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Surface Tension of Alcohol + Water from 20 to 50 °C

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The surface tension of aqueous solutions of methanol, ethanol, 1-propanol, and 2-propanol was measured over the entire concentration range at temperatures of 20−50 °C. The experimental values were correlated with temperature and with mole fraction. The maximum deviation was in both cases always less than 3%.

Introduction

The surface tension of mixtures is a physical property of great importance for mass transfer processes such as distillation, extraction, or absorption. In relation to our research (Vazquez et al., 1990) on how mass transfer is influenced by the Marangoni effect (spontaneous interfacial turbulence generated by surface tension gradients), in this work we measured the surface tension of methanol + water, ethanol + water, 1-propanol + water, and 2-propanol + water over the entire concentration range at temperatures of 20−50 °C.

Experimental Section

Aqueous solutions of methanol, ethanol, 1-propanol, and 2-propanol were prepared with distilled, deionized water. The alcohols were Merck products of nominal purity >99.7%. All the solutions were prepared by weight with deviations of less than 0.3% from the desired concentrations, which are indicated in Tables 1−4 as mole fraction.

Table 1. Surface Tension of Methanol (1) + Water (2)

		$\sigma/(\mathrm{mN\cdot m^{-1}})$ at t/°C						
mass %	x_1	20	25	30	35	40	45	50
0	0.000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
5	0.029	63.46	62.77	61.98	61.14	60.32	59.58	58.77
10	0.059	56.87	56.18	55.41	54.67	54.01	53.27	52.46
15	0.090	51.83	51.17	50.43	49.76	47.04	48.39	47.62
20	0.123	47.86	47.21	46.56	45.84	45.17	44.48	43.76
25	0.158	44.38	43.78	43.14	42.51	41.82	41.21	40.57
30	0.194	41.67	41.09	40.43	39.77	39.14	38.53	37.88
40	0.273	37.02	36.51	35.90	35.36	34.79	34.18	33.62
50	0.360	33.37	32.86	32.33	31.85	31.26	30.77	30.28
60	0.458	30.32	29.83	29.34	28.86	28.44	27.93	27.54
70	0.568	27.91	27.48	26.99	26.56	26.12	25.64	25.23
80	0.692	25.98	25.54	25.06	24.60	24.21	23.72	23.33
90	0.835	24.37	23.93	23.43	22.95	22.57	22.06	21.67
100	1.000	22.95	22.51	22.01	21.52	21.13	20.61	20.21

Table 2. Surface Tension of Ethanol (1) + Water (2)

		$\sigma/(\mathrm{mN\cdot m^{-1}})$ at t/°C						
mass %	x_1	20	25	30	35	40	45	50
0	0.000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
5	0.020	56.41	55.73	55.04	54.36	53.63	52.96	52.16
10	0.042	48.14	47.53	46.88	46.24	45.58	44.97	44.26
15	0.065	42.72	42.08	41.49	40.88	40.27	39.64	38.96
20	0.089	38.56	37.97	37.38	36.83	36.28	35.71	35.12
25	0.115	36.09	35.51	34.96	34.41	33.86	33.31	32.76
30	0.144	33.53	32.98	32.43	31.94	31.42	30.89	30.34
40	0.207	30.69	30.16	29.68	29.27	28.77	28.28	27.82
50	0.281	28.51	27.96	27.53	27.11	26.64	26.21	25.78
60	0.370	26.72	26.23	25.81	25.43	24.97	24.54	24.11
70	0.477	25.48	25.01	24.60	24.21	23.76	23.33	22.92
80	0.610	24.32	23.82	23.39	23.01	22.54	22.12	21.71
90	0.779	23.23	22.72	22.32	21.94	21.53	21.13	20.71
100	1.000	22.31	21.82	21.41	21.04	20.62	20.22	19.82

Table 3. Surface Tension of 1-Propanol (1) + Water (2)

		$\sigma/(\mathrm{mN\cdot m^{-1}})$ at t/°C						
mass %	x_1	20	25	30	35	40	45	50
0	0.000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
5	0.016	42.51	41.83	41.16	40.53	39.86	39.22	38.54
10	0.032	34.86	34.32	33.81	33.26	32.69	32.08	31.48
15	0.050	30.87	30.36	29.88	29.39	28.89	28.36	27.90
20	0.070	28.31	27.84	27.41	26.96	26.51	26.03	25.59
25	0.091	27.08	26.64	26.22	25.79	25.36	24.91	24.49
30	0.114	26.41	25.98	25.56	25.16	24.74	24.29	23.88
40	0.167	25.68	25.26	24.88	24.51	24.09	23.69	23.32
50	0.231	25.18	24.80	24.42	24.02	23.64	23.24	22.86
60	0.310	24.89	24.49	24.11	23.73	23.33	22.92	22.54
70	0.412	24.47	24.08	23.69	23.31	22.93	22.54	22.14
80	0.545	24.23	23.86	23.48	23.09	22.68	22.28	21.91
90	0.730	23.98	23.59	23.21	22.84	22.44	22.04	21.66
100	1.000	23.69	23.28	22.89	22.51	22.11	21.69	21.31

Table 4. Surface Tension of 2-Propanol (1) + Water (2)

		$\sigma/(\mathrm{mN\cdot m^{-1}})$ at t/°C						
mass %	x_1	20	25	30	35	40	45	50
0	0.000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
5	0.016	50.32	49.58	48.88	48.16	47.37	46.66	45.82
10	0.032	41.21	40.42	39.73	39.06	38.43	37.78	37.04
15	0.050	35.27	34.63	34.01	33.38	32.76	32.13	31.51
20	0.070	31.16	30.57	29.98	29.37	28.79	28.18	27.59
25	0.091	28.88	28.28	27.71	27.14	26.58	26.04	25.47
30	0.114	27.38	26.82	26.26	25.73	25.18	24.66	24.11
40	0.167	25.81	25.27	24.74	24.23	23.72	23.21	22.69
50	0.231	24.78	24.26	23.76	23.27	22.78	22.29	21.81
60	0.310	24.05	23.51	22.97	22.54	22.03	21.52	21.01
70	0.412	23.17	22.68	22.18	21.71	21.22	20.76	20.28
80	0.545	22.62	22.14	21.66	21.18	20.71	20.23	19.78
90	0.730	22.21	21.69	21.18	20.66	20.16	19.74	19.23
100	1.000	21.74	21.22	20.72	20.23	19.71	19.21	18.69

Surface tension was determined at 5 °C intervals between 20 and 50 °C, using a Prolabo tensiometer, which employs the Wilhelmy plate principle (Lin et al., 1990; Bogaert et al., 1980), thermostated with a precision of ±0.1 °C. Values shown below are averages of 5−10 measurements; maximum deviations from the average were always less than 0.4%.

Results and Discussion

Tables 1−4 list the measured surface tensions of methanol + water, ethanol + water, 1-propanol + water, and 2-propanol + water of various concentrations at each temperature. In all the systems studied surface tension, σ, decreased with increasing temperature for any given mole fraction of alcohol. The surface tensions of the pure components can be correlated with temperature by fitting

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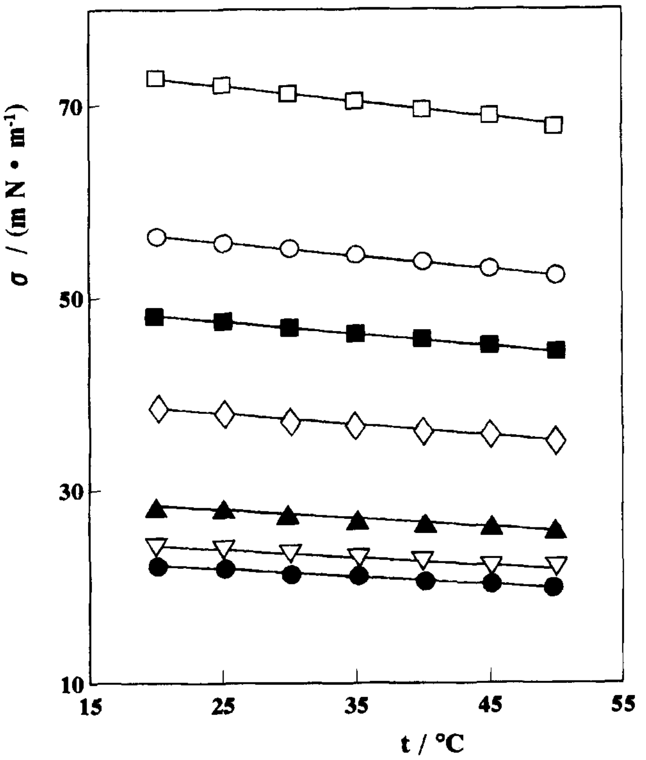

Figure 1. Surface tension as a function of temperature: □, water; ○, 5 mass % ethanol; ■, 10 mass % ethanol; ◇, 20 mass % ethanol; ▲, 50 mass % ethanol; ▽, 80 mass % ethanol; ●, 100 mass % ethanol; —, eq 1.

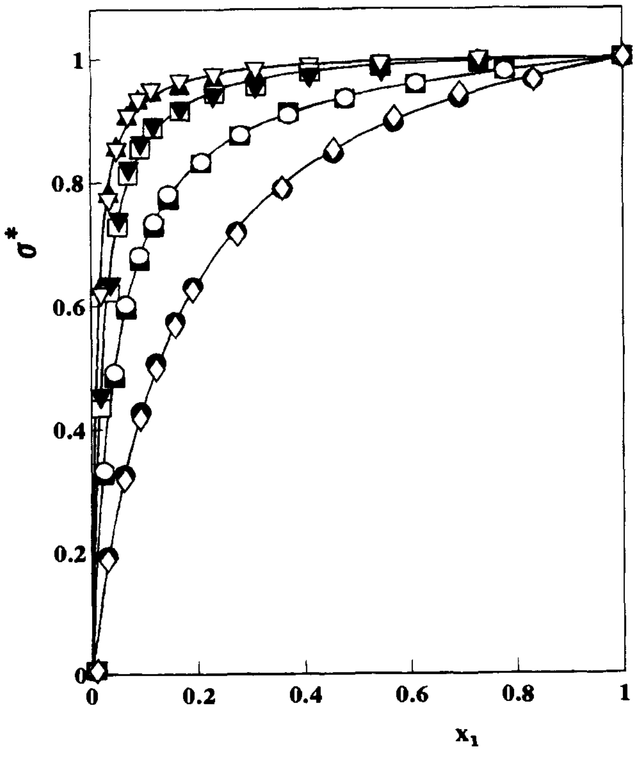

Figure 2. Dimensionless surface tension σ^* plotted against the mole fraction of alcohol: ◇, methanol 20 °C; ●, methanol, 50 °C; ■, ethanol, 20 °C; ○, ethanol, 50 °C; ▽, 1-propanol, 20 °C; ▲, 1-propanol, 50 °C; □, 2-propanol, 20 °C; ▼, 2-propanol, 50 °C.

the following linear expression (Jasper, 1972):

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

Equation 1 also fitted the data of Tables 1–4 for each concentration, with deviations of less than 1%. Figure 1 shows the results for ethanol + water as an example. The fitted values of K_1 and K_2 are listed in Table 5.

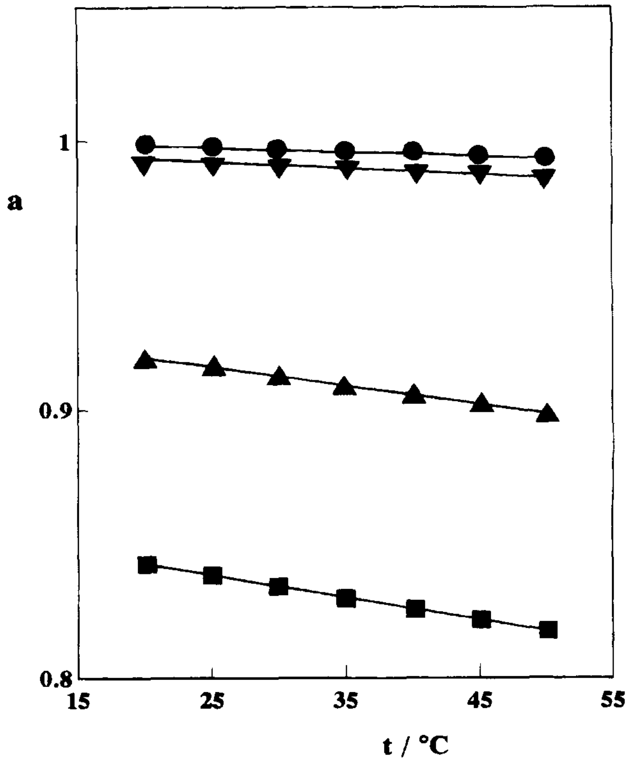

Figure 3. Fitted parameter a (eq 2) as a function of temperature: ■, methanol; ▲, ethanol; ●, 1-propanol; ▼, 2-propanol.

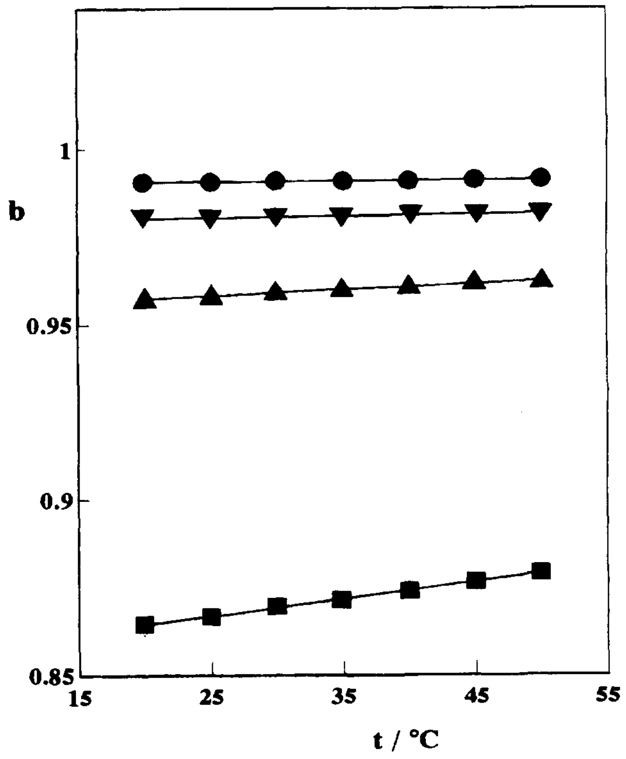

Figure 4. Fitted parameter b (eq 2) as a function of temperature: ■, methanol; ▲, ethanol; ●, 1-propanol; ▼, 2-propanol.

For a given temperature, the surface tension of mixtures studied in this paper decreased as the alcohol concentration increased. This trend was nonlinear, the change in surface tension caused by a given change in alcohol concentration being larger at low concentrations than at high concentra-

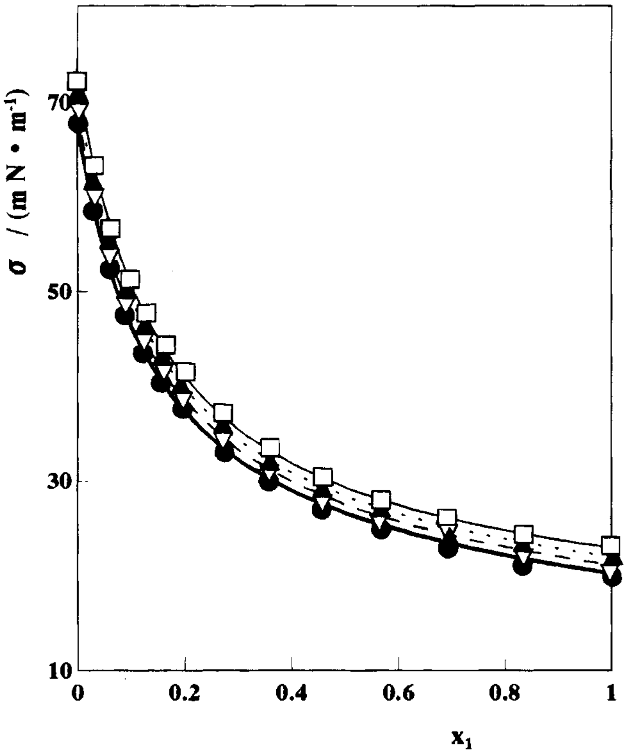

Figure 5. Surface tension of methanol + water plotted against the mole fraction of methanol: □, exptl, 20 °C; —, calcd, 20 °C; ▲, exptl, 30 °C; ···, 30 °C; ▽, exptl, 40 °C; - - -, calcd, 40 °C; ●, exptl, 50 °C; —, calcd, 50 °C.

Table 5. Surface Tension Parameters K_1 and K_2 for Aqueous Organic Mixtures

organic component	x_1	K_1	K_2	x_1	K_1	K_2
methanol	0.000	76.0114	0.1609	0.273	39.3594	0.1149
	0.029	66.6950	0.1584	0.360	35.4515	0.1041
	0.059	59.7657	0.1457	0.458	32.2614	0.0963
	0.090	54.6635	0.1407	0.568	29.8386	0.0938
	0.123	50.6179	0.1379	0.692	27.8830	0.0926
	0.158	47.0057	0.1289	0.835	26.2241	0.0921
	0.194	44.2404	0.1276	1.000	24.7789	0.0918
ethanol	0.000	76.0114	0.1609	0.207	32.5586	0.0949
	0.020	59.2521	0.1407	0.281	30.2507	0.0899
	0.042	50.7436	0.1290	0.370	28.4139	0.0861
	0.065	45.2079	0.1241	0.477	27.1571	0.0849
	0.089	40.8207	0.1139	0.610	25.9242	0.0834
	0.115	38.2868	0.1106	0.779	24.8225	0.0824
	0.114	35.6229	0.1054	1.000	23.8993	0.0819
1-propanol	0.000	76.0114	0.1609	0.167	27.4226	0.0831
	0.016	45.1418	0.1319	0.231	26.8879	0.0821
	0.032	37.0182	0.1092	0.310	26.5612	0.0812
	0.050	32.8536	0.0993	0.412	26.1232	0.0804
	0.070	30.1200	0.0906	0.545	25.8657	0.0798
	0.091	28.8068	0.0864	0.730	25.5904	0.0794
	0.114	28.0933	0.0844	1.000	25.2721	0.0791
2-propanol	0.000	76.0114	0.1609	0.167	27.8879	0.1039
	0.016	53.7768	0.1469	0.231	26.8821	0.1024
	0.032	44.1600	0.1314	0.310	26.0786	0.1014
	0.050	37.7668	0.1252	0.412	25.2489	0.1005
	0.070	33.5471	0.1191	0.545	24.6712	0.0998
	0.091	31.1171	0.1131	0.730	24.1807	0.0993
	0.114	29.5368	0.1086	1.000	23.6891	0.0989

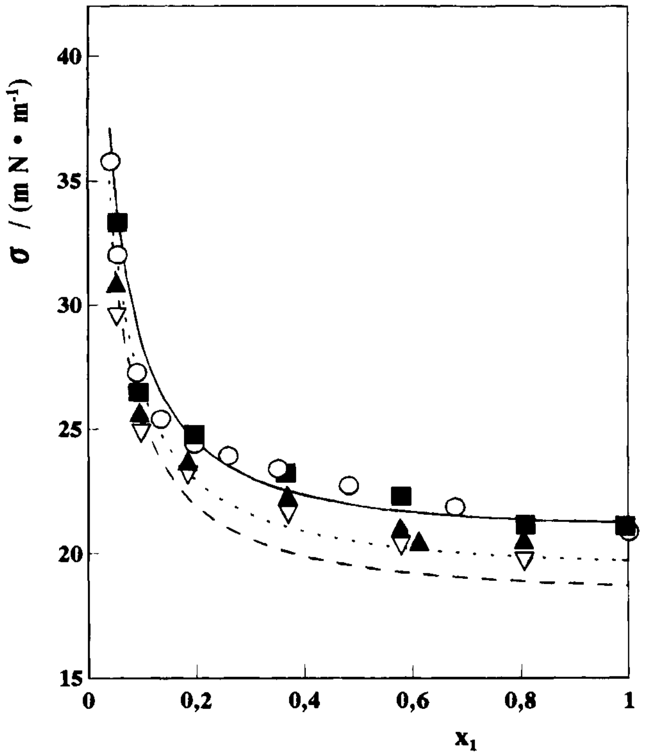

Figure 6. Surface tension of 2-propanol + water against the mole fraction of 2-propanol: ■, Hoke et al., 1991, 25 °C; ▲, Hoke et al., 1991, 40 °C; ▽, Hoke et al., 1991, 50 °C; ○, Cheong et al., 1987, 25 °C; —, eq 2, 25 °C; ···, eq 2, 40 °C; - - -, eq 2, 50 °C.

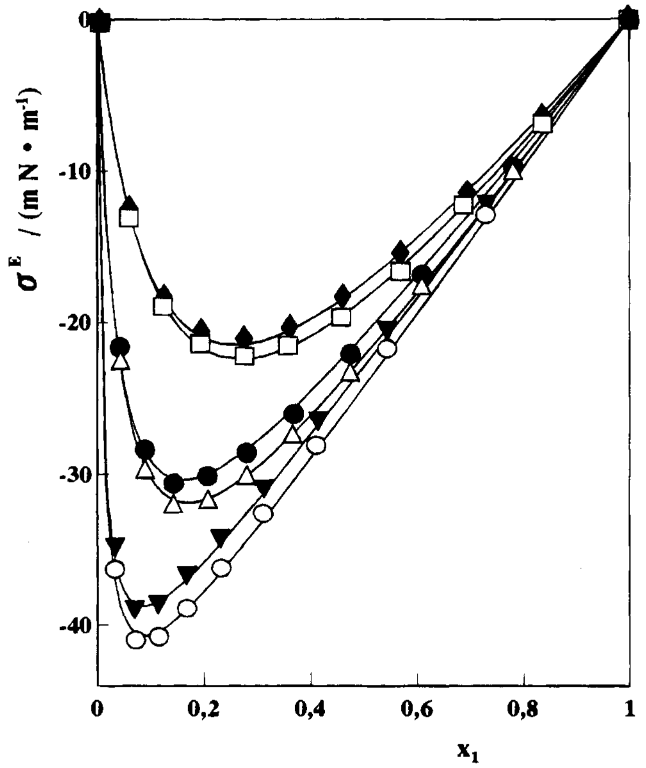

Figure 7. Excess surface tension σ^E as a function of the mole fraction of alcohol: □, methanol, 20 °C; ♦, methanol, 50 °C; △, ethanol, 20 °C; ●, ethanol, 50 °C; ○, 1-propanol, 20 °C; ▼, 1-propanol, 50 °C; — calcd from eqs 2 and 3.

tions. Fitting the equation

$$\sigma^* = \frac{\sigma_w - \sigma}{\sigma_w - \sigma_o} = \frac{1 + ax_2}{1 - bx_2}x_1 \tag{2}$$

to the data for each solute (where σ_w and σ_o are the surface tensions of pure water and pure alcohol, respectively, and x_1 and x_2 are the mole fractions of alcohol and water) yielded $\sigma^* - x_1$ curves like those shown in Figure 2 for temperatures of 20 and 50 °C. The dimensionless surface tension σ^* can be considered as independent of temperature over most of the concentration range. The values of the fitted parameters a and b in eq 2 are linear functions of temperature for each alcohol (see Figures 3 and 4). Figure

5 shows, by way of example, the measured surface tensions of methanol + water in comparison with those calculated by means of eq 2. The deviations are less than 3% in all such plots.

Experimental values obtained by other researchers 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. In the previous reports considered (for methanol + water at 25 °C (Cheong and Carr, 1987), ethanol + water at 25 °C (Ernst et al., 1936), 1-propanol + water at 20, 30, 40, and 50 °C (Martin et al., 1983), and 2-propanol + water at 25 °C (Cheong and Carr, 1987; Hoke et al., 1991) and at 30, 40, and 50 °C (Hoke et al., 1991)), 92% of the values deviate by less than 6% from the predictions of eq 2. The results for 2-propanol + water are shown as an example in Figure 6.

The sensitivity of the surface tension of these systems to the changes in concentration in the low alcohol concentration region reflects the nonideal character of these mixtures. The deviation from ideal behavior can be quantified by the excess surface tension σ^E, defined by

$$\sigma^E = \sigma - (\sigma_w x_w + \sigma_0 x_0) \qquad (3)$$

Plotting σ^E against the mole fraction of organic component (Figure 7 shows typical plots) shows that deviation from ideality increases with the length of the organic molecule and decreases with rising temperature.

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