2}) Pa·s for the PEG-rich phase and from ($4.51 \times 10{-}2$ to 6.54×10^{-2}) Pa·s for the MD-rich phase.

Introduction

Aqueous two-phase systems (ATPS) are formed by mixing either aqueous solutions of different polymers or aqueous solutions of polymers and salts above certain critical thermodynamic conditions. Due to its low interfacial tension, allied to high water content, the ATPS provide mild separations to preserve biological activities of labile compounds, like proteins, cells, or other biological materials.[1] Therefore, the interfacial tension between phases has a decisive influence in the separation and partition mechanism of biomolecules and cells as well as in dispersion, emulsification, flocculation, and solubilization processes. Interfacial tension influences the shape of fluid interfaces and controls their deformability. Data of interfacial tension, viscosity, and other physical properties make possible the prediction of system behavior, velocity of phase formation, phase separation, and reagent composition for the system formation. Tests with the ATPS composed of poly(ethylene glycol) (PEG) and maltodextrin (MD) presented satisfactory results in protein partition as for β-lactoglobulin and bovine serum albumin.[2] Experiments conducted in our laboratory showed that such a system was also effective in cell partition of *Lactobacillus acidophilus* from a fermented broth. The polysaccharide MD can provide a low-cost alternative to substitute the fractioned dextran for the use with PEG in ATPS, making the large-scale application of polymer + polymer ATPS more likely.[3,4] However, there is a lack of interfacial tension data for polymer + polymer ATPS. As far as we know, there is no interfacial tension experimental data for PEG + MD ATPS available in the literature.

The methods for interfacial tension determination can be divided in static (as in the pendant drop technique) and dynamic (as in the spinning drop technique), which was originally introduced by Vonnegut.[5] The spinning drop technique is suitable for systems that present very low interfacial tension values.

Table 1. PEG + MD + Water System Composition

system	w_{PEG}	w_{MD}	M/g·mol^{-1}	system	w_{PEG}	w_{MD}	M/g·mol^{-1}
S_1	12	20	4000	S_6	10	30	8000
S_2	12	20	6000	S_7	8	35	4000
S_3	12	20	8000	S_8	8	35	6000
S_4	10	30	4000	S_9	8	35	8000
S_5	10	30	6000				

Forciniti et al.[6] used the spinning drop technique to study interfacial tension for PEG + dextran (DEX) ATPS. The authors reported a detailed investigation of interfacial tension as a function of temperature, polymer concentration, and PEG + DEX molar mass. The rotational speed range for interfacial tension measurement of each phase was over (2000 to 7000) rpm to guarantee that gyrostatic equilibrium was reached. For systems of the same tie line length, the authors reported an interfacial tension rise on the molar mass increase of one polymer. The authors obtained a linear correlation between the logarithm of the interfacial tension and the difference in DEX concentration between top and bottom phases. The same kind of behavior was also reported for the logarithm of interfacial tension and the difference in PEG concentration between top and bottom phases. Very low values for interfacial tension were found, between ($1.5 \times 10{-}3$ and 0.35) mN·m^{-1}, when compared to other organic extraction systems. For instance, the systems composed of hexane + water, glycerin + hexane, and toluene + water presented interfacial tension values equal to 48.5 mN·m^{-1}, 34.9 mN·m^{-1}, and 35.7 mN·m^{-1}, respectively.[7]

The first report regarding interfacial tension for ATPS was published by Ryden and Albertsson.[8] It analyzed the effect of the tie-line length (TLL) on interfacial tension for PEG + DEX systems, finding a linear relationship between the logarithm of the interfacial tension and the TLL values. The TLL was defined as $[(\Delta PEG)^2 - (\Delta DEX)^2]^{0.5}$, in which ΔPEG and ΔDEX are, respectively, the difference of compound concentration (PEG and DEX) in the two coexisting phases. For such a kind of system: (a) Bamberger et al.[9] studied the interfacial tension

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Table 2. Interfacial Tension for PEG + MD + Water System

n/rpm	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
				γ/mN·m^{-1}					
2000	0.045	0.067	0.094	0.045	0.070	0.106	0.030	0.063	0.081
2500	0.048	0.067	0.085	0.053	0.072	0.105	0.032	0.066	0.086
3000	0.048	0.071	0.090	0.066	0.079	0.117	0.036	0.069	0.082
3500	0.053	0.074	0.090	0.067	0.090	0.124	0.039	0.070	0.086
4000	0.051	0.077	0.102	0.075	0.094	0.129	0.041	0.076	0.090
4500	0.051	0.075	0.093	0.066	0.098	0.131	0.042	0.083	0.091
5000	0.054	0.076	0.092	0.089	0.099	0.138	0.048	0.085	0.095
				γ_{AV}/mN·m^{-1}					
	0.050	0.072	0.092	0.065	0.086	0.121	0.038	0.073	0.087
				σ/mN·m^{-1}					
	0.0032	0.0042	0.0052	0.0014	0.0012	0.0012	0.0064	0.0085	0.0050
				$\Delta\rho$/g·cm^{-3}					
	0.1080	0.1057	0.1032	0.9520	0.1041	0.1137	0.7840	0.1029	0.1030

behavior for different salt concentration. (b) Schluck et al.[10] determined the influence of ionic strength and pH on interfacial tension, verifying a significant interfacial tension increase at high pH values. (c) Wu and Zhu[11] developed a model for interfacial tension prediction by using Forciniti et al.[6] experimental data. The model was able to predict low values of interfacial tension like (1.0×10^{-4} to 1.0) mN·m^{-1}. Some interfacial tension data for PEG + salt systems, from (1.0×10^{-3} to 1.26) mN·m^{-1}, are reported in the literature.[12,13]

Concerning the PEG + MD ATPS viscosity, Szlag and Giuliano[3] and Rao et al.[4] presented some results for PEG (8000 g·mol^{-1}) + MD (1200 g·mol^{-1}, 1800 g·mol^{-1}, and 3600 g·mol^{-1}) and PEG (8000 g·mol^{-1}) + MD (1800 g·mol^{-1}) systems, respectively. A viscosity rise at higher polymer concentration was reported, and also it was observed that the viscosity value of the bottom phase (rich in MD) was higher than the viscosity value of the top phase (rich in PEG). Venâncio et al.[14] verified, for PEG + hydroxypropyl starch (HPS) systems, very high viscosity values for the HPS-rich phase as compared to the PEG-rich phase. Other studies involving PEG + salt ATPS showed that PEG-rich phase viscosities are higher than the viscosity values of the other phase.[15−17] The present study aimed to determine interfacial tension and viscosity data for aqueous two-phase systems composed by PEG (with different molar mass) and MD at 30 °C.

Experimental Section

Materials. The reagents used were MD (2800 g·mol^{-1}, RMB, Brazil) with polydispersity index of 2.85 (previously determined by size exclusion chromatography) and PEG of 4000 g·mol^{-1} (ISOFAR, Brazil), 6000 g·mol^{-1} (ISOFAR, Brazil), and 8000 g·mol^{-1} (Sigma-Aldrich, St. Louis, MO).

Aqueous Two-Phase Systems. PEG + MD ATPS were prepared from stock solutions of PEG and MD with mass fraction (w) equal to 0.50. Appropriate quantities of water, previously distilled and deionized with a Milli-Q device (Millipore, Bedford, MA), and stock solutions of PEG and MD were added to a beaker in order to obtain 200 g of the system. The mixture was magnetically mixed for 2 h. The system was further transferred to a conical separator funnel where the mixture was allowed to settle for 12 h, at 30 °C, to obtain clear phase separation and to reach the equilibrium condition. Phase density measurements were made in triplicate by pycnometry. The pycnometer was previously calibrated with water at the operational temperature (30 °C). The temperature control for each sample was made within ± 0.01 °C by a thermostatic water bath.

Interfacial Tension. The interfacial tension was obtained by using a spinning drop tensiometer (KRÜSS-GmbH, Germany). The experiment was conducted at 30 °C to avoid the MD jellification, which may occur below 28 °C. The experiment was made in triplicate for each system and each rotational speed by the following procedure: (a) The tensiometer temperature was stabilized within ± 0.01 °C by using a thermostatic oil bath. (b) The heavy phase (rich in MD) was gently introduced into a capillary to avoid bubble formation and remaining air presence. (c) The capillary rotation speed was adjusted through the speed controller, and 10 μL of the light phase (rich in PEG) was injected in the capillary, using a microsyringe. The formed drop was centralized on the eyepiece. (d) The lens focus for the drop visualization was found in each measurement. The scale zero point for the diameter reading was coincidentally adjusted with the drop bottom limit. (e) The rotation speed was adjusted for each operational velocity (2000, 2500, 3000, 3500, 4000, 4500, and 5000) rpm. After 10 min, the drop diameter was read with the diameter scale of the instrument, whose unit sdv means scale diameter value.

The PEG + MD ATPS interfacial tension was determined by the Vonnegut equation,[5] as follows:

$$\gamma = e \times (\upsilon \times d)^3 \times n^2 \times \Delta\rho \qquad (1)$$

where γ is the interfacial tension (mN·m^{-1}), e is a constant value (3.427×10^{-6} mN·min^2·mm^{-1}·g^{-1}), υ is a correction factor (0.167 mm·sdv^{-1}), d is the drop diameter measured in the instrument unit (sdv), n is the rotational speed (rpm), and $\Delta\rho$ is the density difference between each phase (g·cm^{-3}).

Princen et al.,[18] studying the relation between the spinning drop shape and interfacial tension, concluded that the Vonnegut equation can be used for systems at high rotation speed. This equation was originally proposed to be applied for a cylindrical drop with hemispherical ends.

Viscosity. The viscosity of each phase of PEG + MD systems, at 30 °C, was measured within ± 0.01 mPa·s by using a rolling ball viscosimeter (Haake-GmbH, Germany). Each viscosity measurement was made in triplicate. The operational temperature was controlled within ± 0.01 °C with a thermostatic water bath.

Results and Discussion

Interfacial Tension. Table 1 shows PEG mass fraction (w_{PEG}), MD mass fraction (w_{MD}), and PEG molar mass (M) for each analyzed system. Table 2 shows the interfacial tension (γ) for PEG + MD ATPS, the average interfacial tension (γ_{AV}), the correspondent standard deviation (σ), and the phase density difference ($\Delta\rho$) for each system and each rotational speed (n) analyzed, adding up 72 measurements. The average interfacial tension was determined as an arithmetic media between

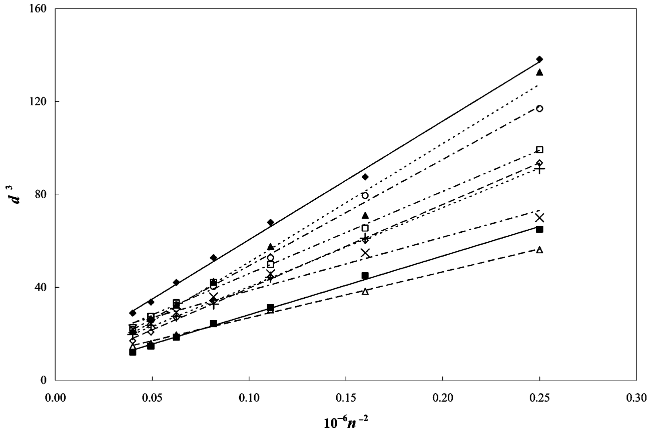

Figure 1. Variation between the (square of rotational speed)$^{-1}$ (n^{-2}) and the cube of drop diameter (d^3) for PEG + MD aqueous two-phase systems: ■, system 1; ◇, system 2; ▲, system 3; ×, system 4; □, system 5; ◆, system 6; △, system 7; +, system 8; ○, system 9.

interfacial tension values at (2000, 2500, 3000, 3500, 4000, 4500, and 5000) rpm. The mean standard deviations found for density and interfacial tension experimental data were of 0.0010 g·cm^{-3} and 0.0025 mN·m^{-1}, respectively.

Figure 1 shows the variation between the (square of rotational speed)$^{-1}$ (n^{-2}) and the cube of drop diameter (d^3) for each system. The linearity presented by each fit demonstrated that gyrostatic equilibrium approached closely enough to possibility the application of eq 1. The linear regression leads to a R^2 superior than 0.94 for all systems. If drop length (l) exceeds 8× its equatorial radius, the simplest operational criterion is the constancy of the product ($n^2 \cdot d^3$) when n is varied.

The results obtained by using eq 1 present a negligible elevation in interfacial tension when the rotational speed was increased. Each average interfacial tension was considered as the value of interfacial tension for the corresponding system. Kim and Rha[12] found the same behavior of interfacial tension for PEG + salt aqueous two-phase systems. The authors observed that the interfacial tension became constant for rotational speed values above 2500 rpm.

Our experimental data, (0.038 to 0.121) mN·m^{-1}, are in good agreement with the range of values found by Ryden and Albertsson[8] for PEG + DEX aqueous two-phase systems of (5.0×10^{-3} to 0.7) mN·m^{-1}.

Kim and Rha[12] also used the spinning drop technique to study the interfacial tension for PEG + salt aqueous two-phase systems, observing an elevation of interfacial tension on the concentration increment of both PEG and salt (potassium phosphate) and on the increase of PEG molar mass. Mishima et al.[13] analyzed the effect of polymer molar mass and temperature on the interfacial tension for PEG + dibasic potassium phosphate aqueous two-phase systems, using the drop volume technique. The temperature effect was not significant, meaning that entropy is probably the main factor governing the process occurring at interface. However, it was reported an interfacial tension rise on the increment of the tie-line length and PEG molar mass.

Figure 2 shows, for our PEG + MD aqueous two-phase systems, the effect of PEG molar mass on interfacial tension. It was observed, for all analyzed systems, that the higher the PEG molar mass, the higher the interfacial tension values.

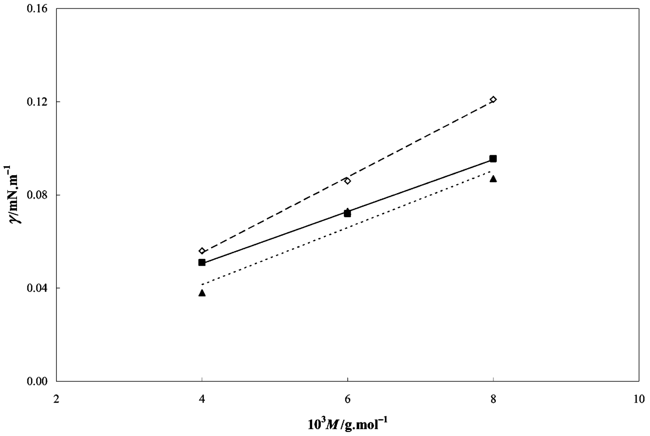

Figure 2. Effect of PEG molar mass (M) on the interfacial tension (γ) of PEG + MD aqueous two-phase systems: ■, PEG (w = 0.12) + MD (w = 0.20); ◇, PEG (w = 0.10) + MD (w = 0.30); ▲, PEG (w = 0.08) + MD (w = 0.35).

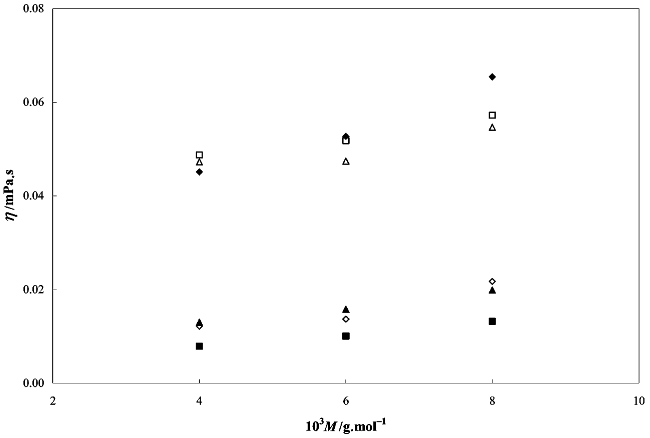

Figure 3. Effect of PEG molar mass (M) on the viscosity (η) of PEG + MD aqueous two-phase systems: ■, PEG (w = 0.12) + MD (w = 0.20) TP; ◇, PEG (w = 0.10) + MD (w = 0.30) TP; ▲, PEG (w = 0.08) + MD (w = 0.35) TP; □, PEG (w = 0.10) + MD (w = 0.30) BP; ◆, PEG (w = 0.12) + MD (w = 0.20) BP; △, PEG (w = 0.08) + MD (w = 0.35) BP. (TP, top phase; BP, bottom phase).

Viscosity. The mean standard deviation found for the viscosity experimental data was 0.02 mPa·s. Figure 3 presents the viscosity of the bottom (rich in MD) and the top (rich in PEG) phases, as a function of PEG molar mass. The bottom phase viscosity was greater than the top phase viscosity, and there was observed a fairly viscosity rise on the PEG molar mass increase. This behavior was also described by Szlag and Giuliano,[3] who reported a viscosity difference of approximately 4.6×10^{-2} Pa·s for systems composed by PEG 8000 g·mol^{-1} + MD 1800 g·mol^{-1}. Venâncio et al. [14] obtained a viscosity difference of approximately 2.7×10^{-1} Pa·s for PEG + HPS ATPS. The bottom phase (rich in HPS) presented very high viscosity values. Figure 3 also shows that the rise of PEG molar mass increased the viscosity of the two phases, with a higher impact over the bottom phase (rich in MD). This effect is possibly due to an elevation of MD concentration in the bottom phase. Szlag et al. [3] observed the same behavior for the bottom phase of PEG + MD ATPS at 25 °C.

Kaul et al.[16] measured, for PEG + potassium phosphate aqueous two-phase systems, viscosity values of 1.98×10^{-2} Pa·s and 2.77×10^{-3} Pa·s for the polymeric phase and the salt phase, respectively. We found viscosity values of 2.50×10^{-2} Pa·s and 2.50×10^{-3} Pa·s for the polymeric phase and the salt phase, respectively, with aqueous two-phase systems composed of PEG 1500 (w = 0.18) + potassium phosphate (w = 0.18).

Conclusions

The interfacial tension and viscosity study for aqueous two-phase systems, composed of PEG with different molar mass and MD, shows that the Vonnegut equation fit very well the experimental data for interfacial tension calculation for all systems analyzed. Also for all systems, the increase of interfacial tension on the PEG molar mass increase was observed. Concerning viscosity, it was verified that the MD-rich phase presented a higher viscosity than the PEG-rich phase and that increasing the PEG molar mass also increased the viscosity.

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