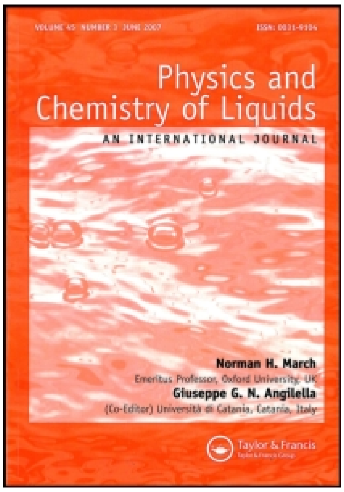

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

A study of the refractive index and surface tension synergy of the binary water/ethanol: influence of concentration

R. Belda[a]; J. V. Herraez[a]; O. Diez[b]
[a] Department of Thermodynamics, Faculty of Pharmacy, University of Valencia 46100 - Burjassot, Valencia, Spain [b] Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, University of Valencia 46100 - Burjassot, Valencia, Spain

To cite this Article Belda, R. , Herraez, J. V. and Diez, O.(2005) 'A study of the refractive index and surface tension synergy of the binary water/ethanol: influence of concentration', Physics and Chemistry of Liquids, 43: 1, 91 — 101
To link to this Article: DOI: 10.1080/00319100512331327342
URL: http://dx.doi.org/10.1080/00319100512331327342

Physics and Chemistry of Liquids
Vol. 43, No. 1, February 2005, 91–101

Taylor & Francis
Taylor & Francis Group

A study of the refractive index and surface tension synergy of the binary water/ethanol: influence of concentration

R. BELDA†,*, J.V. HERRAEZ† and O. DIEZ‡

†Department of Thermodynamics, ‡Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, University of Valencia 46100 – Burjassot, Valencia, Spain

(Received 2 September 2004)

Pure alcohols or alcohols mixed with water are the most widely used solvents in a great variety of industrial applications, including the formulation of pharmaceutical and cosmetic products. As a result of water/alcohol molecular associations, variations result in the physico-chemical characteristics of the system, such as density, viscosity, refractive index and surface tension.

The present study investigates the refractive index and the surface tension of ethanol and water mixtures at a temperature of 25°C, for different molar fractions. The data obtained allow us to study the corresponding refractive index and the surface tension synergies; in this sense, an absolute maximum refractive index is recorded for a molar fraction of 0.667, while maximum synergy (both absolute and relative) is observed for a molar fraction 0.333.

As regards surface tension, minimum absolute and relative synergy is recorded for molar fraction 0.2, since synergy is negative for the surface tensions of the mixtures.

Determinations are also made of the molar refraction of the mixtures and of the variation in refractive indices with temperature.

Keywords: Refractive index; Surface tension; Synergy; Ethanol

1. Introduction

Water is the universal solvent, and the aggregation of amphiphilic molecules within this medium can contribute to enhance our knowledge of stability and solubility processes in water [1], with many practical applications in industry: pharmaceutical and cosmetic formulations, mineral flotation processes, cleaning procedures, etc.

The aggregation of amphiphiles in water is studied in terms of a number of physico-chemical properties: viscosity, density, refractive index, surface tension, specific heat values, etc., as a function of amphiphile concentration. When these properties undergo drastic behavioral changes, aggregates in solution are said to form [2].

Alcohols are the simplest of all amphiphiles, and the behavior of water–alcohol systems is similar to that observed for tensioactive substances in water – thus indicating that these molecules aggregate in water [3–7]. Ethanol is one of the

---

*Corresponding author. Fax: 34-96-3544813. E-mail: Rafael.Belda-Maximino@uv.es

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online
http://www.tandf.co.uk/journals
DOI: 10.1080/00319100512331327342

most widely used alcohols in industry, and has been the subject of a first study exploring the viscosity of mixtures of ethanol and water, and its modification with concentration [8].

With the idea of expanding upon this first evaluation of the physico-chemical properties of ethanol, a second study has been made to investigate the synergy (both absolute and relative) of the refractive index of ethanol and water mixtures at different concentrations. Due to the importance of the molar refraction of liquid mixtures in quality control processes, analytical methods, etc. [9,10], we have also evaluated the molar refraction of these mixtures as a function of molar fraction.

Finally, we have studied the surface tension synergy of these mixtures, along with their corresponding synergy indices.

2. Theoretical considerations

In an earlier study [8] we commented on the method introduced by Kaletunc–Gencer and Peleg [11] for quantifying the viscous synergy of liquid mixtures, defined as the difference between experimental viscosity, η_{exp}, and the theoretical viscosity, η_{mix}, obtained from the equation:

$$\eta_{\mathrm{mix}} = w_{\mathrm{A}}\eta_{\mathrm{A}} + w_{\mathrm{B}}\eta_{\mathrm{B}} \tag{1}$$

where, w_{A} and w_{B} are the fractions by weight of the components A and B of the mixture, and η_{A} and η_{B} are their respective viscosities. With the aim of ensuring more comparable viscous synergy results, we also studied the synergic interaction index (I_η) introduced by Howell [12], and which is defined as:

$$I_\eta = (\eta_{\mathrm{exp}} - \eta_{\mathrm{mix}})/\eta_{\mathrm{mix}} = \Delta\eta/\eta_{\mathrm{mix}} \tag{2}$$

which conceptually represents relative variation of viscous synergy.

In the same way as for viscosity, a definition can be made with respect to the experimentally determined refractive index, n_{exp}, of a theoretical value, n_{mix}, with the corresponding synergy indices, I_n, based on the equations:

$$n_{\mathrm{mix}} = w_{\mathrm{A}}n_{\mathrm{A}} + w_{\mathrm{B}}n_{\mathrm{B}} \tag{3}$$

$$I_n = (n_{\mathrm{exp}} - n_{\mathrm{mix}})/n_{\mathrm{mix}} = \Delta n/n_{\mathrm{mix}} \tag{4}$$

where w_{A} and w_{B} are the fractions by weight of components A and B of the mixture, and n_{A} and n_{B} their refractive indices, respectively.

For calculating the experimental, $[R]_{\mathrm{exp}}$, and the theoretical molar refraction, $[R]_{\mathrm{mix}}$, of the mixtures, we use the following expressions [13]:

$$[R]_{\mathrm{exp}} = \frac{n^2-1}{n^2+2}\cdot\frac{x_{\mathrm{A}}M_{\mathrm{A}} + x_{\mathrm{B}}M_{\mathrm{B}}}{\rho} \tag{5}$$

$$[R]_{\mathrm{mix}} = x_{\mathrm{A}}[R]_{\mathrm{A}} + x_{\mathrm{B}}[R]_{\mathrm{B}} \tag{6}$$

where n is the refractive index of the mixture, x_A and x_B the molar fractions of the components A and B of the system, M_A and M_B the molecular weights, and ρ the density of the mixture.

The resulting surface tension of liquid mixtures does not generally correspond to a pondered mean value of the surface tensions of the components of the mixture [4]. Thus, in the same way as applied to viscosity and refractive index, an absolute synergy value of surface tension could be introduced, likewise defined as the difference between the experimental, σ_{exp}, and the theoretical surface tension, σ_{mix}.

In order to define η_{mix} and n_{mix} according to equations (1) and (3), we took into account that both the viscosity, η, and the refractive index, n, of a pure monoalcohol increase at a given temperature with increasing molecular weight [14]. However, the surface tension remains practically constant (methanol 22.35×10^{-3} N/m, ethanol 22.14×10^{-3} N/m, and propanol 23.30×10^{-3} N/m), thereby indicating that to the effects of surface tension, the amount of molecule present is the most important consideration, not its molecular weight. As a result, a theoretical surface tension, σ_{mix}, is defined by the equation:

$$\sigma_{\text{mix}} = x_A\sigma_A + x_B\sigma_B \tag{7}$$

where x_A and x_B are now the molar fractions of the components of the mixture. The study of the synergy index of surface tension, I_σ, is made in the same way as for viscosity and refractive index, i.e., based on the equation:

$$I_\sigma = (\sigma_{\text{exp}} - \sigma_{\text{mix}})/\sigma_{\text{mix}} = \Delta\sigma/\sigma_{\text{mix}}. \tag{8}$$

3. Experimental method

Ethanol (richness >99.5% by volume) supplied by Aldrich was used. Mixtures of ethanol and water were prepared, with ethanol molar fractions of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1, and each mixture was distributed into three containers – so that each measurement could be performed in triplicate, in order to evaluate possible dispersion of the results. Posteriorly, and with the aim of precisely identifying the maximum values for refractive index and synergy index, and the minimum surface tension synergy index, we also prepared and measured the molar fractions between 0.3 and 0.4 and 0.6 and 0.7, incorporating to table 1 the results corresponding to molar fractions 0.333 and 0.667.

Measurement of the refractive index, n, of the mixtures was carried out with an Abbe refractometer thermostatted for temperatures between 20°C and 70°C [15], while surface tension, σ, was determined using a stalagmometer at a temperature of 25°C.

The measurements obtained (in triplicate) in all cases showed a dispersion of less than 2%.

4. Results

4.1 *Refraction indices*

The results corresponding to n_{exp}, n_{mix}, Δn, I_n, $[R]_{\text{exp}}$ and $[R]_{\text{mix}}$ are shown in table 1. These values have been graphically represented in figures 1–4.

Table 1. Refractive index values: experimental, n_{exp}, theoretical, n_{mix}, and differences, $\Delta n = (n_{\text{exp}} - n_{\text{mix}})$, together with the synergy index of the refractive index, $I_n = (\Delta n / n_{\text{mix}})$, and the experimental, $[R]_{\text{exp}}$, and theoretical, $[R]_{\text{mix}}$, molar refraction values of the mixture of ethanol and water, for the indicated molar fractions of ethanol (x), at a temperature of 25°C.

x	n_{exp}	n_{mix}	Δn	I_n	$[R]_{\text{exp}} \times 10^{-6}$ (m^3)	$[R]_{\text{mix}} \times 10^{-6}$ (m^3)
0.000	1.3326	1.3326	0.000000	0.000000	3.7092	3.7092
0.100	1.3473	1.3389	0.008419	0.006288	4.6101	4.6263
0.200	1.3553	1.3437	0.011600	0.008633	5.5176	5.5434
0.300	1.3599	1.3474	0.012455	0.009243	6.4211	6.4604
0.333	1.3611	1.3485	0.012568	0.009319	6.7405	6.7631
0.400	1.3623	1.3505	0.011804	0.008741	7.3433	7.3775
0.500	1.3631	1.3523	0.010088	0.007456	8.2689	8.2946
0.600	1.3636	1.3551	0.008476	0.006255	9.2103	9.2117
0.667	1.3638	1.3564	0.007442	0.005486	9.8460	9.8261
0.700	1.3636	1.3569	0.006679	0.004922	10.1531	10.1290
0.800	1.3627	1.3585	0.004231	0.003114	11.0740	11.0461
0.900	1.3619	1.3598	0.002083	0.001532	11.9884	11.9632
1.000	1.3610	1.3610	0.000000	0.000000	12.8803	12.8803

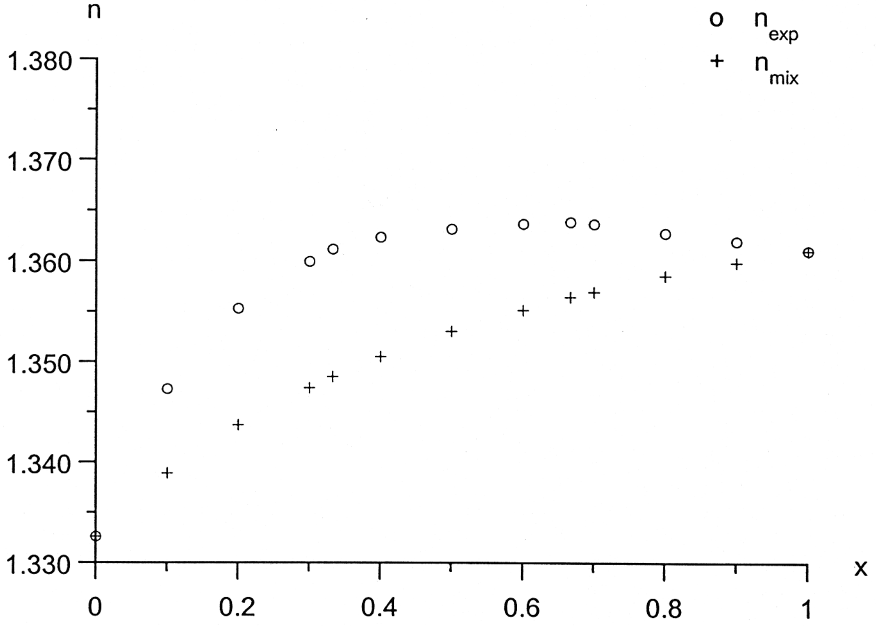

Figure 1. Graphic representation of the values of the refractive index (experimental, n_{exp}, and theoretical, n_{mix}) of the mixture of ethanol and water, as a function of the molar fraction of ethanol (x), at a temperature of 25°C.

In figure 1, showing the values of n_{exp} and n_{mix} as a function of the molar fraction, x, a marked discrepancy is observed between the values of the experimental refractive index, n_{exp}, and the theoretical refractive index, n_{mix}, defined by equation (3). In all cases $n_{\text{exp}} > n_{\text{mix}}$, thus indicating the existence of positive synergy of these mixtures for the refractive index. In this figure, a continuous linear increment is seen in n_{mix}, from the value of the refractive index of water, $n_{\text{water}} = 1.3326$, to that of the pure

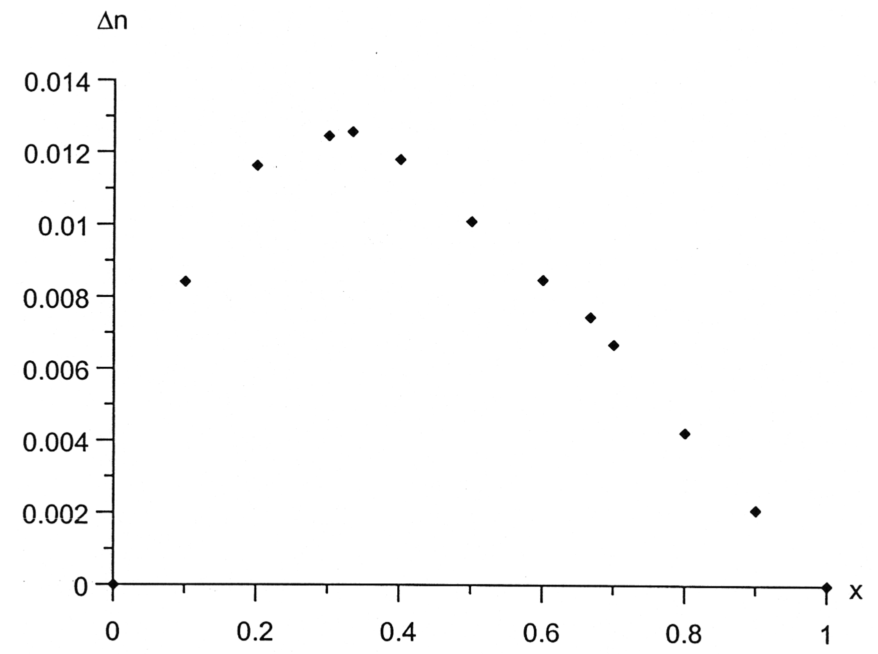

Figure 2. Graphic representation of the absolute synergy of the refractive index, $\Delta n = n_{\mathrm{exp}} - n_{\mathrm{mix}}$, of the mixture of ethanol and water, as a function of the molar fraction of ethanol (x), at a temperature of 25°C.

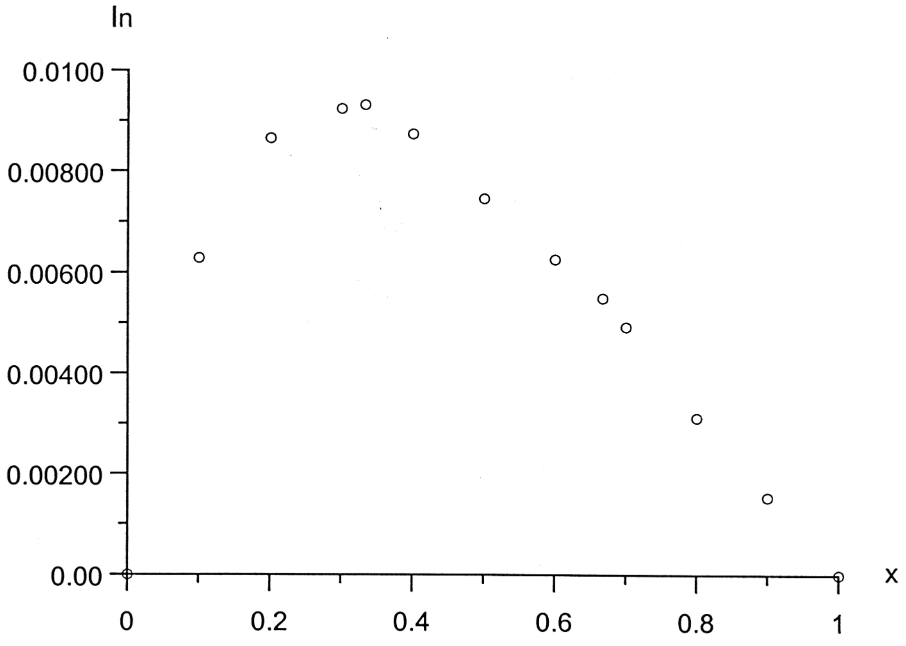

Figure 3. Graphic representation of the relative synergy of the refractive index, $I_n = (\Delta n / n_{\mathrm{mix}})$, of the mixture of ethanol and water, as a function of the molar fraction of ethanol (x), at a temperature of 25°C.

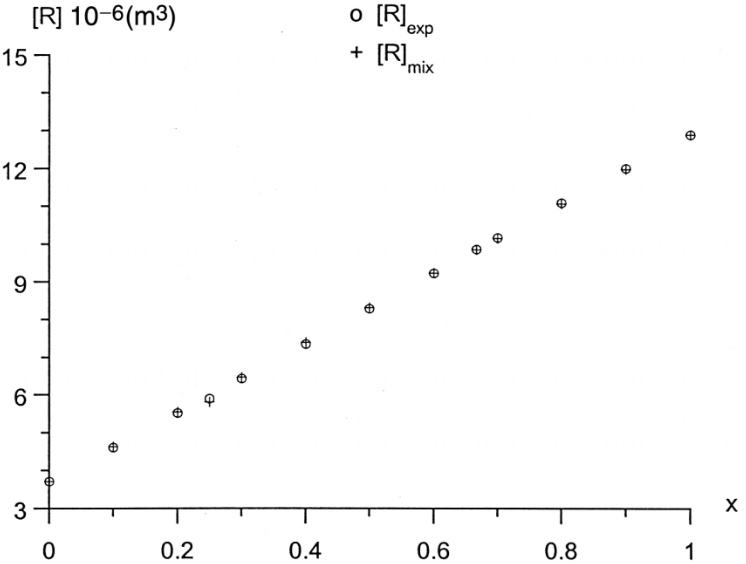

Figure 4. Graphic representation of the values of the molar fraction (experimental, $[R]_{\text{exp}}$, and theoretical, $[R]_{\text{mix}}$), of the mixture of ethanol and water, as a function of the molar fraction of ethanol (x), at a temperature of 25°C.

alcohol, $n_{\text{alcohol}} = 1.3610$, while n_{exp} reaches a maximum value, $n_{\text{maximum}} = 1.3638$, exceeding that of the pure alcohol, and which is reached for molar fraction of 0.667 – corresponding to a proportion of 2 M of alcohol, for every mole of water.

Figures 2 and 3, respectively, show the absolute synergies, $\Delta n = n_{\text{exp}} - n_{\text{mix}}$, and the relative synergies $I_n = \Delta n / n_{\text{mix}}$, where both are seen to exhibit a maximum value for molar fraction 0.333, i.e., a proportion of 2 M of water for every mole of alcohol.

Regarding the molar refraction of the mixtures (figure 4), no synergism is observed – practically total coincidence being observed between the experimental values, $[R]_{\text{exp}}$, obtained by equation (5) and the theoretical values, $[R]_{\text{mix}}$, defined by equation (6). In both cases, growth is strictly linear with increasing molar fraction, x, is as to be expected from equation (6). We have also studied the variation of the refractive index of the mixtures with temperature, for different molar fractions, in the temperature range of 20–70°C. The results are graphically represented in figure 5.

In all the cases, the figure shows a linear decrement in refractive index with temperature, the slope (in absolute terms) increasing with the magnitude of the refractive index of the mixture. In other words, the greatest slope corresponds to molar fraction 0.667, where the greatest refractive index is observed.

4.2 *Surface tension*

On the other hand, the experimentally determined surface tension values, σ_{exp}, are shown in table 2, along with the theoretical values, σ_{mix}, obtained from equation (7), and the values of $\Delta\sigma = \sigma_{\text{exp}} - \sigma_{\text{mix}}$ and I_σ obtained from equation (8).

These values, in turn, yield the graphic representations shown in figures 6–8.

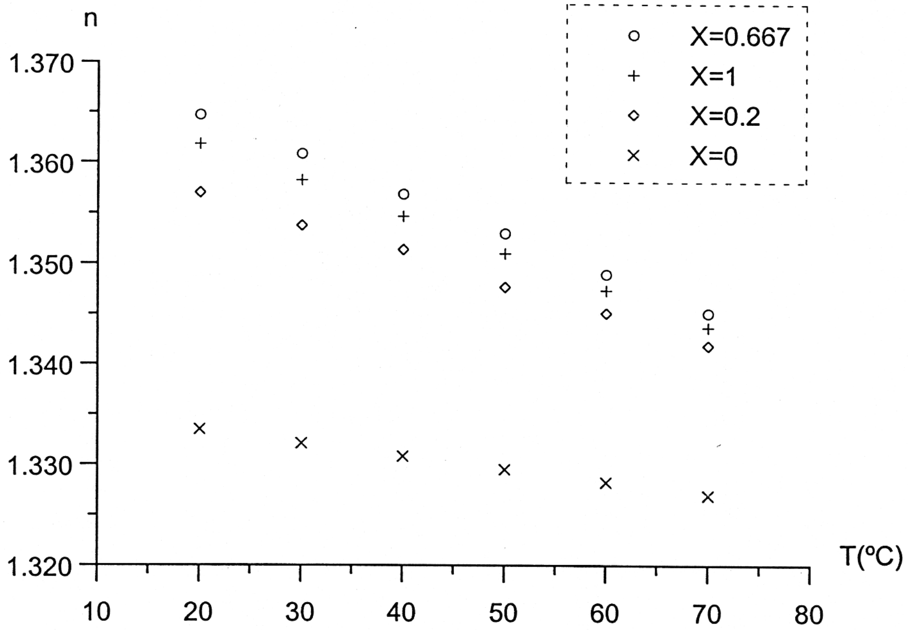

Figure 5. Graphic representation of the experimental values of the refractive index, *n*, of the mixture of ethanol and water, as a function of temperature, for temperatures between 20°C and 70°C, and for molar fractions of 0, 0.2, 0.667 and 1.

Table 2. Surface tension values: experimental, $\sigma_{\rm exp}$, theoretical, $\sigma_{\rm mix}$, and differences, $\Delta\sigma = (\sigma_{\rm exp} - \sigma_{\rm mix})$, together with the synergy index of surface tension, $I_\sigma = (\Delta\sigma/\sigma_{\rm mix})$, of the mixture of ethanol and water, for the indicated molar fractions of ethanol (x), at a temperature of 25°C.

x	$\sigma_{\rm exp} \times 10^{-3}$ (N/m)	$\sigma_{\rm mix} \times 10^{-3}$ (N/m)	$\Delta\sigma \times 10^{-3}$ (N/m)	$I\sigma$
0.000	72.66	72.66	0.00	0.0000
0.100	36.63	67.61	−30.98	−0.4582
0.200	29.89	62.56	−32.67	−0.5222
0.300	27.78	57.50	−29.72	−0.5170
0.400	26.52	52.45	−25.93	−0.4944
0.500	25.56	47.40	−21.84	−0.4607
0.600	24.76	42.35	−17.59	−0.4154
0.700	24.00	37.30	−13.30	−0.3565
0.800	23.35	32.24	−8.89	−0.2759
0.900	22.74	27.19	−4.45	−0.1636
1.000	22.14	22.14	0.00	0.0000

Figure 6 jointly presents the values of $\sigma_{\rm exp}$ and $\sigma_{\rm mix}$, as a function of the molar fraction, x; in this sense, $\sigma_{\rm exp}$ always shows lower values than $\sigma_{\rm mix}$, indicating that the interaction between water and ethanol is characterized by negative synergy of surface tension, in contraposition to the positive synergy of viscosity [8] and the refractive index.

While the experimental values of viscosity, $\eta_{\rm exp}$, show a maximum for molar fraction 0.25, and those of the refractive index, $n_{\rm exp}$, present a maximum for molar fraction 0.667, the experimental values of surface tension, $\sigma_{\rm exp}$, show no relative

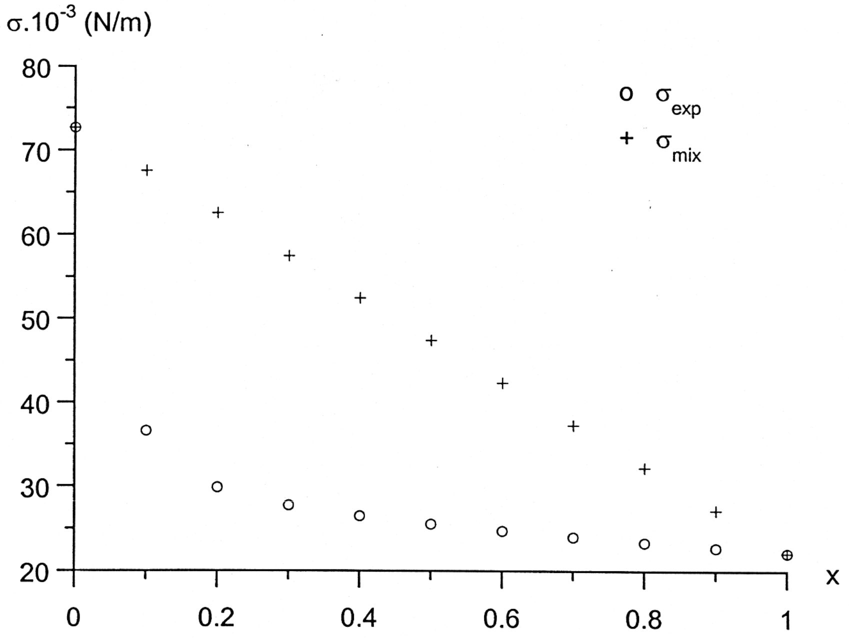

Figure 6. Graphic representation of the values of surface tension (experimental, σ_{exp}, and theoretical, σ_{mix}), of the mixture of ethanol and water, as a function of the molar fraction of ethanol (x), at a temperature of 25°C.

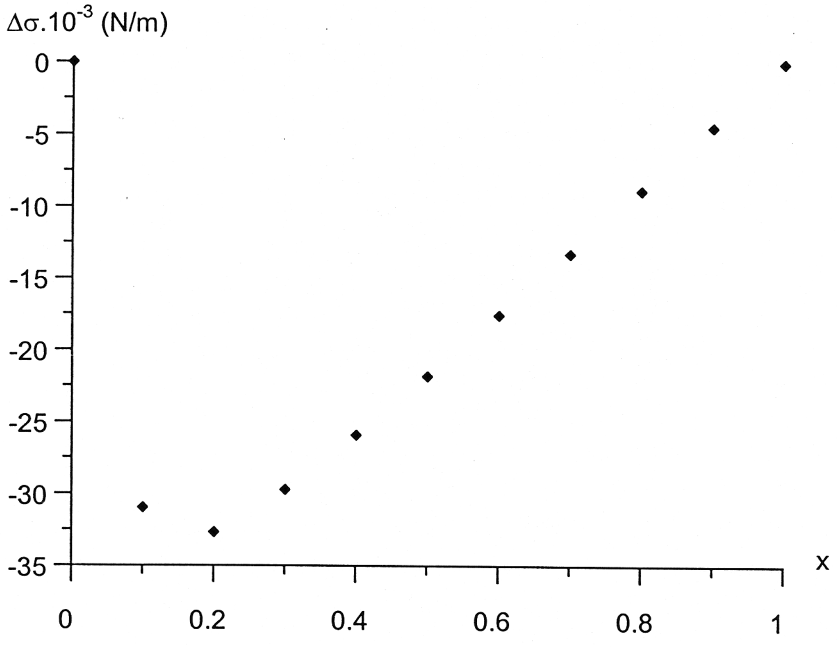

Figure 7. Graphic representation of the absolute synergy of surface tension, $\Delta\sigma = \sigma_{\text{exp}} - \sigma_{\text{mix}}$, of the mixture of ethanol and water, as a function of the molar fraction of ethanol (x), at a temperature of 25°C.

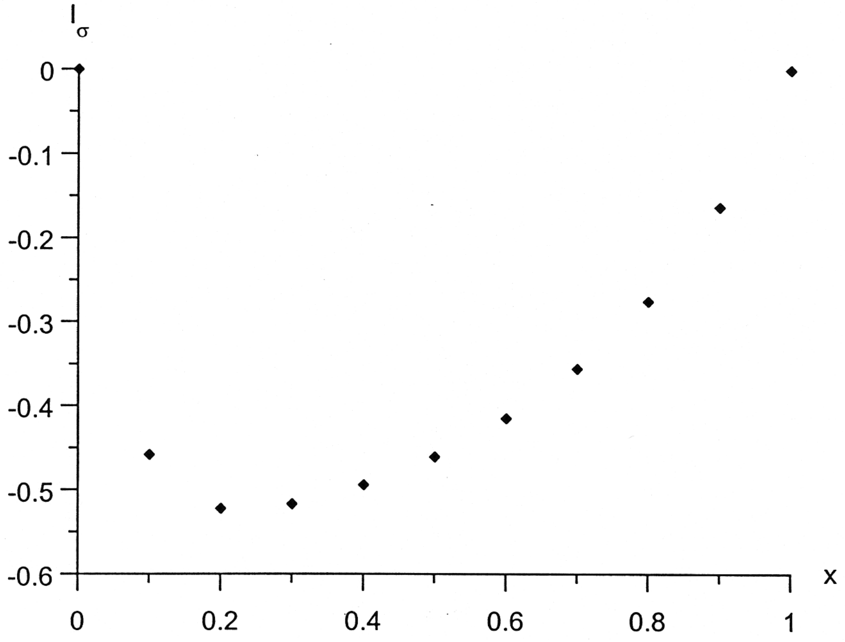

Figure 8. Graphic representation of the relative synergy of surface tension, $I_\sigma = (\Delta\sigma/\sigma_{\text{mix}})$, of the mixture of ethanol and water, as a function of the molar fraction of ethanol (x), at a temperature of 25°C.

minimum – since the values decrease continuously to a low of 22.14×10^{-3} N/m, corresponding to the surface tension of ethanol (which is evidently reached at molar fraction 1).

However, on representing $\Delta\sigma$ and I_σ (figures 7 and 8) as a function of molar fraction, x, we obtain minimum values which, in both cases correspond to molar fraction 0.2.

In our earlier study [8], we explained the enhancement of viscosity of the mixture of ethanol and water as the cause of the formation of molecular packages between alcohol and water molecules.

In the present study, we have observed a certain similarity between the behavior of the refractive index and viscosity, since both the parameters exhibit positive synergy. However, in the case of viscosity, molar fraction 0.25 (3 M of water per mole of alcohol) yielded the highest viscosity value, as well as the maximum values for absolute and relative synergy – while in the case of the refractive index, the maximum value was recorded for molar fraction 0.667 (2 M of alcohol per mole of water), and maximum absolute and relative synergy corresponded to molar fraction 0.333 (2 M of water per mole of ethanol).

In principle, surface tension behaves differently to refractive index and viscosity, since its synergism is negative, due to the rupture of hydrogen bonds between water molecules caused by the presence of alcohol. Likewise, and due to the large difference between the surface tension of water, 72.66×10^{-3} N/m, and that of the alcohol, 22.14×10^{-3} N/m, no minimum in the surface tension of the mixtures is recorded – though a minimum for both absolute and relative synergies is observed, corresponding to molar fraction 0.2.

5. Summary and conclusions

(a) Measurements have been made of the refractive indices of mixtures of ethanol and water for different molar fractions between 0 and 1, observing an absolute maximum, $n_{\mathrm{max}} = 1.3638$, greater than that of the pure alcohol, for molar fraction, $x = 0.667$, corresponding to a proportion of 2 M of alcohol for every mole of water.

(b) A theoretical value has been defined for the refractive index of the mixture, n_{mix}, based on the equation:

$$n_{\mathrm{mix}} = w_{\mathrm{A}} n_{\mathrm{A}} + w_{\mathrm{B}} n_{\mathrm{B}}$$

where n_{A} and n_{B} are the refractive indices of the pure components, and w_{A} and w_{B} the respective fractions by weight of the components of the mixture.

These values of n_{mix} in turn allow us to define absolute synergy, Δn, established as $\Delta n = n_{\mathrm{exp}} - n_{\mathrm{mix}}$, and relative synergy, I_n, established as:

$$I_n = (n_{\mathrm{exp}} - n_{\mathrm{mix}})/n_{\mathrm{mix}} = \Delta n / n_{\mathrm{mix}}$$

(c) The maximum values of the absolute, Δn, and relative synergies, I_n, appear at molar fraction 0.333, i.e., in the proportion of 2 M of water for every mole of ethanol.

(d) Measurements have been made of the variations of the refractive indices with temperature, in the range of 20–70°C, and for the different molar fractions. In all cases, a linear decrease was observed with increasing temperature, the absolute value of the slope increasing with the refractive index of the mixture at 20°C.

(e) Molar refraction increases linearly with molar fraction, in accordance to equation:

$$[R]_{\mathrm{mix}} = x_{\mathrm{A}}[R]_{\mathrm{A}} + x_{\mathrm{B}}[R]_{\mathrm{B}}$$

where $[R]_{\mathrm{A}}$ and $[R]_{\mathrm{B}}$ are the molar refraction values of the pure components, and x_{A} and x_{B} their respective molar fractions; no type of synergy is observed.

(f) Regarding the synergy of surface tension, the same treatment as in the case of the refractive index has been carried out, though defining the theoretical surface tension, σ_{mix}, as:

$$\sigma_{\mathrm{mix}} = x_{\mathrm{A}}\sigma_{\mathrm{A}} + x_{\mathrm{B}}\sigma_{\mathrm{B}}$$

where σ_{A} and σ_{B} are the surface tension values of the components, and x_{A} and x_{B} their respective molar fractions.

(g) The synergies of surface tension (both absolute and relative) appear at molar fraction 0.2, i.e., 4 M of water per mole of ethanol.

References

[1] A.N. Martín. Principios de fisico-química para farmacia y biología, Alhambra, S.L., Madrid (1967).

[2] J. Swarbrik, J.C. Boyland. *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, Inc., New York (1993).

[3] F. Franks, J.E. Desnoyers. *Water Science Reviews*, **1**, 171 (1985).

[4] G. Vazquez, E. Alvarez, J.M. Navaza. *J. Chem. Eng. Data*, **40**, 611 (1995).

[5] C. Faulí I Trillo. Tratado de Farmacia Galénica, Luzán 5, S.A. Madrid (1993).

[6] H.D. Crockford, B. Knight. Fundamentos de fisicoquimica, C.E.C.S.A. Madrid (1968).

[7] R. Voigt. Tratado de tecnología farmacéutica, Acribia, Zaragoza (1982).

[8] R. Belda, J.V. Herraez, O. Diez. *Physics and Chemistry of Liquids*, **42**, 3 (2004).

[9] Y. Jayalakshmi, J.S. Van Duijneneldt, D. Beysens. *J. Chem. Phys.*, **100**, 604 (1994).

[10] F. Jiménez, D. Carreño y, F. Martínez. *Col. Cienc. Quim. Farm*, **21**, 41 (1993).

[11] G. Kaletunc-Gencer, M. Peleg. *J. Texture Studies*, **17**, 61 (1986).

[12] N.K. Howell. *Gums and stabilisers for the food industry*, G.O. Phillips, P.A. Williams, D.J. Wedlock (Eds.), pp. 77–89, Oxford University Press, New York (1994).

[13] S. Glasstone. Tratado de Quimica Física, Aguilar., Madrid (1970).

[14] J.V. Herraez, R. Belda. *Journal of Solution Chemistry*, **33**, **2**, 117 (2004).

[15] T. Catunda, J.P. Andreeto, J.C. Castro. *Sci. Instrum.*, **62**, 1214 (1986).