64 J. Chem. Eng. Data **2009,** *54,* 64–68

Solubilities of Palmitic Acid in Pure Solvents and Its Mixtures

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The solubility of palmitic acid has been measured in ethanol, 2-propanol, acetone, heptane, hexane, 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 a dynamic method, from (290 to 325) K. Solubility data in pure solvents were fitted by the Wilson, NRTL, and UNIQUAC equations and the solubility of palmitic acid in azeotropic mixtures with the NIBS/Redlich−Kister equation. For all calculated results, the root-mean-square deviations of solubility temperatures vary from (0.2 to 0.82) K, depending on the equation used. The solubility in pure solvents decreased in the order: trichloroethylene > 2-propanol > hexane > heptane > acetone > ethanol. The solubility of the palmitic acid increased in azeotropic mixtures compared to the pure solvents, except for the ethanol−trichloroethylene mixture where the solubility was similar to the one in pure trichloroethylene.

Introduction

Palmitic acid (*n*-hexadecanoic acid) is a fatty acid obtained by the hydrolysis of triglycerides of kernel palm, palm, tallow, or coconut oil. It is used in the manufacture of soaps, cosmetic formulations, lube oils, as metallic palpitates as an additive to vegetable oil that can substitute mineral oil as a base fluid in grease making,[1] nondrying oil (surface coatings), and as a phase change material (PCM) for low-temperature latent heat thermal energy storage.[2] The purification and separation of mixtures of saturated fatty acids is carried out by crystallization, so the solubility in solvents is the essential data for designing and controlling the process. In this respect, some studies about its solubility in organic solvents were made.

Solubility data of palmitic acid in some solvents were reported a long time ago using impure products.[3] In relation with the separation of fatty acids by fractional crystallization at low temperatures, Kolb and Brown[4] determined the palmitic acid solubility from (−30 to 10) °C in several solvents. Maeda et al.[5] determined its solubility in ethanol and acetone at four temperatures in the study of the acid precipitation using water as antisolvent. However, it was found that no experimental solubility data of palmitic acid in other solvents were available in the literature over a wide interval of temperatures, so an additional study is needed and also with solvent mixtures searching a synergetic effect on the solubility.

The aim of this work was to study the solid−liquid equilibrium of palmitic acid in pure solvents and in its mixtures, continuing the study on the solubility of fatty acids.[6] The selected solvents have been permitted under the Spanish laws for fats:[7] 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. The activity coefficients calculated from the solubility data were fitted with the usual thermodynamic models.

Table 1. 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	19
hexane	ethanol	331.65	0.6590	20
acetone	hexane	322.75	0.6300	21
acetone	heptane	328.25	0.9000	22
hexane	2-propanol	338.95	0.8429	23
heptane	2-propanol	357.25	0.5450	24
ethanol	trichloroethylene	343.85	0.5259	25
2-propanol	trichloroethylene	348.65	0.4837	26

Experimental Procedure

Palmitic acid (Panreac, Spain > 0.97 mass fraction) was crystallized three times from acetone. Its purity checked by gas chromatography (8700 Perkin-Elmer) was 0.998 mass fraction. The experimental melting temperature (335.8 K) of palmitic acid was 0.1 K from the reported[8] value. When the calculations were made, a value of 53 711 J·mol^{-1} was used for the fusion enthalpy of palmitic acid.[8]

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 1.

The solubility was measured using a dynamic method. Details of the apparatus and its operation have been described elsewhere.[6] Briefly, a mixture of solute and solvent with a fixed composition was first heated quickly to achieve one phase, and then, after being 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 inside a Pyrex glass cell immersed in a glass thermostat. The temperature at which the last crystal disappeared was detected visually, and it was taken as the solid−liquid equilibrium temperature at the fixed composition. All experiments were made at least three

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10.1021/je8005979 CCC: $40.75

Table 2. Palmitic Acid Solubility in Pure Solvents

acetone			ethanol			heptane		
T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1
292.85	3.4236	0.0119	292.15	5.7609	0.0128	294.55	4.6133	0.0145
297.25	2.8237	0.02	295.35	4.7826	0.0170	300.05	3.3161	0.0302
301.65	2.3640	0.0328	297.85	4.2671	0.0232	303.05	2.5691	0.0483
304.05	2.1403	0.0429	302.75	3.3731	0.0393	306.55	2.0628	0.0767
306.55	1.9291	0.0566	304.15	3.0492	0.0454	308.65	1.7958	0.1016
310.25	1.6324	0.086	306.25	2.7657	0.0565	312.05	1.5526	0.1477
312.05	1.4444	0.1096	307.65	2.5332	0.0679	313.75	1.3705	0.1872
315.45	1.2000	0.1649	310.05	2.1783	0.0929	315.65	1.2895	0.2252
317.95	1.0466	0.2221	312.35	1.9497	0.1210	318.25	1.1726	0.2927
321.05	0.9080	0.3115	313.75	1.8156	0.1425	320.55	1.1039	0.3596
322.95	0.9015	0.3768	315.15	1.7266	0.1642	322.25	1.0637	0.4151
			317.05	1.5614	0.2053			
			319.25	1.4679	0.2513			
			321.55	1.3154	0.3241			
			323.65	1.2296	0.3950			

hexane			2-propanol			trichloroethylene		
T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1
293.75	4.0862	0.0154	291.75	2.0135	0.0270	294.20	0.8071	0.0816
297.15	3.1613	0.0257	293.65	1.9294	0.0325	297.10	0.8136	0.1003
299.95	2.6220	0.0379	296.25	1.8278	0.0416	300.30	0.8204	0.1254
304.15	2.0184	0.0663	299.95	1.7124	0.0581	303.50	0.8263	0.1562
306.75	1.6938	0.0947	304.25	1.5163	0.0889	305.50	0.8288	0.1809
309.55	1.5102	0.1284	306.65	1.4032	0.1135	309.20	0.8411	0.2272
311.35	1.3202	0.1658	309.85	1.2979	0.1525	313.10	0.8593	0.2885
314.25	1.2045	0.2200	313.85	1.2274	0.2103	316.55	0.8813	0.3522
317.05	1.1168	0.2846	316.75	1.1911	0.2617	319.55	0.9094	0.4134
319.65	1.0534	0.3561	319.35	1.1617	0.3168	321.45	0.9218	0.4596
322.75	1.0388	0.4384	321.75	1.1259	0.3801	323.75	0.9362	0.522

times, and the results were averaged. The uncertainties of the method were ± 0.1 K and ± 0.0005 mol fraction for the equilibrium temperature and concentration, respectively.

Results and Discussion

Experimental results of the solid−liquid equilibria in pure solvents are listed in Table 2. The experimental solubilities of palmitic acid in acetone and ethanol show slight discrepancies at low temperatures with the values reported by Maeda et al.[5] (Figure 1).

The activity α_i of the ith component in the solid−liquid equilibrium can be calculated[9] by the following equation

$$\ln(\alpha_i) = \ln(\gamma_i x_i) = -\frac{\Delta H_{\text{tp}}}{RT_{\text{tp}}}\left[\frac{T_{\text{tp}}}{T} - 1\right] + \frac{\Delta C_p}{R}\left[\frac{T_{\text{tp}}}{T} - 1\right] - \frac{\Delta C_p}{R}\ln\frac{T_{\text{tp}}}{T} \quad (1)$$

where x_i is the mole fraction solubility and γ_i is the activity coefficient of the ith component at temperature T, respectively. ΔH_{tp} is the molar enthalpy of fusion of the ith solute at the triple-point temperature (T_{tp}), and ΔC_p is the difference in solute heat capacity between the solid and liquid at the triple point. The temperature and the enthalpy of fusion (ΔH_{tp}) at the triple point can be substituted in eq 1 by the atmospheric melting points (T_{f}) and the enthalpy of fusion ΔH_{f} at T_{f}, respectively, because its values present little difference. The contributions of the second and third terms are often minor and negligible. The solubility equation becomes

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

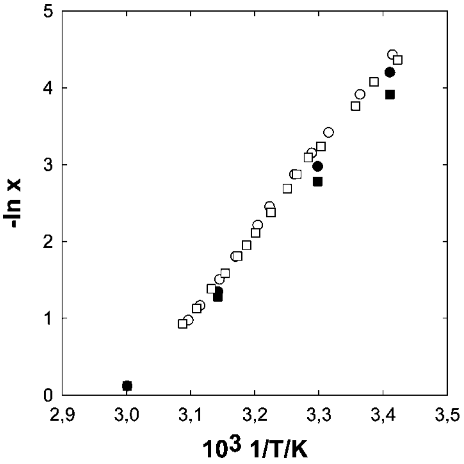

Figure 1. Discrepancy between experimental and reported data for the palmitic acid solubility. In acetone: ○, experimental; ●, Maeda (1997). In ethanol: □, experimental; ■, Maeda (1997).

The activity coefficients of palmitic acid in pure solvents are shown in Table 2. Positive deviations of the ideality were found ($\gamma > 1$) except for trichloroethylene that presents solubility higher than the ideal (Figure 2). This result supports the fact that there is a breaking up of palmitic acid dimers by addition of trichloroethylene that may be due to mutual loss of dipolar associations due to similar dipole moments ($2.56 \cdot 10^{-30}$/C·m trichloroethylene; $2.40 \cdot 10^{-30}$/C·m palmitic acid) and probably to the complexation solute−solvent. A similar result was found with stearic acid.[6] The activity coefficients of palmitic acid in hexane and heptane are high at low temperatures (Table 2) because they were calculated with eq 2, without considering that the palmitic acid dissolves in linear hydrocarbons as a dimer.[6,10−12] The palmitic acid solubilities in ethanol and acetone are lower due to the self-association of the solvent because its molecules would much rather be attracted to each other than to palmitic acid.

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.[13,14] A log plot of the solute solubility as a mole fraction in pure solvents versus

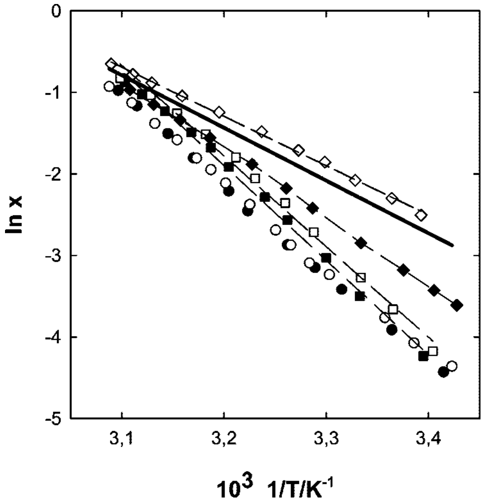

Figure 2. Solubility of palmitic acid in pure solvents: ●, acetone; ○, ethanol; ■, heptane; □, hexane; ◆, 2-propanol; ◇, trichloroethylene. The symbols represent the experimental data and the lines (− −) the Van't Hoff correlation for each solvent. The line (−) represents the calculated ideal solubility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

Table 3. Parameters and Root-Mean-Square Deviation of Wilson, NRTL, and UNIQUAC Correlation Equations for the Palmitic Acid−Pure Solvent Systems

	Wilson			NRTL[a]			UNIQUAC				
system	Λ_1	Λ_2	σ_w/K	A_1	A_2	σ_N/K	a_{12}	a_{21}	b_1	b_{21}	σ_U/K
acetone	0.0565	2.3571	0.92	−3720.00	9086.72	0.55	2554.25	−342.100	−7.2350	0.5369	0.38
ethanol	0.1218	1.5200	0.58	−2111.40	6427.06	0.82	691.98	33.068	−1.2702	−0.5086	0.34
heptane	1.6983	0.9411	0.17	1528.94	2470.25	0.20	44.8634	57.473	0.1304	0.4415	0.21
hexane	1.2634	1.4612	0.23	459.63	1235.75	0.25	56.9038	63.527	0.116	1.1253	0.31
2-propanol	0.2038	1.7796	0.47	2423.96	5140.82	0.54	317.205	125.800	0.1174	0.8992	0.26
trichloroethylene	1.3939	0.9202	0.10	−3632.00	5260.30	0.06	−145.96	−309.439	0.1586	1.6517	0.04

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

Table 4. Palmitic Acid Solubility in Azeotropic Mixtures

ethanol−heptane			hexane−ethanol			ethanol−trichloroethylene		
T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1
292.25	1.0390	0.0543	293.05	0.8837	0.0678	292.05	0.6857	0.0810
295.45	1.0455	0.0685	295.65	0.9067	0.0802	293.75	0.7206	0.0876
298.85	1.0447	0.0880	298.85	0.9224	0.0996	297.95	0.7730	0.1114
300.95	1.0818	0.0988	300.65	0.9251	0.1130	301.05	0.7848	0.1371
304.45	1.0974	0.1246	304.45	0.9380	0.1458	304.95	0.8455	0.1675
308.35	1.1050	0.1619	306.65	0.9494	0.1677	308.65	0.8803	0.2073
311.55	1.1437	0.1939	310.75	0.9835	0.2138	311.55	0.9091	0.2440
314.65	1.1287	0.2410	314.25	0.9639	0.2750	314.95	0.9451	0.2936
318.65	1.1436	0.3078	317.45	0.9483	0.3438	317.65	0.9560	0.3455
320.65	1.1072	0.3608	320.95	0.9680	0.4205	320.45	0.9883	0.3992
323.45	1.1159	0.4262	323.35	0.9966	0.4743	322.65	0.9969	0.4541

acetone−heptane			heptane−2-propanol			acetone−hexane		
T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1
291.45	2.7976	0.0190	292.55	0.8112	0.0711	293.15	1.3938	0.0433
294.05	2.6316	0.0245	294.65	0.8275	0.0816	294.75	1.3656	0.0498
298.25	0.4225	0.0363	296.85	0.8358	0.0950	298.15	1.3737	0.0636
301.55	0.2639	0.0493	300.85	0.8643	0.1227	301.25	1.3371	0.0816
305.65	1.9541	0.0761	304.45	0.8838	0.1547	305.05	1.2351	0.1154
310.65	1.6941	0.1233	308.15	0.9119	0.1935	307.75	1.1720	0.1465
313.55	1.4784	0.1712	311.65	0.9553	0.2337	311.65	1.1382	0.1962
316.45	1.4011	0.2182	314.35	0.9516	0.2803	314.75	1.0752	0.2547
318.85	1.2725	0.2802	317.15	0.9651	0.3314	318.05	1.0797	0.3138
321.25	1.1991	0.3459	320.05	0.9796	0.3927	320.45	1.0516	0.3751
322.65	1.1604	0.3901	322.85	1.0218	0.4485	322.75	1.0636	0.4282

hexanol−2-propanol			2-propanol−trichloroethylene		
T/K	γ_1	x_1	T/K	γ_1	x_1
292.95	0.8746	0.0680	294.05	0.6042	0.1069
295.05	0.8766	0.0793	296.85	0.6502	0.1222
299.75	0.9202	0.1065	301.35	0.7298	0.1506
303.85	0.9333	0.1405	305.95	0.7807	0.1944
307.35	0.9676	0.1727	310.25	0.8322	0.2443
310.35	0.9629	0.2126	313.15	0.8687	0.2838
314.25	0.9626	0.2753	315.85	0.9825	0.3295
316.85	0.9782	0.3207	318.45	0.9146	0.3800
319.25	0.9794	0.3734	320.55	0.9285	0.4276
321.45	1.0047	0.4181	322.25	0.9502	0.4646
323.05	1.0194	0.4552	323.55	0.9484	0.5046

Table 5. Parameters and Root-Mean-Square Deviation of the NIBS−Redlich−Kister Correlation Equation for the Palmitic Acid−Azeotropic Mixture Systems

	NIBS−Redlich−Kister									
system	a_1	b_1	$c_1 \cdot 10^4$	a_2	b_2	$c_2 \cdot 10^4$	a_3	b_3	$c_3 \cdot 10^4$	σ/K
ethanol−heptane	82.5680	−2.2878	26.2360	1055.87	1.5886	4.5910	15.8944	−0.0332	1.3890	0.00008
hexane−ethanol	−912.553	−2.5335	0.6383	5647.86	0.1480	1.4270	0.0090	−0.0032	648.917	0.00016
ethanol−trichloroethylene	105.621	−0.0183	16.5550	−385.736	−7.5110	−234.400	0.0090	−0.0033	0.6706	0.00013
acetone−heptane	13.2013	0.0033	−144.470	27.2843	−0.0012	0.3993	0.1046	−0.0016	219.964	0.00081
heptane−2-propanol	62.1922	−0.1946	0.3901	6.2456	−0.0151	−3.3991	0.0090	−0.3292	3.7303	0.00015
acetone−hexane	−75.4102	0.7495	0.3517	−38.0819	−0.1330	−4.2142	0.0090	−0.0033	−241.077	0.00014
hexane−2-propanol	69.5672	−0.3491	0.3934	82.6808	−0.1381	−0.3490	0.0900	−0.0033	3.6020	0.00013
2-propanol−trichloroethylene	12.1925	0.0069	−1.3727	9.0229	−0.0242	0.0212	1.9026	3.2590	−0.6739	0.00014

$1/T$ should be linear. The corresponding plots are shown in Figure 2. Correlation coefficients of the straight lines are higher than 0.993.

The Wilson, NTRL, and UNIQUAC models were used for the correlation of the activity coefficients of the systems palmitic acid−pure solvent. The exact mathematical forms of the

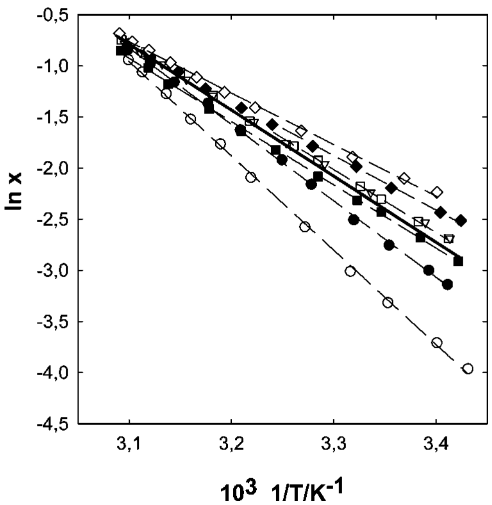

Figure 3. Solubility of palmitic acid in azeotropic mixtures: ○, acetone−heptane; ●, acetone−hexane; ■, ethanol−heptane; □, hexane−2-propanol; ▽, heptane−2-propanol; ◆, ethanol−trichloroethylene; ◇, 2-propanol−trichloroethylene. The lines (− −) represent the Van't Hoff correlation for each mixture. The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

equations were shown in our previous paper.[6] In the UNIQUAC model, the values of R_k and Q_k were taken from Hansen et al.[15]

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

$$\Omega = \sum [T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}}]^2 \tag{3}$$

where T_ν^{exp} and T_i^{cal} are the experimental and calculated equilibrium temperature, respectively.

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

$$\sigma = \left[\sum_{i=1}^{n} (T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}})^2/(n-1)\right]^{1/2} \tag{4}$$

where n is the number of experimental data; T_i^{exp} is the experimental temperature; and T_i^{cal} is the temperature calculated from eq 2 with the γ_i^{cal} values.

The curve-fit parameters of the Wilson, NRTL, and UNIQUAC models and root-mean-square deviations of temperature are listed in Table 3. The best description of solid−liquid equilibrium was given by the UNIQUAC equation with the average root-mean-square deviation of temperature $\bar{\sigma}_U = 0.26$ K. The results of correlations by use of the other models present worse average deviations, $\bar{\sigma}_w = 0.41$ K and $\bar{\sigma}_N = 0.40$ K for the Wilson and NTRL models, respectively.

The solubilities in the azeotropic mixtures of solvents are shown in Tables 4 and 5. As can be observed in Figure 3, the solubility increases by a synergetic effect of the mixtures with respect to pure solvents. Negative deviations of the ideality were found ($\gamma < 1$) except for the mixtures acetone−heptane, acetone−hexane, and ethanol−heptane (Table 4). The solubility increases in mixtures with alcohols 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 hydrogen bonding when it is mixed with the cosolvent, and the mixture achieves an intermediate polarity between its components. When the solvents were mixtures of trichloroethylene with ethanol or 2-propanol, the solubility improved with respect to the pure alcohol being similar to the one in pure trichloroethylene because of the formation of hydrogen bonds, probably. A similar fact was observed for trichloroethylene with branched alcohols.[14]

For the prediction of solute solubilities in the azeotropic mixtures of solvents, the combined nearly ideal binary solvent (NIBS)/Redlich−Kister model suggested by Acree et al.[16−18] was used. That model is expressed as

$$\ln x_A = x_B^0 \ln(x_A^{\mathrm{sat}})_B + x_C^0 \ln(x_A^{\mathrm{sat}})_C + x_B^0 x_C^0 \sum_{i=0}^{N} S_i^*(x_B^0 - x_C^0) \tag{5}$$

where x_B^0 and x_C^0 are the initial mole fractions of the binary solvent as if the solute A is not present and $(x_A^{\mathrm{sat}})_i$ 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

$$S_i^* = a_i + b_i T + c_i T^2 \tag{6}$$

The parameters and the average root-mean-square deviation of temperature are listed in Table 5. For the systems palmitic acid−azeotropic mixtures, the NIBS/Redlich−Kister correlation describes well the solubility curves.

Conclusions

The solubility of palmitic acid in pure solvents decreased in the order: trichloroethylene > 2-propanol > hexane > heptane > acetone > ethanol. The best results for the correlation of the experimental data of palmitic acid solubility in pure solvents were obtained with the UNIQUAC equation. The solubility of the palmitic acid increased in azeotropic mixtures compared to the pure solvents, except for the ethanol−trichloroethylene mixture where the solubility was similar to the one in pure trichloroethylene. The NIBS/Redlich−Kister equation predicted well the solubility in the azeotropic mixtures of solvents.

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Received for review July 31, 2008. Accepted November 14, 2008. The authors gratefully acknowledge financial support for this work provided by Ministerio de Ciencia y Tecnología of Spain, through project PPQ2001-0270-C02-01.

JE8005979