Infinite Dilution Activity Coefficients in Mono-, Di-, and Tripalmitin and Palmitic Acid

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Infinite dilution activity coefficients of several organic solutes in mono-, di-, and tripalmitin and in palmitic acid were measured by gas chromatography, at temperatures between 353 K and 373 K. The solutes include hydrocarbons, chlorinated hydrocarbons, and alcohols. The UNIFAC group contribution model and Flory's combinatorial model, with the addition of a regular solution residual term, were used to correlate the experimental data.

1. Introduction

Triglycerides of long-chain, saturated and unsaturated fatty acids are the main components of vegetable oils. Other constituents are mono- and diglycerides and free fatty acids. A hexane petroleum fraction is the traditional solvent used in the extraction of vegetable oils from oil seeds. The subsequent separation of the solvent from the oil−solvent mixture is industrially accomplished by evaporation and steam stripping, up to residual solvent contents of a few ppm. Knowledge of the vapor−liquid equilibria of these mixtures, especially in the solvent-diluted region, is required for the design and operation of these separation processes.

Experimental values for the activity coefficients of organic solvents infinitely diluted in long-chain glycerides and fatty acids can be obtained by gas chromatography, using the high-boiling glycerides and fatty acids as the column stationary phase. In this work infinite dilution activity coefficients (γ^∞) of several organic solvents in mono-, di-, and tripalmitin and in palmitic acid were measured by this technique.

The differences in the molecular size between the solvents and the long-chain glycerides and fatty acids are indicative of significant entropic contributions to the total values of the infinite dilution activity coefficients. A good representation of these γ^∞ values is expected to be achieved by the use of a thermodynamic model based on Flory's combinatorial model with a regular solution residual contribution or by a group contribution model such as UNIFAC.

2. Experimental Section

The infinite dilution activity coefficients were measured by gas−liquid chromatography (Laub and Pecsok, 1978). The specific retention volume V_g° at 273.15 K, i.e. the normalized volume of carrier gas necessary to elute solute i out of a column with a mass w_s of solvent, is calculated from the measured retention time (t_i) of solute i by

$$V_g^\circ = (t_i - t_a)F(273.15/T_f)((P_f - P_w^s)/P_0)J_3{}^2/w_s \quad (1)$$

where t_a is the inert gas retention time; F is the saturated carrier gas flow, measured at temperature T_f and pressure P_f in a soap-film meter; P_w^s is the vapor pressure of water at T_f; P_0 is the pressure at the column outlet, and $J_3{}^2$ is the James−Martin correction factor for pressure gradient and gas compressibility inside the column (Conder and Young, 1979).

Equation 2, below, gives the thermodynamic relationship between the retention volume V_g° and the infinite dilution activity coefficient γ_i^∞ of solute i in solvent s.

$$\ln \gamma^\infty = \ln(R273.15/(M_s P_i^s V_g^0)) - (B_{ii} - v_i)P_i^s/(RT) \quad (2)$$

In this expression, the virial equation of state has been used to correct for the nonideality of the gas phase. B_{ii}, v_i, and P_i^s represent, respectively, the second virial coefficient, liquid molar volume, and vapor pressure of solute i at column temperature T; R is the universal gas constant; and M_s is the molecular weight of the solvent.

The experimental equipment and technique applied in this study are similar to those used in previous work (Din et al., 1996, Mengarelli et al., 1995). A Varian (Model 3700) gas chromatograph with a FID detector and a Hewlett-Packard (Model 3392) integrator were used in the measurements. The temperatures inside the oven and in the soap-film meter were measured with thermistor thermometers (YSI-400) and read from a digital indicator (Cole Parmer) with a resolution of ±0.1 K. The carrier gas was hydrogen, flowing at about 25 cm^3/min; a soap-film meter was used to quantify the gas flow rates. The column outlet pressure was measured with a quartz transducer (Paroscientific). Pressure drops inside the column ranged from (200 to 300) mbar and were read with a cathetometer from a U-tube manometer. Hamilton gastight syringes, 1 μL capacity, were used to inject the solutes into the carrier gas stream.

The stationary phase for each column was prepared by dissolving, in chloroform, known masses of solvent (mono-, di-, or tripalmitin or palmitic acid) and inert support (Chromosorb W, 60/80 mesh), at a ratio of 3 parts by mass of chromosorb per part of solvent. The chloroform was then slowly evaporated from the solution, in a roto-evaporator under an inert atmosphere. Stainless steel tubes, each 1/8 in. o.d. by 2 m long, were packed with known masses of about (2 to 3) g of each stationary phase.

In order to obtain the dead volume or reference retention time t_a, methane was used as a tracer and was always injected together with each of the solutes studied. The nonretention of methane in each stationary phase was checked against the constancy of the methane retention time (t_a = 30 s) at different column temperatures. Any retention of methane in the stationary phase would affect the value of γ^∞ in a magnitude approximately proportional to the ratio between the distribution coefficients of methane and solute i. For the compound with the lowest retention time, this value will be about 0.01. Therefore, in the worst

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Table 1. Infinite Dilution Activity Coefficients in Monopalmitin

solute	$T = 354.55$ K	$T = 365.05$ K	$T = 375.25$ K
hexane	1.92 ± 0.07	1.92 ± 0.07	1.90 ± 0.09
heptane	2.07 ± 0.05	2.02 ± 0.05	2.02 ± 0.06
isooctane	2.29 ± 0.06	2.23 ± 0.06	2.25 ± 0.07
hexene	1.69 ± 0.06	1.67 ± 0.09	1.66 ± 0.08
benzene	1.00 ± 0.02	0.96 ± 0.02	0.95 ± 0.03
toluene	1.09 ± 0.02	1.05 ± 0.02	1.05 ± 0.03
cyclohexane	1.39 ± 0.03	1.34 ± 0.04	1.34 ± 0.04
methanol	1.17 ± 0.04	1.12 ± 0.04	1.01 ± 0.04
ethanol	1.21 ± 0.03	1.08 ± 0.03	0.97 ± 0.03
1-propanol	1.17 ± 0.02	1.05 ± 0.02	0.95 ± 0.02
2-propanol	1.14 ± 0.03	1.03 ± 0.03	0.93 ± 0.03
1-butanol	1.18 ± 0.02	1.05 ± 0.02	0.95 ± 0.02
2-butanol	1.05 ± 0.02	0.96 ± 0.02	0.88 ± 0.02
acetone	1.26 ± 0.04	1.01 ± 0.04	0.96 ± 0.04
1,2-dichloroethane	1.01 ± 0.02	1.00 ± 0.03	0.96 ± 0.03
trichloroethylene	0.88 ± 0.02	0.89 ± 0.02	0.88 ± 0.02
chloroform	0.97 ± 0.02	0.69 ± 0.02	0.68 ± 0.02
chlorobenzene	1.41 ± 0.02	1.00 ± 0.02	0.97 ± 0.02
benzyl chloride	0.67 ± 0.02	1.42 ± 0.02	1.34 ± 0.02
anisole	1.22 ± 0.02	1.22 ± 0.02	1.16 ± 0.02
ethyl acetate	1.33 ± 0.03	1.28 ± 0.04	1.15 ± 0.04
ethylbenzene	1.20 ± 0.02	1.23 ± 0.02	1.19 ± 0.02

Table 2. Infinite Dilution Activity Coefficients in Dipalmitin

solute	$T = 354.65$ K	$T = 365.15$ K	$T = 375.35$ K
hexane	0.96 ± 0.02	0.89 ± 0.02	0.91 ± 0.02
heptane	0.99 ± 0.02	0.96 ± 0.02	0.96 ± 0.02
isooctane	1.08 ± 0.02	1.05 ± 0.02	1.04 ± 0.02
hexene	0.82 ± 0.01	0.79 ± 0.01	0.80 ± 0.01
benzene	0.52 ± 0.01	0.49 ± 0.01	0.49 ± 0.01
toluene	0.54 ± 0.01	0.53 ± 0.01	0.53 ± 0.01
cyclohexane	0.68 ± 0.01	0.66 ± 0.02	0.66 ± 0.01
methanol	1.04 ± 0.02	0.95 ± 0.02	0.89 ± 0.02
ethanol	1.06 ± 0.02	1.12 ± 0.01	0.93 ± 0.02
1-propanol	0.98 ± 0.02		0.87 ± 0.01
2-propanol	0.94 ± 0.02	1.14 ± 0.01	0.84 ± 0.01
1-butanol	0.97 ± 0.02	0.88 ± 0.02	0.85 ± 0.01
2-butanol	0.85 ± 0.01	0.77 ± 0.01	0.74 ± 0.01
acetone	0.75 ± 0.01	0.73 ± 0.01	0.72 ± 0.01
1,2-dichloroethane	0.57 ± 0.01	0.53 ± 0.01	
trichloroethylene	0.47 ± 0.01	0.45 ± 0.01	0.46 ± 0.01
chloroform	0.53 ± 0.01	0.35 ± 0.01	0.36 ± 0.01
chlorobenzene	0.74 ± 0.01	0.50 ± 0.01	0.50 ± 0.01
benzyl chloride	0.35 ± 0.01	0.71 ± 0.01	
anisole	0.65 ± 0.01	0.59 ± 0.01	0.61 ± 0.01
ethyl acetate	0.72 ± 0.01	0.69 ± 0.01	0.68 ± 0.01
ethyl benzene	0.64 ± 0.01	0.57 ± 0.01	0.60 ± 0.01
limonene	0.26 ± 0.01	0.25 ± 0.01	0.26 ± 0.01

case, the γ^∞ reported in this work could be 1% too high due to this effect.

Reagent grade products from Aldrich Chemical Co. (mono-, di-, and tripalmitin, palmitic acid, hexane, 1-hexene, 1- and 2-propanol, 1,2-dichloroethane, trichloroethylene, ethylbenzene, anisole, limonene), Dorwil (heptane, benzene, toluene, cyclohexane, methanol, ethanol, chloroform, acetone), Mallinkrodt (ethyl acetate), Merck (1-butanol), and Sintorgan (isooctane, 2-butanol, chlorobenzene, and benzyl chloride) were used in the experiments without further purification. Except for limonene (97% purity), the rest of the products had a purity of 99%.

Tables 1−4 contain the experimental values obtained for the infinite dilution activity coefficients of several solutes in mono-, di-, and tripalmitin and in palmitic acid. The values for the second virial coefficients and liquid molar volumes needed in the calculation of γ^∞ by eq 2 were obtained, respectively, from the Hayden−O'Connell and Yenny−Wood correlations (Reid et al., 1977). The Antoine equation, with coefficients taken from the same source, was used for the calculation of the solute vapor pressure.

Table 3. Infinite Dilution Activity Coefficients in Tripalmitin

solute	$T = 350.55$ K	$T = 360.75$ K	$T = 368.05$ K
hexane	0.58 ± 0.02	0.57 ± 0.02	0.57 ± 0.03
heptane	0.61 ± 0.02	0.61 ± 0.02	0.61 ± 0.02
isooctane	0.67 ± 0.02	0.67 ± 0.02	0.67 ± 0.02
hexene	0.52 ± 0.02	0.52 ± 0.02	0.52 ± 0.02
benzene	0.33 ± 0.01	0.33 ± 0.01	0.33 ± 0.01
toluene	0.35 ± 0.01	0.35 ± 0.01	0.35 ± 0.01
cyclohexane	0.44 ± 0.01	0.43 ± 0.01	0.43 ± 0.01
ethanol	1.23 ± 0.07	1.06 ± 0.05	1.11 ± 0.07
1-propanol	1.18 ± 0.04	1.07 ± 0.04	1.04 ± 0.04
2-propanol	1.86 ± 0.05	1.07 ± 0.05	0.98 ± 0.08
1-butanol	1.21 ± 0.05	1.12 ± 0.01	1.01 ± 0.03
2-butanol	1.04 ± 0.03	0.90 ± 0.03	0.86 ± 0.03
acetone	0.77 ± 0.04	0.73 ± 0.04	0.71 ± 0.05
1,2-dichloroethane	0.40 ± 0.01	0.38 ± 0.01	0.37 ± 0.01
trichloroethylene	0.31 ± 0.01	0.30 ± 0.01	0.30 ± 0.01
chlorobenzene	0.35 ± 0.01	0.34 ± 0.01	0.33 ± 0.01
benzyl chloride	0.49 ± 0.01	0.49 ± 0.01	0.48 ± 0.01
chloroform	0.25 ± 0.01	0.24 ± 0.01	0.25 ± 0.01
anisole	0.46 ± 0.01	0.44 ± 0.01	0.43 ± 0.01
ethyl acetate	0.64 ± 0.02	0.63 ± 0.02	0.61 ± 0.02
ethylbenzene	0.40 ± 0.01		0.39 ± 0.01
limonene	0.32 ± 0.01	0.15 ± 0.01	0.17 ± 0.01

Table 4. Infinite Dilution Activity Coefficients in Palmitic Acid

solute	$T = 354.75$ K	$T = 365.25$ K	$T = 374.15$ K
hexane	1.43 ± 0.01	1.47 ± 0.01	1.50 ± 0.01
heptane	1.51 ± 0.01	1.54 ± 0.01	1.59 ± 0.01
isooctane	1.60 ± 0.01	1.64 ± 0.01	1.68 ± 0.01
hexene	1.32 ± 0.01	1.35 ± 0.01	1.39 ± 0.01
benzene	0.96 ± 0.01	0.97 ± 0.01	0.99 ± 0.01
toluene	0.99 ± 0.01	1.00 ± 0.01	1.05 ± 0.01
cyclohexane	1.12 ± 0.01	1.12 ± 0.01	1.15 ± 0.01
methanol	1.94 ± 0.01	1.87 ± 0.01	1.83 ± 0.01
ethanol	1.85 ± 0.01	1.76 ± 0.01	1.73 ± 0.01
1-propanol	1.65 ± 0.01	1.56 ± 0.01	1.53 ± 0.01
2-propanol	1.41 ± 0.01	1.38 ± 0.01	1.35 ± 0.01
1-butanol	1.58 ± 0.01	1.48 ± 0.01	1.45 ± 0.01
2-butanol	1.60 ± 0.01	1.18 ± 0.01	1.16 ± 0.01
acetone	1.60 ± 0.01	1.56 ± 0.01	1.53 ± 0.01
1,2-dichloroethane	1.27 ± 0.01	1.24 ± 0.01	1.25 ± 0.01
trichloroethylene	0.89 ± 0.01	0.90 ± 0.01	0.93 ± 0.01
chloroform	1.01 ± 0.01	0.84 ± 0.01	0.87 ± 0.01
chlorobenzene	1.60 ± 0.01	1.02 ± 0.01	1.04 ± 0.01
benzyl chloride	0.83 ± 0.01	1.67 ± 0.01	1.60 ± 0.01
anisole	1.31 ± 0.01	1.37 ± 0.01	1.30 ± 0.01
ethyl acetate	1.36 ± 0.01	1.32 ± 0.01	1.34 ± 0.01
ethylbenzene	1.11 ± 0.01	1.18 ± 0.01	1.15 ± 0.01
limonene	0.41 ± 0.01	0.45 ± 0.01	0.46 ± 0.01

The uncertainties in the measured variables were estimated to be ±0.7 cm^3/min for the carrier gas flow, ±0.1 K for the temperatures, ±0.1 mbar for the outlet pressure, ±0.13 mbar for the column pressure drops, ±0.002 g for the mass of solvent in the column, and ±0.12 s for the retention times. Application of these uncertainties to a propagation of errors analysis, an overall estimated error of 3 to 5% applies to the experimental infinite dilution activity coefficients reported in Tables 1−4.

3. Thermodynamic Modeling and Discussion

The values of the infinite dilution activity coefficients are reported in Tables 1−4. To the knowledge of the authors, no data are available in the literature for γ^∞ in mono-, di-, or tripalmitin. Data measured by Alessi et al. (1982) for hydrocarbons and alcohols in palmitic acid show differences of 0.07−0.12 in absolute values, with the data reported in Table 4.

The data in Tables 1−4 show rather low values, with a maximum of 2.3 for the γ^∞ of isooctane in monopalmitin. Nearly half have values of γ^∞ lower than unity. For a given

Table 5. Predictions of Infinite Dilution Activity Coefficients at 253 K, for Some Solutes in Palmitic Acid and Mono-, Di-, and Tripalmitin

solute		palmitic acid	mono-palmitin	di-palmitin	tri-palmitin
hexane	experimental	1.43	1.92	0.96	0.58
	UNIFAC	0.91	1.24	0.52	0.34
	Kikic	1.08	1.60	0.81	0.59
hexene	experimental	1.32	1.69	0.85	0.52
	UNIFAC	0.85	1.06	0.45	0.30
	Kikic	1.03	1.40	0.71	0.54
benzene	experimental	0.96	1.00	0.52	0.33
	UNIFAC	0.75	0.66	0.34	0.24
	Kikic	0.99	0.97	0.59	0.48
1-propanol	experimental	1.65	1.17	1.01	1.18
	UNIFAC	1.25	0.64	0.85	1.26
	Kikic	1.64	0.93	1.47	2.51
trichloro-ethylene	experimental	0.89	0.88	0.47	0.31
	UNIFAC	0.84	0.57	0.32	0.25
	Kikic	1.13	0.84	0.58	0.50
chlorobenzene	experimental	1.01	0.97	0.53	0.35
	UNIFAC	1.20	0.70	0.36	0.28
	Kikic	1.50	0.96	0.60	0.52
ethyl acetate	experimental	1.36	1.33	0.74	0.64
	UNIFAC	0.98	0.77	0.49	0.43
	Kikic	1.20	1.03	1.25	0.78

solute, the general trend is a decrease in γ^∞ when the solvent changes from mono- to di- and tripalmitin, i.e. when the molecular weight of the glyceride increases. This indicates a combinatorial effect in the behavior of these mixtures.

Starting from the classical addition of a combinatorial (γ_i^{comb}) plus a residual (γ_i^{res}) term in the expression for the activity coefficient of component i in solution (γ_i)

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} \tag{3}$$

a Flory type model can be used to represent the combinatorial or entropic contribution to γ_i and a local composition or a regular solution approach, to represent the residual or energy-related term.

The UNIFAC (Fredenslund et al., 1975) group contribution model was used to calculate the infinite dilution activity coefficient, applying an exponent $p = 1$ and $p = 2/3$ (Kikic et al., 1980) in the definition of Flory's volume fractions ϕ_i:

$$\phi_i = r_i^p x_i / \sum r_i^p x_i \tag{4}$$

Group interaction parameters from the literature (Gmehling et al., 1982; Macedo et al., 1983; Tiegs et al., 1987) were applied in the calculation of the residual contribution. Table 5 shows some of the results. The experimental and calculated γ^∞ values at 353 K for some typical hydrocarbons, chlorinated hydrocarbons, alcohols, and ethyl acetate are given. Most of the γ^∞ predicted by UNIFAC are appreciably lower than the experimental values, with differences of up to 50%. These results can be attributed to an overestimation of the combinatorial effects when an exponent $p = 1$ is used in eq 4. The effect of introducing a $p < 1$ exponent is equivalent to reducing the size differences between the solute and solvent molecules; this gives lower combinatorial effects and improves UNIFAC predictions of γ^∞. The corrections obtained with $p = 2/3$, though, tend to be too high for some of the solutes in the higher molecular weight glycerides (di- and tripalmitin).

Similar conclusions regarding predictions by the original UNIFAC model and by Kikic's modification to the combinatorial expression, were found by Fornari et al. (1994) and Din et al. (1996) from the vapor−liquid equilibria calculation for several hydrocarbon−vegetable oil mixtures.

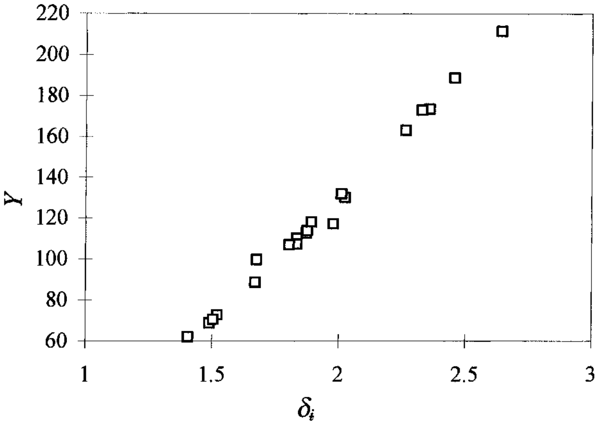

Figure 1. Dependence of the residual function Y on the solute solubility parameter δ_i, for the γ^∞ on dipalmitin.

Table 6. Solubility Parameter (δ_i) for Mono-, Di-, and Tripalmitin and Palmitic Acid

		$10^{-4}\delta_i/(\mathrm{J/m^3})^{0.5}$	
	T/K	Flory	Kikic
monopalmitin	354.55	1.9554	1.9826
dipalmitin	354.55	1.7937	1.8842
tripalmitin	350.55	1.6396	1.7144
palmitic acid	354.65	1.8069	1.8525

When Flory's combinatorial model plus a regular solution residual contribution is applied for the calculation of the infinite dilution activity coefficient of solute i in solvent s, the two terms in eq 3 take the form

$$\ln \gamma_i^{\infty\ \text{comb}} = \ln[(r_i/r_s)^p] + 1 - (r_i/r_s)^p \tag{5}$$

$$\ln \gamma_i^{\infty\ \text{res}} = (v_i/RT)(\delta_i - \delta_s)^2 \tag{6}$$

where v_i is the molar volume of solute i and δ_i and δ_s represent, respectively, the solubility parameters of solute i and solvent s. In Flory's model $p = 1$ and in Kikic's modification $p = 2/3$. In order to apply the regular solution theory, the values of the solubility parameters of palmitic acid and mono-, di-, and tripalmitin have to be estimated. From eqs 1, 5, and 6

$$Y = (2\delta_s/RT)\delta_i - \delta_s^2/RT \tag{7}$$

where

$$Y = \delta_i^2/RT - \ln(\gamma_i^\infty)/v_i + \ln(\gamma_i^{comb})/v_i \tag{8}$$

The solubility parameter δ_s for each of the solvents can be obtained from the slope of eq 7, using the experimental infinite dilution activity coefficients from Tables 1−4, together with v_i *and* δ_i values for the solutes from the literature (Daubert and Danner, 1991). Figure 1 shows a typical Y vs δ_i curve obtained from the γ^∞ data on dipalmitin. Table 6 gives the solubility parameters of palmitic acid and mono-, di-, and tripalmitin obtained from the above procedure. The results include the data regression using $p = 1$ and $p = 2/3$ in the γ_i^{comb} expression.

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