This article was downloaded by: On: 28 January 2011 Access details: Access Details: Free Access Publisher Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37- 41 Mortimer Street, London W1T 3JH, UK

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information: <http://www.informaworld.com/smpp/title~content=t713646857>

Rheological study and thermodynamic analysis of the binary system (water/ethanol): Influence of concentration

R. Beldaª; J. V. Herraezª; O. Diez^b

^a Department of Thermodynamics, 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.(2004) 'Rheological study and thermodynamic analysis of the binary system (water/ethanol): Influence of concentration', Physics and Chemistry of Liquids, 42: 5, 467 — 479 To link to this Article: DOI: 10.1080/00319100410001700850

URL: <http://dx.doi.org/10.1080/00319100410001700850>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use:<http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

RHEOLOGICAL STUDY AND THERMODYNAMIC ANALYSIS OF THE BINARY SYSTEM (WATER/ETHANOL): INFLUENCE OF CONCENTRATION

R. BELDA^{a,*}, J.V. HERRAEZ^a and O. DIEZ^b

^a Department of Thermodynamics, ^b Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, University of Valencia, 46100 – Burjassot, Valencia, Spain

(Received 13 January 2004)

Water is the most widely used solvent in the chemical and pharmaceutical industry, since it is the most physiological and best tolerated excipient. However, in some cases water cannot be used as a solvent because the active substance or solute is insoluble or only slightly soluble in water. For this and other reasons, nonwater solvents may be used possessing the common characteristic of being soluble or mixable in water; as a result, such solvents can be used to prepare binary or tertiary mixtures, etc., with different purposes such as increasing water solubility, or modifying the viscosity or absorption of the dissolved substance, for example.

Ethanol, along with other alcohols either alone or in water–alcohol solutions involving different proportions, are widely used in the pharmaceutical industry as excipients in different formulations, or as solvents.

Ethanol–water systems are characterized by the so-called volume contraction phenomenon, which is in turn accompanied by a considerable increase in the viscosity of the system. This is attributed to the increase in size of the molecular package secondary to solvation or the formation of hydrogen bonds between the alcohol and water – a phenomenon referred to as viscous synergy.

The formation of hydrogen bonds between alcohol and water modifies with temperature, thus leading to variations in the viscosity of the system.

The present study investigates the viscous synergy of systems comprising pure alcohol in water at different concentrations, determining the proportion of alcohol–water at which maximum viscous synergy occurs, along with the correlation between the viscosity increments and density. The ratio between the maximum viscosity reached by the mixture and the viscosity of pure alcohol is expressed by the enhancement index defined as: $E_n = \eta_{\text{max}}/\eta_o$. Likewise, and since the viscosity of these systems varies with temperature, a thermodynamic study has been made to determine the activation energy of the ethanol–water mixture as a function of concentration.

Keywords: Viscosity; Viscous synergy; Ethanol; Solvation; Activation energy

INTRODUCTION

Ethanol is very widely used in the chemical, pharmaceutical, and cosmetic industry, and presently also as an alternative energy source. Knowledge of its physico-chemical characteristics is therefore interesting in order to define its behavior in each concrete case.

^{*}Corresponding author. Tel./Fax: $+34-963544813$. E-mail: Rafael.Belda-Maximino@uv.es

Rheology, the field in physics which studies material deformation and flow, is implicated in the mixing and flow of medicinal formulations and cosmetics, and is increasingly applied to the analysis of the viscous behavior of numerous pharmaceutical products [1–7].

In addition, the rheological and molecular behavior of a formulation can influence aspects such as patient acceptability – since it has been well demonstrated that viscosity and density both influence the absorption rate of such products in the body [8,9].

On the other hand, thermodynamics studies phenomena related to heat and temperature, and in our case is applied to determination of the activation energies of such systems, since temperature is also an important factor [8,10] determining the physicochemical properties of these systems – influencing both product absorption rate and reaction velocity [8,10–12].

The present study investigates and quantifies viscous synergy and volume contraction in mixtures of pure ethanol and water, and their relation to concentration. Likewise, and since the viscosity of these systems varies with temperature, a thermodynamic study has been made of the elements constituting these systems, with the determination of their respective activation energies.

THEORETICAL CONSIDERATIONS

Synergy is defined as mutual enhancement of the physico-chemical, biological, or pharmaceutical activity between different components of a given mixture, as a result of which the combined activity is greater than the simple sum of the activities of the individual constituent components.

For the purposes of the present study, viscous synergy is the term used in application to the interaction between the components of a system characterized by a net viscosity greater than the simple sum of the viscosities of the individual constituent components.

In contraposition to viscous synergy, the term viscous antagonism refers to interaction between the components of a system whereby the net viscosity is less than the simple sum of the viscosities of the individual constituent components. Finally, if the net viscosity of the mixture coincides with the sum of the viscosities of its individual components, then the system is said to lack interaction among its components [13].

From the rheological perspective, the study of viscous synergy is interesting, since many products are formulated with more than a single component in order to yield the desired physical structure and properties [14].

The method most widely used to study the synergistic and antagonic behavior of ethanol–water mixtures was developed by Kaletunc-Gencer and Peleg [15]. This method is able to quantify the synergic interactions taking place in solutions involving components mixed in variable proportions, contrasting the viscosity of the system as determined experimentally, $\eta_{\rm exp}$, with the expected viscosity in the absence of interaction, η_{mix} , defined by the following equation:

$$
\eta_{\text{mix}} = x_A \cdot \eta_A + x_B \cdot \eta_B,\tag{1}
$$

where x_A and x_B are the fraction by weight of A and B in the system, and η_A and η_B are the experimentally determined viscosities of A and B , respectively. Accordingly, when $\eta_{\rm exp} > \eta_{\rm mix}$, viscous synergy exists, while in the event that $\eta_{\rm exp} < \eta_{\rm mix}$, viscous antagonism is defined.

This procedure is used in application to Newtonian fluids, since in the case of non-Newtonian systems shear rate must be taken into account – with the resulting definition of other synergy indices [16].

In order to make viscous synergy results more comparable, we also study the so-called synergic interaction index (I_n) introduced by Howell [17] and defined as:

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

Another aspect to be taken into account is the fact that the viscosity of a product (in our case ethanol) is increased by the simple addition of water. Accordingly, the enhancement index of the viscosity of the mixture (E_n) is defined as the ratio between the maximum viscosity of the solution (η_{max}) and the viscosity of the pure substance (η_o) , i.e.:

$$
E_{\eta} = \eta_{\text{max}}/\eta_o. \tag{3}
$$

The method used to analyze volume contraction is similar to that applied to viscosity, i.e., the density of the mixture is determined experimentally, ρ_{exp} , and a theoretical value is calculated, ρ_{mix} , corresponding to the situation where no volume contraction exists, based on the following equation:

$$
\rho_{\text{mix}} = x_A \cdot \rho_A + x_B \cdot \rho_B,\tag{4}
$$

where x_A and x_B are the fraction by weight of A and B in the system, and ρ_A and ρ_B are the experimentally determined densities of A and B , respectively. Calculations are then made of $\Delta \rho = \rho_{\rm exp} - \rho_{\rm mix}$ the density synergy index, $I_\rho = \Delta \rho / \rho_{\rm mix}$, and the density enhancement index, E_{ρ} .

The mixtures analyzed establish hydrogen bonds between the alcohol and water molecules. These bonds in turn undergo changes with temperature, giving rise to variations in the viscosity of the system. Thus, in order to complete the description of the viscous behavior of such mixtures, a thermodynamic study is required.

The analysis of activation energy is an important and complementary aspect in the rheological study of a product, with implications for the stability of the latter, and moreover affords information on the absorption rate of the system and its velocity of reaction [8,10,12].

Activation energy is defined as the minimum energy necessary for a phenomenon, process, or reaction to take place – i.e., its required initial ''triggering'' energy. In systems with a high-activation energy, only a small proportion of the colliding particles conforming the system have sufficient energy to react, and the reaction process is slow. In contrast, in low-activation energy systems almost all the particles possess sufficient energy to react, and the reaction process is therefore rapid [8]. In our case the activation energy is the energy required to initiate flow among the system molecules.

We have determined the activation energy of the alcohol–water mixture based on the Eyring theory of transport phenomena in liquid systems [18], where viscosity is related

to temperature by the Arrhenius equation:

$$
\eta = A e^{(Ea/R)(1/T)} = A e^{B/T},\qquad(5)
$$

which after linear conversion becomes:

$$
\operatorname{Ln} \eta = \operatorname{Ln} A + (Ea/R) \cdot (1/T),\tag{6}
$$

where: A is a constant characteristic of the substance involved; R is the universal gas constant (cal/mol k); Ea is the activation energy of the system; and T is the absolute temperature of the system.

EXPERIMENTAL METHOD

Ethanol was used as alcohol, with a richness of over 99.5% (v/v), supplied by Aldrich. Ethanol–water mixtures were prepared at concentrations of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100%, (w/w), distributing each preparation in three containers to ensure determinations in triplicate and thus assess possible dispersion of the results obtained. Posteriorly, in order to precisely determine the condition of maximum viscosity, the concentrations between 40 and 50% were also measured, incorporating to our table the results corresponding to a 46% concentration (w/w) of ethanol (equivalent to one ethanol molecule per three water molecules).

The viscosity of the mixtures was determined using a Canon-Fenske viscometer, while density was evaluated with an immersion densitometer. Both instruments were used in the $10-70^{\circ}$ C temperature range – higher temperatures being discarded, since ethanol evaporation prevents stability of the measurements obtained.

The determinations in triplicate in all cases showed a percentage dispersion of under 2% – the mean value being recorded in all cases.

RESULTS

The results corresponding to η_{exp} , η_{mix} , $\Delta \eta$, and $I\eta$ are jointly presented in Table I. For increased clarity, Table I only includes the measures corresponding to temperatures of 10, 30, 50, and 70° C.

Figure 1(*a*) compares experimental viscosity, η_{exp} , with ethanol concentration in the mixture, C (%). As the latter increases, η_{\exp} is seen to increase to a maximum value corresponding to a concentration (w/w) of 46%, beyond which the experimental viscosity values decrease. In all cases these values decrease with increasing temperature.

Figure 1(b) and (c) respectively correspond to $\Delta \eta$ and $I\eta$ as a function of ethanol concentration, C (%); in both cases the behavior is qualitatively similar to that seen in Fig. 1(a). Of note is the fact that the values of $\Delta \eta$, and therefore of I η , are always positive – thus reflecting the viscous synergy phenomenon. It should also be pointed out that maximum viscous synergy is always observed for the 46% ethanol concentration (w/w) , which has already been mentioned as the corresponds to one alcohol molecule per three water molecules. The explanation for this behavior is clearly based on the alcohol solvation phenomenon resulting from the hydrogen bonds formed between the molecules of the two mixture components, with an increase in the volume of the

TABLE I Values corresponding to experimental (η_{exp}) and theoretical viscosity (η_{mix}) , $\Delta \eta = (\eta_{exp} - \eta_{mix})$ differences, and viscous synergy index, $I_{\eta} = (\Delta \eta / \eta_{\text{mix}})$, of the ethanol–water mixtures for the indicated temperatures and concentrations

t (°C)		Concentration in weight of the ethanol $(\%)$													
	θ	10	20	30	40	46	50	60	70	80	90	100			
						$\eta_{\rm exp} \times 10^{-3}$ (Pa s)									
10	1.274	2.342	3.150	3.802	4.168	4.273	4.121	3.611	3.314	2.596		2.134 1.396			
20	1.004	1.602	2.180	2.592	2.879	2.980	2.915	2.669	2.497	2.092	1.711	1.202			
30	0.830	1.263	1.687	1.980	2.161	2.227	2.133	1.982	1.814	1.556	1.222	0.974			
40	0.649	0.927	1.148	1.352	1.466	1.513	1.483	1.442	1.354	1.211	1.010	0.831			
50	0.571	0.798	0.980	1.124	1.219	1.257	1.226	1.177	1.110	0.998		0.853 0.721			
60	0.462	0.614	0.740	0.831	0.891	0.929	0.928	0.896	0.859	0.791	0.694 0.596				
70	0.408	0.512	0.601	0.675	0.728	0.742	0.735	0.716	0.695	0.668		0.605 0.537			
						$\eta_{\rm mix} \times 10^{-3}$ (Pa s)									
10	1.274	1.286	1.298	1.311	1.323	1.330	1.335	1.347	1.359	1.372		1.384 1.396			
20	1.004	1.024	1.044	1.063	1.083	1.095	1.103	1.123	1.143	1.162		1.182 1.202			
30	0.830	0.844	0.859	0.873	0.888	0.896	0.902	0.916	0.931	0.945	0.960 0.974				
40	0.649	0.667	0.685	0.704	0.722	0.733	0.740	0.758	0.776	0.795	0.813 0.831				
50	0.571	0.585	0.599	0.613	0.627	0.636	0.642	0.656	0.670	0.684	0.698 0.712				
60	0.462	0.475	0.489	0.502	0.516	0.524	0.529	0.542	0.556	0.569		0.583 0.596			
70	0.408	0.421	0.434	0.447	0.460	0.467	0.473	0.485	0.498	0.511		0.524 0.537			
					$\Delta \eta = (\eta_{\rm exp} - \eta_{\rm mix}) \times 10^{-3}$ (Pa s)										
10	$\boldsymbol{0}$	1.056	1.852	2.491	2.845	2.943	2.786	2.264	1.955	1.224	$0.750 \quad 0$				
20	$\boldsymbol{0}$	0.578	1.136	1.529	1.796	1.885	1.812	1.546	1.354	0.930	0.529 0				
30	$\boldsymbol{0}$	0.419	0.828	1.107	1.273	1.331	1.231	1.066	0.883	0.611	$0.262 \quad 0$				
40	$\boldsymbol{0}$	0.260	0.463	0.648	0.744	0.780	0.743	0.684	0.578	0.416	0.197 0				
50	$\mathbf{0}$	0.213	0.381	0.511	0.592	0.621	0.584	0.521	0.440	0.314	0.155 0				
60	$\mathbf{0}$	0.139	0.251	0.329	0.376	0.405	0.389	0.354	0.303	0.222	0.111	$\overline{0}$			
70	θ	0.091	0.167	0.228	0.268	0.275	0.262	0.231	0.197	0.157	0.081 0				
						$I_{\eta} = (\Delta \eta / \eta_{\text{mix}})$ (%)									
10	$\boldsymbol{0}$	82.1	142.7	190.0	215.0	221.3	208.7	168.1	143.9	89.2	54.2	$\boldsymbol{0}$			
20	$\boldsymbol{0}$	56.4	108.8	143.8	165.8	172.1	164.3	137.7	118.5	80.0	44.8	$\boldsymbol{0}$			
30	$\mathbf{0}$	49.6	96.4	126.8	143.4	148.5	136.5	116.4	94.8	64.7	27.3	$\boldsymbol{0}$			
40	$\mathbf{0}$	39.0	67.6	92.0	103.0	106.4	100.4	90.2	74.5	52.3	24.2	$\boldsymbol{0}$			
50	$\boldsymbol{0}$	36.4	63.6	83.4	94.4	97.6	91.0	79.4	65.7	45.9	23.1	$\boldsymbol{0}$			
60	$\mathbf{0}$	30.1	51.3	65.5	72.9	77.3	73.5	65.3	54.5	39.0	19.0	$\boldsymbol{0}$			
70	$\overline{0}$	21.6	38.5	51.0	58.3	58.9	55.4	47.6	39.6	30.7	15.5	$\mathbf{0}$			

resulting molecular package. This logically increases both viscosity and the density of the system.

The values obtained from the density measurements, with processing analogous to that employed in the case of viscosity, are shown in Table II. These values allowed us to plot the graphic representation in Figs. 2(a), density, ρ_{\exp} , versus ethanol concentration, C (%); Fig. 2(b), $\Delta \rho$ versus ethanol concentration, C (%); and Fig. 2(c), I_{ρ} versus ethanol concentration, C (%). In all cases the observed behavior was entirely analogous to that seen in the previous figures – thus reflecting the relation between viscous synergy and volume contraction.

This fact becomes apparent on representing $\Delta \eta$ as a function of $\Delta \rho$, as can be seen in Fig. 3, where the linear dependency of both phenomena is clearly seen – each straight line being traced for each of the temperatures studied. These representations have been fitted by means of functions of the type of $\Delta \eta = k \cdot \Delta \rho$, yielding correlation coefficients, r, in excess of 0.991 in all cases. The coefficients, k , i.e., the gradients of the straight lines corresponding to the different temperatures, are shown in Table III. Posteriorly, and

FIGURE 1 (a) Graphic representation of the experimental values for viscosity, $\eta_{exp} \times 10^{-3}$ (Pa s), of the ethanol–water mixtures according to the ethanol concentration involved (w/w), for temperatures of 10, 30, 50, and 70°C. (b) Graphic representation of the viscosity differences, $\Delta \eta \times 10^{-3}$ (Pas), of the ethanol–water mixtures according to the ethanol concentration involved (w/w), for temperatures of 10, 30, 50, and 70°C. (c) Graphic representation of the viscous synergy index, I_n (%), of the ethanol–water mixtures according to the ethanol concentration involved (w/w), for temperatures of 10, 30, 50, and 70°C.

TABLE II Values corresponding to experimental (ρ_{exp}) and theoretical density (ρ_{mix}), $\Delta \rho = (\rho_{exp} - \rho_{mix})$ differences, and density synergy index, $I_\rho = (\Delta \rho / \rho_{\text{mix}})$, of the ethanol–water mixtures for the indicated temperatures and concentrations

t (°C)		Concentration in weight of the ethanol $(\%)$												
	θ	10	20	30	40	46	50	60	70	80	90	100		
						$\rho_{\rm exp}$ $({\rm kg/m^3})$								
10	999.4	985.1	970.2	954.5	936.5	925.4	916.0	891.7	867.6	842.5	817.8	792.1		
20	998.5	983.8	969.0	953.0	934.8	923.8	914.3	890.3	866.1	841.0	816.5	790.8		
30	995.7	980.7	965.9	949.6	931.5	920.4	911.0	887.2	863.1	837.9	813.6	787.9		
40	992.3	977.2	962.4	946.0	927.9	916.9	907.6	884.1	860.1	835.1	811.1	785.6		
50	988.0	972.9	958.1	941.9	924.0	912.9	903.8	880.6	856.9	832.2	808.4	783.2		
60	983.2	968.2	953.7	937.4	919.8	908.8	899.8	877.1	853.8	829.2	805.8	781.0		
70	977.8	962.9	948.5	932.4	915.1	904.3	895.4	872.8	850.1	825.9	802.8	778.4		
						$\rho_{\rm mix}$ (kg/m ³)								
10	999.4	978.7	957.9	937.2	916.5	904.0	895.8	875.0	854.3	833.6	812.8	792.1		
20	998.5	977.7	957.0	936.2	915.4	903.0	894.7	873.9	853.1	832.3	811.6	790.8		
30	995.7	974.8	954.2	933.4	912.6	900.2	891.9	871.1	850.3	829.5	808.8	788.0		
40	992.3	971.6	951.0	930.3	909.6	897.2	889.0	868.3	847.6	826.9	806.3	785.6		
50	988.0	967.5	947.0	926.6	906.1	893.8	885.6	865.1	844.6	824.2	803.7	783.2		
60	983.2	963.0	942.8	922.5	902.3	890.2	882.1	861.9	841.7	821.4	801.2	781.0		
70	977.8	957.9	937.9	918.0	898.0	886.1	878.1	857.8	838.2	818.3	798.3	778.4		
							$\Delta \rho = (\rho_{exp} - \rho_{mix})$ (kg/m ³)							
10	$\boldsymbol{0}$	6.4	12.3	17.3	20.0	21.4	20.2	16.7	13.3	8.9	5.0	$\boldsymbol{0}$		
20	$\boldsymbol{0}$	6.1	12.0	16.8	19.4	20.8	19.6	16.4	13.0	8.7	4.9	$\boldsymbol{0}$		
30	$\boldsymbol{0}$	5.9	11.7	16.2	18.9	20.2	19.1	16.1	12.8	8.4	4.8	$\boldsymbol{0}$		
40	$\boldsymbol{0}$	5.6	11.4	15.7	18.4	19.7	18.6	15.8	12.5	8.2	4.8	$\boldsymbol{0}$		
50	$\boldsymbol{0}$	5.4	11.1	15.3	17.9	19.1	18.2	15.5	12.3	8.0	4.7	$\boldsymbol{0}$		
60	$\boldsymbol{0}$	5.2	10.9	14.9	17.5	18.6	17.7	15.2	12.1	7.8	4.6	$\boldsymbol{0}$		
70	$\mathbf{0}$	5.0	10.7	14.4	17.1	18.2	17.3	15.0	11.9	7.6	4.5	$\mathbf{0}$		
						$I_\rho\!=\!(\Delta\rho/\rho_\text{mix})$ (%)								
10	$\boldsymbol{0}$	0.65	1.28	1.85	2.18	2.37	2.25	1.91	1.55	1.07	0.62	$\boldsymbol{0}$		
20	$\mathbf{0}$	0.64	1.25	1.79	2.12	2.30	2.19	1.87	1.53	1.04	0.61	$\boldsymbol{0}$		
30	$\mathbf{0}$	0.60	1.23	1.74	2.07	2.25	2.14	1.85	1.50	1.02	0.60	$\mathbf{0}$		
40	$\boldsymbol{0}$	0.58	1.20	1.69	2.02	2.19	2.09	1.82	1.48	0.99	0.59	$\boldsymbol{0}$		
50	$\boldsymbol{0}$	0.56	1.17	1.65	1.98	2.14	2.05	1.79	1.46	0.97	0.58	$\boldsymbol{0}$		
60	$\boldsymbol{0}$	0.54	1.16	1.61	1.94	2.09	2.01	1.77	1.44	0.95	0.57	$\boldsymbol{0}$		
70	$\mathbf{0}$	0.52	1.13	1.57	1.90	2.05	1.97	1.74	1.43	0.93	0.56	$\mathbf{0}$		

based on Eq. (3) applied to the values in Table I, we calculated the corresponding viscosity enhancement index, E_n , the results of which are shown in Table IV.

With the aim of amplifying the rheological analysis of the ethanol–water system, and since viscosity of the latter varies with temperature, we carried out a thermodynamic study of the individual elements conforming the system, and also of each of the mixtures evaluated, to determine their corresponding activation energies.

Based on Eq. (6), the values in Table I allowed us to determine the activation energy of each of the systems indicated, since in all cases the distributions of points obtained on representing $\ln \eta = f(1/T)$ were practically linear, with correlation coefficients of over 0.996.

The graphic representations for concentrations of 0, 30, 46, 70, and 100% are shown in Fig. 4, where the equations of the regression straight lines fitted to the experimental points are also presented, with their corresponding correlation coefficients.

From this figure it is deduced that the viscosity of water, ethanol, and of the different mixtures analyzed varies inversely with absolute temperature according to a function of

FIGURE 2 (a) Graphic representation of the experimental values for density, ρ_{exp} (kg/m³), of the ethanolwater mixtures according to the ethanol concentration involved (w/w) , for temperatures of 10, 30, 50, and 70°C. (b) Graphic representation of the density differences, $\Delta \rho$ (kg/m³), of the ethanol–water mixtures according to the ethanol concentration involved (w/w), for temperatures of 10, 30, 50, and 70°C. (c) Graphic representation of the density synergy index, I_{ρ} (%), of the ethanol–water mixtures according to the ethanol concentration involved (w/w), for temperatures of 10, 30, 50, and 70°C.

FIGURE 3 Graphic representation of viscosity differences, $\Delta \eta \times 10^{-3}$ (Pas), according to density differences, $\Delta \rho$ (kg/m³), of the ethanol–water mixtures for temperatures of 10, 30, 50, and 70°C.

TABLE III Values corresponding to k, obtained by fitting linear functions of the type $\Delta \eta = k \cdot \Delta \rho$, in ethanol–water mixtures for the indicated temperatures and concentrations

		T(K)											
	283	293	303	313	323	333	343						
k	141.20	93.90	66.99	41.57	33.51	22.67	15.756						
r	0.997	0.996	0.998	0.992	0.995	0.991	0.991						

TABLE IV Enhancement index values, E_{η} , obtained from Eq. (3), corresponding to the ethanol–water mixtures for the indicated temperatures and concentrations

the type of Eq. (5). Accordingly, the gradient, m, of these straight lines multiplied by the universal gas constant, R, allows us to calculate the corresponding activation energies (with values shown in Table V). These values are graphically illustrated in Fig. 5.

On examining Fig. 5 it can be deduced that the activation energies present a distribution of points similar to that seen in Fig. 1(a), (b), and (c), with a maximum value likewise corresponding to an ethanol concentration of 46% (w/w).

On the other hand, and in order to determine the relation between the synergic interaction indices, power factors, and temperature, the values of η_{exp} , I_{η} , and E_{η} were represented as a function of T, for the 46% concentration (w/w) of ethanol, as can be seen in Fig. 6(a), (b), and (c). Likewise, in Fig. 7(a) representation has been made of $k = (\Delta \eta / \Delta \rho)$ as a function of temperature. Figures 6 and 7 show the distribution of points to be similar, fitting being possible in all cases via functions of the

FIGURE 4 Graphic representation of the Naperian logarithmic values of viscosity, Ln η , as a function of $(1/T) \times 10^{-3}$ (K⁻¹), of the ethanol–water mixtures for concentrations of 0, 30, 46, 70, and 100% (w/w) of ethanol.

TABLE V Activation energy values, Ea (cal/mol), obtained from Eq. (5) , corresponding to the ethanol– water mixtures according to the ethanol concentration (w/w)

	Concentration in weight of the ethanol $(\%)$										
	10	20	30	40	46	50	60	70	80	90	100
Ea (cal/mol) 3660.6 4709.4 5244.4 5503.0 5566.8 5609.9 5489.7 5188.4 4995.5 4439.5 4068.1 3152.6											

FIGURE 5 Graphic representation of the activation energies, Ea (cal/mol), of the ethanol–water mixtures according to the ethanol concentration (w/w) involved.

FIGURE 6 (a) Graphic representation of the experimental viscosity values, $\eta_{exp} \times 10^{-3}$ (Pas), of the ethanol–water mixtures according to the absolute temperature (T), for the 46% concentration (w/w) of ethanol. (b) Graphic representation of the viscous synergy index, I_n (%), of the ethanol–water mixtures according to the absolute temperature (T) , for the 46% concentration (w/w) of ethanol. (c) Graphic representation of the enhancement index values, E_n , of the ethanol–water mixtures according to the absolute temperature (T) , for the 46% concentration (w/w) of ethanol.

FIGURE 7 Graphic representation of the values for $k = \Delta \eta / \Delta \rho$ (m²s⁻¹), of ethanol–water mixtures according to the absolute temperature (T) , for 46% concentration (w/w) of ethanol.

type of Eq. (5) – the coefficients A and B, and their corresponding correlation coefficients, r, being:

Magnitude(Y)		B(K)	
η_{exp} (Pa s)	1.847×10^{-7}	2841.6	0.999
I_{η}	0.1481	2074.8	0.995
E_{η}	0.0360	1248.9	0.992
$K = \Delta \eta / \Delta \rho$ (m ² s ⁻¹)	5.97×10^{-4}	3507.9	0.999

CONCLUSIONS

- 1. Ethanol and water mixtures present positive density and viscous synergies for all temperatures considered – the maximum values for $\Delta \eta$, $\Delta \rho$, I_{η} , and I_{ρ} corresponding to the 46% concentration (w/w) of ethanol, equivalent to the proportion of one alcohol molecule per three water molecules.
- 2. For each temperature, a linear relation is observed between $\Delta \eta$ and $\Delta \rho$, of the following form: $\Delta \eta = k \cdot \Delta \rho$.
- 3. A enhancement index has been defined, based on Eq. (3).
- 4. Calculations have been made of the activation energies of the ethanol–water mixtures, the maximum values likewise corresponding to the 46% concentration, at all temperatures considered.
- 5. The viscosity values of the mixtures, η_{exp} , I_{η} , E_{η} , Ea, and $\Delta \eta / \Delta \rho$, decrease with temperature for all concentrations, according to expressions of the form $Y = A \cdot e^{B/T}$, the coefficients calculated for a 46% (w/w) alcohol concentration being:

RHEOLOGY OF WATER/ETHANOL 479

References

- [1] A.N. Martín (1967). Principios de fisico-química para farmacia y biología. Alhambra, S.L., Madrid.
- [2] J. Ferguson and Z. Kemblonski (1991). Applied Fluid Rheology. Elsevier Science Publishers Ltd., University Press, Cambridge.
- [3] H.A. Barnes, J.F. Hutton and K. Walters (1993). An Introduction to Rheology. Elsevier Science Publishers, BV, Amsterdam.
- [4] C.W. Macosko, (1994). Rheology. Principles. Measurements and Applications. VCH Publishers Inc., New York.
- [5] M. García-Velarde (1994). Revista Española de Física, 9, 12.
- [6] A. Dar (1979). Tecnología farmaceútica. Acribia, Zaragoza
- [7] R. Voight (1982). Tratado de tecnología farmaceútica. Acribia, Zaragoza.
- [8] C. Faulí Trillo (1993). In: S.A. Luzán (Ed.), *Tratado de Farmacia Galénica*. Madrid.
- [9] Swarbrik J. and Boyland J.C. (1993). Encyclopedia of Pharmaceutical Technology. Marcel Dekker, Inc., New York.
- [10] H.D. Crockford and B. Knight (1968). Fundamentos de fisicoquimica. C.E.C.S.A, Madrid.
- [11] J.M. Resa, C. Gonzalez and J. Lanz (2002). Journal of Food Engineering, 51, 2, 113.
- [12] M.J. Assael, N.K. Dalaouti and I. Metaxa (2002). Fluid phase equilibria, 199, 1, 237.
- [13] J. Pellicer (1997). Sinergia viscosa. Ponencia en el curso: Fundamentos de reologı´a. Materiales viscoelásticos. Aplicaciones a las industrias alimentarias y quimico-farmaceúticas. U.I.M.P., Valencia.
- [14] E.R. Morris (1984). Food Gels. Elsevier. Applied Science, London.
- [15] G. Kaletunc-Gencer and M. Peleg (1986). *J Texture Studies*, 17, 61.
- [16] D.D. Christianson (1982). In: Linebak (Ed.), Food Carbohydrates. Conn.
- [17] N.K. Howell (1993). Elucidation of protein-protein interactions in gels and foams. Gums and stabilisers for the food industry. Proceedings of the 7th Internacional Conference. Wales.
- [18] R.B. Bird et al. (1964). In: Reverté (Ed.), *Fenómenos de transporte*. Reverté S.A., Barcelona.