Surface Tension of Some Binary Organic Solutions of Alkylbenzenes and 1-Alkanols

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The surface tensions of binary mixtures of 1-alkanols (C_1–C_8) with benzene, toluene, or xylene were measured. The results were correlated with the activity coefficients calculated through the group contribution method such as UNIFAC, with the maximum deviation from the experimental results less that 5%. The coefficients of the correlation are correlated with the chain length.

Introduction

Surface tension is a property that represents changes in molecular interactions and could thus be used as a means of interpreting behavior of binary mixtures. Although much work has been done in understanding this property, there are few instances where this has been studied by considering a homologous series as one of the components (*1*).

Measurements on a homologous series are made so as to achieve a gradation of values which enable the development of correlations, which is the main purpose of this work. To this end, solutions of benzene, toluene, and xylene with 1-alkanols, respectively, were studied at 25 °C. The chemicals used were of analytical reagent grade except xylene which was a mixture of ortho, meta, and para isomers. The other chemicals with the exception of ethanol were not purified further. A comparison of the physical properties of the components included in this study with those obtained in the literature is given in Table I.

Table I. Physical Properties of Pure Components at 20 °C

		$\rho/(\mathrm{g \cdot cm^{-3}})$		n_D		
compound	purity/%	lit.[a]	measd	lit.[a]	measd	$\eta/(\mathrm{Pa \cdot s})$
benzene	99.8	0.8790	0.8784	1.5011	1.5006	0.646
toluene	99.0	0.8670	0.8670	1.4970	1.4970	0.612
xylene[b]			0.8680		1.4980	0.731
methanol	99.8	0.7917	0.7918	1.3312	1.3313	0.652
ethanol		0.7893	0.8019	1.3624	1.3639	1.484
propan-1-ol	99.00	0.8044	0.8040	1.3854	1.3848	2.176
butan-1-ol	99.00	0.8098	0.8120	1.3993	1.4000	2.907
pentan-1-ol	99.00	0.8144	0.8145	1.4099	1.4102	3.931
hexan-1-ol	99.00	0.8166	0.8187	1.4179	1.4183	5.061
heptan-1-ol	99.00	0.8219	0.8233	1.4241	1.4249	6.616
octan-1-ol	99.00	0.8246	0.8233	1.4292	1.4293	8.397

[a] *Handbook of Chemistry and Physics*, 58th ed.; CRC Press: Cleveland, OH, 1978. [b] Xylene available in the market is a mixture of ortho, meta, and para isomers.

Table II. Surface Tension, σ, for Benzene + 1-Alkanols at 25 °C

system	x_1	$\sigma/(\mathrm{mN \cdot m^{-1}})$	$\sigma_{calcd}/(\mathrm{mN \cdot m^{-1}})$	$100((\sigma - \sigma_{calcd})/\sigma)$
benzene (1) + methanol (2)	0.10	22.43	22.40	+0.13
	0.30	23.37	23.04	+1.41
	0.50	24.51	24.27	+0.98
	0.70	25.83	26.12	−1.12
	0.90	27.35	28.52	−4.28
benzene (1) + ethanol (2)	0.10	20.42	20.71	−1.42
	0.30	21.40	21.21	+0.89
	0.50	22.81	22.26	+2.41
	0.70	24.64	24.00	+2.60
	0.90	26.89	26.31	+2.16
benzene (1) + propan-1-ol (2)	0.10	22.15	22.89	−3.34
	0.30	22.68	23.33	−2.91
	0.50	23.68	24.36	+2.87
	0.70	25.13	26.18	−4.18
	0.90	27.05	28.52	−5.43
benzene (1) + butan-1-ol (2)	0.10	22.14	23.00	−3.88
	0.30	22.62	23.31	−3.05
	0.50	23.59	24.21	−2.63
	0.70	25.05	25.87	−3.27
	0.90	27.01	27.88	−3.22
benzene (1) + pentan-1-ol (2)	0.10	22.22	23.15	−4.19
	0.30	22.53	23.45	−3.64
	0.50	23.42	24.15	−3.12
	0.70	24.87	25.65	−3.14
	0.90	26.94	27.26	−1.19
benzene (1) + hexan-1-ol (2)	0.10	22.16	23.14	−4.42
	0.30	22.20	23.36	−5.23
	0.50	22.99	23.95	−4.18
	0.70	24.51	25.24	−2.98
	0.90	26.77	26.46	+1.16
benzene (1) + heptan-1-ol (2)	0.10	22.78	23.42	−2.81
	0.30	22.95	23.61	−2.88
	0.50	23.71	24.08	−1.56
	0.70	25.05	25.14	−0.36
	0.90	26.99	26.10	+3.30
benzene (1) + octan-1-ol (2)	0.10	23.77	23.94	−0.72
	0.30	24.07	24.03	+0.17
	0.50	24.76	24.42	+1.37
	0.70	25.84	25.36	+1.86
	0.90	27.30	26.07	+4.51

Experimental Section

The surface tension, σ, was measured at 25 °C using both a CAHN 2000 electrobalance and a stalagmometer. The measured value obtained with the CAHN balance agreed to within 1% with that obtained with the stalagmometer. Both instruments reproduced the surface tension of benzene to within 2% of the literature value. The density, ρ, was determined by an ANTON PAAR DMA 55 densitometer to an accuracy of $\pm 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. The accuracy of refractive index, n_D, measurement by an Abbe refractometer was $\pm 10^{-3}$ refractive index unit, that of viscosity, η, measured by an Ostwald viscometer was ±0.2% relative to the standard liquid (water), and the accuracy of the temperature control in all these measurements was within ±0.05 °C of the desired temperature.

Results and Discussion

A generalized correlation of the surface tension data for all the systems studied in this work is attempted. The surface tension, which is the surface free energy per unit area, is

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Table III. Surface Tension, σ, for Toluene + 1-Alkanols at 25 °C

system	x_1	σ/ (mN·m^{-1})	σ_{calcd}/ (mN·m^{-1})	100 (($\sigma - \sigma_{calcd}$)/σ)
toluene (1) + methanol (2)	0.10	22.38	22.43	−0.22
	0.30	23.23	23.17	+0.26
	0.50	24.26	24.34	−0.33
	0.70	25.48	25.84	−1.41
	0.90	26.88	27.55	−2.49
toluene (1) + ethanol (2)	0.10	20.72	20.74	−0.10
	0.30	22.07	21.30	+3.49
	0.50	23.53	22.34	+5.06
	0.70	25.09	23.87	+4.86
	0.90	26.77	25.66	+4.15
toluene (1) + propan-1-ol (2)	0.10	22.10	22.93	−3.76
	0.30	22.52	23.44	−4.09
	0.50	23.41	24.50	−4.66
	0.70	24.76	26.15	−5.61
	0.90	26.57	28.11	−5.80
toluene (1) + butan-1-ol (2)	0.10	22.34	23.00	−2.95
	0.30	23.04	23.44	−1.74
	0.50	24.01	24.37	−1.50
	0.70	25.26	25.93	−2.65
	0.90	26.78	27.71	−3.47
toluene (1) + pentan-1-ol (2)	0.10	22.33	23.16	−3.72
	0.30	22.74	23.50	−3.34
	0.50	23.60	24.32	−3.05
	0.70	24.89	25.77	−3.58
	0.90	26.62	27.24	−2.33
toluene (1) + hexan-1-ol (2)	0.10	22.64	23.15	−2.25
	0.30	23.30	23.41	−0.47
	0.50	24.22	24.12	+0.41
	0.70	25.40	25.39	+0.04
	0.90	26.83	26.52	+1.16
toluene (1) + heptan-1-ol (2)	0.10	23.16	23.43	−1.17
	0.30	23.79	23.66	+0.55
	0.50	24.63	24.25	+1.54
	0.70	25.68	25.35	+1.29
	0.90	26.94	26.15	+2.93
toluene (1) + octan-1-ol (2)	0.10	23.81	23.94	−0.55
	0.30	24.13	24.13	0.00
	0.50	24.75	24.60	+0.61
	0.70	25.68	25.57	+0.43
	0.90	26.92	26.07	+3.16

Table IV. Surface Tension, σ, for Xylene + 1-Alkanols at 25 °C

system	x_1	σ/ (mN·m^{-1})	σ_{calcd}/ (mN·m^{-1})	100(($\sigma - \sigma_{calcd}$)/σ)
xylene (1) + methanol (2)	0.10	22.60	22.46	+0.62
	0.30	23.72	23.22	+2.11
	0.50	24.80	24.32	+1.98
	0.70	25.85	25.54	+1.20
	0.90	26.85	26.75	+0.37
xylene (1) + ethanol (2)	0.10	20.91	20.74	+0.81
	0.30	22.49	21.36	+5.02
	0.50	23.98	22.37	+6.71
	0.70	25.39	23.63	+6.93
	0.90	26.71	25.03	+6.29
xylene (1) + propan-1-ol (2)	0.10	22.21	22.93	−3.24
	0.30	22.75	23.48	−3.21
	0.50	23.64	24.54	−3.81
	0.70	24.87	25.98	−4.50
	0.90	26.43	27.62	−4.50
xylene (1) + butan-1-ol (2)	0.10	22.20	23.00	−3.60
	0.30	22.68	23.48	−3.53
	0.50	23.54	24.44	−3.82
	0.70	24.78	25.84	−4.28
	0.90	26.39	27.41	−3.87
xylene (1) + pentan-1-ol (2)	0.10	22.37	23.17	−3.58
	0.30	22.81	23.54	−3.20
	0.50	23.63	24.40	−3.26
	0.70	24.83	25.71	−3.54
	0.90	26.41	27.11	−2.65
xylene (1) + hexan-1-ol (2)	0.10	22.51	23.15	−2.84
	0.30	22.98	23.45	−2.05
	0.50	23.80	24.20	−1.68
	0.70	24.96	25.39	−1.72
	0.90	26.46	26.52	−0.23
xylene (1) + heptan-1-ol (2)	0.10	22.97	23.44	−2.05
	0.30	23.34	23.71	−1.59
	0.50	24.05	24.33	−1.16
	0.70	25.11	25.38	−1.08
	0.90	26.51	26.23	+1.06
xylene (1) + octan-1-ol (2)	0.10	23.69	23.95	−1.10
	0.30	23.83	24.18	−1.47
	0.50	24.35	24.68	−1.36
	0.70	25.26	25.63	−1.46
	0.90	26.55	26.20	+1.32

expected to be related to the excess free energy of mixing. The latter is a function of the activity coefficients of the components. Therefore, we first calculated the activity coefficients by means of a group contribution method such as UNIFAC (*2*) and correlated them with the respective surface tensions through the following equation:

$$\sigma_{sol}/\sigma_{alc} = C(1.0 + A\gamma_{alc} + B\gamma_{alc}^{2}) \qquad (1)$$

where γ_{alc} is the activity coefficient of the alcohol species in the solution, σ_{alc} and σ_{sol} are the surface tensions of the pure alcohol component and the solution, respectively, and A, B, and C are the adjustable coefficients, each dependent on the chain length of the alcohol component and given by

$$C = 0.88 - 0.03N \qquad (2)$$

$$A = 0.163 + 0.067N + 0.001N^2 \qquad (3)$$

and

$$B = -[0.01 + 0.01N + 0.002N^2] \qquad (4)$$

where N is the number of $-CH_2-$ groups in the alcohol.

The results are presented in Tables II–IV. This correlation is quite accurate, showing a maximum absolute deviation not exceeding 5% from the experimental data. The correlation is specific to 25 °C and is not valid for the calculation of the end-point surface tension.

Literature Cited

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