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Solubilities of Fatty Acids and Triglycerides in 1-Bromopropane

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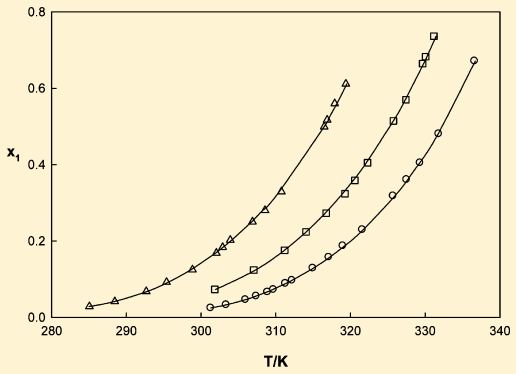
ABSTRACT: The solubilities of the fatty acids, tetradecanoic (myristic), hexadecanoic (palmitic), and octadecanoic (stearic), and of the triglycerides, glyceryl tridodecanoate (trilaurate), glyceryl trimyristate, glyceryl tripalmitate, and glyceryl tristearate, in 1-bromopropane were measured by the dynamic method from (280 to 350) K. The solubility of fatty acids decreased with the increase of molecular weight and was lower than ideal solubility. The systems triglycerides-1-bromopropane presented negative deviations of Raoult's law. The experimental data were correlated with Van Laar, Wilson, nonrandom two-liquid (NRTL), and universal quasichemical activity coefficient (UNIQUAC) equations.



INTRODUCTION

The demand for biodegradable materials has opened a possibility for using vegetable oils as an alternative to petroleum-based materials. Major disadvantages of vegetable oils are inadequate oxidative stability and problems associated with its use in high- or in low-temperature applications.[1] The poor oxidative stability is due to the rapid reactions occurring at the double bond in the oil molecule. In this way, saturated fatty acids have been used as metal-working lubricants.[2] Also, vegetal oil−water emulsions can be used as metalworking fluids[3] that replace the commonly used petroleum-based emulsions and in other applications.[4] The purpose of the emulsion in metal working is to provide maximum cooling with water and at the same time to impart some lubricating properties to reduce friction between the moving chip and the contact surface of any cutting tool; as a result the part being machined has a surface that contains water and oil. The vegetable oils are composed of triglycerides mainly. The cleaning of the metal surface has been made with organic solvents as trichloroethylene, trichloroethane, chlorodifluoroethylene, and fluorodichloroethylene, which have been designated ozone-depleting compounds and their use regulated by legislation. 1-Bromopropane is an alternative intended to replace solvents like trichloroethane and some freons that damage the upper ozone layer.[5]

On the basis of the Fedors method,[6] triglycerides have calculated solubility parameters of approximately 18.8 $(MPa)^{1/2}$. According to Yalkowsky,[7] any two liquids will be completely miscible at room temperature if their solubility parameters do not differ by more than six units. Therefore, any liquid having a solubility parameter between 13 and 24 will be miscible with triglycerides. The solubility parameter of 1-bromopropane is 18.2 $MPa^{1/2}$, falling within this range (Table 1). So, it is of interest to study the solubility of fatty acids and triglycerides in 1-bromopropane for its use as a degreaser.

Experimental solubilities of dodecanoic (lauric) acid in 1-bromopropane were reported in a previous work.[8] However, it was found that no experimental solubility data of tetradecanoic, hexadecanoic, and octadecanoic acids and of the triglycerides, glyceryl trilaurate, glyceryl trimyristate, glyceryl tripalmitate, and glyceryl tristearate in 1-bromopropane were available in the open literature, so an additional study is needed.

The objective of this work was the study of the solid−liquid equilibrium of fatty acids and triglycerides in 1-bromopropane. This led to the experimental determination of solubility data and the correlation of activity coefficient−composition with the usual thermodynamic models.

EXPERIMENTAL SECTION

Materials. The used fatty acids were: myristic acid (Sigma; purity ≥ 0.99 mass fraction; CAS Registry No. 544-63-8), palmitic acid (Panreac; purity 0.98 mass fraction; CAS Registry No. 57-10-3), and stearic acid (Panreac; purity, 0.98 mass fraction, CAS Registry No. 57-11-4). The acids were crystallized three times from acetone. Its purity checked by gas chromatography (8700 Perkin-Elmer FID detector, with a 30 m Stabilwax column of 0.32 ID and oven temperature of (180 to 240) °C at 10 $°C \cdot min^{-1}$) was 0.999 mass fraction.

The used triglycerides were: glyceryl trilaurate (2,3-di(dodecanoyloxy)propyl dodecanoate, Sigma, purity ≥0.99 mass fraction, CAS Registry No. 538-24-9), glyceryl trimyristate (1,3-di(tetradecanoyloxy)propan-2-yl tetradecanoate, Sigma, purity ≥0.99 mass fraction, CAS Registry No. 555-45-3), glyceryl tripalmitate (1,3-di(hexadecanoyloxy)propan-2-yl hexadecanoate, Sigma, purity ≥0.99 mass fraction, CAS Registry No. 555-44-2), and glyceryl tristearate (1,3-di-

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Table 1. Physical Properties of Solutes Used in the Calculations: Molecular Weight MW, Melting Point T_f, Enthalpy of Fusion ΔH_{fus}, Molar Volume MV(298 K), Polarity, Structure Volume Parameter for the UNIQUAC Equation r, and Structure Area Parameter for the UNIQUAC Equation q

substance	MW	T_f / K	ΔH_{fus} / kJ·mol^{-1}	MV / cm^3·mol^{-1}	δ[11] / MPa$^{1/2}$	polarity[11]	r	q
myristic acid	228.38	327.55[15]	45.1[15]	270.62[16]	17.65	0.13	10.2952	8.5520
palmitic acid	256.43	335.95[15]	53.7[15]	300.27[16]	17.54	0.12	11.6440	9.6320
stearic acid	284.48	342.75[15]	61.2[15]	302.39[16]	17.46	0.11	12.9928	10.7120
glyceryl trilaurate	639.01	319.7[17]	123.5[17]	714.79[13]	17.64	0.11	27.7370	22.6920
glyceryl trimyristate	723.17	329.8[17]	148.2[17]	817.15[13]	17.52	0.09	31.7834	25.9320
glyceryl tripalmitate	807.33	338.7[17]	171.7[17]	932.27[13]	17.44	0.08	35.8298	29.1720
glyceryl tristearate	891.49	345.7[16]	196.8[17]	1034.23[13]	17.37	0.07	39.8762	32.4120
1-bromopropane	122.99			90.86[17]	18.08	0.17	3.2199	2.7600

Table 2. Solubility of Fatty Acids (1) in 1-Bromopropane (2) and Activity Coefficients

myristic acid			palmitic acid			stearic acid		
x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
0.0285	285.1	2.9600	0.0730	301.9	1.5529	0.0247	301.3	2.1082
0.0415	288.5	2.5466	0.1240	307.1	1.3222	0.0330	303.4	1.8632
0.0679	292.7	2.0630	0.1758	311.2	1.2305	0.0462	306.0	1.6343
0.0920	295.4	1.8166	0.2235	314.1	1.1835	0.0556	307.4	1.5201
0.1246	298.9	1.6150	0.2726	316.8	1.1511	0.0663	308.9	1.4309
0.1685	302.1	1.4563	0.3234	319.3	1.1261	0.0729	309.7	1.3848
0.1836	302.9	1.4179	0.3585	320.6	1.1119	0.0889	311.3	1.2832
0.2026	303.9	1.3774	0.4048	322.3	1.0956	0.0969	312.2	1.2595
0.2503	306.9	1.3018	0.5141	325.8	1.0645	0.1290	315.0	1.1644
0.2800	308.6	1.2668	0.5698	327.4	1.0514	0.1575	317.1	1.1159
0.3292	310.8	1.2211	0.6644	329.7	1.0326	0.1873	319.0	1.0772
0.4990	316.5	1.1219	0.6825	330.0	1.0294	0.2293	321.6	1.0604
0.5171	316.9	1.1141	0.7362	331.1	1.0209	0.3179	325.7	1.0219
0.5599	317.9	1.0970				0.3607	327.5	1.0197
0.6112	319.4	1.0784				0.4044	329.3	1.0285
						0.4805	331.8	1.0244
						0.6711	336.6	1.0064

(octadecanoyloxy)propan-2-yl octadecanoate, Sigma, purity ≥0.99 mass fraction, CAS Registry No. 555-43-1). The triglycerides were purified by recrystallization in acetone (three times). Its purity (as methyl ester) checked by gas chromatography was 0.998 mass fraction.

1-Bromopropane (Panreac; purity 0.99 mass fraction; CAS Registry No. 106-94-5) was dried over 4 Å molecular sieves (Sigma). The purity, checked by GC (TCD detector at 160 °C, column OV 17, 3 m, 1/8" I.D., oven temperature 65 °C), was higher than 0.995 mass fraction.

The physical properties of materials used in the calculations are listed in Table 1.

Dynamic Method. A mixture of solute and solvent with a fixed composition was prepared by mass with an analytical balance (Mettler H33AR, Zurich, Switzerland) with an uncertainty of 0.0001 g. The mixture was placed in a closed 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, after being cooled to obtain 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 a 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 European Accreditation (EA) and International Laboratory Accreditation Cooperation (ILAC) accepted laboratory. The measurements were carried out in the (280 to 350) K temperature range. All experiments were made at least three times, and the results were averaged. The solubility was reproducible within uncertainties (defined as standard deviation) of ± 0.0005. Meanwhile, the temperature was reproducible within an uncertainty of 0.1 K. The repeatability of the solubility experimental points was ± 0.1 K .

RESULTS AND DISCUSSION

The activity coefficient γ_i of the ith (solute) component in solid−liquid equilibrium can be calculated[9] by the following equation:

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

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Table 3. Solubility of Triglycerides (1) in 1-Bromopropane (2) and Activity Coefficients

trilaurate			trimyristate			tripalmitate			tristearate		
x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
0.0475	289.6	0.1619	0.0297	296.7	0.0772	0.0243	303.5	0.0333	0.0132	308.1	0.0176
0.0572	291.4	0.1852	0.0363	298.6	0.0936	0.0510	310.7	0.0827	0.0239	312.2	0.0266
0.0773	294.0	0.2334	0.0466	301.2	0.1207	0.0778	315.4	0.1518	0.0347	315.2	0.0387
0.1246	299.3	0.3505	0.0539	302.2	0.1401	0.1092	319.7	0.2467	0.0472	318.2	0.0557
0.2225	306.1	0.5692	0.0611	303.6	0.1608	0.1781	325.5	0.4536	0.0549	319.6	0.0688
0.2819	308.8	0.6749	0.0744	305.7	0.2003	0.2270	328.2	0.5773	0.0661	321.8	0.0887
0.3638	311.5	0.7866	0.0788	306.7	0.2144	0.3294	331.4	0.7621	0.0765	323.1	0.1116
0.4123	312.8	0.8366	0.0834	307.2	0.2282	0.4208	333.4	0.8618	0.1158	327.9	0.2104
0.5179	314.8	0.9133	0.1046	309.8	0.2940	0.5614	335.4	0.9442	0.1750	332.6	0.3817
0.6323	316.6	0.9608	0.1844	316.4	0.5230	0.6916	336.7	0.9793	0.2953	337.7	0.6735
0.7686	318.1	0.9884	0.2204	318.2	0.6079				0.3867	340.0	0.8099
			0.2440	319.1	0.6567				0.4762	341.5	0.8914
			0.3749	323.1	0.8437				0.5864	342.9	0.9483
			0.5421	326.0	0.9491				0.6352	343.3	0.9639

Table 4. Parameters and Root-Mean-Square Deviation of Van Laar, Wilson, NRTL, and UNIQUAC for Fatty Acid-1-Bromopropane Systems

	Van Laar			Wilson			NRTL			UNIQUAC			
			σ_{VL}	λ_1	λ_2	σ_W	A_1	A_2		σ_N	A_{12}	A_{21}	σ_M
system	A_1	A_2	K	J·mol^{-1}	J·mol^{-1}	K	J·mol^{-1}	J·mol^{-1}	α	K	J·mol^{-1}	J·mol^{-1}	K
myristic	1.2468	0.3302	0.822	1645.4	1535.6	0.796	1132.9	3269.6	1.58	0.186	802.53	−73.930	0.888
palmitic	0.6065	0.2137	0.414	−484.45	2049.89	0.429	674.98	4922.9	1.55	0.100	1377.6	−584.02	0.465
stearic	1.3314	0.1002	0.096	2844.8	855.31	0.427	8168.7	3542.6	1.92	0.073	453.90	162.060	0.538

where x_i is the mole fraction solubility and γ_i is the activity coefficient of the ith component at temperature T, respectively. $\Delta H^{fus}(T_{tp})$ is the molar enthalpy of fusion of the ith solute at triple-point temperature (T_{tp}), and ΔC_p is the difference in solute heat capacity between the solid and the liquid at the triple point.

The temperature and enthalpy of fusion at the triple point can be substituted in eq 1 by atmospheric melting points T_f and the enthalpy of fusion ΔH^{fus} at T_f, respectively, because their values present little difference. The contributions of the second and third terms are often minor and negligible, because the melting temperature is quite low. Thus, the solubility equation becomes:

$$\ln(x_i\gamma_i) = -\frac{\Delta H^{fus}}{RT_f}\left[\frac{T_f}{T} - 1\right] \quad (2)$$

The activity coefficients of the fatty acids and triglycerides in 1-bromopropane calculated with eq 2 are shown in Tables 2 and 3. The activity coefficients are greater than 1 in fatty acid−1-bromopropane systems, so the solubility of the acid is lower than the ideal one. It indicates that the strength of intermolecular hydrogen bonds between molecules of the acid is greater than the polar−polar interaction between the fatty acid and the 1-bromopropane. The values of the activity coefficients tend to 1 when temperature increases because the strength of molecular bonds decreases, which is a normal behavior.[10] This behavior is similar to that seen in a previous paper[8] for the lauric acid−1-bromopropane system.

The polarity of a substance (X_p) can be defined as follows to account for the contribution from hydrogen bonding and other polar interactions:[11]

$$X_p = 1 - \frac{\delta_d^2}{\delta_{total}^2} \quad (3)$$

where δ_d is the dispersion Hansen solubility parameter and δ_{total} is the total solubility parameter. The polarity of fatty acids decreases from 0.13 to 0.11 when their aliphatic chain length increases from C14 to C18. In comparison with their corresponding fatty acids, triglycerides possess less polarity due to the domination of alkyl groups (Table 1). The polarity of 1-bromopropane is 0.17, so the fatty acids should be more soluble in 1-bromopropane than triglycerides with lower polarities (Table 1). However, the activity coefficients of triglycerides in 1-bromopropane (Table 3) are less than unity for low temperatures. This behavior indicates negative deviations from Raoult's law that must result from effects such as solvation or formation of electron donor−acceptor complexes.

The van Laar, Wilson, nonrandom two-liquid (NTRL), and universal quasichemical activity coefficient (UNIQUAC) models were used for the correlation of the activity coefficients of the systems. In the UNIQUAC model, the values of r and q were taken from Hansen et al.[12] (Table 1)

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

$$\Omega = \sum (T_i^{exp} - T_i^{cal})^2 \quad (4)$$

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

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

$$\sigma = \sum_{i=1}^{n} (T_i^{exp} - T_i^{cal})^2/(n-1) \quad (5)$$

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 van Laar, Wilson, NRTL, and UNIQUAC models[13] and root-mean-square deviations of temperature for fatty acids are listed in Table 4. The best description of solid−liquid equilibrium was given by the NRTL equation with the average root-mean−square deviation of temperature between 0.186 and 0.073, taking α as variable (Figure 1) because the standard deviation of temperature is

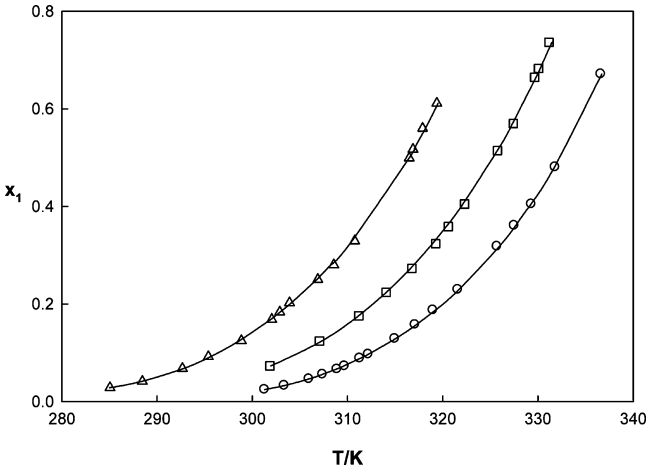

Figure 1. Solubility of fatty acids in 1-bromopropane: ○, stearic acid; □, palmitic acid; △, myristic acid. The symbols represent the experimental data and the lines the NRTL correlation for each fatty acid.

very sensitive to the α value. For example, the standard deviation of temperature deviations in the system myristic acid-1-bromopropane is σ = 0.18 for α = 1.585 and σ = 1.026 for α = 0.3. The results of correlations by use of the other models present worse average deviations (Table 4).

Table 5 displays the parameters and root-mean-square deviations of temperature of the models for triglycerides. The α constant in NTRL equation was calculated to obtain a good data correlation, because the usual values (0.2 or 0.3) did not yield fair results. Figure 2 shows the experimental data and the NRTL correlation for each triglyceride. The good behavior of the van Laar model is noteworthy. In this case, the correlation

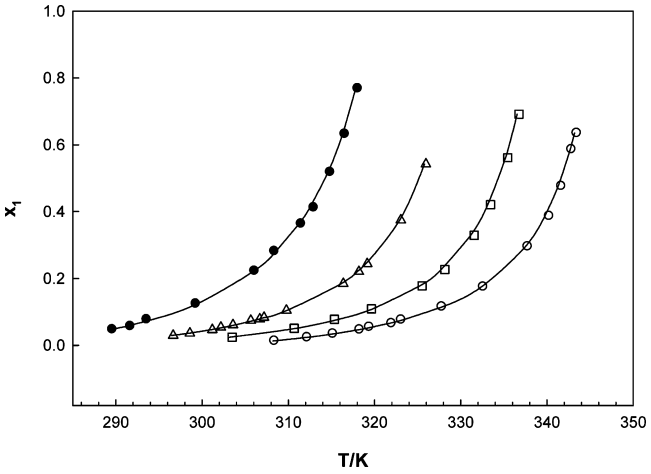

Figure 2. Solubility of triglycerides in 1-bromopropane: ●, glyceryl trilaurate; △, glyceryl trimyristate; □, glyceryl tripalmitate; ○, glyceryl tristearate. The symbols represent the experimental data and the lines the NRTL correlation for each triglyceride.

of results is facilitated because of the parameters of the equation take negative values, corresponding to activity coefficients at infinite dilution less than 1. Similar results were found by Smith et al.[14] for triglyceride−chloroform systems.

CONCLUSIONS

The fatty acid−1-bromopropane systems present positive deviations related to the Raoult law. The triglycerides−1-bromopropane systems present solubilities higher than ideal ones, which suggests that there is solvation or formation of the triglyceride−bromopropane complex. The solubility of triglycerides and fatty acids in 1-bromopropane converge on ideal solubility when the temperature increases. Four methods of correlation were used: van Laar, Wilson, NRTL, and UNIQUAC. In all cases good results were obtained, with the values of standard deviation between 0.09 and 0.88..

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Notes

The authors declare no competing financial interest.

Table 5. Parameters and Root-Mean-Square Deviation of Van Laar, Wilson, NRTL, and Margules for Triglycerides−1-Bromopropane Systems

	Van Laar			Wilson			NRTL			UNIQUAC			
			σ_{VL}	λ_1	λ_2	σ_W	A_1	A_2		σ_N	A_{12}	A_{21}	σ_M
system	A_1	A_2	K	J·mol^{-1}	J·mol^{-1}	K	J·mol^{-1}	J·mol^{-1}	α	K	J·mol^{-1}	J·mol^{-1}	K
trilaurate	−2.6171	−0.6474	0.194	−1215.0	1133.2	0.543	−2063.0	768.59	1.40	0.239	1590.48	−920.05	0.350
trimyristate	−3.5763	−0.5875	0.329	114.42	−105.70	1.012	−1860 0.2	681.67	2.11	0.205	2260.8	−1336.21	0.313
tripalmitate	−4.5999	−0.6967	0.178	−1254.7	1158.99	1.307	−1942.6	3699.8	2.47	0.233	2285.3	−1292.4	0.513
tristearate	−9.8103	−0.1000	0.092	−1252.8	1160.39	0.779	−2392.51	4573.31	1.95	0.089	1616.9	−914.55	0.417

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REFERENCES

(1) Erhan, S. Z.; Asadauskas, S. Lubricant basestocks from vegetable oils. *Ind. Crops Prod.* **2000**, *11*, 277−282.
(2) Adhvaryu, A.; Sung, C.; Erhan, S. Z. Fatty acids and antioxidant effects on grease microstructures. *Ind. Crops Prod.* **2005**, *21*, 285−291.
(3) John, J.; Bhattacharya, M.; Raynor, P. C. Emulsions containing vegetable oils for cutting fluid application. *Colloids Surf., A* **2004**, *237*, 141−150.
(4) McClements, D. J. *Food emulsions. Principles, practices, and techniques*, 2nd ed.; CRC Press: Boca Raton, FL, 2005.
(5) Environmental Protection Agency (EPA). *Rules and Regulations*; Federal Register: Washington, DC, 2007; Vol. *72*, No. 103; pp 30142−30167.
(6) Fedors, R. F. A method for estimating both the solubility parameters and molar volumes of liquids. *Polym. Eng. Sci.* **1974**, *14*, -.
(7) Patton, J. S.; Stone, B.; Papa, C.; Abramowitz, R.; Yalkowsky, S. H. Solubility of fatty acids and other hydrophobic molecules in liquid trioleoylglycerol. *J. Lipid Res.* **1984**, *25*, 189−197.
(8) Cepeda, E. A.; Bravo, R.; Calvo, B. Solubilities of Lauric Acid in n-Hexane, Acetone, Propanol, 2-Propanol, 1-Bromopropane, and Trichloroethylene from (279.0 to 315.3) K. *J. Chem. Eng. Data* **2009**, *54*, 1371−1374.
(9) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular thermodynamics of fluid-phase equilibria*, 3rd ed.; Prentice Hall PTR: Upper Saddle River, NJ, 1999.
(10) Nordstrom, F. L.; Rasmuson, A. C. Prediction of solubility curves and melting properties of organic and pharmaceutical compounds. *Eur. J. Pharm. Sci.* **2009**, *36*, 330−344.
(11) Li, Y. Q.; Taulier, N.; Rauth, A. M.; Wu, X. Y. Screening of lipid carriers and characterization of drug-polymer-lipid interactions for the rational design of polymer-lipid hybrid nanoparticles (PLN). *Pharm. Res.* **2006**, *23*, 1877−1887.
(12) Hansen, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. Vapor-liquid-equilibria by Unifac group contribution 0.5. Revision and extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352−2355.
(13) Walas, S. M. *Phase Equilibrium in Chemical Engineering*; Butterworth-Heinemann: Newton, MA, 1985.
(14) Smith, R. L.; Acosta, G. M.; Arai, K. Prediction and correlation of triglyceride-solvent solid-liquid equilibria with activity coefficient models. *Fluid Phase Equilib.* **1998**, *145*, 53−68.
(15) Daubert, T. E.; Danner, R. P. *Physical and thermodynamic properties of pure chemicals. Data compilation*. Hemisphere Pub. Corp: New York, 1989.
(16) *ChemCAD Professional. 5.2.0*; Chemstations Inc.: Houston, TX, 2002.
(17) Ollivon, M.; Perron, R. Measurements of Enthalpies and Entropies of Unstable Crystalline Forms of Saturated Even Monoacid Triglycerides. *Thermochim. Acta* **1982**, *53*, 183−194.