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MIXTURES FORMED OF ALKYL ACETATES WITH OLIVE OIL AT 298.15 K

Enthalpies of mixing and heat capacities

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Abstract

Enthalpies of mixing and heat capacities of the systems formed of alkyl acetates (ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate and isobutyl acetate) with olive oil were measured at 298.15 K. The mixing of acetates with the oil was strongly endothermic, and the highest measured enthalpies per mole of mixture were 2000 J mol^{-1} for ethyl acetate at an acetate mole fraction of 0.6. The heat capacities of the mixtures were calculated too and values were decreasing as the mole fraction of acetate increases and varied from 296 to 3929 J K^{-1} mol^{-1}.

Keywords: alkyl acetate, enthalpy of mixing, heat capacity, olive oil

Introduction

The heat involved in the mixing process of vegetable oils with several organic solvents shows interest for the oils extraction and refining industry. We are measuring several mixing properties on these systems in a more extensive work [1–5]. In this study, enthalpies of mixing and heat capacities of systems formed of alkyl acetates (ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, and isobutyl acetate) with olive oil at 298.15 K were measured over the whole concentration range. Although a great number of data of specific heats of pure oils or solvents appear in the literature [6–8], no experimental data of mixtures of olive oil with organic solvents have been found in the recent bibliography.

Experimental

Olive oil was supplied by Koipe and was characterized measuring its composition in fatty acids by GLC and other physico-chemical properties using standard Spanish procedures [9]. The results of this analysis appear in Table 1. Solvents were analyti-

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cal quality and were supplied by Fluka. The purities of the solvents were checked by comparing measured density and refractive index data with those reported in the literature [10], and are shown in Table 2. The calorimeter used to measure the change of temperatures on mixing was supplied by Phywe Systeme GMBH 04402.00, with a digital temperature meter with Pt100 probe. The experimental set up and procedure is similar to that described in Zijlema *et al*. [11]. In the measurement of the mixing enthalpies, known masses of component 1 are taken into the Dewar vessel and the needed quantity of component 2 is weighed in a sealed glass cell. Both components are heated until thermal equilibrium is attained at 298.15 K and it is maintained 30 min. After this, component 2 is mixed with component 1 in the Dewar vessel. To avoid mixing problems due to the high differences in viscosity of vegetable oil and acetates, a stirrer blade was inserted in the calorimeter for a perfect mixing of the reactants. The stirring was very intense at the first of the mixing. The heat due to stirring was measured and it was negligible at the short times of the experimental run. The temperature change accompanying the mixing process is sensed by a thermocouple. The accuracy in measuring the temperature was ±0.01 K. All experiments were carried out in a thermostated room which was kept at the same temperature of the experiment (298 K). The enthalpies of mixing and the specific heats were determined by heating the mixture with an electrical device, and measuring the electrical power needed to heat the mixture the same increase of temperature produced when component 1 and 2 were mixed. The electrical heat input was controlled by the power supply. The reliability of the apparatus and the method was established by measuring enthalpies of standard systems, that is, benzene+carbon tetrachloride and chlorobenzene+toluene at 298.15 K. Results were in good agreement with the reported data in the literature [12, 13]. The uncertainty in the measured enthalpies is ±1%.

Table 1 Physical properties of the used oil and solvents measured at 298.15 K

	Density ρ/g cm^{-3}		Refractive index n_D	
	This work	Ref. [10]	This work	Ref. [10]
Olive oil	0.90877	0.909–915^a [14]	1.46701	1.4677–1.4705^a [15]
Ethyl acetate	0.8943	0.89455	1.36968	1.36978
Propyl acetate	0.88206	0.88303	1.38172	1.3828
Isopropyl acetate	0.86645	0.8702	1.37462	1.375
Butyl acetate	0.87605	0.87636	1.39184	1.3918
Isobutyl acetate	0.86725	0.8677	1.38792	1.3880

a: literature data at 293.15 K

Experimental enthalpies of mixing was calculated through the electrical power from $P_{el}=VI$ in which V is the measured potential difference and I is the current through the Ni–Cr wire. An enthalpy balance could be set up for solution in the vessel during an experiment,

$$dH/dt=P_{el} \text{ with } dH=mc_{pm}\,dT \tag{1}$$

in which c_{pm} is the specific heat of mixing at constant pressure. These equations can be used for the calculation of the specific heat from the experimental data. All specific heats were determined in the temperature range 293–298 K at atmospheric pressure.

Table 2 Properties of the used olive oil

Olive oil	
Composition	12.4 palmitic; 2.8 stearic; 77.8 oleic; 7.0 linoleic
Acid value	0.27
Saponification value	189.6
Iodine value	79.6
Peroxide value	9.5
Wetness and volatiles	0.048

Results and discussion

The measured enthalpies of mixing, ΔH_m are plotted in Fig. 1 and the experimental values of the enthalpies, and the heat capacities of the mixtures appear in Table 3. Experimental data of enthalpies have been correlated as a function of composition using Redlich–Kister polynomials. The adjustable parameters A_k have been obtained by a least square method with all points weighted equally. The adjustable parameters and the standard deviation are listed in Table 4.

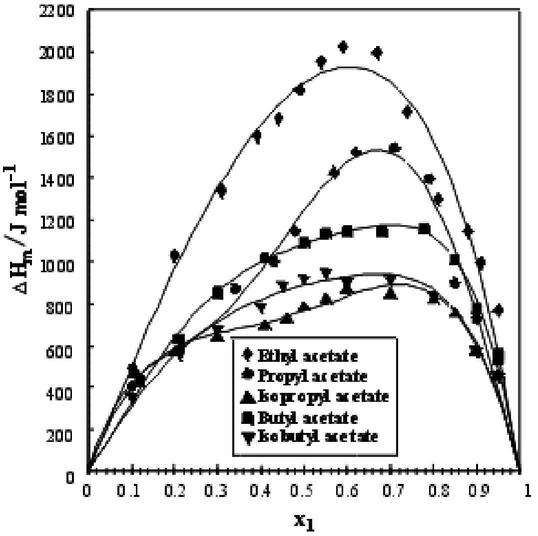

Fig. 1 Enthalpies of mixing of mixtures formed by alkyl acetates with olive oil along mole fraction of acetate at 298.15 K

Table 3 Experimental enthalpies of mixing and heat capacities of alkyl acetates–olive oil mixtures at 298.15 K

x_1	ΔH_m/J mol^{-1}	C_{pm}/J K^{-1} mol^{-1}
	Ethyl acetate–olive oil	
0.102	493.88	2599.35
0.199	1032.56	2458.47
0.310	1337.87	1911.24
0.392	1602.36	1820.86
0.443	1687.04	1653.96
0.491	1819.75	1542.16
0.538	1955.95	1427.70
0.593	2026.96	1299.33
0.674	1998.30	999.15
0.741	1715.44	689.22
0.808	1298.98	548.09
0.877	1145.89	375.70
0.910	996.49	286.35
0.951	766.66	296.01
	Propyl acetate–olive oil	
0.101	405.54	2896.69
0.213	590.58	2271.45
0.344	871.05	1814.69
0.430	999.77	1538.10
0.478	1145.84	1432.30
0.571	1424.48	1499.46
0.623	1522.09	1323.56
0.710	1544.22	989.89
0.793	1395.41	734.43
0.849	897.91	513.09
0.901	729.41	426.56
0.952	524.16	331.74
	Isopropyl acetate–olive oil	
0.119	432.46	3326.63
0.210	629.06	2246.65
0.299	855.55	1989.65
0.412	1018.45	1591.33
0.483	1051.68	1282.54
0.554	1133.47	1122.25
0.605	1145.05	1031.58

Table 3 Continued

x_1	ΔH_m/J mol^{-1}	C_{pm}/J K^{-1} mol^{-1}
0.682	1146.11	818.65
0.783	1157.99	636.26
0.852	1009.63	520.43
0.904	774.82	425.72
0.948	561.60	330.35
	Butyl acetate–olive oil	
0.113	466.07	2912.94
0.202	570.61	2113.38
0.305	638.91	2203.14
0.414	698.57	1486.33
0.462	730.46	1490.74
0.501	784.50	1352.58
0.550	822.19	1284.67
0.599	866.81	1155.74
0.703	848.13	883.47
0.797	820.64	631.26
0.848	751.93	592.07
0.900	571.34	468.31
0.946	455.29	385.84
	Isobutyl acetate–olive oil	
0.098	353.65	3929.50
0.212	560.49	2668.99
0.301	676.96	2115.51
0.398	787.25	1675.01
0.447	886.74	1528.87
0.501	923.17	1442.46
0.553	950.77	1267.69
0.599	904.61	1051.87
0.704	920.49	885.09
0.802	839.07	660.69
0.898	583.41	422.76
0.950	458.79	367.03

Table 4 Least-square parameters A_k and standard deviations σ of acetate–olive oil mixtures at 298.15 K

	A_1	A_2	A_3	A_4	σ/J mol^{-1}
Ethyl acetate	7415.44	–2818.99	1460.87	–1040.87	99.99
Propyl acetate	4977.35	–5530.29	2370.73	5070.86	69.08
Isopropyl acetate	4339.07	–1378.75	3194.98	–3115.34	28.88
Butyl acetate	3052.81	–1337.00	3947.41	–17.56	36.38
Isobutyl acetate	3546.37	–1095.47	2467.29	–1499.05	40.71

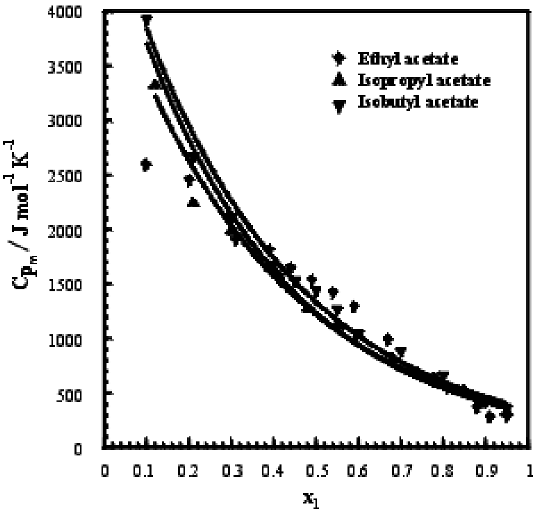

Fig. 2 Heat capacities of mixtures of ethyl acetate, isopropyl acetate, and isobutyl acetate with olive oil along mole fraction of acetate at 298.15 K

Enthalpies of mixing were positive over the entire composition range, illustrating the expenditure of extra energy for breaking the intermolecular association of acetate in order to homogenize it with the weakly polar oil. In the alkyl acetates the interaction between molecules is a dipole-dipole one, and when the molecules are mixed with a weakly polar oil, the bonds are replace by lower interactions and consequently, enthalpies of mixing are positive. The highest measured enthalpies of mixing were 2000 J mol^{-1} for ethyl acetate at an acetate mole fraction of 0.6. Values of enthalpy decreases with the size of acetate molecule, due to a better molecular package related to the decreasing interaction forces in the series of acetates: ethyl>propyl>isopropyl>butyl>isobutyl. From experimental data, the heat capacities of the mixtures were calculated too. Values were decreasing exponentially as the mole fraction of acetate increases (Fig. 2) and varied from 296 to 3929 J mol^{-1} K^{-1}. Values at low concentrations of solvent are not very accurate due to the low experimental ΔT obtained.

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