Study of the Temperature Dependence of Surface Tensions of Some Alkanol + Hexane Mixtures

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Surface tensions of binary mixtures of ethanol, 1-butanol, or 2-butanol with hexane have been measured in the temperature range 283.15 K to 313.15 K with a drop volume tensiometer. The corresponding surface tension deviations have been calculated and correlated. Using the temperature dependence of surface tensions, the entropy change and enthalpy change of surface formation per unit area were evaluated at 298.15 K.

Introduction

It is well-known that the properties and the behavior of the surface region of a liquid substance are substantially different from those of the bulk. Because of this, a complete thermodynamic study of any substance has to incorporate surface investigations. Surface tension measurements and their variation with composition and temperature are very useful for this purpose because any other important properties like the entropy change and enthalpy change of surface formation per unit surface can be evaluated from the experimental results.

Alcohols are strongly associated with hydrogen bonding, and it has been found helpful to consider the changes in the thermodynamic functions, which occur during the dilution of an alcohol with a nonpolar solvent, as partly due to the breaking of the hydrogen bonds and partly due to the mixing of the alcohol with the solvent. Due to its interesting characteristics, the mixture alkane + alcohol has attracted the attention of the scientific community, and several thermodynamic properties, including surface tension measurements, have been obtained before. There are previous studies in which the surface tensions of alkanol + alkane mixtures have been measured,[1−5] including two references reporting measurements at 298.15 K for the mixture ethanol + hexane[4,5] and one for the mixture 1-butanol + hexane.[4] However, there have been few studies of the temperature dependence of surface tension for these kinds of mixtures.

The surface behavior of mixtures formed by ethanol, 1-butanol, or 2-butanol with hexane between 283.15 K and 313.15 K via surface tension measurements has been studied. From the experimental results, surface tension deviations have been calculated and correlated. From the study of the dependence of surface tensions with temperature, the entropy change and enthalpy change of surface formation per unit surface have been estimated.

Experimental Methods

The liquids used were ethanol (99.8 %), 1-butanol (>99.8 %), 2-butanol (>99 %), and hexane (≥99 %) provided by Aldrich. The purities of these compounds were checked by measuring several thermophysical properties such as density and refractive index. No further purification was considered necessary, although the isomeric butanols were dried with activated molecular sieves (0.3 nm) from Merck.

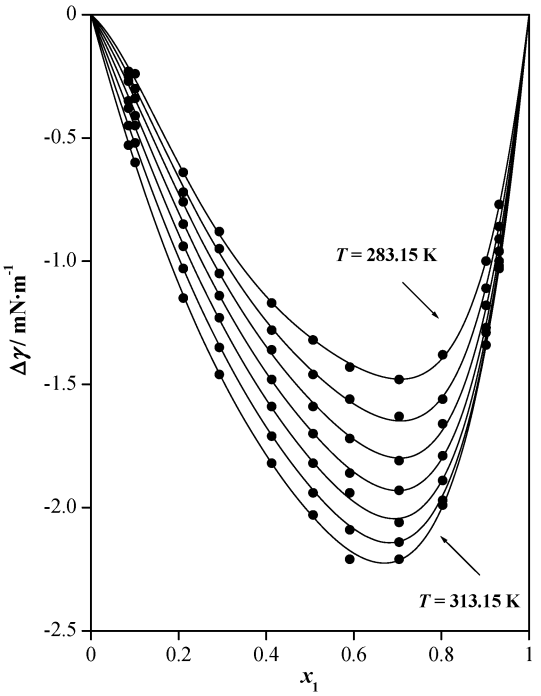

Figure 1. Surface tension deviations, $\Delta\gamma$, of the mixture ethanol (1) + hexane (2).

The surface tensions, γ, of the pure liquids and their mixtures were determined using a drop volume tensiometer (Lauda TVT-2).[6] Measurements were carried out in a range of temperatures from 283.15 K to 313.15 K with an interval of 5 K between each temperature. The tensiometer measures the volume of a drop detaching from a capillary of known diameter. The temperature was kept constant by means of an external Lauda E-200 thermostat. The uncertainty in temperature is ± 0.01 K. Densities needed to calculate surface tensions from volume drop determinations were measured using an Anton Paar DMA-58 vibrating tube densimeter. The uncertainty of the surface tension measurement is ± 0.01 mN·m^{-1}. Details of the experimental procedure can be found in a previous paper.[7] Surface tensions

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10.1021/je700215z CCC: $37.00

Table 1. Surface Tensions, γ, of the Pure Compounds

	γ/mN·m^{-1}							
	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K		T = 303.15 K	T = 308.15 K	T = 313.15 K
compound	exptl	exptl	exptl	exptl	lit	exptl	exptl	exptl
ethanol	23.12	22.75	22.28	21.86	21.8[a]	21.49	21.15	20.66
1-butanol	25.55	25.12	24.78	24.25	24.20[b]	23.95	23.55	23.15
2-butanol	24.37	23.95	23.56	23.08	23.1[a]	22.75	22.39	21.97
hexane	19.63	19.04	18.52	18.06	17.90[b]	17.53	16.74	16.47

[a] Ref 8. [b] Ref 5.

Table 2. Experimental Surface Tensions, γ, and Surface Tension Deviations, $\Delta\gamma$, of the Binary Mixtures

	T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K	
	γ	$\Delta\gamma$	γ	$\Delta\gamma$	γ	$\Delta\gamma$	γ	$\Delta\gamma$	γ	$\Delta\gamma$	γ	$\Delta\gamma$	γ	$\Delta\gamma$
x_1	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}
Ethanol (1) + Hexane (2)														
0.0855	19.70	−0.23	19.11	−0.25	18.57	−0.27	18.03	−0.35	17.49	−0.38	16.67	−0.45	16.30	−0.53
0.1006	19.74	−0.24	19.11	−0.30	18.56	−0.34	18.03	−0.41	17.48	−0.45	16.66	−0.52	16.29	−0.60
0.2107	19.73	−0.64	19.1	−0.72	18.55	−0.76	18.01	−0.85	17.42	−0.94	16.64	−1.03	16.2	−1.15
0.2928	19.77	−0.88	19.18	−0.95	18.57	−1.05	18.03	−1.14	17.46	−1.23	16.68	−1.35	16.24	−1.46
0.4128	19.90	−1.17	19.29	−1.28	18.71	−1.36	18.15	−1.48	17.57	−1.59	16.85	−1.71	16.38	−1.82
0.5071	20.08	−1.32	19.46	−1.46	18.84	−1.59	18.29	−1.70	17.72	−1.82	17.04	−1.94	16.56	−2.03
0.5909	20.26	−1.43	19.67	−1.56	19.02	−1.72	18.45	−1.86	17.93	−1.94	17.26	−2.09	16.74	−2.21
0.7036	20.61	−1.48	20.02	−1.63	19.36	−1.81	18.80	−1.93	18.26	−2.06	17.70	−2.14	17.21	−2.21
0.8032	21.05	−1.38	20.46	−1.56	19.88	−1.66	19.32	−1.79	18.82	−1.89	18.31	−1.97	17.85	−1.99
0.9021	21.78	−1.00	21.28	−1.11	20.73	−1.18	20.22	−1.27	19.81	−1.29	19.38	−1.34	18.91	−1.34
0.9320	22.11	−0.77	21.64	−0.86	21.11	−0.91	20.64	−0.96	20.22	−1.00	19.82	−1.03	19.36	−1.02
1-Butanol (1) + Hexane (2)														
0.0519	19.78	−0.16	19.15	−0.21	18.6	−0.24	18.11	−0.27	17.55	−0.31	16.75	−0.34	16.40	−0.42
0.0875	19.87	−0.28	19.26	−0.31	18.7	−0.37	18.2	−0.40	17.61	−0.48	16.80	−0.54	16.43	−0.62
0.1959	20.17	−0.62	19.58	−0.65	19.03	−0.72	18.52	−0.75	17.92	−0.87	17.13	−0.94	16.74	−1.04
0.2999	20.41	−1.00	19.88	−0.98	19.35	−1.05	18.84	−1.08	18.28	−1.18	17.52	−1.26	17.12	−1.35
0.3990	20.69	−1.30	20.14	−1.33	19.65	−1.37	19.10	−1.43	18.62	−1.47	17.91	−1.55	17.48	−1.66
0.4914	20.93	−1.61	20.40	−1.63	19.96	−1.64	19.43	−1.67	18.92	−1.76	18.29	−1.80	17.83	−1.92
0.5974	21.44	−1.73	20.90	−1.77	20.44	−1.82	19.91	−1.85	19.43	−1.94	18.82	−1.99	18.39	−2.07
0.7044	22.14	−1.66	21.63	−1.69	21.18	−1.75	20.6	−1.82	20.17	−1.88	19.59	−1.95	19.12	−2.06
0.8027	23.09	−1.29	22.54	−1.38	22.13	−1.41	21.54	−1.49	21.13	−1.55	20.60	−1.61	20.15	−1.68
0.9088	24.37	−0.64	23.85	−0.72	23.44	−0.77	22.87	−0.82	22.51	−0.85	22.06	−0.87	21.60	−0.94
0.9530	24.93	−0.34	24.47	−0.36	24.07	−0.42	23.53	−0.43	23.18	−0.47	22.76	−0.47	22.37	−0.47
2-Butanol (1) + Hexane (2)														
0.0493	19.75	−0.11	19.16	−0.12	18.62	−0.15	18.11	−0.20	17.52	−0.27	16.69	−0.33	16.33	−0.41
0.1057	19.84	−0.29	19.24	−0.32	18.7	−0.35	18.14	−0.45	17.53	−0.55	16.66	−0.68	16.26	−0.79
0.2083	20.00	−0.62	19.36	−0.70	18.8	−0.77	18.21	−0.90	17.62	−1.00	16.81	−1.11	16.41	−1.21
0.3004	20.18	−0.87	19.52	−0.99	18.95	−1.08	18.37	−1.20	17.82	−1.28	17.08	−1.36	16.70	−1.42
0.4002	20.43	−1.10	19.77	−1.23	19.21	−1.33	18.67	−1.40	18.16	−1.46	17.50	−1.50	17.13	−1.54
0.4962	20.72	−1.26	20.13	−1.35	19.60	−1.42	19.09	−1.46	18.6	−1.52	18.01	−1.53	17.62	−1.58
0.5948	21.10	−1.35	20.57	−1.39	20.13	−1.39	19.61	−1.44	19.18	−1.45	18.60	−1.50	18.22	−1.52
0.6968	21.64	−1.29	21.20	−1.26	20.76	−1.27	20.26	−1.30	19.84	−1.33	19.33	−1.35	18.92	−1.38
0.8018	22.35	−1.08	21.90	−1.08	21.52	−1.04	21.04	−1.05	20.67	−1.05	20.18	−1.09	19.74	−1.14
0.8964	23.18	−0.70	22.74	−0.70	22.34	−0.70	21.88	−0.68	21.52	−0.69	21.12	−0.68	20.73	−0.67
0.9492	23.73	−0.40	23.31	−0.39	22.9	−0.40	22.43	−0.39	22.11	−0.37	21.73	−0.37	21.33	−0.36

of the pure compounds at work temperatures together with literature[5,8] values at 298.15 K are shown in Table 1.

The mixtures were prepared by mass using a Mettler H20T balance. The estimated uncertainty in the mole fraction is ± 1·10^{-4}.

Results and Discussion

Surface tension deviations, $\Delta\gamma$, have been calculated from experimental measurements of surface tension according to the following equation

$$\Delta\gamma = \gamma - x_1\gamma_1 - x_2\gamma_2 \qquad (1)$$

where γ is the surface tension of the mixture and x_i and γ_i are the mole fraction and surface tension of component i, respectively. The values of surface tensions and surface tension deviations are given in Table 2, and surface tension deviations are graphically represented in Figures 1 to 3.

The surface tension deviations were correlated with temperature and composition by means of the following equation[9]

$$\Delta\gamma = x_1(1 - x_1)\sum_{i=0}^{r}\sum_{j=0}^{p} A_{ij}(T - T_0)^i(2x_1 - 1)^j \qquad (2)$$

where x_1 is the mole fraction of alcohol; T is the temperature; T_0 is a reference temperature, T_0 = 283.15 K; and A_{ij} are adjustable parameters determined by the method of least-squares. The values of these parameters are given in Table 3 together with the corresponding standard deviations.

Surface tension deviation for all the studied mixtures presents negative values in the whole range of compositions. The position of the minimum value of surface tension deviation for the mixtures containing ethanol or 1-butanol is displaced from the equimolar composition to a region richer in alcohol ($0.6 < x_1 < 0.7$). In the case of mixtures formed by ethanol, surface tension deviations at 313.15 K are the largest ones in absolute

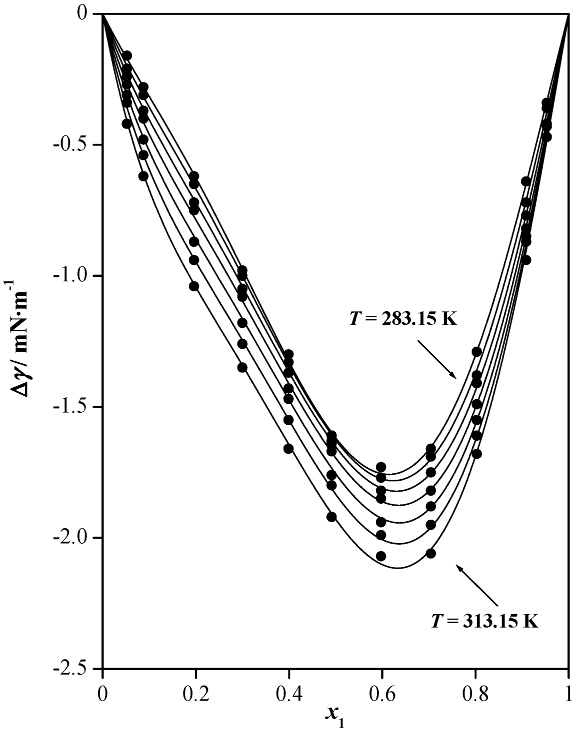

Figure 2. Surface tension deviations, $\Delta\gamma$, of the mixture 1-butanol (1) + hexane (2).

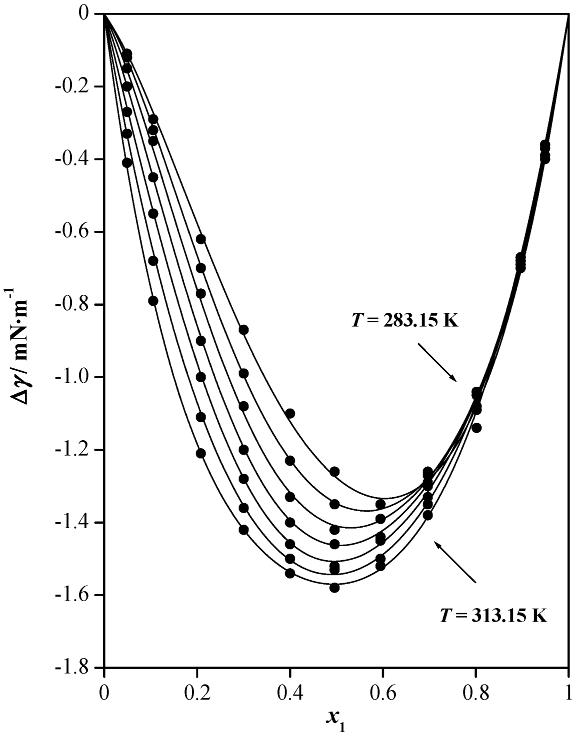

Figure 3. Surface tension deviations, $\Delta\gamma$, of the mixture 2-butanol (1) + hexane (2).

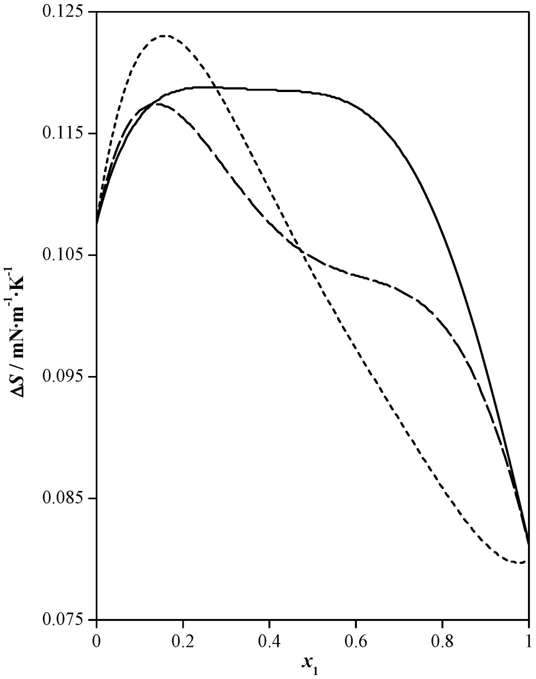

Figure 4. Entropy change of surface formation, ΔH, of the studied mixtures at 298.15 K: solid line, ethanol (1) + hexane (2); dashed line, 1-butanol (1) + hexane (2); dotted line, 2-butanol (1) + hexane (2).

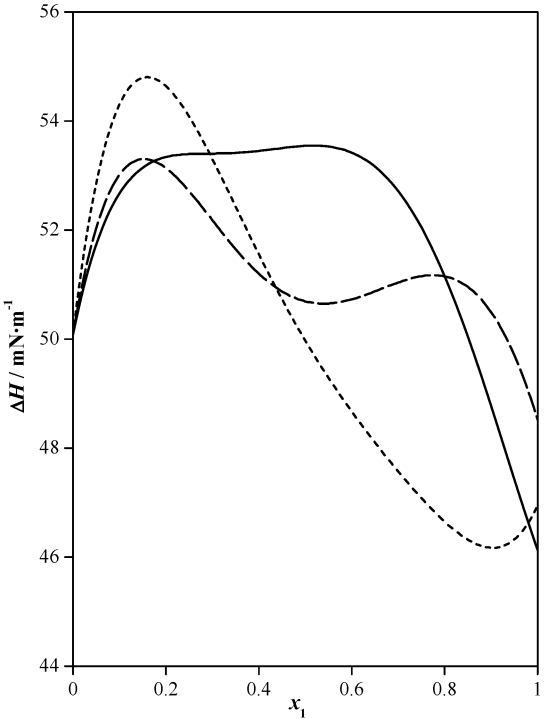

Figure 5. Enthalpy change of surface formation, ΔH, of the studied mixtures at 298.15 K: solid line, ethanol (1) + hexane (2); dashed line, 1-butanol (1) + hexane (2); dotted line, 2-butanol (1) + hexane (2).

value, whereas for the mixture containing 2-butanol, absolute values of surface tension deviation are the smallest. In general, if the number of carbon atoms of the alcohol increases, the value of surface tension deviation becomes less negative. An increase of the ramification of the chain of the alcohol produces the same effect. For all the studied mixtures, when the temperature increases, values of the surface tension deviation decrease, becoming more negative. The effect of temperature is more perceptible for the mixture ethanol + hexane. It is also noticeable that for the mixture containing 2-butanol surface tension deviation for mole fractions of alcohol larger than 0.8 depends very slightly on temperature. As we have mentioned before, our $\Delta\gamma$ results for ethanol or 1-butanol with hexane at 298.15 K are in good agreement with those of the literature, showing errors between our experimental data and the literature data of 0.4 %[4] and 0.7 %[5] for the mixture ethanol + hexane, whereas for the surface tensions of the mixture 1-butanol + hexane, the error between the two data is 0.9 %.[4]

Table 3. Parameters of Equation 2, A_{ij}, and Standard Deviations, $s(\Delta\sigma)$

A_{00}	A_{01}	A_{02}	A_{03}	A_{10}	A_{11}	A_{12}	A_{13}	A_{20}	A_{21}	A_{22}	A_{23}	$s(\Delta\sigma)$
Ethanol (1) + Hexane (2)												
−5.2326	−2.7746	−2.8502	−3.7906	−0.1045	−0.1301	−0.0934	0.0203	0.0003	0.0029	0.0014	0.0014	0.01
1-Butanol (1) + Hexane (2)												
−6.4752	−4.5607	1.2298	2.8776	0.0006	−0.1082	−0.1861	−0.0431	−0.0014	0.0002	0.0023	0.0031	0.01
2-Butanol (1) + Hexane (2)												
−5.1071	−2.1509	−0.2343	−1.3854	−0.0601	0.1858	0.0551	−0.2030	0.0007	−0.0037	−0.0042	0.0094	0.01

From the surface tension measurements, the entropy change and enthalpy change of surface formation per unit surface area can be evaluated by applying

$$\Delta S = -\left(\frac{\partial \gamma}{\partial T}\right)_{p,x_2} \tag{3}$$

$$\Delta H = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{p,x_2} \tag{4}$$

In Figures 4 and 5, the entropy change and enthalpy change of surface formation of the studied mixtures at 298.15 K are shown. The entropies and enthalpies of surface formation are positive at all temperatures over the whole composition range for all the mixtures. Results show that the shape of the entropy change and enthalpy change of surface formation graphics is almost the same for each mixture and at each temperature. At 298.15 K, entropy change and enthalpy change values of surface formation of the mixture formed by ethanol and hexane show an extended maximum located between 0.2 and 0.7 in mole fraction. When the mixture is formed by 1-butanol and hexane, at the temperature of 298.15 K, there are two maximum points and one minimum point of enthalpy change of surface formation. One of the maximum points is located at compositions of 0.2 in mole fraction of alcohol, and the other one is at compositions of 0.8 approximately. If the mixture contains 2-butanol, there is only one maximum point, which is located between 0.1 and 0.2 in mole fraction of alcohol and one minimum point for the enthalpy change of surface formation located near a composition of 0.9 in mole fraction of alcohol.

Due to the Gibbs adsorption phenomenon, the component of a binary mixture with lower surface tension will tend to migrate to the surface while the other component will tend to stay in the bulk. As a result, we should expect negative surface tension deviation values, and the bigger the difference between surface tension of pure components, the more negative surface tension deviations should be. However, during the mixing process, other effects can affect the surface behavior, such as repulsion or attraction between unlike molecules or modification in the structure of components.[10−11] These effects can cause, for instance, the component with lower surface tension to interact with the other component and remain in the bulk leading to positive values of surface tension deviations.

In these mixtures, surface tension values of all the studied mixtures are negative, and this could be because of the Gibbs adsorption phenomenon: hexane presents lower surface tension values than the alcohols studied here; therefore, it is more surface active and is expected to be displaced to the surface, whereas alcohol molecules will tend to stay in the bulk. Analyzing the difference between surface tension of pure components at the studied temperatures, we can notice that the bigger differences are found for the mixture formed by 1-butanol and hexane, with the smallest ones being for the mixture containing ethanol. Furthermore, differences increase if temperature does. Therefore, the Gibbs adsorption phenomenon should be one of the main processes that occurs during the surface formation.

Conclusions

In this paper, surface tensions of binary mixtures of ethanol, 1-butanol, or 2-butanol with hexane have been experimentally measured in the temperature range 283.15 K to 313.15 K. Their corresponding surface tension deviations have been calculated and correlated. Using the temperature dependence of surface tensions, the entropy change and enthalpy change of surface formation per unit area were evaluated at 298.15 K. We have analyzed the results in terms of the molecular characteristics of the components of the mixtures, and we have concluded that the Gibbs adsorption phenomenon should be one of the main processes that occurs during the surface formation, with hexane being the more surface active component of the studied mixtures.

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Received for review April 24, 2007. Accepted May 31, 2007. We are grateful for financial assistance from D.G.A. and Universidad de Zaragoza (INFR 423-06). Ana Villares thanks the predoctoral grants from Ministerio de Educación y Ciencia.

JE700215Z