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Phase Equilibria of Long-Chain Carboxylic Acids in Supercritical Propane

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ABSTRACT: This paper presents data on the phase behavior of long-chain acids (octanoic acid, decanoic acid, dodecanoic acid, hexadecanoic acid, octadecanoic acid, and docosanoic acid) in supercritical propane. The data were measured for acid mass fractions w_{acid} = (0.0149 to 0.652) in the temperature range T = (375 to 412) K, and the phase transition occurred at pressures in the range p = (3.7 to 11.2) MPa. The data showed no temperature inversions yet does hint toward possible three-phase regions at low temperatures for acids with 10 or more carbon atoms. The data shows a linear relationship between the phase transition pressure and the temperature at constant composition. Additionally, for acids with 10 or more carbon atoms, at constant temperature and mass fraction, a linear relationship exists between the phase transition pressure and the number of carbon atoms.

INTRODUCTION

Recent studies have shown that supercritical fluid separation is an attractive alternative technique for the separation and fractionation of high molecular mass compounds.[1,2] Applications in the petrochemical industry include, but are not limited, to the fractionation of paraffin and synthetic wax,[3,4] the fractionation of wax-like alcohol ethoxylates,[5,6] and the separation of detergent range alkanes and alcohols.[7] In addition, a multitude of studies on the supercritical fluid extraction and/or fractionation of oils and other high molecular mass compounds from natural products have been conducted (see reviews of Brunner[2] and Temelli[8] for selected examples). Typical compounds encountered include alkanes, alcohols, acids, and/or esters, and these may be aliphatic or aromatic in nature with varying degrees of saturation. Triglycerides are also often encountered in natural products. Supercritical fluid extraction and/or fractionation are well-suited to these type of separations as they are able to process thermally sensitive materials with a very low solvent residue and usually with a high selectivity.[2]

Supercritical carbon dioxide is the most popular supercritical solvent and is nontoxic and nonflammable. A number of studies have been conducted on the phase behavior of liquid phase long-chain carboxylic acids in supercritical carbon dioxide. However, due to its dipole moment, carbon dioxide is not a good solvent of long-chain carboxylic acids (see for example Sparks et al.,[9] Ghaziaskar and Nikravesh,[10] Heo et al.,[11] Buyn et al.,[12] and Kramer and Thodos[13,14]). In many cases very high pressures (in excess of 30 MPa) are required for total solubility of these acids, and as the molecular mass of the compound increases, so does the pressure required for total solubility.

Propane is an attractive alternative supercritical solvent. Studies of the phase behavior of the homologous series of long-chain alkanes and alcohols in supercritical propane[15−17] have shown that high molecular mass alkanes and alcohols require considerably lower pressures for total solubility than in supercritical carbon dioxide.[18,19] In addition, comparing the phase behavior of tetradecanoic acid in propane[20] with the trends observed for the solubility of tetradecanoic acid in supercritical carbon dioxide, it can be seen that the pressure required for total solubility is much lower for propane than for carbon dioxide. However, considerably less experimental data have been published for long-chain acids (octadecanoic acid and higher) in propane than in carbon dioxide.

A review of the literature has shown that phase equilibrium data have been published for the homologous series propane/*n*-alkane as well as propane/1-alcohol. However, for the homologous series of propane/acids, to the best of our knowledge, only a single set of data has been published (propane/tetradecanoic acid (C14-COOH))[20] for acids with 6 or more carbon atoms.

The aim of this paper is to present phase equilibrium data for the homologous series of long-chain saturated carboxylic acids in supercritical propane between temperatures of T = (375 and 411) K and for mass fractions between w_{acid} = (0.015 and 0.65). The temperature range was selected as it is just above the critical temperature of propane (369.8 K)[21] as, ideally, a supercritical fluid extraction/fractionation process should operate just above the critical temperature of the solvent. The mass fractions were selected so that the critical region can be well-characterized and that the measured data can be used for thermodynamic modeling of the systems with specific focus on the critical behavior, as required for supercritical fluid extraction/fractionation processes.

EXPERIMENTAL SECTION

Experimental Setup and Method. A static synthetic method, using a previously constructed setup, consisting of a variable volume high-pressure view cell, was used to measure the phase equilibria. The design of the view cell is based on a piston-cylinder setup and has been described in detail in a previous publication.[15] The view cell has a maximum volume of 45 cm^3 and is able to operate between T = (300 and 460) K and up to pressures (p) =

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Table 1. Acids Used, Their Acronyms, Chemical Formulae, Catalog Numbers, and Purity (As Provided by the Suppliers)

alcohol	chemical formula	catalog number	purity
octanoic acid (caprylic acid)	$CH_3(CH_2)_6COOH$	Sigma C2875	0.99
decanoic acid (capric acid)	$CH_3(CH_2)_8COOH$	Fluka 21409	0.995
undecanoic acid (hendecanoic acid)	$CH_3(CH_2)_9COOH$	Aldrich 171476	0.99
dodecanoic acid (lauric acid)	$CH_3(CH_2)_{10}COOH$	Sigma L4250	0.99
hexadecanoic acid (palmitic acid)	$CH_3(CH_2)_{14}COOH$	Sigma P5585	0.99
octadecanoic acid (stearic acid)	$CH_3(CH_2)_{16}COOH$	Fluka 85679	0.995
docosanoic acid (behenic acid)	$CH_3(CH_2)_{20}COOH$	Aldrich 216941	0.995

Table 2. Phase Equilibria Measurements for the System Propane (1)/Octanoic Acid (2) (w_2 = Mass Fraction of Component 2)

			pressure−temperature relationship		
			$p = AT + B$ (p in MPa, T in K)		
w_2	T/K	p/MPa	A	B	R^2
0.652	380.2	3.78	0.05350	−16.576	0.999
	394.6	4.50			
	408.6	5.30			
0.554	382.1	4.31	0.06487	−20.487	0.999
	395.4	5.13			
	408.3	6.01			
0.452	380.9	4.53	0.07183	−22.846	0.999
	393.9	5.41			
	407.5	6.44			
0.384	380.9	4.59	0.07373	−23.494	1.000
	394.4	5.57			
	408.3	6.61			
0.302	382.0	4.80	0.07510	−23.896	1.000
	394.9	5.74			
	408.1	6.76			
0.229	380.4	4.78	0.07626	−24.218	1.000
	394.3	5.86			
	408.2	6.90			
0.179	382.1	4.95	0.07141	−22.328	1.000
	395.3	5.91			
	409.4	6.90			
0.121	380.8	4.90	0.06789	−20.932	0.999
	394.3	5.87			
	407.9	6.74			
0.0814	380.8	4.95	0.06368	−19.291	1.000
	395.1	5.88			
	408.6	6.72			
0.0510	381.2	5.00	0.05576	−16.236	0.999
	395.1	5.82			
	409.0	6.55			
0.0287	379.8	4.95	0.04689	−12.832	0.995
	393.5	5.67			
	407.1	6.23			
0.0176	380.2	4.79	0.03690	−9.223	0.997
	393.8	5.34			
	407.3	5.79			

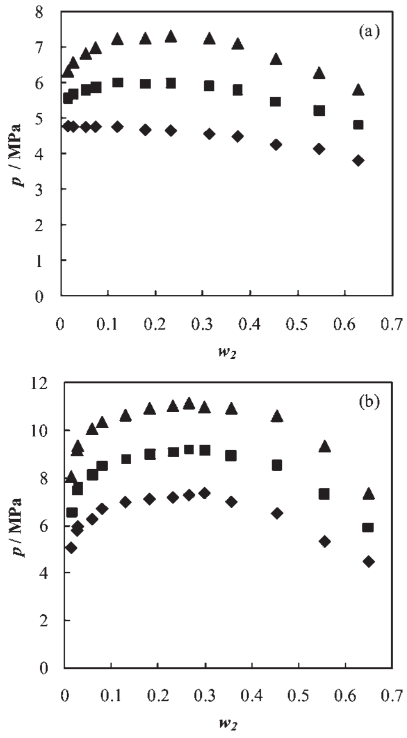


Figure 1. Phase behavior of (a) propane (1)/decanoic acid (2) and (b) propane(1)/docosanoic(2) acid in propane at T = (378, 393, and 408) K; ◆, 378 K; ■, 393 K; ▲, 408 K.

27.5 MPa. The accuracy of the measurements in the cell can be summarized as follows:[15]

- The uncertainty in the phase transition pressure measurement is approximately 0.06 MPa.
- The accuracy of the temperature measurement is better than 0.2 K.
- It is estimated that the maximum error in the mass fraction is approximately 0.01 times the value. This error is based on the accuracy and repeatability of the balances used for the measurement as well as the accuracy with which the compounds can be transferred to the phase equilibrium cell.

The experimental procedure can be summarized as follows: A known amount of the acid is loaded into the phase equilibrium cell, after which the cell is closed, evacuated, and flushed with propane. Liquid propane is then added quantitatively, and the inlet valve is securely closed. The cell is then heated to the required temperature using circulating heating fluid. Once the cell content reaches thermal equilibrium, the pressure is increased until the cell content is in the single phase region. The pressure is

Table 3. Phase Equilibria Measurements for the System Propane (1)/Decanoic Acid (2)

			pressure−temperature relationship		
			$p = AT + B$ (p in MPa, T in K)		
w_2	T/K	p/MPa	A	B	R^2
0.628	376.7	3.72	0.06756	−21.738	1.000
	393.7	4.85			
	409.7	5.95			
0.545	376.5	4.04	0.07231	−23.200	0.999
	393.4	5.21			
	408.7	6.37			
0.454	377.0	4.19	0.08129	−26.474	0.999
	392.4	5.39			
	409.0	6.79			
0.374	376.7	4.40	0.08782	−28.706	0.999
	393.4	5.79			
	409.6	7.29			
0.314	376.3	4.41	0.09027	−29.560	1.000
	393.5	5.96			
	409.2	7.38			
0.232	377.7	4.61	0.08926	−29.086	0.999
	394.4	6.16			
	410.2	7.51			
0.179	376.8	4.57	0.08643	−27.990	1.000
	393.3	6.01			
	409.2	7.37			
0.120	377.6	4.71	0.08320	−26.685	0.999
	393.9	6.13			
	409.7	7.38			
0.0739	377.3	4.70	0.07470	−23.470	1.000
	393.5	5.95			
	409.3	7.09			
0.0531	376.9	4.66	0.06938	−21.468	0.999
	393.4	5.87			
	409.2	6.90			
0.0266	375.8	4.59	0.06060	−18.135	0.993
	391.8	5.70			
	407.5	6.51			
0.0156	376.5	4.68	0.05177	−14.786	0.997
	392.7	5.60			
	408.2	6.32			

Table 4. Phase Equilibria Measurements for the System Propane (1)/Undecanoic Acid (2)

			pressure−temperature relationship		
			$p = AT + B$ (p in MPa, T in K)		
w_2	T/K	p/MPa	A	B	R^2
0.653	380.2	4.04	0.05633	−17.379	1.000
	394.6	4.84			
	408.6	5.64			
0.557	382.1	4.43	0.07248	−23.293	0.997
	395.4	5.30			
	408.3	6.33			
0.452	380.9	4.54	0.09092	−30.055	0.998
	393.9	5.82			
	407.5	6.96			
0.387	380.9	4.67	0.09742	−32.407	0.999
	394.4	6.06			
	408.3	7.34			
0.306	382.0	4.87	0.09999	−33.316	1.000
	394.9	6.18			
	408.1	7.48			
0.237	380.4	5.06	0.09173	−29.807	0.999
	394.3	6.40			
	408.2	7.61			
0.184	382.1	5.13	0.09293	−30.324	0.996
	395.3	6.50			
	409.4	7.67			
0.125	380.8	5.20	0.09077	−29.353	1.000
	394.3	6.45			
	407.9	7.66			
0.0771	380.8	5.14	0.08025	−25.400	1.000
	395.1	6.33			
	408.6	7.37			
0.0472	381.2	5.12	0.07374	−22.981	1.000
	395.1	6.16			
	409.0	7.17			
0.0289	379.8	4.99	0.06997	−21.548	0.996
	393.5	6.05			
	407.1	6.90			
0.0180	380.2	4.99	0.06016	−17.842	0.994
	393.8	5.92			
	407.3	6.62			

then slowly reduced until the transition point between the single and the two-phase region is observed and temperature and pressure are logged. The procedure is repeated at a number of temperatures. During the heating procedure, as well as while conducting the measurements, the cell contents are stirred with a magnetic stirrer to ensure proper mixing. Further details pertaining to the experimental procedure as well as comparison with high quality data from other reputable research groups have been described in a previous publication.[15]

Materials Used. Propane was obtained from Air Liquide at a purity of 0.9995, and the acids were obtained from Sigma-Aldrich. The acids used, their acronyms, chemical formulas, catalog numbers, and purities (as provided by the suppliers) are given in Table 1. All compounds were used without further purification.

■ RESULTS AND DISCUSSION

High-pressure phase equilibrium measurements of propane with octanoic acid (C8-COOH), decanoic acid (C10-COOH), dodecanoic acid (C12-COOH), hexadecanoic acid (C12-COOH), octadecanoic acid (C18-COOH), and docosanoic acid (C22-COOH) were conducted for mass fractions $w_{\mathrm{acid}} = (0.0149$ to $0.654)$ and temperatures $T = (375.1$ to $411.9)$ K resulting in bubble/dew point pressures in the range $p = (3.78$ to $11.20)$ MPa. All measurements were conducted above the melting temperature of the acid as well as the critical temperature of propane, and as such, all measurements were fluid−liquid in nature. Although the temperature was constant throughout the measurement of an experimental data point, not all of the data

Table 5. Phase Equilibria Measurements for the System Propane (1)/Dodecanoic Acid (2)

			pressure−temperature relationship		
			$p = AT + B$(p in MPa, T in K)		
w_2	T/K	p/MPa	A	B	R^2
0.648	380.9	4.04	0.06357	−20.185	0.999
	396.1	4.96			
	410.3	5.91			
0.550	380.7	4.40	0.07602	−24.551	1.000
	395.4	5.48			
	409.5	6.59			
0.448	381.0	4.82	0.08609	−27.988	1.000
	394.9	5.98			
	409.7	7.29			
0.389	379.8	4.85	0.09412	−30.916	0.999
	393.8	6.10			
	407.2	7.43			
0.300	380.7	5.00	0.09962	−32.911	1.000
	394.2	6.37			
	409.5	7.87			
0.231	381.4	5.17	0.10037	−33.085	0.999
	394.9	6.59			
	408.4	7.88			
0.181	380.2	5.05	0.09726	−31.905	1.000
	395.0	6.54			
	409.0	7.85			
0.125	381.2	5.26	0.09200	−29.797	1.000
	395.0	6.56			
	408.7	7.79			
0.0804	379.2	5.05	0.08531	−27.270	0.999
	393.5	6.35			
	407.8	7.49			
0.0519	380.3	5.17	0.08084	−25.550	0.999
	394.1	6.34			
	407.4	7.36			
0.0281	379.5	5.01	0.06947	−21.315	0.996
	395.0	6.20			
	409.2	7.07			
0.0149	377.0	4.78	0.05978	−17.739	0.999
	392.9	5.79			
	407.8	6.62			

Table 6. Phase Equilibria Measurements for the System Propane (1)/Hexadecanoic Acid (2)

			pressure−temperature relationship		
			$p = AT + B$ (p in MPa, T in K)		
w_2	T/K	p/MPa	A	B	R^2
0.655	380.2	4.18	0.06604	−20.931	1.000
	395.7	5.18			
	408.8	6.07			
0.571	379.6	4.73	0.08564	−27.799	0.999
	393.6	5.86			
	408.1	7.17			
0.463	381.1	5.19	0.11187	−37.432	1.000
	395.2	6.78			
	408.1	8.21			
0.392	381.8	5.46	0.11653	−38.990	0.998
	397.1	7.35			
	409.5	8.68			
0.305	380.4	5.81	0.11628	−38.389	0.999
	394.5	7.54			
	408.1	9.03			
0.231	379.8	5.73	0.11594	−38.256	0.998
	394.2	7.53			
	407.6	8.95			
0.184	379.7	5.83	0.11332	−37.157	0.998
	392.9	7.43			
	406.0	8.81			
0.122	378.1	5.43	0.11575	−38.279	0.997
	392.5	7.25			
	406.2	8.68			
0.0829	379.3	5.38	0.10588	−34.743	0.998
	392.9	6.92			
	406.5	8.26			
0.0532	381.8	5.57	0.09615	−31.107	0.999
	394.8	6.90			
	407.7	8.06			
0.0274	380.3	5.28	0.07933	−24.838	0.995
	393.2	6.44			
	408.2	7.50			
0.0199	376.4	4.94	0.08005	−25.176	0.999
	392.4	6.27			
	406.9	7.38			
0.0184	380.9	5.39	0.06947	−21.040	0.998
	394.4	6.41			
	408.8	7.33			

could be measured at exactly the same temperature due to variations in the ambient conditions and the fact that the temperature controller controls the heating fluid temperature, which in turn regulates the temperature of the cell contents. It is known that for alkanes and alcohols in supercritical ethane and propane a linear relationship exists between the phase transition pressure and temperature[15,17] within a limited temperature range, and this linear relationship can be used to interpolate between measurements to obtain isothermal data. This type of linear relationship was applied to the measured data and thus allowed the generation of isothermal data. The R^2 (Pearson R^2 value for fit of linear relationship) values of the linear pressure−temperature relationships (0.984 to 1.000) indicate that the assumption of the linear pressure−temperature relationships holds true in the desired temperature range. The phase behavior measurements as well as the linear pressure−temperature relationships are given in Tables 2 to 8.

Figure 1 shows the phase behavior of C10-COOH and C22-COOH in supercritical propane at various temperatures. These plots were constructed using the linear pressure−temperature relationship given in Tables 3 and 8, respectively. In all cases an increase in temperature leads to an increase in phase transition pressure. At certain acid mass fractions a maximum exists for the phase transition pressure. This maximum, or mixture critical point, is mostly between acid mass fractions w_{acid} = (0.10 to 0.35)

Table 7. Phase Equilibria Measurements for the System Propane (1)/Octadecanoic Acid (2)

			pressure−temperature relationship		
			$p = AT + B$ (p in MPa, T in K)		
w_2	T/K	p/MPa	A	B	R^2
0.638	376.4	4.08	0.08161	−26.664	0.999
	392.5	5.32			
	409.0	6.74			
0.547	375.4	4.62	0.11289	−37.771	1.000
	391.9	6.45			
	410.4	8.57			
0.454	376.4	5.25	0.12730	−42.628	0.999
	392.7	7.44			
	409.0	9.40			
0.370	376.7	5.71	0.12707	−42.098	0.997
	394.5	8.16			
	409.6	9.88			
0.307	375.8	5.85	0.13422	−44.519	0.997
	394.7	8.61			
	409.9	10.41			
0.234	376.2	5.97	0.13301	−43.975	0.995
	392.2	8.37			
	409.6	10.42			
0.180	375.1	5.72	0.12750	−42.042	0.998
	391.3	7.97			
	409.4	10.10			
0.120	375.1	5.41	0.11717	−38.478	0.997
	395.1	7.95			
	411.9	9.71			
0.0735	376.9	5.35	0.11223	−36.878	0.995
	392.5	7.32			
	408.0	8.84			
0.0394	377.0	5.21	0.10741	−35.222	0.996
	392.6	7.07			
	408.1	8.55			
0.0299	376.5	5.16	0.10229	−33.305	0.998
	391.7	6.85			
	407.0	8.28			
0.0274	376.9	5.09	0.09399	−30.221	0.984
	393.5	6.99			
	409.7	8.17			
0.0153	376.9	5.06	0.09110	−29.263	1.000
	392.9	6.55			
	408.3	7.92			

Table 8. Phase Equilibria Measurements for the System Propane (1)/Docosanoic Acid (2)

			pressure−temperature relationship		
			$p = AT + B$ (p in MPa, T in K)		
w_2	T/K	p/MPa	A	B	R^2
0.649	375.5	4.25	0.09610	−31.858	0.999
	392.0	5.76			
	406.9	7.27			
0.555	376.1	5.03	0.13382	−45.269	0.999
	392.1	7.27			
	407.2	9.19			
0.454	375.9	6.16	0.13658	−45.124	0.998
	391.4	8.45			
	406.8	10.38			
0.356	377.8	6.91	0.13100	−42.532	0.998
	393.4	9.10			
	408.5	10.93			
0.299	377.0	7.22	0.12051	−38.200	1.000
	392.9	9.17			
	408.7	11.04			
0.266	378.1	7.23	0.12883	−41.429	0.998
	393.2	9.33			
	408.9	11.20			
0.232	376.9	6.97	0.12842	−41.374	0.998
	393.3	9.25			
	408.7	11.05			
0.182	377.6	7.01	0.12701	−40.906	0.999
	393.5	9.16			
	409.1	11.01			
0.131	377.8	6.88	0.12180	−39.067	0.998
	393.5	8.98			
	413.8	11.28			
0.0808	377.1	6.51	0.12135	−39.175	0.995
	393.1	8.68			
	408.6	10.33			
0.0595	372.8	5.57	0.12665	−41.621	1.000
	390.8	7.92			
	407.4	9.95			
0.0289	376.8	5.76	0.11360	−36.997	0.998
	393.1	7.75			
	408.6	9.37			
0.0275	375.3	5.41	0.11271	−36.824	0.996
	391.1	7.39			
	406.8	8.96			
0.0150	377.9	5.06	0.09966	−32.619	1.000
	393.7	6.58			
	409.0	8.16			

with the lower acid mass fractions observed at lower temperatures and for lower molecular mass acids.

Although three phases were not observed experimentally, there are indications of possible three-phase behavior at low temperatures and low acid mass fractions for systems between C10-COOH and C18-COOH. As the mass fraction of acid decreased, the nature of the phase transition measurement changed from first liquid to critical and then to vapor after which a liquid-like nature was once again observed. In addition, at the transition from vapor to liquid a pressure minima is noted. The observation of this second region of liquid-like behavior indicates the presence of three-phase behavior. Peters[22] discussed the phase behavior of various homologous series in, among others, supercritical propane and plotted data of the upper critical end points (UCEP) and lower critical end points (LCEP) of C16-COOH to C22-COOH in propane. The presence of an UCEP or a LCEP, even if hidden by solidification, is a prerequisite for three-phase behavior to occur. The observation of the possible three-phase behavior in C16-COOH and C18-COOH is in agreement with the results of Peters. In addition, the absence of the observation of three-phase behavior for C22-COOH can be explained by the fact that the UCEP temperature (approximately T = (371 to 372) K) is lower than the temperatures measured in this work (T > 375 K). Extrapolation of the data by Peters shows that a tricritical point (where the UCEP and LCEP are identical) may occur at approximately C12-COOH or possibly lower, depending on the method of extrapolation. However, possible three-phase behavior was observed for both C12-COOH and C10-COOH, and thus the tricritical point is most probably at an acid with molecular mass less than that of C10-COOH. There was no indication of three-phase behavior in the system with C8-COOH.

No temperature inversions were observed, and neither does the data indicate the presence thereof. In all cases the gradients of the linear pressure−temperature relationships (at constant composition) are positive, and as the molecular mass increases, so does the gradient, indicating that for heavier acids the increase in phase transition pressure with temperature becomes even larger.

Van Konynenberg and Scott[23] proposed five types of phase behavior; Streett[24] later added a sixth type, and subsequently the nomenclature for phase diagrams has been standardized by the International Union of Pure and Applied Chemistry (IUPAC).[25] From the data presented here, one is tempted to classify the measured systems into one of these classes, yet only a limited region of the phase diagram has been measured. However, from the measured data together with the information presented by Peters[22] an indication of the type of phase behavior can be obtained. For C10-COOH to C18-COOH there exists the possibility of a three-phase region, and for C22-COOH a three-phase region may exist at temperatures lower than those measured in this work. Gardeler et al.[26] and Schwarz and Knoetze[17] proposed that the homologous series propane/1-alcohol are either type III, IV, or V. All three of these types of phase behavior occur in highly asymmetrical systems, and as the homologous series propane/acid is more asymmetric than propane/1-alcohol, it may be concluded that the propane/acid systems for acids C10-COOH and larger are either type III, IV, or V. With respect to the IUPAC[25] nomenclature the phase diagrams of propane with C10-COOH to C22-COOH could thus be any type with 2^P and 2^C in their name as the indication that two critical lines are present. This is based on the fact that an UCEP and a LCEP is present and that the UCEP and the three-phase regions occur at temperatures above the critical temperature of propane (from the work of Peters[22]). Further classification is not possible with the current information as only a selected region of the phase diagram has been studied. The system propane/C8-COOH does not display a three-phase region in the range measured in this work, and as a result the propane/C8-COOH system may be, in addition to type III, IV, or V, also type II or I. Classification according to IUPAC[25] would depend on the type of phase behavior that the higher alkanes in propane display and will most probably be either the same type or a simplification thereof.

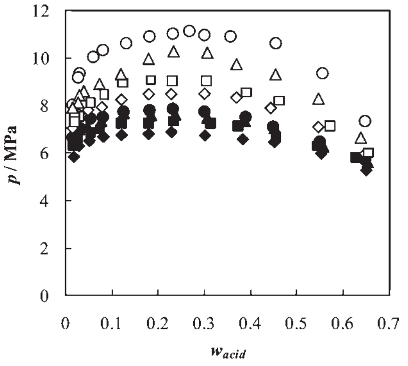


Figure 2. Comparison of the phase behavior of various acids at T = 408 K; ◆, C9-COOH; ■, C10-COOH; ▲, C11-COOH; ●, C12-COOH; ◇, C14-COOH;[20] □, C16-COOH; △, C18-COOH; ○, C22-COOH.

A comparison of the phase behavior of various acids at constant temperature is shown in Figure 2 for 408 K. For the entire range studied the phase transition pressure increases with increasing molecular mass. Similar trends have been observed for the phase behavior of n-alkanes and 1-alcohols in supercritical propane.[16,17] These studies have shown that there is a generally linear relationship between the phase transition pressure and the number of carbon atoms. The question now arises as to whether such a linear relationship also holds true for the homologous series propane/acids. Although it may seem as if this linear pressure−carbon number relationship is arbitrarily applied, the concept is based in the idea of group contribution: the addition of a -CH_2- group to an existing acid results in, at the same temperature and acid mass fraction, the same increase in pressure, irrespective of whether it has been added to a molecule with a hydrocarbon backbone of 10 or of 20 carbon atoms. Figure 3 shows three typical pressure−carbon number plots at constant temperature and mass fraction acid over the entire mass fraction range studied. As seen, from C10-COOH upward there is a generally linear relationship between the number of carbon

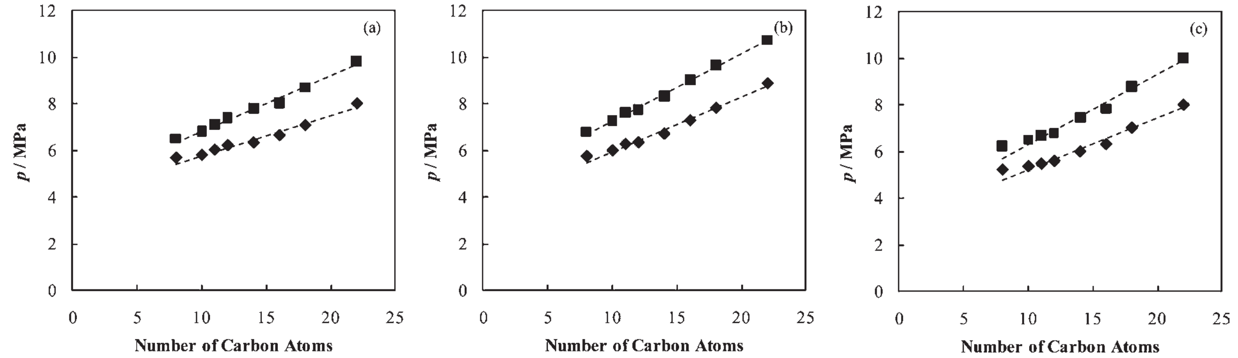


Figure 3. Pressure−carbon number plot for (a) w_{acid} = 0.05, (b) w_{acid} = 0.15, and (c) w_{acid} = 0.50 at T = (◆, 393 K and ■, 408) K, dashed line fitted correlation from Table 9.

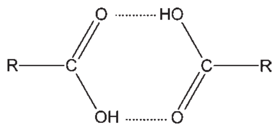
atoms and the phase transition pressure, but C8-COOH seems to deviate from this trend. The deviation may be attributed to the fact that for C8-COOH the polar carboxylic acid group plays a significantly larger effect in the nonpolar solvent than in larger acids resulting in higher phase transition pressures. In addition, C8-COOH probably displays a different type of phase behavior.

Due to the fact that the C8-COOH data does not lie on a straight line with the other data and probably follows a different type of phase behavior, these data have been omitted from the linear pressure−carbon number relationships. Using the measured data, together with the literature data for the system propane/tetradecanoic acid[20] the pressure−carbon number relationships at T = (393 and 408) K were constructed and are given in Table 9. A set of pressure−carbon number relationships at lower temperatures has been omitted. As the temperature decreases, the gradient of the pressure−carbon number relationships decreases, and the effect of the experimental error becomes significant. As can be seen the linear relationships at T = (393 and 408) K fit the data quite well with an average R^2 value of 0.981. Reconstruction of the data showed that the linear pressure−carbon number plots fit the experimental data with an average error of 0.1 MPa with only 5 of 266 points showing an error larger than 0.3 MPa. Within the range C10-COOH to C22-COOH the pressure−carbon numbers can thus be used with confidence to provide a reasonable estimation of the phase behavior. Schwarz et al.[27] showed that for the homologous series propane/n-alkane the linear relationships can be extrapolated to higher carbon numbers to provide a good first-order estimation of the phase equilibria. Limited extrapolation of the given linear pressure−carbon number plots is thus possible to provide an indication of the phase behavior for higher acids.

Table 9. Pressure−Carbon Number Plots Valid for Decanoic Acid to Docosanoic Acid at T = (393 and 408) K Where CN = the Number of Carbon Atoms in the Hydrocarbon Backbone of the Acid

	pressure−carbon number plot: $p = A \cdot \mathrm{CN} + B$ (p in MPa)					
	T = 393 K			T = 408 K		
w_{acid}	A	B	R^2	A	B	R^2
0.600	0.1427	3.391	0.975	0.2034	3.725	0.967
0.550	0.1889	3.132	0.980	0.2680	3.356	0.977
0.500	0.2237	2.945	0.981	0.2998	3.316	0.985
0.450	0.2557	2.785	0.979	0.3277	3.312	0.987
0.400	0.2588	2.942	0.978	0.3201	3.675	0.988
0.350	0.2703	2.957	0.984	0.3240	3.827	0.988
0.300	0.2845	2.907	0.987	0.3290	3.910	0.980
0.250	0.2750	3.099	0.982	0.3303	3.944	0.982
0.200	0.2632	3.249	0.989	0.3178	4.079	0.989
0.150	0.2394	3.519	0.990	0.2911	4.346	0.997
0.125	0.2225	3.716	0.981	0.2729	4.536	0.994
0.100	0.2127	3.738	0.972	0.2676	4.438	0.993
0.080	0.2050	3.750	0.960	0.2640	4.342	0.988
0.060	0.1838	3.936	0.970	0.2520	4.356	0.988
0.050	0.1740	4.012	0.973	0.2406	4.419	0.988
0.040	0.1650	4.063	0.973	0.2309	4.425	0.980
0.030	0.1549	4.125	0.967	0.2183	4.460	0.966
0.025	0.1285	4.383	0.982	0.1883	4.703	0.975
0.020	0.1090	4.554	0.984	0.1705	4.805	0.989

Figure 4 shows an interesting phenomena: Here the phase behavior of C16-COOH and dotriacontane (C32 alkane), C18-COOH, and hexatriacontane (C36 alkane) as well as C22-COOH and tetratetracontane (C44 alkane) in propane[16] are compared, and it can be seen that the acid behaves very similar to an alkane with double the amount of carbon atoms. It is well-known that acids associate to form strong hydrogen bonds between two molecules in solution. The hydroxyl group of one acid and the double-bonded oxygen of the other acid, and vice versa, form hydrogen bonds resulting in the molecules occurring as double molecules. It should be noted that this association does not result in chemical bonds but rather two molecules that are attached to each other by strong hydrogen bonds that result in behavior similar to a single molecule. The concept of this type of association, also employed in thermodynamic models such as those of the SAFT[28] family, can be represented schematically as follows:



From the results presented in Figure 4, it can thus be postulated that in supercritical solution association of acids also occurs and therefore two acid molecules associate and behave like a single molecule with double the number of carbon atoms

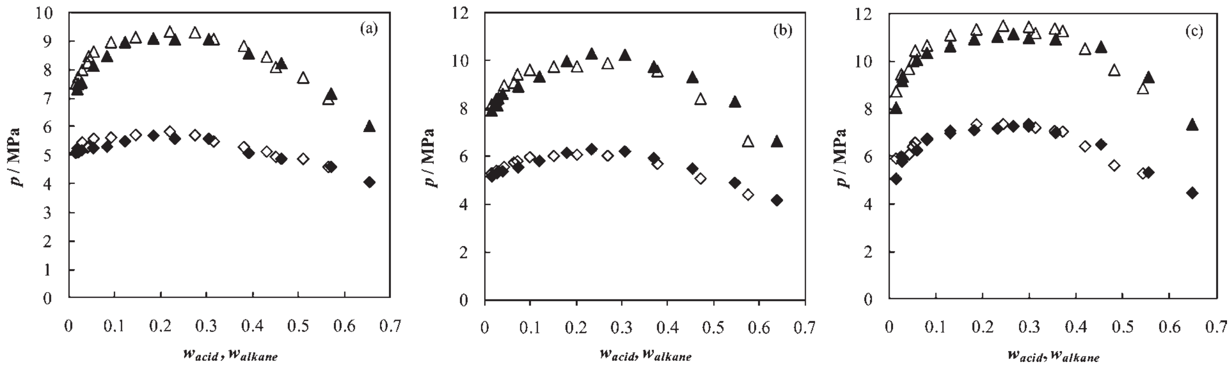


Figure 4. Pressure−composition plot at constant temperature for (a) hexadecanoic acid (◆, 378 K; ▲, 408 K) and dotriacontane[16] (◇, 378 K; △, 408 K), (b) octadecanoic acid (◆, 378 K; ▲, 408 K) and hexatriacontane[16] (◇, 378 K; △, 408 K), and (c) docosadecanoic acid (◆, 378 K; ▲, 408 K) and tetratetracontante[16] (◇, 378 K; △, 408 K) (w_{alkane} = mass fraction alkane in supercritical solvent).

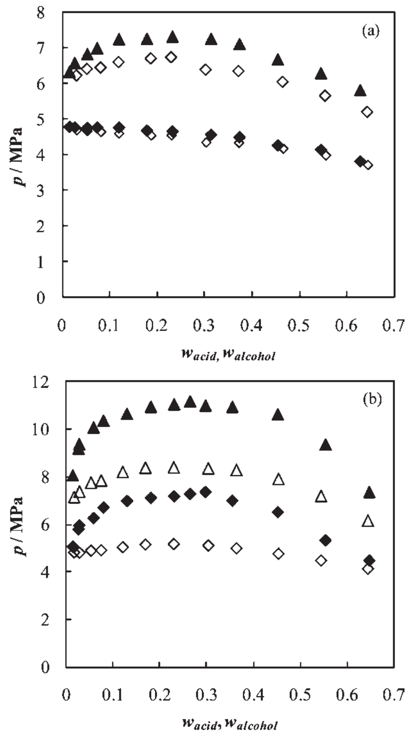


Figure 5. Pressure−composition plot at constant temperature for (a) decanoic acid (◆, 378 K; ▲, 408 K) and 1-decanol[17] (◇, 378 K; △, 408 K) and (b) docosadecanoic acid (◆, 378 K; ▲, 408 K) and 1-docosanol[17] at (◇, 378 K; △, 408 K) ($w_{alcohol}$ = mass fraction alcohol in supercritical solvent).

and a functional end group in the middle of the atom. Functional groups in the middle of molecule are very well shielded in supercritical solutions,[29] and due to the location of this functional end group the hydrocarbon backbone shields the functional group sufficiently, and the resultant "double acid" molecule behaves very much like an *n*-alkane.

The question arises as to whether supercritical propane is able to separate acids from other high molecular mass compounds. Consider Figure 5 where the phase behavior of C10-COOH and C22-COOH is compared to 1-decanol (C10 1-alcohol) and 1-docosanol (C22 1-alcohol), respectively. The higher the temperature and the greater the molecular mass, the larger the difference in phase behavior. However, even when comparing C10-COOH and 1-decanol at a lower temperature the acid is consistently, albeit only marginally, at higher phase transition pressures. This fact, together with previous results[20] that showed that the difference between an acid and an ester or *n*-alkane is larger than that between an acid and an alcohol indicates that supercritical propane has the ability to separate high molecular acids from other molecules with similar hydrocarbon backbones but different functional groups.

CONCLUSIONS

This study provided phase equilibrium data for long-chain acids in supercritical propane. From the magnitude of the pressure it can be seen that supercritical propane is able to solubilize long-chain acids at moderate pressures and that supercritical propane is able to distinguish between acids and other functional end groups. Interestingly, in supercritical propane the acids behave very similar to alkanes of double their number of carbon atoms, suggesting that the carboxylic acid groups of two molecules associate with one another to form a double molecule. In the future it is recommended that phase behavior measurements of acids in supercritical ethane be conducted. These data, together with literature information on the phase behavior of alkanes in supercritical ethane as well as alkanes and acids in supercritical carbon dioxide, may shed light as to whether association of acids is a common occurrence in supercritical solution. In addition, future work will also include the measurement of phase equilibria of other long-chain compounds (such as esters and alcohols) as well as triglycerides (important in the extraction of natural product) in supercritical ethane, propane, and carbon dioxide.

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