Excess Molar Volumes and Refractive Indices of Mixtures Formed by Acetates with Sunflower Oil at Different Temperatures

Cristina González*, José M. Resa, Juan Lanz, and M. Angeles Fanega

Chemical Engineering Department, Faculty of Pharmacy, University of Basque Country, Vitoria, Spain

ABSTRACT: The aim of this work is to measure the densities and refractive indices of mixtures formed of acetates (ethyl, vinyl, propyl, isopropyl, and butyl acetate) with sunflower oil. From these measurements, excess molar volumes and variations of the refractive index of the mixtures have been calculated. The properties were measured at temperatures varying from 288.15 to 298.15 K. The excess molar volumes and variations of refractive index data were correlated vs. composition with Redlich–Kister polynomials. Densities of the mixtures were predicted by the Rackett and modified Rackett equations. Refractive indices of the mixtures were predicted by several mixing rules and compared with experimental values. In all cases, SD between predicted and experimental data were less than 5%.

Paper no. J10106 in *JAOCS 79,* 539–542 (June 2002).

KEY WORDS: Acetate, excess molar volume, refractive index, sunflower oil.

In the refining and extraction oils industry, properties of mixtures of organic solvents with vegetable oils are needed. This work is part of a more extensive investigation on mixing properties of organic solvents with edible oils (1–7). Here, excess molar volumes, refractive indices, and variations of the refractive indices at different temperatures (between 288.15 and 298.15 K) of alkyl acetates (ethyl, propyl, isopropyl, and butyl acetate) and vinyl acetate in mixtures with sunflower oil are shown. Thermodynamic excess/mixing functions, such as excess volume, enthalpy, variation of refractive index, or isentropic compressibility, frequently have been studied with strictly binary mixtures (8–11). The purpose of this paper was to investigate whether these "mixing functions" work well in pseudobinary mixtures, in which vegetable oil is one component. Several mixing rules have been used to predict the properties (density, refractive index) of the mixtures. Although the oil is a mixture of different compounds, it has been considered as a single compound to predict the final properties.

EXPERIMENTAL PROCEDURES

Sunflower oil was a commercial refined oil supplied by Koipesol (Jaén, Spain). Alkyl acetates were analytical grade reagents supplied by Fluka (Buchs, Switzerland). Samples of different concentrations in acetate were prepared by weighing in a Salter ER-182A balance (Tokyo, Japan). The accuracy of the balance was $\pm 5 \times 10^{-4}$ g. Density of the mixtures was measured at different temperatures with an Anton Paar DMA 58 (Graz, Austria) densitometer with a precision of ±0.00001 g·cm^{-3} and the refractive index with a Mettler Toledo RE 50 with a precision of ±0.00002. The temperature of the densitometer and refractometer cells was controlled by a Peltier element, with an accuracy of $\pm 1 \times 10^{-2}$ K. Excess volumes were accurate to $\pm 2 \times 10^{-3}$ cm^{3}mol^{-1}. Experimental and literature (12) densities and refractive indices of the solvents used and sunflower oil are listed in Table 1. The FA composition of the sunflower oil was determined by a Shimadzu GC-14B (Kyoto, Japan) gas chromatograph equipped with an FID. The chromatographic technique and the chemical procedure for the preparation of FA were described previously (5). The oil composition obtained was: palmitic acid, 8.4%; stearic acid, 3.9%; oleic acid, 28.9%; linoleic acid, 58.3%; and linolenic acid, 0.6%. The uncertainty in mole percentage for these results was less than 0.1%. From this composition, the average molar mass of this oil was computed in accordance with the following expression:

$$M_{\text{oil}} = 3\left(\sum_{i=1}^{N} x_i M_i\right) + M_{\text{CH–C–CH}} \qquad [1]$$

where x_i is the molar fraction, M_i the molar mass of each FA in the analysis, N the number of FA found by analysis, and $M_{\text{CH–C–CH}}$ the molar mass contribution of the glycerol molecule fraction. The computed average molar mass of sunflower oil samples was 874.12 g·mol^{-1}. The variation in the composition due to different samples affects mainly the monounsat-

TABLE 1
Comparison of Experimental Data for Density (ρ) and Refractive Index (n_D) with Literature Values (12) for Pure Solvents and Sunflower Oil at 298.15 K

	ρ (g·cm^{-3})		n_D	
Compound	Exp	Lit	Exp	Lit
Sunflower oil	0.91545	0.920–0.925[a]	1.47244	1.472–1.474
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
Vinyl acetate	0.92565	0.92634	1.39254	1.3934

[a]At 293.15 K (Ref. 16). Abbreviations: Exp, experimental data; Lit, literature value.

*To whom correspondence should be addressed at Chemical Engineering Department, Faculty of Pharmacy, University of Basque Country, Apdo. 450, Vitoria, Spain. E-mail: iqpgoorc@vc.ehu.es

urated FA and PUFA, with the change in molar mass being less than ±1 g·mol^{-1} and in excess molar volume less than ±2 × 10^{-3} cm^{3}mol^{-1}.

RESULTS AND DISCUSSION

From experimental density data of the mixtures, excess molar volumes (V^E) were calculated. In Figures 1 and 2, excess molar volumes at 298.15 K of different mixtures of acetates/oil and excess molar volume of vinyl acetate/sunflower oil mixtures at different temperatures, respectively, are plotted. From the experimental refractive indices, the variation of the refractive index (Δn_D) with respect to the pure compounds was calculated. The variation of the refractive index of the mixtures with mole fraction of acetate at 298.15 K appears in Figure 3.

The excess volume data and the variation of the refractive index were correlated as a function of composition using a Redlich–Kister expansion:

$$V^E, \text{ in cm}^3\cdot\text{mol}^{-1} \left(\text{or } \Delta n_D\right) = x_1 x_2 \sum_{k\geq 0} a_k \left(x_1 - x_2\right)^k \qquad [2]$$

where x_1 and x_2 are the mole fractions of the higher- and lower-volatility compounds, respectively, and a_k are the adjustable parameters obtained by the least squares method. Table 2 summarizes the values of the parameters a_k together with the standard deviations (σ) of the differences between experimental values and those calculated from Equation 2. The parameters of Equation 2 were used to calculate the solid curves in Figures 1–3. For both excess volume and variation of the refractive index, the Redlich–Kister equation fits the experimental data well, as can be observed in the three figures. In Figure 1, the excess molar volumes of the mixtures with mole fraction of acetate at 298.15 K are presented. The system ethyl acetate/sunflower oil showed a behavior very close to ideality, with excess volumes very close to zero. The oil molecules are voluminous but not compact, which means that there are spaces between the nonpolar chains where small molecules with low interaction could be introduced. The higher M.W. acetates showed negative excess molar volumes, resulting from better molecular packing. With vinyl acetate, a higher excess volume was observed, but this effect decreased with increasing temperature

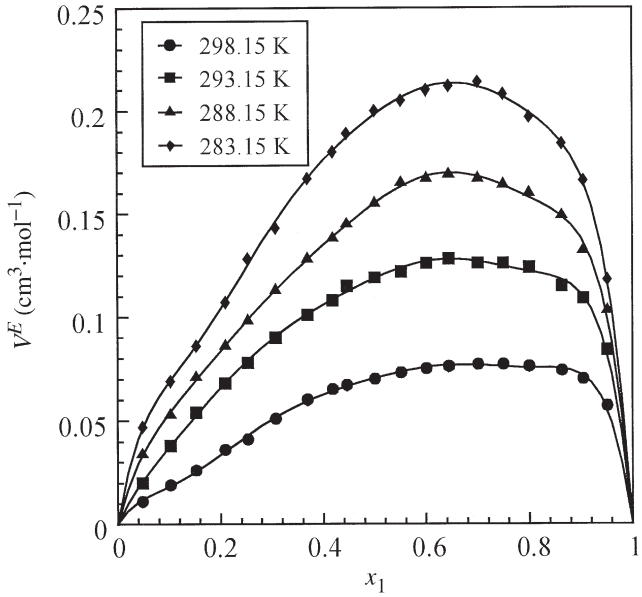

FIG. 2. Excess molar volumes (V^E) of vinyl acetate/sunflower oil at different temperatures. Symbols, experimental data; solid lines, Redlich–Kister fit.

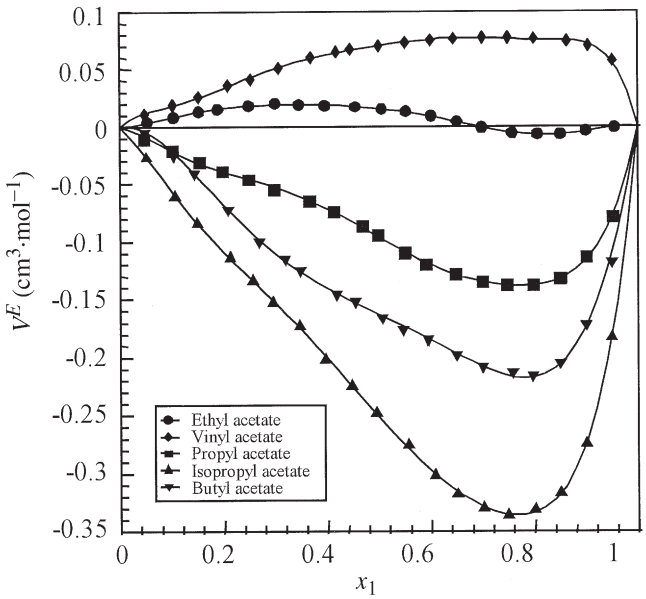

FIG. 1. Excess molar volumes (V^E) of mixtures of sunflower oil with various acetates at 298.15 K with mole fraction of acetate (x_1). Symbols, experimental data; solid lines, Redlich–Kister fit. The straight line at $V^E = 0$ represents the ideal case.

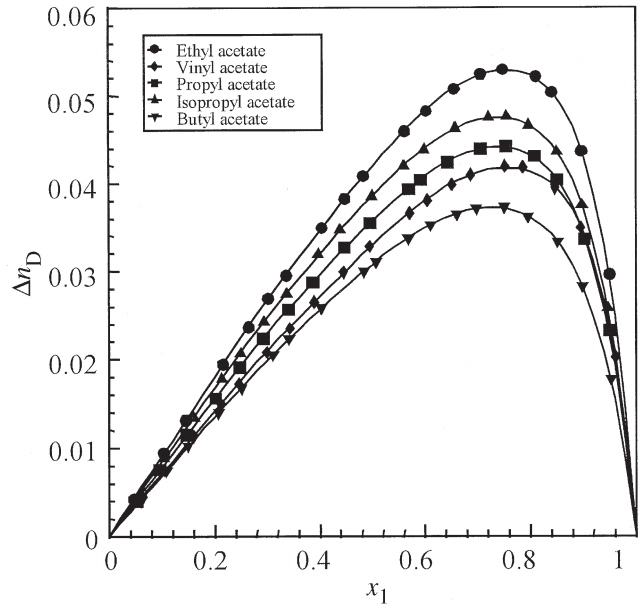

FIG. 3. Variation of the refractive index (Δn_D) of mixtures of sunflower oil with various acetates at 298.15 K with mole fraction of acetate (x_1). Symbols, experimental data; solid lines, Redlich–Kister fit.

TABLE 2
Redlich–Kister Parameters (a_k) at 298.15 K for the V^E and Δn_D vs. Mole Fraction Data[a]

	Parameters of V^E vs. mole fraction curves							
	a_0	a_1	a_2	a_3	a_4	a_5	a_6	σ
Ethyl acetate	0.062	0.127	–0.138	–0.050	0.115			$4.8\cdot10^{-4}$
Vinyl acetate	0.288	–0.083	–0.062	–0.440	0.640			$9.8\cdot10^{-4}$
Propyl acetate	–0.386	0.429	–0.313	0.325	–0.430			$1.2\cdot10^{-3}$
Isopropyl acetate	–1.008	0.886	–0.730	0.930	–0.873			$1.6\cdot10^{-3}$
Butyl acetate	–0.659	0.422	–0.544	0.987	–0.224			$1.9\cdot10^{-3}$
	Parameters of Δn_D vs. mole fraction curves							
Ethyl acetate	0.16768	–0.14008	0.11840	–0.04691	0.01701	–0.16463	0.15401	$1.3\cdot10^{-4}$
Vinyl acetate	0.13164	–0.11245	0.09745	–0.02739	–0.00437	–0.14849	0.15056	$1.7\cdot10^{-4}$
Propyl acetate	0.14275	–0.11421	0.09730	–0.04878	0.00809	–0.09656	0.10123	$1.7\cdot10^{-4}$
Isopropyl acetate	0.15405	–0.12288	0.10122	–0.05132	0.01633	–0.10848	0.10889	$1.0\cdot10^{-4}$
Butyl acetate	0.12294	–0.09523	0.07445	–0.03729	0.01723	–0.07072	0.06428	$6.9\cdot10^{-5}$

[a]V^E, excess molar volume.

(Fig. 2). In all of the mixtures, similar behavior was observed: V^E decreased when temperature increased. The molecular structure stated by the dipole-dipole interactions was disturbed when the acetate molecules had more energy. Therefore, addition of sunflower oil did not disturb molecular organization as much as in a cooler, well-ordered structure. Therefore, V^E were smaller at higher temperatures.

The densities of the mixtures were calculated by the Rackett equation (13) and the modified Rackett equation (14), which is an improved equation for prediction of saturated liquid density. The modified Rackett equation is given as

$$V = \left(RT_c/P_c\right)Z_{\mathrm{RA}}^{\left[1+(1-T_r)^{2/7}\right]} \qquad [3]$$

where V is the molar volume, T_r is the reduced temperature, T_c and P_c are the critical properties, and Z_{Ra} is an acentric factor that varies according to the molecular structure parameter. In Table 3, the average SD (δρ) for estimated densities of the mixtures with respect to the experimental data at 298.15 K are shown. On the basis of these SD, it can be concluded that the more accurate equation to predict the density of the mixtures is the modified Rackett equation. In these cases, SD were less than 3%. The deviations using the Rackett equation were less than 5%.

The experimental refractive indices have been compared with the estimated ones by means of the mixing rules (15) proposed by Lorentz-Lorenz (Eq. 4), Dale and Gladstone (Eq. 5), and Eykman (Eq. 6):

TABLE 3
Average SD (δρ) for Predicted Densities with Respect to Experimental Data for Binary Mixtures of Sunflower Oil with Various Acetates at 298.15 K

Solvent	δρ [Rackett (13)]	δρ (modified Rackett, Eq. 3)
Ethyl acetate	0.03034	0.01106
Vinyl acetate	0.01934	0.00729
Propyl acetate	0.02157	0.00644
Isopropyl acetate	0.02410	0.00619
Butyl acetate	0.01169	0.01416

TABLE 4
Average SD (δn_D) for Predicted Refractive Indices with Respect to Experimental Data for the Mixtures of Acetates with Sunflower Oil at 298.15 K

Solvent	δn_D (Eq. 4)	δn_D (Eq. 5)	δn_D (Eq. 6)
Ethyl acetate	0.00052	0.00008	0.00018
Vinyl acetate	0.00018	0.00017	0.00011
Propyl acetate	0.00049	0.00015	0.00023
Isopropyl acetate	0.00080	0.00032	0.00047
Butyl acetate	0.00051	0.00018	0.00028

$$\frac{n_D^2-1}{n_D^2+2} = \sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right] \qquad [4]$$

$$n_D - 1 = \sum_{i=1}^{N}\left[\phi_i\left(n_{Di}-1\right)\right] \qquad [5]$$

$$\frac{n_D^2-1}{n_D^2+0.4} = \sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2-1}{n_{Di}^2+0.4}\right)\right] \qquad [6]$$

where

$$\phi_i = \frac{\left(x_i M_i/\rho_i\right)}{\sum_{i=1}^{N}\left(x_i M_i/\rho_i\right)} \qquad [7]$$

The results of the comparison with the experimental data appear in Table 4, in which the average deviation (δn_D) between experimental and estimated data are shown. A good agreement is observed, with only small differences in all cases. As can be observed in Table 4 for 298.15 K, the deviations corresponding to the mixture rules proposed by different authors were less than 5% for the binary mixtures with respect to the experimental values. From these data one can see that the same mixing rules applied to binary mixtures of pure compounds can be used for the pseudobinary mixtures formed by oil and an organic solvent, that the behavior of the mixtures shows the same tendency vs. mole fraction as pure binary mixtures, and that the Redlich–Kister equation fits the experimental data well.

ACKNOWLEDGMENT

The authors thank the Ministerio de Educación y Cultura for financial support of this work (project PB 97-0623).

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 (C6–C9) or Alcohol (C2–C4)) + 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 (C2–C4) + Olive Oil Mixtures, *J. Food. Eng*. *50*:47–58 (2001).
6. Resa, J.M., C. González, M. Fanega, S. Ortiz de Landaluce, and J. Lanz, Enthalpies of Mixing, Specific Heats, and Viscosities of Alcohol (C1–C4) + Olive Oil Mixtures at 298.15 K, *Ibid. 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. Comelli, F., R. Francesconi, and C. Castellari, Densities, Viscosities, and Excess Molar Enthalpies of Binary Mixtures Containing Essential Oils at (298.15 and 313.15) K. The (*S*)-(−)-Limonene + Cineol, (*S*)-(−)-Limonene + Linalool, and Cineole + Linalool Systems, *J. Chem. Eng. Data 46*:868–872 (2001).
9. Cominges, B.E., M.M. Piñeiro, L. Mosteiro, T.P. Iglesias, J.L. Legido, and M.I. Paz Andrade, Temperature Dependence of Thermophysical Properties of Hexane + 1-Hexanol, *Ibid. 46*: 1206–1210 (2001).
10. Chandrasekhar, G., P. Venkatesu, and M.V. Prabhakara Rao, Excess Molar Volumes and Speed of Sound of Ethyl Acetate and Butyl Acetate with 2-Alkoxyethanols at 308.15 K, *Ibid. 45*: 590–593 (2000).
11. Brocos, P., E. Calvo, A. Piñeiro, R. Bravo, A. Amigo, A.H. Roix, and G. Roux-Desgranges, Heat Capacities, Excess Enthalpies, and Volumes of Mixtures Containing Cyclic Ethers. 5. Binary Systems {1,3-dioxolane + 1-alkanols}, *Ibid. 44*: 1341–1347 (1999).
12. 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.
13. Rackett, H.G., Equation of State for Saturated Liquids, *J. Chem. Eng. Data 15*:514–517 (1970).
14. Reid, R.C., J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids,* 4th edn., McGraw-Hill, Singapore, 1988, p. 67.
15. Iglesias, M., B. Orge, and J. Tojo, Refractive Indices and Densities of the Ternary Mixtures Acetone + Methanol + Water and Acetone + Methanol + 1-Butanol at 298.15 K, *Fluid Phase Equilib. 126*:203–223 (1996).
16. Karleskind, A. (ed.) *Oils & Fats Manual: A Comprehensive Treatise,* Lavoisier, Paris, 1996, p. 121.

[Received September 27, 2001; accepted March 15, 2002]