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Volumetric and Surface Tension Behavior of Aqueous Solutions of Polyvinylpyrrolidone in the Range (288 to 303) K

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ABSTRACT: Experimental results have been obtained for the equilibrium liquid–vapor surface tension of the binary system composed of water + polyvinylpirrolidone (PVP). In this work we studied two different samples of PVP, at concentrations of (0.000002, 0.000018, 0.000102, 0.000499, 0.000999, 0.002003, 0.003018, 0.004021, and 0.005111) mass fraction of the polymer, at (288.15, 293.15, 298.15, and 303.15) K. The density has also been determined experimentally, for the same aqueous solutions in the same temperature range studied of surface tension, using two Anton Paar vibrating-tube densimeters (models DMA 60 and DMA 4500M). The values of the surface tension of the binary system decrease as the PVP concentration increases and as the temperature increases. The surface tension results of the binary system were correlated simultaneously as a function of temperature and PVP concentration. From the density results, the partial molar volume and the infinite dilution partial molar volume of the polymer have been calculated, which were correlated successfully with a general equation which takes into account the influence of the polymer concentration and temperature.

INTRODUCTION

Surface tension of water-soluble polymers is an important thermodynamic property, which characterizes interfaces between two miscible substances, frequently encountered in many scientific, technological, and industrial applications. Many research groups have focused their attention on obtaining information on the thermodynamic properties of aqueous solutions containing a macromolecular nonelectrolyte compound as solute since such properties are important for understanding solute–solvent and solute–solute interactions. They can give an indirect insight into the conformational features of the polymer, which is often used in biotechnical, biomedical, and other industrial applications.[1,2] Several research groups have determined thermodynamics properties of a class of nonionic water-soluble polymers such as polyvinylcaprolactam (PVCAP)[3] and polyvinylpyrrolidone (PVP)[4] because these polymers possess important properties such as good resistance to hydrolysis,[5] formation of complexes with dyes and proteins.[6] PVCAP is distinguished by its complete miscibility in water at low temperatures and phase separation at higher temperatures with a lower consulate temperature.[7] PVP binds to polar molecules exceptionally well, owing to its polarity, which has led to application in coatings for photoquality inkjet papers and transparencies, as well as, in inks for inkjet printers. PVP is also used in the formulation of personal care products, such as shampoos, hair sprays, and toothpastes. Figure 1 shows the structural formula of PVP, the latter is also known as [2-pyrrolidinone, 1-ethynyl-homopolymer]. Thermodynamic properties such as density and viscosity of this nonionic water-soluble polymeric cyclicamide have been reported in the literature as a function of concentration and temperature: PVP (average molar mass of 10 000 $g \cdot mol^{-1}$);[8] PVP10, PVP50, PVP1000, and PVP 1000FL (average molar mass of (9411, 57 980, 97 3500, and 1 146 000) $g \cdot mol^{-1}$, respectively);[9] PVP (average molar mass of 10 000 $g \cdot mol^{-1}$) + methanol, + ethanol, or +1-propanol;[10] PVP (average molar mass of 10 000 $g \cdot mol^{-1}$).[11] Other thermophysical properties such as surface tension, interfacial tension and dynamic surface tension have also been reported for: PVP (average molar mass of 1 300 000 $g \cdot mol^{-1}$);[12] PVP10 and PVP55 (average molar mass of (10 000 and 55 000) $g \cdot mol^{-1}$, respectively);[4] PVP (average molar mass of 40 000 $g \cdot mol^{-1}$);[13] PVP K30 and PVP K12 (average molar mass of (44 000 and 5000) $g \cdot mol^{-1}$, respectively);[14] and PVP (average molar mass of 29 000 $g \cdot mol^{-1}$).[15]

Currently our laboratory has undertaken a project to study the complex phase transition and inhibition of natural gas chlatrates hydrates. Several different substances with surface active properties are being studied as low dose kinetic inhibitors (LDKI) and as antiagglomerants of hydrates to evaluate the most effective electrolyte and nonelectrolyte compounds, pure and mixed, for specific applications in the oil and gas industries, since hydrate plugs often occur in oil and gas transportation pipelines leading to highly dangerous and costly blockages.[16] Economic and environmental concerns suggest that low dosage hydrate inhibitors, including kinetic inhibitors and antiagglomerants, should be selected for solving the question of the hydrate plugs.[17] PVP is a homopolymer that can be studied to determine its characteristics as LDKI.

Hence, reliable data, either experimental or predicted, on hydrate plug location are very important for the continuous operation of deep oil production together with natural gas processing units. Other areas of interest related to the study of hydrates include storage of natural gas, sequestration of CO_2 on the ocean floor, and separation of greenhouse gas from flue gas. However, although the kinetics of hydrates formation is understood, the inhibition mechanism of kinetic inhibitors is not very clear yet. The initial hydrate formation usually occurs at the gas–liquid interface,[18–20] which clearly indicates that the gas–liquid interfacial tension plays an

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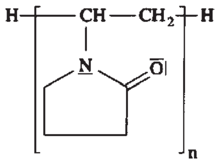

Figure 1. Formula of polyvinylpyrrolidone.

important role in the different stages of hydrate formation processes. The experimental investigation of interfacial tension at the gas−liquid interface of selected systems is capable of providing helpful information for revealing the mechanism of hydrate formation and inhibition. However, interfacial tension data near hydrate formation conditions for different systems are relatively scarce in the literature.

Therefore, because of the lack of reports on the thermophysical properties of systems which are of interest for the study of hydrates, particularly of aqueous polymers which are of scientific and industrial interest, in this study we have measured density and surface tension of the binary systems formed by water + PVP at concentrations of (0.000002, 0.000018, 0.000102, 0.000499, 0.000999, 0.002003, 0.003018, 0.004021, and 0.005111) mass fraction of the polymer, at (288.15, 293.15, 298.15, and 303.15) K, under atmospheric pressure. The concentration of the polymer studied in this work is relatively low because of its possible use as a LDKI, hence to make it economically profitable.

EXPERIMENTAL SECTION

Materials. Two samples of PVP were employed in this work: PVP10 with general formula $(C_6H_9NO)_x$, also known as polyvidone and povidone, (average molar mass of 10 000 $g \cdot mol^{-1}$) was obtained from Sigma-Aldrich, lot 1117K0692 (CAS No. 9003-39-8), and PVP K15 (average molar mass of 10 000 $g \cdot mol^{-1}$) which was obtained as a gift from International Specialty Products Mexico (ISP), lot 05500136852. Water was obtained from EMD Chemical Inc., HPLC grade (lot 47115). The ethylene glycol used in the calibration of the densimeter was obtained from Merck with a mole purity of 99.5 % (lot 5001KPGK), heptane and pentane were obtained from Aldrich with a mole purity of > 99.5 % (lots 03355DQ and 12870CO, respectively). Diethanolamine and hexadecane for density tests were obtained from J.T. Baker with a mole purity of 99.9 % (lots 9227-03 and N105-07, respectively).

Preparation of Solutions. All of the binary solutions of known concentration were prepared by mass in sealed vials using an electronic Sartorius analytical balance (model 2006 MP) with a precision and accuracy of ± 0.0001 g. The values for the studied systems have an uncertainty of ± 0.02 % in mass fraction.[21] The polymer was used without further purification. The water was degassed before use for calibration or mixture preparation purposes, utilizing an ultrasound bath for a period of one hour. Both the polymer and water were charged in sealed vials with a magnetic bar that allows stirring of the sample with the aid of a Thermolyne Sybron heating and stirring plate. The equilibrium solubility process for each binary system was established after a stirring period of 48 h.[22]

Density. Density values were obtained using two Anton Paar vibrating-tube densimeters (models DMA 60 and DMA 4500 M), which work under the technique of the mechanical oscillator developed by Kratky and co-workers.[23] The temperature of the samples in the DMA 60 densimeter was controlled by means of a PolyScience, model 9501, digital refrigerated circulating bath within ± 0.002 K of the reported values and measured in thermowells at the rear inlet and exit of the densimeter with a digital thermometer Systemteknik AB, model S1220, with a platinum resistance probe with a precision of ± 0.001 K. The readings from this thermometer were compared with those from a calibrated Hart Scientific thermometer (model 1529 Chub-E4) whose accuracy is ± 0.005 K, traceable to the U.S. NIST (National Institute of Standards and Technology). The achieved accuracy for the temperature measurements through narrow range comparisons with the reference thermometer was ± 0.02 K.

The DMA 60 was calibrated at each studied temperature with both dry nitrogen and ethylene glycol, whose density as a function of temperature were obtained from the literature.[24,25] The working equation of the densimeter is

$$\rho = A + B\tau^2 \tag{1}$$

where ρ is the density in $kg \cdot m^{-3}$ of the system under study, A and B are constants obtained from the calibration at a given temperature, and τ is the vibrating period of the densimeter corresponding to the system under study.

For each temperature studied, the reported density results for both pure solvents and solutions of known concentration were obtained from the average period of vibration, which was in turn obtained from at least 20 stable measurements, with a stability of ± 0.0005 ms^{-1}, so that with that average value and the parameters A and B from the calibration, the density corresponding to each sample was determined. The final uncertainty of the density results was evaluated through a complete statistical analysis on the propagation of uncertainties for all the known variables involved that considered the use of the so-called Student's t distribution. Therefore, the uncertainty reported in this work was always determined with a 95 % confidence for the best values of density experimentally determined. The estimated combined uncertainty for the experimental density values of this work is ± 0.02 % in the ranges of both concentration and temperature.[26,27]

The DMA 4500 M densimeter also works under the oscillating U-tube method for obtaining density values.[28−30] The sample is introduced into a U-shaped borosilicate glass tube that is being excited electronically to vibrate at its characteristic frequency. The characteristic frequency changes depending on the density of the sample. Through a precise determination of the characteristic frequency and a mathematical conversion, the density of the sample can be measured. The instrument uses two integrated Pt 100 platinum thermometer together with Peltier elements which provide an extremely precise thermostatting of the sample. The DMA 450 M provides density values with an accuracy of ± 0.05 $kg \cdot m^{-3}$ and repeatability of ± 0.01 $kg \cdot m^{-3}$.

The DMA 4500 M readings were validated at each studied temperature with heptane,[31,32] hexadecane,[33−35] and ethylene glycol,[25,32,36,37] whose density values as a function of temperature were obtained from the literature.

Surface Tension. Equilibrium surface tension values were obtained with the pendant drop method using a FTA200 contact angle system.[21,38,39] The main components of the apparatus include a light source, a computer-controlled dosing system, a thermal cell with cuvette, and a video system mounted on an optical platform which shows live on the computer screen the pendant drop of the system under study, so that the images are captured for analysis with a special software for fitting the

Table 1. Comparison of Density (ρ/kg·m^{-3}) Values of Two Pure Compounds, at Different Temperatures[a]

T		ρ						AARD
		kg·m^{-3}						
K	substance	this work	ref 31	ref 32	ref 40	ref 41	ref 33	%[b]
288.15	pentane	630.5				630.62		0.019
293.15		625.6		626.24		625.75	626.2	0.074
298.15		621.1		621.39		620.83	621.3	0.040
288.15	water	999.2		999.101				0.009
298.15		997.2	997.210	997.047				0.008
303.15		995.8	995.805	995.650	995.7	995.7		0.010
								0.027

[a] All measurements performed with densimeter DMA 60. [b] Average absolute relative deviation in percent.

Table 2. Comparison of Density (ρ/kg·m^{-3}) Values of Aqueous Solutions of Diethanolamine (DEA) at Different Concentrations, at 293.15 K[a]

C_{DEA}	T	ρ		ARD
		kg·m^{-3}		
% in mass	K	this work	ref 42	%[b]
10	293.15	1011.0	1010.1	0.089
20	293.15	1021.6	1022.0	0.039
30	293.15	1034.0	1034.2	0.019

[a] All measurements performed with densimeter DMA 60. [b] Absolute relative deviation in percent.

Laplace–Young equation to the drop shape coordinates. The automatic image analysis that allows obtaining accurate surface tension values is based on the following working equation:

$$\gamma = \frac{\Delta\rho g(d_e)^2}{H} \tag{2}$$

where $\Delta\rho$ is the difference of density between the liquid under study and vapor, g the local acceleration of gravity, d_e the maximum diameter of the pendant drop, and $1/H$ is the form factor calculated by the software.

The temperature of the samples was controlled by means of a PolyScience (model 9501) digital refrigerated circulating bath with a thermometer Systemteknik AB, model S1220, with a platinum resistance probe with a precision of ± 0.001 K. The readings from this thermometer in the studied range were compared with those from the reference thermometer cited above. The obtained accuracy for the temperature measurements with the Systemteknik thermometer was ± 0.02 K.

In this work, for obtaining each set of measurements of surface tension, under constant temperature, the apparatus was previously calibrated using a reference system whose density and surface tension values are accurately known. Water was used as reference throughout the range of temperature studied.[21,22,32,33]

The experimental surface tension value reported in this work for each studied aqueous system of known concentration corresponds to an average of 100 values determined from the images analysis. These values were obtained for 10 fresh drops, and in turn 10 values of the surface tension are obtained for each drop. After carrying out an error analysis it was estimated that the reported surface tension values have an uncertainty of ± 0.18 mN·m^{-1}.[21,22,38,39]

■ RESULTS AND DISCUSSION

Density. The accuracy of the experimental results obtained in this work was established through the determination of the density of two pure compounds (pentane and water), and of aqueous solutions of (10, 20, and 30) % in mass of DEA, at (288.15, 293.15, 298.15, and 303.15) K for pentane and water and 293.15 K for the aqueous solutions, respectively. These systems were studied with the Anton Paar densimeter model DMA 60. Tables 1 and 2 present the density results for the pure compounds and the aqueous solutions, respectively. The Tables also include data previously reported in the literature for comparison purposes. It can be observed that our results for pentane and water present an absolute mean deviation with respect to the data reported by Muhammand et al.,[31] Riddick and Bunger,[32] Pery and Chilton,[40] NIST,[41] and Vargaftik[35] that guarantee an accuracy of ± 0.027 %, and for the aqueous solutions of DEA the comparison gives an absolute deviation with respect to the data reported by Rinker et al.[42] of ± 0.089 % at 10 % in mass, ± 0.039 % at 20 % in mass, and of ± 0.019 % for 30 % in mass. These values are of the same order of magnitude as the estimated combined uncertainty for our experimental density results given above.

To establish the accuracy of the experimental results obtained in this work with the Anton Paar densimeter, model DMA 4500 M, we determined the density for three pure compounds in the temperature range from (288.15 to 303.15) K. Table 3 presents the density results for the pure compounds. The Table also includes data previously reported in the literature for comparison purposes. It can be observed that our results for heptane have an absolute mean deviation with respect to the data reported by Riddick and Bunger[32] and NIST[41] of 0.008%, for hexadecane our results have an absolute mean deviation of 0.011 % with respect to the data reported by Bolotnikov et al.[34] Vargaftik.,[33] and API,[35] whereas for ethylene glycol have an absolute mean deviation of 0.007 % with respect to the data reported by George and Sastry,[25] Riddich and Bunger,[32] Azizian and Bashavard,[36] and Tsierkezos and Molinou.[37] These values are of the same order of magnitude as the estimated combined uncertainty for our experimental density results given above.

We have obtained in this work new experimental results for the density of aqueous solutions of PVP K15 at concentrations of (0.000002, 0.000018, 0.000102, 0.000499, 0.000999, 0.002003, 0.003018, 0.004021, and 0.005111) mass fraction of the polymer obtained from ISP. The studied temperatures are (288.15, 293.15, 298.15, and 303.15) K, under atmospheric pressure, using two Anton Paar densimeters, DMA 60 and DMA 4500 M. The results of density given in Table 4 were obtained with densimeter model DMA 60 whereas Table 5 gives the experimental results of density obtained with densimeter DMA 4500 M.

Figure 2 shows the experimental results of density obtained with densimeter DMA 60. It is possible to observe in this figure that the density results of the aqueous PVP K15 solutions studied show a linear dependence with PVP concentration. Since the density of pure water is always lower than that corresponding to aqueous PVP solutions in the range of temperature considered, then the density values of the studied solutions increases as the PVP concentration

Table 3. Comparison of Density ($\rho/\mathrm{kg\cdot m^{-3}}$) Values of Three Pure Compounds, at Different Temperatures[a]

system	T	ρ								AARD
	K	$\mathrm{kg\cdot m^{-3}}$ this work	ref 32	ref 41	ref 36	ref 33	ref 37	ref 38	ref 25 and 35	%[b]
heptane	288.15	688.1		688.02						0.012
	293.15	683.8	683.76	683.82						0.004
	298.15	679.6	679.51	679.60						0.007
hexadecane	303.15	766.6			766.55	766.5	766.5			0.011
ethyleneglycol	288.15	1116.9	1117.1							0.018
	293.15	1113.4	1113.5					1113.34	1113.23	0.010
	298.15	1109.9	1110.0					1109.87	1109.96	0.006
	303.15	1106.4	1106.6					1106.36		0.011

[a] All measurements performed with densimeter DMA 4500M. [b] Average absolute relative deviation in percent.

Table 4. Experimental Density ($\rho/\mathrm{kg\cdot m^{-3}}$) Results for Aqueous Solutions of PVP K15, as a Function of Temperature[a]

C_{PVP}		288.15 K	293.15 K	298.15 K	303.15 K
		ρ	ρ	ρ	ρ
mass fraction	$x_2\cdot 10^6$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{kg\cdot m^{-3}}$
0.000002	0.0036	999.1	998.2	997.0	995.7
0.000018	0.0324	999.1	998.2	997.1	995.7
0.000102	0.184	999.1	998.2	997.1	995.7
0.000499	0.899	999.2	998.3	997.2	995.7
0.000999	1.8	999.3	998.4	997.3	995.9
0.002003	3.61	999.5	998.6	997.5	996.1
0.003018	5.44	999.7	998.9	997.7	996.3
0.004021	7.25	1000.0	999.1	997.9	996.5
0.005111	9.21	1000.2	999.3	998.1	996.8

[a] All measurements performed with densimeter DMA 60.

Table 5. Experimental Density ($\rho/\mathrm{kg\cdot m^{-3}}$) Results For Aqueous Solutions of PVP K15, as a Function of Temperature[a]

C_{PVP}		288.15 K	293.15 K	298.15 K	303.15 K
		ρ	ρ	ρ	ρ
mass fraction	$x_2\cdot 10^6$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{kg\cdot m^{-3}}$	$\mathrm{kg\cdot m^{-3}}$
0.000002	0.0036	999.3	998.4	997.2	995.8
0.000018	0.0324	999.3	998.3	997.2	995.8
0.000102	0.184	999.3	998.4	997.2	995.8
0.000499	0.899	999.3	998.4	997.3	995.9
0.000999	1.8	999.5	998.6	997.4	996.0
0.002003	3.61	999.6	998.6	997.5	996.1
0.003018	5.44	999.7	998.8	997.5	996.1
0.004021	7.25	1000.0	999.1	997.9	996.5
0.005111	9.21	1000.0	999.1	997.9	996.5

[a] All measurements performed with densimeter DMA 4500M.

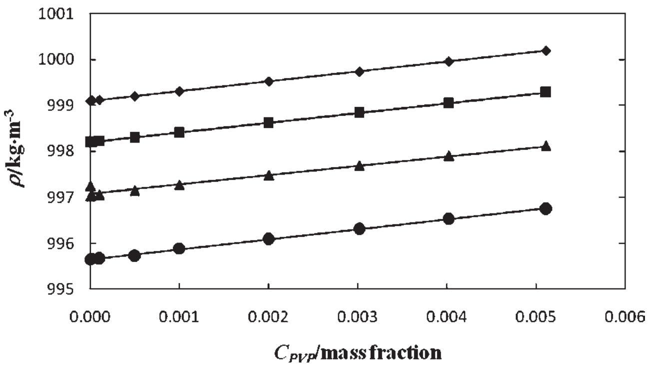

Figure 2. Experimental density (ρ) results of this work for aqueous solution of PVP K15 as a function of concentration, at different temperatures: ◆, 288.15 K; ■, 293.15 K; ▲, 298.15 K; ●, 303.15 K. The full lines represent calculated values with a first-degree equation. All measurements performed with densimeter DMA60.

increases, whereas for a given known concentration of the aqueous solution the density decreases as the temperature increases.

On the other hand, to establish if the source of the polymer could be a possible cause for giving different density values it was necessary to determine the density of aqueous solutions of the polymer PVP10, obtained from Sigma-Aldrich. The circumstantial arrival of the densimeter DMA 4500 M to our laboratory led us to perform the study of a second sample of PVP, at 298.15 K and nine different concentrations.

The experimental density results are shown in Table 6[23,26,27] together with a set of results for the PVP K15 sample. From the results in Table 6 it is possible to observe that there is a very small difference between both sets of values, since the average absolute relative deviation is 0.01 % for the density values obtained at nine different concentrations with both densimeters. These results allow concluding that both samples can be considered to be essentially the same.

This test is of high relevance when considering that very large amounts of LDKI's are used in the oil industry to ensure the flow of hydrocarbons, hence if a change of manufacturer involves different properties of the inhibitors then the risk of hydrate appearance can lead to disastrous effects.

Equilibrium Surface Tension. To establish the accuracy of the experimental results obtained in this work, we have determined the surface tension for aqueous solutions of DEA at three concentrations (10, 20, and 30) % in mass, at 293.15 K. Table 7 contains a comparison between our experimental results of surface tension and those reported by Águila-Hernández et al.[38] and Rinker et al.[42] It can be observed that our results present relative mean deviations of 0.19 % at 10 % in mass, 0.15 % at 20 % in mass, and 0.19 % at 30 % in mass, which is of the same order of magnitude as the experimental uncertainty.

After having established that the two samples of PVP present the same density behavior, the equilibrium surface tension was

Table 6. Comparison of Density (ρ/kg·m^{-3}) Results of Aqueous Solutions of PVP K15, Obtained From ISP, and PVP10, Obtained From Sigma-Aldrich, at Nine Different Concentrations, at 298.15 K

		ρ
		kg·m^{-3}
C_{PVP}	DMA 60	DMA 4500M
mass fraction	ISP	Sigma-Aldrich
0.000002	997.0	997.2
0.000018	997.1	997.2
0.000102	997.1	997.2
0.000499	997.2	997.3
0.000999	997.3	997.4
0.002003	997.5	997.6
0.003018	997.7	997.8
0.004021	997.9	998.0
0.005111	998.1	998.2
AARD/%		0.01

Table 7. Comparison of Surface Tension (γ) Values for Aqueous Solutions of Diethanolamine (DEA), as a Function of Concentration and Temperature

		γ			
		mN·m^{-1}			
C_{DEA}	T				ARD
% in mass	K	this work	ref 34	ref 35	%[a]
10	293.15	63.98	64.14	63.90	0.19
20	293.15	66.55	66.45		0.15
30	293.15	61.77	61.84	61.94	0.19
AARD/%					0.18

[a] Absolute relative deviation in percent.

determined for aqueous solutions of PVP, at concentrations of (0.000002, 0.000018, 0.000102, 0.000499, 0.000999, 0.002003, 0.003018, 0.004021, and 0.005111) mass fraction of PVP K15, obtained from ISP, at (288.15, 293.15, 298.15, and 303.15) K. It was observed that the surface tension values obtained at relatively short time after having formed the pendant drop were not constants, hence, after several tests to establish the equilibrium of the binary system it was concluded that the surface tension values were constant, repeatable, and reproducible for measurements taken 30 min after formation of the liquid−vapor interface. The surface tension results are given in Table 8 and plotted as a function of PVP K15 concentration in Figure 3. It is observed that the surface tension results, at the four temperatures, decrease when the PVP K15 concentration increases in the low concentration range [i.e., (0.000002 to 0.000102) mass fraction], whereas from 0.000499 mass fraction of PVP K15 the surface tension results are constant, within the experimental uncertainty, throughout the rest of concentration range studied. This behavior is reminiscent of the equilibrium surface tension-concentration profiles observed with typical surfactants at the critical micelle point. From the results in Table 8 it is observed that the rate of change of the values of surface tension with temperature is larger than that with the polymer concentration. To obtain these values of surface tension we employed the density results from densimeter DMA 4500 M.

Table 8. Experimental Results of the Equilibrium Surface Tension (γ) for Water (1) + PVP K15 (2), as a Function of Polymer Concentration and Temperature[a]

	γ			
C_{PVP}	mN·m^{-1}			
mass fraction	288.15 K	293.15 K	298.15 K	303.15 K
0	73.56	72.58	71.84	71.04
0.000002	73.18	69.96	69.42	68.35
0.000018	71.48	69.77	69.17	65.61
0.000102	71.09	69.71	68.38	65.59
0.000499	71.15	69.84	68.36	65.56
0.000999	71.19	69.82	68.45	65.67
0.002003	71.15	69.85	68.45	65.69
0.003018	71.18	69.79	68.42	65.57
0.004021	71.16	69.81	68.37	65.59
0.005111	71.13	69.76	68.42	65.73

[a] All measurements taken 30 min after formation of the interface.

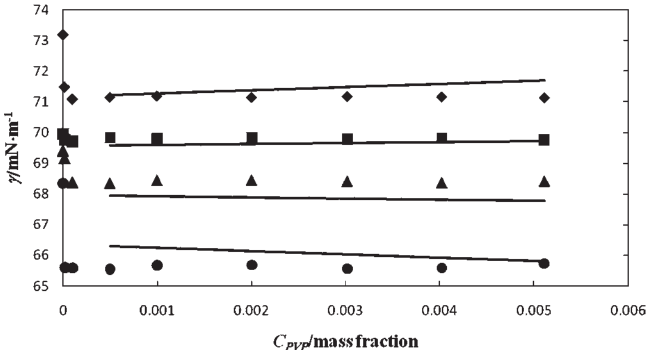

Figure 3. Experimental results of the equilibrium surface tension (γ) for aqueous solutions of PVP K15, as a function of polymer concentration. All measurements were taken 30 min after formation of the interface. The polymer was obtained from ISP: ◆, 288.15 K; ■, 293.15 K; ▲, 298.15 K; ●, 303.15 K. Full lines represent calculated values from eq 3, with 24 experimental points regressed.

Table 9. Parameters of eq 3 for the Correlation of the Experimental Results of Surface Tension and Density for the Aqueous Solutions of PVP K15

		surface tension				
	T					*σ
points	K	a_1	a_2	b_1	b_2	mN·m^{-1}
36	288.15 to 303.15	185.98	0.33	−0.40	−0.35	0.59
24	288.15 to 303.15	187.68	0.38	−0.40	−0.01	0.29
				density		*σ/g·cm^{-3}
36	288.15 to 303.15	1.0934	0.0018	−0.0003	0.0006	0.0004

[*] Standard deviation of the fit.

The experimental surface tension results obtained in this work were correlated as a function of both PVP concentration and temperature. The equation used to correlate the experimental results is[21,27]

$$\gamma = a_1 + a_2 C_{PVP} + [b_1 + b_2 C_{PVP}]T \qquad (3)$$

where γ is the surface tension in mN·m^{-1}, T the temperature in K, C_{PVP} the concentration in mass fraction of PVP, and the parameters a_1, a_2, b_1, and b_2 are adjustable.

Table 10. Experimental Density Results (ρ/kg·m^{-3}) and Derived Polymer Partial Molar Volume (ϕ_2/cm^3·mol^{-1}) for Aqueous Solutions of PVP, as a Function of Temperature

		288.15 K		293.15 K		298.15 K		303.15 K	
C_{PVP}		ρ	ϕ_2	ρ	ϕ_2	ρ	ϕ_2	ρ	ϕ_2
mass fraction	$x_2 \cdot 10^6$	kg·m^{-3}	cm^3·mol^{-1}	kg·m^{-3}	cm^3·mol^{-1}	kg·m^{-3}	cm^3·mol^{-1}	kg·m^{-3}	cm^3·mol^{-1}
0.000002	0.0036	999.2	10002	998.3	10012	997.1	10023	995.7	10037
0.000018	0.0324	999.2	10002	998.3	10012	997.1	10023	995.7	10037
0.000102	0.184	999.2	10002	998.3	10011	997.1	10023	995.7	10037
0.000499	0.899	999.2	10002	998.4	10011	997.2	10022	995.8	10036
0.000999	1.8	999.4	10000	998.5	10009	997.3	10021	995.9	10035
0.002003	3.61	999.5	9999	998.6	10008	997.5	10020	996.1	10034
0.003018	5.44	999.7	9997	998.8	10006	997.6	10018	996.2	10032
0.004021	7.25	1000.0	9995	999.1	10004	997.9	10015	996.5	10029
0.005111	9.21	1000.1	9993	999.2	10002	998.0	10014	996.6	10028

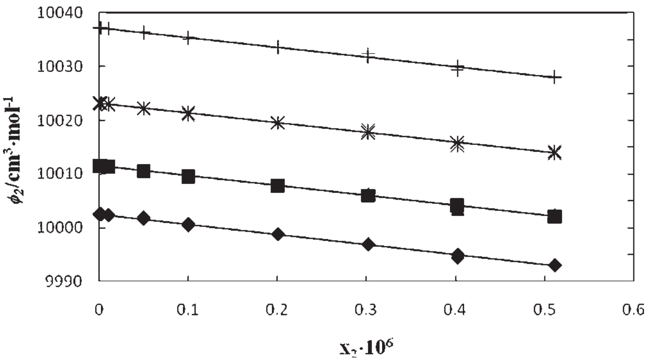

Figure 4. Partial molar volume (ϕ_2) of PVP, at different temperatures: ♦, 288.15 K; ■, 293.15 K; □, 298.15 K; and +, 303.15 K. Full lines represent calculated values with eq 5.

Table 11. Infinite Dilution Partial Molar Volume and Standard Deviation of eq 5 for PVP Aqueous Solutions, at Different Temperatures

T	ϕ_2^∞		σ^a
K	cm^3·mol^{-1}	b	cm^3·mol^{-1}
288.15	10003	−3625	0.3
293.15	10012	−3477	0.3
298.15	10023	−3367	0.4
303.15	10037	−3318	0.4

[a] Standard deviation of the fit.

The adjusted parameters, together with the standard deviation of the fit, are given in Table 9. The equation reproduces the experimentally derived surface tension at the four temperatures considered in this study within a mean standard deviation of ± 0.59 mN·m^{-1} for 36 surface tension points, and within ± 0.29 mN·m^{-1} considering only 24 surface tension points in the region where the surface tension is independent of PVP concentration.

Volumetric Behavior. The partial molar volume of PVP (ϕ_2) was calculated on the basis of the density of the aqueous solution, molar mass of water and polymer, and mole fraction of the polymer through the following linear equation:[43]

$$\phi_2 = \frac{M_2}{\rho} - \frac{M_1 + x_2(M_2 - M_1)}{\rho^2}\frac{\partial \rho}{\partial x_2}(1 - x_2) \qquad (4)$$

where M_1 and M_2 are the molar mass of water and polymer, respectively, in g·mol^{-1}, ρ the density of the solution in g·cm^{-3} (we used here the average value of density from both densimeters), and x_2 the mole fraction of the polymer.

The density, in g·cm^{-3}, was then expressed as a function of x_2, the mole fraction of PVP. With the least-squares fitting technique, a first-degree equation gave the best fit to the 36 experimental points given in Table 10: $\rho = 1.000 + 0.317x_2$, with standard deviation of 0.001 g·cm^{-3}. The derived values of ϕ_2 are also included in the Table 10, and plotted in Figure 4. The 36 density results were also regressed, as a function of both mass fraction and temperature, to an equivalent function as that for surface tension. The four adjusted parameters and the standard deviation of the fit are presented in Table 9.

The ϕ_2 values were fitted to the following linear equation:[43]

$$\phi_2 = \phi_2^\infty + b_2 x_2 \qquad (5)$$

where ϕ_2^∞ is the partial molar volume of polymer at infinite dilution, b_2 is an empirical parameter which depends on solute, solvent, and temperature.

Values of ϕ_2^∞ with the standard deviation of the fits are included in Table 11.

Figure 4 shows that for a given temperature the partial molar volumes of PVP in water decreases as the concentration of polymer increases. This behavior can be interpreted as a manifestation of strong attractive interactions due to the hydrogen bonding of water with the nitrogen in PVP.

■ CONCLUSIONS

Experimental density and surface tension values have been measured for PVP + water binary system, at four different temperatures (288.15, 293.15, 298.15, and 303.15) K. Through the density results it was established that the samples of PVP from two different sources were essentially the same polymer. From density measurements partial molar volume and infinite dilution partial molar volume of the polymer have been computed. Partial molar volume values of the system studied increase with increasing temperature, and decrease with increasing mole fraction of polymer. This behavior indicates that loss of solvation of the PVP increases with increasing temperature. Partial molar volume values have been correlated with a linear equation. The experimental surface tension and density results obtained in this work were satisfactorily correlated with a very simple equation which incorporates both the concentration of PVP and temperature dependence.

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