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Activity coefficient at infinite dilution measurements for organic solutes (polar and non-polar) in fatty compounds – Part II: C18 fatty acids

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ABSTRACT

In this work, activity coefficients at infinite dilution (γ_{13}^{∞}) have been measured for 21 solutes (subscript 1) (alkanes, cycloalkanes, alkenes, aromatic compounds, alcohols, esters, ketones, and halogenated hydrocarbons), in four solvents (subscript 3), namely one saturated fatty acid and three unsaturated fatty acids: stearic (octadecanoic) acid – C18:0, oleic (*cis*-9-octadecenoic) acid – C18:1 9c, linoleic (*cis*,*cis*-9,12-octadecadienoic) acid – C18:2 9c12c, and linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acid – C18:3 9c12c15c, by gas–liquid chromatography. The measurements were carried out at temperatures from (303.13 to 368.19) K and the partial molar excess Gibbs free energy ($\Delta G_1^{E,\infty}$), enthalpy ($\Delta H_1^{E,\infty}$), and entropy ($\Delta S_1^{E,\infty}$), at infinite dilution were calculated from experimental γ_{13}^{∞} values obtained over the temperature range. The uncertainties in determination of γ_{13}^{∞} and $\Delta H_1^{E,\infty}$ are 4% and 20%, respectively. The results for stearic acid obtained in this study have been compared to those available in the Dortmund Data Bank (DDB). The real behaviour of fatty systems could be better understood through the results obtained in this work.

1. Introduction

Fatty acids, esterified to glycerol, are the main constituents of oils and fats. Most commodity oils contain fatty acids with carbon chain lengths between C16 and C22, with C18 fatty acids dominating in most plant oils [1]. This paper studies C18 fatty acids most commonly found in nature, their nomenclature and additional information are shown in table 1 and the chemical structures are illustrated in figure 1.

Table 1 also illustrates one of the effects of unsaturation, the melting point of C18 fatty acids decreases with increasing unsaturation.

Storage fats (seed oils and animal adipose tissue) consist chiefly (>98%) of triacylglycerols, with the fatty acids distributed among different molecular species. The minor components are partial acylglycerols and free fatty acids, and they may also include phospholipids, sterols, tocopherols, and carotenoids [1,3–5].

Figure 1 shows that, as in case of other fatty acids, the basic structure of C18 fatty acids consists of a hydrophobic hydrocarbon chain, in this case, with 18 carbons (which can be saturated or unsaturated) with a hydrophilic polar group at one end. It endows fatty acids and their derivatives with distinctive properties, reflected in both their food and industrial use [1,3]. The most reactive sites in fatty acid molecules are the carboxyl group and double bonds, which are important to the body metabolism and to the reactions used in the food and oleochemical industry [1]. In their pure form as well as in not too dilute solutions, fatty acids are nearly completely dimerized in the liquid phase [6].

Oleic, linoleic, and linolenic acids can also be called ω-9, ω-6, and ω-3 fatty acids, respectively. The last two can also be classified as polyunsaturated fatty acids (PUFA), which are produced only by plants and phytoplankton and are essential to all higher organisms, including mammals and fish, because ω-3 and ω-6 fatty acids cannot be interconverted, and both are essential nutrients [7].

In recent years, there is an increasing interest in the thermodynamic property and phase equilibrium data of fatty systems, such as mixtures containing: fatty acids, methyl and ethyl esters of fatty acids, glycerol, partial acylglycerols, triacylglycerols, and multicomponent systems, such as edible oils, fats, and biodiesel. All these compounds are directly involved in industrial extraction

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TABLE 1
Nomenclature and associated data of C18 fatty acids.

Fatty acid nomenclature			$M^{b,c}/(\mathrm{g \cdot mol^{-1}})$	Melting point[b]/K	Significant sources[d]
IUPAC	Trivial	Symbol[a]			
Octadecanoic acid	Stearic acid	C18:0	284.483	342.50	Cocoa butter, tallow
cis-9-Octadecenoic acid	Oleic acid	C18:1 9c	282.467	289.15	Cottonseed, olive, palm, rapeseed oils
cis,*cis*-9,12-Octadecadienoic acid	Linoleic acid	C18:2 9c12c	280.451	268.15	Corn, soybean, sunflower oils
cis,*cis*,*cis*-9,12,15-Octadecatrienoic acid	Linolenic acid	C18:3 9c12c15c	278.435	262.03	Linseed oil

[a] Cx:y, x = chain length, y = number of double bonds followed by respective position, and c = configuration *cis*.
[b] From DDB [2].
[c] M = molar mass.
[d] Ref. [1].

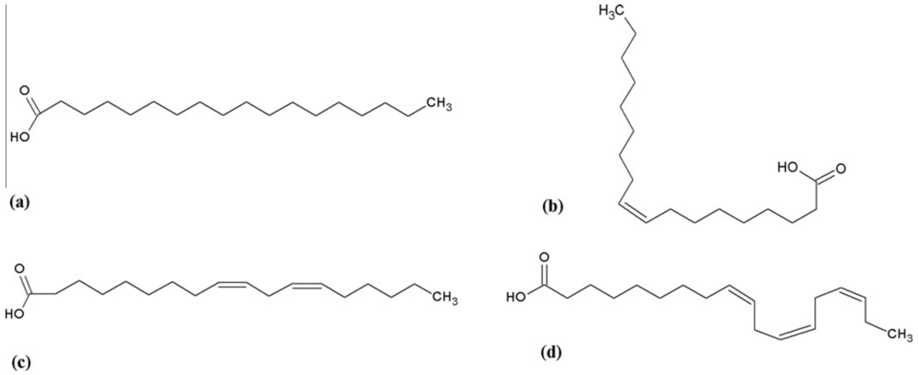

FIGURE 1. Structure of the C 18 fatty acids: (a) stearic acid; (b) oleic acid; (c) linoleic acid, and (d) linolenic acid.

and refining of edible vegetable oils [8–12], the production and purification of partial acylglycerols [13–17] and in the processing of biodiesel [18–21], all of which are submitted to several separation and purification stages which play an important role in the economics of the processes. This is especially true in case of very high purity requirements, which result in increased investment and operating costs.

From practical and theoretical points of view, the activity coefficient at infinite dilution or the limiting activity coefficient (γ_{13}^{∞}) represents an important property to the practicing chemist and process engineer [22–24]. From the industrial viewpoint, it offers a wider applicability than any measurement at finite concentration, since experimental values at infinite dilution are better suited to predict the phase behaviour of a mixture over the entire concentration range than vice versa [25]. They are also especially useful for the selection of selective solvents (e.g. extraction, absorption, and extractive distillation) and for reliable design, optimisation and modelling of thermal separation processes [24,26–28]. From a theoretical point of view, the activity coefficients at infinite dilution are important for the development of new thermodynamic models and also for the adjustment of reliable model parameters [24,28,29].

In our previous work [30], the γ_{13}^{∞} of several solutes in saturated fatty acids: capric acid (C10:0), lauric acid (C12:0), myristic acid (C14:0), and palmitic acid (C16:0) were measured and different trends for polar and non-polar solutes could be identified, both in the series of fatty acids and as function of temperature. This paper is a continuation of that work, and it discusses the role of the double bonds in the structure of the fatty acid (solvent) in the solvent–solute interaction with the aim to contribute to the pool of knowledge available to develop a greater understanding of the correlation between structure and function for the various fatty acids.

We report here activity coefficients at infinite dilution, γ_{13}^{∞}, for 21 solutes (alkanes, cycloalkanes, alkenes, aromatic compounds, alcohols, esters, ketones, and halogenated hydrocarbons) in four C18 fatty acids:

- stearic (octadecanoic) acid – C18:0;
- oleic (*cis*-9-octadecenoic) acid – C18:1 9c or ω-9;
- linoleic (*cis*,*cis*-9,12-octadecadienoic) acid – C18:2 9c12c or ω-6;
- linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acid – C18:3 9c12c15c or ω-9.

The values of γ_{13}^{∞} were determined at temperatures from (303.13 to 368.19) K. Experimental γ_{13}^{∞} data were used to calculate the values of partial molar excess Gibbs free energy, $\Delta G_1^{E,\infty}$, enthalpy, $\Delta H_1^{E,\infty}$, and entropy, $\Delta S_1^{E,\infty}$, at infinite dilution.

2. Experimental

2.1. Materials

Table 2 presents the list of fatty acids (solvents), their purity and the suppliers; they were not subjected to further purification. The solutes had purities above 0.99 in mass fraction and were used also without further purification since the GLC technique allows the separation of any impurities on the column. As solid support material for all stationary phases, Chromosorb P-AW-DMCS 60/80 mesh, supplied by CS-Chromatographie Service GmbH (Germany) was used. Dry helium (>0.9999 mass fraction purity) was used as carrier gas.

2.2. Apparatus and experimental procedure

A homemade gas–liquid chromatography was used for the measurements of activity coefficients at infinite dilution. A detailed description is presented by Knoop *et al.* [31]. This apparatus follows the same principle as presented by Letcher [32]. Due to the negligible vapour pressure of fatty acids [33], there was no need for carrier gas pre-saturation, since problems of mass loss are

TABLE 2
Information about the solvents studied.

Solvent	Purity (GC) mass fraction	Supplier
Stearic acid	>0.985	Sigma
Oleic acid	>0.99	Sigma Aldrich
Linoleic acid	>0.995	Aldrich
Linolenic acid	>0.99	Sigma

minimised. Our GLC is equipped with a thermal conductivity detector (Gow-Mac, model 10285) and a catharometer (Pye Unicam) as electrical supply.

The unsaturated solvents were stocked at temperature below -20 °C. For these compounds, the entire procedure for preparation of the column was carried out under inert atmosphere (nitrogen) and with a minimum exposure to light, since they are sensitive to oxidation [34].

A pre-weighed amount of a pre-dried solid support was coated with a known quantity of solvent (stearic, oleic, linoleic, or linolenic acid) with chloroform (0.999 fraction mass purity dried over molecular sieve) as a solubilizer in a rotary evaporator. All chloroform was then removed by slow evaporation (for unsaturated fatty acids under nitrogen atmosphere) and the mixture (fatty acid + chromosorb) was subjected to a low pressure of approximately 5 kPa at T = 310 K for at least 15 h.

The column (304 grade stainless steel, length 25 cm and internal diameter 4.1 mm) was carefully filled with a known mass (about 2 g) of coated solid support. As described in [31], before and after the measurements the masses of solvent and solid support were determined gravimetrically using an analytical balance (Sartorius, model CP225D, Germany), accurate to ±0.00001 g. The solid support material was coated with around 20% to 30% (w/w) of the solvent. These loadings were deemed to be large enough to avoid residual adsorption effects. For each solvent investigated, two different loadings were used.

An adaptation was made in the equipment described by Knoop *et al.* [31]: a calibrated Agilent digital gas flow meter (uncertainly of 0.1 $\text{cm}^3 \cdot \text{min}^{-1}$) was installed at the inlet of the column for the control and measurement of the carrier gas flow rate. The helium flow rates were within the range (0.65 to 0.85) $\text{cm}^3 \cdot \text{s}^{-1}$ and corrected for the calibration parameters of the digital flow meter (101.325 kPa and T = 295.15 K). In all assays, the flow rate was compared to the value obtained by a soap bubble flow meter installed at the outlet of the column (from original version) and both values were found to be in good agreement. Before the beginning of the retention time determination, the flow rate was set and allowed to stabilize for at least 30 min.

The sample volumes of injected solutes were varied from (0.1 to 0.3)10^{-3} cm^3, as recommended by Laub *et al.* [35], therefore the solute could be considered to be at "infinite dilution" on the column. Air was used as a non-retainable component, since the GLC apparatus was equipped with a TCD (Thermal Conductivity detector). Thus, together with the solute, about (0.7 to 0.9)10 cm^{-3} of air were injected, using a syringe with a total capacity of 10^{-3} cm^3 (SGE Analytical Science). It was first verified that this quantity of air would not interfere with the obtained retention times.

A Hewlett-Packard HP 3990A integrator was used for the detection of retention times. To ensure reproducibility and stability of the system during the runs, triple analyses of the solute retention times were performed. The reproducibility obtained was generally within 0.1% to 2%, depending on the temperature and the solute. The column temperature was maintained constant within ±0.1 K and it was controlled by a thermostatic bath (Lauda) equipped with two platinum resistance thermometers (PT-100), with an uncertainly of ±0.01 K. The column inlet (P_i) and outlet pressure (P_o) were measured by a pressure gauge (accuracy ± 0.3 kPa) and a capacitive absolute pressure gauge (accuracy ± 0.2 kPa), respectively. Depending on the flow rate of the carrier gas and the column temperature, the column pressure drop ($P_i - P_o$) varied between (5 and 10) kPa.

The experiments were carried out at different temperatures in the range from (303.13 to 368.19) K, and to verify the reproducibility, at a given temperature, for some solutes, the experiment was repeated twice (with different loadings). The results for the solvent stearic acid were compared to the available literature values. Taking into account the possible errors when determining the retention time (<1%), the solute vapour pressure (<0.5%), the number of moles of solvent on GLC column (<2%) and the cross virial coefficient (<0.2%), the estimated overall errors in γ_{13}^{∞} and $\Delta H_1^{E,\infty}$ were less than 4% and 20%, respectively.

3. Theoretical background

The equation proposed by Everett [36] and Cruickshank *et al.* [37] was used in this paper to calculate the activity coefficients at infinite dilution, γ_{13}^{∞}, for solutes in C18 fatty acids, as shown below:

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3 RT}{V_N P_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_o J_2^3 (2B_{12} - V_1^{\infty})}{RT}, \tag{1}$$

where R is the gas constant; T is the absolute column temperature and V_N refers to the net retention volume of the solute. In this expression, the subscriptions 1, 2 and 3 refer to solute, carrier gas and solvent (in this case the C18 fatty acid), respectively. Other quantities occurring in equation (1) are: n_3, the number of moles of solvent on the column packing; P_1^*, the vapour pressure of pure solute; $B_{1i}(i = 1, 2)$, the second virial coefficient and cross coefficient; V_1^*, the molar volume of pure solute; P_o is the column outlet pressure; V_1^{∞}, the partial molar volume of the solute at infinite dilution in the solvent (in this work $V_1^{\infty} \approx V_1^*$, as suggested by Everett and Stoddart [38]). The J_2^3 denotes the pressure-correction term (James–Martin [39] coefficient) calculated by equation (2). All temperature and pressure dependent variables were taken at the column temperature T and column outlet pressure P_o.

$$J_2^3 = \frac{3}{2}\,\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}, \tag{2}$$

where P_i and P_o are the inlet and outlet pressures of the column, respectively.

The net retention volume of solute, V_N, is given by

$$V_N = J_2^3 F_c (t_R - t_G), \tag{3}$$

where t_R and t_G are the retention times for the solute and an unretained gas (in this case air), respectively; and F_c is the column outlet flow rate, corrected for the temperature and pressure calibration of the flow meter by

$$F_c = F\left(\frac{P_o}{P_{fm}}\right)\left(\frac{T_{fm}}{T}\right), \tag{4}$$

where F is the flow rate measured with a calibrated flow meter; P_o is the outlet pressure and P_{fm} is the calibration pressure of the flow meter, *i.e.* 1013.25 Pa; T is the absolute temperature of the column; and T_{fm} is the calibration temperature of the flow meter, *i.e.* T = 295.15 K.

The thermophysical properties required for developing the activity coefficients at infinite dilution were taken from the Dortmund Data Bank (DDB) [2] and the Design Institute for Physical Properties (DIPPR) data bank [40]. The cross second virial coefficients (B_{12}) were estimated from the Tsonopoulos corresponding states correlation [29] coupled with Hudson–McCoubrey mixing rules [41,42], the ionisation energies used in the calculation of $T_{C,12}$ (cross critical temperature) were taken from reference [43], whereas the second virial coefficients of pure solutes were calculated from the DIPPR correlations. The vapour pressures were calculated from Antoine constants stored in the DDB and the liquid molar volumes were also calculated from the DIPPR correlations. The values of P_1^*, V_1^*, B_{11} and B_{12} for all solutes in stearic acid at studied range temperature are given in table S1 in table S1 in the supplementary data (SD).

The activity coefficients at infinite dilution were determined as a function of temperature, therefore, $\ln \gamma_{13}^{\infty}$ can be directly related with excess thermodynamics functions at infinite dilution by the following expression:

$$\ln \gamma_{13}^{\infty} = \frac{\Delta \mu_1^{E,\infty}}{RT} = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R}. \quad (5)$$

Assuming a linear dependence of $\ln \gamma_{13}^{\infty}$ on the reciprocal absolute temperature ($\ln \gamma_{13}^{\infty} = \alpha/T + b$), the partial molar excess enthalpy at infinite dilution, $\Delta H_1^{E,\infty}$, can be estimated from the slope "*a*", and the partial molar excess entropy at infinite dilution, $\Delta S_1^{E,\infty}$, from the intercept "*b*".

TABLE 4
Experimental limiting activity coefficients, $\gamma_{13}^{\infty\,a}$, for solutes in oleic (*cis*-9-octadecenoic) acid, C18:1 9c, at different temperatures.

Solute *T*=	338.36 K	348.29 K	348.36 K	358.28 K
n-Hexane	1.401	1.329	1.341	1.302
n-Heptane	1.516	1.428	1.469	1.369
Isooctane	1.627	1.519	1.544	1.477
Hex-1-ene	1.213	1.205	1.194	1.152
Toluene	0.925	0.893	0.865	0.852
Cyclohexane	1.062	1.001	1.011	1.352
Ethylbenzene	1.052	0.991	0.964	0.962
Methanol	1.573		1.476	1.491
Ethanol	1.451		1.373	1.382
Propan-1-ol	1.355		1.267	1.244
Butan-1-ol	1.260		1.226	1.224
Propan-2-ol	1.199		1.122	1.113
Butan-2-ol	1.019		0.987	0.975
Chloroform	0.653	0.676		0.628
Trichloroethylene	0.803	0.783		0.742
Chlorobenzene	0.930	0.905		0.877
1,2-Dichloroethane	1.090	1.077		1.011
Benzyl chloride		1.439		1.385
Ethyl acetate	1.201	1.130		1.091
Acetone	1.311	1.292		1.197
Anisole	1.204	1.170		1.153

[a] Uncertainty 4%.

4. Results and discussion

Tables 3 to 6 list the average γ_{13}^{∞} experimental values for different solutes in the investigated fatty acids: stearic (octadecanoic) acid, oleic (*cis*-9-octadecenoic) acid, linoleic (*cis*,*cis*-9,12-octadecadienoic) acid, and linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acid over temperature range from (303.13 to 368.19) K, respectively.

Table 3 also shows, in addition to the experimental data of this work, the values of γ_{13}^{∞} for stearic acid from available literature [44,45], as stored in DDB (Dortmund Data Bank) [2]. For most solutes, we observe good agreement between literature values and those obtained in this work. Comparing γ_{13}^{∞} in stearic acid from this work to the results obtained by Alessi *et al.* [44] (by interpolation), we can find differences of less than 0.02 to 0.21 in absolute values (or mean difference less than 6%). Comparing our result and those obtained by Alessi *et al.* [45], for methanol the difference is by nearly 24%. In fact, if we compare the data from these two available sources, it is possible to check the inconsistence of both values of γ_{13}^{∞} itself and as function of temperature.

The discrepancy between the earlier published γ_{13}^{∞} values for some solutes and one listed in table 3 is probably due to different methods used to obtain the retention time, the use of different equations and different references of thermodynamic properties for calculating γ_{13}^{∞}, and the use of different inert carrier gases for the measurements. Since the new values were determined several

TABLE 3
Experimental limiting activity coefficients, $\gamma_{13}^{\infty\,a}$, for solutes in stearic (octadecanoic) acid, C18:0, at different temperatures and literature values.

Solute	This work						Alessi *et al.* [44]			Alessi *et al.* [45]			
T/K	349.47	349.48	358.39	358.46	367.93	368.13	354	384	413	347	357	367	377
n-Hexane	1.258		1.239[c]			1.186	1.16	1.12	1.10	1.25	1.27	1.27	1.30
n-Heptane	1.346		1.332[c]			1.279	1.13	1.23	1.22				
Isooctane	1.419		1.407[c]		1.365[d]	1.354							
Hex-1-ene	1.151		1.134[c]			1.085	1.04	1.03	0.96				
Toluene	0.903	0.892	0.872			0.869	0.85	0.83	0.81				
Cyclohexane	0.985		0.968[c]			0.959[d]	0.91	0.90	0.84				
Ethylbenzene	1.029		1.014[c]		1.020[d]	0.982							
Methanol		1.964	1.924			1.751	1.97	1.55	1.14	2.44	2.24	2.08	1.98
Ethanol		1.811	1.713			1.549	1.70	1.30	1.01				
Propan-1-ol	1.555[b]	1.582		1.461	1.363	1.387	1.58	1.21	0.98				
Butan-1-ol	1.501[b]	1.481		1.363	1.307	1.315	1.52	1.17	0.97				
Propan-2-ol	1.337[b]			1.262	1.175	1.142[d]							
Butan-2-ol	1.176[b]	1.197		1.088	1.019	1.006[d]							
Chloroform	0.734		0.704			0.694	0.70	0.69	0.64	0.73			
TCE		0.789	0.776		0.741								
Chlorobenzene	0.954		0.936[c]			0.924[d]							
1,2-DCE	1.157	1.142	1.102	1.121[c]	1.096[d]	1.062							
Benzyl Chloride	1.559	1.545	1.486			1.452							
Ethyl acetate		1.245	1.189		1.076	1.090[d]	1.17	1.07	0.97				
Acetone		1.480	1.391			1.304	1.37	1.12	1.06				
Anisole	1.216	1.224	1.189	1.194[c]	1.173[d]	1.157							

TCE = trichloroethylene.
1,2-DCE = 1,2-dichloroethane.
[a] Uncertainty 4%.
[b] T = 349.38 K.
[c] T = 358.40 K.
[d] T = 368.19 K.

TABLE 5
Experimental limiting activity coefficients, γ_{13}^{∞} [a], for solutes in linoleic (*cis*,*cis*-9,12-octadecadienoic) acid, C18:2 9c12c, at different temperatures.

Solute *T*=	338.28 K	338.28 K	348.31 K	348.28 K	358.30 K
n-Hexane	2.196		2.556	2.524	2.932
n-Heptane	2.322		2.736	2.678	3.232
Isooctane	2.434		2.975	2.962	3.632
Hex-1-ene	1.726		1.982	2.003	2.360
Toluene	1.097	1.094	1.165	1.192	1.263
Cyclohexane	1.493	1.486	1.709	1.704	2.026
Ethylbenzene	1.271		1.363	1.353	1.487
Methanol	1.454		1.328		
Ethanol	1.362			1.222	1.231
Propan-1-ol	1.288		1.242		1.220[b]
Butan-1-ol	1.187			1.181	
Propan-2-ol	1.134			1.136	1.127[b]
Butan-2-ol	1.089		1.101		1.100
Chloroform	0.642	0.644	0.674	0.689	0.734
Trichloroethylene					
Chlorobenzene	1.002	0.996	1.072	1.069	1.162
1,2-Dichloroethane	1.048	1.057	1.055	1.082	1.112
Benzyl chloride			1.531	1.540	1.608
Ethyl acetate	1.228			1.267	1.115[b]
Acetone	1.213			1.161	1.133[b]
Anisole	1.242		1.292	1.317	1.369

[a] Uncertainty 4%.
[b] $T = 358.33$ K.

TABLE 6
Experimental limiting activity coefficients, γ_{13}^{∞} [a], for solutes in linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acid, C18:3 9c12c15c, at different temperatures.

Solute *T*=	303.13 K	313.24 K	313.25 K	323.26 K
n-Hexane	3.699		2.911	3.306
n-Heptane	3.834		3.066	3.264
Isooctane	4.570		3.535	4.012
Hex-1-ene	2.520	2.123	2.187	2.454
Toluene			1.171	1.204
Cyclohexane	2.356	1.913	1.880	2.041
Ethylbenzene				
Methanol	1.164		1.291[b]	1.357
Ethanol	1.070		1.216	1.316
Propan-1-ol				1.271
Butan-1-ol				
Propan-2-ol			1.081	1.121
Butan-2-ol				
Chloroform	0.613		0.621[b]	0.623[c]
Trichloroethylene				
Chlorobenzene				
1,2-Dichloroethane	1.053	1.035	1.020	0.996
Benzyl chloride				
Ethyl acetate	1.312		1.160[b]	1.178[c]
Acetone	1.099	1.057	1.101	1.111
Anisole				

[a] Uncertainty 4%.
[b] $T = 313.24$ K.
[c] $T = 323.24$ K.

times and using different loadings for most of the solutes the results show good agreement with references, we believe them to be more accurate.

In a previous work [30], we have already noted that the combination of a rather long non-polar hydrocarbon chain and the strongly polar carboxylic acid group enables fatty acids to dissolve easily both polar and non-polar compounds. In this study we could observe the influence of the presence and number of *cis* double bonds in fatty acids in the interaction with several solutes. A *cis* double bond introduces a pronounced bend in fatty acid chain and therefore causes a distinct kink in the polyunsaturated fatty acids alkyl chain [1]. The effect of the quantity of fatty acid *cis* double bonds can be seen on magnitude and trend of γ_{13}^{∞} when comparing the results obtained in saturated and mono-saturated fatty acids (stearic and oleic acids, respectively) with data from polyunsaturated fatty acids (linoleic and linolenic acids).

In terms of the overall magnitude of the γ_{13}^{∞} values (maximum around 4.6 for linolenic acid), it can be noted that unlike our previous work with saturated fatty acids [30], the values of γ_{13}^{∞} present more pronounced deviations from ideal mixture behaviour. For all solvents investigated, the lowest values of γ_{13}^{∞} are observed for chloroform followed by other chlorine-containing compounds (trichloroethylene, chlorobenzene, and 1,2-dichloroethane) which means that independent of the presence of *cis* double bonds in the fatty acid chain, chloroform has a strong interaction with fatty acids (unsaturated or not), that can be result from van der Waals forces and polarity effects. It is also worth mentioning that chlorine-containing compounds are naturally found in fatty acids as in many other biomolecules [46].

Figures 2 to 5 show the limiting activity coefficients in stearic (octadecanoic), oleic (*cis*-9-octadecenoic), linoleic (*cis*,*cis*-9,12-octadecadienoic), and linolenic (*cis, cis, cis*-9,12,15-octadecatrienoic) acids as function of the absolute temperature for several investigated solutes.

For all solvents studied, the values of γ_{13}^{∞} for alkane (*n*-hexane, *n*-heptane, and isooctane) increase with increasing solute alkyl chain and for alcohols the converse is true, *i.e.* γ_{13}^{∞} values decrease with increasing solute alkyl chain. For all solvents investigated, toluene shows the smallest γ_{13}^{∞} values from the hydrocarbons series studied. This is the result of the interaction between the slightly polar portion of fatty acid molecules with the localised or delocalised π-electrons clouds in benzene structure. Analysing the values

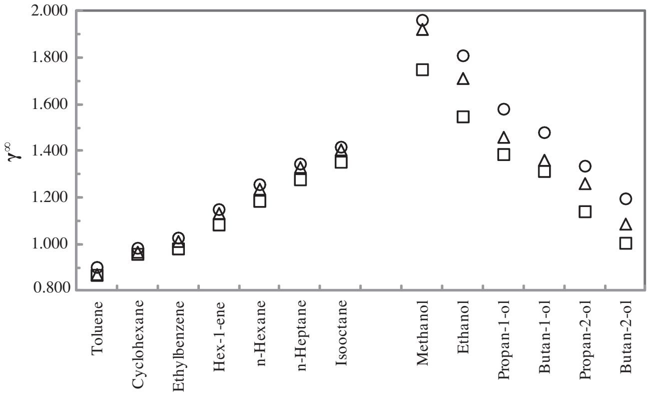

FIGURE 2. Plot of γ_{13}^{∞} in stearic (octadecanoic) acid versus *T* for hydrocarbons and alcohols, ○ at $T = 349.5$ K; Δ at $T = 358.4$ K; and □ at $T = 368.1$ K.

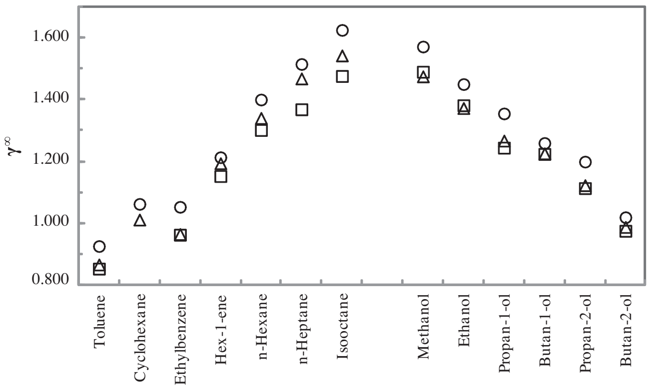

FIGURE 3. Plot of γ_{13}^{∞} in oleic (*cis*-9-octadecenoic) acid *versus* *T* for hydrocarbons and alcohols, ○ at $T = 338.4$ K; Δ at $T = 348.4$ K; and □ at $T = 358.3$ K.

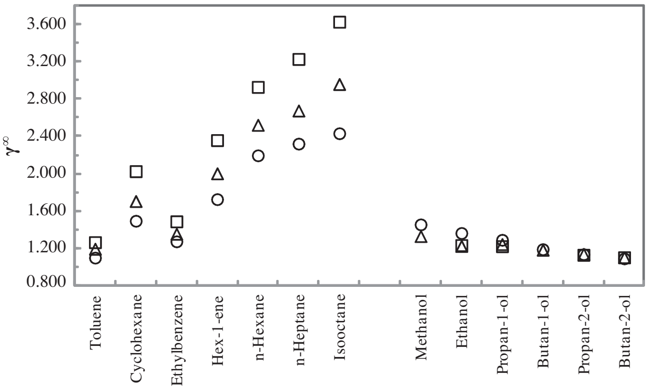

FIGURE 4. Plot of γ_{13}^{∞} in linoleic (*cis*,*cis*-9,12-octadecadienoic) acid *versus T* for hydrocarbons and alcohols, ○ at $T = 338.3$ K; Δ at $T = 348.3$ K; and □ at $T = 358.3$ K.

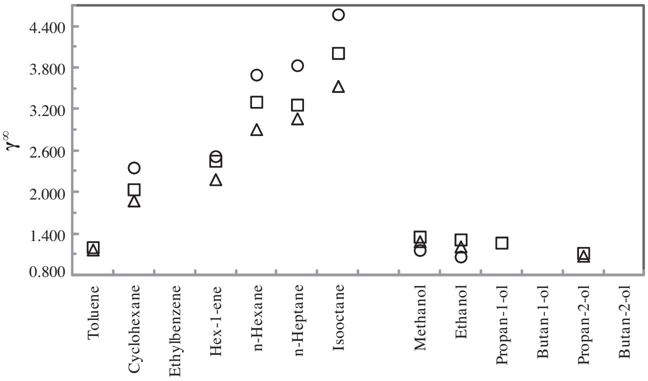

FIGURE 5. Plot of γ_{13}^{∞} in linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acid versus *T* for hydrocarbons and alcohols, ○ at $T = 303.1$ K; Δ at $T = 313.3$ K; and □ at $T = 323.3$ K.

of γ_{13}^{∞} for alkane, alkene, and cycloalkane with the same carbon number, it was found the follow hierarchy for the γ_{13}^{∞} values in increasing order: cyclohexane < hex-1-ene < *n*-hexane. In the case of cycloalkanes, it should be considered that their molar volumes are smaller than those of linear alkane and alkene with the same number of carbons atoms, therefore the packing effect additionally increases the interaction with fatty acids, the same was observed in previous work [30] and for others solvents as ionic liquids [47–49]. The alkene double bond leads to stronger mutual interactions between the fatty acids and the solute hex-1-ene than between the fatty acids and *n*-hexane.

As mentioned above the influence of the number of *cis* double bonds follows typical trends for some solutes: for the series of hydrocarbons (non-polar solutes), the values of γ_{13}^{∞} increase with increasing number of *cis* double bonds in the fatty acid alkyl chain. In case of alcohols (polar solutes), γ_{13}^{∞} values decrease with increasing number of *cis* double bonds in the carbon chain of the solvent. We can deduce that the increase in the *cis* double bonds in fatty acid alkyl chain implies the increase of solvent polarity, which reduces the intermolecular interaction with non-polar solvents and increases the interaction with polar solvents, as reflected in the values of γ_{13}^{∞}.

If we compare the magnitude of γ_{13}^{∞} values for non-polar and polar solutes in stearic, oleic, linoleic, and linolenic acids, it is possible to observe a significant change in values of γ_{13}^{∞} due the presence of *cis* double bonds in fatty acids (see profiles of γ_{13}^{∞} values for these solutes in figures 2 to 5). For stearic acid (saturated fatty acid) higher interactions (lower γ_{13}^{∞} values) are observed with non-polar solutes, while for oleic acid (monounsaturated fatty

TABLE 7
Limiting values of the partial molar excess enthalpy, $\Delta H_1^{E,\infty}$[a], entropy, $\Delta S_1^{E,\infty}$, and Gibbs free energy, $\Delta G_1^{E,\infty}$, for solutes in stearic, oleic, linoleic, and linolenic acid at reference temperature 298.15 K.

Solute	Stearic acid			Oleic acid			Linoleic acid			Linolenic acid		
	$\Delta G_1^{E,\infty}$ / (kJ · mol^{-1})	$\Delta H_1^{E,\infty}$ / (kJ · mol^{-1})	$T_{ref}\Delta S_1^{E,\infty}$ / (kJ · mol^{-1})	$\Delta G_1^{E,\infty}$ / (kJ · mol^{-1})	$\Delta H_1^{E,\infty}$ / (kJ · mol^{-1})	$T_{ref}\Delta S_1^{E,\infty}$ / (kJ · mol^{-1})	$\Delta G_1^{E,\infty}$ / (kJ · mol^{-1})	$\Delta H_1^{E,\infty}$ / (kJ · mol^{-1})	$T_{ref}\Delta S_1^{E,\infty}$ / (kJ · mol^{-1})	$\Delta G_1^{E,\infty}$ / (kJ · mol^{-1})	$\Delta H_1^{E,\infty}$ / (kJ · mol^{-1})	$T_{ref}\Delta S_1^{E,\infty}$ / (kJ · mol^{-1})
n-Hexane	5.69	3.38	−2.31	6.18	3.72	−2.46	−29.31	−14.53	14.77			
n-Heptane	4.75	2.97	−1.78	8.65	5.15	−3.50	−33.36	−16.62	16.74			
Isooctane	3.92	2.59	−1.33	8.01	4.89	−3.12	−40.10	−20.14	19.97			
Hex-1-ene	5.93	3.39	−2.54	4.40	2.60	−1.80	−30.94	−15.73	15.21			
Toluene							−13.69	−7.16	6.54			
Cyclohexane	2.90	1.54	−1.36				−29.45	−15.13	14.32	25.45	13.87	−11.58
Ethyl benzene	4.88	2.67	−2.21	8.08	4.36	−3.73	−15.36	−7.85	7.51			
Methanol										−12.77	−6.23	6.53
Ethanol	15.17	8.98	−6.18				8.80	5.08	−3.72	−16.86	−8.40	8.46
Propan-1-ol	12.89	7.55	−5.34	6.72	3.80	−2.92	4.57	2.76	−1.81			
Butan-1-ol	12.74	7.40	−5.34									
Propan-2-ol	14.80	8.38	−6.43									
Butan-2-ol	16.40	9.08	−7.32				5.91	3.25	−2.66			
Chloroform	6.66	3.17	−3.49				−11.09	−6.48	4.61	−0.12	−0.67	−0.55
TCE[b]	7.31	3.63	−3.68	7.99	3.97	−4.03						
CB[c]	5.43	2.87	−2.56	5.78	2.98	−2.80	−14.11	−7.50	6.61			
1,2−DCE[d]				6.83	3.76	−3.08				4.39	2.28	−2.11
Ethyl acetate	6.20	3.93	−2.27									
Acetone	14.78	8.27	−6.50	8.74	4.88	−3.86				4.04	2.15	−1.89
Anisole	12.45	7.24	−5.21	7.92	4.58	−3.34	6.03	3.45	−2.57			

[a] Uncertainty 20%.
[b] TCE = trichloroethylene.
[c] CB = chlorobenzene.
[d] 1,2-DCE = 1,2-Dichloroethane.

acid) polar and non-polar solutes have the same interaction (about same magnitude of γ_{13}^{∞} values) and for linoleic and linolenic acids (polyunsaturated fatty acids) polar solutes now have higher interaction with the solvent (lower γ_{13}^{∞} values) than non-polar solutes. This is probably consequence of the presence of the hydrogen atom of *cis* double bond in fatty acid, which shows stronger acidic properties and the π-electron of double bond causes an increase of interactions between unsaturated fatty acids with polar solutes.

For stearic and oleic acids the influence of temperature follows a typical trend for most of the solutes with increasing temperature was observed a decrease in γ_{13}^{∞} value. While for linoleic acid the opposite effect was noted for hydrocarbons solutes, in which the temperature increase was followed by an increase in γ_{13}^{∞} value. For linolenic acid, the effect of the temperature on the magnitude of γ_{13}^{∞} was more difficult to fit into a pattern.

The partial molar excess enthalpy, $\Delta H_1^{E,\infty}$, entropy, $\Delta S_1^{E,\infty}$, and Gibbs free energy, $\Delta G_1^{E,\infty}$, at infinite dilution calculated from stearic (octadecanoic), oleic (*cis*-9-octadecenoic), linoleic (*cis*,*cis*-9,12-octadecadienoic), and linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acids experimental results are shown in table 7.

In case of the solvents stearic and oleic acids, positive values of $\Delta G_1^{E,\infty}$, and $\Delta H_1^{E,\infty}$ were found for all solutes and the entropy values are relative small and negative. The positive values for $\Delta H_1^{E,\infty}$ mean a weak association between the solutes studied and these two fatty acids. However for stearic acid, we could see the same trend as observed for other saturated fatty acids in our previous study [30]. Both for alkanes and for alcohol solutes, the calculated values of $\Delta H_1^{E,\infty}$ decrease with an increase in carbon number of the solute. Furthermore, for alcohols the decreasing $\Delta H_1^{E,\infty}$ values occur with decrease of γ_{13}^{∞} values and the opposite is observed for alkanes. In the case of polyunsaturated fatty acids, we obtained negative $\Delta H_1^{E,\infty}$ values for some solutes. The negative values of partial molar excess enthalpies at infinite dilution indicate that interactions of solute–solvent pairs are higher than for solute–solute pairs. For linolenic acid, the strong association occurred with alcohols (polar solute), whereas for linoleic acid, as observed also in figure 4, the strong negative $\Delta H_1^{E,\infty}$ values is a result of the stark increase of γ_{13}^{∞} values with increasing temperature. It should be noted that the $\Delta H_1^{E,\infty}$ values for the polyunsaturated fatty acids were calculated from different ranges of temperature.

5. Conclusions

Limiting values of activity coefficients at infinite dilution for 21 solutes in four saturated and unsaturated fatty acids were measured by gas–liquid chromatography at temperatures from (303.13 to 368.19) K and compared to available literature data. The thermodynamic functions at infinite dilution for the same solutes were derived for stearic (octadecanoic), oleic (*cis*-9-octadecenoic), linoleic (*cis*,*cis*-9,12-octadecadienoic), and linolenic (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic) acids. For all solvents, different trends could be identified for polar and non-polar compounds as a function of temperature. It appears that both the presence and the number of *cis* double bonds in the fatty acid alkyl chain have influence on the solvent–solute and solute–solute interactions and hence on the values of γ_{13}^{∞}. These results allow a more accurate description of the real behaviour of fatty systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2012.12.009.

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