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Refractive Index, Surface Tension, and Density of Aqueous Mixtures of Carboxylic Acids at 298.15 K

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Refractive indices (n), densities (ρ), and surface tensions (σ) for {formic acid, acetic acid, propionic acid, or butyric acid + water} mixtures at 298.15 K and normal atmospheric pressure have been determined as a function of mole fractions. From the experimental data, excess molar volumes (V^{E}) and deviations of refractive index from linear behavior (Δn_{ϕ}) have been calculated. The magnitude of these experimental quantities is discussed in terms of nature and type of intermolecular interactions in binary mixtures. Besides, the interpretation of the ratio of molar volume to molar refraction V/R as a measure of the degree of free volume appears to be a useful tool for qualitative considerations concerning volumetric and refractometric data. To analyze the behavior of surface tensions, the Extended Langmuir (EL) model was used.

Introduction

Thermodynamic properties of carboxylic acids + water are of considerable theoretical and practical interest, and they have been widely analyzed, especially in the case of formic and acetic acid + water mixtures. Interactions between water and carboxylic acids are extremely complex, being the analysis of the hydrogen bonding interactions of complexes of this kind of systems of great interest.[1−3]

The easy with which the refractive index of a liquid can be measured accurately and precisely has led to increased interest in the theoretical and empirical correlations of this property with others that are more difficult to measure directly, particularly with excess properties in binary mixtures. Another thermodynamic property that is also easy to measure and usually presents a very strong dependence on both the compounds constituting the mixture and their relative concentrations is the surface tension. We placed special priority on the experimental determination in the diluted region of the binary mixtures. Our research group has taken a keen interest in the analysis of surface tension data in the diluted region because, based on these measurements and taking into account the refractive indices and density values, we can very precisely assess properties such as standard energy of adsorption, parachor, molar refraction, or the activity coefficient at infinite dilution of the mixture components. None of the research literature that we analyzed presents an acceptable density of experimental points in the diluted region and that is what motivated us to study these systems. The majority of the surface tension determinations that we consulted (all very outdated) were conducted under non-equilibrium conditions between the vapor and liquid phases. The experimental technique that we used consists of a hermetically sealed cell allowing for the attainment of a saturated atmosphere and preventing the solute loss at the concentrated surface. This issue is particularly important when conducting measurements in systems with high vapor pressures, which is the case of the first of the members of the series of carboxylic acids.

We have measured densities (ρ), refractive indices (n), and surface tensions (σ) of {formic, acetic, propionic, or butyric acid + water} mixtures at 298.15 K and atmospheric pressure. From the experimental data, excess molar volumes (V^{E}) and deviations of refractive index from linear behavior (Δn_{ϕ}) have been calculated. The discussion of results examines the influence of the size of the carboxylic acid hydrocarbon chain on the excess properties. Besides, the interpretation of the ratio of molar volume to molar refraction (V/R) as a measure of the degree of free volume appears to be a useful tool for qualitative considerations concerning volumetric and refractometric data. To analyze the behavior of surface tensions, the Extended Langmuir (EL) model was used. The EL model is based on a modification of the Langmuir isotherm combined with a mixing rule and includes two adjustable parameters with clear physical meaning.

Experimental Section

The source and purity of the chemical compounds are shown in Table 1, together with the experimental densities, refractive indexes, surface tensions, and values reported by other authors.[4−9] The liquids were used without further purification other than being kept over molecular sieves to remove water. The ultrapure water was obtained by using an ELIX 3 system from Millipore. The water surface tension value at 298.15 K was 71.89 $\mathrm{mN{\cdot}m^{-1}}$, and the density and refractive index were taken as $\rho = 997.048$ $\mathrm{kg{\cdot}m^{-3}}$ and $n = 1.33254$, respectively. 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 uncertainty in the mole fraction was estimated to be $<1{\cdot}10^{-4}$.

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Table 1. Source, Purity, Density (ρ), Refractive Index (n), and Surface Tension (σ) for the Pure Liquids at 298.15 K

			$10^{-3}\cdot\rho$ (kg·m^{-3})		n_D		σ (mN·m^{-1})	
compound	source	purity/%	this work	lit.	this work	lit.	this work	lit.
formic acid	Fluka	≥98	1.21129	1.21405[4] 1.21346[5] 1.2138[6]	1.37459	1.36938[4] 1.36943[6]	38.17	37.03[9]
acetic acid	Fluka	>99.8	1.04395	1.043924[4] 1.04322[5] 1.0440[6]	1.36969	1.3698[4] 1.37046[6] 1.3707[7]	27.08	27.12[9]
propionic acid	Fluka	≥99.5	0.98833	0.98808[4] 0.98793[5] 0.9903[6] 0.987847[8]	1.38484	1.3843[4] 1.38479[6] 1.3850[7]	26.15	26.17[9] 26.2[4]
butyric acid	Fluka	≥99.5	0.95317	0.9532[4]	1.39599	1.3958[4] 1.3963[7]	26.19	26.2[4]

Experimental densimetric and refractometric techniques have been described in detail in previous works.[10−12] Densities were measured with a vibrating-tube densimeter from Anton Paar (model DMA 60/602) operated in the static mode and calibrated with bidistilled and deionized water and dry air on a daily basis. The uncertainties of ρ and V^E are less than 10^{-2} kg·m^{-3} and $4\cdot10^{-9}$ m^3·mol^{-1}, respectively. For refractive index measurements at the wavelength of the D-line of sodium, we have used a Mettler Toledo refractometer (model RA-510M) having an uncertainty of 10^{-5}, calibrated with bidistilled and deionized water. The solutions were prethermostated at 298.15 K before the experiments in order to achieve a quick thermal equilibrium. Surface tension of pure liquids and mixtures at the liquid−vapor interface was determined using a Lauda drop volume tensiometer, described in detail in a previous paper,[12] which also discussed procedure and handling of data. The temperature of the measurement cell was controlled within 0.01 K by a water thermostat. The uncertainty obtained in σ values is less than 0.03 mN·m^{-1}.

Results and Discussion

Table 2 contains the experimental results at 298.15 K for ρ, V^E, n, Δn_ϕ, and σ, in terms of the carboxylic acid mole fraction. Deviations of refractive index from linear behavior, Δn_ϕ, were calculated by using

$$\Delta n_\phi = n - (\phi_1 n_1 + \phi_2 n_2) \tag{1}$$

where ϕ_i is the volume fraction of component i in the mixture. Excess molar volumes (V^E) were calculated from the density of the mixture (ρ), densities (ρ_i), and molar masses (M_i) of the pure compounds and the corresponding molar fractions (x_i) by means of

$$V^E = x_1\left(\frac{M_1}{\rho} - \frac{M_1}{\rho_1}\right) + x_2\left(\frac{M_2}{\rho} - \frac{M_2}{\rho_2}\right) \tag{2}$$

V^E and Δn_ϕ were fitted with a function of the form

$$F = x(1-x)\sum_{i=0}^{n-1} A_i x^{i/2} \tag{3}$$

where F is either V^E or Δn_ϕ. The coefficients A_i and standard deviations $s(F)$ listed in Table 3 were estimated by the least-squares method. These parameters were used to obtain the calculated curves in Figures 1 and 3.

Refractive Indices. Figure 1 shows that for all systems studied Δn_ϕ is positive over the whole range of mole fractions and becomes less positive as the length of the hydrocarbon chain of the acid increases, with the exception of the binary mixture {formic acid + water}. This apparent anomaly can be explained by taking into account the negative correlation between Δn_ϕ and the ratio of molar volume to molar refraction V/R, proposed as a measure of the degree of free volume.[13,14] The equation defining the molar refraction $R = V(n^2 - 1)/(n^2 + 2)$ can be rewritten in such a way that the correlation between the refractive index n and the ratio V/R appears unmasked:

$$n^2 - 1 = \frac{3}{\dfrac{V}{R} - 1} \tag{4}$$

It is remarkable that refractive index deviations show a similar trend, although with opposite sing, that the ratio V/R for the binary mixtures {acetic acid, propionic acid, or butyric acid + water}. The excess volume of the system {formic acid + water} is much smaller than the corresponding values for the other binary mixtures of this series, being responsible of the aforementioned anomaly, shown in Figure 1. Figure 2 shows the curves $\Delta(V/R)$ versus x for the analyzed mixtures. The quantity $\Delta(V/R)$ was obtained by using the following equation:[13,14]

$$\Delta\left(\frac{V}{R}\right) = \frac{V}{R} - \frac{V_{id}}{R_{id}} = \frac{n^2+2}{n^2-1} - \frac{x_1V_1 + x_2V_2}{x_1R_1 + x_2R_2} \tag{5}$$

Excess Molar Volumes. The excess molar volume V^E in aqueous solutions of carboxylic acids is always negative and large in magnitude, as can be seen in Figure 3. Our results compare well with the literature data;[5,8,15−17] however, the results of Apelblat et al.[5] and Casanova et al.[15] for the mixture {formic acid + water} at the central part of the V^E curve are more negative than ours. These differences may be attributed to the different purity of the formic acid utilized. The behavior of the mixture {formic acid + water} does not follows the general trend for the other members of the series.

In general, the sign of V^E depends on the relative magnitude of contractive and expansive effects that arise on the mixing process. The large negative V^E for these mixtures leads to the conviction that the factors causing the volume contraction prevail over the factors responsible for volume expansion, being the hydrophobic hydration the most effective factor in volume reduction, as recently pointed out by Motin et al.[18]

Surface Tension. Figure 4 shows the experimental surface pressures ($\pi = \sigma_{water} - \sigma$) versus the carboxylic acid mole fraction for the mixtures analyzed in this work. The surface tension of all mixtures studied decreases as the acid concentration increases. This trend was nonlinear, the change in surface tension caused by a change in acid concentration being larger at low concentrations than at high. The binary mixture {butyric acid + water} shows the typical behavior of a tensoactive substance in water. As the hydrocarbon chain of the acid

Table 2. Experimental Densities (ρ), Excess Molar Volumes (V^{E}), Refractive Indices (n), Deviations of Refractive Index from Linear Behavior (Δn_{ϕ}), and Surface Tensions (σ) at 298.15 K

x	$10^{-3}\cdot\rho$ / $\mathrm{kg\cdot m^{-3}}$	V^{E} / $\mathrm{cm^{3}\cdot mol^{-1}}$	n	Δn_{ϕ}	σ / $\mathrm{mN\cdot m^{-1}}$	x	$10^{-3}\cdot\rho$ / $\mathrm{kg\cdot m^{-3}}$	V^{E} / $\mathrm{cm^{3}\cdot mol^{-1}}$	n	Δn_{ϕ}	σ / $\mathrm{mN\cdot m^{-1}}$
(x) Formic Acid + (1 − x)Water											
0.0007	0.99752	−0.0031	1.33265	0.00005	71.48	0.1098	1.05276	−0.2232	1.34454	0.00334	57.29
0.0015	0.99802	−0.0054	1.33269	0.00002	71.14	0.1539	1.06949	−0.2603	1.34829	0.00412	55.23
0.0028	0.99879	−0.0087	1.33271	0.00005	70.65	0.2040	1.08651	−0.2942	1.35223	0.00497	52.74
0.0067	1.00127	−0.0225	1.33343	0.00030	69.45	0.3004	1.11430	−0.3366	1.35863	0.00614	49.18
0.0106	1.00360	−0.0332	1.33440	0.00093	68.59	0.4178	1.14155	−0.3618	1.36478	0.00695	47.25
0.0154	1.00631	−0.0444	1.33496	0.00108	67.53	0.5101	1.15859	−0.3528	1.36885	0.00744	45.73
0.0277	1.01384	−0.0859	1.33633	0.00141	65.46	0.6133	1.17483	−0.3343	1.37220	0.00731	43.41
0.0442					63.13	0.7058	1.18706	−0.3034	1.37444	0.00681	41.42
0.0538	1.02693	−0.1308	1.33912	0.00209		0.8162	1.19840	−0.2245	1.37543	0.00491	40.12
0.0755					59.92	0.8967	1.20413	−0.1185	1.37543	0.00302	39.13
(x)Acetic Acid + (1 − x) Water											
0.0001					71.79	0.0746					47.25
0.0005					71.18	0.1086					43.43
0.0007	0.99741	−0.0048	1.33285	0.00023	71.04	0.1108	1.03157	−0.4612	1.35281	0.00972	43.39
0.0008					70.84	0.1513	1.04090	−0.6205	1.35708	0.01109	40.12
0.0012	0.99788	−0.0118	1.33312	0.00044	70.37	0.1814	1.04655	−0.7255	1.36009	0.01218	39.24
0.0060	0.99892	−0.0182	1.33422	0.00098	66.17	0.2288	1.05246	−0.8401	1.36386	0.01328	38.17
0.0066					65.76	0.3053	1.05874	−0.9767	1.36818	0.01398	36.50
0.0119	1.00078	−0.0371	1.33576	0.00185	62.57	0.4129	1.06349	−1.0991	1.37230	0.01408	34.80
0.0138					61.57	0.5160	1.06454	−1.1285	1.37456	0.01333	33.23
0.0234					58.26	0.6068	1.06364	−1.0910	1.37543	0.01202	31.87
0.0257	1.00439	−0.0704	1.33874	0.00332	57.45	0.7035	1.06107	−0.9762	1.37543	0.01008	30.32
0.0404					53.14	0.8067	1.05700	−0.7710	1.37459	0.00750	29.32
0.0516	1.01191	−0.1577	1.34364	0.00562	50.64	0.9076	1.05189	−0.4811	1.37257	0.00403	28.42
(x) Propionic Acid + (1 − x) Water											
0.0008	0.99747	−0.0083	1.33292	−0.01117	68.52	0.0989	1.01717	−0.5322	1.35796	−0.53531	34.71
0.0016	0.99764	−0.0118	1.33304	−0.01466	66.47	0.2016	1.02207	−0.8521	1.37093	−0.85531	32.25
0.0029	0.99815	−0.0220	1.33367	−0.02493	63.66	0.3008	1.02151	−1.0351	1.37840	−1.03833	31.12
0.0044	0.99868	−0.0328	1.33422	−0.03574	60.98	0.4003	1.01887	−1.1315	1.38294	−1.13483	30.19
0.0064	0.99929	−0.0456	1.33485	−0.04850	57.91	0.5009	1.01433	−1.1158	1.38564	−1.11919	29.36
0.0103	1.00060	−0.0730	1.33606	−0.07588	53.54	0.6039	1.01012	−1.0691	1.38690	−1.07250	28.56
0.0179	1.00271	−0.1194	1.33850	−0.12237	48.16	0.7020	1.00503	−0.9173	1.38721	−0.92064	27.91
0.0272	1.00551	−0.1828	1.34145	−0.18581	44.12	0.7666	1.00283	−0.8552	1.38709	−0.85858	27.52
0.0470	1.00686	−0.2326	1.34689	−0.23564	38.89	0.8784	0.99668	−0.5506	1.38599	−0.55393	26.92
0.0618	1.00897	−0.2950	1.35074	−0.29808	36.93						
(x) Butyric Acid + (1 − x) Water											
0.00004	0.99714	−0.0019	1.33256	0.00001	71.12	0.0596	1.00055	−0.3202	1.35359	0.00552	28.35
0.0001	0.99728	−0.0046	1.33259	0.00001	70.47	0.0865	0.99876	−0.3933	1.35959	0.00635	28.23
0.0006	0.99735	−0.0080	1.33282	0.00008	66.32	0.1034	0.99768	−0.4366	1.36283	0.00674	28.15
0.0016	0.99739	−0.0127	1.33325	0.00020	60.32	0.2033	0.99250	−0.6788	1.37695	0.00848	27.92
0.0028					55.12	0.2997	0.98771	−0.8493	1.38524	0.00914	27.73
0.0056	0.99824	−0.0447	1.33514	0.00083	46.34	0.3810	0.98312	−0.9144	1.38923	0.00853	27.66
0.0075					42.12	0.5038	0.97720	−0.9632	1.39330	0.00755	27.56
0.0136	0.99983	−0.1084	1.33877	0.00204	35.88	0.5763	0.97362	−0.9346	1.39471	0.00669	27.42
0.0201	1.00084	−0.1553	1.34064	0.00209	31.94	0.7036	0.96747	−0.7977	1.39625	0.00509	27.13
0.0299	1.00179	−0.2170	1.34506	0.00388	29.24	0.8019	0.96235	−0.5775	1.39667	0.00360	26.90
0.0480	1.00161	−0.2932	1.35064	0.00508	28.48	0.9189	0.95718	−0.2946	1.39654	0.00163	26.51

decreases, this behavior is less evident. Fitting the equation[9]

$$\pi = \pi^{0}\left(1 + \frac{a(1-x)}{1-b(1-x)}\right)x \qquad (6)$$

to the experimental results for each system yielded the π−x curves shown in Figure 4. The values of the fitted parameters a and b are shown in Table 4.

The σ values obtained by Álvarez et al.[9] for {formic, acetic, or propionic acid + water} as well as those obtained by Drucker[19] for {formic or acetic acid + water} agree well with our experimental values. The values obtained by Glagoleva[20] for {formic or acetic acid + water} systems show much greater deviations. Figure 5 shows the surface tension data at $x = 0.5$ for the binary mixtures studied in this work together with literature data[9,19−22] for comparison.

The EL[23] model was applied to these mixtures in order to interpret the results obtained. The EL model allows for the behavior analysis of binary systems that deviate either positively or negatively from ideality.[24−26] Briefly, it considers the surface of a binary liquid mixture as a thin but finite layer and starts by developing the following expression for the relationship between the volume fractions of component B in the surface

Table 3. Coefficients of Equation 3 and Standard Deviations (s)

	A_0	A_1	A_2	A_3	A_4	s
Formic Acid + Water						
Δn_{ϕ}	0.0817	−0.231	0.321	−0.138		$14\cdot10^{-5}$
V^{E}	−3.82	6.16	−3.93			0.0071
Acetic Acid + Water						
Δn_{ϕ}	0.1712	−0.2743	0.1527			$12\cdot10^{-5}$
V^{E}	0.708	−30.96	55.9	−31.8		0.015
Propionic Acid + Water						
Δn_{ϕ}	0.166	−0.117	−0.566	1.059	−0.525	$14\cdot10^{-5}$
V^{E}	−4.62	−10.9	29.7	−19.8		0.022
Butyric Acid + Water						
Δn_{ϕ}	0.1935	−0.522	0.572	−0.226		$25\cdot10^{-5}$
V^{E}	−13.69	56.1	−122.8	120.3	−43.8	0.011

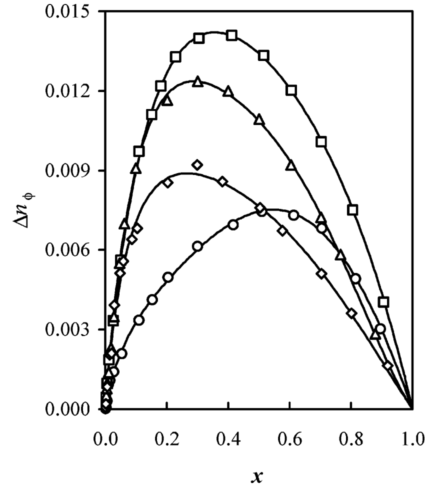

Figure 1. Plot of Δn_ϕ (eq 1) at 298.15 K for {(*x*) carboxylic acid + (1 − *x*) water} mixtures: ○, formic acid; □, acetic acid; △, propionic acid; ◇, butyric acid.

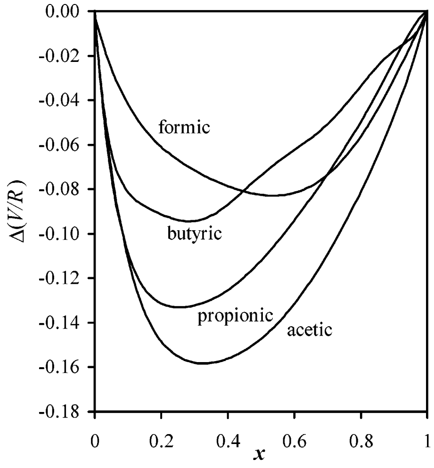

Figure 2. Plot of Δ(*V*/*R*) calculated by using eq 5 for the analyzed mixtures.

and the bulk, ϕ_B^S and ϕ_B, respectively:

$$\phi_B^S = \beta\phi_B/(1 - \phi_B + \beta\phi_B) \tag{7}$$

where the parameter $\beta = (\phi_B^S/\phi_B)/(\phi_A^S/\phi_A)$ is a measure of the lyophobicity of B relative to A. The second ingredient of the EL model is a mixing rule with a Margules-type term:

$$\sigma = \phi_A^S\sigma_A + \phi_B^S\sigma_B - \lambda\phi_A^S\,\phi_B^S\pi^0 \tag{8}$$

where σ_A and σ_B are the surface tensions of the pure components A and B, π^0 is the positive difference between them (A is the component of higher surface tension), and λ is a parameter that represents the effect of unlike-pair interactions on the surface tension of the mixture and is zero when this effect is negligible. From eq 8 the surface pressure π can be written as

$$\pi = \pi^0\phi_B^S(\alpha\phi_A^S + \phi_B^S) \tag{9}$$

where $\alpha = \lambda + 1$; and substituting for ϕ_B^S and $\phi_A^S(= 1 - \phi_B^S)$ from eq 7 yields

$$\pi = \pi^0\beta[\beta + \alpha(\phi_A/\phi_B)]/[\beta + (\phi_A/\phi_B)]^2 \tag{10}$$

Table 5 shows the values of parameters α and β obtained after adjusting the experimental values of surface tension to the above equation. For all the systems of this series except for the one containing butyric acid, $\alpha = 1$ (or $\lambda = 0$) and $\beta > 1$, which implies that the heteromolecular interactions do not affect significantly the surface tension of the solution. A value of $\beta > 1$ indicates that the concentration of the acid is higher at the surface, in regard to the bulk concentration. The value of the

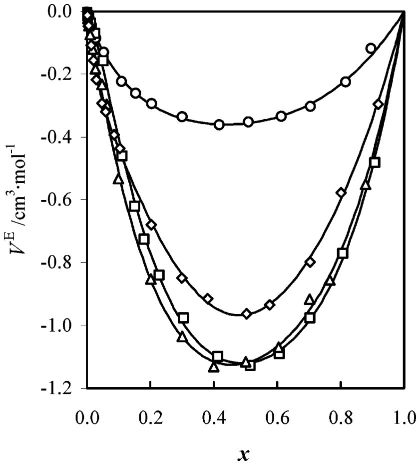

Figure 3. Plot of excess molar volumes, V^E (eq 2), at 298.15 K for {(*x*) carboxylic acid + (1 − *x*) water} mixtures: ○, formic acid; □, acetic acid; △, propionic acid; ◇, butyric acid.

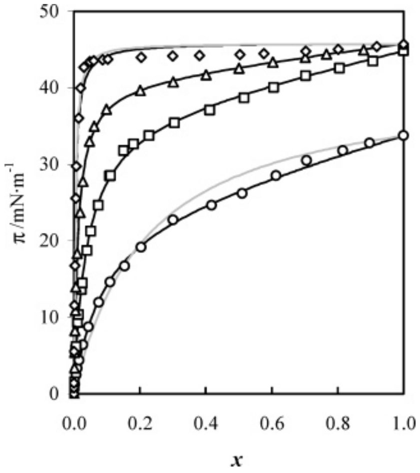

Figure 4. Surface pressures π at 298.15 K for {(*x*) carboxylic acid + (1 − *x*) water} mixtures: ○, formic acid; □, acetic acid; △, propionic acid; ◇, butyric acid; black lines, calculated by using eq 6; gray lines, curves obtained with the Extended Langmuir model, eq 10.

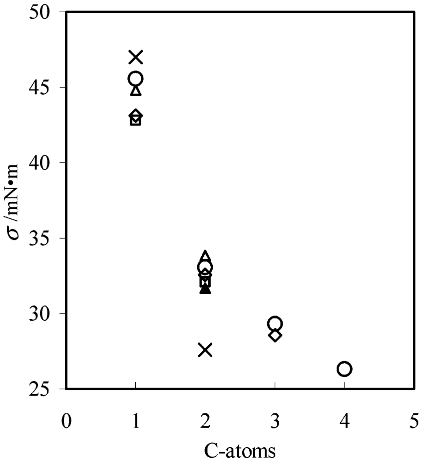

Figure 5. Plot at $x = 0.5$ of surface tension, σ, against the C-atom number of the carboxylic acid: ○, this work; ◇, ref 9; □, ref 21 (303.15 K); △, ref 19; ▲, ref 22 (293.15 K); ×, ref 20.

Table 4. Values of the Parameters *a* and *b* Obtained by Fitting Equation 6 to Surface Pressure Data and Standard Deviations *s*

	a	*b*	*s*
formic acid + water	0.606	0.922	0.42
acetic acid + water	0.760	0.963	0.43
propionic acid + water	0.873	0.9878	0.38
butyric acid + water	0.998	0.9958	1.04

Table 5. Values of the Parameters α and *β* Obtained by Fitting Equation 10 to Surface Pressure Data and Standard Deviations *s*

	α	*β*	*s*
formic acid + water	1	2.62	1.36
acetic acid + water	1	4.73	1.96
propionic acid + water	1	14.00	1.83
butyric acid + water	1.74	22.50	0.80

parameter β increases as the hydrocarbon chain of the acid increases. For the mixture {butyric acid + water}, λ is clearly > 0 and $\beta > 1$. This means that the interactions in the mixtures decrease the σ value and that the compound prevalently adsorbed is the acid. In Figure 4 the fitting curves corresponding to the systems {formic or butyric acid + water} are included as an example of the ability of the EL model to describe the surface tension behavior.

Literature Cited

(1) Zhou, Z.; Shi, Y.; Zhou, X. Theoretical studies on the hydrogen bonding interaction of complexes of formic acid with water. *J. Phys. Chem.* **2004**, *108*, 813−822.

(2) Wei, D.; Truchon, J.-F.; Sirois, S.; Salahub, D. Solvation of formic acid and proton transfer in hydrated clusters. *J. Chem. Phys.* **2002**, *116*, 6028−6038.

(3) Velardez, G. F.; Ferrero, J. C.; Beswick, J. A.; Daudey, J. P. Ab initio study of the structures and $\pi^* \leftarrow n$ electronic transition in formic acid−(water)$_n$ ($n = 3$, 4, and 5) hydrogen bonded complexes. *J. Phys. Chem. A* **2001**, *105*, 8769−8774.

(4) Riddick, J. A., Bunger, W. B., Sakano, T. K., Eds. *Organic Solvents* (*in Techniques of Chemistry*); Weissberger, A., Ed.; Wiley-Interscience: New York, 1986; Vol. II.

(5) Apelblat, A.; Manzurola, E. Excess molar volume of formic acid + water, acetic acid + water and propionic acid + water systems at 288.15, 298.15, and 308.15 K. *Fluid Phase Equilib.* **1987**, *32*, 163−193.

(6) Cases, A. M.; Gómez Marigliano, A. C.; Bonatti, C. M.; Sólimo, H. N. Density, viscosity, and refractive index of formamide, three carboxylic acids, and formamide + carboxylic acid binary mixtures. *J. Chem. Eng. Data* **2001**, *46*, 712−715.

(7) Bernardo-Gil, G.; Esquivel, M.; Ribeiro, A. Densities and refractive indices of pure organic acids as a function of temperature. *J. Chem. Eng. Data* **1990**, *35*, 202−204.

(8) Estrada-Baltazar, A.; De León-Rodríguez, A.; Hall, K. R.; Ramos-Estrada, M.; Iglesias-Silva, G. A. Experimental densities and excess volumes for binary mixtures containing propionic acid, acetone and water from 283.15 to 323.15 K at atmospheric pressure. *J. Chem. Eng. Data* **2003**, *48*, 1425−1431.

(9) Álvarez, E.; Vázquez, G.; Sánchez-Vilas, M.; Sanjurjo, B.; Navaza, J. M. Surface tension of organic acids + water binary mixtures from 20 °C to 50 °C. *J. Chem. Eng. Data* **1997**, *42*, 957−960.

(10) Calvo, E.; Brocos, P.; Bravo, R.; Pintos, M.; Amigo, A.; Roux, A. H.; Roux-Desgranges, G. Heat capacities, excess enthalpies, and volume of mixtures containing cyclic ethers. 1. *J. Chem. Eng. Data* **1998**, *43*, 105−111.

(11) Brocos, P.; Calvo, E.; Amigo, A.; Bravo, R.; Pintos, M.; Roux, A. H.; Roux-Desgranges, G. Heat capacities, excess enthalpies, and volume of mixtures containing cyclic ethers. 2. *J. Chem. Eng. Data* **1998**, *43*, 112−116.

(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) Brocos, P.; Piñeiro, Á.; Bravo, R.; Amigo, A. Refractive indices, molar volume and molar refractions of binary liquid mixtures: concepts and correlations. *Phys. Chem. Chem. Phys.* **2003**, *5*, 550−557.

(14) Brocos, P.; Amigo, A. Critical review on treatment of refractive indices and related properties in liquid mixtures. *Recent Res. Dev. Chem. Eng.* **2005**, *6*, 47−84.

(15) Casanova, C.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. Excess volumes and excess heat capacities of (water + alkanoic acid). *J. Chem. Thermodyn.* **1981**, *13*, 241−148.

(16) Korpela, J. Densities and compression isotherms of formic acid−water, acetic acid−water, propionic acid−water, and isobutyric acid−water mixtures. *Acta Chem. Scand.* **1971**, *25*, 2852−2864.

(17) Campbell, A. N.; Kartzmark, E. M.; Gieskes, J. M. T. M. Vapor−liquid equilibriums, densities, and refractivities in the system acetic acid-chloroform-water at 25 °C. *Can. J. Chem.* **1963**, *41*, 407−429.

(18) Motin, M. A.; Kabir, M. H.; Huque, E. M. Densities and excess molar volumes of formic acid, acetic acid and propionic acid in pure water and in water + Surf Excel solutions at different temperatures. *Phys. Chem. Liq.* **2005**, *43*, 277−288.

(19) Drucker, K. Studies on aqueous solutions of aliphatic acids. *Phys. Chem. Stoechiom. Verwandschaftsl.* **1905**, *52*, 641−704.

(20) Glagoleva, A. A. Surface tension of the binary systems $HCOOH-H_2O$ and $CH_3COOH-H_2O$ *Zh. Obsch. Khim.* **1947**, *17*, 1044−1047.

(21) Morgan, J. L. R.; Neidle, M. The weight of a falling drop and the laws of tate, XVIII. The drop weights, surface tensions and capillary constants of aqueous solutions of ethyl, methyl and amyl alcohols, and of acetic and formic acid. *J. Am. Chem. Soc.* **1913**, *35*, 1856−1865.

(22) Grunmach, L. Determination of the surface tension and other physical constants of mixtures of acetic acid and water. *Ann. Phys.* **1909**, *28*, 217−258.

(23) Piñeiro, Á.; Brocos, P.; Amigo, A.; Gracia-Fadrique, J.; Guadalupe Lemus, M. Extended Langmuir isotherm for binary liquid mixtures. *Langmuir* **2001**, *17*, 4261−4266.

(24) Brocos, P.; Gracia-Fadrique, J.; Amigo, A.; Piñeiro, Á. Application of the Extended Langmuir model to surface tension data of binary liquid mixtures. *Fluid Phase Equilib.* **2005**, *237*, 148−159.

(25) Gaman, A. I.; Napari, I.; Winkler, P. M.; Vehkamäki, H.; Wagner, P. E.; Strey, R.; Viisanen, Y.; Kulmala, M. Homogeneous nucleation of *n*-nonane and *n*-propanol mixtures: A comparison of classical nucleation theory and experiments. *J. Chem. Phys.* **2005**, *123*, 244502.

(26) Azizian, S.; Bashavard, N.; Yahyaei, B. Surface properties of dilute solution of alkanes in benzyl alcohol. *J. Chem. Eng. Data* **2006**, *51*, 56−59.

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