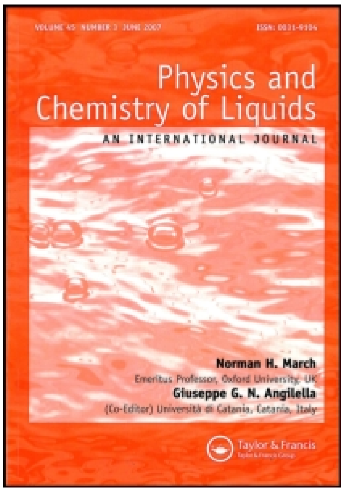

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Temperature dependence of surface tension of 2-methyl-1-propanol and 2-methyl-2-propanol+*n*-hexane mixtures

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Temperature dependence of surface tension of 2-methyl-1-propanol and 2-methyl-2-propanol + *n*-hexane mixtures

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Surface tensions of binary mixtures of 2-methyl-1-propanol or 2-methyl-2-propanol with *n*-hexane have been measured in the temperature range 283.15 K–313.15 K for mixtures containing 2-methyl-1-propanol and from 298.15 K to 313.15 K for mixtures formed by 2-methyl-2-propanol, with a drop volume tensiometer. The corresponding surface tension deviations have been calculated and correlated. Using the temperature dependence of surface tensions, the entropy and enthalpy of surface formation per unit area were evaluated at the studied temperatures.

Keywords: surface tension; surface formation; 2-methyl-1-propanol; 2-methyl-2-propanol; *n*-hexane

1. Introduction

Study of surface tension and its variation with composition and temperature is very interesting, not only from the experimental point of view but also because some other important properties like the entropy and enthalpy of surface formation per unit surface can be evaluated from the experimental results. Surface tension can be considered as the balance of several phenomena that can take place in both the surface of a liquid and also in the bulk. Comprehension about structure and cohesion forces of the pure compounds and their mixtures can be obtained from surface tension data as well as information about specific molecular interactions because this property depends basically on the variation in molecular forces and that of the density of packing or molecular size [1].

This work is a part of an extensive work related to the temperature dependence of surface tension of some mixtures. In previous papers [2,3], we have presented the surface behaviour of mixtures containing *n*-hexane, bromobutane and some alcohols such as ethanol or isomeric butanols. In this case, the surface behaviour of mixtures formed by 2-methyl-1-propanol and 2-methyl-2-propanol with *n*-hexane between 283.15 K and 313.15 K (or from 298.15 K to 313.15 K in the case of mixtures formed by 2-methyl-2-propanol) via surface tension measurements has been studied. From the experimental results, surface tension deviations have been calculated and correlated. Entropy and enthalpy of surface formation per unit surface have also been estimated.

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A revision of the literature has shown that these mixtures have not been measured before and there is no such study.

2. Experimental

The liquids used were: 2-methyl-1-propanol (99.5%), and 2-methyl-2-propanol (>99.5%) and *n*-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 sieve, type 0.3 nm, from Merck.

The surface tension, γ, of the pure liquids and their mixtures were determined using a drop volume tensiometer Lauda TVT-2 [4]. Measurements were carried out in a range of temperatures from 283.15 K to 313.15 K in the case of the mixture formed by 2-methyl-1-propanol and from 298.15 K to 313.15 K for the mixture formed by 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 [5]. Surface tensions of the pure compounds at work temperatures together with literature values [6,7] 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 $\pm 1 \times 10^{-4}$.

3. Results and discussion

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

$$\Delta\gamma = \gamma - x_1\gamma_1 - x_2\gamma_2, \tag{1}$$

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 and 2.

The surface tension deviations were correlated with temperature and composition by means of the following equation [8]:

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

where x_1 is the mole fraction of alcohol, T is the temperature, T_0 is a reference temperature, $T_0 = 283.15$ K for the mixture containing 2-methyl-1-propanol, $T_0 = 298.15$ K for 2-methyl-2-propanol mixture 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.

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	Exp.	Exp.	Exp.	Exp.	Lit.	Exp.	Exp.	Exp.
2-Methyl-1-propanol	23.65	23.33	22.92	22.47	22.37[a]	22.17	21.83	21.45
2-Methyl-2-propanol				20.30	20.1[a]	19.85	19.41	18.93
n-Hexane	19.63	19.04	18.52	18.06	17.90[b]	17.53	16.74	16.47

Notes: [a]Reference [6]. [b]Reference [7].

Table 2. Experimental surface tensions, γ, and surface tension deviations, $\Delta\gamma$, of the binary mixtures.

2-Methyl-1-propanol (1) + *n*-hexane (2)														
	$T = 283.15$ 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	
x_1	γ (mN m^{-1})	$\Delta\gamma$ (mN m^{-1})	γ (mN m^{-1})	$\Delta\gamma$ (mN m^{-1})	γ (mN m^{-1})	$\Delta\gamma$ (mN m^{-1})	γ (mN m^{-1})	$\Delta\gamma$ (mN m^{-1})	γ (mN m^{-1})	$\Delta\gamma$ (mN m^{-1})	γ (mN m^{-1})	$\Delta\gamma$ (mN m^{-1})	γ (mN m^{-1})	$\Delta\gamma$ (mN m^{-1})
0.0582	19.56	−0.30	19.00	−0.29	18.50	−0.28	18.04	−0.27	17.53	−0.27	16.76	−0.27	16.48	−0.28
0.0945	19.57	−0.44	19.02	−0.43	18.51	−0.42	18.05	−0.42	17.54	−0.43	16.78	−0.44	16.49	−0.46
0.2053	19.74	−0.71	19.19	−0.73	18.67	−0.76	18.18	−0.79	17.65	−0.83	16.91	−0.88	16.56	−0.93
0.2781	19.93	−0.82	19.37	−0.86	18.84	−0.91	18.33	−0.96	17.80	−1.02	17.07	−1.08	16.70	−1.15
0.3865	20.27	−0.91	19.72	−0.98	19.17	−1.05	18.65	−1.12	18.14	−1.19	17.45	−1.25	17.08	−1.32
0.5076	20.74	−0.93	20.21	−1.01	19.68	−1.08	19.16	−1.14	18.69	−1.20	18.07	−1.25	17.70	−1.29
0.6424	21.43	−0.78	20.94	−0.85	20.43	−0.92	19.92	−0.97	19.49	−1.02	18.96	−1.05	18.59	−1.08
0.7037	21.81	−0.65	21.34	−0.72	20.84	−0.78	20.33	−0.83	19.92	−0.88	19.40	−0.92	19.03	−0.95
0.8274	22.66	−0.30	22.23	−0.36	21.75	−0.41	21.24	−0.47	20.84	−0.52	20.37	−0.58	19.96	−0.63
0.9226	23.28	−0.05	22.90	−0.09	22.44	−0.13	21.95	−0.18	21.58	−0.23	21.16	−0.28	20.74	−0.33
0.9494	23.43	−0.01	23.07	−0.04	22.62	−0.07	22.14	−0.11	21.79	−0.14	21.39	−0.18	20.97	−0.23
0.0506	–	–	–	–	–	–	20.07	−0.12	19.53	−0.20	19.01	−0.26	18.50	−0.31
0.0876	–	–	–	–	–	–	19.89	−0.21	19.34	−0.31	18.78	−0.40	18.23	−0.48
0.1892	–	–	–	–	–	–	19.43	−0.44	18.89	−0.52	18.28	−0.63	17.69	−0.78
0.2956	–	–	–	–		–	19.01	−0.63	18.52	−0.65	17.88	−0.74	17.30	−0.90
0.3852	–	–	–	–	–	–	18.72	−0.72	18.23	−0.73	17.58	−0.80	17.04	−0.94
0.4948	–	–	–	–	–	–	18.43	−0.76	17.90	−0.80	17.21	−0.87	16.73	−0.98
0.6017	–	–	–	–	–	–	18.22	−0.73	17.62	−0.83	16.87	−0.94	16.41	−1.04
0.6933	–	–	–	–	–	–	18.09	−0.66	17.44	−0.80	16.61	−0.94	16.14	−1.09
0.7929	–	–	–	–	–	–	18.00	−0.52	17.33	−0.68	16.44	−0.85	15.93	−1.05
0.9058	–	–	–	–	–	–	17.98	−0.29	17.36	−0.38	16.46	−0.53	15.97	−0.73
0.9543	–	–	–	–	–	–	18.00	−0.16	17.43	−0.20	16.57	−0.29	16.16	−0.42

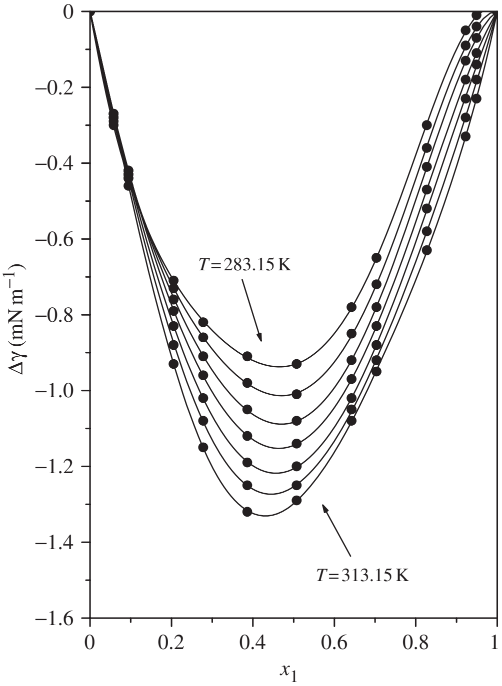

Figure 1. Surface tension deviations, $\Delta\gamma$, of the mixture 2-methyl-1-propanol (1) + *n*-hexane (2).

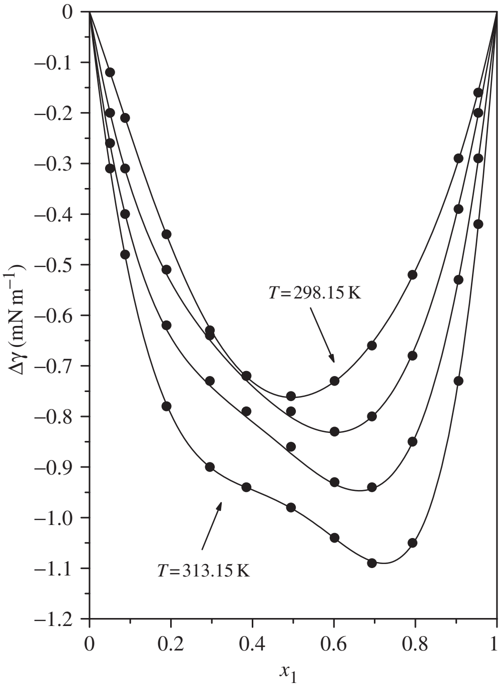

Figure 2. Surface tension deviations, $\Delta\gamma$, of the mixture 2-methyl-2-propanol (1) + *n*-hexane (2).

Table 3. Parameters of Equation (2), A_{ij}, and standard deviations, $s(\Delta\gamma)$.

Mixture	A_{00} A_{10} A_{20}	A_{01} A_{11} A_{21}	A_{02} A_{12} A_{22}	A_{03} A_{13} A_{23}	$s(\Delta\gamma)$
2-Methyl-1-propanol (1) + *n*-Hexane (2)	−3.7221	−0.6352	0.9467	−2.8890	
	−0.0645	0.0131	0.0480	0.1051	0.003
	0.0005	−0.0017	−0.0022	0.0019	
2-Methyl-2-propanol (1) + *n*-Hexane (2)	−3.0441	0.0315	−0.0170	−0.7978	
	−0.0209	−0.2757	−0.2633	0.5099	0.005
	−0.0026	0.0140	−0.0047	−0.0347	

Surface tension deviations for all the studied mixtures present negative values in all range of composition. The position of the minimum value of surface tension deviation for the mixtures containing 2-methyl-2-propanol is displaced from the equimolar composition to a region richer in alcohol ($0.7 < x_1 < 0.8$). In general, the mixture containing 2-methyl-1-propanol shows that surface tension deviation absolute values are greater for the mixture formed by 2-methyl-2-propanol than for the whole range of temperatures analysed. For all the mixtures, when the temperature increases, values of the surface tension deviation decrease, becoming more negative.

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

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

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

In Figures 3–6, the entropy and enthalpy of surface formation of the mixtures at the studied temperatures are shown. The entropies and enthalpies of surface formation are positives at all temperatures over the whole composition range for all the mixtures. In the case of enthalpy of surface formation, figures from 298.15 K to 313.15 K, present two maximum points located at molar fractions of 0.1 and 0.7, respectively, and a minimum point at $\sim x_1 = 0.4$ in mole fraction. At lower temperatures, there is only one maximum point located at molar fraction of 0.1 in alcohol and a minimum point situated at very high molar fractions of alcohol. A similar behaviour is observed for the entropy of surface formation, although in this case, the two maximum points are observed only at the temperatures of 308.15 K and 313.15 K.

This results can be compared to that obtained previously for mixtures formed by *n*-hexane and 1-butanol or 2-butanol [3]. We can affirm that absolute values of surface tension deviations are smaller for the studied mixtures containing 2-methyl-1-propanol or 2-methyl-2-propanol. It is also noticeable that the behaviour of entropy and enthalpy of surface formation of the mixture *n*-hexane and 2-butanol is quite similar to the present ones. Although this behaviour is not common, the presence of two or more minimum or maximum points in representation of the entropy and enthalpy of surface formation as a function of composition has been observed before [1,3,9]. In light of the rich behaviour found, it has been suggested that the unexpected variations of surface entropy could be

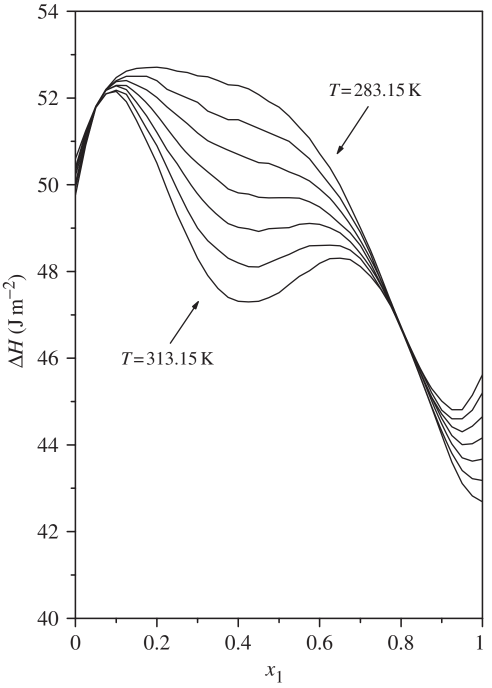

Figure 3. Enthalpy of surface formation, ΔH, of the mixture 2-methyl-1-propanol (1) + *n*-hexane (2) at the studied temperatures.

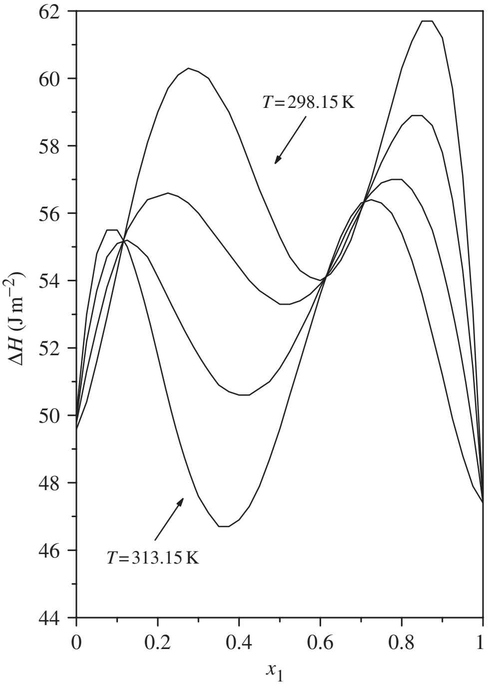

Figure 4. Enthalpy of surface formation, ΔH, of the mixture 2-methyl-2-propanol (1) + *n*-hexane (2) at the studied temperatures.

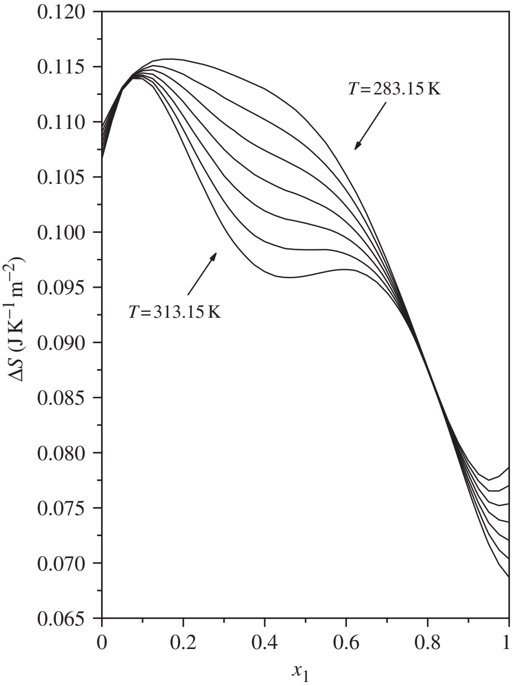

Figure 5. Entropy of surface formation, ΔS, of the mixture 2-methyl-1-propanol (1) + *n*-hexane (2) at the studied temperatures.

caused by structural changes similar to those of phase transition. These changes are related to the packing of the molecules at the interface and are caused by specific interactions. According to this hypothesis, symmetrical molecules will only show one entropy maximum, while non-symmetrical ones, due to the different conformations they can adopt while their surface concentration increases, may show several maximum points. Minimum values of entropy and enthalpy of surface formation have sometimes been related to the complex formation between components of the mixture [9].

Analysing the results obtained for the surface tension deviations, Gibbs adsorption phenomenon seems to be predominant; *n*-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 while alcohol molecules will tend to stay in the bulk. Taking into account 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 2-methyl-1-propanol and *n*-hexane, being smaller for the mixture containing 2-methyl-2-propanol 1. Furthermore, differences increase if temperature does. Therefore, Gibbs adsorption phenomenon should be one of the main processes that occur during the surface formation.

4. Conclusions

In this article, the surface behaviour of mixtures formed by 2-methyl-1-propanol with *n*-hexane between 283.15 K and 313.15 K and 2-methyl-2-propanol with *n*-hexane between

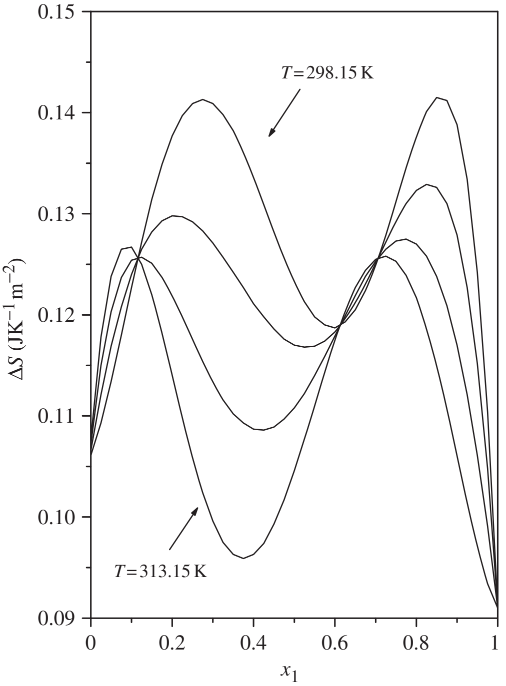

Figure 6. Entropy of surface formation, ΔS, of the mixture 2-methyl-2-propanol (1) + n-hexane (2) at the studied temperatures.

298.15 K and 313.15 K *via* surface tension measurements has been studied. Their corresponding surface tension deviations have been calculated and correlated. Using the temperature dependence of surface tensions the entropy and enthalpy of surface formation per unit area were evaluated at the studied temperatures. We have analysed the results and we have concluded that Gibbs adsorption phenomenon should be one of the main processes that occur during the surface formation, being n-hexane the more surface active component of the studied mixtures.

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