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Application of the Extended Langmuir Model for the Determination of Lyophobicity of 1-Propanol in Acetonitrile

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Abstract Surface tensions (σ) of binary liquid mixtures of acetonitrile (ACN) with 1-propanol (PrOH) were measured over the entire composition range at eight different temperatures, 278.15 K, 283.15 K, 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, and 313.15 K. The lyophobicities (β) of the surfactant PrOH relative to that of ACN as well as the surface mole fractions (x_2^S) of PrOH at various temperatures were derived using the extended Langmuir model (Langmuir **17**, 4261, 2001). The β values indicate the greater affinity of PrOH for the surface, and this trend slightly increases with rising temperature. The determined x_2^S values indicate that the surface concentration of PrOH is always higher than its bulk concentration and consequently confirm that the surface is enriched with PrOH.

Keywords Acetonitrile · Binary mixtures · Langmuir model · Lyophobicity · 1-Propanol · Surface tension

1 Introduction

The thermodynamic properties of liquid mixtures were extensively used during recent years for the characterization of molecular interactions between the components [1–3]. Among the experimental methods for the investigation of molecular interactions in liquid mixtures, the surface tension can be distinguished because of its simplicity and its precision. Surface tension data for liquid mixtures are widely used for chemical engineering applications [4–6] because surface properties play an important role in mass transfer processes such as liquid–liquid extraction, gas absorption, distillation,

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and condensation. A critical review of the available literature reveals that there is a large database on surface properties for a number of binary liquid mixtures over wide temperature and concentration ranges [7–13].

The present work reports the surface tensions (σ) of binary mixtures of acetonitrile (ACN) with 1-propanol (PrOH) at eight different temperatures, 278.15 K, 283.15 K, 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, and 313.15 K. The surface mole fraction (x_2^S) and the lyophobicity (β) of surfactant PrOH relative to that of ACN were derived using the extended Langmuir model. ACN/PrOH binary mixtures are often used as solvents in modern chemical technology [14]. A survey in the literature shows that, except for the work of Tahery et al. [15], which reports surface tensions for the ACN/PrOH binary mixtures at 293.15 K, detailed surface investigations for the ACN/PrOH binary system over a wide range of temperatures are still scare. Therefore, the aim of the present work is a study of the surface properties of the ACN/PrOH binary system in the temperature range from 278.15 K to 313.15 K.

2 Experimental

2.1 Materials

ACN (Merck, puriss) and PrOH (Merck, puriss) were used without further purification. The solvents were dried over 0.4 nm molecular sieves before use. The purity of the liquids was assessed by comparing their experimental surface tensions (σ) with available literature values. The σ value of 22.9 $mN \cdot m^{-1}$ measured in the work for PrOH at 303.15 K is in very good agreement with the literature value of 22.93 $mN \cdot m^{-1}$ reported by Johnson et al. [16]. Furthermore, the σ value of 29.3 $mN \cdot m^{-1}$ found in the present work for ACN at 293.15 K is also in a good agreement with the σ value of 29.25 $mN \cdot m^{-1}$ reported by Tahery et al. [15]. A comparison of the experimental σ values obtained in the present work for the ACN/PrOH binary mixtures at 293.15 K with the σ values reported by Tahery et al. [15] is presented graphically in Fig. 1. As can be observed in Fig. 1, the agreement is very satisfactory.

2.2 Solutions

The binary mixtures were prepared by mass using an analytical balance with a precision of ± 0.0001 g. The mole fraction of each mixture was obtained from the measured masses of the components with an uncertainty of 0.0001. All molar quantities are based on the relative atomic mass table of 1985 issued by IUPAC.

2.3 Apparatus and Procedures

The surface tensions were measured using a Du Nouy tensiometer, A. Krüss (K8600), equipped with a platinum–iridium ring having a wire diameter of 0.37 mm. The platinum–iridium ring was cleaned with chromosulfuric acid and boiling distilled water. The tensiometer was calibrated with distilled water in the temperature range

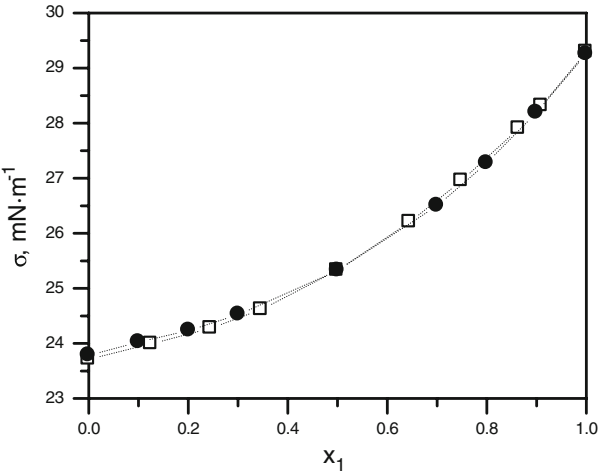

Fig. 1 Surface tension (σ) *versus* mole fraction of ACN (x_1) for ACN/PrOH binary mixtures at $T = 293.15$ K. The symbols are denoted as follows: σ values from the present work (□) and literature σ values reported by Tahery et al. (●) [15]

from 278.15 K to 313.15 K, and a correction factor was employed in all cases. The surface tensions of the water at different temperatures were taken from the literature [17]. The samples were introduced into a double-walled glass cell connected to a water-bath thermostat. A precision digital thermometer was used to read the cell temperature with an uncertainty of 0.01 K. The estimated uncertainty of the measured surface tension was $0.1\ \mathrm{mN \cdot m^{-1}}$.

The densities were measured with an Anton Paar digital precision densimeter (DMA 58) with a built-in solid state thermostat. The cell was calibrated with dry air and doubly distilled water in the temperature range from 278.15 K to 313.15 K. The thermostat temperature was constant to ±0.01 K. The estimated uncertainty of the measured density was $0.00005\ \mathrm{g \cdot cm^{-3}}$.

3 Results and Discussion

The experimental values of the surface tension (σ) and density (d) for the ACN/PrOH binary mixtures at 278.15 K, 283.15, 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, and 313.15 K are listed in Tables 1 and 2, respectively. The values of σ are presented graphically *versus* the mole fraction of ACN (x_1) in Fig. 2. There is a systematic nonlinear increase of σ with the increase of the mole fraction of ACN. Furthermore, the variation of σ with temperature was found to be linear with a negative temperature coefficient, $(\partial\sigma/\partial T)_p < 0$, a result which is in agreement with the studies of Jasper and others [18–20]. Representative curves of the variation of σ with T for the binary mixtures with the compositions, $x_1 = 0.0000$, $x_1 = 0.2452$, $x_1 = 0.4995$, $x_1 = 0.7492$, and $x_1 = 1.0000$, are shown in Fig. 3. The slope $(\partial\sigma/\partial T)_p$ was found to be independent of temperature and corresponds to the surface entropy per unit surface area (S^{S}), according to the modified thermodynamic equation of

Table 1 Mole fractions of ACN (x_1) and surface tensions (σ) of ACN/PrOH binary mixtures in the temperature range from 278.15 K to 313.15 K

x_1	σ (mN · m^{-1})							
T (K):	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
0.0000	24.9	24.5	24.1	23.7	23.3	22.9	22.5	22.2
0.1255	25.2	24.8	24.4	24.0	23.6	23.2	22.8	22.4
0.2452	25.4	25.0	24.7	24.3	23.9	23.5	23.1	22.7
0.3466	25.8	25.4	25.0	24.6	24.2	23.8	23.4	23.0
0.4995	26.5	26.1	25.7	25.3	24.9	24.5	24.2	23.8
0.6449	27.4	27.0	26.6	26.2	25.8	25.4	25.0	24.6
0.7492	28.1	27.7	27.3	26.9	26.6	26.2	25.8	25.4
0.8645	29.1	28.7	28.3	27.9	27.5	27.1	26.7	26.3
0.9101	29.5	29.1	28.7	28.3	27.9	27.5	27.1	26.8
1.0000	30.5	30.1	29.7	29.3	28.9	28.5	28.1	27.7

Table 2 Mole fractions of ACN (x_1) and densities (d) of ACN/PrOH binary mixtures in the temperature range from 278.15 K to 313.15 K

x_1	d (g · cm^{-3})							
T (K):	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
0.0000	0.81630	0.81240	0.80860	0.80361	0.79958	0.79548	0.79280	0.78702
0.1255	0.81341	0.80944	0.80555	0.79941	0.79674	0.79249	0.78947	0.78374
0.2452	0.81066	0.80661	0.80264	0.79656	0.79401	0.78962	0.78630	0.78062
0.3466	0.80833	0.80422	0.80018	0.79415	0.79170	0.78718	0.78362	0.77799
0.4995	0.80481	0.80061	0.79646	0.79051	0.78821	0.78351	0.77956	0.77401
0.6449	0.80147	0.79718	0.79293	0.78705	0.78490	0.78002	0.77571	0.77023
0.7492	0.79907	0.79472	0.79039	0.78457	0.78252	0.77752	0.77295	0.76752
0.8645	0.79642	0.79200	0.78759	0.78182	0.77989	0.77475	0.76989	0.76452
0.9101	0.79537	0.79092	0.78648	0.78074	0.77885	0.77366	0.76868	0.76334
1.0000	0.79330	0.78880	0.78430	0.77830	0.77675	0.77150	0.76630	0.76100

Clapeyron for liquid surfaces: $S^{\mathrm{S}} = -(\partial\sigma/\partial T)_p$ [21]. Considering that the surface enthalpy (H^{S}) is the sum of the surface Gibbs energy required to extend the surface, namely σ and the latent heat (q) required to maintain isothermal conditions, the enthalpy H^{S} can be estimated according to the equation: $H^{\mathrm{S}} = \sigma + q = \sigma + T S^{\mathrm{S}}$. The obtained S^{S}(0.078 mJ · m^{-2} · K^{-1}) for ACN/PrOH binary mixtures appears to be constant and independent of the temperature and solvent composition [22]. In contrast, the calculated H^{S} seems to be independent of the temperature but increases nonlinearly with the increase of the mole fraction of ACN (Fig. 4).

For the investigation of the influence of the bulk composition on the surface tension of the binary mixtures, the extended Langmuir model was applied [23–25]. According to this model, the surface of the liquid mixture is considered to be a thin layer of finite

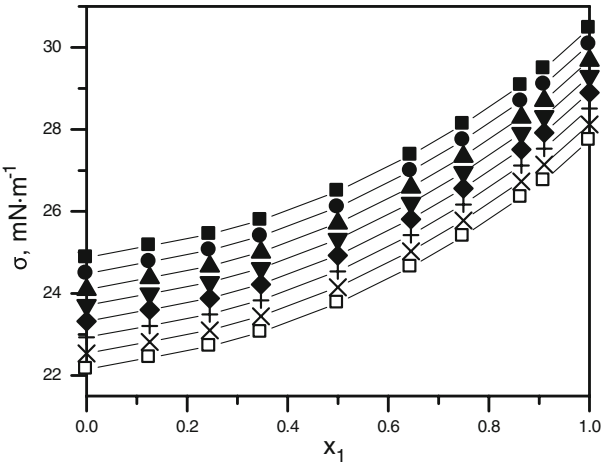

Fig. 2 Surface tension (σ) *versus* the mole fraction of ACN (x_1) for ACN/PrOH binary mixtures at $T = 278.15$ K (■), $T = 283.15$ K (●), $T = 288.15$ K (▲), $T = 293.15$ K (▼), $T = 298.15$ K (♦), $T = 303.15$ (+), $T = 308.15$ K (x), and $T = 313.15$ K (□)

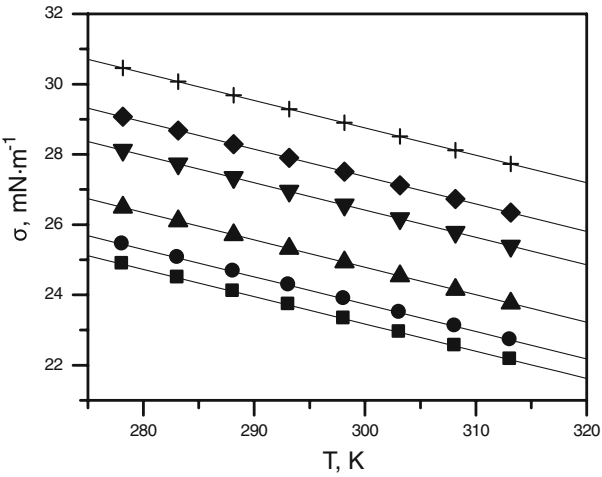

Fig. 3 Surface tension (σ) *versus* the temperature (T) for ACN/PrOH binary mixtures with the following compositions: $x_1 = 0.0000$ (■), $x_1 = 0.2452$ (●), $x_1 = 0.4995$ (▲), $x_1 = 0.7492$ (▼), $x_1 = 0.8645$ (♦), and $x_1 = 1.0000$ (+)

depth. At equilibrium, the relation between the surface volume fraction (φ_2^{S}) and the bulk volume fraction (φ_2) of the surfactant PrOH is given by the following equation:

$$\varphi_2^S = \frac{\beta\varphi_2}{[1 + (\beta - 1)\,\varphi_2]} \tag{1}$$

where β is a measure of the lyophobicity of the surfactant PrOH relative to that of ACN and represents its tendency to be adsorbed by the surface. A value of β close to unity

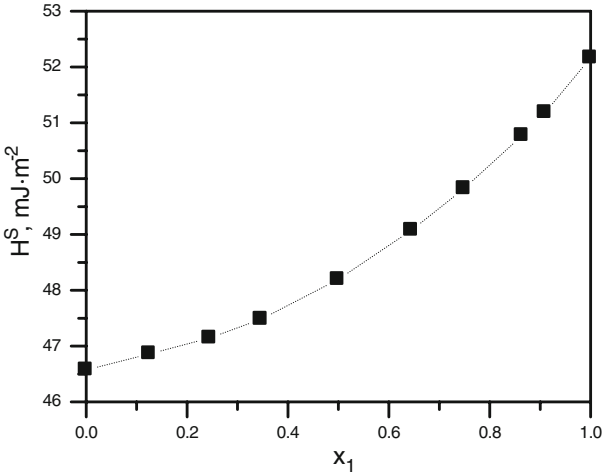

Fig. 4 Surface enthalpy (H^S) *versus* the mole fraction of ACN (x_1) for ACN/PrOH binary mixtures in the temperature range from 278.15 K to 313.15 K

shows the same affinity of the surfactant component for both the bulk-phase region and the surface, whereas $\beta > 1$ demonstrates the greater affinity of the surfactant component for the surface. The bulk volume fraction of PrOH (φ_2) is obtained from the following equation:

$$\varphi_2 = \frac{x_2 V_2}{(x_1 V_1 + x_2 V_2)} \tag{2}$$

where V_1 and V_2 are the molar volumes of ACN and PrOH, respectively. According to this model, the surface tension of the binary mixture is related with the corresponding surface volume fractions of the components by the following equation:

$$\sigma = \varphi_1^S \sigma_1 + \varphi_2^S \sigma_2 - \lambda \varphi_1^S \varphi_2^S (\sigma_1 - \sigma_2) \tag{3}$$

where σ is the surface tension of the binary mixture, σ_1 and φ_1^S are the surface tension and surface volume fraction of ACN, respectively, and σ_2 and φ_2^S are the surface tension and surface volume fraction of PrOH, respectively. The factor λ represents the effect of the unlike pair interactions on the surface tension of the mixture which is related to structural changes. If we assume that the structural changes upon mixing are insignificant (consequently λ becomes 0), Eq. 3 simplifies to

$$\sigma = \varphi_1^S \sigma_1 + \varphi_2^S \sigma_2 \tag{4}$$

Equation 4 offers the opportunity to calculate the surface volume fraction of the surfactant component in the binary liquid mixtures. The combination of Eqs. 1 and 4 results in the following relation:

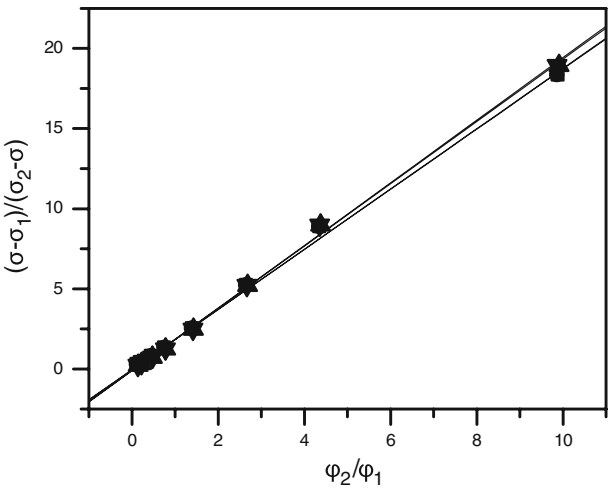

Fig. 5 Plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ *versus* φ_2/φ_1 for ACN/PrOH binary mixtures at $T = 278.15$ K (■), $T = 288.15$ K (●), $T = 298.15$ K (▲), and $T = 308.15$ K (▼)

Table 3 Values of lyophobicity (β) of surfactant PrOH relative to that of ACN in the temperature range from 278.15 K to 313.15 K

T (K)	β	T (K)	β
278.15	1.9	298.15	1.9
283.15	1.9	303.15	2.0
288.15	1.9	308.15	2.0
293.15	1.9	313.15	2.0

$$\frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma)} = \beta \left(\frac{\varphi_2}{\varphi_1}\right) \tag{5}$$

For the binary mixture investigated in the present work, the plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ *versus* φ_2/φ_1 was found to be linear in the composition range: $0.09 < x_2 < 0.87$ (Fig. 5) suggesting that the effect of the unlike pair interactions on the surface tension of the mixture is negligible and consequently that $\lambda = 0$ in this composition region. The slope of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ *versus* φ_2/φ_1 is equal to the value of lyophobicity (β) of the surfactant PrOH relative to that of ACN. The obtained β values in the temperature range from 278.15 K to 313.15 K are listed in Table 3. The observed β values ($\beta > 1$) confirm the greater affinity of PrOH for the surface. Furthermore, the β values slightly increase, and consequently, the affinity of PrOH for the surface increases, with rising temperature. The extracted β values are in accordance with the x_2^S values (see Table 4).

The surface volume fractions (φ_2^S) of surfactant PrOH in the composition range $0.09 < x_2 < 0.87$ were calculated from the following equation:

$$\varphi_2^S = \frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma_1)} \tag{6}$$

Table 4 Bulk mole fractions (x_2) and surface mole fractions (x_2^S) of PrOH in ACN/PrOH binary mixtures in the bulk composition range of $0.09 < x_2 < 0.87$ and the temperature range from 278.15 K to 313.15 K

x_2	x_2^S							
T(K):	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
0.8745	0.9278	0.9278	0.9279	0.9306	0.9301	0.9321	0.9304	0.9304
0.7548	0.8609	0.8610	0.8611	0.8636	0.8631	0.8650	0.8637	0.8636
0.6534	0.7833	0.7834	0.7836	0.7849	0.7852	0.7870	0.7861	0.7860
0.5005	0.6327	0.6329	0.6331	0.6352	0.6342	0.6358	0.6354	0.6353
0.3551	0.4649	0.4651	0.4653	0.4676	0.4660	0.4672	0.4672	0.4671
0.2508	0.3360	0.3362	0.3364	0.3378	0.3368	0.3377	0.3379	0.3378
0.1355	0.1887	0.1888	0.1890	0.1895	0.1891	0.1897	0.1899	0.1898
0.0899	0.1300	0.1301	0.1302	0.1302	0.1303	0.1307	0.1308	0.1308

which results from Eq. 4 after rearrangement and considering that $\varphi_1^S + \varphi_2^S = 1$. The surface volume fractions (φ_2^S) were converted to surface mole fractions (x_2^S) using the following equation:

$$\varphi_2^S = \frac{x_2^S V_2}{\left(x_1^S V_1 + x_2^S V_2\right)} \tag{7}$$

where x_1^S is the surface mole fraction of ACN and x_2^S is the surface mole fraction of PrOH. The values of x_2^S for PrOH are given in Table 4 and presented graphically *versus* the bulk mole fraction (x_2) in Fig. 6. The x_2^S data imply that the surface concentration of PrOH in ACN/PrOH binary mixtures is higher than its bulk concentration, and consequently, the surface can be considered to be enriched with PrOH. However, the x_2^S values change almost insignificantly with temperature. The results confirm the "preference" of the PrOH molecules being present at the surface. The x_2^S results are in full accordance with the β values (Table 3).

4 Conclusions

The present work reports the investigation of the surface of ACN/PrOH binary mixtures in the temperature range from 278.15 K to 313.15 K. The lyophobicities (β) of surfactant PrOH relative to those of ACN as well as the surface mole fractions (x_2^S) of PrOH were determined using the extended Langmuir model in binary mixtures of ACN/PrOH in the temperature range from 278.15 K to 313.15 K. The extracted β values indicate the greater affinity of PrOH for the surface, and this trend is amplified with an increase of temperature. The x_2^S results confirm that the surface concentration of PrOH is higher than its bulk concentration.

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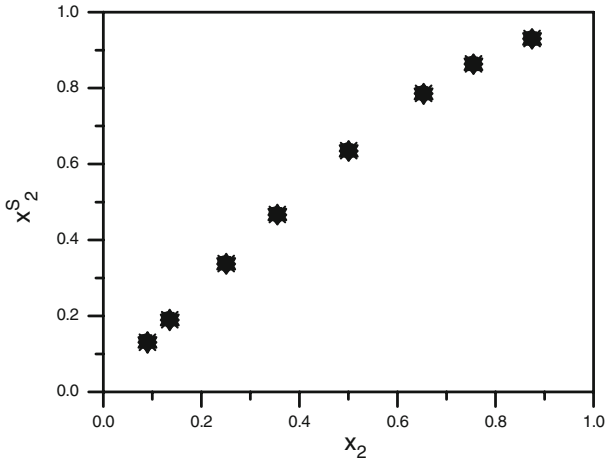

Fig. 6 Surface mole fraction (x_2^S) *versus* bulk mole fraction (x_2) of PrOH in ACN/PrOH binary mixtures in the bulk composition range $0.09 < x_2 < 0.87$ at $T = 278.15$ K (■), $T = 283.15$ K (•), $T = 288.15$ K (▲), $T = 293.15$ K (▼), $T = 298.15$ K (♦), $T = 303.15$ (+), $T = 308.15$ K (x), and $T = 313.15$ K (□)

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