Enthalpies of Mixing and Heat Capacities of Mixtures Containing Alcohols and *n*-Alkanes with Corn Oil at 298.15 K

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ABSTRACT: Enthalpies of mixing for mixtures containing alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol) plus corn oil or *n*-alkanes (*n*-hexane, *n*-heptane, and *n*-octane) plus corn oil were measured at 298.15 K and atmospheric conditions. The enthalpy was measured in the range of concentrations in which alcohols were miscible with the vegetable oil. Results were correlated by the Redlich–Kister equation. The mixing of alcohols with corn oil was strongly endothermic, whereas values obtained for the binaries containing *n*-alkanes were slightly endothermic. Thus, heat capacities were calculated for all the systems studied.

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KEY WORDS: Alcohol, *n*-alkane, corn oil, enthalpy of mixing, heat capacity, mixtures.

Edible oils are important components of the diet and also provide characteristic flavors and textures to foods. During extraction, purification, and usage, oils undergo a variety of processing operations, including frying, distillation, and chemical modification, which may alter their properties. Prediction of the behavior of oils under real processing conditions is possible by measuring bulk properties such as density, viscosity, speed of sound, and so on, which are related to industrial processes by semiempirical equations. Such properties of edible oils depend on the composition and temperature. Studies related to oil technology and to the technologies used in the processing of high-quality edible oils utilize organic solvents for extraction and refining.

In the last few years considerable work has been done in the field of calorimetry to investigate the thermodynamic properties of oils and their mixtures with different solvents. Knowledge of the heat involved in the mixing process of organic solvents with vegetable oils is useful for designing equipment for the extraction and refining of edible oils. When solvents are mixed with the oil, a heat of solution is involved. In these cases, a loss of heat usually takes place, an endothermic effect that is a consequence of the interaction between oil and solvent molecules.

This study is part of a more extensive project in which different physicochemical properties of mixtures formed by organic solvents with vegetable oils are being measured (González and colleagues, Refs. 1–5). In this study, the enthalpy of mixing of systems composed of alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol) or *n*-alkanes (*n*-hexane, *n*-heptane, and *n*-octane) with corn oil were measured at 298.15 K and at atmospheric pressure. For some of the alcohols, immiscibility occurs at certain composition values; hence, enthalpies of mixing were measured in the concentration ranges at which both components were miscible. Heat capacities were also calculated using the experimental values of the enthalpies of mixing. Several studies by different authors [Kowalski (6), Tan and Che Man (7), Morad *et al.* (8), and Coupland and McClements (9)] have involved the heat capacities of pure vegetable oils (usually determined by DSC), and data on the heat capacities of pure FA and their binary and ternary mixtures have been determined by Cedeño *et al.* (10).

MATERIAL AND METHODS

Reactives. Chemicals were supplied by Panreac (Barcelona, Spain), except 2-propanol, which was supplied by Prolabo (Fontenay, France). Before measurement, pure solvents were degassed by ultrasound, kept in dark bottles, and dried over molecular sieves (type 3a, 1/16 in.; Fluka, Buchs, Switzerland).

Corn oil was supplied by Koipe (Jaén, Spain), and the FA composition was analyzed using a Shimadzu model GC-14B gas chromatograph (Kyoto, Japan) equipped with an FID. The chromatographic technique and the chemical procedure for the preparation of FAME were described in a previous study (1). The oil composition obtained *via* GC analysis is shown in Table 1 and compared with literature values. The uncertainty of the data in this table is ±0.1 mol%. From the experimental composition, the average molar mass (M_w) of corn oil was calculated as $M_w = 872.08 \pm 0.05\ \text{g}\cdot\text{mol}^{-1}$. Differences between the experimental composition data and that supplied by other authors were due to factors such as seed origin, type of farming, soil conditions, climate, and method used to obtain the oil. Other characteristics of the oil such as acid value, saponification value, iodine value, PV, and moisture content and volatiles also were measured following standard Spanish procedures (Unified Spanish Rules, see Ref. 16). The results are presented in Table 2 along with those reported in the literature.

Preparation and procedures. To determinate the mixing enthalpy of the mixtures, all experiments were carried out using a

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TABLE 1
FA Composition of Corn Oil (mol%)

FA	Palmitic	Stearic	Arachidic	Oleic	Linoleic	Linolenic
Experimental	11.97	2.34	0.77	29.09	54.97	0.86
Literature (11)	13.6	1.7	—	37.2	45.6	0.6
Literature (12)	15.71	3.12	—	36.45	43.83	0.42
Literature (12)	12.89	2.62	—	35.63	48.85	—
Literature (12)	11.75	3.54	—	40.07	44.65	—
Literature (12)	15.49	2.40	—	34.64	47.47	—
Literature (12)	11.45	3.12	—	38.02	47.44	—
Literature (13)	10.7	2.4	<1.0	27.1	55.8	1.0
Literature (14)	11	2	—	28	58	1
Literature (15)	13	3	—	31	52	1
Literature (16)	9–17	1–3	<1.0	22–40	45–65	<1.5
Literature (17)	8–13	1–4	—	24–32	55–62	<2

Dewar calorimeter and associated equipment (the whole set supplied by Phywe Systeme Gmbh, Göttingen, Germany). The experimental setup and procedure were similar to that of Zijlema *et al.* (18), as described in detail by Resa *et al.* (5). For weighing the individual components of these mixtures, a Model HF-20006 AND (Oxford, United Kingdom) electronic balance with an accuracy of $\pm 2\cdot 10^{-3}$ g was used, taking care that no solvent evaporation occurred. The accuracy of temperature measurements was ±0.01 K. The reliability of the apparatus and the method were established by measuring the enthalpies of standard systems, that is, benzene + carbon tetrachloride and chlorobenzene + toluene, at 298.15 K. Results were in good agreement with data reported in the literature [*cf.* Nicolaides and Eckert (19) and Tanaka and Benson (20)]. The uncertainty in the measured enthalpies was ±1%.

Determination of ΔH^m *and* C_p^m. When n_1 mol of component 1 (organic solvent) was mixed with n_2 mol of component 2 (corn oil), a temperature change was observed ($\Delta T_{\exp}$) because of the interactions between liquids. Heat was added as electrical power (W_{el}) to the mixture to produce a temperature increase (ΔT_{ind}) as close as possible to the experimental value. Experimental enthalpies of mixing (Δh^m) were calculated as follows:

$$\Delta h^m = Q_{\exp} = W_{el} \cdot \left(\frac{\Delta T_{\exp}}{\Delta T_{ind}} \right) \tag{1}$$

The molar enthalpy of mixing, ΔH^m, is given as

$$\Delta H^m = \frac{\Delta h^m}{n_1 + n_2} \tag{2}$$

Heat capacities of the mixtures can be calculated using Equation 3:

$$\Delta H^m = C_p{}^m \cdot (T_2 - T_1) = C_p{}^m \cdot \Delta T_{\exp} \quad \text{or} \quad C_p{}^m = \frac{\Delta H^m}{\Delta T_{\exp}} \tag{3}$$

RESULTS AND DISCUSSION

Molar enthalpies of mixing. The change in enthalpy observed when two liquids are mixed is the sum of the changes in enthalpy that occur during the mixing process. The mixing enthalpy, ΔH^m, is influenced by the interactions of all the molecules involved, which in turn are a function of the mixing ratio. The enthalpy of mixing is zero if there are no interactions between the molecules (so-called ideal mixtures). Tables 3 and 4 report experimental molar enthalpies of mixing, ΔH^m, and calculated heat capacities of mixing $\Delta C_p{}^m$, for the binary system. Experimental data for the enthalpies of mixing were fitted as a function of composition using the Redlich–Kister polynomial (21):

$$\Delta H^m = x_1 x_2 \sum_{k \geq 0} A_k (x_1 - x_2)^k \tag{4}$$

$$\sigma = \left(\frac{\Sigma(\Delta H_{calc} - \Delta H_{\exp})^2}{n} \right)^{1/2} \tag{5}$$

where ΔH^m is the enthalpy of mixing, x_1 and x_2 are mole fractions of the organic solvent and oil, and A_k are the fitting parameters. The values of A_k were obtained by a least squares method with all points weighted equally. The parameters A_k

TABLE 2
Properties of Corn Oil

Property	Experimental	Literature (13)	Literature (15)	Literature (16)	Literature (17)
Acid value	0.14			<0.2	
PV	9.2			<10	
Wetness and volatiles	0.04			<0.1	<0.1
Saponification value	198	190	187–195	187–195	187–195
Iodine value	123.7	120	107–128	100–135	103–128

TABLE 3
Experimental Enthalpies of Mixing (H^m) and Calculated Heat Capacities ($C_p{}^m$) of the Studied Mixtures (alcohols + corn oil) at 298.15 K as a Function of the Solvent Molar Fraction (x_1)

x_1	ΔH^m (J/mol)	$C_p{}^m$ (J/mol°C)	x_1	ΔH^m (J/mol)	$C_p{}^m$ (J/mol°C)
		Methanol + corn oil			
0.087	1113.9	2931.4	0.378	2273.1	1313.9
0.134	1194.3	2024.2	0.409	2425.4	1283.3
0.190	1502.6	1788.8	0.452	2581.0	1252.9
0.234	1833.5	1682.1	0.499	2555.3	1145.9
0.277	1870.1	1461.0	0.547	2313.7	956.1
0.329	2187.6	1448.7			
		Ethanol + corn oil			
0.107	1421.0	2329.5	0.506	2802.4	1094.7
0.215	2008.8	1716.9	0.560	2783.2	1004.8
0.319	2396.0	1409.4	0.638	2596.9	835.0
0.401	2697.5	1309.4	0.702	2430.9	727.8
0.416	2740.7	1274.7	0.750	2179.8	631.8
0.451	2834.1	1232.2			
		1-Propanol + corn oil			
0.064	1067.4	3049.8	0.510	3078.2	1107.3
0.126	1459.3	2146.1	0.553	3028.1	1033.5
0.221	2165.8	1820.0	0.637	2869.4	856.6
0.309	2709.8	1566.4	0.700	2688.0	744.6
0.404	2928.2	1337.1	0.799	2239.9	554.4
0.453	3062.8	1240.0	0.850	1929.8	478.9
		2-Propanol + corn oil			
0.106	1128.3	1849.7	0.699	3145.0	768.9
0.211	2133.1	1734.2	0.749	2858.7	660.2
0.313	2688.5	1477.2	0.800	2549.8	565.4
0.409	3061.6	1314.0	0.850	2176.2	468.0
0.497	3215.1	1116.3	0.898	1627.2	375.8
0.601	3289.0	939.7			
		1-Butanol + corn oil			
0.107	1275.4	2237.5	0.550	2984.4	1032.7
0.224	2124.0	1741.0	0.604	3002.1	950.0
0.307	2560.1	1505.9	0.702	2689.5	755.5
0.411	2839.8	1296.7	0.801	2251.7	586.4
0.463	2952.9	1210.2	0.900	1493.6	391.0
0.500	2949.6	1125.8	0.950	1043.4	303.3
		2-Butanol + corn oil			
0.107	1102.5	1807.3	0.557	3419.5	1005.8
0.203	1920.3	1561.2	0.600	3471.8	928.3
0.303	2623.6	1433.6	0.701	3334.5	756.1
0.400	3066.5	1226.6	0.800	2821.9	583.0
0.451	3332.0	1185.8	0.850	2392.2	486.2
0.501	3409.9	1079.1	0.949	1428.3	318.8

and the SD σ, calculated with Equation 5, are listed in Table 5. Figures 1 and 2 show experimental and correlated values of ΔH^m as a function of the solvent molar fraction for mixtures of alcohols or *n*-alkanes with corn oil, respectively.

Molar heat capacities of mixing. $C_p{}^m$ values were obtained with Equation 3 using enthalpy data and were calculated as a function of composition using an exponential equation for mixtures involving alcohols (Eq. 6), and a linear equation for those containing *n*-alkanes (Eq. 7):

$$C_p{}^m = b \cdot e^{a \cdot x_1} \qquad [6]$$

$$C_p{}^m = a \cdot x_1 + b \qquad [7]$$

The values of the constants *a* and *b* for the studied mixtures are given in Table 6.

For some concentrations, alcohols were not miscible with oil, so the enthalpy was measured only for soluble mixtures (Fig. 1). The results showed high enthalpies of mixing, depending on the concentration. The maximum appeared for 0.55–0.60 mol fractions of alcohol in oil. Alcohols are polar molecules that form hydrogen bonds among themselves, whereas vegetable oils are triesters of glycerol having constituent

TABLE 4
Experimental Enthalpies of Mixing (H^m) and Calculated Heat Capacities (C_p^m) of the Studied Mixtures (*n*-alkanes + corn oil) at 298.15 K, as a Function of the Solvent Molar Fraction (x_1)

x_1	ΔH^m (J/mol)	C_p^m (J/mol°C)	x_1	ΔH^m (J/mol)	C_p^m (J/mol°C)
		n-Hexane + corn oil			
0.160	176.2	1602.1	0.643	508.8	848.0
0.310	282.0	1343.0	0.701	513.2	703.0
0.393	336.0	1199.9	0.798	459.5	560.4
0.450	386.7	1104.8	0.901	377.4	373.6
0.502	421.0	1026.8	0.952	331.8	301.6
0.550	472.0	943.9			
		n-Heptane + corn oil			
0.102	82.0	1639.8	0.594	465.0	894.2
0.202	182.4	1520.3	0.651	499.9	819.5
0.303	247.1	1300.7	0.718	517.1	708.4
0.400	353.4	1178.1	0.797	493.6	567.3
0.502	412.8	1032.0	0.900	423.3	419.1
0.549	444.2	945.2	0.949	338.4	341.8
		n-Octane + corn oil			
0.101	69.6	1739.1	0.602	528.6	911.4
0.191	175.4	1594.8	0.698	573.6	764.8
0.292	256.8	1426.6	0.798	539.4	606.1
0.409	361.0	1164.5	0.900	425.8	443.5
0.503	461.3	1072.8			

TABLE 5
Fitting Parameters (A_k) of Equation 7 and SD (σ) for the Studied Mixtures (organic solvents + corn oil) at 298.15 K

Solvent	A_0	A_1	A_2	A_3	A_4	A_5	σ (J·mol^{-1})
Methanol	10072.51	−4175.05	−25746.46	−30316.02			64.9
Ethanol	11335.15	253.90	−2409.03	118.84	13854.63		23.4
1-Propanol	12143.75	603.15	4196.31				73.4
2-Propanol	13033.30	2981.94	3465.71				40.0
1-Butanol	11815.95	1653.04	4999.46				76.0
2-Butanol	13489.38	2895.30	4320.46	6194.87			95.3
n-Hexane	1760.59	1384.12	−813.03	413.66	4972.80		26.2
n-Heptane	1668.43	1558.90	449.52	−1354.87	2276.19	4491.50	13.2
n-Octane	1811.91	1602.94	958.59	1138.74	797.90		10.5

FA. The endothermic effect observed in all cases can be explained as a consequence of the disruption of hydrogen bonding among alcohol molecules, augmented by a dipole–dipole type among alcohols and the triesters of the oil. A positive ΔH^m suggests that the overall amount of interaction diminished upon mixing. Upon increasing the length of the alcohol, an increase in ΔH^m is clearly observed.

Mixtures of *n*-alkanes with corn oil showed the same trend (Fig. 2), i.e., an endothermic effect that increased with the size of the alkane. Maximal ΔH^m obtained for the curves of methanol and 2-butanol were 2581 and 3472 J·mol^{-1}, respectively. Comparing these values with the maximal ΔH^m observed for *n*-octane mixtures, 574 J·mol^{-1}, we concluded that the absorption of energy of the hydrocarbons was very small. These kinds of molecules are very apolar and are bonded by very weak London forces. They had no tendency to establish new bonds with the polar groups of the oil molecules and long hydrocarbon chains of the triesters.

The evolution of heat capacities of the mixtures as a function of mole fraction for alcohols or *n*-alkanes with corn oil is plotted in Figures 3 and 4. Note that very few differences

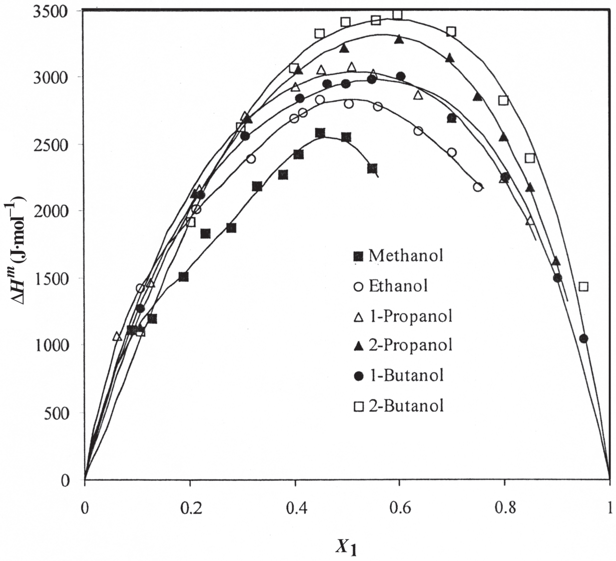

FIG. 1. Enthalpies of mixing (H^m) of the alcohol–corn oil mixtures vs. the mole fraction of alcohol at 298.15 K. Lines represent best fit to Equation 4.

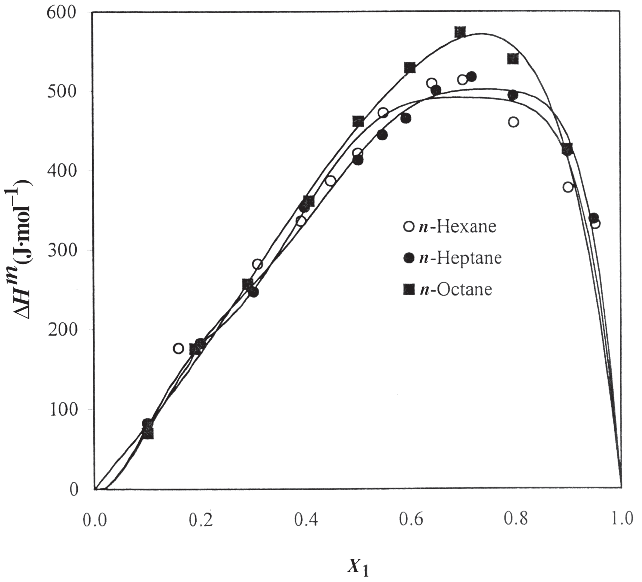

FIG. 2. Enthalpies of mixing (H^m) of the *n*-alkane–corn oil mixtures vs. the mole fraction of *n*-alkane at 298.15 K. Lines represent best fit to Equation 4.

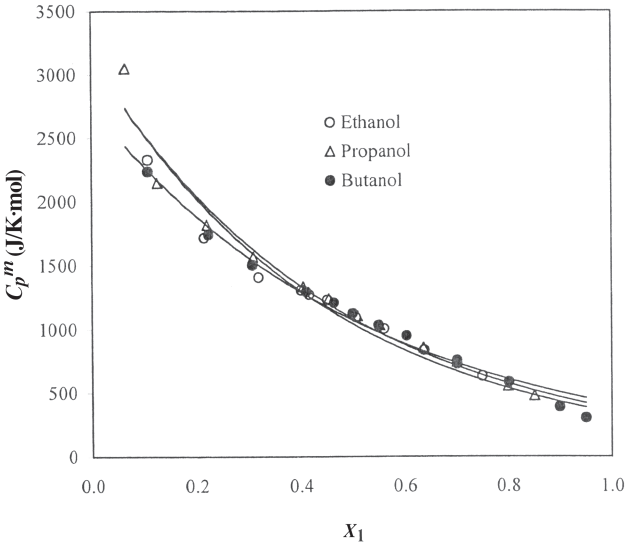

FIG. 3. Heat capacities of mixing (C_p^m) for the binary systems alcohol + corn oil as function of the alcohol mole fraction at 298.15 K.

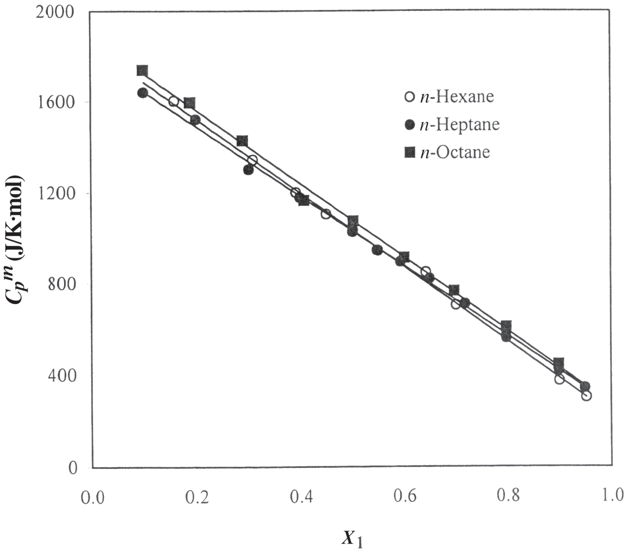

FIG. 4. Heat capacities of mixing (C_p^m) for the binary systems *n*-alkane + corn oil as function of the *n*-alkane mole fraction at 298.15 K.

between the different alcohols were observed. The trend in heat capacities with composition for the studied mixtures did not vary with the type of alcohol or *n*-alkane.

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TABLE 6
Fitting Parameters (*a, b*) of Heat Capacities–Mole Fraction of Solvent for Systems [alcohols + corn oil (Eq. 9) and *n*-alkanes + corn oil (Eq. 10)] and Their Regression Coefficients (*r*)

	a	*b*	*r*
Methanol	−1.934	2795.7	0.954
Ethanol	−1.883	2750.1	0.993
1-Propanol	−2.115	3128.9	0.992
2-Propanol	−1.956	2689.4	0.978
1-Butanol	−2.212	3155.6	0.980
2-Butanol	−1.905	2570.7	0.969
n-Hexane	−1625.7	1849.9	0.999
n-Heptane	−1531.3	1798	0.999
n-Octane	−1617.1	1887.7	0.998

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