

Surface Tensions of Three Amyl Alcohol + Ethanol Binary Mixtures from (293.15 to 323.15) K

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ABSTRACT: The surface tension of (2-methyl-2-butanol + ethanol), (3-methyl-1-butanol + ethanol), and (2-methyl-1-butanol + ethanol) binary solutions was measured over the entire composition range and at temperatures from (293.15 to 323.15) K. The experimental data were correlated with the temperature, the maximum deviation being less than 0.4 %.

INTRODUCTION

In the few last years our investigation group has carried out some diverse experimental studies to determine the surface tension of different substances with a great interest in the chemical industry: alcohol or glycols,¹ organic acids,² and alkanolamines,^{3,4} in the pure state or aqueous solution. In this work, continuing with this research, we have studied the surface tension of three binary mixtures of amyl alcohol + ethanol, over the entire concentration range and at different temperatures.

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. Many authors 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. In our research concerning how mass transfer is influenced by the Marangoni effect,^{5,6} we have induced the interfacial turbulence by the deposition of alcohols or organic acids on the gas–liquid interface. To extend these investigations to other liquids, such as amyl alcohols, we need to determine their surface tensions.

Amyl alcohol describes any saturated aliphatic alcohol containing five carbon atoms. This class consists of eight structural isomers C₅H₁₂O: four primary, three secondary, and one tertiary alcohols. The amyl alcohols are used like solvent for surfaces and lacquer baths, inks to print, and dyes for wool, as well as in the chemical production of photographic and pharmaceutical substances.⁷ They are also used for the perfume composition and the synthesis of fruit essence. Finally, another significant application of amyl alcohols is for the production of amyl acetates⁸ and other amyl esters.

Amyl alcohols are soluble in different organic solvents, such as ethanol, diethylether, or acetone, and insoluble in water. Therefore, in this work surface tensions of binary mixtures of (2-methyl-2-butanol + ethanol), (3-methyl-1-butanol + ethanol), and (2-methyl-1-butanol + ethanol) have been determined over the entire concentration range, at temperatures between (293.15 and 323.15) K. These data represent the continuation of a previous work on these binary mixtures.⁹

Table 1. Review of the Literature Data for the Surface Tension, σ , of Pure Ethanol

T/K	σ / mN·m ⁻¹		T/K	σ / mN·m ⁻¹	
	this work	lit.		this work	lit.
293.15	22.31	22.28 ^a	313.15	20.62	20.66 ^a
		22.30 ^b			20.64 ^c
		22.36 ^c			
298.15	21.82	21.86 ^a	318.15	20.22	20.50 ^b
		21.80 ^b			20.20 ^c
		21.78 ^d			
303.15	21.41	21.49 ^a	323.15	19.82	20.00 ^b
		21.40 ^b			19.79 ^c
308.15	21.04	21.15 ^a			
		21.10 ^b			

^a Giner et al.¹⁰ ^b Azizian and Hemmati.¹¹ ^c Gonçalves et al.¹² ^d Fu et al.¹³
^e Muratov.¹⁴

EXPERIMENTAL SECTION

Materials. 2-Methyl-1-butanol (CAS Registry No. 137-32-6), 2-methyl-2-butanol (CAS Registry No. 75-85-4), and 3-methyl-1-butanol (CAS Registry No. 123-51-3) were supplied by Sigma-Aldrich with a nominal mass fraction purity ≥ 0.99 for all compounds. Ethanol has been supplied by Panreac Química (CAS Registry No. 64-17-5) with a nominal mass fraction purity of >0.995 . All solutions were prepared by mass using an analytical balance (Kern 770) with a precision of $\pm 10^{-4}$ g. The maximum uncertainty of the sample's preparations in mole fraction was ± 0.0003 .

Methods. The surface tension of pure ethanol was determined in a previous paper¹ using a Prolabo tensiometer, which employs the Wilhemmy plate principle, while the surface tension of mixtures and pure amyl alcohols was determined using a Krüss K-11

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Table 2. Experimental Values of Surface Tension σ , at Temperature T , and Mole Fraction x , for the Liquid Mixture 2-Methyl-1-butanol (1) + Ethanol (2)^a

x_1	$\sigma / \text{mN} \cdot \text{m}^{-1}$						
	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$	$T/K = 313.15$	$T/K = 318.15$	$T/K = 323.15$
0.0000	22.31	21.82	21.41	21.04	20.62	20.22	19.82
0.0268	22.48	22.10	21.71	21.39	21.04	20.68	20.36
0.0549	22.65	22.25	21.90	21.56	21.22	20.90	20.55
0.0845	22.76	22.37	21.99	21.67	21.33	21.00	20.64
0.1156	22.86	22.47	22.10	21.75	21.44	21.08	20.73
0.1484	22.96	22.54	22.17	21.82	21.49	21.12	20.81
0.1830	23.01	22.62	22.23	21.89	21.54	21.20	20.86
0.2584	23.15	22.72	22.35	22.00	21.61	21.24	20.91
0.3433	23.28	22.86	22.46	22.11	21.76	21.37	20.98
0.4395	23.43	22.98	22.58	22.22	21.83	21.44	21.05
0.5495	23.56	23.09	22.69	22.30	21.94	21.54	21.15
0.6765	23.72	23.25	22.82	22.41	22.02	21.61	21.27
0.8247	23.89	23.38	22.96	22.54	22.13	21.70	21.33
1.0000	24.09	23.61	23.14	22.69	22.30	21.86	21.44

^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x) = 0.0003$, and the combined expanded uncertainty U_c is $U_c(\sigma) = 0.05 \text{ mN} \cdot \text{m}^{-1}$ (0.95 level of confidence).

Table 3. Experimental Values of Surface Tension σ , at Temperature T , and Mole Fraction x , for the Liquid Mixture 2-Methyl-2-butanol (1) + Ethanol (2)^a

x_1	$\sigma / \text{mN} \cdot \text{m}^{-1}$						
	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$	$T/K = 313.15$	$T/K = 318.15$	$T/K = 323.15$
0.0000	22.31	21.82	21.41	21.04	20.62	20.22	19.82
0.0268	22.50	22.05	21.67	21.34	20.93	20.58	20.22
0.0549	22.66	22.23	21.85	21.51	21.16	20.82	20.48
0.0845	22.78	22.36	21.98	21.64	21.30	20.97	20.62
0.1156	22.88	22.46	22.08	21.75	21.41	21.07	20.72
0.1484	22.97	22.54	22.16	21.83	21.48	21.14	20.79
0.1830	23.04	22.61	22.23	21.89	22.54	21.20	20.84
0.2584	23.16	22.73	22.34	21.99	22.64	21.28	20.92
0.3433	23.28	22.84	22.45	22.09	21.73	21.36	21.00
0.4395	23.41	22.97	22.56	22.19	21.82	21.45	21.08
0.5495	23.55	23.10	22.68	22.29	21.92	21.53	21.16
0.6765	23.70	23.24	22.81	22.40	22.02	21.62	21.23
0.8247	23.88	23.41	22.96	22.53	22.15	21.73	21.34
1.0000	24.04	23.61	23.14	22.69	22.30	21.86	21.44

^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x) = 0.0003$, and the combined expanded uncertainty U_c is $U_c(\sigma) = 0.05 \text{ mN} \cdot \text{m}^{-1}$ (0.95 level of confidence).

tensiometer, which also employs the Wilhelmy plate method, at temperatures ranging from (293.15 to 323.15) K, at 5 K intervals. The plate employed was a commercial platinum plate supplied by Krüss, which was cleaned with water and acetone and was flame-dried before each measurement. The surface tension was measured with an uncertainty of $\pm 0.05 \text{ mN} \cdot \text{m}^{-1}$, and the temperature was controlled using a thermostat-cryostat bath, with a precision of ± 0.1 K. Each surface tension value reported came from an average of 10 measurements. Before surface tension measurements, the samples were thermostatted in a stirred vessel that was closed to prevent evaporation.

The measured surface tensions of the pure ethanol, to the temperature of the work, are included in Table 1 and are compared with values published by other authors.^{10–14} A good agreement can be observed in the aforementioned table between our data and most of the bibliographical results. On the other hand, in the literature we have not found data on the surface tension of pure amyl alcohols to compare to our experimental data.

RESULTS AND DISCUSSION

Surface tension data of 2-methyl-1-butanol + ethanol, 2-methyl-2-butanol + ethanol, and 3-methyl-1-butanol + ethanol are

Table 4. Experimental Values of Surface Tension σ , at Temperature T , and Mole Fraction x , for the Liquid Mixture 3-Methyl-1-butanol (1) + Ethanol (2)^a

x_1	$\sigma / \text{mN} \cdot \text{m}^{-1}$						
	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$	$T/K = 313.15$	$T/K = 318.15$	$T/K = 323.15$
0.0000	22.31	21.82	21.41	21.04	20.62	20.22	19.82
0.0268	22.56	22.09	21.70	21.35	20.95	20.56	20.17
0.0549	22.78	22.32	21.94	21.59	21.19	20.81	20.44
0.0845	22.98	22.54	22.17	21.81	21.41	21.04	20.67
0.1156	23.17	22.73	22.36	22.01	21.62	21.24	20.87
0.1484	23.33	22.90	22.53	22.17	21.78	21.41	21.04
0.1830	23.49	23.05	22.68	22.32	21.92	21.55	21.17
0.2584	23.75	23.32	22.95	22.58	22.18	21.80	21.42
0.3433	23.96	23.54	23.17	22.79	22.39	22.01	21.63
0.4395	24.13	23.72	23.36	22.97	22.57	22.19	21.81
0.5495	24.25	23.85	23.49	23.10	22.70	22.33	21.95
0.6765	24.34	23.96	23.61	23.21	22.82	22.44	22.06
0.8247	24.41	24.05	23.71	23.29	22.89	22.51	22.12
1.0000	24.50	24.15	23.80	23.36	22.96	22.57	22.17

^a Standard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(x) = 0.0003$, and the combined expanded uncertainty U_c is $U_c(\sigma) = 0.05 \text{ mN} \cdot \text{m}^{-1}$ (0.95 level of confidence).

Table 5. Adjustable Parameters K_1 and K_2 (in eq 1) with the Standard Deviations, σ_{st} ^a

x_1	K_1			K_2			K_1			K_2		
	$\text{mN} \cdot \text{m}^{-1}$	$\text{mN} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	σ_{st}	$\text{mN} \cdot \text{m}^{-1}$	$\text{mN} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	σ_{st}	$\text{mN} \cdot \text{m}^{-1}$	$\text{mN} \cdot \text{m}^{-1}$	σ_{st}	$\text{mN} \cdot \text{m}^{-1}$	$\text{mN} \cdot \text{m}^{-1}$	σ_{st}
	2-Methyl-1-butanol (1) + Ethanol (2)			2-Methyl-2-butanol (1) + Ethanol (2)			3-Methyl-1-butanol (1) + Ethanol (2)					
0.0000	46.259	8.1857	0.031	46.259	8.1857	0.031	46.259	8.1857	0.031			
0.0268	44.151	7.3710	0.024	44.482	7.5143	0.032	45.508	7.8429	0.029			
0.0549	42.768	6.8290	0.019	43.651	7.1786	0.035	45.331	7.7071	0.028			
0.0845	41.962	6.4930	0.021	43.543	7.1000	0.034	45.332	7.6357	0.021			
0.1156	41.468	6.2714	0.018	43.412	7.0214	0.035	45.375	7.5857	0.022			
0.1484	41.115	6.1071	0.012	43.899	7.1571	0.034	45.565	7.5929	0.022			
0.1830	41.013	6.0286	0.014	44.160	7.2214	0.032	45.907	7.6571	0.020			
0.2584	40.943	5.9286	0.017	44.724	7.3714	0.030	46.343	7.7143	0.015			
0.3433	41.014	5.8857	0.014	45.262	7.5143	0.029	46.622	7.7357	0.012			
0.4395	41.293	5.9143	0.011	45.917	7.6929	0.030	46.758	7.7214	0.010			
0.5495	41.897	6.0500	0.013	46.684	7.9071	0.031	46.713	7.6643	0.010			
0.6765	42.633	6.2286	0.011	47.612	8.1714	0.030	46.691	7.6214	0.012			
0.8247	43.617	6.4786	0.021	48.522	8.4214	0.034	46.988	7.6929	0.023			
1.0000	44.819	6.7929	0.020	49.784	8.7790	0.032	47.548	7.8500	0.028			

^a $\sigma_{\text{st}} = [\sum(\sigma_{\text{cal}} - \sigma_{\text{exp}})^2 / (N - n)]^{1/2}$, where σ represents the surface tension, N is the number of data, and n is the number of parameters.

presented in Tables 2, 3, and 4, respectively. The experimental data shows that the surface tension decreases linearly with increasing temperature for any mass fraction of amyl alcohol. This behavior is common, and it has been detected for different systems.^{11,15} For this reason, the experimental data were correlated with temperature by the expression developed by Jasper:¹⁶

$$\sigma_m / \text{mN} \cdot \text{m}^{-1} = K_1 - K_2 \cdot T / K \quad (1)$$

where σ is the surface tension, T is the temperature, and K_1 and K_2 are two fit parameters whose values are listed in Table 5, with the standard deviation (σ_{st}) between the experimental and the calculated values

With regard to the influence of concentration, the experimental trends shown in Figure 1 indicate that, for each temperature, an increase in amyl alcohol concentration produces an increase of the value of surface tension. Moreover, the addition of a given quantity of amyl alcohol produces an increase in the surface tension, which is larger for the 2-methyl-1-butanol than for the 3-methyl-1-butanol or 2-methyl-2-butanol.

This trend is very similar than the behavior observed in a previous paper for alcoholic solutions of amines¹⁷ and is so different than the trend observed for aqueous solutions of ethanol (Figure 2). In aqueous solutions, pure water has a value of surface tension greater than the corresponding value for pure ethanol ($\sigma_{\text{water}} / \sigma_{\text{ethanol}} > 3$), and therefore, the addition of a

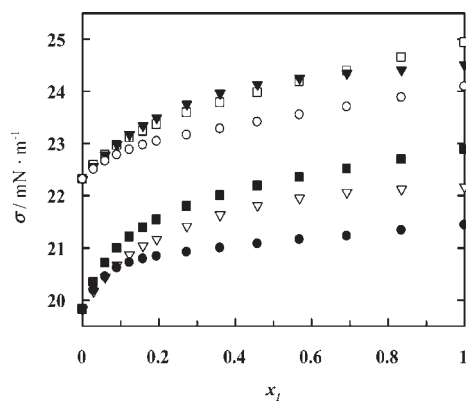


Figure 1. Variation of the surface tension, σ , with the composition at 293.15 K: \square , 2-methyl-1-butanol (1) + ethanol (2); \blacktriangledown , 3-methyl-1-butanol (1) + ethanol (2); \circ , 2-methyl-2-butanol (1) + ethanol (2), and at 323.15 K: \blacksquare , 2-methyl-1-butanol (1) + ethanol (2); \blacktriangledown , 3-methyl-1-butanol (1) + ethanol (2); \bullet , 2-methyl-2-butanol (1) + ethanol (2).

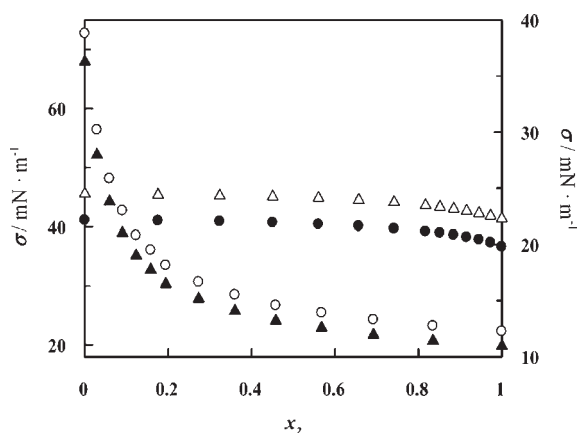


Figure 2. Surface tension dependence with composition for binary mixtures of 3-methyl-1-butanol (1) + ethanol (2): \triangle , 293.15 K; \bullet , 323.15 K, and for aqueous binary mixtures of ethanol (2): \circ , 293.15 K; \blacktriangle , 323.15 K.

small quantity of alcohol produces a significant decrease in the value of surface tension.

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