Short Articles

Solubilities of Lauric Acid in *n*-Hexane, Acetone, Propanol, 2-Propanol, 1-Bromopropane, and Trichloroethylene from (279.0 to 315.3) K

Emilio A. Cepeda,* Raquel Bravo, and Beatriz Calvo

Department Ingeniería Química, Facultad de Farmacia, Universidad del País Vasco, Paseo de la Universidad 7,
01005 Vitoria, Spain

The solubilities of lauric acid in *n*-hexane, acetone, 2-propanol, propanol, 1-bromopropane, and trichloroethylene have been measured using a dynamic equilibrium method from (279.0 to 315.3) K. All systems present positive deviations of the ideal behavior. The solvent that presented the lowest average deviation, concerning the ideality of the system, was trichloroethylene, and the highest value of deviation was found in acetone. The experimental solubility data were correlated with the NRTL, Wilson, and UNIQUAC models. In the *n*-hexane case, the correction for the existence of dimers was applied. The best results were obtained using UNIQUAC with 0.26 K average root-mean-square deviation of temperature. The solubility in pure solvents decreased in the order: trichloroethylene > 1-bromopropane > 2-propanol > propanol > acetone > *n*-hexane.

Introduction

Lauric acid (dodecanoic acid, C12:0) is one of the three most widely distributed saturated fatty acids found in nature (14:0, 16:0, and 18:0). It is found in oils and fats as triacylglycerol. Coconut oil [(45 to 50) %] and palm kernel oil [(45 to 55) %] are the oils used as foods with a higher content of lauric acid.[1] Its main application is the manufacture of soaps, shampoos, and other surface active agents (foaming agents or emulsifiers)[2] including special lubricants. Also, it is employed as phase change material in eutectic mixtures with other fatty acids.[3] Lauric acid as a monoglyceride is known to the pharmaceutical industry for its good antimicrobial properties.[4]

Mixtures of lauric and myristic oils are obtained after fractional crystallization of kernel palm oil and coconut oil.[5] The acids are obtained by hydrolysis at high temperature and pressure. The acid is purified by distillation.[6] The separation of the acids can be carried out by solvent fractionation and fractional crystallization. Recently, Maeda et al.[7,8] have researched the separation based in a combined process of liquid−liquid separation and crystallization in a liquid−liquid−solid process, for fatty acids−ethanol and water. In the separation process, the solubility in solvent 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 lauric acid in some solvents were reported a long time ago using impure products.[9] Privett et al.[10] determined the acid solubility in acetone at low temperatures. Maeda et al.[11] 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 lauric acid in other solvents were available in the literature at higher temperatures, so an additional study is needed.

Table 1. Experimental Solubility of Lauric Acid in Mole Fraction

hexane		acetone		2-propanol	
T/K	x_1	T/K	x_1	T/K	x_1
279.9	0.0292	286.6	0.0794	279.2	0.0797
282.5	0.0408	290.1	0.1075	282.7	0.1041
283.6	0.0502	293.1	0.1457	285.9	0.1301
286.9	0.0736	293.3	0.1465	289.1	0.1638
289.7	0.1078	298.0	0.2242	293.1	0.2199
291.7	0.1339	299.9	0.2835	297.1	0.2832
293.9	0.1712	301.9	0.3395	301.0	0.3610
296.4	0.2231	303.4	0.3890	303.0	0.4089
297.5	0.2516	305.1	0.4489	304.4	0.4581
300.1	0.3221	306.7	0.5123	306.1	0.5135
301.8	0.3795	308.1	0.5679	308.1	0.5857
303.8	0.4424	309.1	0.6138	309.8	0.6477
305.9	0.5188	310.9	0.6780	311.2	0.7116
308.0	0.5926	312.0	0.7349	312.6	0.7774
311.0	0.7107	313.0	0.7950	314.1	0.8417
312.5	0.7775	314.4	0.8571	314.9	0.8959
314.2	0.8583	315.2	0.8955		

propanol		trichloroethylene		1-bromopropane	
T/K	x_1	T/K	x_1	T/K	x_1
287.1	0.1298	282.0	0.1436	280.6	0.0756
289.6	0.1533	283.1	0.1568	283.8	0.0997
292.8	0.1920	284.6	0.1713	287.8	0.1504
295.1	0.2254	288.4	0.2162	289.9	0.1847
297.9	0.2747	291.0	0.2582	293.1	0.2386
299.9	0.3175	293.0	0.2947	295.2	0.2753
301.5	0.3527	296.0	0.3372	298.8	0.3399
303.5	0.4057	298.2	0.3885	301.4	0.4041
304.7	0.4403	301.2	0.4407	304.3	0.4732
306.5	0.5088	303.3	0.5156	305.3	0.5281
307.4	0.5406	306.7	0.5910	307.3	0.5734
308.7	0.5969	308.6	0.6662	309.3	0.6453
309.9	0.6444	310.5	0.7246	310.5	0.7090
310.7	0.6903	312.5	0.8058	312.5	0.7748
312.1	0.7491	313.5	0.8547	313.8	0.8591
313.4	0.8178				
314.2	0.8730				

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* Corresponding author. Fax: 34 945 013014. E-mail: emilio.cepeda@ehu.es.

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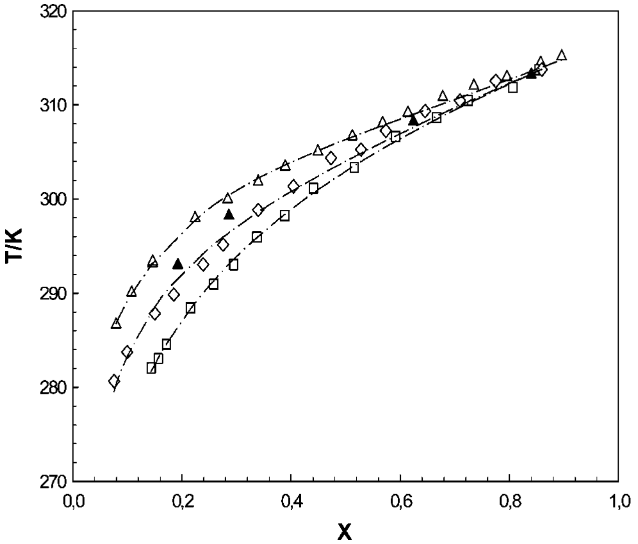

Figure 1. Experimental and reported data for the mole fraction solubility of lauric acid in pure solvents: Δ, acetone; ◇, 1-bromopropane; □, trichloroethylene; ▲, Maeda (1998) data for acetone. The lines (—•—) represent the calculated solubilities with the UNIQUAC correlation.

The objective of this work was the study of the solid−liquid equilibrium of lauric acid in six pure solvents, continuing the study on the solubility of fatty acids.[12] The solvents selected were *n*-hexane, acetone, propanol, 2-propanol, 1-bromopropane, and trichloroethylene. These solvents were chosen because they have been used in the process of fractionation: trichloroethylene was used also for cleaning, and 1-bromopropane is a solvent intended to replace solvents like trichloroethane and some freons that damage the upper ozone layer. This led to the experimental determination of solubility data and the correlation activity coefficients−composition with the usual thermodynamic models.

Materials and Methods

Lauric acid (Panreac, Spain > 0.97 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 (317.2 K) of lauric acid was 0.1 K of that reported.[13] When the calculations were made, a value of 36295 $\mathrm{J \cdot mol^{-1}}$ was used for the fusion enthalpy of lauric acid.[13]

All solvents (Panreac, analytical grade) were dried over 4Å molecular sieves. The purity, checked by GC, was higher than 0.999 mass fraction.

The solubility was measured using a dynamic method. Briefly, a mixture of solute and solvent with a fixed composition was first heated quickly to achieve one phase and then cooled to obtain the acid crystallization in the solvent. The sample was heated again slowly (less than 0.1 °C each 30 min) with continuous stirring inside a Pyrex glass cell immersed in a glass thermostat (with 0.1 °C subdivisions) totally immersed in the thermostatting liquid. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The accuracy of the temperature measurements was ± 0.1 K, and the reproducibility was also ± 0.1 K. The error in the mole fraction did not exceed 0.0005. 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. The measurements were carried out in the (279.0 to 315.3) K temperature range. All experiments were performed at least three times, and the results were averaged.

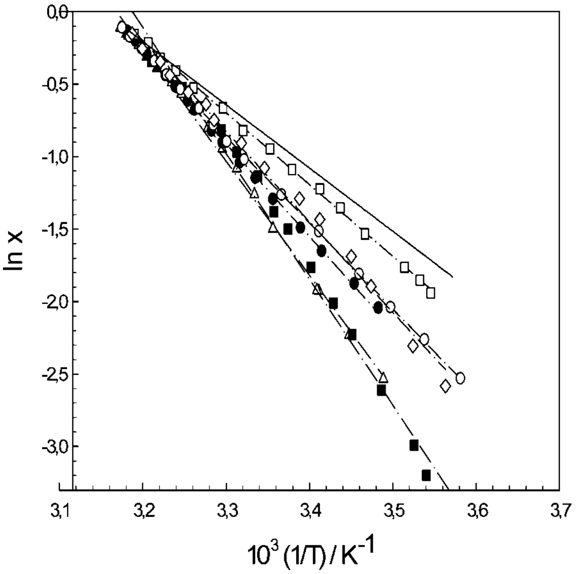

Figure 2. Van't Hoff plot for the lauric acid solubility in: ■, hexane; △, acetone; ●, propanol; ○, 2-propanol; ◇, 1-bromopropane; □, trichloroethylene. The symbols represent the experimental data and the lines (--) the straight line of regression. The line (—) represents the calculated ideal solubility (eq 2).

Table 2. Van't Hoff Regression ($\ln x = A + B/T$) and Coefficient of Determination for the Lauric Acid Solubilities in Solvents

solvent	A	B/K	r^2
n-hexane	27.815	−8722.8	0.9881
acetone	24.896	−7856.5	0.9967
n-propanol	20.210	−6400.2	0.9991
2-propanol	18.743	−5941.3	0.9998
trichloroethylene	15.574	−4929.7	0.9992
1-bromopropane	19.819	−6255.2	0.9937

Results and Discussion

Experimental results of the solid−liquid equilibria are listed in Table 1. The presented data are within the same order as reported by other authors. The lauric acid solubilities in acetone reported by Maeda et al.[11] (Figure 1) presented values higher than those measured by us at low temperatures, and there were little differences at high temperatures. The discrepancy could be due to the purity of the acid.

The activity coefficient γ_i of the ith component in the solid−liquid equilibrium can be calculated by the general solubility equation[14]

$$\ln(\gamma_i x_i) = -\frac{\Delta H_{\mathrm{tp}}}{RT_{\mathrm{tp}}}\left[\frac{T_{\mathrm{tp}}}{T} - 1\right] - \frac{\Delta C_p}{R}\left(\ln\frac{T_{\mathrm{tp}}}{T} - \frac{T_{\mathrm{tp}}}{T} + 1\right) - \frac{\Delta V}{RT}(P - P_{\mathrm{tp}}) \quad (1)$$

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}); ΔC_p is the difference in solute heat capacity between the solid and liquid at the triple point; ΔV is the difference between the specific volumes of the condensed phases; and $P - P_{\mathrm{tp}}$ is the difference between the pressure of the system and the pressure in the triple point. The temperature and the enthalpy of fusion (ΔH_{tp}) at the triple

Table 3. Parameters and Root-Mean-Square Deviation (σ) of Correlation Equations for the Lauric Acid−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_{12}	b_{21}	σ_{ij}/K
hexane	0.1668	2.2551	0.39	−2930.20	5445.43	0.53	80.7416	117.8156	−0.3194	0.7333	0.13
acetone	0.2809	0.8698	0.42	−122.38	3283.26	0.47	107.2307	378.5470	−0.7729	1.6932	0.31
2-propanol	0.6386	0.7172	0.45	1084.65	732.45	0.42	79.4748	425.4725	−1.2827	2.0471	0.24
n-propanol	0.6961	0.5908	0.16	1691.41	427.09	0.16	163.6714	157.5477	−0.5980	1.1062	0.07
trichloroethylene	0.5174	1.3117	0.32	−1014.41	1911.30	0.32	48.9758	68.2144	−0.4706	0.5940	0.33
1-bromopropane	0.2344	1.3586	0.80	−1338.04	3893.14	0.87	−148.3689	1058.1668	−2.2922	4.3105	0.50

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

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

$$\ln(\gamma_i x_i) = -\frac{\Delta H_f}{RT_f}\left[\frac{T_f}{T} - 1\right] \tag{2}$$

where ΔH_f is the molar enthalpy of fusion of i solute at the melting point temperature (T_f).

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.[15,16] A log plot of the solute solubility as mole fraction in pure solvents versus $1/T$ should be linear. The corresponding plots are shown in Figure 2. Except in the case of *n*-hexane ($r^2 = 0.9881$), no deviation from linearity is observed ($r^2 > 0.9937$). The slopes and intercepts are shown in Table 2. The anomalous behavior of lauric acid in *n*-hexane can be due to dimer formation. Also, in Figure 2 it is shown that the acid solubilities were lower than the ideal solubility in all solvents, thus positive deviations of the ideality ($\gamma_1 > 1$) were found.

Wilson, NTRL, and UNIQUAC models were used for the correlation of the activity coefficients of the systems lauric acid−solvent. The exact mathematical forms of the equations were shown in our previous paper.[12] In the UNIQUAC model, the values of R_k and Q_k were taken from Hansen et al.[17]

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_i^{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

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

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 and root-mean-square deviations of temperature are listed in Table 3. In the *n*-hexane case, the existence of lauric acid dimers[18−20] was taken into consideration and quantified replacing in eq 2 the mole fraction (x_i) by the effective mole fraction $x_i' = x_i/(2 - x_i)$ and the enthalpy of fusion ΔH_f by $2\Delta H_f$, decreasing the high root-mean-square deviation of temperature (Wilson, 0.71 to 0.39; NRTL, 1.19 to 0.53; UNIQUAC, 0.41 to 0.13). The assumptions done are not rigorous because the acid can be as an equilibrium monomer−dimer, and the average enthalpy of fusion can be a difference of twice that of the monomer. The best description of solid−liquid equilibrium was given by the UNIQUAC equation with the average root-mean-square deviation of temperature $\bar{\sigma}_U = 0.26$. The correlation for the three systems is shown in Figure 1. The results using other models present worse average deviations, $\bar{\sigma}_w = 0.42$ and $\bar{\sigma}_N = 0.46$ for the Wilson and NTRL models, respectively.

Conclusions

The solubility of lauric acid has been measured in six common organic solvents, *n*-hexane, acetone, propanol, 2-propanol, 1-bromopropane, and trichloroethylene, between (279 and 315.3) K. On the basis of solubility data, it can be concluded that lauric acid is more soluble in trichloroethylene and less soluble in *n*-hexane than in any of the organic solvents investigated. The best results for the correlation of the experimental data of lauric acid solubility were obtained with the UNIQUAC equation. Other models resulted in the following ranking in descending order: Wilson and NRTL.

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