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Solubilities of Stearic Acid in Organic Solvents and in Azeotropic Solvent Mixtures

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The solubility of stearic acid was measured in ethanol, 2-propanol, heptane, hexane, acetone, and trichloroethylene and in the azeotropic mixtures of the solvents (ethanol−heptane; hexane−ethanol; ethanol−trichloroethylene; acetone−heptane; heptane−2-propanol; acetone−hexane; hexane−2-propanol; 2-propanol−trichloroethylene), by the phase disappearance method, from (290 to 325) K. The stearic acid−pure solvent experimental data were correlated with the Van Laar, Wilson, NRTL, and UNIQUAC equations and the solubility of stearic acid in azeotropic mixtures with the NIBS/Redlich−Kister equation. The UNIFAC solubility prediction improved when the correction for the existence of stearic acid dimers was applied except for systems with trichloroethylene and 2-propanol. The solubility of stearic acid increased in azeotropic mixtures regarding pure solvents except for the heptane−acetone and hexane−acetone mixtures.

Introduction

Stearic acid (octadecanoic acid) is a fatty acid obtained from hydrogenated fat or vegetable oils by hydrolysis at high temperature and pressure. The acid is purified by distillation. Its molecule is amphiphilic, although it has hydrophobic character, mainly due to its long hydrocarbon chain. The mentioned acid is a raw material used to make soaps, paints, and cosmetics. In pharmacy, stearic acid is used for ointments, suppositories, enteric pills, and bitter remedies coatings.[1] It is also used as a lubricant to work with some metals. In this respect, some studies about its solubility in organic solvents were conducted.

In relation to the separation of fatty acids by fractional crystallization at low temperatures, Kolb and Brown[2] determined the stearic acid solubility from (−30 to 10) °C in several solvents. Brandret and Johnson[3] also determined its solubility in fluorocarbon, chlorocarbons, and ethanol. Beckmann et al.[1] measured the solubility of three polymorphs of the acid in decane, methanol, and butanone. Domanska[4] determined the solubility of stearic acid in several solvents and binary mixtures. Mirmehrabi and Rohani[5] measured the solubility of stearic acid polimorphs in methanol, 2-butanone, decane, and hexane. However, a closer examination of data shows different values of solubility. Therefore, an additional study on solubility of stearic acid in pure solvents and with mixtures of solvents that might have a synergetic effect on the solubility is needed.

The objective of this work is the study of the solid–liquid equilibrium of stearic acid in pure solvents and in azeotropic mixtures of solvents, as part of a project for obtaining the acid from vegetable oil. This led to (a) the experimental determination of solubility data, (b) the correlation of activity coefficients−composition with the usual thermodynamic models, and (c) the prediction study using the UNIFAC method. The pure solvents selected were ethanol, 2-propanol, acetone, heptane, hexane, and trichloroethylene. The mixtures of solvents were chosen at the azeotropic concentration because they are easily regenerated by distillation with a constant composition. The azeotropic mixtures (101.325 kPa) chosen were: ethanol−heptane; hexane−ethanol; ethanol−trichloroethylene; acetone−heptane; heptane−2-propanol; acetone−hexane; hexane−2-propanol; and 2-propanol−trichloroethylene.

Solid−Liquid Equilibrium Models

Correlation of Solid–Liquid Equilibrium. The activity α_i of the i component in the solid–liquid equilibrium can be calculated[6] by the following equation

$$\ln(\alpha_i) = \ln(\gamma_i x_i) = -\frac{\Delta H_\mathrm{t}}{RT_\mathrm{t}}\left[\frac{T_\mathrm{t}}{T}-1\right] + \frac{\Delta C\mathrm{p}}{R}\left[\frac{T_\mathrm{t}}{T}-1\right] - \frac{\Delta C\mathrm{p}}{R}\ln\frac{T_\mathrm{t}}{T} \tag{1}$$

where α_i is the activity; γ_i is the activity coefficient; x_i is the mole fraction in the liquid phase; ΔH_t is the molar enthalpy of fusion of the i solute at the triple point temperature T_t; and $\Delta C\mathrm{p}$ is the difference in solute heat capacity between the solid and liquid at the melting point. As there is little difference between the triple point temperature and the normal point melting temperature and between the enthalpies of fusion at these two temperatures, the enthalpy and temperature at the triple point can be substituted by its values at the normal melting point. Moreover, the two terms of the eq 1 containing $\Delta C\mathrm{p}$ almost cancel each other, and they are less important than the remaining terms. Therefore, if a solid–solid phase transition does not occur, the following equation can be used to calculate the activity coefficient

$$\ln(\gamma_i x_i) = -\frac{\Delta H_\mathrm{f}}{RT_\mathrm{f}}\left[\frac{T_\mathrm{f}}{T}-1\right] \tag{2}$$

where ΔH_f is the enthalpy of fusion at the normal melting point (T_f). The obtained activity coefficients were correlated using models that describe the Gibbs energy excess of mixing. For the correlation of the activity coefficients of the binary systems, stearic acid−pure solvent, Van Laar, Wilson, NTRL, and

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UNIQUAC models were used. The used equations for the activity coefficients are listed in Table 1.

For the prediction of solute solubilities in the azeotropic mixtures of solvents, the NIBS/Redlich–Kister equation suggested by Acree et al.[7–9] was used

$$\ln x_{\mathrm{A}} = x_{\mathrm{B}}^{0} \ln\left(x_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{B}} + x_{\mathrm{C}}^{0} \ln\left(x_{\mathrm{A}}^{\mathrm{sat}}\right)_{\mathrm{C}} + x_{\mathrm{B}}^{0} x_{\mathrm{C}}^{0} \sum_{i=0}^{N} S_i^{*}\left(x_{\mathrm{B}}^{0} - x_{\mathrm{C}}^{0}\right) \quad (3)$$

where $x_{\mathrm{B}}{}^0$ and $x_{\mathrm{C}}{}^0$ are the initial mole fractions of the binary solvent as if the solute A is not present and $(x_{\mathrm{A}}{}^{\mathrm{sat}})_i$ is the mole fraction solubility of the A solute in pure solvent i. S_i* is the parameter of the model, and it is expressed as the following

$$S_i^{*} = a_i + b_i T + c_i T^2 \quad (4)$$

The parameters of the equations were calculated using Marquardt's maximum neighbor method of minimization of the objective function Ω

$$\Omega = \sum \left[\ln(\gamma_i x_i)^{\mathrm{exptl}} - \ln(\gamma_i x_i)^{\mathrm{calcd}}\right]^2 \quad (5)$$

where $(\gamma_i x_i)^{\mathrm{exptl}}$ and $(\gamma_i x_i)^{\mathrm{calcd}}$ are the products of the mole fraction and the experimental and calculated activity coefficients, respectively.

The root-mean-square deviation of temperature (σ) between experimental and calculated values was defined by the following equation

$$\sigma = \left[\sum_{i=1}^{n} \left(T_i^{\mathrm{exptl}} - T^{\mathrm{calcd}}\right)^2 / (n-1)\right]^{1/2} \quad (6)$$

where n is the number of experimental data; T_i^{exptl} is the experimental temperature; and T_i^{calcd} is the temperature calculated from eq 2 with the $\gamma_i{}^{\mathrm{calcd}}$ values.

Predictive UNIFAC Mode. The nonideality of the solid phase will be described by the predictive UNIFAC method of group contribution.[6] In this model, the activity coefficient has two parts, combinatorial and residual. The combinatorial part describes the dominant entropic contribution, and the residual part is due to intermolecular forces and is responsible for the enthalpy of mixing:

$$\ln \gamma_i = \gamma_i{}^{\mathrm{C}} + \ln \gamma_i{}^{\mathrm{R}} \quad (7)$$

$$\ln \gamma_i^{\mathrm{C}} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (8)$$

where

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad (9)$$

The coordination number z is taken to be 10. The values of θ and Φ are related to mole fraction

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (10)$$

These are given by k group contributions R_k and Q_k according to

$$r_i = \sum_k v_k^{(i)} R^k \qquad q_i = \sum_k v_k^{(i)} Q_k \quad (11)$$

The residual contribution to activity coefficient is given by

$$\ln \gamma_i{}^{\mathrm{R}} = \sum_k \upsilon_k{}^{(i)} [\ln \Gamma_k - \ln \Gamma_k] \quad (12)$$

where Γ_k is the group residual activity coefficient and is related with the composition and temperature through

Table 1. Activity Coefficient Models for Binary Systems

model		binary parameters	symbol definitions	$\ln \gamma_1$
Van Laar	A_1, A_2		x_1 mole fraction of 1 component. γ_1 activity coefficient of 1 component. T/K temperature.	$\ln \gamma_1 = x_2^2[1 / A_1 x_1 + A_2 x_2 + \mathrm{x}_1 - (A_1 - A_2) / (A_1 x_1 + A_2 x_2)^2]$
Wilson	A_{12}, A_{21}		Binary parameters of Van Laar and Wilson were considered independent of the temperature.	$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2(\Lambda_{12} / x_1 + \Lambda_{12} x_2 - \Lambda_{21} / \Lambda_{12} x_1 + x_2)$
NRTL	A_{12}, A_{21}	$\tau_{12} = A_{12} / RT$; $G_{12} = \exp(-\alpha\tau_{12})$	$A_{12} = g_{12} - g_{22}$; g_{ij}/J·mol^{-1} is an energy parameter characteristic of the ij interaction. $\alpha = \alpha_{12} = \alpha_{21}$ is related to the nonrandomness in the mixture.	$\ln \gamma_1 = x_2^2[\tau_{21}(G_{21} / x_1 + x_2 G_{21})^2 + \tau_{12} G_{12} / (x_2 + x_2 G_{12})^2]$
UNIQUAC	a_{12}, b_{12}, a_{21}, b_{21}	$A_{12} = a_{12} + b_{12}T$; $\tau_{12} = \exp(-A_{12} / T)$; $l_1 = (z/2)(r_1 - q_1) - (r_1 - 1)$; $\theta_1 = q_1 / \Sigma^2 q_j x_j$; $\Phi_1 = r_1 x_1 / \Sigma^2 r_j x_j$	$A_{12} = (u_{12} - u_{22})/R$; u_{ij}/J·mol^{-1} is an energy parameter characteristic of the ij interaction. R/J·mol^{-1}·K^{-1} is the gas constant. z is the coordination number equal to 10. $q_j = \Sigma k v_k Q_k$; υ_k is the number of groups k in the molecule j, and Q_k/m^2 is the k group area. $r_j = \Sigma k v_k R_k$; υ_k is the number of groups k in the molecule j, and R_k/m^3 is the k group volume. $\gamma_1{}^{\mathrm{C}}$ and $\gamma_1{}^{\mathrm{R}}$ are the combinatorial and residual contributions to activity coefficient of 1 component, respectively.	$\ln \gamma_1 = \ln \gamma_1^{\mathrm{C}} + \ln \gamma_1^{\mathrm{R}}$; $\ln \gamma_1^{\mathrm{C}} = \ln \Phi_1 / x_1 + z / 2q_1 \ln \theta_1 / \Phi_1 + l_1 - \Phi_1 / x_1 \Sigma_j^2 x_j l_j$; $\ln\gamma_1^{\mathrm{R}} = q_1[1 - \ln(\Sigma_j^2 \theta_j \tau_{j1}) - \Sigma_j^2 \theta_j \tau_{1j} / \Sigma_k^2 \theta_1 \tau_{1k}]$

$$\ln \Gamma_k = Q_k\left[1 - \ln \sum_m \theta_m \psi_{mk} - \sum_m \left(\frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}}\right)\right] \qquad (13)$$

In this equation

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad (14)$$

where X_m is the mole fraction of group m. The group interaction parameter Ψ_{mn} is given by

$$\psi_{mn} = \exp - \left[\frac{U_{mn} - U_{nn}}{RT}\right] = \exp - (a_{mn}/T) \qquad (15)$$

where U_{mn} is a measure of the energy of interaction between groups m and n. The values of the parameters R_k, Q_k, and Ψ_{mn} were taken from Hansen et al.[10]

Experimental Procedure

Materials. Stearic acid has four polymorphs.[11] Polymorph C is thermodynamically the most common and stable. Form C can be obtained by crystallization from a polar solvent.[5] Stearic acid (Panreac, Spain > 0.979 mass fraction) was crystallized three times from acetone. Its purity checked by gas chromatography (8700 Perkin-Elmer) was 0.999 mass fraction. The experimental melting temperature (342.65 K) of stearic acid was 0.1 K of the reported.[4] When the calculations were made, a value of 61.209 kJ·mol^{-1} was used for the fusion enthalpy of stearic acid.[12]

All solvents (Panreac, analytical grade) were dried over 4 Å molecular sieves. The purity, checked by GC, was higher than 0.999 mass fraction. The compositions of the azeotropic mixtures of solvents (101.325 kPa) used in this work are given in Table 2.

Dynamic Method. The solubility was measured using a dynamic method. A mixture of solute and solvent with a fixed composition was prepared by mass. The masses of the samples and solvents were determined using an analytical balance (Mettler H33AR, Switzerland) with an uncertainty of 0.0001 g. The mixture was placed in a Pyrex glass cell immersed in a glass thermostat. Continuous stirring was achieved with a magnetic stir bar. The mixture was first heated quickly to achieve one phase, and then, to be cooled to obtain the acid crystallization in the solvent, the sample was heated again very slowly (less than 0.1 K every 30 min) with continuous stirring. The temperature at which the last crystal disappeared during the second or third heating cycle was detected visually, and it was taken as the solid–liquid equilibrium temperature. This temperature was measured with a thermometer (Afora, Spain) with works certificate, subdivided in 0.1 K, immersed in the liquid. The standards used in the thermometer calibration were certified by the German Official Calibration Ludwig Schneider Messtechnik GmbH Nr DKD-K-0670, which is an EA and ILAC accepted laboratory. The measurements were carried out in a (290 to 325) K temperature range. All experiments were made at least three times, and the results were averaged. The uncertainties of the method were ± 0.1 K and ± 0.0005 mole fraction for the equilibrium temperature and concentration, respectively.

Table 2. Azeotropic Composition of the Binary Solvent Systems in Mole Fraction

solvent 1	solvent 2	T/K	x_1	ref
ethanol	heptane	344.89	0.6180	14
hexane	ethanol	331.65	0.6590	15
acetone	hexane	322.75	0.6300	16
acetone	heptane	328.25	0.9000	17
hexane	2-propanol	338.95	0.8429	18
heptane	2-propanol	357.25	0.5450	19
ethanol	trichloroethylene	343.85	0.5259	20
2-propanol	trichloroethylene	348.65	0.4837	21

Results and Discussion

Experimental results of the solid–liquid equilibria are listed in Table 3 and Table 4. The presented data are within the same order as that reported by other authors. The experimental solubilities of stearic acid in heptane, acetone, 2-propanol, and trichloroethylene agree with the values reported by Domanska.[4] However, slight discrepancies between experimental and reported solubilities were observed for ethanol[3,4] and hexane[5] (Figure 1).

The accuracy of experimental data for a small temperature interval can be checked supposing that ΔH_f in eq 2 was constant, then the Van't Hoff equation can be applied.[12,13] A log plot of the solute solubility as mole fraction in pure solvents versus $1/T$ should be linear. The corresponding plot is shown in Figure 2. Correlation coefficients of the straight lines are between 0.988 and 0.999.

The acid solubilities were lower than the ideal solubility in pure solvents, thus positive deviations of the ideality were found ($\gamma_1 > 1$), except for trichloroethylene (Figure 2). This can be explained because the carbon in the trichloroethylene molecule can participate in hydrogen bonding because it is bounded to electronegative atoms of chlorine.

The UNIFAC solubility prediction of stearic acid in pure solvents was not good (high values of σ, Table 5) except for 2-propanol and trichloroethylene. The prediction improved when the existence of dimers of stearic acid was taken into consideration and quantified, replacing in eq 2 the mole fraction (x_i)

Table 3. Stearic Acid Solubility in Pure Solvents

acetone		ethanol		heptane		hexane		2-propanol		trichloroethylene	
T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1
291.95	0.0042	291.45	0.0025	293.45	0.0023	293.75	0.0034	292.35	0.0099	292.75	0.0230
294.75	0.0055	294.95	0.0031	297.35	0.0053	294.95	0.0045	295.75	0.0124	295.25	0.0299
298.05	0.0077	299.85	0.0057	300.65	0.0089	298.45	0.0073	299.65	0.0172	298.05	0.0437
301.15	0.0103	304.85	0.0103	304.65	0.0163	300.65	0.0103	302.15	0.0231	301.65	0.0603
304.85	0.0152	309.45	0.0180	307.35	0.0227	303.55	0.0161	303.75	0.0282	305.55	0.0908
307.65	0.0204	312.35	0.0280	309.85	0.0366	307.25	0.0295	308.35	0.0452	308.55	0.1178
311.05	0.0313	314.75	0.0406	313.45	0.0562	310.05	0.0460	311.25	0.0625	310.65	0.1367
313.95	0.0456	316.25	0.0498	314.55	0.0661	313.45	0.0710	313.35	0.0814	313.25	0.1644
316.45	0.0638	316.85	0.0560	315.85	0.0779	315.05	0.0856	315.45	0.1027	314.85	0.1854
319.05	0.0845	318.55	0.0731	317.55	0.1005	316.75	0.1076	317.15	0.1223	317.05	0.2122
320.35	0.1059	319.95	0.0926	319.35	0.1279	319.05	0.1423	318.75	0.1435	321.05	0.2643
321.55	0.1260	321.95	0.1241	322.05	0.1786	321.55	0.1873	321.05	0.1789	323.25	0.2985
322.55	0.1475	323.65	0.1546	324.85	0.2401	323.55	0.2397	321.95	0.2101		

Table 4. Stearic Acid Solubility in Azeotropic Mixtures

ethanol + heptane		hexane + ethanol		ethanol + trichloroethylene		acetone + heptane		heptane + 2-propanol		acetone + hexane		hexane + 2-propanol		2-propanol + trichloroethylene	
T/K	x_1	*T*/K	x_1	*T*/K	x_1	*T*/K	x_1	*T*/K	x_1	*T*/K	x_1	*T*/K	x_1	*T*/K	x_1
292.35	0.0273	295.05	0.0369	293.45	0.0424	293.15	0.0083	297.75	0.0306	289.15	0.0107	293.25	0.0346	293.65	0.0610
295.45	0.0347	299.45	0.0539	296.65	0.0519	298.15	0.0145	294.55	0.0390	293.25	0.0180	295.05	0.4000	295.85	0.0686
298.95	0.0485	302.95	0.0696	301.05	0.0717	300.75	0.0200	297.55	0.0487	298.25	0.0267	299.35	0.0568	300.25	0.0891
303.05	0.0659	305.05	0.797	306.65	0.1021	305.05	0.0289	300.35	0.0606	302.15	0.0380	302.35	0.0694	304.35	0.1114
306.35	0.0853	308.15	0.1016	309.95	0.1236	306.65	0.0351	303.25	0.0753	307.65	0.0584	305.65	0.0827	308.05	0.1376
311.25	0.1178	311.65	0.1302	311.25	0.1357	311.45	0.0571	306.15	0.0905	309.95	0.0740	308.95	0.1043	310.55	0.1555
314.65	0.1459	314.35	0.1576	313.05	0.1521	313.45	0.0715	307.95	0.1039	312.25	0.0919	310.85	0.1192	312.75	0.1743
316.75	0.1678	316.55	0.1805	316.15	0.1809	315.55	0.0925	311.55	0.1329	316.35	0.1353	312.95	0.1392	315.25	0.1991
318.85	0.1947	318.95	0.2094	318.05	0.2052	317.85	0.1150	314.85	0.1630	318.75	0.1732	315.35	0.1692	318.25	0.2346
320.05	0.2101	319.85	0.2275	320.05	0.2329	319.75	0.1436	318.55	0.2074	319.75	0.1887	317.95	0.2019	320.45	0.2651
321.35	0.2261	321.55	0.2521	322.05	0.2575	320.75	0.1631	321.85	0.2522	322.05	0.2247	320.25	0.2379	322.35	0.2959
322.45	0.2500	323.85	0.2938	323.55	0.2795	322.45	0.1913	323.35	0.2811	323.05	0.2504	322.75	0.2784		

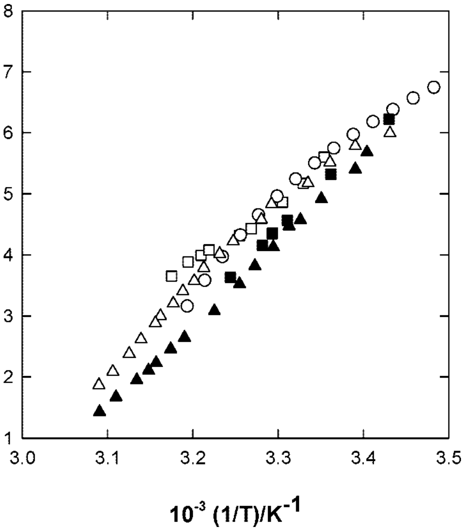

Figure 1. Discrepancy between experimental and reported data for the stearic acid solubility. In ethanol: △, experimental; ○, Domanska, 1987; ■, Bandreth, 1971. In hexane: ▲, experimental; □, Mirmehrabi, 2004.

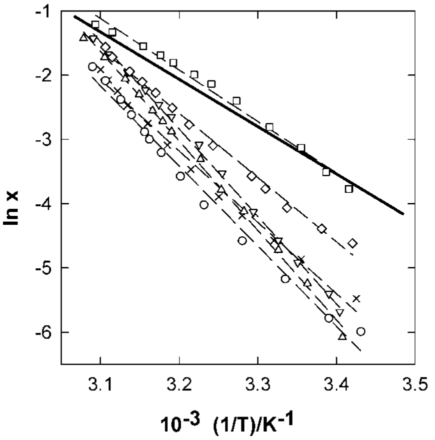

Figure 2. Solubility of stearic acid in pure solvents: x, acetone; ○, ethanol; ▽, hexane; △, heptane; ◇, 2-propanol; □, trichloroethylene. The symbols represent the experimental data, and the lines (- -) the Van't Hoff correlation for each solvent. The line (—) represents the calculated ideal solubility (eq 2).

Table 5. Root-Mean-Square Deviation (σ) of UNIFAC Prediction

	UNIFAC prediction	
system	σ_{UNIFAC}/K	$\sigma_{\mathrm{UNIFAC}}{}^{2a}$/K
acetone	11.37	5.30
ethanol	6.85	4.59
heptane	13.32	2.05
hexane	12.47	3.55
2-propanol	1.19	6.68
trichloroethylene	1.33	5.47
ethanol + heptane	5.15	2.60
hexane + Ethanol	7.68	4.12
ethanol + trichloroethylene	2.47	4.29
acetone + heptane	11.73	7.09
heptane + 2-propanol	3.77	2.05
hexane + acetone	12.73	8.79
hexane + 2-propanol	6.88	3.46
2-propanol + trichloroethylene	2.41	4.69

[a] $\sigma_{\mathrm{UNIFAC}}{}^2$ value when it was considered that the stearic acid was a dimer in the solution.

by the effective mole fraction, $x_i' = x_i/(2 - x_i)$ and the enthalpy of fusion ΔH_f by $2\Delta H_f$. The root-mean-square deviations ($\sigma_{\mathrm{UNIFAC}}{}^2$) are collected in Table 5. This result supports the fact that there is a breaking up of stearic acid dimers by the

Table 6. Parameters and Root-Mean-Square Deviation (σ) of Correlation Equations for the Stearic Acid−Solvent Systems

	Van Laar			Wilson			NRTL[a]			UNIQUAC				
system	A_1	A_2	σ_{VL}/K	Λ_1	Λ_2	σ_W/K	A_1	A_2	σ_N/K	a_{12}	a_{21}	b_{12}	b_{21}	σ_U/K
acetone	2.6236	0.5628	0.46	0.0867	1.6437	0.33	−2883.20	8419.81	0.47	48.9893	68.2194	−0.4431	0.3554	0.26
ethanol	2.9814	0.4387	1.10	0.0444	1.7712	0.76	−3240.60	10178.7	1.33	57.0320	179.270	−0.3335	0.6824	0.60
heptane	−2.7793	−1.8990	0.31	0.8123	1.7345	0.31	−839.043	−395.213	0.31	12.0000	37.0000	−0.4053	0.3288	0.34
hexane	−2.1749	−1.2665	0.31	0.7097	2.1327	0.31	−1733.01	170.936	0.23	−222.920	299.673	−0.1519	0.1901	0.20
2-propanol	4.4425	0.9147	0.38	0.1291	1.9548	0.39	−3167.52	7267.34	0.45	−120.300	96.2140	0.4973	−0.2231	0.40
trichloroethylene	5.6539	−10.5804	1.36	0.0805	3.1875	0.56	852.600	−1151.80	1.55	107.200	619.090	1.1932	−2.7415	0.43

[a] Calculated with the third nonrandomness parameter $\alpha = 0.3$.

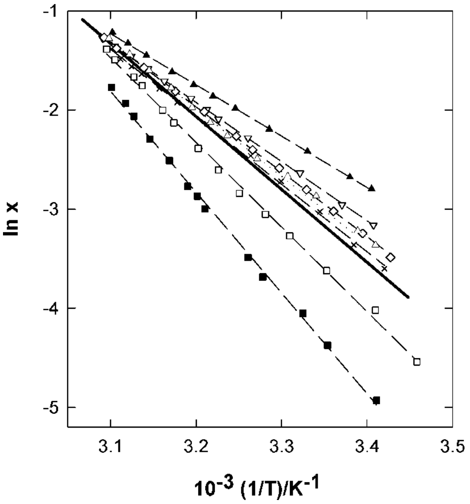

Figure 3. Solubility of stearic acid in azeotropic mixtures: x, ethanol + heptane; ▽, ethanol + trichloroethylene; □, heptane + acetone; ◇, heptane + 2-propanol; ■, hexane + acetone; Δ, hexane + 2-propanol; ▲, 2-propanol + trichloroethylene. The lines (- -) represent the Van't Hoff correlation for each mixture. The line (—) represents the calculated ideal solubility (eq 2).

addition of trichloroethylene and 2-propanol that may be due to mutual loss of dipolar associations and difference in size and form of unlike molecules. The prediction for acetone−stearic acid presented the higher deviations.

From the UNIFAC results, the low solubility in hexane and heptane was explained considering that the stearic acid dissolves as a dimer or monomer depending on the nature of solvent. So, in linear hydrocarbons, probably the acid is a dimer, and then corrections should be done for the enthalpy of fusion and for x_2 (eq 2), but in trichloroethylene, acetone, and alcohols, probably the acid is a monomer due to the polarity of solvents. The difference in hydrogen bonding between trichloroethylene and alcohols or ketones explains its behavior. Acetone and alcohol molecules are more polar and would much rather be attracted to each other than to stearic acid.

Van Laar, Wilson, NRTL, and UNIQUAC (the values of R_k and Q_k were taken from Hansen et al.[10]) models were used to correlate the binary experimental data. According to the UNIFAC results, dimer data and heat of fusion dimer were used for hexane and heptane. The curve-fit parameters and root-mean-square deviations of temperature are listed in Table 6. The best description of solid–liquid equilibrium was given by the UNIQUAC equation with the average root-mean-square deviation of temperature $\bar{\sigma}_U = 0.37$ K. The results of correlations by use of other models present worse average deviations, $\bar{\sigma}_{VL} = 0.65$ K, $\bar{\sigma}_w = 0.44$ K and $\bar{\sigma}_N = 0.72$ K for the Van Laar, Wilson, and NTRL models, respectively.

With the binary azeotropic mixtures, the stearic acid solubility increased with respect to pure solvents with a clear synergetic effect (Table 4). The solubility in mixtures with alcohols increased with respect to pure solvents in ethanol + heptane, hexane + ethanol, heptane + 2-propanol, and hexane + 2-propanol systems, probably because the alcohol interrupts its self-association by a hydrogen bond when it is mixed with the cosolvent. When the solvents were mixtures of trichloroethylene with ethanol or 2-propanol (Figure 3), the solubility improved with respect to pure solvents, with values above the ideal solubility, because the dimers were breaking up. A similar fact was observed for trichloroethylene with branched alcohols.[13]

For the stearic acid−azeotropic mixtures, the NIBS/Redlich–Kister correlation describes well the solubility curves. The parameters and the average root-mean-square deviation of temperature are listed in Table 7. In this case, the consideration of the dimers existence does not improve the description of the solubility and was not considered.

Conclusions

The solubility of stearic acid has been measured in six common organic solvents and eight binary systems, between (290 and 325) K. The application of corrections for the existence of dimers in solid–liquid equilibrium calculations improves the UNIFAC prediction mainly in heptane and hexane and was considered in the calculation. The best results for the correlation of the experimental data of stearic acid solubility in pure solvents were obtained with the UNIQUAC equation. Other models resulted in the following ranking in descending order: Wilson, Wilson NRTL, and Van Laar. Eight binary azeotropic mixtures of solvents revealed great synergetic effects on solubility. The biggest enhancement of the solubility of fatty acids was observed

Table 7. Parameters and Root-Mean-Square Deviation of Correlation Equations for the Stearic Acid−Azeotropic Mixture Systems

	NIBS/Redlich–Kister									
system	a_1	b_1	$c_1 \cdot 10$	a_2	b_2	$c_2 \cdot 10^4$	a_3	b_3	$c_3 \cdot 10^4$	σ/K
ethanol + heptane	101.2300	−0.2853	−0.1691	0.1933	−0.0650	612.04	0.0086	−0.0033	−0.0801	8.9E−07
hexane + ethanol	103.3194	−0.2961	10.0871	0.8579	−0.0275	−29.3770	0.2299	0.0090	−18.1400	0.00012
ethanol + trichloroethylene	28.5152	0.0381	−1.1759	−2.8751	−0.1802	−50.7150	−0.9748	3.1027	20.1060	0.00015
acetone + heptane	75.7487	0.0183	23.6720	3.4234	−1.5045	−60.4920	2.1065	−0.0734	−52.5750	0.00015
heptane + 2-propanol	2.7486	−0.0302	0.3672	1.4426	3.0172	−87.6800	1.3066	0.0034	−0.9078	0.00015
hexane + acetone	72.0000	−0.2723	−0.0574	2.4185	−0.0710	7.9928	2.1226	−0.0178	2.1000	0.00015
hexane + 2-propanol	−8.7013	5.8795	−52.6890	−6.4093	−5.6967	147.0800	−4.0781	−2.8820	−139.7900	0.00015
2-propanol + trichloroethylene	71.1633	−0.1736	−0.5269	48.9093	−0.2648	0.14718	−0.1374	0.3777	−0.1398	0.00006

on hydrocarbons + alcohols. The NIBS/Redlich–Kister equation predicted well the solubility in the azeotropic mixtures of solvents.

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