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SHORT COMMUNICATION

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Influence of temperature on the composition of mixed monolayer formed at the methyl alcohol/acetic acid aqueous solution–air interface

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Abstract The influence of temperature on the composition of mixed monolayer formed at the methyl alcohol/acetic acid aqueous solution was examined by surface tension measurements. Surface tension of various two-component solutions was obtained at 10, 20 and 28 °C temperatures in the 0–0.5 M range of bulk concentration of alcohol and acid, respectively. Three independent methods, i.e., the Gibbs adsorption equation (GAE), regular solution approximation (RSA) and Butler adsorption isotherm (BAI) were applied to calculate surface composition of the methyl alcohol/acetic acid mixed monolayer. It was shown that in the temperature range of 10–28 °C the surface molar fraction of the solutes remained constant for the fixed bulk concentration of alcohol and acid. Additionally, based on the RSA and BAI methods, we showed there were no interactions between solute molecules in the mixed monolayer in the studied range of concentrations.

Key words Air–aqueous solution interface – methyl alcohol/acetic acid mixed adsorbed monolayer – surface tension vs. temperature dependence – Gibbs free energy of adsorption

Introduction

In all systems where the interface between any two phases is formed, a phenomenon of adsorption of solute components plays an important role influencing properties of this interface [1, 2]. Thus, understanding of this process is essential in the prediction of physicochemical properties of the investigated system. This way, one can control the adsorption phenomenon during technological processes by making molecular layers that can either prevent or enhance adsorption of solute, depending on what is needed. The largest number of data have been collected for adsorption of "synthetic" or biological surface active compounds at liquid–air or liquid–solid interface [3, 4]. These studies concentrate mainly on long aliphatic chain compounds [5, 6]. However, a few of them deal with short-chain species only [1]. They consider surface concentration and interactions in mixed solution–air interface of aliphatic alcohols [1], their derivatives [7–9] and aliphatic acids [10]. Contrary to long-chain or physiological active compounds, influence of neither molecular structure nor temperature on surface properties of short-chain species have been investigated so far. Hence we studied aliphatic alcohol/aliphatic acid mixed monolayer and changes in its properties by the introduction of a $-CH_2-$ group to the hydrocarbon chain of both compounds [11–14]. The system has been tested by three independent thermodynamic methods, namely, the Gibbs adsorption equation (GAE), the regular solution approximation (RSA) and the Butler adsorption isotherm (BAI).

The results obtained encouraged us to further investigate, especially the influence of temperature on surface properties. For purposes of comparison, we have chosen an already studied system.

In this paper we report the surface tension of methyl alcohol/acetic acid aqueous solution in the 10–28 °C range of temperature. The surface tension of the mixtures was measured as a function of the bulk composition and analysed by GAE, RSA and BAI. The adsorption behavior of the mixtures is discussed by considering surface composition, molecular interaction parameter and the Gibbs free energy of adsorption of the components. In our work we decided to keep the conditions of the experiments consistent with previous papers [7–14]. Due to surface potential measurements in previous works, aqueous 0.1 M KCl solution has been chosen as the solvent of the mixed systems. However, the presence of electrolyte has not been taken into account in further calculations. This was owing to the fact that a 0.1 M KCl changes the surface tension of the aqueous solution of 0.24 mN/m without changing the shape of the surface tension vs. concentration curves. Therefore, the studied solutions can be treated as pure aqueous solutions.

Experimental

Aqueous 0.1 M KCl solution was used as the solvent in the methyl alcohol/acetic acid mixed system. Water was distilled twice and its purity was tested by conductivity and surface tension measurements. The salt, purchased from POCh (Poland), was purified by roasting at 400 °C (6 h) followed by recrystallization (twice) from aqueous solution. Methyl alcohol and acetic acid were purchased from POCh (Poland). Prior to use methyl alcohol was purified by distillation over freshly activated molecular sieves (4A). Acetic acid was recrystallized twice as described previously [11–13]. Purity of the compounds were checked by refractive index. Additionally, surface tension of 0.1 M KCl and the chosen dilute one-component solutions of alcohol and acid were measured. Obtained results were in agreement with the literature data [15]. Surface tension was calculated by the drop weight method at 10, 20 and 28 °C by using Harkins-Brown corrections.

The radius of the tip of the stalagmometer was 3.375×10^{-3} m. The stalagmometer was placed inside the termostated cell described previously [11–14]. However, instead of a manual drop formation, every drop was formed by using an electrical step motor controlled by a PC computer. The accuracy of the drop weight was $\pm 10^{-5}$ g, that gives an error in the surface tension calculations of ± 0.1 mN/m.

The measurements were carried out in the 0–1.6 M and 0–0.9 M ranges of concentrations of alcohol and acid, respectively, in one-component solutions and in the 0–0.5 M range of concentration of both solutes in two-component solutions.

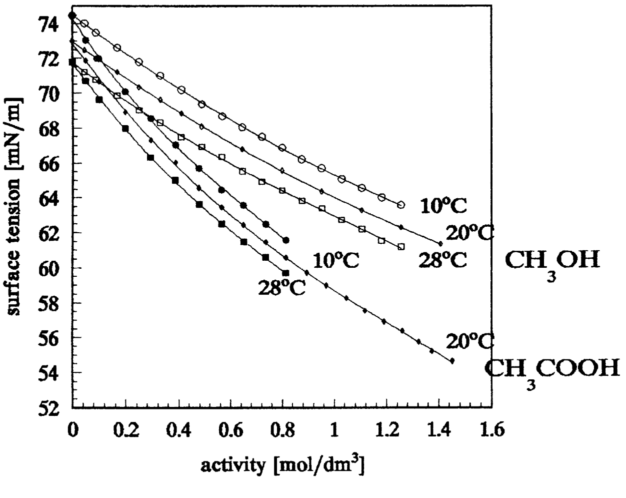
Results and discussion

In Fig. 1 the dependence of surface tension versus activity of methyl alcohol and acetic acid in one-component solutions measured at 10, 20 and 28 °C is shown. As it is clearly seen in the figure, obtained values of surface tension for these solutions decrease by 0.1–0.15 mN/(m °C) when temperature is raised from 10 to 20 and then to 28 °C.

Similar measurements of dependence of surface tension on the activity of the solutes in two-component solutions at 10, 20 and 28 °C were shown in Figs. 2–4, respectively. Here, every curve represents the dependence of surface tension upon changes in activity of acetic acid while the activity of methyl alcohol is held constant. These curves follow the general pattern observed previously [11–13]. As expected, acetic acid, being the more surface active agent, had stronger influence on the surface tension of the mixture than methyl alcohol. Thus, increase in acid concentration causes a more dramatic decrease in surface tension than the same increase in concentration of alcohol. Results presented in Figs. 2–4 show clearly that temperature strongly influences surface tension. As is evident from Figs. 2–4 surface tension changes by 1.3 mN/m when temperature is raised by 10 °C. Similar results were obtained for one-component solutions (vide supra). Data presented in Figs. 2–4 allowed to calculate surface composition, molecular interaction parameter and the Gibbs free energy of adsorption of the components.

Table 1 compares mean molar fractions of acetic acid in the 10–28 °C range of temperature, calculated by

Fig. 1 Dependence of surface tension on the activity of methyl alcohol and acetic acid in one-component solutions at 10, 20, 28 °C



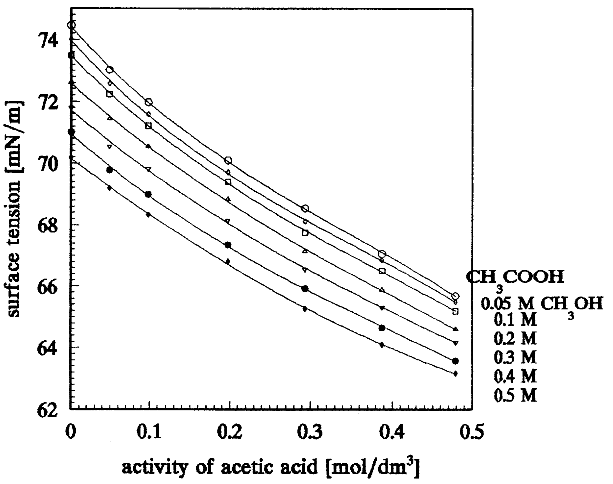


Fig. 2 Dependence of surface tension on the activity of acetic acid in methyl alcohol/acetic acid mixed system at 10 °C

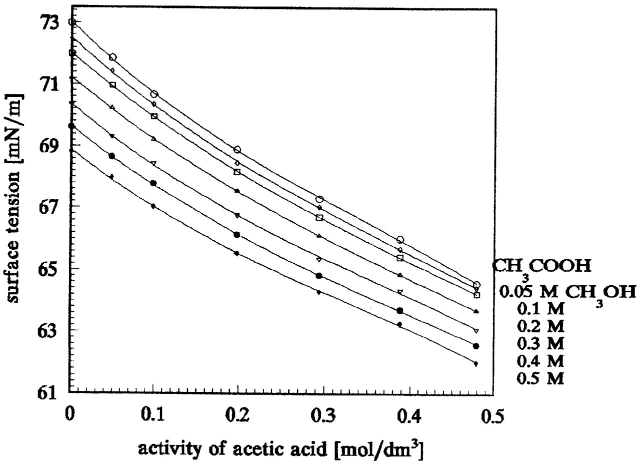


Fig. 3 Dependence of surface tension on the activity of acetic acid in methyl alcohol/acetic acid mixed system at 20 °C

GAE (X_i^{GAE}), RSA (X_i^{RSA}) and BAI (X_i^{BAI}) methods. To make it easier to follow, below we show briefly how to calculate these values. X_i^{GAE} is obtained from

$$X_i^{\mathrm{GAE}} = \frac{\Gamma_i^{(1)}}{\Gamma_i^{(1)} + \Gamma_j^{(1)}} , \quad i,j = 1,2 , \tag{1}$$

where $\Gamma_i^{(1)}$ is the Gibbs surface excess calculated on the basis of surface tension versus activity dependence [11–13].

Independently, RSA, the statistical thermodynamical description of the two-component liquid state, was applied to estimate the composition and interactions in multicomponent mixed micelles and mixed adsorbed monolayer [7–13]. X_i^{RSA} reported in Table 1 is expressed as follows:

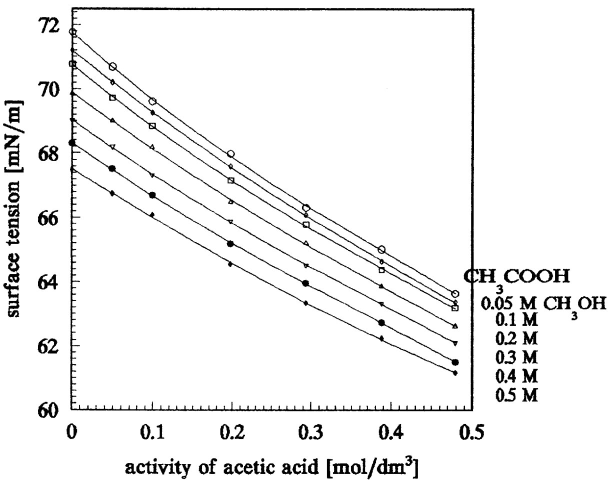


Fig. 4 Dependence of surface tension on the activity of acetic acid in methyl alcohol/acetic acid mixed system at 28 °C

$$\left(\frac{X_i^{\mathrm{RSA}}}{1 - X_i^{\mathrm{RSA}}}\right)^2 \frac{\ln(a_1/a_1^0 \cdot X_i^{\mathrm{RSA}})}{\ln[a_2/a_2^0 \cdot (1 - X_i^{\mathrm{RSA}})]} = 1 , \tag{2}$$

where a_i is the bulk activity of the solute, a_i^0 denotes the activity of the ith solute in one-component solution when the surface pressure is equal to the surface pressure of the mixture. a_i^0 is known from surface tension vs. activity dependence in one-component solution at 10, 20 and 28 °C temperatures. X_i^{BAI}, Table 1, was calculated following BAI [12, 13] written in the form:

$$\sum_i X_i \exp\left[\frac{-(\gamma^0 - \gamma)\cdot A_i - \Delta G_i}{RT}\right] = \sum_i X_i^{\mathrm{s}} = 1 , \quad i = 1,2,3 , \tag{3}$$

where X_i and X_i^{s} denote bulk and surface molar fractions respectively, A_i is a partial molar surface area, and ΔG_i is defined as

$$\Delta G_i = \Delta G_i^0 + RT \ln f_i^{\mathrm{s}} . \tag{4}$$

ΔG_i^0 and f_i^{s} represent the standard Gibbs free energy of adsorption and surface activity coefficient, respectively. In order to calculate the surface composition of the mixture and Gibbs free energy of adsorption of the solutes, overestimated system of linear equations of type Eq. (3) must be solved, for the details see [12, 13]. The area per molecule for methyl alcohol, acetic acid and water amount to 16, 24 and 9.8 Å² [16–18]. BAI concerns three components (methyl alcohol, acetic acid and water), thus relative

Table 1 Mean molar fractions of acetic acid, in 10–28 °C range of temperature, calculated on the basis of GAE, RSA and BAI methods

CH$_3$COOH CH$_3$OH	0.05	0.1	0.2	0.3	0.4	0.5	X
0.05	0.71	0.84	0.90	0.93	0.95	0.97	X_i^{GAE}
	0.68	0.80	0.89	0.94	0.96	0.96	X_i^{RSA}
	0.70	0.82	0.90	0.93	0.94	0.95	X_i^{BAI}
0.1	0.54	0.71	0.82	0.87	0.90	0.93	$\mathrm{X}_i^{\mathrm{GAE}}$
	0.53	0.69	0.82	0.88	0.92	0.93	X_i^{RSA}
	0.54	0.70	0.82	0.87	0.89	0.91	X_i^{BAI}
0.2	0.36	0.54	0.69	0.77	0.82	0.85	X_i^{GAE}
	0.37	0.54	0.70	0.78	0.83	0.86	X_i^{RSA}
	0.37	0.53	0.69	0.76	0.81	0.83	X_i^{BAI}
0.3	0.28	0.43	0.59	0.67	0.74	0.79	X_i^{GAE}
	0.29	0.44	0.61	0.70	0.76	0.80	X_i^{RSA}
	0.27	0.43	0.59	0.68	0.73	0.77	X_i^{BAI}
0.4	0.24	0.37	0.52	0.61	0.68	0.75	X_i^{GAE}
	0.23	0.37	0.54	0.63	0.70	0.74	X_i^{RSA}
	0.22	0.35	0.52	0.61	0.67	0.71	X_i^{BAI}
0.5	0.22	0.33	0.47	0.57	0.64	0.72	X_i^{GAE}
	0.19	0.32	0.48	0.58	0.65	0.70	X_i^{RSA}
	0.18	0.30	0.46	0.55	0.62	0.66	X_i^{BAI}

surface molar fractions of solutes, X_i^{BAI}, are finally expressed by

$$X_i^{\mathrm{BAI}} = \frac{X_i^{\mathrm{s}}}{X_i^{\mathrm{s}} + X_j^{\mathrm{s}}}, \quad i,j = 1,2 \; . \tag{5}$$

As was expected, from the general behavior of surface active components, the higher the bulk concentration, the more are the molecules present at the surface and higher the surface concentration, see Table 1. Furthermore, the more the surface active agent, the higher is its molar surface fraction by the fixed bulk concentration of both components.

Studies on the influence of the temperature on the surface composition prove that although the temperature strongly influences the surface tension of the solutions, simultaneously, for the fixed bulk concentration, the relative surface molar fraction remains constant. This can be easily seen in Fig. 5, where we compare mean surface molar fractions calculated on the basis of X_i^{GAE}, X_i^{RSA}, X_i^{BAI} for the 10, 20, 28 °C temperatures, respectively. The differences in mean surface molar fractions for 10, 20 and 28 °C temperatures amount on average to 0.01.

Although X_i^{GAE}, X_i^{RSA} , X_i^{BAI} are obtained by different thermodynamical calculations, their mean values within a 10–28 °C range of temperature, remains in good agreement. The differences in surface molar fractions calculated by GAE, RSA and BAI amount on average to 0.03 for the system at 20 °C and 0.02 for the system at 10 and 28 °C.

Additionally, BAI calculations, Eqs. (3) and (4), allow to determine standard Gibbs free energy of adsorption of the components, ΔG_i^0 in one- and two-component solutions, Table 2. However, it is not possible to determine f_i^{s} from Eq. (4), since our previous considerations about adsorption of –CH$_2$– group [12, 13] in aliphatic alcohol/aliphatic acid mixed system allow us to claim that ΔG_i and ΔG_i^0, Eq. (4), are equal. Standard Gibbs free energy of adsorption of the solvent is not included in Table 2 due to its low value – about 1 cal/mol. The negative sign of ΔG_i^0 implies that the process of adsorption is spontaneous. As we expected, standard Gibbs free energy of adsorption of acetic acid, of more surface active substance is lower than

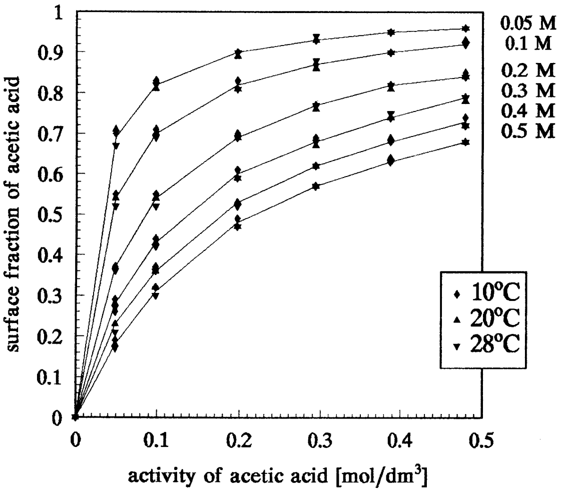


Fig. 5 Dependence of surface molar fraction on the activity of acetic acid in methyl alcohol/acetic acid mixed system at 10, 20 and 28 °C

Table 2 Gibbs free energies of adsorption [kcal/mol^{-1}] of methyl alcohol and acetic acid in two- and one-component aqueous solutions

System	Two-component solution		One-component solution	
$CH_3OH + CH_3COOH$	CH_3OH	CH_3COOH	CH_3OH	CH_3COOH
10 °C	− 1.52	− 2.04	− 1.48	− 2.03
20 °C	− 1.53	− 2.04	− 1.49	− 2.03
28 °C	− 1.53	− 2.05	− 1.50	− 2.06

that determined for methyl alcohol. Gibbs free energy of adsorption is a function of size, shape, distribution of molecules and molecular interactions. In the case of our study, the temperature influences, in the range of error, neither ΔG_i^0 (Table 2) nor surface composition. Moreover, this points out that the temperature does not influence the molecular structure of the interface and surface orientation of the molecules. Calculations of ΔG_i^0 show that its values determined for one- and two-component solutions are equal within the range of error. This indicates that the forces acting on the monolayer formed at the one-component solution do not change by addition of the second solute. Hence we were interested in calculating the interaction parameter β, defined by RSA method [5–13]:

$$\beta = \frac{\ln(a_1/a_1^0 X_i^{\mathrm{RSA}})}{(1 - X_i^{\mathrm{RSA}})^2} \, . \tag{6}$$

For the methyl alcohol/acetic acid mixed systems, β amounts on average to 0.0 at 10 and 20 °C, and 0.1 at 28 °C. Simultaneously, surface activity coefficients of alcohol and acid reach values 1.0 ± 0.1. This result prove that no interactions are expected between solute molecules adsorbed at the interface. Going further, in the formation of the adsorbed layer solvent–solvent and solute–solvent interactions are involved.

Conclusions

Methyl alcohol/acetic acid mixed system in the 0–0.5 M range of bulk concentration was analyzed by three independent thermodynamic methods, namely, GAE, RSA and BAI. Consistent results of surface composition were obtained at the fixed temperature. Moreover, surface composition does not change in the 10–28 °C range of temperature. Application of BAI and RSA methods indicate that solute molecules adsorbed at the interface do not interact with each other, which was pointed out by ΔG_i^0 and molecular interaction parameter β calculations. To summarize, temperature does not influence the molecular structure of the interface and surface orientation of the molecules in methyl alcohol/acetic acid mixed monolayer.

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