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Measuring surface tension of binary mixtures of water + alcohols from the diffraction pattern of surface ripples

H. Ghahremani [1*], A. Moradi[2], J. Abedini-Torghabeh[3], S.M. Hassani[4]

[1]*Young Researcher Club, Islamic Azad University, Quchan Branh, Quchan, Iran*
[2]*Department of Physics, Islamic Azad University, Quchan Branch, Quchan, Iran*
[3]*Recycle Organization of Mashhad Municipality, Iran*
[4]*Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran*

ABSTRACT

Surface tension data of binary mixtures of water + alcohols was measured at a temperature of 25ºC using the optical diffraction method. The experimental values were correlated with temperature and mole fraction. T he surface tension of these binary mixtures decreases with the increase in linear alcohol content. Surface tensions for methanol, ethanol, 1-propanol and 2-propanol were determined at various temperatures and normal atmospheric pressure. The magnitude of these experimental quantities is discussed in terms of the nature and type of intermolecular interactions and hydrogen bonding in the binary mixtures. Distilled water at the temperature range of 0 to 100ºC had surface tensions of 75.99 to 58.93mN/m. Temperature was plotted against surface tension, and the general polynomial trend of the lines was found to be y = -0.167x+76.25 for water and y=-0.080x+24.13, y=-0.082x+24.10, y=-0.078x+25.38 and y=-0.077x+22.8 for methanol, ethanol, 1-propanol and 2-propanol, respectively. The logarithm of mole fraction of alcohols in water was plotted against the surface tension, and the general polynomial trend of the lines for water+ methanol, ethanol, 1-propanol and 2-propanol were found to be $y = 11.53x^3 + 26.54x^2 - 10.08x + 22.48$, $y = -3.059x^3 + 2.415x^2 - 6.841x + 21.94$, $y = -6.306x^3 - 8.661x^2 - 5.119x + 23.15$ *and* $y = -7.555x^3 - 8.668x^2 - 6.579x + 20.87$, *respectively.*

Key words: surface tension; binary mixtures alcohol; diffraction; temperature; mole fraction.

INTRODUCTION

The study of the mechanical properties of liquid mixtures containing water and alcohols has increased notably over the past several years given the interest that industry has shown in this type of compound. Specifically, recent research [1] has measured the surface tension of water in the diffraction pattern of surface ripples. Moreover, the analysis of properties, such as, surface tension, is very important from a theoretical point of view in that it sheds light on the structure of these liquid mixtures [2].

Mixtures of water with alcohols are important in numerous engineering applications. Tension caused by the polarity of water and alcohol, self-association of water and alcohol as well as the cross-association between water and alcohol are visible in such complex mixtures. These features have a significant impact on physical and chemical properties, especially, the phase equilibrium behavior and hence the interfacial properties. Calculating the surface and interfacial tension of liquid mixtures is very important, because these properties play an important role in interfacial heat and mass transfer. These figures also contain information on the structure and energy of the surface region [3-6].

The surface tension of liquid mixtures has been investigated by several researchers [7-17]. Recently, surface tension of binary mixtures of linear chain alcohols with ethylene glycol was studied by Azizian [18] and by Jimenez et al [19] P. Lucas and A. Hillel [20] have described, following Weisbuch and Garbay [21], an experimental set up to study the generation of ripples on surface of water and measure the surface tension of water. In 1894, Lord Rayleigh measured the surface tension of water by analyzing ripples [22]. Rayleigh's result of 74mN/m was remarkably close to the accepted value of 72.75mN/m for the surface tension of a water-air interface at 20 ^{0}C [23].

In the present study the surface tension (σ) was examined for the binary mixtures {water + methanol, ethanol, 1-propanol and 2-propanol} throughout the entire range of molar fractions at a temperature of 25ºC. The surface tension of these mixtures, were measured by setting up surface ripples with an oscillating wire attached to a speaker driven by a function generator. Exploiting the fact that the ripples behave like a diffraction grating, a laser was reflected off the surface and the interference spots measured from a gradient image. This technique permitted accurate measurement of the spots, and eliminated most of the fluctuations due to vibrations which were not completely isolated by the air table [24].

MATERIALS AND METHODS

By setting up ripples on the surface of the sample, the surface tension can be measured. A small wire connected to a speaker cone driven by a function generator sets up the surface ripples, and a He-Ne laser is angled at the sample surface. The ripples act as a diffraction grating yielding interference spots on a screen. By varying the mole fractions of alcohols in mixtures and making the frequency and amplitude of the function generator constant, the variation in the interference spot spacing can be measured and from this the surface tension can be obtained.

Table 1: Source, purity, density *(ρ)* and surface tension *(σ)* for the pure liquids

Liquid	Source and purity	ρ (g /ml)	σ (mN/ m)
Methanol	Merck , > 99.9%	0.7915	22.454
Ethanol	Merck , > 99.8%	0.7894	22.380
1- propanol	Merck , > 99.5%	0.8035	23.706
2- propanol	Merck , > 99.8%	0.7800	21.700

The source and purity of the chemical compounds are shown in Table 1, together with the densities, ρ, surface tensions, σ, and the values. All binary mixtures of water + alcohols were prepared by volume with a sampler precision of ±1 × 10^{-3} cm^{3}. The surface tension of samples was measured with the diffraction pattern of surface ripples. The temperature of the measurement cell was controlled within 0.01°C by a water thermostat and a 10◦C temperature interval between 0 and 100◦C was considered. Each value reported was an average of at least 10 measurements with a standard deviation of ±0.1 (mN/m). Densities were measured with an

Anton Paar digital precision densitometer (Model DMA 4500) operated in the static mode and calibrated with bi-distilled water.

As shown in Fig. 1, a petridish of about 20 cm diameter is filled with the experimental liquid to a depth of 1cm. A metal pin with its blunt end glued vertically upright to the diaphragm of a loud speaker (held above the petridish) is placed as an exciter. When slightly immersed in the liquid and driven by a low frequency sinusoidal signal generator, the exciter vibrates vertically up and down and generates the desired liquid surface waves. To study the profile of surface waves we place the petridish-loud-speaker assembly on the prism-table of a spectrometer in order to choose a diffracting element at any position on the liquid surface and to record the corresponding position from the prism-table scale (with a minimum count of 0.1 degree). Light from a 5mW He-Ne laser (λ= 632.8 nm) having a beam diameter of 1.8 mm is directed to fall on the liquid surface at an angle of incidence, of 86°as noted in our experiment. The laser beam incident on the dynamical phase grating formed on the liquid surface produces Fraunhofer diffraction patterns which is observed on a screen placed at a fairly large distance (12.4 meters in our case) from the diffraction center [25]. During our experiment, the room temperature was recorded at $25^{\circ}C$.

The dispersion relation for waves on liquid surfaces is [26]:

$$\omega^2 = \left(gk + \frac{\sigma}{\rho}k^3\right)\tanh(kD) \qquad (1)$$

where ω and k are the angular frequency and wave number, respectively. $\sigma$and ρ are the surface tension and density of the liquid while g is the gravitational acceleration and D is the depth of the liquid .The $\tanh(kD)$ factor is approximately 1 for deeper depth and/or larger wave number. The wave number k is acquired by the equation [21]:

$$k = \frac{2\pi}{\lambda}\sin\frac{\varphi}{2}[\sin(\theta - \frac{\varphi}{2}) + \sin(\theta + \frac{\varphi}{2})] \qquad (2)$$

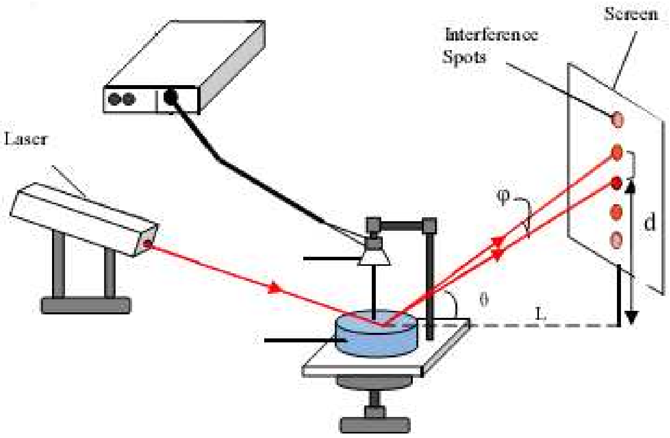

Fig. 1: A laser beam is aimed at a reservoir containing the sample, with ripples induced by a wire attached to a speaker driven by a function generator. The surface ripples act as a diffraction grating causing the interference spots on the screen.

The angle of the laser beam measured from the horizontal axis is θ. At small angles $(\sin\theta \cong \theta \ and \ \sin\varphi \cong \varphi)$ simplified to:

$$k = \frac{2\pi}{\lambda}\theta\varphi \qquad (3)$$

Where θ and φ are in radians and $\theta = \frac{h}{L}, \varphi = \frac{d}{L}$. d is the distance between adjacent interference spots and h is the perpendicular height of the central order spot from the liquid surface level.

In this experiment, λ is of order 10^{-7}m, φ is 10^{-3},θ is 10^{-2}, and D is of order 10^{-2}m. Thus kD is of order 10^{1} and so the tanh (kD) term in Eq. 1 is simply 1 and we have:

$$\omega^2 = gk + \frac{\sigma}{\rho}k^3 \qquad (4)$$

Similarly, we note that the gk term due to gravity is of order 10^{4} while the surface tension term $\frac{\sigma}{\rho}k^3$is of order 10^{10} to 10^{13}. Thus we can neglect the gravity term and simply use

$$\omega^2 = \frac{\sigma}{\rho}k^3 \qquad (5)$$

The final equation (6) obtained from eq.3 and 5 is:

$$\sigma = \left(\frac{\omega^2 \lambda^3 L^6}{0\pi^3 h^3}\right)\frac{\rho}{d^3} \qquad (6)$$

RESULTS AND DISCUSSION

The values of densities, ρ, and surface tension, σ, for several mixtures are reported in Table 2 and compared with literature values [23]. This Table lists the measured surface tension of water, methanol, ethanol, 1-propanol, 2-propanol at various temperature (in the temperature range investigated) fig 2 and 3.

Fig.2 and 3 show a comparison of references [27] and experimental data of the system water and alcohols at various temperatures.

Our special interest was the temperature dependence of the surface tension, which can be understood on the grounds of thermodynamic. In all systems studied, the surface tension decreased in line with temperature (in the temperature range investigated). The results of Table 2 show this correlation. Distilled water at these temperatures had surface tension (mN/m) of 75.99 to 58.93. The temperature was plotted against the surface tension and the general trend of the line was found to be

$y = -0.167x+76.25$, and for methanol, ethanol, 1-propanol and 2-propanol to be
$y=-0.080x+24.13$, $y=-0.082x+24.10$, $y=-0.078x+25.38$ and $y=-0.077x+22.8$, respectively.

The surface tension data of several alcohol-water mixtures at $25^{\circ}C$ are presented in table 3. These are shown in fig 3. The surface tension decreases with the mole fraction of alcohol. This rapid decrease is typical for the aqueous system with surface-active solutes and this character increases with the length of the hydrocarbon chain. In the aqueous solutions of normal alcohols, the surface active character increases with the length of the hydrocarbon tail [28]. In the systems studied here the surface active character increases slightly with the size of the hydrocarbon ring. Therefore, the surface tension of ethanol increases more rapidly than that of methanol as shown in fig 3 (this trend is nonlinear).

Table 2: Experimental density ρ, spot distance d, surface tension σ_{Exp}, reference surface tension σ_{Ref} and surface tension deviations $(\Delta\sigma)$ for the systems {water, methanol, ethanol, 1-propanol and 2-propanol}at various temperatures.

t [°C]	$\rho [\frac{g}{ml}]$	d [mm]	$\sigma_{exp} [\frac{mN}{m}]$	$\sigma_{ref} [\frac{mN}{m}]$	$\Delta\sigma [\frac{mN}{m}]$
			Water		
0	0.9998	35.5	75.99	75.64	0.35
10	0.9997	35.7	74.71	74.23	0.48
20	0.9982	36.0	72.75	72.75	0.00
30	0.9957	36.2	71.37	71.20	0.17
40	0.9922	36.5	69.38	69.60	0.22
50	0.9880	36.7	67.97	67.94	0.03
60	0.9832	36.9	66.54	66.24	0.30
70	0.9778	37.2	64.59	64.47	0.12
80	0.9718	37.4	63.17	62.67	0.50
90	0.9654	37.7	61.26	60.82	0.44
100	0.9584	38.1	58.93	58.91	0.02
			Methanol		
0	0.8157	48.6	24.16	24.00	0.16
10	0.8042	48.9	23.39	23.23	0.16
20	0.7925	49.2	22.63	22.45	0.18
30	0.7807	49.8	21.49	21.68	0.19
40	0.7685	50.1	20.78	20.91	0.13
50	0.7562	50.5	19.97	20.14	0.17
60	0.7435	50.6	19.51	19.36	0.15
			Ethanol		
0	0.8121	48.5	24.21	24.05	0.16
10	0.8014	49.1	23.02	23.22	0.20
20	0.7905	49.2	22.57	22.39	0.18
30	0.7793	49.6	21.72	21.55	0.17
40	0.7680	50.0	20.89	20.72	0.17
50	0.7564	50.7	19.74	19.89	0.15
60	0.7446	50.9	19.20	19.06	0.14
70	0.7324	51.4	18.34	18.23	0.11
			1-propanol		
0	0.8252	47.9	25.53	25.26	0.27
10	0.8151	48.2	24.75	24.48	0.27
20	0.8048	48.8	23.55	23.71	0.16
30	0.7943	48.9	23.10	22.93	0.17
40	0.7837	49.5	21.97	22.15	0.18
50	0.7729	49.6	21.54	21.38	0.16
60	0.7619	50.0	20.73	20.60	0.13
70	0.7506	50.6	19.70	19.82	0.12
80	0.7391	50.8	19.17	19.04	0.13
90	0.7273	51.2	18.43	18.27	0.16
			2-propanol		
0	0.8092	49.2	23.10	22.90	0.20
10	0.7982	49.8	21.98	22.11	0.13
20	0.7869	50.2	21.15	21.32	0.17
30	0.7755	50.6	20.35	20.53	0.18
40	0.7638	51.0	19.58	19.74	0.16
50	0.7519	51.4	18.83	18.96	0.13
60	0.7397	51.6	18.31	18.17	0.14
70	0.7272	52.1	17.49	17.38	0.11
80	0.7143	52.6	16.69	16.59	0.10

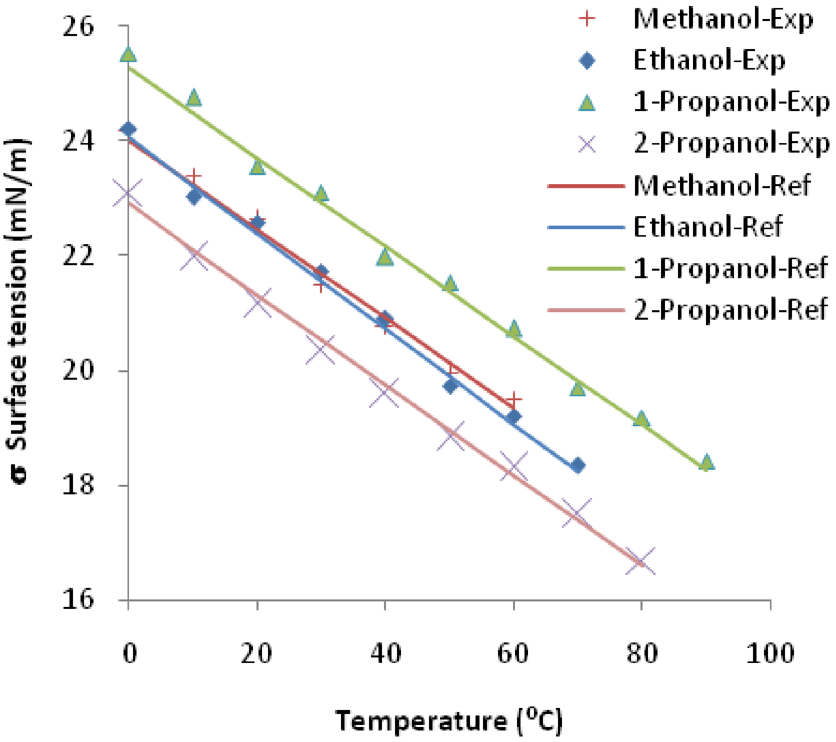

Fig.2. surface tension (σ) of ethanol, methanol, 1-propanol and 2-propanol as a function of temperature

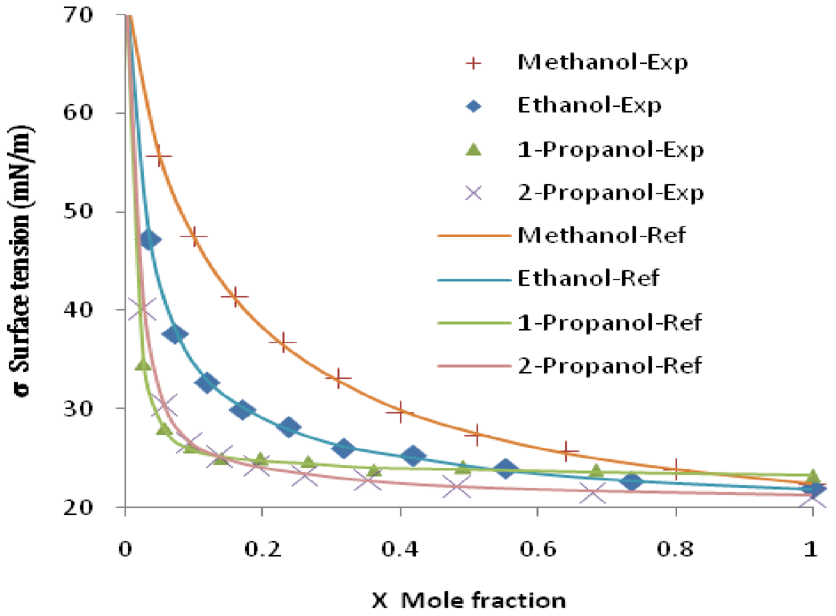

Fig.3.surface tension (σ) of binary mixture of methanol, ethanol, 1-propanol and 2-propanol with water as a function of mole fraction at $25^{\circ}C$

Table 3 Experimental density ρ, spot distance d, surface tension σ_{Exp}, reference surface tension σ_{Ref} and surface tension deviations $(\Delta\sigma)$ for the binary systems {water+ ethanol, methanol, 1-propanol and 2-propanol} at $25^{\circ}C$

x	$\rho[\frac{g}{ml}]$	d [mm]	$\sigma_{exp}[\frac{mN}{m}]$	$\sigma_{ref}[\frac{mN}{m}]$	$\Delta\sigma[\frac{mN}{m}]$
Water +Methanol					
0.0000	0.9970	36.1	72.10	72.01	0.09
0.0473	0.9872	39.1	55.61	56.18	0.57
0.1004	0.9761	40.9	47.56	47.21	0.35
0.1606	0.9636	42.5	41.47	41.09	0.38
0.2293	0.9493	43.9	36.80	36.51	0.29
0.3086	0.9328	45.1	33.17	32.86	0.31
0.4010	0.9136	46.5	29.57	29.83	0.26
0.5102	0.8909	47.4	27.25	27.48	0.23
0.6410	0.8637	47.9	25.77	25.54	0.23
0.8007	0.8305	48.8	23.76	23.93	0.17
1.0000	0.7915	49.4	22.33	22.51	0.18
Water +Ethanol					
0.0000	0.9970	36.1	72.10	72.01	0.09
0.0333	0.9711	41.3	47.17	47.53	0.36
0.0718	0.9632	44.2	37.67	37.97	0.30
0.1171	0.9539	46.0	32.68	32.98	0.30
0.1711	0.9428	47.0	29.96	30.16	0.20
0.2364	0.9293	47.6	28.18	27.96	0.22
0.3171	0.9127	48.5	26.02	26.23	0.21
0.4194	0.8916	48.6	25.24	25.01	0.23
0.5533	0.8640	49.0	24.02	23.82	0.20
0.7359	0.8264	49.5	22.72	22.72	0.00
1.0000	0.7894	49.6	22.00	21.82	0.18
Water + 1- propanol					
0.0000	0.9970	36.1	72.10	72.01	0.09
0.0261	0.9829	45.8	34.64	34.32	0.32
0.0570	0.9686	48.8	28.07	27.84	0.23
0.0938	0.9490	49.6	26.19	25.98	0.21
0.1387	0.9288	50.0	25.04	25.26	0.22
0.1946	0.9013	49.7	24.95	24.80	0.15
0.2660	0.8875	49.5	24.71	24.49	0.22
0.3605	0.8654	49.7	23.87	24.08	0.21
0.4914	0.8470	49.2	24.05	23.86	0.19
0.6850	0.8240	49.0	23.79	23.59	0.20
1.0000	0.8035	49.0	23.22	23.28	0.06
Water + 2- propanol					
0.0000	0.9970	36.1	72.10	72.01	0.09
0.0254	0.9816	43.6	40.06	40.42	0.36
0.0554	0.9696	47.5	30.29	30.57	0.28
0.0913	0.9464	49.2	26.63	26.82	0.19
0.1352	0.9302	49.8	25.08	25.27	0.19
0.1900	0.9037	49.9	24.33	24.26	0.07
0.2602	0.8824	50.2	23.31	23.51	0.20
0.3537	0.8638	50.1	22.86	22.68	0.18
0.4840	0.8341	50.3	22.01	22.14	0.13
0.6785	0.8063	50.2	21.55	21.69	0.14
1.0000	0.7800	50.1	21.09	21.22	0.13

In a recent research, Koga et al. propose that hydrophobic hydration locally enhances the hydrogen bond network but associates with the reduction of the hydrogen bond probability of bulk H_2O that is relatively far away from solutes [29]. The order of relative hydrophobic nature of alcohols is established by Koga et al. as: methanol < ethanol < 2-propanol < 1-propanol that is also observed in the order of mole fraction X. It is interesting to note that all of the curves of surface tension break like the critical micelle concentration for surfactants at the end point of these ranges, as shown in Fig 4.This figure shows a comparison of references [30] and experimental data of the mixture systems (water+ methanol,ethanol,1-propanol and 2-propanol in various mole fraction.

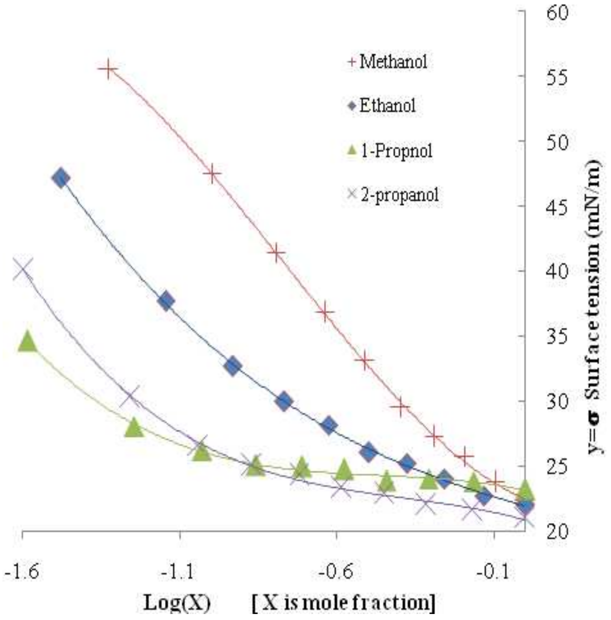

Fig.4: Experimental surface tension (σ) as a function of logarithm of mole fraction X and general trend of lines

Fig.4 shows experimental surface tension as a function of logarithm of mole fraction X and polynomial trend of lines at various volumes (10 to 100%) of alcohols in water. The dependence of the surface tension $\sigma\ (mN/m)$ for methanol, ethanol, 1-propanol and 2-propanol as a function of X, logarithm of mole fraction in water, can be given as:

$$\sigma = ax^3 + bx^2 + cx + d \qquad (7)$$

Where a, b, c and d are constants and x=log(X). The coefficients a, b, c and d are reported in Table 4.

Table 4.Coefficients of Eq. (7) fitted to the surface tension σ for binary systems

System	A	b	c	d
Water + Ethanol	11.53	26.54	-10.08	22.48
Water + methanol	-3.059	2.415	-6.841	21.94
Water+1-Propanol	-6.306	-8.661	-5.119	23.15
Water+2-Propanol	-7.555	-8.668	-6.579	20.87

The surface tension data was correlated with the position of hydroxyl groups in the solute and the results were used to evaluate the effect of alcohols on the water structure.

The surface tension decreases with the mole fraction of alcohol and temperature. A rapid decrease is typical for aqueous systems with surface-active solutes and this character increases with the length of the hydrocarbon chain.

CONCLUSION

In dilute alcohol aqueous solutions, hydrophobic hydration induces a surface excess of the alcohol. When a monolayer is completely formed, the solute molecules, either on the surface or in the bulk, feel tightest and the bulk solution starts to lose ideality; that is, the solute molecules start to aggregate. Gradually, the hydrogen bond network in water is destroyed by the growing aggregations. Consequently, the surface excess decreases as the molecular interactions in bulk weaken.

The experimental results show that there is a nonlinear decrease in surface tension with the addition of alcohols. The fundamental surface properties are demonstrated in the relative enrichment of the volatile component in the surface. This enrichment strongly depends on composition of the liquid phase. The surface tension of water and alcohols were correlated with temperature proposed for pure components. The results obtained show that temperature greatly influences the surface tension with a linear relationship.

REFERENCES

[1] S. sarker, PhD thesis, Indian institute of technology (Bombay, India, **2005**).
[2] E. Calvo, M. Pintos, A. Amigo, R. Bravo, *J. Colloid and Interface Sci*., **2004**, 272, 438.
[3] S. Enders, H. Kahl, *Fluid Phase Equib*, **2008**, 263, 160.
[4] J. Lyklema, Fundamentals of interface and colloid science: liquid-fluid interfaces, (Academic press, London, **2000**) 268.
[5] H.T. Davis, Statistical mechanism of phases interfaces, and thin films, Wiley-VCH, **1995**.
[6] I.C. Sanchez, Physics of polymer surfaces and interfaces, Butterworth Heinermann, Boston, **1992**.
[7] Papaioannou, C. Panayiotou, *J. Colloid Interface Sci*., **1989**, 130, 432.
[8] J.A.V. Butler, A. Wightman, *J. Chem. Soc*, **2001**, 1932. 2089.
[9] D.E. Goldsack, C.D. Sarvas, *Can. J. Chem*. **1981**, 59, 2969.
[10] D.E. Goldsack, B.R. White, *Can. J. Chem*. **1983**, 61, 1725.
[11] R. Defay, I. Prigogine, A. Bellemans, D.H. Everett, Surface tension and adsorption (John Wiley and Sons, Inc., New York, **1966**) 432.
[12] E.A. Guggenheim, *Trans. Faraday Soc*., **1945**, 41, 150.
[13] F.B. Sprow, J.M. Prausnitz. *Trans. Faraday Soc*., **1966**, 62, 1105.
[14] J.G. Eberhart, *J. Phys. Chem*., **1966**, 70, 1183.
[15] J.L. Shereshefsky, *J Colloid and Interface Sci*, **1967**, 24, 317.
[16] J.T. Suarez, C. Torres-Marchal, P. Rasmussen, *Chem. Eng. Sci*., **1989**, 44, 782.
[17] S. Azizian, N. Bashavard, *J. Colloid Interface Sci*. **2005**, 282, 428.
[18] S. Azizian, M. Hemmati, *J. Chem. Eng. Data*, **2003**, 48, 662.
[19] E. Jimenez, M. Cabanas, L. Segade, S. Garcia-Garabal, H. Casas, *Fluid Phase Equilib*. **2001**, 180, 151.
[20] P. Lucas, A. Hillel, *J. Phys. C*., **1974**, 7, 3341.
[21] G. Weisbuch, F. Garbay, *Am. J. phys*., **1979**, 47, 355.
[22] G.L. Trigg, E.H. Immergut, Encyclopedia of Applied Physics, **1992**, 6, 258.
[23] D.R. Lide, CRC Handbook of Chemistry and Physics, **1996**, 77.
[24] S. Poprocki, *Am. J. Phys*., **2006**, 47, 401.

[25] T.K. Barik, P.R. Chaudhuri, A. Roy, S. Kar, *IOP Journal*, **2006**, 17, 1553.
[26] Klemens, *Amer. J. Phys*., **1996**, 64, 758.
[27] J.G. Speight, Lange's Handbook of Chemistry, **2005**, 272.
[28] J. Glinski, G. Charepeyer, J.K. Platten, P. Smet, *J. Chem. Phys*., **1998**, 109, 5050.
[29] F. Yohko Yano, *J Colloid and Interface Sci*., **2005**, 284, 255.
[30] D.R. Lide, CRC Handbook of Chemisry and Physics, **2004**, 1141.