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Surface Tension of Organic Acids + Water Binary Mixtures from 20 °C to 50 °C

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The surface tensions of aqueous solutions of formic acid, acetic acid, and propionic acid were measured over the entire concentration range at temperatures (20 to 50) °C. The experimental values were correlated with temperature and mole fraction. Maximum deviations were in both cases always less than 1%.

Introduction

The recovery of acetic, formic and propionic acids from aqueous mixtures is economically important in industries that utilize these acids as raw materials or solvents for reactions. Aqueous solutions of acetic acid are used in cellulose acetate manufacture (used in the production of textile fibers, lacquers, photograph films, ...) and vinyl acetate production (used in latexes, paints, adhesives, ...), formic acid is used in the leather and textile industries, and propionic acid is used as a catalyst in the manufacture of polyester resins (Markley, 1960; Lowry and Aguiló, 1974; Aguiló and Horlenko, 1980).

Recovery of the acids from aqueous solutions can be realized by direct distillation, azeotropic distillation, and solvent extraction. The selection of recovery method depends on the estimated cost of the separation. If the acid concentrations are low, the most economical method will be extraction due to lower steam costs.

Surface tension has an important role in mass transfer processes such as distillation, extraction, and absorption since it can influence the rate of mass transfer across the interface. The diffusion of solute often causes an interfacial turbulence that is not related to the turbulence in the bulk of the flowing fluid. The interfacial turbulence, convective motions promoted by interfacial tension gradients, can give an increase in the rate of interfacial mass transfer (Lewis and Pratt, 1953). Sternling and Scriven (1959) analyzed the hydrodynamic aspects of interfacial turbulence and suggested that interfacial tension is usually promoted by solute transfer into the phase of lower viscosity. Others authors (Gross and Hixson, 1969; Vázquez et al., 1990, 1996) have indicated that surface tension gradients along a gas−liquid interface can accompany mass transfer, and the resulting interfacial turbulence (Marangoni effects) can significantly accelerate the mass transfer process.

Our research concerns how mass transfer is influenced by the Marangoni effect (interfacial turbulence generated by surface tension gradients). The absorption of CO_2 by water at a plane interface was measured in the presence and in the absence of the Marangoni effect induced by deposition of some liquids of low surface tension (aqueous solutions of alcohols) on the gas−liquid interface, and the surface velocity distributions resulting from the induced convection were measured and used to calculate a Reynolds number quantifying convection and mean surface times residence, correlating the Reynolds number with the ratio of Marangoni and Schmidt numbers (Vázquez et al., 1990, 1996). In order to extend these investigations to other liquids, such as organic acids, we need to determine their surface tensions. In this work we present measurements of the surface tension of formic acid + water, acetic acid + water, and propionic acid + water mixtures over the entire concentration range at temperatures of (20 to 50) °C.

Table 1. Surface Tension of Formic Acid (1) + Water (2)

	σ/(mN m^{-1})						
x_1	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
0.020	68.86	68.11	67.33	66.57	65.72	65.02	64.18
0.042	65.54	64.82	64.02	63.31	62.48	61.82	61.01
0.065	62.24	61.91	61.14	60.46	59.67	58.98	58.23
0.089	60.02	59.33	58.61	57.92	57.16	56.52	55.76
0.115	57.73	57.07	56.36	55.68	54.98	54.33	53.60
0.144	55.87	55.21	54.52	53.86	53.14	52.53	51.79
0.207	52.31	51.68	51.06	50.42	49.71	49.12	48.46
0.281	49.52	48.88	48.23	47.61	46.96	46.38	45.68
0.370	46.76	46.18	45.58	44.97	44.33	43.78	43.13
0.477	44.28	43.73	43.10	42.57	41.96	41.38	40.82
0.610	41.87	41.31	40.68	40.12	39.51	39.01	38.42
0.779	39.68	39.14	38.54	38.01	37.46	36.93	36.38
1.000	37.58	37.03	36.47	35.94	35.39	34.87	34.34

Experimental Section

Aqueous solutions of formic acid, acetic acid and propionic acid were prepared with distilled−deionized water. The acids were Merck products of nominal purity >98%. All the solutions were prepared by mass with an uncertainty less than 0.3%, which are listed in Tables 1−3 as mole fractions.

Surface tension was determined at 5 °C intervals between (20 and 50) °C, using a Traube stalagmometer and a Prolabo tensiometer, which employs the Wilhelmy plate principle (Lin et al., 1990; Van der Bogaert and Joos, 1980). The stalagmometer and the tensiometer were calibrated with distilled−deionized water, and the detailed experimental procedure has been described elsewhere (Vázquez et al., 1995a,b). Each value reported was an average of 5−10 measurements, where maximum deviations from the average value were always less than 0.4%. All solutions were thermostated with a precision ±0.05 K, and the accuracy of the measurements was ±0.05 mN·m^{-1}.

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Table 2. Surface Tension of Acetic Acid (1) + Water (2)

	σ/(mN m^{-1})						
x_1	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
0.016	62.42	61.72	60.93	60.13	59.31	58.62	57.76
0.032	56.28	55.58	54.88	54.16	53.38	52.71	51.87
0.050	51.83	51.24	50.53	49.86	49.16	48.48	47.76
0.070	48.64	48.01	47.32	46.68	46.02	45.34	44.68
0.091	46.13	45.44	44.84	44.16	43.54	42.82	42.24
0.114	44.06	43.46	42.82	42.18	41.60	40.93	40.37
0.167	40.92	40.34	39.73	39.14	38.57	37.96	37.33
0.231	38.38	37.62	37.31	36.66	36.14	35.58	35.00
0.310	36.33	35.79	35.28	34.71	34.16	33.62	33.08
0.412	34.44	33.82	33.40	32.86	32.34	31.86	31.23
0.545	32.51	32.03	31.44	30.92	30.46	29.89	29.41
0.730	30.28	29.76	29.27	28.78	28.26	27.74	27.23
1.000	27.61	27.12	26.63	26.11	25.64	25.13	24.66

Table 3. Surface Tension of Propionic Acid (1) + Water (2)

	σ/(mN m^{-1})						
x_1	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
0.013	53.18	52.44	51.71	51.01	50.24	49.50	48.77
0.026	45.34	44.62	43.88	43.23	42.51	41.82	41.11
0.041	41.12	40.44	39.76	39.12	38.46	37.76	37.08
0.057	38.41	37.76	37.17	36.53	35.89	35.24	34.56
0.075	36.54	35.92	35.34	34.72	34.08	33.46	32.84
0.094	35.23	33.63	34.01	33.41	32.81	32.21	31.61
0.140	33.33	32.76	32.18	31.62	31.04	30.48	29.92
0.196	32.01	31.47	30.94	30.36	29.83	29.27	28.76
0.267	30.96	30.43	29.92	29.37	28.84	28.34	27.81
0.362	30.04	29.52	29.01	28.48	27.96	27.41	26.93
0.493	29.10	28.58	28.08	27.56	27.07	26.57	26.06
0.686	28.02	27.51	27.03	26.52	26.01	25.54	25.02
1.000	26.66	26.17	25.68	25.18	24.69	24.19	23.68

Table 4. Surface Tension Parameters K_1 and K_2 (Eq 1) for Aqueous−Organic Acid Mixtures

organic component	x_1	K_1	K_2	x_1	K_1	K_2
formic acid	0.000	76.0114	0.1609	0.207	54.8736	0.1281
	0.020	72.0068	0.1561	0.281	51.9018	0.1236
	0.042	68.5939	0.1515	0.370	49.1272	0.1192
	0.065	65.5618	0.1468	0.477	46.6336	0.1159
	0.089	62.8439	0.1411	0.610	44.0829	0.1124
	0.115	60.4518	0.1364	0.779	41.9025	0.1100
	0.144	58.4800	0.1326	1.000	39.6950	0.1067
acetic acid	0.000	76.0114	0.1609	0.167	43.3596	0.1194
	0.016	65.4871	0.1537	0.231	40.7315	0.1148
	0.032	59.2404	0.1462	0.310	38.5231	0.1088
	0.050	54.6881	0.1375	0.412	36.4971	0.1042
	0.070	51.2853	0.1321	0.545	34.5604	0.1026
	0.091	48.6845	0.1288	0.730	32.2939	0.1008
	0.114	46.5776	0.1246	1.000	29.5836	0.0987
propionic acid	0.000	76.0114	0.1609	0.140	35.6121	0.1141
	0.013	56.1200	0.1471	0.196	34.1859	0.1086
	0.026	48.0868	0.1390	0.267	33.0567	0.1049
	0.041	43.8174	0.1343	0.362	32.0875	0.1028
	0.057	41.0293	0.1291	0.493	31.1053	0.1010
	0.075	39.0671	0.1242	0.686	30.0168	0.0996
	0.094	37.6318	0.1198	1.000	28.6411	0.0989

Results and Discussion

Tables 1−3 list the measured surface tensions of formic acid + water, acetic acid + water, and propionic acid + water mixtures of various concentrations at each temperature. In all the systems studied the surface tension, σ, decreased with increasing temperature for any given mole fraction of acid. The experimental values were correlated with temperature by means of the following linear expression

$$\sigma/(\mathrm{mN{\cdot}m^{-1}}) = K_1 - K_2{\cdot}t/°\mathrm{C} \qquad (1)$$

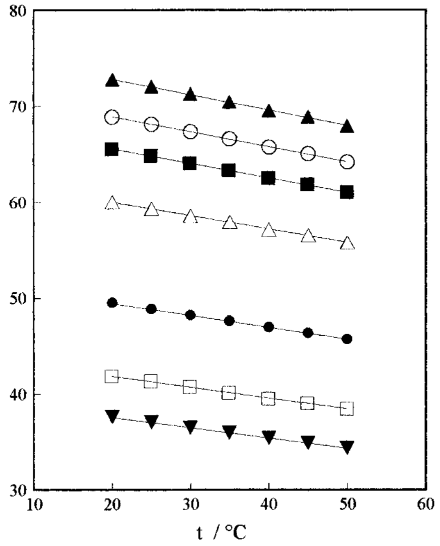

Figure 1. Surface tension as a function of temperature: (▲) water; (○) 5 mass % formic acid; (■) 10 mass % formic acid; (△) 20 mass % formic acid; (●) 50 mass % formic acid; (□) 80 mass % formic acid; (▼) 100 mass % formic acid; (—) calculated from eq 1.

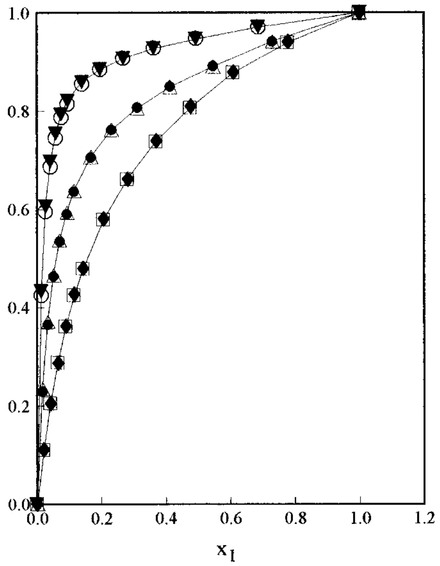

Figure 2. Dimensionless surface tension σ* plotted against mole fraction of acid: (♦) formic acid, 20 °C; (□) formic acid, 50 °C; (●) acetic acid, 20 °C; (△) acetic acid, 50 °C; (○) propionic acid, 20 °C; (▼) propionic acid, 50 °C.

proposed for the pure components (Jasper, 1972). This equation also fitted the data of Tables 1−3 for each concentration with deviations of less than 1%, and the fitted values of K_1 and K_2 are listed in Table 4. Figure 1 shows the results for formic acid + water mixtures as an example.

For a given temperature, the surface tension of all mixtures studied decreased as the acid concentration increased. This trend was nonlinear, the change in surface tension caused by a given change in acid concentration being larger at low concentrations than at high. Fitting the equation

$$\sigma^* = \frac{\sigma_2 - \sigma}{\sigma_2 - \sigma_1} = \left(1 + \frac{a x_2}{1 - b x_2}\right) x_1 \qquad (2)$$

to the results for each solute (where σ_2 and σ_1 are the surface tensions of pure water and pure acid respectively and x_1 and x_2 are the mole fractions of acid and water)

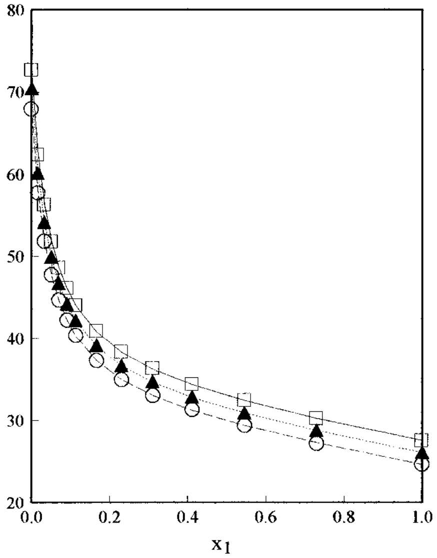

Figure 3. Surface tension of acetic acid + water mixtures plotted against mole fraction of acetic acid: (□) experimental, 20 °C; (—) calculated, 20 °C; (▲) experimental, 35 °C; (···) calculated, 35 °C; (○) experimental, 50 °C; (---) calculated, 50 °C.

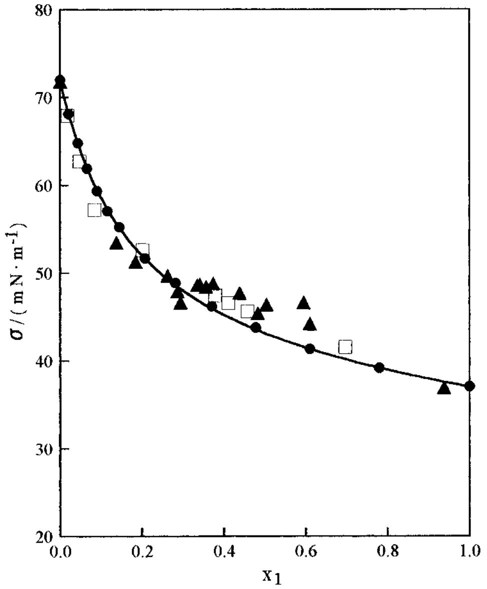

Figure 4. Surface tension of formic acid+water mixtures against mole fraction of formic acid : (●) experimental, 25 °C; (□) Drucker, 25 °C; (▲) Glagoleva, 25 °C; (—) calculated from eq 2, 25 °C.

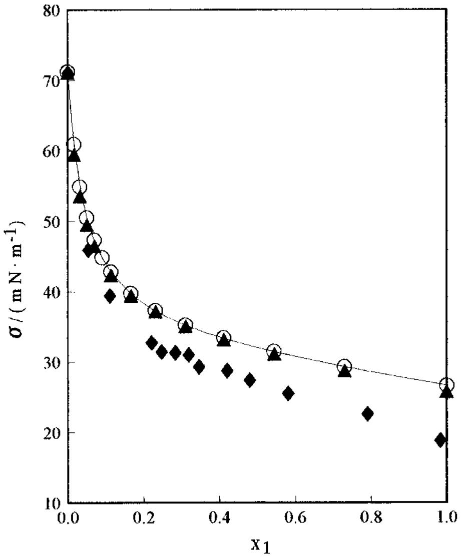

Figure 5. Surface tension of acetic acid + water mixtures against mole fraction of acetic acid: (○) experimental, 30 °C; (♦) Glagoleva, 30 °C; (▲) Morgan, 30 °C; (—) calculated from eq 2, 30 °C.

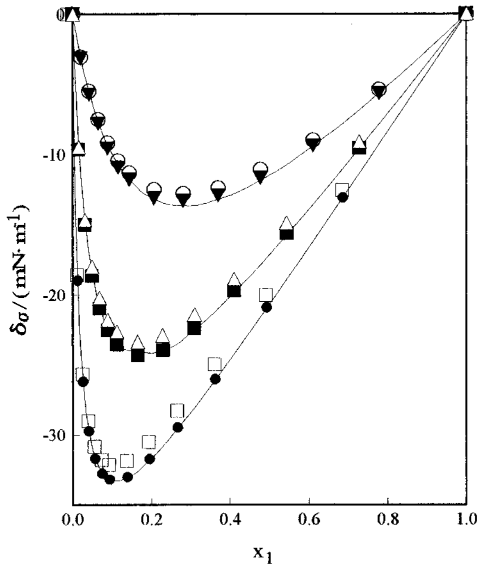

Figure 6. Surface tension deviation, δ_{σ}, as a function of mole fraction of acid: (▼) formic acid, 20 °C; (○) formic acid, 50 °C; (■) acetic acid, 20 °C; (△) acetic acid, 50 °C; (●) propionic acid, 20 °C; (□) propionic acid, 50 °C; (—) calcd from eqs 2 and 3.

Table 5. Surface Tension Parameters *a* and *b* (Eq 2) for Aqueous−Organic Acid Mixtures

organic component	*t*/°C	*a*	*b*	organic component	*t*/°C	*a*	*b*
formic acid	20	0.7538	0.8442	propionic acid	20	0.9103	0.9848
	25	0.7512	0.8457		25	0.9096	0.9850
	30	0.7488	0.8473		30	0.9089	0.9852
	35	0.7466	0.8488		35	0.9081	0.9854
	40	0.7443	0.8504		40	0.9073	0.9856
	45	0.7423	0.8521		45	0.9066	0.9857
	50	0.7401	0.8536		50	0.9058	0.9860
acetic acid	20	0.7928	0.9556				
	25	0.7913	0.9562				
	30	0.7896	0.9568				
	35	0.7879	0.9573				
	40	0.7868	0.9575				
	45	0.7861	0.9579				
	50	0.7852	0.9582				

yielded $\sigma^{*}-x_1$ curves like those shown in Figure 2 for temperatures (20 and 50) °C; the dimensionless surface tension σ^{*} is a weak function of temperature over most of the concentration range. The values of the fitted parameters *a* and *b* (Table 5) are linear functions of temperature for each acid. Figure 3 shows the measured surface tensions of acetic acid + water mixtures in comparison with those calculated by means of eq 2; the deviations are less than 1% in all such plots.

An important number of experimental values obtained by other authors cannot be directly compared with the values reported in this paper because of differences in the concentrations used. They can, however, be compared with values predicted by eq 2, finding that for the three systems at 25 and 35 °C (Drucker, 1905) and for the formic acid + water and acetic acid + water systems at 30 °C (Morgan and Neidle, 1913) the values present deviations less than 5% from the predictions of eq 2. The values obtained by Glagoleva (1947) for the formic acid + water at 20, 25 and 30 °C and acetic acid + water at 20 and 30 °C systems show much greater deviations. The experimental surface tension (reported in this work and in those of other reseachers) and the one calculated by means of eq 2 are graphically shown, as an example, in Figures 4 (acetic acid + water at 25 °C) and 5 (formic acid + water at 30 °C).

The surface tension deviation is defined as the difference between the surface tension of the mixture and those expected on the basis of a mole fraction average

$$\delta\sigma = \sigma - (\sigma_2 x_2 + \sigma_1 x_1) \qquad (3)$$

Plotting δ_σ against the mole fraction of organic component (Figure 6 shows typical plots) shows that the deviation from a mole fraction average increases with the length of the organic molecule and decreases with rising temperature.

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