Physical properties and their corresponding changes of mixing for the ternary mixture acetone + n-hexane + water at 298.15 K

Jhoany Acosta-Esquijarosa, Ivonne Rodríguez-Donis *, Eladio Pardillo-Fontdevila

Centro de Química Farmacéutica, 200 y 21, Atabey, Apdo 16042, Playa, Ciudad de la Habana, Cuba

Abstract

Experimental density and the refractive index of the ternary mixture acetone + n-hexane + water, and their binary systems were experimentally measured and correlated at 298.15 K and atmospheric pressure. A maximum in refractive indices has been observed for the acetone + water system while the excess molar volume and the molar refraction change are all negative. For the mixture acetone + n-hexane, the excess molar volume is always positive and the molar refraction change of mixing showed a S-shaped dependence on acetone composition. The excess molar volumes and molar refraction changes of mixing were correlated using the Redlich–Kister expression and Cibulka equation. The coefficients and standard deviation between the experimental and fitted values were estimated. Good agreement between both results was obtained.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Excess molar volume; Density; Refractive index; Water; n-Hexane; Acetone

1. Introduction

Pure organic solvents and their mixtures have been employed in purification processes commonly encountered in the pharmaceutical industry. The mixture acetone + n-hexane is generated as a by-product in the liquid–liquid chromatographic purification step of the Prostaglandin F2α (PGF2α) [1]. The separation of acetone + n-hexane mixture is not possible by conventional distillation because they form a minimum boiling temperature azeotrope [2], but an hybrid process involving solvent extraction and distillation steps by using water as entrainer has been established for this purpose [3,4]. Therefore, the knowledge of the physical properties of the binary and ternary mixtures composed by acetone, n-hexane and water is very useful for the calculation of multicomponent phase equilibrium data allowing the design of a more reliable technological procedure.

A complete characterization of any mixture can be performed by means of its thermophysical properties. Hence, some of them can be used for an indirect determination of their composition. Commonly, only one property has to be selected to determine the composition of a binary mixture. However, in the case of ternary mixture at least two properties must be determined considering that the isolines of both physical properties should be orthogonal [5].

The binary system n-hexane + water exhibits a great immiscibility gap over almost all composition range. Therefore, a wide liquid–liquid region remains into the resulting ternary mixture in spite of acetone addition. Due to the large liquid–liquid envelope in the ternary system, an especial care must be taken in order to determine the physical properties into the homogeneous region avoiding that the ternary composition provides two liquid phases.

In this paper, we determine experimentally two physical properties, density and refractive index, at 298.15 K and atmospheric pressure of the ternary mixture acetone + n-hexane + water and theirs respective homogeneous binary mixtures. The results are used to calculate excess molar volumes and molar refraction changes of mixing at the temperature of 298.15 K and atmospheric pressure. These quantities are also fitted using the Redlich–Kister polynomial [6] and Cibulka equation [7]. As far as we know, these physical properties for the ternary mixture acetone + n-hexane + water have not been published before, while the corresponding data for the binary mixture acetone + n-hexane are only available in the literature at the temperatures of 298.15 K [8] and 308.15 K [9].

Table 1
Comparison of densities ρ and refractive indexes n_D of pure components with literature data at 298.15 K and atmospheric pressure

Component	ρ (g cm^{-3})		n_D	
	Experimental	Literature	Experimental	Literature
Water	0.9970	0.99704[a]	1.3325	1.33250[a]
n-Hexane	0.6551	0.65484[a]	1.3724	1.37226[a]
Acetone	0.7849	0.78440[a]	1.3560	1.35596[a]

[a] Riddick et al. (1986).

2. Experimental

2.1. Materials

Acetone and *n*-hexane were supplied as chromatographic grade by Merck with purities exceeding 99.5% and they were used without previous purification. However, purities of the solvents were checked by gas chromatography. Deionised water was supplied from our own laboratory. Experimental data of density and refractive index are given in Table 1. These results agree well with the published data [10].

2.2. Apparatus and experimental procedure

The samples were prepared by weight in a Sartorius balance with a precision of ± 0.1 mg. The physical properties of the ternary system were determined using pseudobinary mixtures. The pseudobinary mixtures were prepared starting from a binary acetone + water mixture with a fixed amount of acetone in the mass composition interval from 0.7 to 0.9 and adding small quantities of *n*-hexane in order to avoid the liquid–liquid splitting.

Densities of the ternary mixture were measured with a precision of ± 0.0001 g cm^{-3} in an Anton Paar DMA-38 vibrating tube densimeter, which was previously calibrated with air and water. The refractive index was also measured using Abbe's refractometer with accuracy of ± 0.0001 units. During all measurements, temperature was kept at 298.15 ± 0.02 K with a Haake Thermostat.

3. Results and discussion

The experimental values of densities (ρ) and refractive index (n_D), measured for binary and the ternary system are reported in Tables 2 and 3, respectively. Experimental density and refractive index data of each binary and the pseudobinary mixture were correlated with the mole fraction of acetone (x_1) taking into account the following polynomial model [5]:

$$y = \sum_{i=0}^{n} A_i x^i \tag{1}$$

were y is the physical property to be correlated (density or refractive index), x the mole fraction of acetone and, A_i and i are the fitting constant and the degree of the polynomial model, respectively.

Table 2
Densities ρ, refractive indexes n_D, excess molar volumes V^E and changes of mixing ΔR for binary systems at 298.15 K and atmospheric pressure

x_1 (acetone mole fraction)	ρ (g cm^{-3})	n_D	V^E (cm^{-3} mol^{-1})	ΔR (cm^{-3} mol^{-1})
Acetone + *n*-hexane				
0.0504	0.6572	1.3709	0.332	0.011
0.0994	0.6597	1.3699	0.563	0.019
0.1511	0.6629	1.3688	0.738	0.025
0.1999	0.6663	1.3679	0.859	0.029
0.2497	0.6701	1.3668	0.949	0.030
0.3006	0.6744	1.3660	1.016	0.031
0.3518	0.6790	1.3651	1.059	0.030
0.4006	0.6837	1.3643	1.081	0.028
0.4476	0.6887	1.3635	1.084	0.025
0.4995	0.6945	1.3627	1.067	0.021
0.5498	0.7007	1.3618	1.032	0.017
0.5976	0.7070	1.3611	0.982	0.012
0.6479	0.7141	1.3603	0.915	0.008
0.6970	0.7217	1.3595	0.836	0.003
0.7503	0.7305	1.3587	0.737	−0.001
0.7998	0.7394	1.3580	0.635	−0.004
0.8499	0.7491	1.3572	0.518	−0.006
0.8979	0.7593	1.3568	0.388	−0.007
0.9507	0.7717	1.3561	0.214	−0.005
Acetone + water				
0.0502	0.9770	1.3422	−0.379	−0.009
0.0993	0.9593	1.3499	−0.696	−0.016
0.1502	0.9422	1.3549	−0.961	−0.023
0.1996	0.9266	1.3583	−1.158	−0.028
0.2496	0.9118	1.3604	−1.301	−0.033
0.3007	0.8976	1.3616	−1.393	−0.036
0.3507	0.8848	1.3621	−1.441	−0.039
0.4003	0.8731	1.3623	−1.452	−0.041
0.4509	0.8621	1.3621	−1.435	−0.043
0.4992	0.8525	1.3618	−1.396	−0.043
0.5489	0.8435	1.3614	−1.335	−0.043
0.5990	0.8350	1.3609	−1.255	−0.043
0.6506	0.8270	1.3603	−1.152	−0.041
0.7014	0.8196	1.3597	−1.028	−0.039
0.7467	0.8134	1.3591	−0.900	−0.036
0.8015	0.8063	1.3583	−0.721	−0.031
0.8460	0.8008	1.3577	−0.560	−0.026
0.8969	0.7949	1.3569	−0.364	−0.019
0.9451	0.7899	1.3564	−0.180	−0.011

The correlation of the experimental results with the Eq. (1) was done by using the least-squares regression where the significance of each coefficient was determined applying Fisher's criterion [11]. Table 4 displays the calculated coefficients and the mean standard deviation between the experimental and fitted values for binary and ternary mixtures.

From density and refractive index data, we determine the corresponding mixture properties such as excess molar volumes (V^E) and molar refraction changes of mixing (ΔR) and they are also reported in Tables 2 and 3. Excess molar volumes (V^E) of the ternary mixture were calculated by the following Eqs. (2) and (3):

$$V^E = V - \sum_i x_i V_i \tag{2}$$

Table 3

Densities ρ, refractive indexes n_D, excess molar volumes V^E and changes of mixing ΔR for acetone (1) + n-hexane (2) + water (3) at 298.15 K and atmospheric pressure

x_1	x_2	ρ (g cm^{-3})	n_D	V^E (cm^{-3} mol^{-1})	ΔR (cm^{-3} mol^{-1})
0.0000	1.0000	0.6551	1.3724	0.000	0.000
0.0919	0.8980	0.6597	1.3702	0.600	0.044
0.1793	0.8009	0.6657	1.3684	0.950	0.072
0.2698	0.7003	0.6729	1.3665	1.255	0.085
0.3600	0.6002	0.6821	1.3646	1.356	0.082
0.4486	0.5019	0.6939	1.3634	1.225	0.064
0.5403	0.4000	0.7086	1.3624	0.979	0.033
0.6304	0.3000	0.7249	1.3603	0.771	−0.003
0.7189	0.2016	0.7433	1.3585	0.595	−0.032
0.8100	0.1005	0.7666	1.3573	0.304	−0.039
0.9005	0.0000	0.7945	1.3572	0.000	0.000
0.0000	1.0000	0.6551	1.3724	0.000	0.000
0.6417	0.1990	0.7482	1.3601	0.605	−0.016
0.6779	0.1538	0.7592	1.3598	0.482	−0.014
0.7199	0.1014	0.7734	1.3594	0.327	−0.011
0.7602	0.0511	0.7887	1.3594	0.169	−0.008
0.8011	0.0000	0.8062	1.3592	0.000	0.000
0.0000	1.0000	0.6551	1.3724	0.000	0.000
0.6299	0.0996	0.7815	1.3603	0.365	−0.002
0.6649	0.0497	0.7995	1.3602	0.181	−0.002
0.6996	0.0000	0.8199	1.3602	0.000	0.000

where V_i represents the molar volume of pure component i and V refers to the molar volume of the mixture calculated by:

$$V = \frac{\sum x_i M_i}{\rho} \tag{3}$$

where x_i and M_i are the mole fraction and the molecular weight of component i in the mixture. Density of the mixture ρ is the experimental data.

The molar refraction changes of mixing, ΔR, were calculated by the following expression:

$$\Delta R = R - \sum_i x_i R_i \tag{4}$$

where R_i is the molar refraction of pure component i and R represents the molar refraction of the mixture that was calculated

using the traditional Lorentz–Lorenz equation [12]:

$$R = V \frac{n_D^2 - 1}{n_D^2 + 2} \tag{5}$$

where n_D is the experimental refractive index of the mixture.

Once we have determined the excess molar volume and the change of refractive index of mixing, we can correlate them by the polynomials of Redlich–Kister for binary and ternary systems and by Cibulka equation only for the ternary mixture.

For binary systems, the data of excess molar volumes (V^E) and the change of refractive index of mixing (ΔR) were correlated with mole composition by using the following general equation:

$$Q_{ij} = x_i x_j \sum_k A_k (x_i - x_j)^k \tag{6}$$

where Q_{ij} is V^E or ΔR, x_i the mole fraction of more volatile component i, x_j the mole fraction of component j, A_k the polynomial coefficients and k is the number of the polynomial coefficient.

For the ternary system the Redlich–Kister equation is:

$$\begin{aligned}Q_{ijk} = {} & Q_{ij} + Q_{jk} + Q_{ik} + x_i x_j x_k (A + B(x_i - x_j) \\ & + C(x_j - x_k) + D(x_i - x_k) + E(x_i - x_j)^2 \\ & + F(x_j - x_k)^2 + G(x_i - x_k)^2 + \cdots)\end{aligned} \tag{7}$$

where Q_{ijk} represents V^E or ΔR for the ternary mixture acetone (1) + n-hexane (2) + water (3), and Q_{ij} is the Redlich–Kister polynomial coefficient calculated from the binary data for the same property.

On the other hand, the excess molar volume and the change of refractive index of mixing can be fitted by the Cibulka equation as follow:

$$Q_{ijk} = Q_{ij} + Q_{kj} + Q_{ik} + x_i x_j x_k (A + Bx_i + Cx_j) \tag{8}$$

Eqs. (6)–(8) were fitted to the appropriate parameters by least-squares regression, and the Fisher's test was used to establish the number of coefficients.

Fig. 1 and Table 2 display the experimental values of ρ, n_D, V^E and ΔR for the binary system acetone + water, which are plotted against the mole fraction of acetone. As we can see in Fig. 1, there is a lineal relationship between density and molar fraction

Table 4

Polynomial coefficients (A_i) and standard deviations (σ) determined by the fitting of Eq. (1) to each binary and pseudobinary mixture

x^a	A_0 (g cm^{-3})	A_1 (g cm^{-3})	A_2 (g cm^{-3})	A_3 (g cm^{-3})	A_4 (g cm^{-3})	σ (g cm^{-3})
Density						
1.0000[b]	0.65462	0.06149	0.01856	0.01965	0.02995	0.00036
0.9005	0.65497	0.04657	0.05819	0.06837	–	0.00043
0.8011	655099	0.13722	−0.19653	0.32536	–	0.00003
0.6996	0.65510	−0.15673	0.50164	–	–	0.00025
Refractive index						
1.0000[b]	1.37267	−0.01781	−0.01543	0.03987	−0.02257	0.00010
0.9005	1.37237	−0.04334	0.07490	−0.05060	–	0.00017
0.8011	1.37234	−0.05857	0.05178	–	–	0.00037
0.6996	1.37229	−0.01800	–	–	–	0.00034

[a] Mole fraction of acetone in the acetone + water mixture.

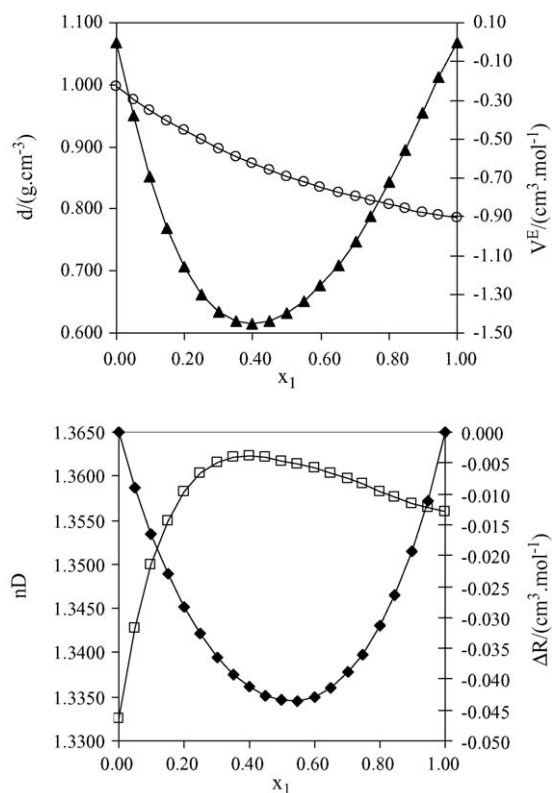[b] Mole fraction of n-hexane in the mixture n-hexane + acetone.

Fig. 1. (a) Density ρ ($\bigcirc$) and excess molar volumes V^E ($\blacktriangle$), (b) refractive index n_D ($\square$), and ΔR ($\blacklozenge$) of acetone (1) + water (3) at 298.15 K and atmospheric pressure.

while the curve of refractive index versus mole fraction exhibits a maximum value. Therefore, the refractive index of this binary mixture cannot be used as a calibration curve to calculate the composition of unknown concentration because different compositions show the same refractive index. On the other hand, the excess molar volume and the molar refraction change of mixing are negative in all range of composition reaching a minimum point at −1.453 and −0.043 cm^3 mol^{-1}, respectively. Besides, the same properties for the binary mixture acetone + n-hexane are reported in Table 2. In this case, the values of V^E are all positive exhibiting a maximum point at 1.080 cm^3 mol^{-1}. This behaviour indicates the occurrence of physical interactions which involves mainly dispersion forces producing a positive contribution in the excess molar volume. As we can see in Table 2, the molar refraction changes of mixing has a S-shaped dependence on acetone composition involving positive and negative values into the range of −0.003 to +0.0158 cm^3 mol^{-1}.

Accordingly to the results reported in Table 3, ternary system exhibits bigger and positive excess molar volume values than those obtained for the binary mixtures showing a maximum value at 1.35 cm^3 mol^{-1}. However, ΔR takes negative and positive values being 0.085 cm^3 mol^{-1} the maximum value.

Isolines of density, refraction index and excess molar volume were obtained by using the Eq. (1) described above in order to estimate the compositions at a given value of each property. Figs. 2–4 show the curves of constant density, refractive index and excess molar volume, respectively, where the compositions
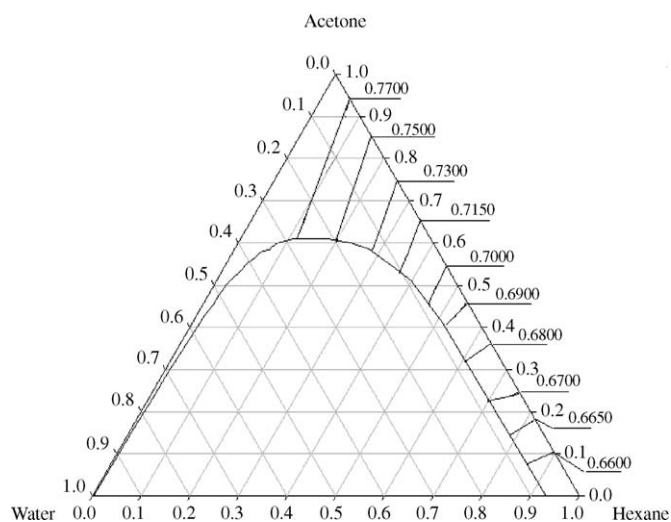

Fig. 2. Density isolines for acetone + n-hexane + water system at 298.15 K and atmospheric pressure.
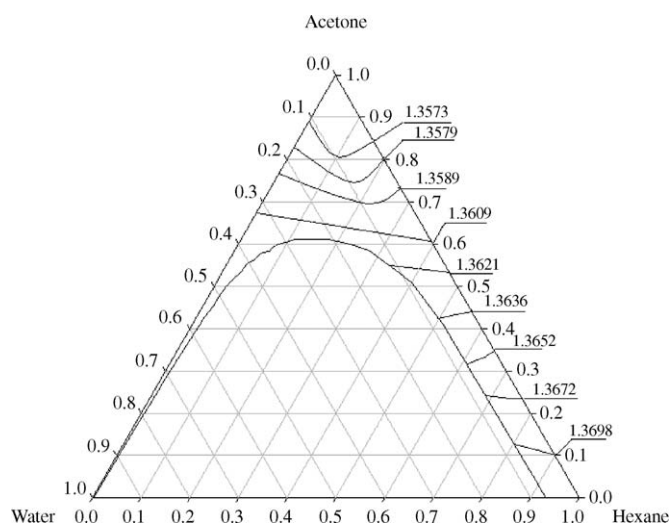

Fig. 3. Refractive index isolines for acetone + n-hexane + water system at 298.15 K and atmospheric pressure.
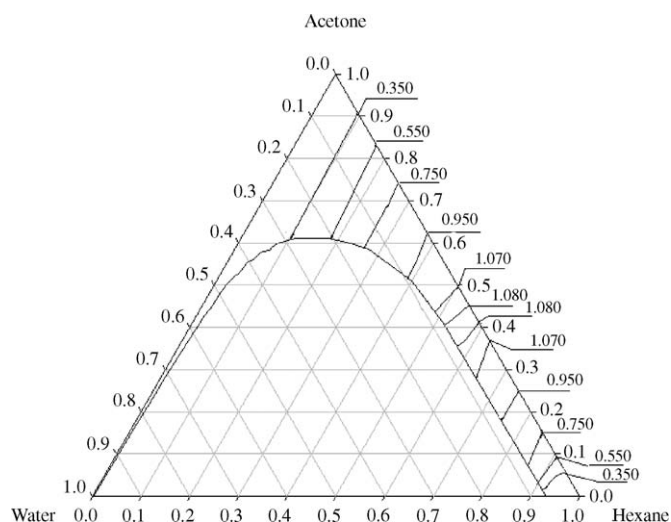

Fig. 4. Excess molar volume isolines for acetone + n-hexane + water system at 298.15 K and atmospheric pressure.

Table 5
Polynomial coefficients (A_k) and standard deviations (σ) for Redlich–Kister equation fitted from experimental data of binary systems to calculate V^E (cm^3 mol^{-1}) and ΔR (cm^3 mol^{-1})

Property	A_0 (cm^{-3} mol^{-1})	A_1 (cm^{-3} mol^{-1})	A_2 (cm^{-3} mol^{-1})	A_3 (cm^{-3} mol^{-1})	A_4 (cm^{-3} mol^{-1})	σ (cm^{-3} mol^{-1})
Acetone (1) + n-hexane (2)						
V^E	4.266	−1.041	0.528	−0.361	1.609	0.013
ΔR	0.084	−0.159	−0.020	−0.031	–	0.001
Acetone (1) + water (2)						
V^E	−5.581	2.055	−1.465	0.561	1.656	0.003
ΔR	−0.174	−0.016	−0.036	–	–	0.001

Table 6
Polynomial coefficients and standard deviations (σ) for Eqs. (7) and (8) fitted from experimental data of the ternary system acetone + n-hexane + water to determine V^E (cm^3 mol^{-1}) and ΔR (cm^3 mol^{-1})

Property	A (cm^{-3} mol^{-1})	B (cm^{-3} mol^{-1})	C (cm^{-3} mol^{-1})	D (cm^{-3} mol^{-1})	E (cm^{-3} mol^{-1})	F (cm^{-3} mol^{-1})	G (cm^{-3} mol^{-1})	σ (cm^{-3} mol^{-1})
Redlich–Kister Eq. (7)								
V^E	60.923	−94.453	53.855	−114.359	146.748	−126.797	–	0.016
ΔR	17.744	5.669	−134.738	−127.742	−154.269	245.494	298.779	0.008
Cibulka Eq. (8)								
V^E	121.582	−186.918	−26.320	–	–	–	–	0.050
ΔR	−28.153	31.988	29.281	–	–	–	–	0.033

values x_i are in mole fraction. The liquid–liquid envelope was estimated by using the UNIFAC method with the commercial program ProPhy Plus [13]. As we can see in Figs. 2 and 3, the density and the refractive index isolines of this ternary mixture are only orthogonal in the region limited by the acetone molar composition of 0.7–0.9 and 0–0.1 of water. Then, a combination of both physical properties defines a particular ternary mixture where the composition is given by the point of intersection of the corresponding density and refractive index isolines when we are working into of the orthogonal region. However, when the ternary composition lies out of the orthogonal region, we can use the isolines of the excess molar volume because they exhibit a similar tendency that the density isolines (see Figs. 2 and 4).

These coefficients and their mean standard deviation are listed in Table 5 for binary mixtures and in Table 6 for the ternary system. As we can see in Table 5, the Redlich–Kister polynomial provided a satisfactory correlation of the binary data. In the case of the ternary system, the Redlich–Kister equation gives a better correlation that those obtained by the Cibulka equation, which can be inferred by the lower value of the mean standard deviation (Table 6).

4. Conclusions

Excess molar volume and the molar refraction change of mixing were evaluated for the ternary mixture acetone + n-hexane + water and their respective binary homogeneous mixtures at 298.15 K and atmospheric pressure from new experimental data of density and refractive index. A maximum in refractive indices was observed for the acetone + water system, where samples with different composition showed the same refractive index. The excess molar volume and the

molar refraction change of mixing are all negative for the acetone + water mixture showing a minimum point at −1.453 and −0.043 cm^3 mol^{-1}, respectively. However, the excess molar volume is always positive and the molar refraction change of mixing takes negative and positive values having a S-shaped dependence on acetone composition for acetone + n-hexane mixture. In the case of the ternary mixture acetone + n-hexane + water, the excess molar volume takes higher and positive values while negative and positive values were obtained for the molar refraction change of mixing. In all cases, the data were satisfactorily correlated by the Redlich–Kister polynomials.

References

[1] Y. Rivas, J.A. González, R. Avila, R. Ruiz, L. Sordo, M. Castro, Acta Farm. Bonaerense 18 (1999) 165–172.

[2] J. Gmehling, J. Menke, J. Krafczyk, K. Fischer, Azeotropic Data, Part I, VCH Editor, Weinheim, 1994, 500 pp.

[3] I. Rodriguez-Donis, J. Acosta-Esquijarosa, V. Gerbaud, E. Pardillo-Fondevila, X. Joulia, Chem. Eng. Process. 44 (2005) 131–137.

[4] I. Rodriguez-Donis, U. Jáuregui-Haza, E. Pardillo-Fondevila, LAAR 29 (1999) 119–127.

[5] A. Arce, M. Blanco, E. Rodil, A. Soto, J.A. Vieitez, J. Sol. Chem. 27 (1998) 601–619.

[6] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345–348.

[7] I. Cibulka, Collect. Czech. Chem. Commun. 47 (1982) 1414–1419.

[8] J. Acosta-Esquijarosa, A. Arce, E. Rodil, A. Soto, J. Chem. Eng. Data 46 (2001) 1176–1180.

[9] S.A. Levinchev, Fiz khim Svoisteva Rastvorov (1964) 219–226.

[10] J.A. Riddick, W.B. Bunger, T. Sakano, Organic Solvents, John Wiley, New York, 1986, pp. 74, 92–93, 336–337.

[11] S.L. Ajnazarova, V.V. Kafarov, Methods for Experimental Optimization in Chemical Technology, Vishaia Shkola, Moscow, 1985, pp. 120–153.

[12] H.A. Lorentz, Theory of Electrons, Teubner, Leipzig, 1909.

[13] ProSim S.A. http://www.prosim.net. Reference Manual, 2000.