

**DETERMINATION OF THE SPECIFIC MASS OF TERNARY MIXTURE OF AOT/ORGANIC SOLVENT ALCOHOL AND THE EXCESS MOLAR VOLUME OF BINARY MIXTURE ORGANIC SOLVENT/ALCOHOL**

**DETERMINACIÓN DE LA MASA ESPECÍFICA DE MEZCLA TERNATIVA DE ALCOHOL SOLVENTE AOT/ORGÁNICO Y EL EXCESO MOLAR VOLUMEN DE MEZCLA BINARIA SOLVENTE / ALCOHOL ORGÁNICO**

G.M.S. Gomes<sup>1</sup>, C.M. Veloso<sup>2</sup>, R.C.I Fontan<sup>2</sup>, O.R.R. Gandolfi<sup>2</sup>,

G.R.F. Gonçalves<sup>2</sup>, V.S. Sampaio<sup>2</sup>, R.C.F. Bonomo<sup>2\*</sup>

<sup>1</sup>Rural Federal University of Pernambuco, Academic unit of Garanhuns, Bom Pastor Avenue S/N, Boa Vista, 55292-270, Garanhuns-PE, Brazil.

<sup>2</sup>State University of Southwest of Bahia, Spring Square 40, Spring District, 45700-000 Itapetinga, BA, Brazil.

Received June 1, 2017; Accepted July 26, 2017

**Abstract**

The objective of this work was to determine specific mass of ternary mixtures, using diotyl sodium sulfosuccinate (AOT) as a surfactant, iso-octane and hexane as organic solvent, and butanol and isopropanol as alcohol. The excess molar volume ( $V_m^E$ ) was obtained only for binary systems of solvent and alcohol. It was observed that specific masses of pure liquids varied with temperature from 696.281 kg.m<sup>-3</sup> (15 °C) to 679.761 849 kg.m<sup>-3</sup> (35 °C) for iso-octane; 671.849 kg.m<sup>-3</sup> (15 °C) to 653.533 kg.m<sup>-3</sup> (35 °C), for hexane; 814.228 kg.m<sup>-3</sup> (15 °C) to 798.842 kg.m<sup>-3</sup> (35 °C), for butanol; 790.463 kg.m<sup>-3</sup> (15 °C) to 773.426 kg.m<sup>-3</sup> (35 °C) for isopropanol. The same was observed for binary mixtures, which presented the following variations: from 710.404 kg.m<sup>-3</sup> (15 °C) to 693.654 kg.m<sup>-3</sup> (35 °C), for iso-octane/butanol; from 706.286 kg.m<sup>-3</sup> (15 °C) to 688.972 kg.m<sup>-3</sup> (35 °C), for iso-octane/isopropanol; from 700.970 kg.m<sup>-3</sup> (15 °C) to 682.817 kg.m<sup>-3</sup> (35 °C), for hexane/butanol; from 694.169 kg.m<sup>-3</sup> (15 °C) to 675.125 kg.m<sup>-3</sup> (35 °C) for hexane/isopropanol. For  $V_m^E$  of binary mixtures, it was verified they varied from 15 to 35 °C, from -1.47504x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> to -1.50475x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> for iso-octane/butanol; from 2.09222x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> to 2.31939x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> for iso-octane/isopropanol; from -3.82449x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> to -4.04924x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> for hexane/butanol; from 4.34134x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> to 4.61050x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> for hexane/isopropanol.

**Keywords:** interactions, linear chain, branched chain, micelle.

**Resumen**

El objetivo de este trabajo fue determinar las masas específicas de mezclas ternarias, empleando dioctil sulfosuccinato de sodio (AOT), como surfactante, iso-octano y hexano, como disolvente orgánico y butanol y isopropanol, como co-solvente. El volumen molar de exceso ( $V_m^E$ ) se obtuvo sólo para los sistemas binarios comprendidos por disolvente y alcohol. Se observó que las masas específicas de los líquidos puros redujeron con la temperatura de 696.281 kg.m<sup>-3</sup> (15 °C) a 679.761 kg.m<sup>-3</sup> (35 °C) para iso-octano; 671.849 kg.m<sup>-3</sup> (15 °C) a 653.533 kg.m<sup>-3</sup> (35 °C), para hexano; 814.228 kg.m<sup>-3</sup> (15 °C) a 798.842 kg.m<sup>-3</sup> (35 °C), para butanol; 790.463 kg.m<sup>-3</sup> (15 °C) a 773.426 kg.m<sup>-3</sup> (35 °C), para isopropanol. El mismo comportamiento se observó para las mezclas binarias, las cuales presentaron la siguiente variación: 710.404 kg.m<sup>-3</sup> (15 °C) a 693.654 kg.m<sup>-3</sup> (35 °C), para iso-octano / butanol; 706.286 kg.m<sup>-3</sup> (15 °C) a 688.972 kg.m<sup>-3</sup> (35 °C), para iso-octano/isopropanol; 700.970 kg.m<sup>-3</sup> (15 °C) a 682.817 kg.m<sup>-3</sup> (35 °C), para hexano/butanol; 694.169 kg.m<sup>-3</sup> (15 °C) a 675.125 kg.m<sup>-3</sup> (35 °C) para hexano/isopropanol. Para los  $V_m^E$  de las mezclas binarias, se verificó que éstos varían entre 15 a 35 °C de -1.47504x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> a -1.50475x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> para iso-octano/butanol; 2,09222x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> a 2.31939x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> para iso-octano/isopropanol; -3.82449x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> a -4.04924x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> para hexano/butanol; 4.34134x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> a 4.61050x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> para hexano/isopropanol.

**Palabras clave:** interacciones, cadena lineal, cadena ramificada, micela.

\* Autora para la correspondencia. E-mail: bonomorcf@yahoo.com.br

doi: 10.24275/uam/izt/dcbj/revmexingquim/2018v17n1/Gomes

issn-e: 2395-8472

## 1 Introduction

---

Ternary mixtures of surfactant/organic solvent/alcohol are used in extraction processes by reverse micelles which are formed after adding water. Several recent works show the application of reverse micelles in the extraction of proteins, enzymes, antibiotics and pigment (Chávez-Castilla and Aguilar, 2015; Ding *et al.*, 2016; Gaikawai *et al.*, 2012; He *et al.*, 2015; Liu *et al.*, 2008; Mathew *et al.*, 2007; Mohd-Setapar *et al.*, 2009; Sun *et al.*, 2008; Wan *et al.*, 2016). Among the advantages presented in extraction by reverse micelles, it is important to emphasize the workability guarantee of encapsulated biomolecules, due to the aqueous centers found in the micelle.

Application and control of separation processes, as well as equipment development may be more difficult due to the lack of information on the changes of thermophysical properties with composition and temperature (Minim *et al.*, 2010). Specific mass and excess molar volume are important properties for understanding processes involving mass transference, energy transference as heat, fluid flow, and mainly, molecular interaction among mixture components (Ali *et al.*, 2007; Blanco *et al.*, 2010).

Through specific mass measuring it is possible to obtain measures of volumetric properties. In turn, these properties depend not only on interaction among solute-solute, solvent-solvent and solute-solvent, but also on the structural effects resulting from interstitial accommodations due to differences of molar volume and free volume among components in the solution (Astaría *et al.*, 1983).

The objective of this work was to determine specific masses of ternary mixtures using diotyl sodium sulfosuccinate (AOT) as a surfactant; iso-octane and hexane as an organic solvent, and butanol and isopropanol as an alcohol. The excess molar volume was only obtained for binary systems of solvent and alcohol.

## 2 Materials and methods

---

### 2.1 Materials

Dietyl sodium sulfosuccinate (AOT) was obtained from Sigma Aldrich; iso-octane, hexane from F Maia, and isopropanol and 1-butanol from F Maia and Vetec

Química Fina, respectively. All reagents were used in analytical degree.

### 2.2 System obtainment

Twenty ternary systems were prepared with concentrations from 1 to 20 % (w/w) AOT and the relation among organic solvent and alcohol concentrations remained constant, 75 % and 25 % (w/w), respectively. Two types of organic solvents were used, iso-octane with branched carbonic chain (C<sub>8</sub>H<sub>18</sub>) and hexane with linear carbonic chain (C<sub>6</sub>H<sub>14</sub>). Also, two alcohols were used, butanol (C<sub>4</sub>H<sub>10</sub>O) and isopropanol (C<sub>3</sub>H<sub>7</sub>OH), with linear and branched chain, respectively. Each reagent was separately weighed using an analytical balance (Shimadzu Ay220 ± 0.001 g). In sequence, AOT was mixed to the organic solvent and alcohol, and homogenized. For preparing binary systems, only solvent and alcohols were used in the proportions of 75 % and 25 % (w/w).

### 2.3 Specific mass

Specific mass was determined for 15, 20, 25, 30 and 35 °C. For determining specific mass, a digital workbench hydrometer DMA 5000M (Anton paar), precision of ± 5x10<sup>-3</sup> kg.m<sup>-3</sup> and repeatability of ± 1x10<sup>-3</sup> kg.m<sup>-3</sup>, and operation range of 0 a 3 g.cm<sup>-3</sup>. The temperature ranged from 0°C and 90°C, precision of ± 0.01 °C and repeatability of ± 0.001 °C.

### 2.4 Excess molar volume ( $V_m^E$ )

Excess molar volumes ( $V_m^E$ ) were indirectly determined through measuring specific masses of pure components and binary mixtures.  $V_m^E$  was calculated using Eq. (1):

$$V_m^E = x_1 M_1 \left( \frac{1}{\rho} - \frac{1}{\rho_1} \right) + x_2 M_2 \left( \frac{1}{\rho} - \frac{1}{\rho_2} \right) \quad (1)$$

which  $V_m^E$  (m<sup>3</sup>.mol<sup>-1</sup>) represents excess molar volume;  $\rho$  (kg.m<sup>-3</sup>) represents specific mass;  $x$  represents the molar ratio; and  $M$  (kg.mol<sup>-1</sup>) represents molar mass. Variables with indexes 1 and 2 correspond to solvent and alcohol, respectively.

### 2.5 Experimental planning

Specific masses data of ternary systems were obtained in triplicate using complete factorial with five temperature levels (T) and twenty levels of alcohol

molar fraction ( $x$ ), for four systems, completing 400 experiments. For binary systems, data was obtained in triplicate. Also, a complete factorial planning was used utilizing five T levels for four systems, completing twenty experiments. All statistical analyses were conducted using the software SAS Universal Edition. The adaptation of adjusted equations was evaluated by the significance level ( $p$ ) and the coefficient of determination ( $R^2$ ).

### 3 Results and discussion

#### 3.1 Specific mass

In Table 1 it is possible to observe that specific masses for pure liquids varied with temperature, from 696.281 kg.m<sup>-3</sup> (15 °C) to 679.761 kg.m<sup>-3</sup> (35 °C), for iso-octane; from 671.849 kg.m<sup>-3</sup> to 653.533 kg.m<sup>-3</sup> (35 °C), for hexane; from 814.228 kg.m<sup>-3</sup> (15 °C) to 798.842 kg.m<sup>-3</sup> (35 °C), for butanol; from 790.463 kg.m<sup>-3</sup> (15 °C) to 773.426 kg.m<sup>-3</sup> (35 °C), for isopropyl alcohol. The same was observed for binary mixtures, which presented the following variation: from 710.404 kg.m<sup>-3</sup> (15 °C) to 693.654 kg.m<sup>-3</sup> (35 °C) for iso-octane/butanol; from 706.286 kg.m<sup>-3</sup> (15 °C) to 688.972 kg.m<sup>-3</sup> (35 °C) for iso-octane/isopropanol; from 700.970 kg.m<sup>-3</sup> (15 °C) to 682.817 kg.m<sup>-3</sup> (35 °C) for hexane/butanol; from 694.169 kg.m<sup>-3</sup> (15 °C) to 675.125 kg.m<sup>-3</sup> (35 °C) for hexane/isopropanol.

For binary mixtures, it was verified that values of specific mass were closer to the specific mass of the pure organic solvent, due to the higher proportion of the last in the mixture. However,

specific masses obtained experimentally for binary mixtures are lower than those obtained by the direct proportion calculation, which means, considering that the resulting specific mass was 75 % of the organic solvent specific mass, and 25 % of the alcohol. This is due to the fact that new thermodynamic interactions were formed from the substances combination, because if these are stronger, the molecules are closer. Therefore, the volume occupied by the same mass will be lower and, consequently, specific mass will be higher. The opposite case may also occur. The results found for specific masses of ternary mixtures are shown in Table 2 and 3.

It was observed that specific masses for ternary systems, AOT/iso-octane/butanol, with molar fraction from 0.002 to 0.054 varied from 724.595 kg.m<sup>-3</sup> to 782.803 kg.m<sup>-3</sup> (15 °C) and from 707.894 kg.m<sup>-3</sup> to 766.021 kg.m<sup>-3</sup> (35 °C); AOT/iso-octane/isopropanol, with molar fractions from 0.002 to 0.050 varied from 717.748 kg.m<sup>-3</sup> to 775.889 kg.m<sup>-3</sup> (15 °C) and from 700.193 kg.m<sup>-3</sup> to 758.419 kg.m<sup>-3</sup> (35 °C); AOT/hexane/butanol, with molar fraction from 0.002 to 0.038 varied from 708.192 kg.m<sup>-3</sup> to 768.780 kg.m<sup>-3</sup> (15 °C) and from 690.061 kg.m<sup>-3</sup> to 750.419 kg.m<sup>-3</sup> (35 °C); AOT/hexane/isopropanol, with molar fraction from 0.002 to 0.042 varied from 695.985 kg.m<sup>-3</sup> to 761.625 kg.m<sup>-3</sup> (15 °C) and from 676.868 kg.m<sup>-3</sup> to 742.679 kg.m<sup>-3</sup> (35 °C).

It is possible to observe that temperature not only influences specific masses of pure liquids and all systems under analysis, but also specific masses of ternary mixture were influenced by the increase of AOT molar fraction. This behavior is in accordance to Morávková *et al.*, (2011), Zhou *et al.*, (2010), Ku and Tu (2005).

Table 1. Specific masses for pure liquids iso-octane (1), hexane (2), butanol (3), isopropanol (4) and for binary mixtures of iso-octane/butanol (13), iso-octane/isopropanol (14), hexane/butanol (23), hexane/isopropanol (24).

T (°C)	$\rho$ (kg.m <sup>-3</sup> )											
	$\rho_1$		$\rho_2$		$\rho_3$		$\rho_4$		$\rho_{13}$	$\rho_{14}$	$\rho_{23}$	$\rho_{24}$
	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit				
15	696.281		671.849		814.228		790.463		710.404	706.286	700.97	694.169
20	692.185	691.7a	667.329	659.94b	810.431	809.60a	786.308	785.45f 786.91g	706.269	702.028	696.505	689.499
25	688.067		662.771	654.81c 655.32b	806.601	806.06d	782.082	782.45g 782.70h	702.098	697.72	691.989	684.774
30	683.928	683.5a	658.176	649.7c 650.71b	802.745	802.03d 801.90a	777.789		697.896	693.371	687.428	679.983
35	679.761		653.533	644.8c	798.842	798.25e	773.426		693.654	688.972	682.817	675.125

a. Torín-Ollarves *et al.*, 2012; b. Baraldi *et al.*, 2002; c. Nayak *et al.*, 2003; d. Yang *et al.*, 2006; e. Nain, 2007; f. Riddick *et al.*, 1986; g. Soujanya *et al.*, 2016; h. Lladosa *et al.*, 2007.

Table 2. Specific Mass ( $\rho$ ) ( $\text{kg}\cdot\text{m}^{-3}$ ) of ternary mixtures iso-octane/butanol/AOT (135), iso-octane/isopropanol/AOT (145).

<b>Iso-octane/butanol/AOT</b>					
<b>x1</b>	<b>15 °C</b>	<b>20 °C</b>	<b>25 °C</b>	<b>30 °C</b>	<b>35 °C</b>
0.002	724.595	720.477	716.318	712.129	707.894
0.005	728.276	724.154	719.987	715.786	711.553
0.007	730.164	726.043	721.879	717.679	713.449
0.009	732.983	728.85	724.681	720.478	716.239
0.012	736.295	732.163	727.991	723.787	719.555
0.014	739.689	735.565	731.399	727.199	722.963
0.017	742.305	738.162	733.975	729.771	725.53
0.019	744.562	740.425	736.257	732.054	727.81
0.022	747.963	743.822	739.64	735.441	731.204
0.025	750.676	746.531	742.353	739.227	734.977
0.027	753.191	749.049	744.875	740.669	736.43
0.03	755.709	751.561	747.384	743.177	738.94
0.033	759.693	755.551	751.375	747.169	742.928
0.036	762.701	758.559	754.379	750.172	745.928
0.038	764.898	760.754	756.553	752.361	748.117
0.041	767.177	763.037	758.856	754.646	750.4
0.044	770.302	766.147	761.959	757.753	753.513
0.047	777.001	772.874	768.694	764.475	760.213
0.05	780.218	776.064	771.879	767.702	763.619
0.054	782.803	778.656	774.468	770.266	766.021
<b>Iso-octane/isopropanol/AOT</b>					
<b>x1</b>	<b>15 °C</b>	<b>20 °C</b>	<b>25 °C</b>	<b>30 °C</b>	<b>35 °C</b>
0.002	717.748	713.444	709.072	704.661	700.193
0.004	720.41	716.178	711.815	707.401	702.937
0.006	723.366	719.059	714.693	710.277	705.812
0.009	726.247	721.922	717.563	713.144	708.69
0.011	729.449	725.135	720.772	716.358	711.907
0.013	731.296	726.982	722.621	718.211	713.75
0.016	736.365	733.683	729.323	724.916	720.46
0.018	739.038	736.152	730.51	726.119	721.662
0.02	740.053	735.747	731.386	726.98	722.524
0.023	743.241	738.918	734.56	730.158	725.707
0.025	745.247	740.926	736.567	732.164	727.708
0.028	748.822	744.511	740.15	735.744	731.294
0.03	753.564	749.26	744.897	740.501	736.055
0.033	755.738	751.435	747.079	742.68	738.238
0.036	758.977	754.66	750.296	745.884	741.442
0.039	762.387	758.069	753.718	749.333	744.884
0.041	765.544	761.222	756.858	752.464	748.021
0.044	770.559	766.353	762.015	757.595	753.117
0.047	772.138	767.83	763.476	759.087	754.651
0.05	775.889	771.584	767.235	762.845	758.419

Table 3. Specific Mass ( $\rho$ ) ( $\text{kg}\cdot\text{m}^{-3}$ ) of ternary mixtures hexane/butanol/AOT (235), hexane/isopropanol/ AOT (245).

<b>Hexane/butanol/AOT</b>					
<b>x1</b>	<b>15 °C</b>	<b>20 °C</b>	<b>25 °C</b>	<b>30 °C</b>	<b>35 °C</b>
0.002	708.192	703.735	699.237	694.68	690.001
0.004	711.796	707.329	702.785	698.233	693.625
0.006	714.538	710.064	705.553	700.995	696.389
0.008	718.109	713.647	709.129	704.566	699.956
0.009	721.272	716.813	712.306	707.755	703.148
0.011	722.81	718.357	713.837	709.277	704.659
0.013	723.75	719.279	714.773	710.224	705.549
0.016	725.662	721.196	716.69	712.137	707.459
0.017	730.244	725.791	721.287	716.739	712.061
0.019	735.459	731.012	726.499	721.93	717.311
0.021	737.785	733.311	728.793	724.233	719.627
0.023	742.14	737.676	733.151	728.589	723.964
0.024	746.492	741.993	737.468	732.901	728.29
0.026	750.077	745.7	741.2	736.63	732.002
0.028	752.293	747.939	743.449	738.87	734.228
0.03	754.677	751.095	746.551	741.9	737.206
0.032	758.685	754.337	749.792	745.152	740.43
0.034	760.676	756.252	751.757	747.194	742.571
0.036	762.39	757.929	755.049	750.806	746.709
0.038	768.78	764.334	759.759	755.113	750.419
<b>Hexane/isopropanol/AOT</b>					
<b>x1</b>	<b>15 °C</b>	<b>20 °C</b>	<b>25 °C</b>	<b>30 °C</b>	<b>35 °C</b>
0.002	695.985	691.317	686.58	681.799	676.868
0.004	702.375	697.709	692.982	688.187	683.258
0.005	705.728	701.06	696.336	691.548	686.623
0.007	708.577	703.911	699.182	694.398	689.482
0.009	710.611	705.943	701.227	696.463	691.591
0.011	715.11	710.445	705.746	701.025	696.345
0.013	716.886	712.23	707.51	702.729	697.848
0.015	718.021	713.359	708.647	703.868	698.956
0.017	721.934	717.279	712.563	707.851	703.145
0.019	728.144	723.499	718.786	714.018	709.102
0.021	731.148	726.51	721.803	717.033	712.2
0.023	733.712	729.052	724.34	719.573	714.749
0.025	737.158	732.503	727.795	723.032	718.209
0.028	742.857	738.252	733.495	728.652	723.727
0.03	748.514	743.815	738.958	734.021	728.939
0.032	750.841	746.221	741.481	736.661	731.749
0.035	751.391	746.744	742.047	729.998	732.483
0.037	758.839	754.897	748.714	743.854	738.947
0.039	760.18	755.514	750.746	745.896	740.976
0.042	761.625	757.022	752.308	747.526	742.679

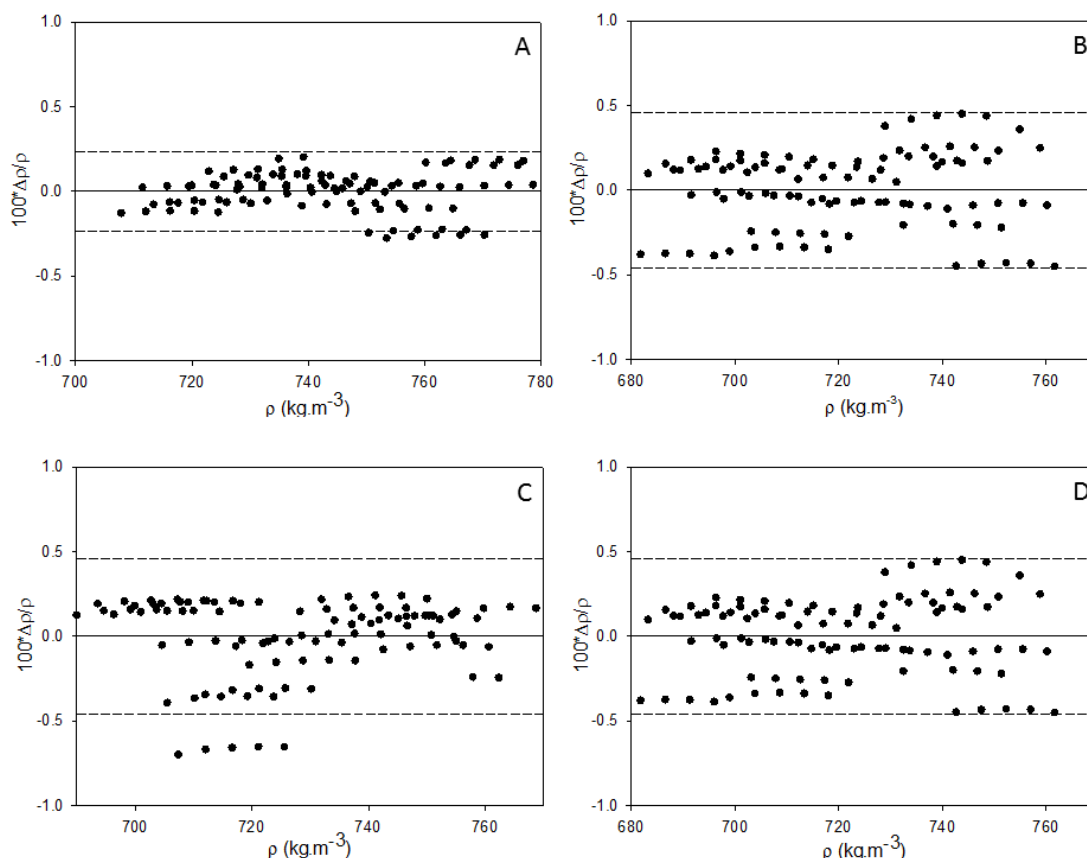


Fig. 1. Graph of residual  $100 * \Delta\rho = (\rho \text{ exp} - \rho \text{ pred})$  of experimental specific masses of ternary systems as a function of specific masses calculated from models: (a) iso-octane/butanol/AOT e (b) iso-octane/isopropanol/AOT; (c) hexane/butanol/AOT e (d) hexane/isopropanol/AOT. Trace lines represent two standard deviations from adjustments.

The decrease in density with increasing temperature can be increased mobility of liquid molecules provided increased energy as heat, making the interactions within the weaker system, which causes the volume expansion and reduced interactions molecular consequently reducing the density (Siongo *et al.*, 2010).

The increase of specific mass for ternary systems with increase of AOT concentration may be attributed to new and stronger dipole-dipole interaction and hydrogen bonds between solute-solvent than those between solvent-solvent, considering the final result of mass increase contributed more effectively than volume increase.

Polynomial models were used for correlating specific mass variations ( $\rho$ ) with temperature (T), of pure liquids and binary mixtures, and with temperature and surfactant composition for ternary mixtures. Models were adjusted to experimental data, considering that the quadratic general model, Eq. (2),

was analyzed for the first case and Equation 3 for the second. The model was selected based on the significance of the t-test (Student) parameters,  $p < 0,05$ , coefficient of determination ( $R^2$ ), and residual analysis, only for ternary mixtures.

$$\rho_{ij} = \beta_0 + \beta_1 T + \beta_2 T^2 \quad (2)$$

$$\rho_{ijk} = \beta_0 + \beta_1 T + \beta_2 x_1 + \beta_3 x_1 T + \beta_4 x_1^2 + \beta_5 T^2 \quad (3)$$

Adjustments presented in Table 4 demonstrate a linear behavior for specific masses and negative effect for temperature for all systems under analysis, binary and ternary, which indicates that temperature increase causes a reduction of the thermodynamic property under evaluation. It was also observed that temperature's influence on binary and ternary mixtures was greater than on pure liquids. Based on this behavior, it is possible to imply that interactions between solvent-alcohol in the mixture are stronger

Table 4. Adjusted models for specific masses of pure liquids, iso-octane (1), hexane (2), butanol (3) and isopropanol (4), of binary mixtures of iso-octane/butanol (13), iso-octane/isopropanol (14), hexane/butanol (23), hexane/isopropanol (24) and ternary mixtures, iso-octane/butanol/AOT (135), iso-octane/isopropanol/AOT (145), hexane/butanol/AOT (235), hexane/isopropanol/ AOT (245).

Model	R <sup>2</sup>
$\rho_1 = 708.6929 - 0.8259 T$	0.9999 (3)
$\rho_2 = 685.6241 - 0.9157 T$	0.9999 (4)
$\rho_3 = 825.7984 - 0.7692 T$	0.9999 (5)
$\rho_4 = 803.3101 - 0.8519 T$	0.9999 (6)
$\rho_{13} = 723.0007 - 0.8375 T$	0.9999 (7)
$\rho_{14} = 719.3179 - 0.8657 T$	0.9999 (8)
$\rho_{23} = 714.6333 - 0.9076 T$	0.9999 (9)
$\rho_{24} = 708.5120 - 0.95210 T$	0.9999 (10)
$\rho_{135} = 735.4699 + 1112.6639 x_1 - 0.8343 T$	0.9976 (11)
$\rho_{145} = 729.0630 + 1210.7134 x_1 - 0.8738 T$	0.9971 (12)
$\rho_{235} = 717.4804 + 1689.5208 x_1 - 0.9003 T$	0.9929 (13)
$\rho_{245} = 710.0578 + 1655.4229 x_1 - 0.9526 T$	0.9938 (14)

Table 5. Excess molar volume ( $V_m^E$ ) of binary mixtures iso-octane/butanol (13), iso-octane/isopropanol (14), hexane/butanol (23), hexane/isopropanol (24).

$V_m^E$ (m <sup>3</sup> .mol <sup>-1</sup> )	Temperature (°C)				
	15	20	25	30	35
$V_{13m}^E$	-1.475×10 <sup>-6</sup>	-1.485×10 <sup>-6</sup>	-1.493×10 <sup>-6</sup>	-1.500×10 <sup>-6</sup>	-1.505×10 <sup>-6</sup>
$V_{14m}^E$	2.092×10 <sup>-6</sup>	2.143×10 <sup>-6</sup>	2.198×10 <sup>-6</sup>	2.257×10 <sup>-6</sup>	2.319×10 <sup>-6</sup>
$V_{23m}^E$	-3.824×10 <sup>-6</sup>	-3.881×10 <sup>-6</sup>	-3.936×10 <sup>-6</sup>	-3.992×10 <sup>-6</sup>	-4.049×10 <sup>-6</sup>
$V_{24m}^E$	4.341×10 <sup>-6</sup>	4.407×10 <sup>-6</sup>	4.474×10 <sup>-6</sup>	4.542×10 <sup>-6</sup>	4.611×10 <sup>-6</sup>

than interaction between solvent-solvent. In relation to system composition, temperature coefficients for hexane/isopropanol systems were greater than those found in iso-octane/isopropanol systems. Possibly, there is a stronger interaction between hexane and isopropanol, and the increase of temperature causes such a structural disarrangement that volume alteration becomes more obvious.

In addition, ternary mixtures presented positive coefficient for molar fraction, which confirms that the presence of AOT in systems contributes for specific mass increase. Moreover, for systems with iso-octane, the coefficient was even higher than in systems with Hexane. Probably, the molecular interactions between AOT molecules and the first system were stronger, and the effect of the system final mass overcomes its increase in volume.

Residual analysis represents the difference between model and experimental results (Fig. 1). Randomness of points is an indication of how well adjustments represent experimental results and they can be use to predict specific mass for ternary systems

as a function of temperature and molar fraction within a range under study. This analysis was not conducted for binary systems, once there was not sufficient data.

### 3.2 Excess molar volume

The results found for  $V_m^E$  are presented in Table 5. It was observed that excess molar volume for binary mixtures varied from 1.475x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (15 °C) to -1.505x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (35 °C) for iso-octane/butanol; from 2.092x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (15 °C) to 2.319x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (35 °C) for iso-octane/isopropanol; from -3.824x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (15 °C) to -4.049x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (35 °C) for hexane/butanol; from 4.341x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (15 °C) to 4.610x10<sup>-6</sup> m<sup>3</sup>.mol<sup>-1</sup> (35 °C) for hexane/isopropanol.

It was verified that values for  $V_m^E$  were positive for systems containing isopropanol, both in those with iso-octane and hexane (Fig. 2). Adding Isopropanol contributed to the increase of binary mixtures within all temperature range, considering that in those containing hexane,  $V_m^E$  was higher once compared

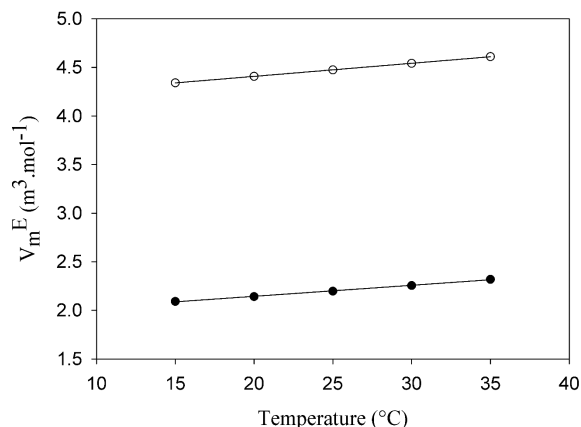


Fig. 2. Excess molar volume for binary mixtures of isopropanol/organic (hexane,o; iso-octane, ●).

to iso-octane mixtures. The presence of alcohol in pure solvents leads to changes in solvent-solvent interactions, dispersion forces, and leads to dipole-dipole and hydrogen bonds interactions.

According to Dubey *et al.* (2008), positive  $V_m^E$  is attributed to weak interactions among molecules, characterizing volume increase of the final system.

As stated by Liu *et al.* (1999), hexane molecular volume is 217 Å and iso-octane is 274 Å. The difference is related to the structure of each hydrocarbon, the first containing linear chain and the second containing branched chain. Therefore, hexane molecules become closer, more organized and conduct more intense interaction, contrary to iso-octane, which presents branched chain.

Adding isopropanol to a system with hexane causes greater modification in the structure of such solvent which cause the alcohol modification to prevent intense contact among hexane molecules, leaving weak interactions.

On the other hand, iso-octane is a solvent containing free space in its structure due to branching, which may make alcohol molecules' accommodation easier. Therefore, the contribution to volume increase is lower.

It is also observed that with the increase of temperature occurred in an elevation of  $V_m^E$ . This may be due to the decrease of the molecular interactions of the system (weak interactions), with the increase of the energy in the form of heat, causing an increase of the free volume and consequently an increase in the  $V_m^E$ .

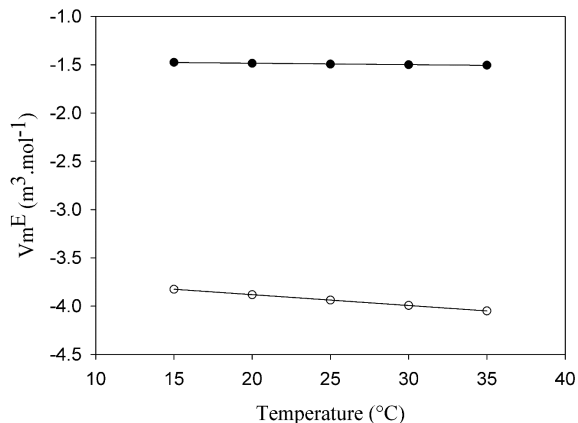


Fig. 3. Excess molar volume of binary mixtures of butanol/organic solvent (iso-octane, ●; hexane,o).

For butanol systems,  $V_m^E$  values were negative for both solvents, iso-octane and hexane, for all temperature range (Fig. 3). Thus, alcohol addition decreased the volume of binary mixtures. Also,  $V_m^E$  for systems containing hexane, reduction was even higher.

Butanol is a linear chain alcohol, in which molecules are closer and strongly interacting with Hexane molecules, which also contain linear chain. Hence, there is a contribution for greater contraction of the final volume. The contrary goes for iso-octane, whose branched chain prevents strong interactions with alcohol molecules.

Generally, adding alcohol to pure solvents causes changes in solvent-solvent interactions, once new interactions such as solute-solvent take place. In addition, volume increase is attributed to weak interaction, and the contrary for volume reduction.

It is observed in the butanol system that the  $V_m^E$  decreased with increasing temperature for both organic solvents. When the temperature increased, the structural factors had a favorable effect, where the solution presented a more compact structure, causing a greater packaging between the different components of the mixture.

Polynomial models for excess molar volume ( $V_m^E$ ) as a function of temperature were adjusted to experimental data of binary mixtures. Non-significant parameters were eliminated based on t-test (Student),  $p < 0,001$ , coefficient of determination ( $R^2$ ) and agreement to the phenomena.

In Table 6,  $V_m^E$  models for binary mixtures are presented.



Table 6. Models adjusted to excess molar volume of binary mixtures of iso-octane/butanol (13), iso-octane/isopropanol (14), hexane/butanol (23) and hexane/isopropanol (24).

Model	R <sup>2</sup>
$V_{13m}^E = -1.4545 \times 10^{-6} - 1.4828 \times 10^{-9} T$	0.9833 (15)
$V_{14m}^E = 1.9177 \times 10^{-6} + 1.1364 \times 10^{-8} T$	0.9983 (16)
$V_{23m}^E = -3.6561 \times 10^{-6} - 1.1217 \times 10^{-8} T$	0.9999 (17)
$V_{24m}^E = 4.1387 \times 10^{-6} + 1.3453 \times 10^{-8} T$	0.9997 (18)

## Conclusions

Specific mass increases with the AOT molar fraction and decreases with temperature for all systems under study.  $V_m^E$  was determined for binary mixtures containing Iso-octane or Hexane/Butanol or Isopropanol. Positive values for systems containing Isopropanol characterized the existence of weak interactions, while negative values for systems with Butanol indicated the presence greater intensity interactions. Therefore, the effect of interactions' intensity on structural molecular arrangements and dipolar momentum of binary mixtures was the responsible for  $V_m^E$  behavior. Obtained equations are in accordance with experimental data, and therefore,  $\rho$  and  $V_m^E$  estimative can be determined for any temperature and mass fraction within the range under study.

## Nomenclature

AOT	diotyl sodium sulfosuccinate
$V_m^E$	excess molar volume, m <sup>3</sup> .mol <sup>-1</sup>
x	molar ratio
M	molar mass, kg.mol <sup>-1</sup>
T	temperature, °C
R <sup>2</sup>	correlation coeficiente
$\rho$	density, kg.m <sup>-3</sup>

## Agradecimientos

El primer autor agradece el apoyo al Centro de Catálisis, Petróleo y Petroquímica de la Facultad de Ciencias, Universidad Central de Venezuela por el soporte técnico prestado en el Laboratorio de Tamices Moleculares. Los autores agradecen a INTEVEP S.A por el permiso concedido para publicar la presente contribución.

## References

- Ali, A., Khan, S., Hyder, S. and Tariq, M. (2007). Interactions of some  $\alpha$ -amino acids with tetra-n-alkylammonium bromides in aqueous medium at different temperatures. *Journal of Chemical Thermodynamics* 39, 613-620.
- Astaria, G., Savage, D. W. and Bisio, A. (1983). Gas treating with chemical solvents.
- Baraldi, P., Giorgini, M. G., Manzini, A. M. and Tassi, L. (2002). Density, refractive index, and related properties for 2-butanone + n-hexane binary mixtures at various temperatures. *Journal of Solution Chemistry* 31, 873-893.
- Blanco, A., García-Abuín, A., Gómez-Díaz, D., Navaza, J. M. and Vidal-Tato, I. (2010). Influence of Temperature and Composition upon Density, Viscosity, Speed of Sound, and Refractive Index of Aqueous Solutions of 1-Ethyl-2-pyrrolidinone. *Journal of Chemical and Engineering Data* 55, 962-965.
- Chávez-Castilla, L. and Aguilar O. (2015). Effect of mineral supplementation and type of starch on the production of prodigiosin from a culture of *Serratia marcescens* BS303. *Revista Mexicana de Ingeniería Química* 14, 641-652.
- Ding, X., Cai, J. and Guo, X. (2016). Extraction of ovalbumin with gemini surfactant reverse micelles - Effect of gemini surfactant structure. *Separation and Purification Technology* 158, 367-373.
- Dubey, G. P. and Sharma, M. (2008). Study of molecular interactions in binary liquid mixtures of 1-octanol with n-hexane, n-octane, and n-decane using volumetric, viscometric, and acoustic properties. *Journal of Chemical Thermodynamics* 40, 991-1000.

- Gaikaiwari, R. P., Wagh, S. A. and Kulkarni, B. D. (2012). Efficient lipase purification using reverse micellar extraction. *Bioresource Technology* 108, 224-230.
- He, S., Shi, J., Walid, E., Zhang, H., Ma, Y. and Xue, J. S. (2015). Reverse micellar extraction of lectin from black turtle bean (*Phaseolus vulgaris*): Optimisation of extraction conditions by response surface methodology. *Food Chemistry* 166, 93-100.
- Ku, H.-C. and Tu, C.-H. (2005). Densities and viscosities of binary and ternary mixtures of ethanol, 2-butanone, and 2,2,4-trimethylpentane at T = (298.15, 308.15, and 318.15) K. *Journal of Chemical and Engineering Data* 50, 608-615.
- Liu, D., Ma, J., Cheng, H. and Zhao, Z. (1999). Conducting properties of mixed reverse micelles. *Colloids and Surfaces A* 148, 291-298.
- Liu, Y., Dong, X. and Sun, Y. (2008). New development of reverse micelles and applications in protein separation and refolding. *Chinese Journal of Chemical Engineering* 16, 949-955.
- Lladosa, E., Montón, J. B., Burguet, M. C. and Muñoz, R. (2007). Effect of pressure and the capability of 2-methoxyethanol as a solvent in the behavior of a diisopropyl ether-isopropyl alcohol azeotropic mixture. *Fluid Phase Equilibria* 262, 271-279.
- Mathew, D. S. and Juang, R.-S. (2007). Role of alcohols in the formation of inverse microemulsions and back extraction of proteins/enzymes in a reverse micellar system. *Separation and Purification Technology* 53, 199-215.
- Minim, L. A., Bonomo, R. C. F., Amaral, I. V., Reis, M. F. T., Oliveira, A. A. A. and Minim, V. P. R. (2010). Density and viscosity of binary and ternary mixtures of poly(ethylene glycol) and poly(acrylic acid, sodium salt) at temperatures of (288.15 to 318.15) K. *Journal of Chemical and Engineering Data* 55, 2328-2332.
- Mohd-Setapar, S. H., Wakeman, R. J. and Tarleton, E. S., (2009). Penicillin G solubilisation into AOT reverse micelles. *Chemical Engineering Research & Design* 87, 833-842.
- Morávková, L., Wagner, Z., Sedláková, Z. and Linek, J. (2011). Volumetric behaviour of binary and ternary liquid systems composed of ethanol, isooctane, and toluene at temperatures from (298.15 to 328.15) K. Experimental data and correlation. *Journal of Chemical Thermodynamics* 43, 1906-1916.
- Nain, A. K. (2007). Densities and volumetric properties of binary mixtures of formamide with 1-butanol, 2-butanol, 1,3-butanediol and 1,4-butanediol at temperatures between 293.15 and 318.15 K. *Journal of Solution Chemistry* 36, 497-516.
- Nayak, J. N., Aralaguppi, M. I. and Aminabhavi, T. M. (2003). Density, viscosity, refractive index, and speed of sound in the binary mixture of 1,4-dioxane + ethanediol, + hexane, + tributylamine, or + triethylamine at (298.15, 303.15, and 308.15) K. *Journal of Chemical and Engineering Data* 48, 1152-1156.
- Riddick, J. A., Bunger, W. B. and Sakano, T. K. (1986). *Organic Solvents: Physical Properties and Methods of Purification*. Fourth edition. John Wiley and Sons, New York, NY, Pages: 1343.
- Siongco, K. R., Leron, R. B. and Li, M.-H. (2013). Densities, refractive indices, and viscosities of N,N-diethylethanol ammonium chloride-glycerol or -ethylene glycol deep eutectic solvents and their aqueous solutions. *Journal of Chemical Thermodynamics* 65, 65-72.
- Soujanya, J., Reddy, Ch.A., Satyanathi, B. and Sankarshana, T. (2016). Experimental vapour - liquid equilibrium data of the quaternary system methanol (1) + isopropyl alcohol (2) + water (3) + glycerol (4) along with isopropyl alcohol (2) + glycerol (4) and isopropyl alcohol (2) + water (3) binary data at atmospheric and sub-atmospheric pressures. *Fluid Phase Equilibria* 409, 327-333.
- Sun, X.-H., Zhu, K.-X. and Zhou, H.-M. (2008). Protein extraction from defatted wheat germ by reverse micelles: Optimization of the forward extraction. *Journal of Cereal Science* 48, 829-835.
- Torín-Ollarves, G., Segovia, J. J., Martín, M. C. and Villamañán, M. A. (2012). Thermodynamic

- characterization of the mixture (1-butanol + iso-octane): Densities, viscosities, and isobaric heat capacities at high pressures. *Journal of Chemical Thermodynamics* 44, 75-83.
- Wan, J., Guo, J., Miao, Z. and Guo, X. (2016). Reverse micellar extraction of bromelain from pineapple peel - Effect of surfactant structure. *Food Chemistry* 197, 450-456.
- Yang, C., Lai, H., Liu, Z. and Ma, P. (2006). Density and viscosity of binary mixtures of diethyl carbonate with alcohols at (293.15 to 363.15) K and predictive results by UNIFAC-VISCO group contribution method. *Journal of Chemical and Engineering Data* 51, 1345-1351.
- Zhou, Q., Song, Y., Yu, Y., He, H. and Zhang, S. (2010). Density and excess molar volume for binary mixtures of naphthenic acid ionic liquids and ethanol. *Journal of Chemical and Engineering Data* 55, 1105-1108.