Experimental and Predicted Enthalpies of Mixing of Mixtures Formed from Alcohols and Sunflower Oil at 298.15 K

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ABSTRACT: The enthalpies of mixing of systems formed from alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol) and sunflower oil at 298.15 K are presented. Enthalpies were measured in the composition range in which the compounds were miscible. From the experimental measurements, we calculated the heat capacities of the mixtures. Several group contribution models were applied to estimate the enthalpies of mixing of these mixtures. The average deviations varied from 10 to 60%, depending on the model and compound. The best prediction in all cases was the Nitta model, with average deviations from 10 to 30%. The novelty of the work is that models of this type have not been applied previously to predict enthalpies of such large molecules, and the results of the estimates are of the same order as other types of compounds (pure compounds of small size).

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KEY WORDS: Alcohol, enthalpies of mixing, group contribution method, prediction, sunflower oil.

Recently, we have been interested mainly in studying the mixing properties of mixtures involving organic solvents with vegetable oils (1–8). The present work is part of a series in which enthalpies of mixing of the mentioned compounds are measured. When experimental data are missing, group-contribution methods can be successfully applied to predict important properties such as enthalpies, vapor–liquid equilibria, and density. In group-contribution methods, it is assumed that the mixture consists not of molecules but of functional groups. Different group-contribution methods, such as the analytical solution of groups (ASOG) (9) and universal quasi-chemical functional group activity coefficients (UNIFAC) (10), have been suggested. In both methods, the required activity coefficient is calculated by a combinatorial and a residual part. The UNIFAC method shows some weakness because poor results are obtained with compounds that are very different in size. To eliminate most of the mentioned weaknesses, some modifications of the UNIFAC method have been developed [see Dang and Tassios (10), Larsen *et al.* (11), and Weidlich and Gmehling (12)]. The UNIFAC group-contribution model was originally developed by Fredenslund *et al.* (13) using the universal quasi-chemical (UNIQUAC) equation by Abrams and Prausnitz (14). The activity coefficients in this model are calculated as the addition of two terms. The first one is combinatorial and takes into account the differences in shape and size of the molecules. The second one is a residual term describing the energetic interactions present in the mixture. The adjustable parameters in this model are the energetic interaction parameters between groups. Dang and Tassios (10) modified the original model, and their version is focused only on excess molar enthalpy estimations. In the version of Larsen *et al.* (11), the interaction parameters become temperature dependent, and the combinatorial term is modified. As a result, this version can predict other properties, such as Gibbs potential and phase equilibria. Weidlich and Gmehling (12) also modified the temperature dependence of the parameters, recalculated interaction parameters using a wider database, and fitted them simultaneously to liquid–liquid and vapor–liquid equilibria, excess enthalpies, and infinite dilution activity coefficients. For every version of the UNIFAC model, the parameters used in this work for estimation were those provided by the authors in the original works, except those of the Gmehling version of UNIFAC, which were presented in a later work (15). These methods have been used in the literature to predict enthalpies of binary systems formed by pure compounds and molecules of small size. In this work, we have tested these methods with very large molecules, such as oil, and their interaction with small ones, such as alcohols.

The Nitta–Chao group-contribution model (16) is based on the cell theory for thermodynamic properties of polar and nonpolar liquids and their solutions, including excess properties, activity coefficients, and PVT relations. The model applies the cell theory introduced by Flory *et al.* (17), in which the repulsive forces between molecules are expressed by means of a cell partition function, derived from the rigid spheres equation of state by Carnahan and Starling (18), as well as the quasi-chemical approximation of Guggenheim (19).

The objective of this work was to test all these methods to predict the enthalpies of alcohol–sunflower oil systems. The enthalpies of mixing are important in the oil industry for designing equipment such as tubing, mixers, and so on. We report the enthalpies of mixing and heat capacities of mixtures of methanol,

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ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol with sunflower oil at 298.15 K. The UNIFAC model [in the versions of Dang and Tassios (10), Larsen *et al.* (11), and Weidlich and Gmehling (12)] and the Nitta *et al*. model (16) were used to estimate the experimental enthalpies. No previous work predicts the enthalpies of mixing of those types of mixtures.

EXPERIMENTAL PROCEDURES

Commercially refined sunflower oil was supplied by Koipesol (Jaén, Spain). It was characterized by measuring its composition in FA by GLC and by other physicochemical properties. The FA composition was analyzed by means of a Shimadzu 4B gas chromatograph equipped with a flame detector. Before introducing the oil in the column, FA were converted into methyl esters by sodium methanoate and extracted with hexane. The chromatographic technique and the chemical procedure for the preparation of FA were described in a previous work (2). The uncertainty in mol% for these results was less than 0.1%. Other characteristics of the oils—acid value, saponification value, iodine value, PV, and wetness and volatiles—also were measured. These were analyzed following standard Spanish procedures (14), and the values obtained are as follows: composition (%), 8.4 palmitic, 3.9 stearic, 28.9 oleic, 58.3 linoleic, and 0.5 linolenic; acid value, 0.148; saponification value, 190.3; iodine value, 125; PV, 13.4; wetness and volatiles, 0.0098. Alcohols were of analytical quality, supplied by Fluka (Buchs, Switzerland), and their measured physical properties (density and refractive indices) along with literature values appear in Table 1.

The calorimeter used to measure the change of temperatures on mixing was supplied by Phywe Systeme GmbH (04402.00; Göttingen, Germany) and included a digital temperature meter with a Pt100 probe. The experimental setup and procedure were similar to those described in Zijlema *et al.* (20). To measure the mixing enthalpies, a known mass of component 1 was placed in the Dewar vessel and the needed quantity of component 2 was weighed in a sealed glass cell. Both components were heated until thermal equilibrium was attained at 298.15 K; it was maintained for 30 min. After this, component 2 was mixed with component 1 in the Dewar vessel. The temperature change accompanying the mixing process was sensed by a thermocouple. The accuracy in measuring the temperature was ±0.01 K. All experiments were carried out in a temperature-controlled room that was kept at the same temperature as the experiment (298 K). The enthalpies of mixing and the heat capacities were determined by heating the mixture with an electrical device and then measuring the electrical power needed to heat the mixture through the same increase of temperature produced when components 1 and 2 were mixed. The electrical heat input was controlled by the power supply. Experimental enthalpies of mixing were calculated from the electrical power as $P_{el} = V \cdot I$ 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 the solution in the vessel during an experiment,

$$\Delta H/\Delta t = P_{el} \tag{1}$$

with

$$\Delta H = m\, c_{pm}\, \Delta T \tag{2}$$

in which c_{pm} is the heat capacity of the mixture at constant pressure. These equations can be used to calculate the heat capacity from the experimental data. All heat capacities were determined in the temperature range of 293–298 K at atmospheric pressure. The uncertainty in the measured enthalpies was ±1%.

RESULTS AND DISCUSSION

Table 2 lists the measured molar enthalpies of mixing at 298.15 K, ΔH_m exp., and predicted enthalpies based on the models developed by Dang and Tassios (ΔH_m Dang), Larsen *et al.* (ΔH_m Larsen), Weidlich and Gmeling (ΔH_m Weidlich), and Nitta *et al.* (ΔH_m Nitta). The deviations among experimental and predicted enthalpies for each point for the different models are included as well as the average deviation for the system. Table 3 reports the calculated heat capacities of mixing for the binary systems from enthalpy data. Experimental enthalpy data vs. composition were fitted to Redlich–Kister polynomials (21) of the form

$$\Delta H_m = x_1 x_2 \sum_{k\geq 0} a_k (x_1 - x_2)^k \tag{3}$$

where x_1 is the mole fraction of alcohol, x_2 is the mole fraction of the oil, a_k are the adjustable parameters obtained by a least

TABLE 1
Physical Properties of the Oil and Solvents Used, Measured at 298.15 K

	Density/g·cm^{-3}		Refractive index	
	Exp.	Lit.[a]	Exp.	Lit.[a]
Sunflower oil	0.91545	0.920–925[b]	1.47244	1.472–74[c]
Methanol	0.78660	0.78637	1.32644	1.32652
Ethanol	0.78521	0.78493	1.35923	1.35941
1-Propanol	0.79950	0.79960	1.38304	1.38370
2-Propanol	0.78079	0.78126	1.37486	1.37520
1-Butanol	0.80644	0.80575	1.39703	1.39741
2-Butanol	0.80250	0.80241	1.39506	1.39530

[a] From Riddick *et al.* (22).
[b] At 293.15 K (Ref. 23).
[c] Reference 24.

TABLE 2
Experimental, Predicted Enthalpies of Mixing (several models)[a], and Deviations Among Experimental and Predicted Enthalpies of Alcohols with Sunflower Oil at 298.15 K

x_1	ΔH_m (J·mol^{-1}) exp.	ΔH_m (J·mol^{-1}) Dang	Dev. (%)	ΔH_m (J·mol^{-1}) Larsen	Dev. (%)	ΔH_m (J·mol^{-1}) Weidlich	Dev. (%)	ΔH_m (J·mol^{-1}) Nitta	Dev. (%)
				Methanol					
0.110	1061	2103	98.3	618	41.7	818	22.9	810	23.7
0.202	1780	2978	67.3	1060	40.5	1414	20.6	1406	21.0
0.319	2243	3548	58.2	1508	32.8	2038	9.1	2043	8.9
0.413	2455	3697	50.6	1760	28.3	2412	1.8	2437	0.7
0.458	2484	3691	48.6	1843	25.8	2545	2.4	2582	3.9
0.511	2563	3627	41.5	1904	25.7	2659	3.8	2715	5.9
		Av. dev. (%)	60.8	Av. dev. (%)	32.5	Av. dev. (%)	10.1	Av. dev. (%)	10.7
				Ethanol					
0.113	1245	2333	87.4	630	49.4	795	36.1	789	36.7
0.204	1931	3255	68.6	1063	45.0	1349	30.2	1345	30.3
0.311	2434	3825	57.2	1473	39.5	1884	22.6	1893	22.2
0.410	2707	4003	47.9	1744	35.6	2251	16.8	2284	15.6
0.448	2838	3999	40.9	1816	36.0	2355	17.0	2401	15.4
0.511	2879	3918	36.1	1894	34.2	2476	14.0	2544	11.6
0.547	2859	3831	34.0	1913	33.1	2514	12.1	2597	9.2
0.602	2696	3647	35.3	1902	29.4	2526	6.3	2635	2.3
0.704	2440	3146	28.9	1743	28.6	2375	2.7	2532	3.8
0.803	1808	2458	35.9	1388	23.2	1974	9.2	2161	19.5
		Av. dev. (%)	47.2	Av. dev. (%)	35.4	Av. dev. (%)	16.7	Av. dev. (%)	16.7
				1-Propanol					
0.105	1100	2414	119.4	588	46.5	723	34.3	716	35.0
0.204	1899	3544	86.7	1062	44.1	1310	31.0	1303	31.4
0.311	2598	4170	60.5	1472	43.3	1827	29.7	1834	29.4
0.403	2794	4364	56.2	1728	38.1	2158	22.8	2184	21.8
0.449	2911	4364	49.9	1818	37.5	2279	21.7	2319	20.4
0.502	3030	4294	41.7	1887	37.7	2377	21.5	2437	19.6
0.568	3012	4111	36.5	1917	36.4	2432	19.3	2521	16.3
0.626	3038	3868	27.3	1885	37.9	2411	20.6	2528	16.8
0.701	2704	3443	27.3	1757	35.0	2277	15.8	2432	10.1
0.800	2211	2683	21.3	1413	36.1	1882	14.9	2073	6.2
0.847	1875	2232	19.0	1171	37.6	1591	15.2	1786	4.8
		Av. dev. (%)	49.6	Av. dev. (%)	39.1	Av. dev. (%)	22.4	Av. dev. (%)	19.2
				2-Propanol					
0.103	1166	2510	115.2	580	50.3	710	39.1	756	35.2
0.154	1680	3229	92.2	837	50.2	1026	38.9	1099	34.6
0.200	2053	3716	81.0	1049	48.9	1289	37.2	1385	32.5
0.249	2377	4103	72.6	1254	47.2	1544	35.1	1666	29.9
0.302	2801	4393	56.8	1450	48.2	1789	36.1	1943	30.6
0.347	2980	4552	52.8	1593	46.5	1970	33.9	2151	27.8
0.401	3112	4650	49.4	1735	44.3	2152	30.8	2369	23.9
0.446	3226	4662	44.5	1826	43.4	2272	29.6	2521	21.9
0.504	3407	4592	34.8	1904	44.1	2380	30.2	2668	21.7
0.553	3298	4465	35.4	1933	41.4	2426	26.4	2751	16.6
0.602	3273	4278	30.7	1925	41.2	2428	25.8	2787	14.8
0.648	3222	4050	25.7	1881	41.6	2385	26.0	2776	13.9
0.699	3091	3738	20.9	1787	42.2	2282	26.2	2703	12.6
0.751	2783	3353	20.4	1638	41.1	2111	24.1	2552	8.3
0.803	2590	2895	11.8	1430	44.8	1865	28.0	2308	10.9
0.847	2227	2442	9.7	1204	45.9	1591	28.6	2015	9.5
		Av. dev. (%)	47.1	Av. dev. (%)	45.1	Av. dev. (%)	31.0	Av. dev. (%)	21.5

(Continued)

TABLE 2 (Continued)

x_1	ΔH_m (J·mol^{-1}) exp.	ΔH_m (J·mol^{-1}) Dang	Dev. (%)	ΔH_m (J·mol^{-1}) Larsen	Dev. (%)	ΔH_m (J·mol^{-1}) Weidlich	Dev. (%)	ΔH_m (J·mol^{-1}) Nitta	Dev. (%)
				1-Butanol					
0.064	626	1683	168.9	369	41.0	442	29.4	439	29.9
0.110	1229	2446	99.0	615	50.0	737	40.0	735	40.2
0.203	2021	3467	71.6	1060	47.6	1274	37.0	1276	36.9
0.305	2573	4058	57.7	1456	43.4	1758	31.7	1770	31.2
0.398	2942	4256	44.7	1722	41.5	2088	29.0	2124	27.8
0.451	3021	4252	40.8	1828	39.5	2223	26.4	2276	24.7
0.499	3068	4186	36.4	1891	38.3	2308	24.8	2380	22.4
0.547	3040	4063	33.7	1923	36.8	2354	22.6	2448	19.5
0.602	2969	3859	30.0	1915	35.5	2356	20.6	2476	16.6
0.700	2705	3331	23.2	1773	34.5	2205	18.5	2377	12.1
0.796	2183	2608	19.5	1448	33.7	1832	16.1	2041	6.5
0.903	1536	1510	1.7	828	46.1	1083	29.5	1276	16.9
0.954	1132	819	27.7	424	62.6	571	49.6	700	38.2
		Av. dev. (%)	50.4	Av. dev. (%)	42.3	Av. dev. (%)	28.9	Av. dev. (%)	24.8
				2-Butanol					
0.048	806	1413	75.4	281	65.1	337	58.2	355	56.0
0.111	1319	2590	96.3	624	52.7	748	43.3	791	40.1
0.203	2136	3665	71.5	1067	50.0	1282	40.0	1363	36.2
0.310	2863	4321	50.9	1484	48.1	1790	37.5	1926	32.7
0.403	3249	4528	39.3	1749	46.2	2117	34.8	2307	29.0
0.448	3449	4530	31.3	1840	46.6	2232	35.3	2449	29.0
0.502	3495	4459	27.6	1915	45.2	2329	33.4	2583	26.1
0.547	3556	4343	22.1	1946	45.3	2372	33.3	2655	25.3
0.599	3474	4148	19.4	1942	44.1	2376	31.6	2695	22.4
0.701	3331	3582	7.5	1801	45.9	2221	33.3	2603	21.9
0.804	2843	2753	3.1	1447	49.1	1805	36.5	2215	22.1
0.905	1905	1627	14.6	847	55.5	1077	43.4	1411	25.9
0.952	1487	936	37.0	466	68.6	601	59.5	821	44.8
		Av. dev. (%)	38.2	Av. dev. (%)	51.0	Av. dev. (%)	40.0	Av. dev. (%)	31.7

[a] Dang: Dang and Tassios (10); Larsen: Larsen *et al.* (11); Weidlich: Weidlich and Gmehling (12); Nitta: Nitta *et al.* (16).

squares fit method, and k is the degree of polynomial expansion. The changes in experimental enthalpies of mixing at 298.15 K with a mole fraction of alcohol are graphically represented in Figure 1 (points), and solid curves were calculated with the coefficients a_k. The evolution of heat capacities of mixtures along the mole fraction of alcohol for methanol and 1-butanol at 298.15 K is shown in Figure 2. Solid curves were obtained with an exponential fit to the experimental data.

Table 4 lists the parameters a_k with their SD, σ. The σ are defined as follows:

$$\sigma = \sqrt{\frac{\Sigma(Z_{\text{cal}} - Z_{\text{exp}})_i^2}{N - m}} \qquad [4]$$

where N is the number of experimental data, m is the number of equation parameters, and Z is the property considered (ΔH_m).

Some curves are truncated because sunflower oil was not miscible at all concentrations with some alcohols, such as methanol, ethanol, and 2-propanol. Enthalpies of mixing were positive over the whole concentration range, with a maximum close to $x = 0.55$, and higher values were found for 2-butanol, with 3556 J·mol^{-1} at the maximum.

Figure 3 compares the experimental and predicted values of enthalpies of mixing for the various models of 2-propanol with sunflower oil at 298.15 K. As shown in Table 2, the worst predictions were found for the Dang and Tassios (10) and Larsen *et al.* (11) methods, with average deviations around 40–50% in most of the binary systems. The best fits were for the Weidlich and Gmehling (12) and Nitta *et al.* (16) methods, with deviations from 10–40% of the average. Lower values were obtained for the shorter-chain alcohols, and higher deviations were obtained for the longer-chain ones. The low deviation values yielded by the Nitta calculation must be emphasized, as well as the correct description of the asymmetry induced by the self-association rearrangement effects caused by the alcohol molecules. The application of these theoretical methods in this case differs greatly from the usual application of group-contribution models. For instance, as has been pointed out before, sunflower oil itself is not a pure compound but a multicomponent mixture that includes a variable composition of several FA. Thus, treating it as a single component and calculating the total number of functional groups requires performing a statistical calculation to determine how many ester, methyl, methylene, and tertiary aliphatic carbons are present. In this way, the total number of functional groups constituting the sunflower oil, in this case, is larger than 50 (the exact number depends in every case

TABLE 3
Calculated Heat Capacities of the Mixtures Formed of Alcohols with Sunflower Oil at 298.15 K

x_1	c_{pm} (J·K^{-1}mol^{-1})	x_1	c_{pm} (J·K^{-1}mol^{-1})
Methanol		1-Butanol	
0.110	2210	0.064	2158
0.202	1835	0.110	2120
0.319	1447	0.203	1821
0.413	1272	0.305	1550
0.458	1145	0.398	1337
0.511	1059	0.451	1213
		0.499	1136
Ethanol		0.547	1057
0.113	2147	0.602	940
0.204	1772	0.700	766
0.311	1466	0.796	567
0.410	1259	0.903	392
0.448	1228	0.954	300
0.511	1134		
0.547	1007	2-Butanol	
0.602	905	0.048	2985
0.704	716	0.111	2199
0.803	527	0.203	1751
		0.310	1491
1-Propanol		0.403	1289
0.105	1965	0.448	1202
0.204	1711	0.502	1135
0.311	1528	0.547	1040
0.403	1276	0.599	947
0.449	1198	0.701	766
0.502	1139	0.804	589
0.568	984	0.905	404
0.626	889	0.952	314
0.701	739		
0.800	542		
0.847	457		
2-Propanol			
0.103	1881		
0.154	1787		
0.200	1656		
0.249	1544		
0.302	1490		
0.347	1426		
0.401	1291		
0.446	1208		
0.504	1136		
0.553	1005		
0.602	917		
0.648	828		
0.699	740		
0.751	630		
0.803	561		
0.847	463		

on the specific functional group assignment of each model). This value is much larger than the number of groups involved in the usual calculations done with this kind of model. The low deviations obtained show that they are a useful tool for thermophysical (and even phase equilibrium) estimates for natural oils, in this case, and extend their potential range of application to other families of complex molecules, including long linear chains and branched structures.

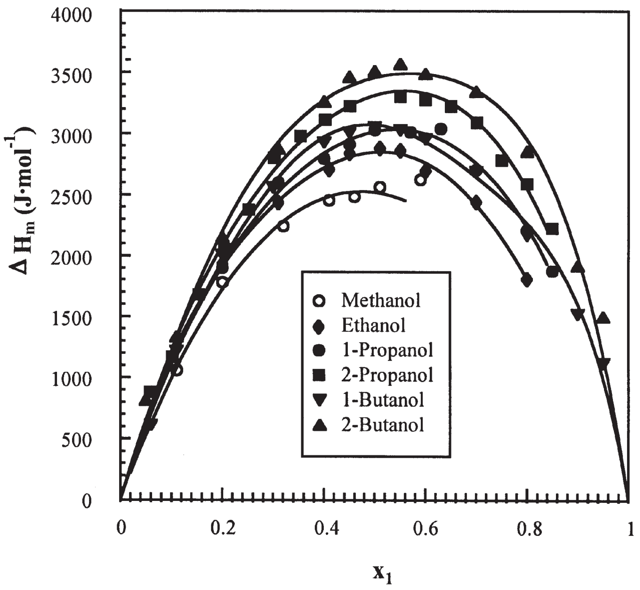

FIG. 1. Experimental enthalpies of mixing at 298.15 K of mixtures of alcohol with sunflower oil along the mole fraction of alcohol. Points, experimental values; solid curves, fit to the Redlich–Kister equation (21).

The heat capacities of the mixtures also were calculated and were plotted vs. mole fraction of alcohol in Figure 2. Values decreased as the mole fraction of alcohol increased and varied from 300 to 2984 J/mol K.

Thus, the group-contribution methods predict the behavior of mixtures with average deviations similar to those of other binary systems of molecules of simpler structure.

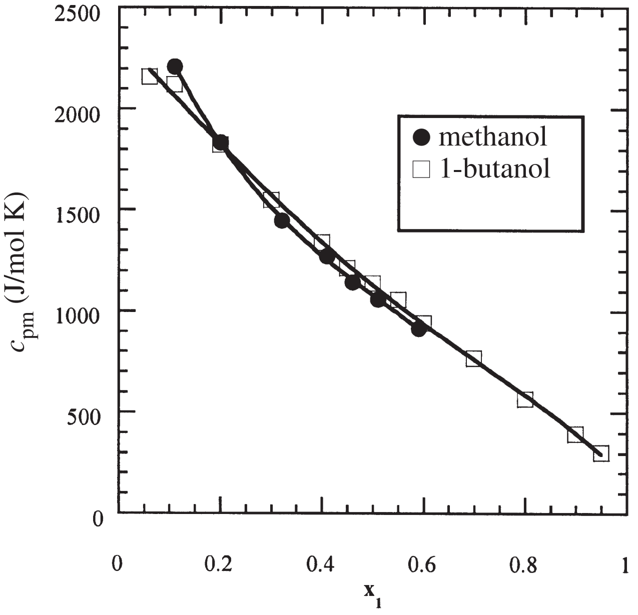

FIG. 2. Calculated heat capacities at 298.15 K of mixtures of methanol and 1-butanol with sunflower oil vs. the mole fraction of alcohol. Points, experimental values; solid curves, fit to exponential curves.

TABLE 4
Redlich–Kister Parameters at 298.15 K for the ΔH_m vs. Mole Fraction Data

	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	2-Butanol
a_1	10085.4	11392.0	12062.9	13250.1	12285.5	13827.2
a_2	1081.3	−536.7	−1666.3	−2431.0	680.1	−1984.9
a_3	82.8	668.9	2535.5	3445.5	95.4	6324.4
a_4		2969.5			−6398.4	−5350.2
a_5					6662.2	
σ (J/mol)	40	30	45	67	63	115

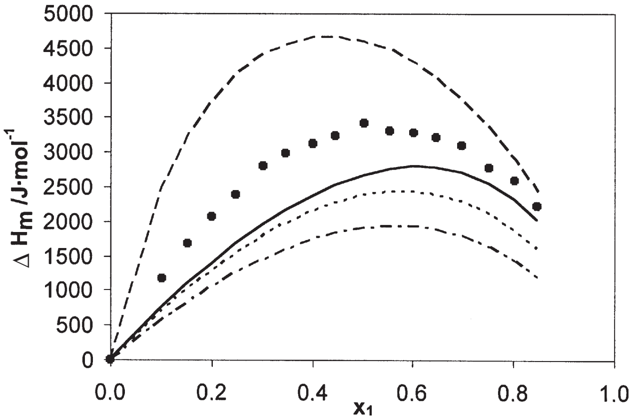

FIG. 3. Comparison between experimental (•) and predicted values of enthalpies of mixing for several models studied [---, Weidlich and Gmehling (12), –·–, Larsen *et al.* (11), – –, Dang and Tassios (10), ——, Nitta *et al.* (16)] of mixtures of 2-propanol with sunflower oil at 298.15 K.

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REFERENCES

1. González, C., J.M. Resa, A. Ruiz, and J.I Gutiérrez, Densities of Mixtures Containing *n*-Alkanes with Sunflower Seed Oil at Different Temperatures, *J. Chem. Eng. Data 41*:796–798 (1996).
2. González, C., J.M. Resa, A. Ruiz, and J.I. Gutiérrez, Excess Molar Volumes of Mixtures of Hexane + Natural Oils from 298.15 K to 313.15 K, *Ibid. 42*:339–341 (1997)
3. González, C., M. Iglesias, J. Lanz, and J.M. Resa, Temperature Dependence of Excess Molar Volumes in (*n*-Alkane (C_6–C_9) or Alcohol (C_2–C_4)) + Olive Oil Mixtures, *Thermochim. Acta 328*:277–296 (1999).
4. González, C., J.M. Resa, and J. Lanz, Excess Volumes of Binary Mixtures That Contain Olive Oil with Alkyl and Vinyl Acetates, *J. Am. Oil Chem. Soc. 77*:985–990 (2000).
5. González, C., M. Iglesias, J. Lanz, G. Marino, B. Orge, and J.M. Resa, Temperature Influence on Refractive Indices and Isentropic Compressibilities of Alcohol (C_2–C_4) + Olive Oil Mixtures, *J. Food Eng. 50*:29–40 (2001).
6. Resa, J.M., C. González, M.A. Fanega, S. Ortiz de Landaluce, and J. Lanz, Enthalpies of Mixing, Heat Capacities, and Viscosities of Alcohol (C_1–C_4) + Olive Oil Mixtures at 298.15 K, *J. Food Eng. 51*:113–118 (2001).
7. González, C., J.M. Resa, J. Lanz, and M.A. Fanega, Speeds of Sound and Isentropic Compressibilities of Organic Solvents with Sunflower Oil at 298.15 K, *J. Am. Oil Chem. Soc. 79*:543–548 (2002).
8. González, C., J.M. Resa, J. Lanz, and M.A. Fanega, Excess Molar Volumes and Refractive Indices of Mixtures Formed by Acetates with Sunflower Oil at Different Temperatures, *J. Am. Oil Chem. Soc. 79*:539–542 (2002).
9. Kojima, K., and K. Tochigi, *Prediction of Vapor–Liquid Equilibria by the ASOG Method*, Elsevier, Tokyo, 1979.
10. Dang, D., and D.P. Tassios, Prediction of Enthalpies of Mixing with a UNIFAC Model, *Ind. Eng. Chem. Process. Des. Dev.* 25:22–31 (1986).
11. Larsen, B.L., P. Rasmussen, and A. Fredeslund, A Modified UNIFAC Group Contribution Model for Prediction of Phase Equilibria and Heats of Mixing, *Ind. Eng. Chem. Res. 26*:2274–2286 (1987).
12. Weidlich, U., and J. Gmehling, A Modified UNIFAC Model. 1. Prediction of VLE, h^E, and γ^∞, *Ind. Eng. Chem. Res. 26*:1372–1381 (1987).
13. Fredenslund, A., J. Gmehling, and P. Rasmussen, *Vapor–Liquid Equilibria Using UNIFAC*, Elsevier, New York, 1977.
14. Abrams, D.S., and J.M. Prausnitz, Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems, *AIChE J. 21*:116–128 (1975).
15. Gmehling, J., J. Li, and M. Schiller, A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties, *Ind. Eng. Chem. Res. 32*:178–193 (1993).
16. Nitta, T., E.A. Turek, R.A. Greenkorn, and K.C. Chao, A Group Contribution Molecular Model for Liquids and Solutions Composed of the Groups Methyl, Methylene, Hydroxy, and Carbonyl, *AIChE J. 23*:144–160 (1977).
17. Flory, P.J., R.A. Orwoll, and A. Vrij, Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons, *J. Am. Chem. Soc. 86*:3507–3514 (1964).
18. Carnahan, N.F., and K.E. Starling, Equation of State for Non-attracting Rigid Spheres, *J. Chem. Phys. 51*:635–636 (1969).
19. Guggenhein, E.A., *Mixtures*, Clarendon Press, Oxford, 1952.
20. Zijlema, T.G., G.J. Witkamp, and G.M. van Rosmalen, Specific Heats and Enthalpies of Mixing of Amine–H_2O and Amine–H_2O–NaCl Mixtures, *J. Chem. Eng. Data 44*:1335–1337 (1999).
21. Redlich, O., and A.T. Kister, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, *Ind. Eng. Chem. 40*:345–348 (1948).
22. Riddick, J.A., W.B. Bunger, and T.K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, 4th edn., John Wiley & Sons, New York, 1986.
23. Karleskind, A., *Oils and Fats Manual*, Ed. Afeca, Paris, 1996, Vol. 2.
24. AMV Ediciones, Produccion, análisis y control de calidad de aceites y grasas comestibles, AMV Ediciones, Madrid, 1987.

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