J. Chem. Eng. Data **2010,** *55,* 2905–2908 **2905**

Surface Tension Data of Aqueous Binary Mixtures of Methyl, Ethyl, Propyl, and Butyl Acetates at 298.15 K

Carolina Bermúdez-Salguero and Jesús Gracia-Fadrique*

Facultad de Química, Departamento de Fisicoquímica, Universidad Nacional Autónoma de México, México, D.F., 04510, Mexico

Alfredo Amigo*

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, E-15782, Santiago de Compostela, Spain

---

Surface tension of aqueous solutions of aliphatic esters (methyl, ethyl, propyl, and butyl acetate) were determined at a temperature of 298.15 K and atmospheric pressure over the mole fraction range reaching the solubility limit in the aqueous phase. The discussion of results examines the influence of the size of the ester hydrocarbon chain on the surface tension. Experimental results have been analyzed using the Langmuir model, and the ability of the Langmuir equation to describe the concentration dependence of surface tension has been tested.

Introduction

Thermodynamic properties of aqueous solutions of aliphatic esters are of considerable theoretical and practical interest, and they have been widely analyzed, especially in the case of methyl, ethyl, and butyl acetates.

Methyl acetate and ethyl acetate are organic compounds with a characteristic sweet smell like certain glues or nail polish removers, in which they are used. Propyl acetate and butyl acetate are known by their characteristic odors of pear and banana, respectively. Knowledge of the surface tensions of aqueous systems containing aliphatic esters is essential in many fields because these compounds are used as solvents in different applications, in chemical reactions, extractive processes, and also as a flavor enhancer in foods. Surface tension measurement is simple and precise and is helpful in understanding and interpreting the nature of interaction between the molecules of the mixtures.

Surface tensions, σ, for the binary systems {methyl, ethyl, propyl, or butyl acetate + water} were measured at 298.15 K under atmospheric pressure, over the short mole fraction range where the aliphatic esters are soluble in water. Literature concerning this physical property is scarce and, in some cases, very outdated. The discussion of results examines the influence of the size of the ester hydrocarbon chain on surface tension. In addition, the Langmuir model was used to analyze the surface tension behavior. This phenomenological model has two adjustable parameters with clear physical significance, one representing the lyophobicity of the solvent relative to the water and the other containing information about the maximum surface concentration of the surface active compound.

Experimental Section

The organic compounds used were typically of the highest purity-grade commercially available, and no further purification was carried out. The name, CAS Registry Number, origin, and purity of compounds are shown in Table 1, together with the experimental surface tensions and values reported by other authors.[1−11] As can be observed, the measurements obtained coincide well with literature values. The measured water surface tension at 298.15 K was 71.57 mN·m^{-1}, while density was determined as ρ = 997.048 kg·m^{-3}. Liquid mixtures were prepared by mass in airtight stoppered bottles, bearing in mind the vapor pressures of the components when establishing the filling sequence. The mole fraction uncertainty was estimated as < 1·10^{-4}.

Surface tensions of the pure liquids and their mixtures at the liquid−vapor interface were measured using a Lauda TVT2 automated tensiometer based on the pending drop volume principle. This technique consists of measuring the volume of a drop detaching from a capillary with a circular cross section. The detailed instrumentation design for the preceding model TVT1 which, as concerns the measuring device, differs from the TVT2 only in the unit control, has been described in a previous paper[12] also addressing the procedure and the handling

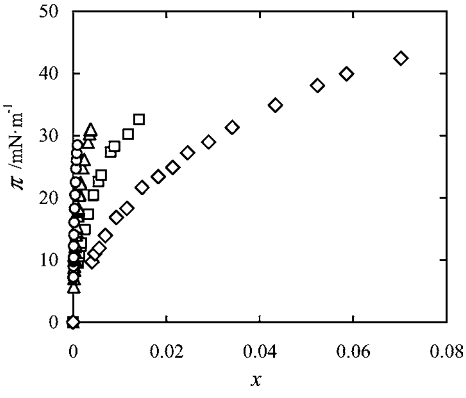

Figure 1. Plot of surface pressures π at 298.15 K for {(x) aliphatic ester + (1 − x) water} mixtures. ◇, methyl acetate; □, ethyl acetate; △, propyl acetate; ○, butyl acetate.

---

* To whom correspondence should be addressed. E-mail: jgraciaf@servidor.unam.mx; fax: 52 55 56162010. E-mail: alfredo.amigo@usc.es; fax: 34 981520676.

10.1021/je900962v © 2010 American Chemical Society
Published on Web 05/06/2010

Table 1. Source, Purity, Surface Tension (σ^0), and Surface Pressure (π^0) of Pure Liquids at the Temperature 298.15 K (Otherwise Indicated)

				this work		literature	
	CAS Registry No.	source	purity	σ^0 (mN·m^{-1})	π^0 (mN·m^{-1})	σ^0 (mN·m^{-1})	method
water				71.57		71.35[1]	drop volume
						71.80[2]	
						71.84[3]	Du Noüy ring
						71.95[4]	Du Noüy ring
methyl acetate	[79-20-9]	Sigma-Aldrich	0.99	24.79	46.78	21.926[5,a]	drop weight
						24.10[2]	
						24.58[6,b]	
						25.231[5,c]	drop weight
ethyl acetate	[141-78-6]	J.T. Baker	0.9987	23.93	47.64	22.55[2,d]	
						23.70[4]	Du Noüy ring
						23.75[2,b]	
						23.82[7]	capillarity
propyl acetate	[109-60-4]	Sigma-Aldrich	0.995	24.22	43.35	23.10[2,d]	
						23.91[8]	pendant drop
						23.99[9]	pendant drop
						24.28[2,b]	
butyl acetate	[123-86-4]	Sigma-Aldrich	0.995	24.91	46.66	23.29[10,d]	Du Noüy ring
						23.98[2,d]	
						24.30[11]	capillarity
						24.89[9]	pendant drop
						25.09[2,d]	

[a] Measured at $T = 307.35$ K. [b] Measured at $T = 293.15$ K. [c] Measured at $T = 283.15$ K. [d] Measured at $T = 303.15$ K.

Table 2. Experimental Surface Tension (σ), Surface Pressure (π), and Reduced Surface Pressure (π^*) for the Binary Aqueous Mixtures

x	σ / mN·m^{-1}	π / mN·m^{-1}	π^*	x	σ / mN·m^{-1}	π / mN·m^{-1}	π^*
			Methyl Acetate (x) + Water ($1 - x$)				
0	71.57	0	0	0.0214	46.68	24.89	0.53
0.0040	61.87	9.70	0.21	0.0245	44.35	27.22	0.58
0.0047	60.57	11.00	0.24	0.0290	42.63	28.94	0.62
0.0056	59.67	11.90	0.25	0.0341	40.26	31.31	0.67
0.0069	57.62	13.95	0.30	0.0433	36.64	34.93	0.75
0.0093	54.72	16.85	0.36	0.0523	33.49	38.08	0.81
0.0115	53.25	18.32	0.39	0.0586	31.61	39.96	0.85
0.0147	49.91	21.66	0.46	0.0702	29.12	42.45	0.91
0.0183	48.18	23.39	0.50	1	24.79	46.78	1
			Ethyl Acetate (x) + Water ($1 - x$)				
0	71.57	0	0	0.0044	51.16	20.42	0.43
0.0011	62.08	9.49	0.20	0.0054	48.98	22.59	0.47
0.0013	60.95	10.62	0.22	0.0061	47.92	23.65	0.50
0.0014	60.43	11.14	0.23	0.0080	44.22	27.35	0.57
0.0017	59.33	12.24	0.26	0.0089	43.31	28.26	0.59
0.0018	58.80	12.77	0.27	0.0118	41.37	30.20	0.63
0.0025	56.64	14.93	0.31	0.0141	38.97	32.60	0.68
0.0033	54.17	17.41	0.37	1	23.93	47.64	1
			Propyl Acetate (x) + Water ($1 - x$)				
0	71.57	0	0	0.00104	53.70	17.87	0.38
0.00017	65.86	5.71	0.12	0.00114	53.49	18.08	0.38
0.00023	64.54	7.03	0.15	0.00116	53.22	18.35	0.39
0.00031	62.64	8.93	0.19	0.00142	50.93	20.64	0.44
0.00031	63.23	8.34	0.18	0.00142	51.11	20.46	0.43
0.00038	61.64	9.93	0.21	0.00158	49.17	22.40	0.47
0.00041	61.43	10.14	0.21	0.00159	49.30	22.27	0.47
0.00049	60.29	11.28	0.24	0.00208	46.76	24.81	0.52
0.00052	59.40	12.17	0.26	0.00239	45.44	26.13	0.55
0.00057	59.02	12.55	0.27	0.00318	42.65	28.92	0.61
0.00071	57.47	14.10	0.30	0.00355	41.31	30.26	0.64
0.00074	56.94	14.63	0.31	0.00367	40.63	30.94	0.65
0.00083	56.17	15.41	0.33	0.00380	40.55	31.02	0.66
0.00103	54.38	17.19	0.36	1	24.22	47.35	1
			Butyl Acetate (x) + Water ($1 - x$)				
0	71.57	0	0	$2.16 \cdot 10^{-4}$	57.50	14.07	0.30
$7.97 \cdot 10^{-5}$	63.74	7.83	0.17	$2.74 \cdot 10^{-4}$	55.53	16.04	0.34
$7.99 \cdot 10^{-5}$	64.49	7.08	0.15	$3.43 \cdot 10^{-4}$	53.31	18.26	0.39
$8.76 \cdot 10^{-5}$	63.71	7.86	0.17	$4.39 \cdot 10^{-4}$	51.12	20.45	0.44
$8.81 \cdot 10^{-5}$	64.30	7.27	0.16	$5.36 \cdot 10^{-4}$	49.09	22.48	0.48
$1.04 \cdot 10^{-4}$	62.60	8.97	0.19	$6.70 \cdot 10^{-4}$	46.90	24.67	0.53
$1.24 \cdot 10^{-4}$	61.81	9.76	0.21	$7.54 \cdot 10^{-4}$	45.57	26.00	0.56
$1.31 \cdot 10^{-4}$	61.47	10.10	0.22	$8.10 \cdot 10^{-4}$	44.42	27.15	0.58
$1.42 \cdot 10^{-4}$	61.15	10.42	0.22	$9.33 \cdot 10^{-4}$	43.10	28.47	0.61
$1.73 \cdot 10^{-4}$	59.30	12.27	0.26	1	24.91	46.66	1

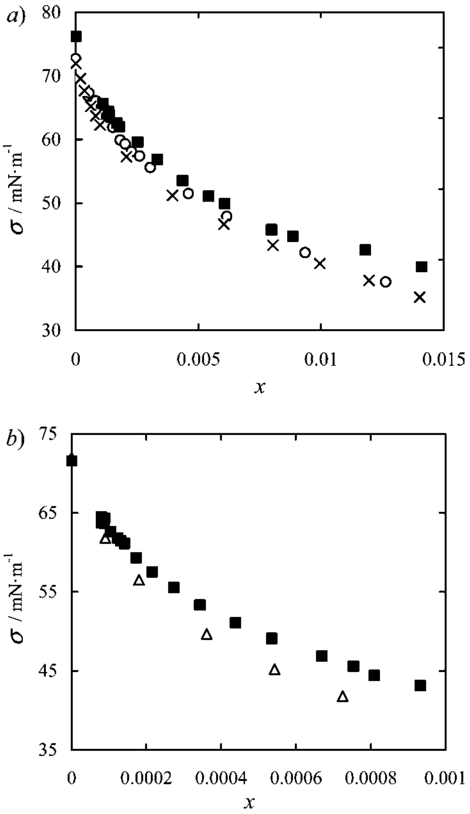

Figure 2. Comparison of surface tension measurements with literature values at 298.15 K: (a) {(x) ethyl acetate + (1 − x) water}. ■, this work; ○, ref 14, T = 293.15 K; ×, ref 4. (b) {(x) butyl acetate + (1 − x) water}. ■, this work; △, ref 11.

of data. The experimental technique used consists of a hermetically sealed cell allowing for the attainment of a saturated atmosphere and preventing solute loss at the concentrated surface. The temperature of the measurement cell was controlled within 0.01 K by a water thermostat. The uncertainty obtained in σ values was less than 0.04 mN·m^{-1}.

Results and Discussion

Table 2 contains the experimental surface tension at 298.15 K in terms of the ester mole fraction. We have included the surface pressure values in this table ($\pi = \sigma_{\text{water}} - \sigma$) and the reduced surface pressures ($\pi^* = \pi/(\sigma_{\text{water}} - \sigma_{\text{ester}}) = \pi/\pi^0$). Figure 1 shows the plot of surface pressures against the aliphatic ester mole fraction for the mixtures analyzed in this work. The surface tension for all of the mixtures studied decreases as the ester concentration increases. This trend was nonlinear, as the change in surface tension caused by a change in ester concentration was larger at low concentrations than at high ones. It is important to note that the water solubility of the esters is quite low and decreases as the hydrocarbon chain increases.

The σ values obtained by Belton[13] for {methyl acetate + water} and by Bigelow and Washburn[14] and Habrdova et al.[4] for {ethyl acetate + water} coincide with our experimental values. The values obtained by Washburn and Shildneck[11] for {butyl acetate + water} show much larger deviations as shown in Figure 2. In contrast with the experimental data of Washburn and Shildneck (1933) for butyl acetate and Belton's data (1940) for methyl acetate, the experimental data reported in this work are distributed along the entire available composition interval, limited by the miscibility of the systems. Moreover, a higher density of points in the diluted regions was achieved.

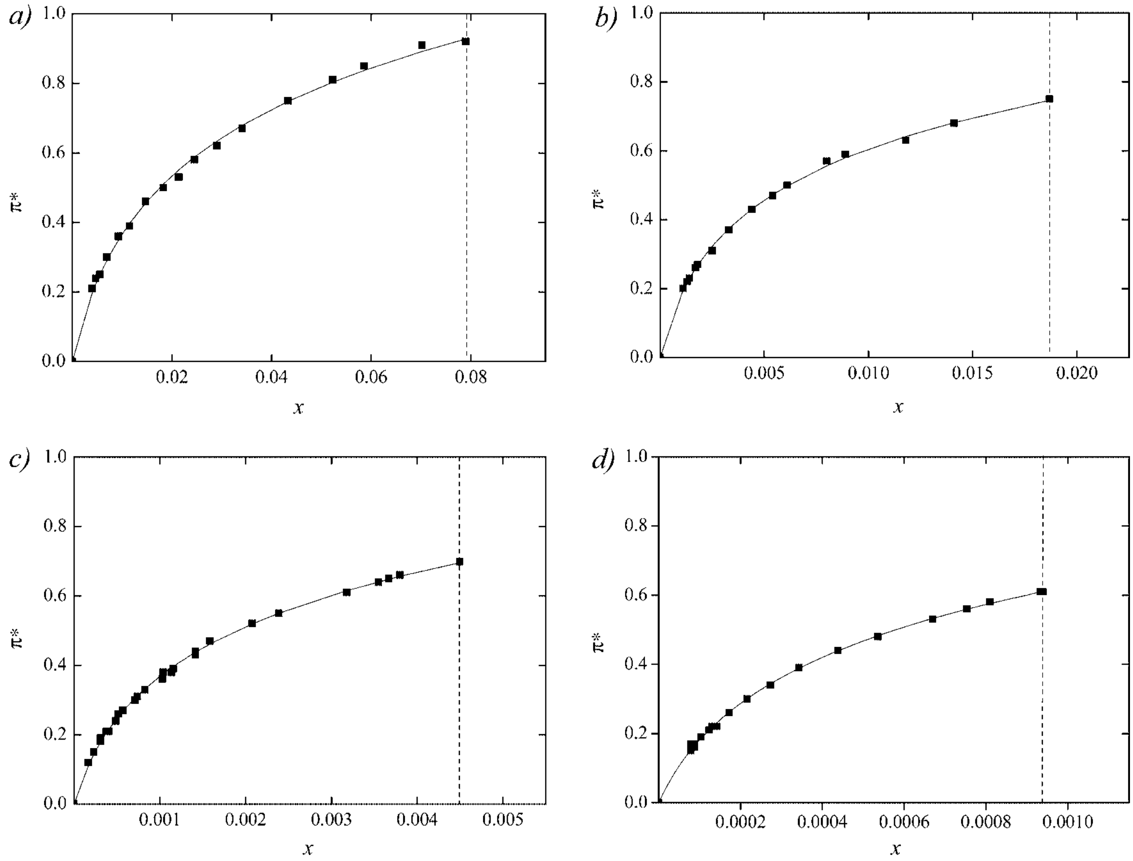

Figure 3. Experimental reduced surface pressures π^* at 298.15 K for {(x) aliphatic ester + (1 − x) water} mixtures. (a) Methyl acetate. (b) Ethyl acetate. (c) Propyl acetate. (d) Butyl acetate. Solid lines stand for the fit to Langmuir eq 2. Dotted lines separate the one- and two-phase regions; the region to the right is the two-phase region.

Table 3. Langmuir Parameters Obtained from π^* Versus x Regressions: Compressibility Factor ($Z_0 = \pi^0/\Gamma_s RT$), Hydrophobic Parameter (β), and $\ln(\pi^*/x)_{x\to 0}$

	$Z_0^{-1} = \Gamma_s RT/\pi^0$	±	$\Gamma_s RT$ (mN·m^{-1})	Z_0	β	±	$\ln(\pi^*/x)_{x\to 0} = \ln(Z_0^{-1}\beta)$
methyl acetate	0.327	0.008	15.297	3.06	200	10	4.18
ethyl acetate	0.241	0.005	11.481	4.15	1130	60	5.61
propyl acetate	0.250	0.004	11.838	4.00	3400	100	6.75
butyl acetate	0.260	0.004	12.120	3.85	10100	310	7.87

Table 4. Surface Tension of the Saturated Aqueous Phase (σ_{sat}) and Prediction of Its Composition (x_{sat}) at 298.15 K with the Langmuir Equation

	σ_{sat} mN·m^{-1}	π_{sat} mN·m^{-1}	π_{sat}^*	$x_{sat,Lang}$	$x_{sat,lit}$
methyl acetate	28.42	43.15	0.92	0.0790	0.0731[2]
ethyl acetate	35.99	35.58	0.75	0.0187	0.0158[17] 0.0163[18] 0.0176[2]
propyl acetate	38.45	33.12	0.70	0.0045	0.0038[17] 0.0041[2]
butyl acetate	43.12	28.45	0.61	0.00094	0.00090[17] 0.000995[18] 0.0011[2]

The Langmuir model[15,16] was applied to these mixtures to interpret the results obtained. Briefly, the Langmuir isotherm in fluid−fluid interfaces, coupled with the Gibbs equation, leads to

$$\theta = \frac{x}{\Gamma_s RT}\left(\frac{d\pi}{dx}\right)_T = \frac{\beta x}{1 + \beta x} \qquad (1)$$

where θ is the surface coverage ($\theta = \Gamma/\Gamma_s$), Γ is the Gibbsian surface concentration, Γ_s is the saturation surface concentration, π is the surface pressure, R is the gas constant, T is the absolute temperature, x is the bulk concentration in mole fraction for the surface-active solute, and β is equivalent to the Henry constant in two dimensions and is a measure of the lyophobicity of the solute relative to the water.

The integral form of eq 1 leads to the corresponding surface equation of state

$$\pi = \Gamma_s RT \ln(1 + \beta x) \quad \text{or} \quad \pi^* = \frac{\Gamma_s RT}{\pi^0}\ln(1 + \beta x) = Z_0^{-1}\ln(1 + \beta x) \qquad (2)$$

Table 3 shows the values of parameters Z_0^{-1} and β obtained after fitting the experimental values of surface tension to the above equation. The value of parameter β increases as the hydrocarbon chain of the ester increases, implying that the lyophobicity of the apliphatic ester increases with the C-atom count. Parameter Z_0 represents the bidimensional compressibility coefficient and is nearly constant for ethyl, propyl, and butyl acetates, being slightly smaller for the first member of the homologous family. In Figure 3, the fitting curves corresponding to the systems {methyl, ethyl, propyl, and butyl acetate + water} are included as an example of the ability of the Langmuir model to describe the surface tension behavior of this kind of binary mixture. We have also determined the surface tensions of the saturated aqueous phase for these binary mixtures. The saturated water-aliphatic ester solutions, in two phases, were prepared in a separating funnel and shaken vigorously to ensure a thorough mixture. The solutions were placed in a water thermostat (at 298.15 K) for approximately 24 h to ensure that the equilibrium between the two phases was reached before surface tension measurements in the water-rich phase were taken. The saturated surface tension values and the corresponding compositions, calculated by using eq 2, are summarized in Table 4. The literature values[2,17,18] coincide with those calculated using the Langmuir equation.

Literature Cited

(1) Rilo, E.; Pico, J.; García-Garabal, S.; Varela, L. M.; Cabeza, O. Density and Surface Tension in Binary Mixtures of CnMIM-BF_4 Ionic Liquids with Water and Ethanol. *Fluid Phase Equilib.* **2009**, *285*, 83–89.

(2) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986; Vol. II.

(3) Lampreia, I. M. S.; Santos, A. F. S.; Barbas, M. J. A.; Santos, F. J. V.; Matos, M. L. S. Changes in Aggregation Patterns Detected by Difussion, Viscosity, and Surface Tension in Water + 2-(Diethylamino)ethanol Mixtures at Different Temperatures. *J. Chem. Eng. Data* **2007**, *52*, 2388–2394.

(4) Habrdova, K.; Hovorka, S.; Bartovska, L. Concentration Dependence of Surface Tension for Very Dilute Aqueous Solutions of Organic Nonelectrolytes. *J. Chem. Eng. Data* **2004**, *49*, 1003–1007.

(5) Morgan, J. L. R.; Schwartz, F. W. The Weight of a Falling Drop and the Laws of Tate VII. The Drop Weight of Some of the Lower Esters, and the Surface Tensions and Molecular Weights Calculated from Them. *J. Am. Chem. Soc.* **1911**, *33*, 1041–1060.

(6) Richards, T. W.; Mathews, J. H. The Relation Between Compressibility, Surface Tension and Other Properties of Material. *J. Am. Chem. Soc.* **1908**, *30*, 8–13.

(7) Shipp, W. E.; Hemmati, M. Surface Tension of Binary Mixtures of Several Organic Liquids at 25 °C. *J. Chem. Eng. Data* **1970**, *15*, 308–311.

(8) Deng, J.; Tan, H.; Yang, Y.; Zai, S.; Ouyang, G.; Huang, Z. Densities and Surface Tensions of Propyl Acetate + Xylenes or + Ethylbenzene from (298.15 to 308.15) K. *J. Chem. Eng. Data* **2007**, *52*, 1131–1135.

(9) Yang, Y.; Deng, J.; Yang, H.; Zheng, X.; Che, G.; Huang, Z. Densities, Surface Tensions, and Derived Surface Thermodynamic Properties of (Trimethylbenzene + Propyl Acetate, or Butyl Acetate) from T = 298.15 to 313.15 K. *J. Chem. Thermodyn.* **2007**, *39*, 438–448.

(10) Johnson, I.; Costa, H. F.; Ferreira, A. G. M.; Fonseca, I. M. A. Density, Viscosity, and Surface and Interfacial Tensions of Mixtures of Water + *n*-Butyl Acetate + 1-Propanol. *Int. J. Thermophys.* **2008**, *29*, 619–633.

(11) Washburn, E. R.; Shildneck, C. H. Surface Tension Studies with *n*-Butyl Acetate. *J. Am. Chem. Soc.* **1933**, *5*, 2354–2357.

(12) Piñeiro, Á.; Brocos, P.; Amigo, A.; Pintos, M.; Bravo, R. Surface Tensions and Refractive Indices of (Tetrahydrofuran + *n*-Alkanes) at T = 298.15 K. *J. Chem. Thermodyn.* **1999**, *31*, 931–942.

(13) Belton, J. W. The Surface Tensions of Methyl Acetate Solutions. *Trans. Faraday Soc.* **1940**, *35*, 493–495.

(14) Bigelow, S. L.; Washburn, E. R. Variations in the Surface Tension of Solutions. *J. Phys. Chem.* **1928**, *32*, 321–480.

(15) Langmuir, I. The Constitution and Fundamental Properties of Solids and Liquids. II. Liquids. *J. Am. Chem. Soc.* **1917**, *39*, 1848–1906.

(16) Gracia-Fadrique, J. Langmuir-BET Surface Equation of State in Fluid-Fluid Interfaces. *Langmuir* **1999**, *15*, 3279–3282.

(17) Stephenson, R.; Stuart, J. Mutual Binary Solubilities: Water-Alcohols and Water-Esters. *J. Chem. Eng. Data* **1986**, *31*, 56–70.

(18) Donahue, D. J.; Bartell, F. E. The Boundary Tension at Water-Organic Liquid Interfaces. *J. Phys. Chem.* **1952**, *56*, 480–484.

Received for review November 10, 2009. Accepted April 28, 2010. This work was supported by DGAPA, Programa de Apoyo a Proyectos de Investigación e Innovación Tecnológica, PAPIIT-UNAM, under the Projects IN103108 and IN100808 and Grant FIS2007-63479 from MEC, Spain.

JE900962V