Surface Properties of Binary Liquid Mixtures of Water and Formic acid

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Abstract:

For a binary liquid mixture, water + formic acid, the formic acid adsorption at the air/liquid interface lowers the surface tension (γ) of the solution. Based on experimental data reported in the literature, the interface thermodynamics (surface excess) of the system (water/formic acid) were studied, where the Gibbs convention for the surface was employed. In Gibbs convention the two phases α and β are separated by an ideal interface σ which is infinitely thin. The surface thermodynamic quantities of the mixture; the surface entropy, the surface enthalpy, the surface excess concentration (Γ_{max}) of formic acid, and the area per molecule (in A^{o2}) at interface have been calculated. The surface tensions data over the entire concentration range at temperatures 20 to 50 °C was considered. The surface tension decreased with increasing temperature for any given mole fraction of acid. Data confirms the adsorption of formic acid molecules at the interface and increasing the mixture temperature lead to increase the area per molecule. At 20 °C the area per molecule = 32.94 A^{o2} and at 50 °C the area per molecule = 36.33 A^{o2}.

Key words: Thermodynamic properties, surface tension, surface excess concentration.

1. Introduction:

Experimental data of physical properties in mixtures of liquids are required for a full understanding of their thermodynamic properties as well as for use in the chemical engineering industry. The surface tension of liquid mixtures is an important property that reveals information on the structure and energetic of the surface region between two phases and exerts a considerable influence on the transfer of mass and energy across the interface. The intermolecular interaction (attraction or repulsion between neighboring molecules) is considered an important property to determine the properties of binary liquid mixtures, and the surface tension is one of the important things that may need to investigate the intermolecular interactions [1,2,3]. Knowing the surface tension and focusing on the system structure is required in many mass transfer processes such as distillation, absorption, liquid-liquid extraction, and condensation [1,2]. In previous study, they found that the surface tension can effect on the mass transfer rate because of the surface tension gradients along the interface, and increasing the interfacial turbulence can accelerate the mass transfer process [4,5].

In liquid mixtures either binary or multi-component mixture any small change in its structure will accompany with change on its surface tension. The surface tension, as known, is depending on the surface structures rather than the bulk structures. Then the surface structure depends on the surface concentration of the solution components, therefore the adsorption and desorption processes completely effect the surface tension and this was described on Figure (1), [6, 7, 8, 9]. Thus, the surface behavior seems to be very sensitive to the amount of adsorbed components. So, it is essential to know the surface tension over an entire composition range for any liquid mixtures that used for chemical engineering applications. In chemical industries, it determines the quality of the products (i.e. coatings, paints, detergents, cosmetics and agrochemicals).

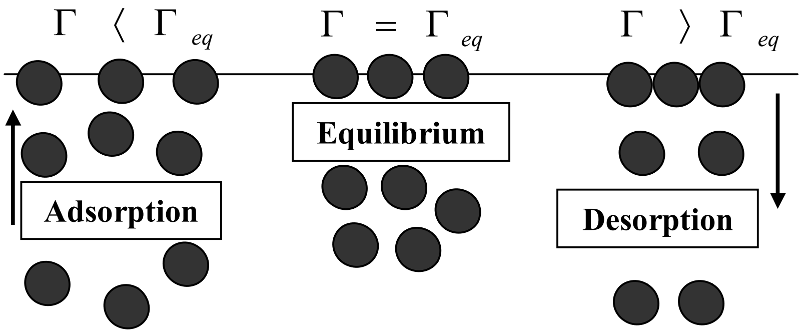

Figure (1): Shows the solute molecules motion between the interface and the bulk.

In this study, an experimental data [5] of water-formic acid, binary liquid, in the temperature range from 20 °C to 50 °C, was used for more understanding the method of recovering or extracting the formic acid from waste water streams. Formic acid is used in the textile industry, in tanning, in runner processing and in the manufacture of pharmaceuticals. So, such systems may often be dealt with using the Langmuir isotherm [4, 7, 8, 9]:

$$\frac{\Gamma}{\Gamma_{\max}} = \frac{\alpha C_B}{1 + \alpha C_B}$$

Where, C_B is the concentration of B in the bulk solution, Γ is the number of moles of B per unit area at the surface, $\Gamma_{\max}$ is the value of Γ when the surface is saturated, and α is the Langmuir equilibrium constant, and to investigate the surface tension of binary solutions of formic acid and water. Since most of the changes in surface tension of binary mixture occur at very low concentration of the solute, this study investigated the behavior of the formic acid molecules at the liquid/air interface.

2. Modeling and calculations procedure

From the Gibbs adsorption isotherms equation, the differential form for the surface tension can be described as following [7,8]:

$$-d\gamma = \bar{s}dT - \tau dp + \sum_{c=1}^{N_c} \Gamma_c d\mu_c \qquad (1)$$

Where the excess coefficients are defined as:

$$\bar{s} = \frac{1}{A}(S - \lambda^{\alpha}\bar{S}^{\alpha} - \lambda^{\beta}\bar{S}^{\beta})$$

$$\tau = \frac{1}{A}(V - \lambda^{\alpha} - \lambda^{\beta})$$

$$\Gamma_c = \frac{1}{A}(n_c - \lambda^{\alpha}C^{\alpha} - \lambda^{\beta}C^{\beta})$$

Where; A is the interfacial area, S, V, n_c the entropy, volume and mole-number of component c in the two phases α *and* β. λ^{α} and λ^{β} are the Gibbs distance parameters, shown the distance between Gibbs dividing surfaces.

In this study the system is liquid-gas(air) system. Therefore, applying the Gibbs convention is very sufficient in this work. So, $\tau = 0, \quad \Gamma_1 = 0$.

Then at constant temperature and one solvent the equation (1) become:

$-d\gamma = \Gamma_2 d\mu_2$ for an ideal solution

$$\therefore \quad \Gamma_2 = -\frac{1}{RT}\frac{d\gamma}{d\log C_2} \qquad (2)$$

R is the ideal gas constant [=] $8.314\,J.K^{-1}.mol^{-1}$, and T is the system temperature in K.

The term $\frac{d\gamma}{d\log C_2}$ has a physical meaning of surface activity. If the surface tension does not change with changing concentration, $\frac{d\gamma}{d\log C_2} = 0,\ \Gamma_2 = 0$ it means that such these compounds are not surface active. But if the surface tension decreases with increasing concentration of solute, $\frac{d\gamma}{d\log C_2} \prec 0,\ \Gamma \succ 0$ means these compounds are surface active, this is called adsorption [8,9], figure (1).

The Langmuir isotherm for the solution 2 in 1 determined by considering the equilibrium between the adsorption and desorption of 2 at the surface. So, the desorption velocity are equal the adsorption velocity [8, 9, 10]:

$$V_{ads} = k_{ads}(1-\theta)X_2$$

$$V_{des} = k_{des}\theta$$

$\theta = \frac{\Gamma_2}{\Gamma_{\max}}$, k_{ads} *and* k_{des} are constants, and X_2 is the mole fraction of 2; at equilibrium $V_{ads} = V_{des}$

In terms of concentration $\frac{\Gamma_2}{\Gamma_{\max}} = \frac{\alpha C_2}{1+\alpha C_2}$ (3)

From equation (2):

$d\pi = \Gamma_{\max} RT \log(1+\alpha C_2)$, $d\pi = -d\gamma$

And $\pi = \gamma - \gamma_o$, γ_o is the surface tension of the pure water.

From equation (1) the temperature derivative of surface tension corresponds to excess surface entropy per unit area at constant concentration is

$\bar{s} = -(\frac{d\gamma}{dT})$ (4)

The process was under constant pressure.

The surface enthalpy $(\overline{H})$ is the sum of the Gibbs surface energy that required extending the surface, which is the surface tension (γ) and the latent heat required to maintain isothermal condition, the enthalpy $(\overline{H})$ can be calculated according to the next equation:

$\overline{H} = \gamma + q = \gamma + T\overline{S}$ (5)

Using Excel spreadsheets performed the calculations.

3. Results and discussion

The experimental data of surface tension for water/formic acid binary mixture at 20 ˚C, 25 ˚C, 30 ˚C, 35 ˚C, 40 ˚C, 45 ˚C, and 50 ˚C are listed in table (1). The value of surface tensions are presented graphically versus the mole fraction of formic acid (X_2) in Figure (2), for a given temperature, the surface tension of all mixtures decreased as the acid concentration increased. This trend was nonlinear; the change in surface tension is larger at low concentrations than at high. There is a systematic nonlinear decrease of surface tension (γ) with the increase of the mole fraction of formic acid.

The variation of surface tension with system temperature for the binary mixture with the formic acid compositions, x_2 =0.000, x_2 =0.020, x_2 =0.042, x_2 =0.065, x_2 =0.144, x_2 =0.37, and x_2 =0.779 are shown in figure (3). The slope ($^{d\gamma}/_{dT}$) was found independent of temperature and corresponds to the surface entropy per unit area $\bar{S}$, according to the equation number (4). The excess surface entropy $\bar{S}$ was found equal to: 0.12 mJ.m^{-2}.k^{-1} for water/formic acid binary mixtures, and it appears to be constant and independent of the temperature and solvent concentration. In contrast, the calculated ($\bar{H}$) seems to be independent of the temperature but decrease nonlinearly with the increase of the mole fraction of formic acid, Figure (4).

The results obtained from the equation (2); the maximum surface excess concentration (Γ_{max}) of formic acid, and the area per molecule (in A^{o2}) at interface were determined at different temperatures and listed in the table (2). At high temperatures the surface excesses are less than that at low temperatures, the reason is; the area that occupied by each molecule at high temperature is higher than the area per molecule at low temperature and that is because the molecules have a great mobility at high temperatures. Therefore they occupy more space.

Table (1): The surface tension of the formic acid + water mixture at different temperatures and different compositions:

Surface tension (mN/m)

X1	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0	72.75	72.01	71.21	70.42	69.52	68.84	67.92
0.02	68.86	68.11	67.33	66.57	65.72	65.02	64.18
0.042	65.54	64.82	64.02	63.31	62.48	61.82	61.01
0.065	62.24	61.91	61.14	60.46	59.67	58.98	58.23
0.089	60.02	59.33	58.61	57.92	57.16	56.52	55.76
0.115	57.73	57.07	56.36	55.68	54.98	54.33	53.6
0.144	55.87	55.21	54.52	53.86	53.14	52.53	51.79
0.207	52.31	51.68	51.06	50.42	49.71	49.12	48.46
0.281	49.52	48.88	48.23	47.61	46.96	46.38	45.68
0.37	46.76	46.18	45.58	44.97	44.33	43.78	43.13
0.477	44.28	43.73	43.1	42.57	41.96	41.38	40.82
0.61	41.87	41.31	40.68	40.12	39.51	39.01	38.42
0.779	39.68	39.14	38.54	38.01	37.46	36.93	36.38
1	37.58	37.03	36.47	35.94	35.39	34.87	34.34

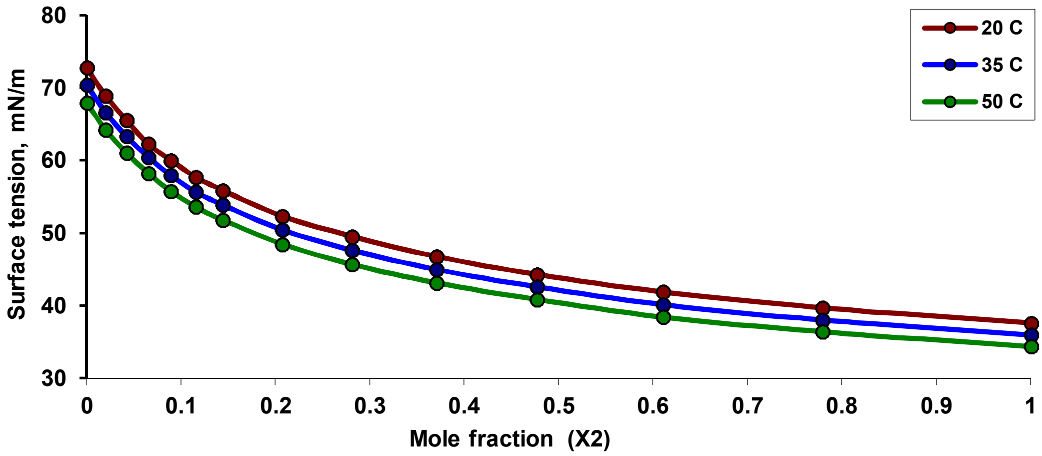

Figure (2): Surface tension of water/formic acid mixture at different concentrations and temperatures.

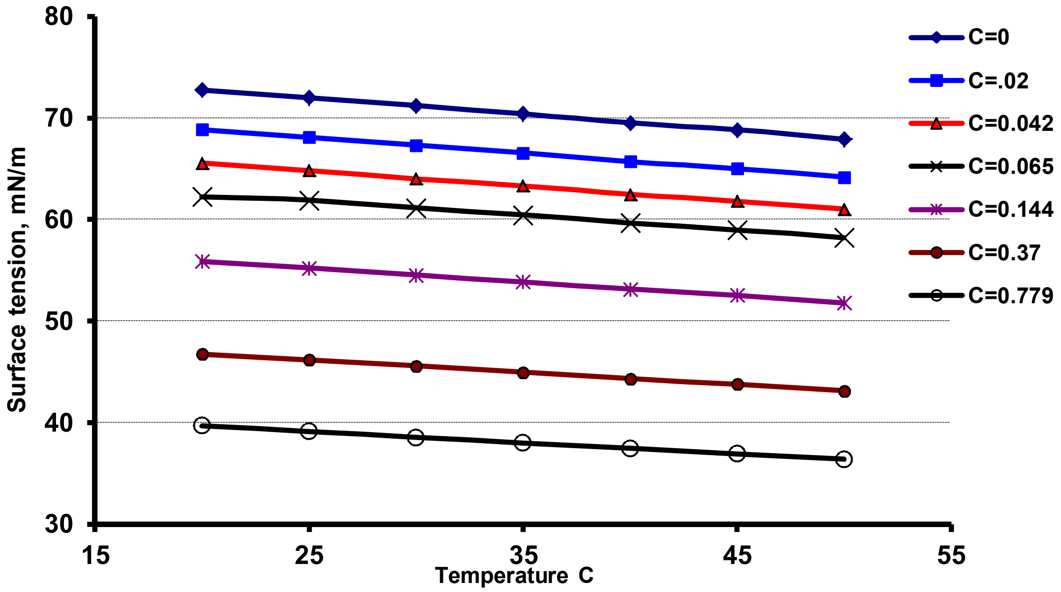

Figure (3): Surface tension of water/formic acid mixture at different temperatures and concentrations.

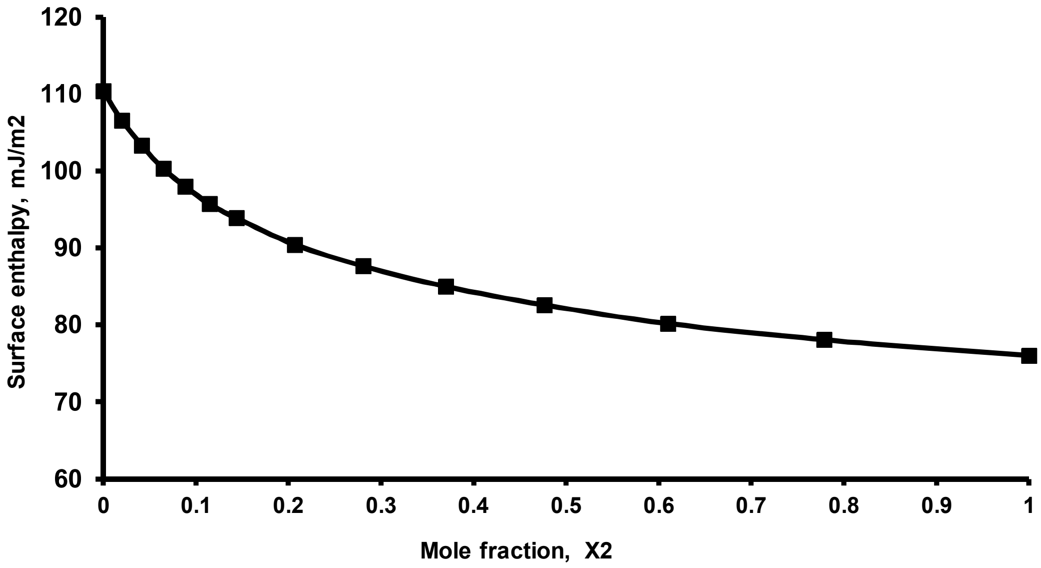

Figure (4): Surface enthalpy $(\overline{H})$ of formic acid/water mixtures, in the range from 20 C° to 50 C°, at different concentrations.

Table (2): The maximum surface excess in mol/m^2 and the area per molecule in A^{o2} at interface in the range from 20 C° to 50 C°:

T (C°)	$\Gamma_{\max} \times 10^6 \left(mol/m^2\right)$	**Area/molecule (** A^{o^2} **)**
20	5.04	32.94
35	4.79	34.66
50	4.57	36.33

4. Conclusion:

Experimental data from literature were used to study the thermo-physical properties of formic acid/water mixtures. The surface tension decreased with increasing temperature for any given mole fraction of acid. For a given temperature, the surface tension of all mixtures decreased as the acid concentration increased. The γ vs. X_2 data confirm that the surface concentration of formic acid is higher than its bulk concentration. In other words, for the formic acid + water mixtures, the tendency of formic acid molecules for migration to the liquid/air interface is higher at higher temperature. As a result of spreading formic acid molecules over the interface, the mass transfer performance devices such as; packed distillation column and liquid-liquid extraction unit can improve the overall efficiency of the process.

The excess surface entropy $\bar{S}$ for the binary mixtures = 0.12 $mJ.m^{-2}.k^{-1}$, and it was constant and independent of the temperature and solvent concentration. The calculated $(\overline{H})$ was independent of the temperature and was decreased nonlinearly by increasing the formic acid concentration.

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