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Sylvia J. Rodríguez[a]; Diana M. Cristancho[a]; Paula C. Neita[a]; Edgar F. Vargas[b]; Fleming Martínez[a]

[a] Grupo de Investigaciones Farmacéutico-Fisicoquímicas, Departamento de Farmacia, Facultad de Ciencias, Universidad Nacional de Colombia, Bogotá D.C., Colombia [b] Laboratorio de Termodinámica de Soluciones, Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Bogotá D.C., Colombia

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Sylvia J. Rodríguez[a], Diana M. Cristancho[a], Paula C. Neita[a],
Edgar F. Vargas[b] and Fleming Martínez[a]*

[a]*Grupo de Investigaciones Farmacéutico-Fisicoquímicas, Departamento de Farmacia,
Facultad de Ciencias, Universidad Nacional de Colombia, A.A. 14490, Bogotá D.C.,
Colombia;* [b]*Laboratorio de Termodinámica de Soluciones, Departamento de Química,
Facultad de Ciencias, Universidad de los Andes, Bogotá D.C., Colombia*

In this article, the excess molar volumes and partial molar volumes
of components of the binary system octyl methoxycinnamate (OMC) +
ethyl acetate (AcOEt) were investigated from density measurements on the
entire range of mass fractions for this system at 298.15, 303.15, 308.15,
313.15, and 318.15 K. The results of excess molar volumes were fitted by
the Redlich–Kister equation using third degree polynomials. The system
exhibited negative excess volumes (up to $-0.926 \, cm^3 \, mol^{-1}$ at 318.15 K),
probably due to interactions like dispersion forces between unlike
molecules or some differences in the molar volumes of pure components.
The effect of temperature on the different volumetric properties studied was
also analysed. Besides, the volumetric thermal expansion coefficients were
also calculated finding values varying from $7.53 \times 10^{-4} \, K^{-1}$ for pure OMC
up to $1.38 \times 10^{-3} \, K^{-1}$ for pure AcOEt at 308.15 K.

Keywords: octyl methoxycinnamate; ethyl acetate; binary liquid mixtures;
excess volumes; partial volumes

1. Introduction

Solvent mixtures have been widely used in pharmacy and cosmetic science in order
to increase the solubility of active ingredients poorly soluble in water [1]. As it is
well known, solubility is an important physicochemical property to be considered
along the design of fluid cosmetic formulations, such as lotions [2]. As an example
of cosmetic aid, octyl methoxycinnamate (OMC; Figure 1), which is an ingredient
in some sunscreens and lip balms, is an organic solvent. It is widely used to absorb
UV–B rays from the sun, thus protecting the skin from possible damage [3]. It is also
used in dermatology to reduce the appearance of scars [3]. Ethyl acetate (AcOEt) is a
common organic solvent, miscible in almost all the organic solvents used in cosmetic
design, because it has a low dielectric constant (6.02 at 293.15 K) [4].

On the other hand, almost all the solvent mixtures obtained are highly non-ideal
due to increased interactions between unlike molecules and large differences in the
molar volumes of pure components, which leads to non-additive volumes on

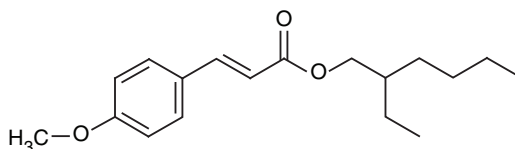*Corresponding author. Email: fmartinezr@unal.edu.co

Figure 1. Molecular structure of octyl methoxycinnamate.

mixing [5,6]. For this reason, it is necessary to characterise the volumetric behaviour of binary mixtures as a function of temperature, in order to expand the physicochemical information available for liquid mixtures used in cosmetic science, including those with possible dangerous behaviour. This information is useful to analyse the intermolecular interactions present inside liquid organic systems [7].

For these reasons, in this article, the excess molar volumes and the partial molar volumes of the binary system OMC + AcOEt at various temperatures, in addition to other volumetric properties, were calculated according to the modified procedures widely exposed in literature [8–10].

2. Experimental

2.1. *Materials*

In this investigation, OMC [CAS: 54-77-3] obtained from BASF and AcOEt AR grade [CAS: 141-78-6] obtained from Merck, Germany, were used without further purification.

2.2. *Solvent mixtures preparation*

All OMC + AcOEt solvent mixtures were prepared in quantities of 40.00 g by mass using an Ohaus Pioneer TM PA214 analytical balance with sensitivity ±0.1 mg, in concentrations from 0.125 to 0.875 varying in 0.125 in mass fraction, in order to study seven mixtures and the pure solvents.

2.3. *Density determination*

Density was determined using a DMA 45 Anton Paar digital density meter connected to a Neslab RTE 10 Digital Plus (Thermo Electron Company) recirculating thermostatic water bath. The equipment was calibrated according to the instruction manual using air and water at the different temperatures studied [11]. All mixture preparations and density measurements were repeated at least three times and the results were averaged. From the density values, all volumetric properties were calculated as it will be indicated later.

3. Results and discussion

In Table 1, the composition of OMC + AcOEt mixtures, in mass and mole fractions, and density values at several temperatures studied are presented. Our density values for AcOEt are in good agreement with those presented by Hu *et al.* [12] at 298.15 K (0.89449 g cm^{-3}) and 303.15 K (0.88836 g cm^{-3}) and those presented by

Table 1. Densities[ab] for OMC + AcOEt mixtures at various temperatures.

OMC		Temperature (K)				
Mass fraction	Mole fraction	298.15	303.15	308.15	313.15	318.15
0.000	0.0000	0.8944	0.8885	0.8824	0.8761	0.8702
0.125	0.0415	0.9085	0.9029	0.8971	0.8912	0.8855
0.250	0.0918	0.9228	0.9175	0.9120	0.9063	0.9008
0.375	0.1540	0.9374	0.9323	0.9271	0.9217	0.9166
0.500	0.2328	0.9522	0.9474	0.9425	0.9374	0.9325
0.625	0.3358	0.9664	0.9617	0.9571	0.9523	0.9476
0.750	0.4765	0.9800	0.9756	0.9713	0.9668	0.9623
0.875	0.6799	0.9933	0.9891	0.9851	0.9810	0.9769
1.000	1.0000	1.0067	1.0028	0.9991	0.9954	0.9916

Notes: [a]Units, $g\,cm^{-3}$; [b]The mean SD was $0.0001\,g\,cm^{-3}$.

Nikam *et al.* [13] at 298.15 K ($0.8946\,g\,cm^{-3}$), 303.15 K ($0.8885\,g\,cm^{-3}$), and 308.15 K ($0.8825\,g\,cm^{-3}$). According to Table 1, in all cases the density decreases linearly as the temperature increases.

3.1. *Molar volumes and excess molar volumes*

In Table 2, the molar volumes for OMC + AcOEt binary mixtures calculated from Equation (1) at all tested temperatures are presented.

$$V = \frac{x_1 M_1 + x_2 M_2}{\rho}, \tag{1}$$

where x_1 and x_2 are the mole fractions and M_1 and M_2 the molar masses, for both components ($290.40\,g\,mol^{-1}$ for OMC and $88.10\,g\,mol^{-1}$ for AcOEt, respectively), and ρ is the solvent mixture density.

On the other hand, the excess volumes calculated from Equation (2) at all temperatures studied are also presented in Table 2. This behaviour is shown graphically in Figure 2 at all temperatures tested.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right), \tag{2}$$

where ρ_1 and ρ_2 are the densities of pure components.

In the same way as the behaviour obtained in other similar investigations using other solvents [5,14], the excess volumes obtained are negative (with a minimum value around 0.35 in mole fraction of OMC, where it is near to $-0.93\,cm^3\,mol^{-1}$ at 318.15 K) indicating a contraction in volume. Unfortunately, there is no information for this system and thus no comparison is possible. As was already said [5], according to Fort and Moore [15], a negative excess volume is an indication of strong heteromolecular interactions in the liquid mixtures and is attributed to charge transfer, dipole–dipole, dipole-induced–dipole interactions, and hydrogen bonding between unlike components.

Table 2. Molar volumes, excess molar volumes, and partial molar volumes of components for OMC + AcOEt mixtures at several temperatures.

Temperature (K)	OMC Mass fraction	OMC Mole fraction	Molar volume[ab]	Excess volume[ab]	$\left(\dfrac{\partial v}{\partial \mu_{OMC}}\right)^c$	$\bar{V}_{OMC}$[ab]	$\bar{V}_{AcOEt}$[ab]
298.15	0.000	0.0000	98.50	0.000	−0.1466	282.09	98.50
	0.125	0.0415	106.22	−0.167	−0.1413	283.75	98.53
	0.250	0.0918	115.60	−0.346	−0.1359	285.08	98.46
	0.375	0.1540	127.22	−0.537	−0.1306	286.10	98.30
	0.500	0.2328	141.97	−0.744	−0.1252	286.80	98.04
	0.625	0.3358	161.46	−0.841	−0.1198	287.44	97.76
	0.750	0.4765	188.26	−0.762	−0.1145	288.02	97.46
	0.875	0.6799	227.16	−0.499	−0.1091	288.40	97.11
	1.000	1.0000	288.48	0.000	−0.1038	288.48	96.66
303.15	0.000	0.0000	99.16	0.000	−0.1512	282.94	99.16
	0.125	0.0415	106.88	−0.189	−0.1456	284.63	99.17
	0.250	0.0918	116.27	−0.378	−0.1399	286.02	99.10
	0.375	0.1540	127.91	−0.569	−0.1343	287.11	98.94
	0.500	0.2328	142.69	−0.788	−0.1287	287.84	98.66
	0.625	0.3358	162.25	−0.862	−0.1231	288.55	98.38
	0.750	0.4765	189.10	−0.788	−0.1175	289.14	98.06
	0.875	0.6799	228.11	−0.509	−0.1118	289.53	97.69
	1.000	1.0000	289.59	0.000	−0.1062	289.59	97.21
308.15	0.000	0.0000	99.85	0.000	−0.1561	283.79	99.85
	0.125	0.0415	107.57	−0.202	−0.1503	285.52	99.86
	0.250	0.0918	116.98	−0.392	−0.1444	286.97	99.79
	0.375	0.1540	128.63	−0.593	−0.1386	288.08	99.61
	0.500	0.2328	143.44	−0.817	−0.1328	288.84	99.33
	0.625	0.3358	163.04	−0.886	−0.1270	289.59	99.05
	0.750	0.4765	189.95	−0.811	−0.1212	290.19	98.72
	0.875	0.6799	229.04	−0.526	−0.1154	290.59	98.33
	1.000	1.0000	290.65	0.000	−0.1096	290.65	97.83
313.15	0.000	0.0000	100.56	0.000	−0.1610	284.70	100.56
	0.125	0.0415	108.28	−0.212	−0.1550	286.46	100.56
	0.250	0.0918	117.71	−0.406	−0.1491	287.96	100.49
	0.375	0.1540	129.38	−0.618	−0.1431	289.09	100.31
	0.500	0.2328	144.22	−0.841	−0.1371	289.89	100.02
	0.625	0.3358	163.85	−0.908	−0.1311	290.67	99.73
	0.750	0.4765	190.83	−0.825	−0.1251	291.29	99.39
	0.875	0.6799	230.00	−0.538	−0.1191	291.69	98.99
	1.000	1.0000	291.74	0.000	−0.1132	291.74	98.48
318.15	0.000	0.0000	101.24	0.000	−0.1656	285.63	101.24
	0.125	0.0415	108.98	−0.223	−0.1595	287.43	101.25
	0.250	0.0918	118.43	−0.417	−0.1533	288.99	101.18
	0.375	0.1540	130.10	−0.650	−0.1472	290.11	100.98
	0.500	0.2328	144.98	−0.869	−0.1410	290.96	100.69
	0.625	0.3358	164.67	−0.926	−0.1348	291.79	100.40
	0.750	0.4765	191.72	−0.831	−0.1287	292.44	100.05
	0.875	0.6799	230.96	−0.560	−0.1225	292.81	99.62
	1.000	1.0000	292.87	0.000	−0.1163	292.87	99.10

Notes: [a]Units, $cm^3 mol^{-1}$. [b]The mean SD for V and V^E was 0.01 $cm^3 mol^{-1}$ while for $\bar{V}_{OMC}$ and $\bar{V}_{AcOEt}$ was close to 0.03 $cm^3 mol^{-1}$. [c]Unit, $cm^3 g^{-1}$.
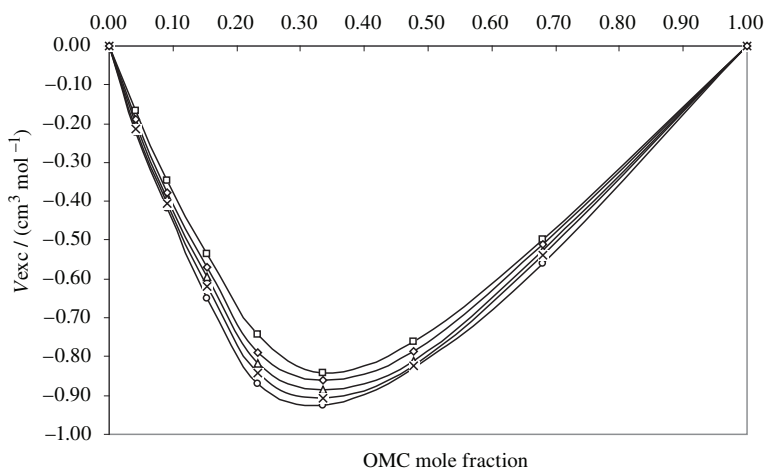
Figure 2. Excess molar volumes of OMC + AcOEt mixtures at several temperatures. 298.15 (□), 303.15 (◇), 308.15 (Δ), 313.15 (×), and 318.15 K (○).

In the evaluated system, where the non-specific interactions predominate, the contraction in volume has been interpreted basically in qualitative terms considering the following events: first, expansion due to separation of OMC molecules by addition of AcOEt; second, contraction due to free volume difference of unlike molecules; and third, contraction due to non-specific interactions between OMC and AcOEt.

Thus, the negative values of excess volumes over the free volume contribution indicate that the weak interactions (with predominance of London dispersive forces between OMC and AcOEt) are greater than the original non-specific interactions between OMC–OMC and AcOEt–AcOEt.

The excess molar volumes become more negative as the temperature is raised for all the mixtures studied indicating greater volume contraction, which points out the increase in the interactions between OMC and AcOEt with increase in temperature.

3.2. *Partial molar volumes*

The partial molar volumes for OMC ($\bar{V}_{OMC}$) and AcOEt ($\bar{V}_{AcOEt}$) were calculated by multiplying the respective specific partial volumes ($\bar{v}_{OMC}$ and $\bar{v}_{AcOEt}$) and molar masses. In this way, the $\bar{v}_{OMC}$ and $\bar{v}_{AcOEt}$ values were obtained by using the Bakhuis–Roozeboom method by means of Equations (3) and (4) applied to the variation of the respective specific volumes as a function of OMC mass fraction, μ (Table 2), and adjusting polynomials by least squares regression analyses. Polynomials of second or third degree order are the most widely used in these cases, based upon their good statistical parameters, specially their determination coefficients (Figure 3). The first derivatives were taken out on the polynomials obtained and solved at each composition point expressed in mass fraction.

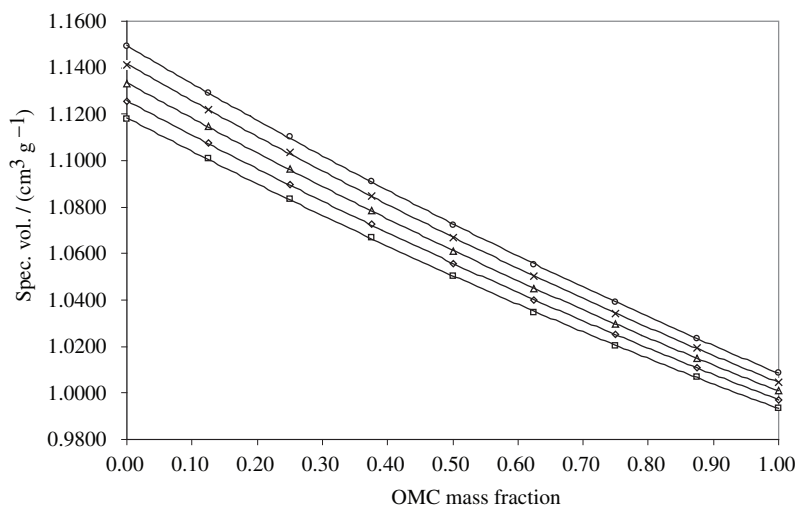$$\bar{v}_{OMC} = v + \mu_{AcOEt} \frac{dv}{d\mu_{OMC}} \qquad (3)$$

Figure 3. Specific volume of OMC + AcOEt mixtures as a function of the mixtures composition at several temperatures. 298.15 ($\square$), 303.15 ($\diamondsuit$), 308.15 (Δ), 313.15 ($\times$), and 318.15 K ($\circ$).

$$\bar{v}_{AcOEt} = v - \mu_{AcOEt} \frac{dv}{d\mu_{OMC}}. \tag{4}$$

The values of $\bar{V}_{OMC}$ and $\bar{V}_{AcOEt}$ are also presented in Table 2, in addition to the slopes ($dv/d\mu_{OMC}$) obtained at each composition and temperature. Almost in all cases the partial molar volumes for OMC and AcOEt in the mixtures are lower than those for the pure solvents (except for AcOEt in the mixture with 0.875 in mass fraction of AcOEt at 303.15 and 318.15 K). In mixtures, the partial molar volumes for OMC varied from 283.75 cm^3 mol^{-1} (for 0.125 in mass fraction of OMC at 298.15 K) to 292.81 cm^3 mol^{-1} (for 0.875 in mass fraction of OMC at 318.15 K), and for AcOEt it varied from 97.11 cm^3 mol^{-1} (for 0.875 in mass fraction of AcOEt at 298.15 K) to 101.25 cm^3 mol^{-1} (for 0.125 in mass fraction of AcOEt at 318.15 K). The results obtained for $\bar{V}_{OMC}$ and $\bar{V}_{AcOEt}$ are in agreement with the negative excess volumes obtained. The variation of this property is presented in Figure 4 as a function of OMC mole fraction at 308.15 K for OMC and AcOEt, respectively. These values were calculated as the difference between partial molar volumes and molar volumes presented in Table 2. For both solvents, the partial molar volume diminishes as their respective proportion in the mixtures diminishes.

At this point, it is important to consider that partial volumes were obtained by using specific volumes and mass fractions, in an opposite way to that done previously with ethanol + water mixtures [16] and 1,2-propanediol + water mixtures [14]. For the OMC + AcOEt system, straight lines were obtained for molar volume *versus* mole fraction, which apparently indicates no variation of partial molar volumes with respect to molar volumes as pure compounds. For this reason, the classical method based on molar volumes and mole fractions was not used in this article.
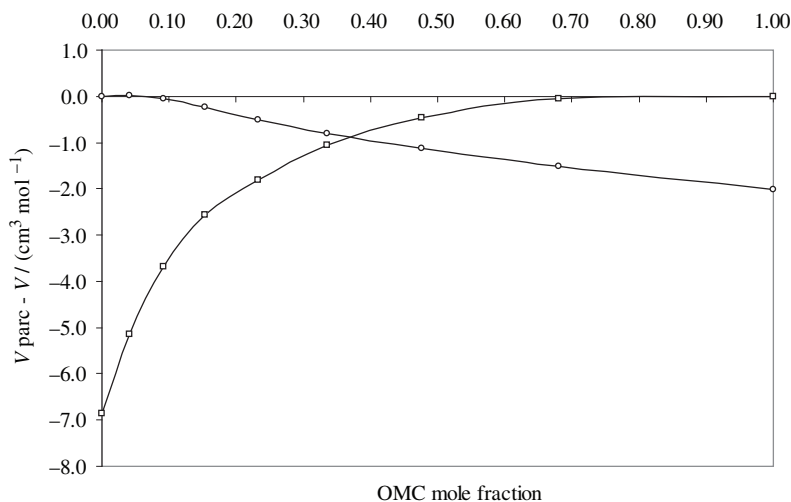
Figure 4. Partial molar volumes of OMC ($\circ$) and AcOEt ($\square$) calculated as differences with respect to pure solvent volumes in OMC + AcOEt mixtures at 308.15 K.

3.3. *Redlich–Kister equation*

As was already said [5], Redlich and Kister [17] introduced Equation (5) to facilitate the representation of thermodynamic properties and the classification of solutions in multicomponent systems. The Redlich–Kister equation has been used widely for studying several kinds of physicochemical values of mixtures, such as excess volumes, excess viscosities, and solubilities in cosolvent mixtures, among others.

$$V^{E} = x_1 x_2 \sum a_i (x_1 - x_2)^i. \tag{5}$$

For the analysis of excess volumes presented in Table 2, Equation (5) was used in the form of third degree polynomial equations using least square analyses, and therefore, obtaining four coefficients, as presented in Equation (6). Polynomials of third degree are the most widely used in these cases, because of their relevant statistic parameters, such as determination coefficients and standard deviations (SDs).

$$\frac{V^{E}}{x_1 x_2} = a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2 + a_3(x_1 - x_2)^3. \tag{6}$$

The Redlich–Kister parameters for OMC + AcOEt mixtures at all temperatures tested are presented in Table 3, in addition to determination coefficients and SDs calculated according to Equation (7) (where D is the number of compositions studied and N is the number of terms used in the regression, that is 7 and 4, respectively). Figure 5 shows the Redlich–Kister equation applied to OMC + AcOEt data at 308.15 K.

$$\sigma(V^{E}) = \sqrt{\frac{\sum (V^{E}_{\text{expt}} - V^{E}_{\text{calc}})^2}{D - N}}. \tag{7}$$

Table 3. Redlich–Kister regression results for the excess volumes of OMC + AcOEt mixtures at several temperatures in mole fraction.

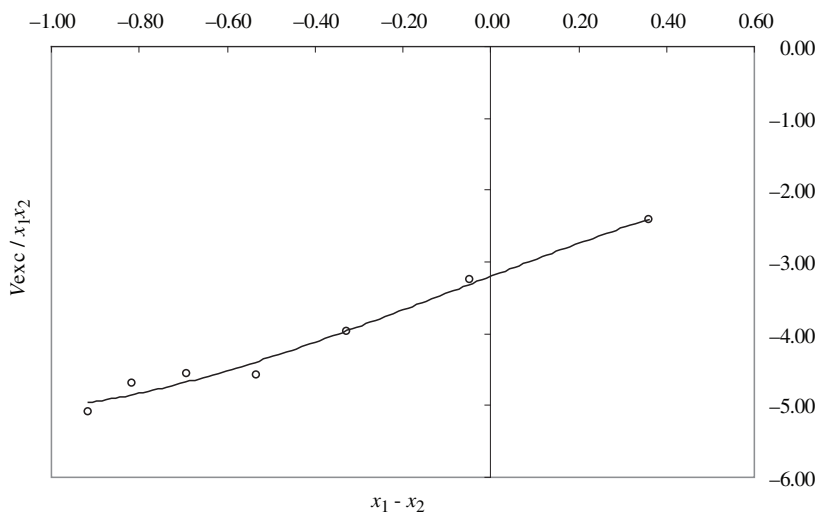| Temperature (K)	a_0	a_1	a_2	a_3	r^2	$\sigma(\mathrm{cm^3\,mol^{-1}})$
298.15	−2.9956	2.3101	−0.3362	−1.6430	0.9914	0.015
303.15	−3.0949	2.3451	−0.2362	−1.0194	0.9879	0.020
308.15	−3.2003	2.3443	−0.1330	−0.6468	0.9831	0.024
313.15	−3.2569	2.4113	−0.2740	−0.6514	0.9830	0.024
318.15	−3.2796	2.4656	−0.8706	−1.0992	0.9779	0.026

Figure 5. Regression at 308.15 K adjusted to Redlich–Kister equation using four terms for OMC + AcOEt mixtures with composition expressed in mole fraction.

At all the temperatures tested, the variation coefficients are greater than 0.98, which indicates that the obtained regular polynomials regressions describe adequately the excess volumes, because the SDs are similar to those presented in literature for other mixtures [8–10].

3.4. *Volume thermal expansion*

In pharmaceutical and cosmetic preformulation studies, it is very important to predict the variation of physicochemical properties related to commercial products, with respect to any change in temperature; in particular, those properties, which affect the concentration of active ingredients in the formulations to be developed. For this reason, the volume thermal expansion coefficients (α) were calculated by means of Equation 8 [18] by using the variation of molar volumes with temperature (Table 2).

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,x}. \tag{8}$$

Table 4. Volume thermal expansion coefficients of OMC + AcOEt mixtures at 308.15 K.

OMC			
Mass fraction	Mole fraction	$\partial V/\partial T(\text{cm}^3\,\text{mol}^{-1}\,\text{K}^{-1})$	α ($\times 10^{-3}\,\text{K}^{-1}$)
0.000	0.0000	0.1379	1.381
0.125	0.0415	0.1385	1.288
0.250	0.0918	0.1419	1.213
0.375	0.1540	0.1448	1.126
0.500	0.2328	0.1506	1.050
0.625	0.3358	0.1621	0.994
0.750	0.4765	0.1743	0.918
0.875	0.6799	0.1899	0.829
1.000	1.0000	0.2188	0.753

Table 4 summarises the $(\partial V/\partial T)$ and α values for all mixtures and pure solvents at 308.15 K. For all mixtures and pure solvents, linear models were used to correlate molar volumes and temperatures, obtaining determination coefficients greater than 0.999. The α values varied from $7.53 \times 10^{-4}\,\text{K}^{-1}$ in OMC up to $1.38 \times 10^{-3}\,\text{K}^{-1}$ in pure AcOEt.

4. Conclusions

This study presents experimental volumetric information about the OMC + AcOEt solvent system, which was not available earlier. As was said, this information could be employed in several engineering processes and for the theoretical understanding of the behaviour of solvent mixtures used in the chemical and pharmaceutical industries. In general terms, based on our results, it can be concluded that OMC + AcOEt mixtures show non-ideal behaviour with negative deviations in molar volume in all the compositions and temperatures tested, and thus, the partial molar volumes calculated for both components are lower than those obtained for the pure solvents. This behaviour is probably due to interactions such as dispersion forces between unlike molecules or some differences in the molar volumes of pure components. These observations demonstrate that it is necessary to systematically characterise this important binary system in order to have complete experimental information about the physical and chemical properties useful in the understanding of liquid pharmaceutical and cosmetic systems. It is important to keep in mind that the experimental information obtained for binary solvent mixtures could be employed to estimate the physicochemical behaviour of ternary and quaternary mixtures by means of theoretical methods such as the one described by Mehlman *et al.* [19] based on artificial neural networks, among others. Ultimately, based on thermophysical properties of liquids, Marcus [20] described some methods to understand the preferential solvation of biologically active solutes in binary solvent mixtures.

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