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Influence of High Pressure on the Liquidus Curve Shape in Binary Hydrocarbon Mixtures: Experimental Data, Correlation, and Prediction[†]

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(Solid + liquid) phase equilibria (SLE) of (tridecane + 3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene) at pressures up to about 1.0 GPa have been investigated in the temperature range from 293 K to 353 K. A thermostated apparatus was used for the measurements of transition pressures from the liquid to the solid state in two-component isothermal solutions. A polynomial pressure−temperature−composition relation for the high-pressure (solid + liquid) equilibria based on the general solubility equation at atmospheric pressure was found to correlate the data satisfactorily. Additionally, the SLE of binary systems (tridecane + 3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene) at normal pressure were measured by the dynamic (synthetic) method. The results at high pressure were compared for every system to those at normal pressure. The influence of the hydrocarbons' (with six carbon atoms) structure is discussed. Small effects are observed at high pressure (600 MPa). The main aim of this work was to predict the mixture behavior using only pure-component data and a cubic equation of state for the wide range of pressure studied, far above the pressure range to which cubic equations of state are normally applied. The fluid-phase behavior is described moderately well by the corrected SRK EOS and the van der Waals one-fluid mixing rules.

Introduction

The (solid + liquid) phase equilibria (SLE) of alkane systems have gained increasing interest in this decade. Most petroleum reservoir fluids contain heavy hydrocarbons that may precipitate as a waxy solid phase when conditions of temperature and pressure change. For the petroleum compositions, mixtures of alkanes with branched-chain hydrocarbons, aromatic hydrocarbons, or 1-alkynes seem to be very important, especially over wide ranges of temperature and pressure. Phase equilibrium data of alkane systems with these solvents are of importance for the safe and efficient operation of chemical plants. They are necessary for high-pressure polymerization processes and for the design of oil-recovery processes. New high-pressure SLE data of alkanes systems also offer new perspectives for modern technologies. Besides its importance for technological processes such as crystallization and purification at high pressure, SLE provides a good tool for examining the thermodynamic nature of many systems. The ultimate aim of this work is to investigate the influence of the solvents'—C_6 hydrocarbons—shape and chemical character on the solubility of long-chain hydrocarbons.

From a historical perspective, the very first (solid + liquid) equilibria measurements of organic liquids at high pressure were presented by Baranowski and co-workers.[1−4] Simultaneously, results for different organic mixtures were presented by Nagaoka and Makita,[5−7] Nagaoka and co-workers,[8] and Tanaka and Kawakami.[9] Recently, Yang et al. presented results involving alkane mixtures with alcohols.[10,11] The pressure effect on the phase behavior of binary mixtures of fatty acids up to 200 MPa was measured and well described by Inoue et al.[12]

Modeling of (solid + liquid) equilibrium under high pressure is presented by different authors using the chain delta lattice parameter model,[13] the Sako−Wu−Prausnitz EOS (SWP),[14,15] or the van der Waals EOS.[16] For the prediction of solid−fluid phase diagrams of light gas−heavy hydrocarbon systems up to 200 MPa using an equation of state, the G^E model is developed and presented by Pauly and co-workers.[17,18]

Mainly, simple eutectic mixtures with complete miscibility in the liquid phase and immiscibility in the solid phase were tested in a wide temperature range from 243 K to 373 K (i.e., the binary system (benzene + thiophene)[8]). SLE of binary mixtures were measured by an optical method from 278 K to 343 K and pressures up to 500 MPa for the organic liquid systems (benzene + 2-methyl-2-propanol)[5] or (carbon tetrachloride + *p*-xylene or benzene)[6] and (α-methylnaphthalene + β-methylnaphthalene).[7] The eutectic mixtures become richer in the component with the highest slope $\mathrm{d}p/\mathrm{d}T$ of the melting curve, and the eutectic temperature rises with increasing pressure; different compositions of the eutectic point are also observed.[8,9] It is expected as well that at higher pressure the melting temperature of a congruently melting compound increases and sometimes the nature of the compound may change to an incongruently melting compound.[6] The solid system (chlorobenzene + bromobenzene), which shows complete miscibility in the solid phase, does not present a maximum or minimum on solidus or liquidus curves throughout the whole composition and pressure ranges.[8] The first results of binary mixtures of alkanes were presented for eutectic mixtures of (tetradecane, or hexadecane + cyclohexane, or benzene) at high pressures up to 120 MPa by Tanaka and

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Table 1. Physical Constants of Pure Compounds^a

compound	$T_{\text{fus},1}$ K	$\Delta_{\text{fus}}H_1$ J·mol^{-1}	$T_{\text{tr},1}{}^a$ K	$\Delta_s^l C_{p,\text{m}}$ J·mol^{-1}·K^{-1}	$\Delta_{\text{tr}}H_1{}^a$ J·mol^{-1}	$T_{\text{cr}}{}^b$ K	$P_{\text{cr}}{}^b$ bar	ω^b	$V_\text{m}{}^b$ cm^3·mol^{-1}
tridecane	268.79^c 269.01^e	28501.0^c	255	−105.94^c	9162	675.84	17.23	0.6186	244.56
3-methylpentane	110.25^c	5303.2^c		53.96^c		504.47	31.24	0.2772	130.69
2,2-dimethylbutane	174.28^c	579.0^c		10.03^c		488.82	30.81	0.2339	133.77
1-hexyne	141.29^b	4205.8^b				516.24	36.20	0.3327	115.49
benzene	278.61^d 279.05^e	9834.1^d		4.01^d		562.20	48.98	0.2100	89.52
cyclohexane	279.82^c	2676.9^c		14.63^c		553.62	40.73	0.2096	108.91
hexane	177.84^c	13 079.6^c		44.12^c		507.47	30.12	0.3046	131.37

[a] Melting temperature, $T_{\text{fus},1}$; molar enthalpy of fusion, $\Delta_{\text{fus}}H_1$; solid−solid phase transition temperature, $T_{\text{tr},1}$; heat capacity change at the melting temperature, $\Delta_s^l C_{p,\text{m}}$; molar enthalpy of transition, $\Delta_{\text{tr}}H_1$; critical temperature, T_{cr}; critical pressure, P_{cr}; acentric factor, ω; molar volume, V_{m}. [a] Reference 23. [b] Reference 24. [c] Reference 25. [d] Reference 26. [e] This work.

Table 2. Experimental (Solid + Liquid) Equilibrium Temperatures of {Tridecane (1) + 3-Methylpentane or 2,2-Dimethylbutane or 1-Hexyne (2)} Systems at 0.1 MPa^a

x_1	$T_{1\alpha}$/K	x_1	$T_{1\alpha}$/K	x_1	$T_{1\beta}$/K	x_1	$T_{1\beta}$/K
			3-Methylpentane				
1.0000	269.01	0.6474	260.55	0.4776	254.59	0.2325	245.52
0.9537	268.08	0.6044	259.33	0.4593	254.25	0.1774	243.33
0.8968	267.11	0.5854	258.62	0.4464	254.01	0.1553	241.93
0.8421	265.85	0.5633	258.00	0.4181	253.39	0.1227	239.70
0.8003	264.65	0.5413	257.14	0.3872	252.53	0.0962	237.79
0.7794	264.08	0.5200	256.29	0.3364	250.68		
0.7457	263.17	0.5076	255.80	0.3145	249.45		
0.7217	262.60	0.4898	255.00	0.2837	248.77		
0.6783	261.48			0.2591	246.93		
			2,2-Dimethylbutane				
1.0000	269.01	0.5738	258.41	0.4861	254.11	0.2593	246.94
0.9591	268.33	0.5469	257.05	0.4730	253.83	0.2349	245.94
0.9138	267.36	0.5303	255.98	0.4546	253.45	0.2084	244.66
0.8881	267.01	0.5073	255.18	0.4321	252.88	0.1841	243.30
0.8436	266.32	0.4921	254.20	0.4118	252.40	0.1563	240.54
0.8044	265.17			0.3804	251.36	0.1471	239.96
0.7721	264.37			0.3608	250.78	0.1316	238.65
0.7216	263.27			0.3432	250.03	0.1184	237.34
0.6764	262.09			0.3241	249.45	0.0981	235.68
0.6201	260.64			0.3071	248.64	0.0862	234.62
0.6035	259.75			0.2846	247.93	0.0552	228.55
			1-Hexyne				
1.0000	269.01	0.6397	262.05	0.3828	254.37	0.1744	248.79
0.9697	268.81	0.6053	260.95	0.3702	254.12	0.1473	247.76
0.9203	268.13	0.5745	260.06	0.3556	253.81	0.1057	245.25
0.8774	267.47	0.5451	259.37	0.3457	253.77	0.0665	240.75
0.8372	266.74	0.5056	258.44	0.3321	253.55	0.0035	231.94
0.8093	266.00	0.4714	257.43	0.3058	253.15		
0.7731	265.30	0.4480	256.65	0.2904	252.69		
0.7338	264.45	0.4282	255.78	0.2593	251.64		
0.6957	263.31	0.4103	255.32	0.2314	250.91		
0.6663	262.72			0.1981	249.62		

[a] T_1: liquidus equilibrium temperatures for α and β crystalline forms.

Kawakami.[9] The SLE coexistence curve and the eutectic point shift to higher temperatures with an increasing pressure. Changing the pressure from 0.1 MPa to 120 MPa increases the temperature of the eutectic point for (tetradecane or hexadecane + benzene) by 25 K and 30 K, respectively. For (tetradecane or hexadecane + cyclohexane), it is 30 K and 35 K, respectively. The composition of the eutectic point shifts to a higher concentration of the alkane. The pressure dependence of the solubilities of anthracene and phenanthrene in water shows a decrease in the partial molar volumes of these solutes in water with increasing pressure up to 200 MPa, as was shown recently.[19]

In this article, we present high-pressure SLE results obtained with a piston-cylinder apparatus, which is described in detail in our previous work.[20−22] New data were measured for tridecane with four hydrocarbons, each with six carbon atoms in the molecule, (3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene), and were compared with two additional C_6 hydrocarbons, cyclohexane[21] and hexane,[22] which were presented previously. The data were measured at very high pressures, up to 1.0 GPa, and over wide temperature range, from 293 K to 363 K.

The experimental data were described using the predictive method proposed by Pauly et al.,[18] which was corrected for an improved description of the phase behavior at very high pressures. The performance of the modified model is also tested on our data for (alkanes + cyclohexane) published previously.[21,22] The (solid + liquid) coexistence curves of these systems were also correlated by the equation proposed by Yang et al.[10,11] For the comparison, new SLE data were measured under normal pressure for (tridecane + 3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene) and were described with Wilson, NRTL, and UNIQUAC equations. The effect of the solubility of long-chain alkanes in C_6-structure hydrocarbons at high pressures (>300 MPa) is expected, as is the possibility of a pure prediction of SLE at such high pressures.

Experimental Section

Materials. The origins of the chemicals and its purity are tridecane (Koch-Light Laboratory, +99%), 3-methylpentane (Aldrich, +99%), 2,2-dimethylbutane (Aldrich, +99%), 1-hexyne (Aldrich, +97%), and benzene (Aldrich, +99%). Alkane has been used directly, without purification. The solvents were purified by fractional distillation under low pressure after prolonged reflux over different drying reagents and were stored over freshly activated molecular sieves of type 4A (Union Carbide). After the distillation, all compounds were checked by GLC analysis, and no significant impurities were found (less than 0.2 mass %). The water contamination was determined using the Karl Fischer technique. The water content was less than 0.02 mol %. Physical properties of pure compounds used in calculations are collected in Table 1.

Procedure. The (solid + liquid) phase equilibrium of (tridecane + 3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene) binary systems at atmospheric pressure (0.1 MPa) has been determined using a dynamic (synthetic) method, which was described in detail previously.[27,28] The thermometer was calibrated on the basis of the ITS-90 temperature scale. The accuracy of the temperature measurements was ±0.01 K, whereas the error in the mole fraction did not exceed $\delta x_1 = 0.0005$. The uncertainty of the temperature measurements was ±0.05

Table 3. Experimental (Solid + Liquid) Equilibria Temperatures of the {Tridecane (1) + Benzene (2)} System at 0.1 MPa[a]

x_1	$T_{1\alpha}$/K	x_1	$T_{1\alpha}$/K	x_1	$T_{1\beta}$/K	x_1	T_2/K	x_1	T_2/K
				Benzene					
1.0000	269.01	0.5910	259.35	0.4836	256.30	0.4592	256.23	0.1517	271.44
0.9489	268.15	0.5692	258.99	0.4757	255.71	0.4381	257.11	0.1351	272.32
0.9229	267.51	0.5496	258.62			0.4226	258.04	0.1201	273.06
0.8893	266.92	0.5309	258.05			0.3955	259.65	0.1042	273.70
0.8633	266.27	0.5019	257.02			0.3618	261.45	0.0861	274.67
0.8022	264.83					0.3242	263.50	0.0682	275.68
0.7733	264.17					0.2966	265.01	0.0588	276.17
0.7418	263.32					0.2804	265.90	0.0492	276.68
0.7087	262.57					0.2504	266.91	0.0407	277.27
0.6702	261.65					0.2210	268.36	0.0323	277.80
0.6300	260.55					0.1960	269.57	0.0000	279.05
0.6135	260.01					0.1745	270.49		

[a] T_1: tridecane liquidus for α and β crystalline forms. T_2: benzene liquidus curve.

K, and that of the mole fraction did not exceed ±0.0005. The results are shown in Tables 2 and 3 as x_1, the mole fraction of tridecane in saturated solution as a function of T_2 or T_1 (α, β crystalline forms of tridecane). T_2 is the temperature of the liquidus of the solid benzene in binary solution equilibrium, and T_1 is the temperature of the liquidus of the solid tridecane in binary solution equilibrium.

A simple piston−cylinder device, presented in detail in our previous paper,[20−22] was used. The mobile piston was moved by a hydraulic press. The device was thermostated with water thermostat steering by the thermocouple, and the temperature was measured by a Pt-resistance thermometer (Delta HD 9215, Poland). The pressure was measured up to 1.5 GPa. The uncertainties in temperature and pressure measurements were ±0.5 K and 10 MPa, respectively. (Liquid + solid) phase transitions were determined by discontinuities in volume−pressure curves. The accuracy of the discontinuity in $P-V$ curves follows the measurement of pressure at the crystallization point and is assumed to be ±2%. The initiation of freezing was noticed at a higher pressure than the equilibrium value of this phase transition, observed as an "overpressure" effect (the intersection between the lines of the one- and two-phase regions). The equilibrium point was the first from the solid-phase line (see our previous work).[20] The published results are the average of three or more measurements at the intersection point.

Results and Discussion

(Solid + liquid) phase equilibria of the (tridecane + hexane or cyclohexane) binary systems at normal pressures were measured previously.[21,22] In this work, the data of additional binary mixtures with tridecane are presented. For crystals with simple structures, the pressure dependence of the melting point can be described with the semiempirical equation of Simon,[29] as was shown in our previous work.[21,22] The behavior of pure substances can also be purely predicted with very good accuracy using the model described previously.[22]

The effect of pressure on the (solid + liquid) phase equilibria of the binary mixtures has been measured at various constant compositions and temperatures. The liquid−solid transitions were determined for the whole alkane concentration range from $x_1 = 0$ up to $x_1 = 1$. The experimental high-pressure SLE results of these binary systems are collected in Tables 4−7 for every solvent tested and in Figures 1−8.

Table 4. Freezing Pressures, P, for Mole Fractions, x_1, at Different Temperatures from T = 293.15 K to T = 343.15 K for the {Tridecane (1) + 3-Methylpentane (2)} System

T/K	293.15	303.15	313.15	323.15	333.15	343.15
x_1	P/MPa					
1.0000	133.01	197.13	265.40	337.83	414.42	495.18
0.9788	148.10	214.95	285.92	361.00	440.20	523.52
0.8995	150.38	218.70	290.31	365.19	443.36	524.80
0.8185	173.71	238.27	308.25	383.67	464.52	550.80
0.7382	180.78	245.04	316.60	395.44	481.58	575.01
0.6594	201.26	267.38	339.93	418.93	504.38	596.26
0.5798	217.95	285.83	360.59	442.23	530.76	626.17
0.4995	238.20	312.10	391.81	477.31	568.63	665.75
0.4159	267.71	343.21	425.68	515.10	611.47	714.80
0.3404	297.21	374.32	459.55	552.88	654.31	763.86
0.2588	349.06	438.36	533.35	634.05	740.45	852.55
0.1687	400.92	502.39	607.15	715.22	826.58	941.24
0.1001	511.92	644.02	777.77	913.16	1050.21	1188.90
0.0624	622.92	785.65	948.38	1111.11	1273.84	1436.57

Table 5. Freezing Pressures, P, for Mole Fractions, x_1, at Different Temperatures from T = 293.15 K to T = 343.15 K for the {Tridecane (1) + 2,2-Dimethylbutane (2)} System

T/K	293.15	303.15	313.15	323.15	333.15	343.15
x_1	P/MPa					
1.0000	133.01	197.13	265.40	337.83	414.42	495.18
0.9777	135.82	200.93	270.08	343.27	420.51	501.78
0.8971	147.00	216.65	286.73	361.76	441.74	526.67
0.8197	151.57	230.77	309.26	387.03	464.09	540.42
0.7392	172.50	247.06	323.03	400.41	479.21	559.43
0.6587	193.44	263.34	336.79	413.79	494.33	578.43
0.5780	216.13	286.01	363.05	447.23	538.57	637.07
0.5001	226.54	291.90	369.72	460.00	562.73	677.91
0.4198	255.76	333.53	416.72	505.34	599.38	698.85
0.3401	288.59	374.53	466.35	564.04	667.61	777.06
0.2602	334.89	423.96	520.72	625.17	737.30	857.13
0.1803	399.29	491.18	590.83	698.25	813.42	936.36
0.0882	522.93	638.46	754.00	869.54	985.07	1100.61

Calculations

Modeling. The condition of equilibrium between the solid and liquid phases is given by the equality of the fugacities in both phases for each individual component, i:

$$f_i^{\mathrm{l}}(T, P, x_i^{\mathrm{l}}) = f_i^{\mathrm{s}}(T, P, x_i^{\mathrm{s}}) \qquad (1)$$

For this particular system, the solid phase will be a pure compound, whereas the liquid phase is a binary mixture.

The general (solid + liquid) phase equilibrium (SLE) equation relates, for the crystallizing compound, the fugacities of both phases in the standard state, $f_i(P_{\mathrm{o}})$, to the pure

Table 6. Freezing Pressures, P, for Mole Fractions, x_1, at Different Temperatures from T = 293.15 K to T = 343.15 K for the {Tridecane (1) + 1-Hexyne (2)} System

T/K	293.15	303.15	313.15	323.15	333.15	343.15
x_1	P/MPa					
1.0000	133.01	197.13	265.40	337.83	414.42	495.18
0.9791	138.18	205.25	276.07	350.65	428.98	498.10
0.9001	149.10	218.70	290.04	363.10	437.90	514.42
0.8084	162.00	229.34	299.82	376.76	460.16	550.03
0.7391	170.90	241.22	315.73	394.44	477.35	564.45
0.6587	184.21	254.49	329.29	408.61	492.45	580.81
0.5616	199.01	270.76	349.67	435.74	528.97	620.90
0.4994	206.59	284.74	367.32	454.35	545.82	641.73
0.4196	226.70	311.94	394.50	482.92	577.19	677.32
0.3403	247.51	330.80	419.35	513.18	599.60	707.00
0.2589	274.93	359.53	445.06	531.50	618.87	748.00
0.1798	334.43	423.04	509.62	594.18	676.72	786.50
0.1007	393.93	486.55	574.19	656.86	734.56	825.00
0.0312	505.23	599.85	688.49	776.12	863.82	969.26

Table 7. Freezing Pressures, P, for Mole Fractions, x_1, at Different Temperatures from T = 293.15 K to T = 343.15 K for the {Tridecane (1) + Benzene (2)} System

T/K	293.15	303.15	313.15	323.15	333.15	343.15
x_1	P/MPa					
1.0000	133.01	197.13	265.40	337.83	414.42	495.18
0.9024	150.68	215.72	286.00	361.54	442.33	528.38
0.8164	167.28	231.95	302.67	379.42	462.22	551.05
0.7373	179.34	248.94	319.49	399.82	481.10	566.27
0.6587	196.05	261.16	333.95	414.44	502.62	598.50
0.5762	208.35	278.33	354.75	437.60	526.90	622.64
0.5008	220.05	293.27	371.10	458.84	553.65	660.41
0.4735	228.84	304.20	381.57	469.99	565.48	680.10
0.4196	216.44	285.75	360.88	441.82	528.58	621.15
0.3723	198.15	266.09	335.84	407.47	497.95	585.48
0.3379	180.66	248.68	310.16	366.16	453.84	540.64
0.2642	148.19	203.15	252.18	314.13	382.70	457.91
0.1788	115.27	161.60	211.90	266.17	324.42	386.63
0.0967	90.35	128.04	170.06	216.43	267.13	322.18
0.0210	60.31	100.13	142.24	186.64	233.32	282.30
0.0000	53.62	92.22	133.29	176.82	222.81	271.27

component thermophysical properties:[30]

$$\ln\frac{f_i^{\mathrm{l}}(P_{\mathrm{o}})}{f_i^{\mathrm{s}}(P_{\mathrm{o}})} = \frac{\Delta_{\mathrm{fus}}H_i}{RT_{\mathrm{fus},i}}\left(\frac{T_{\mathrm{fus},i}}{T}-1\right) + \frac{\Delta_{\mathrm{tr}}H_i}{RT_{\mathrm{tr},i}}\left(\frac{T_{\mathrm{tr},i}}{T}-1\right) - \frac{\Delta_{\mathrm{s}}^{\mathrm{l}}C_{p,\mathrm{m}}}{R}\left(\ln\frac{T}{T_{\mathrm{fus},i}}+\frac{T_{\mathrm{fus},i}}{T}-1\right) \quad (2)$$

Because the only compound studied in this work—tridecane—presents solid−solid phase transitions, the second term of eq 2 will be used for the measured systems. The fugacity of the solid phase at pressure P can be obtained through correcting the standard-state fugacity with the Poynting correction by the integration of the solid-phase molar volume

$$\ln f_i^{\mathrm{s}}(P) = \ln f_i^{\mathrm{s}}(P_{\mathrm{o}}) + \frac{1}{RT}\int_{P_{\mathrm{o}}}^{P} V_i^{\mathrm{s}_{\mathrm{o}}}\,\mathrm{d}P \quad (3)$$

Because no equation of state for the solid phase is available, the solid-phase molar volume will be taken as proportional to the corresponding pure-liquid molar volume:

$$V_i^{\mathrm{s}_{\mathrm{o}}} = \beta V_i^{\mathrm{l}_{\mathrm{o}}} \quad (4)$$

In previous work,[17,31−34] a constant value of β was used, with very good results, up to 100 MPa. Preliminary calculations showed that this simplification would not hold above 250 MPa. Because pressures much higher than these were used in this work, a new approach to β was adopted.[22]

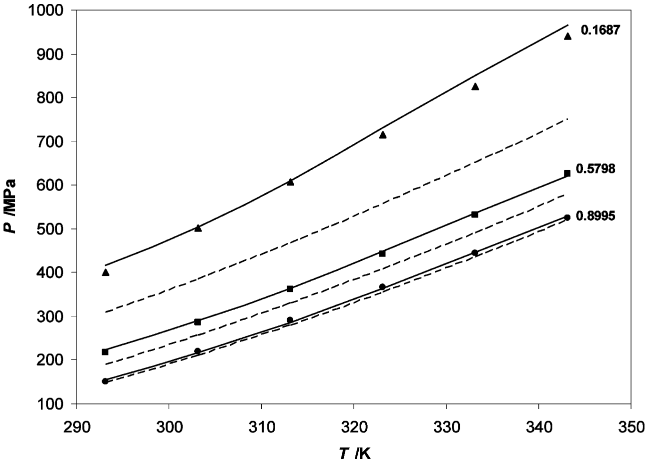

Figure 1. Experimental data, correlation, and prediction for the system {tridecane (1) + 3-methylpentane (2)} at constant mole fractions: ●, 0.8995; ■, 0.5798; ▲, 0.1687; −, correlation with eq 19; - - -, prediction.

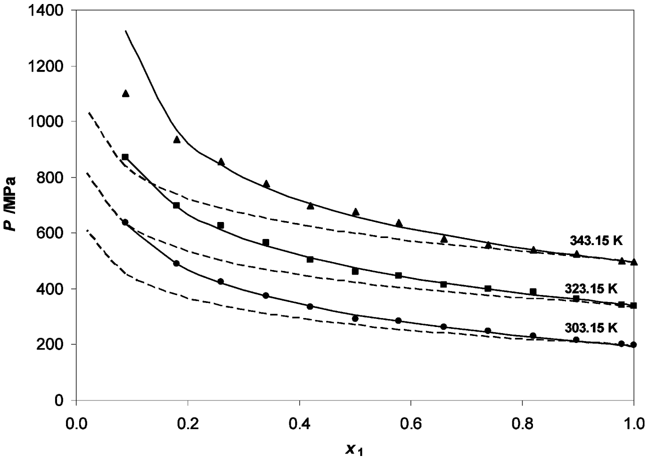

Figure 2. Freezing pressures of the {tridecane (1) + 2,2-dimethylbutane (2)} system at different temperatures: ●, 303.15 K; ■, 323.15 K; ▲, 343.15. Comparison of the prediction (- - -) and correlation with eq 19 (−).

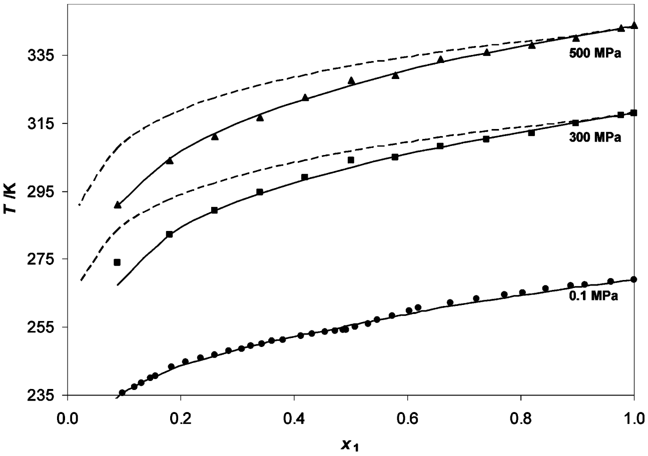

Figure 3. Freezing temperatures of the {tridecane (1) + 2,2-dimethylbutane (2)} system at different pressures: ●, 0.1 MPa; ■, 300 MPa; ▲, 500 MPa. Comparison of the prediction (- - -) and correlation (−). At 0.1 MPa correlation with the Wilson equation and at high pressure with the eq 19.

Knowing from the experimental measurements that dP/dT is fairly constant for a broad range of pressures and that the enthalpy of melting is fairly pressure-independent according to some authors,[35] it follows from

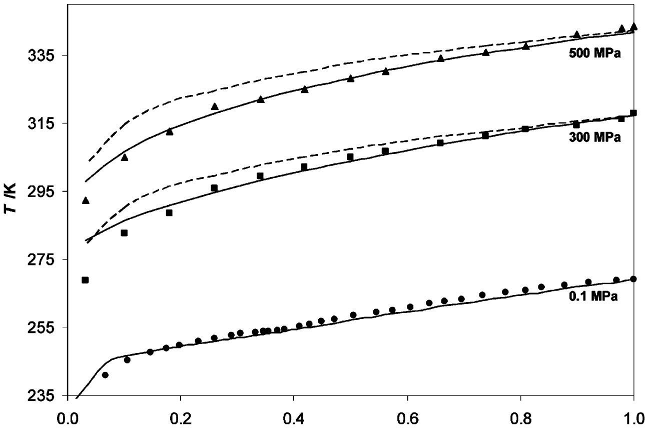

Figure 4. Freezing temperatures of the {tridecane (1) + 1-hexyne (2)} system at different pressures: ●, 0.1 MPa; ■, 300 MPa; ▲, 500 MPa. Comparison of the prediction (- - -) and correlation at 0.1 MPa with the Wilson equation and at high pressure with eq 19 (−).

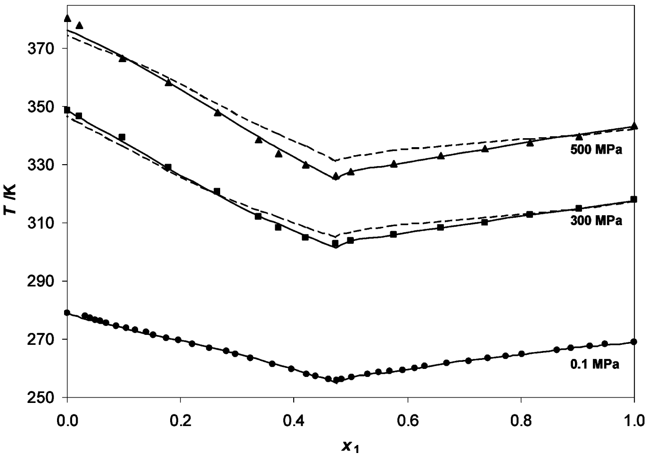

Figure 5. Freezing temperatures of the {tridecane (1) + benzene (2)} system at different pressures: ●, 0.1 MPa; ■, 300 MPa; ▲, 500 MPa. Comparison of the prediction (- - -) and correlation at 0.1 MPa with the Wilson equation and at high pressure with eq 19 (−).

the Clapeyron equation that

$$T(V_i^{l} - V_i^{s_o}) = \alpha \tag{5}$$

with α being constant. Using eq 4, a new expression for β is then obtained

$$\beta = \frac{V_i^{l}}{V_i^{s_o}} - \frac{\alpha}{TV_i^{l}} \cong 1 - \frac{\alpha}{TV_i^{l_o}} \tag{6}$$

Note that within this new approach β is still pressure-independent and the integration of the Poynting correction is not affected.

The evaluation of liquid fugacities is performed with the Soave−Redlich−Kwong equation of state[36] corrected by the volume translation of Peneloux[37]

$$P = \frac{RT}{(V' - b)} - \frac{a(T)}{V'(V' + b)} \tag{7}$$

with

$$V_i = V_i' + C_i \tag{8}$$

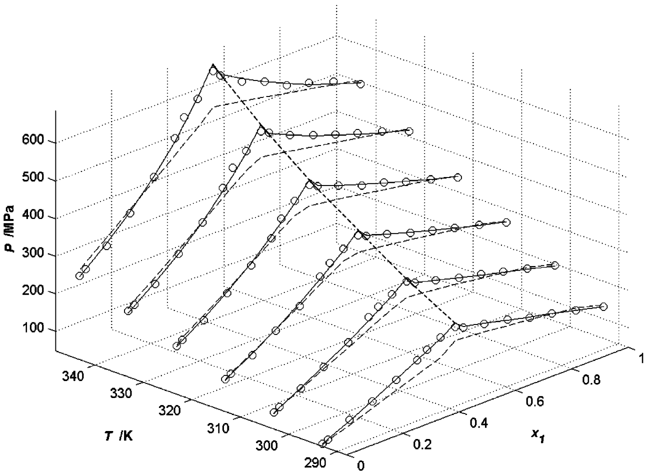

Figure 6. Prediction (- - -), correlation with eq 19 (−), and experimental data of the {tridecane (1) + benzene (2)} system on a 3D diagram.

where V' is the molar volume calculated from the SRK-EOS. C_i is calculated from the GCVOL group contribution method[38] at atmospheric pressure by

$$C_i = V_i^{\mathrm{GCVOL}} - V_i^{\mathrm{EOS}}$$

For mixtures, the van der Waals one-fluid mixing rules were used

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{9}$$

$$b = \sum_i x_i b_i \tag{10}$$

with the k_{ij}'s obtained from the group contribution method by Jaubert and Mutelet.[39]

For crystallizing compounds, the equilibrium constant for the solid phase in the case of a pure solid phase is thus given by[18]

$$K_i^{s} = \frac{x_i^{s}}{x_i^{l}} = \phi_i^{l}[P](\phi_i^{l_o}[P_o])^{\beta - 1}(\phi_i^{l_o}[P])^{-\beta}\left(\frac{P}{P_o}\right)^{1-\beta} \exp\left\{\frac{(1-\beta)C_i(P - P_o)}{RT} + \frac{\Delta_{\mathrm{fus}}H_i}{RT_{\mathrm{fus},i}}\left(\frac{T_{\mathrm{fus},i}}{T} - 1\right) + \frac{\Delta_{\mathrm{tr}}H_i}{RT_{\mathrm{tr},i}}\left(\frac{T_{\mathrm{tr},i}}{T} - 1\right) - \frac{\Delta_{\mathrm{s}}^{l}C_{p,\mathrm{m}}}{R}\left(\ln\frac{T}{T_{\mathrm{fus},i}} + \frac{T_{\mathrm{fus},i}}{T} - 1\right)\right\} \tag{11}$$

with the liquid-phase fugacity coefficients, ϕ_i^{l}, calculated from the equation of state. P_o is the reference pressure taken as atmospheric pressure.

Correlation at Normal Pressure. The solubility of solid 1 with the solid−solid phase transition in a liquid may be expressed in a very general way by eq 12

$$-\ln x_1 = \frac{\Delta_{\mathrm{fus}}H_1}{R}\left(\frac{1}{T_1} - \frac{1}{T_{\mathrm{fus},1}}\right) + \frac{\Delta_{\mathrm{tr}}H_1}{R}\left(\frac{1}{T_1} - \frac{1}{T_{\mathrm{tr},1}}\right) - \frac{\Delta_{\mathrm{fus}}C_{p_1}}{R}\left(\ln\frac{T_1}{T_{\mathrm{fus},1}} + \frac{T_{\mathrm{fus},1}}{T_1} - 1\right) + \ln\gamma_1 \tag{12}$$

where x_1, γ_1, $\Delta_{\mathrm{fus}}H_1$, $\Delta_{\mathrm{fus}}C_{p_1}$, $T_{\mathrm{fus},1}$, and T_1 are the mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between the solid and liquid at the

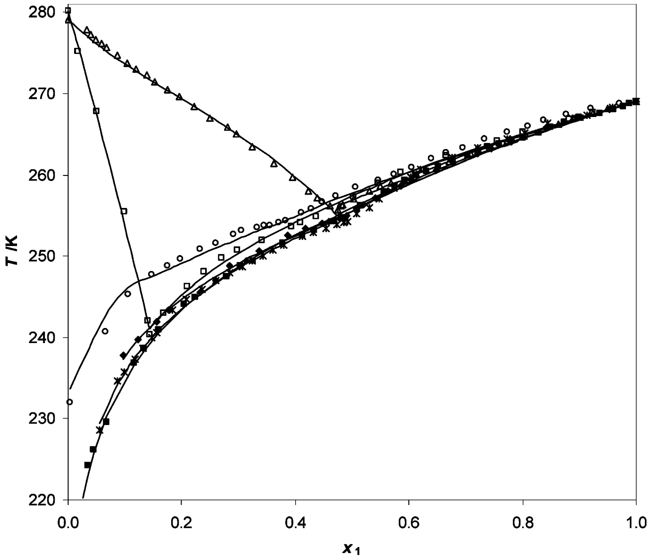

Figure 7. (Solid + liquid) equilibrium of {tridecane (1) + solvent (2)} at 0.1 MPa: ♦, 3-methylpentane; *, 2,2-dimethylbutane; ○, 1-hexyne; △, benzene; ■, hexane;[22] □, cyclohexane.[21] Solid lines were calculated with the Wilson equation.

melting point, melting temperature of the solute (1), and equilibrium temperature, respectively. $\Delta_{\text{tr}}H_1$, and $T_{\text{tr},1}$ are the enthalpy of the solid−solid phase transition and transition temperature of the solute (here tridecane), respectively. The solubility equation for temperatures below that of the phase transition must include the effect of the transition. Equation 12 may be used by assuming simple eutectic behavior with full miscibility in the liquid phase and immiscibility in the solid phase.

In this study, three methods are used to derive the solute activity coefficients, γ_1, from the so-called correlation equations that describe the Gibbs energy of mixing, (G^{E}): the Wilson,[40] NRTL,[41] and UNIQUAC[42] equations.

The two adjustable parameters of the equations were found by an optimalization technique

$$\Omega = \sum_{i=1}^{n} [T_i^{\text{exptl}} - T_i^{\text{calcd}}(x_{1i}, P_1, P_2)]^2 \tag{13}$$

where Ω is the objective function, n is the number of experimental points, and T_i^{exptl} and T_i^{calcd} denote, respectively, the experimental and calculated equilibrium temperatures corresponding to concentration x_{1i}. P_1 and P_2 are model parameters resulting from the minimization procedure. The root-mean-square deviation of temperature was defined as follows:

$$\sigma_{\text{T}} = \left(\sum_{i=1}^{n} \frac{(T_i^{\text{exptl}} - T_i^{\text{calcd}})^2}{n-2}\right)^{1/2} \tag{14}$$

Parameters r_i and q_i of the UNIQUAC model were calculated with the following relationships

$$r_i = 0.029281V_{\text{m}} \tag{15}$$

$$q_i = \frac{(Z-2)r_i}{Z} + \frac{2(1-l_i)}{Z} \tag{16}$$

where V_{m} is the molar volume of pure component i at 298.15 K. The molar volumes of tridecane, V_{m} (298.15), and solvents are presented in Table 1. Coordination number Z was assumed to be equal to 10, and bulk factor l_i was assumed to be equal to 1. Values of model parameters obtained by fitting solubility curves of the {tridecane (1) + 3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene (2)} system are given in Table 8 together with the corresponding standard deviations. The melting temperature, $T_{\text{fus},1}$, and solid−solid phase transition temperature, $T_{\text{tr},1}$, were taken from the SLE experimental curves. In binary system {tridecane (1) + benzene (2)}, the solid−solid transition temperature, $T_{\text{tr},1,}$ was very close to the eutectic point and was difficult to observe. The solid lines in Figures 3−6 show the solubility curves correlated by the Wilson equation.

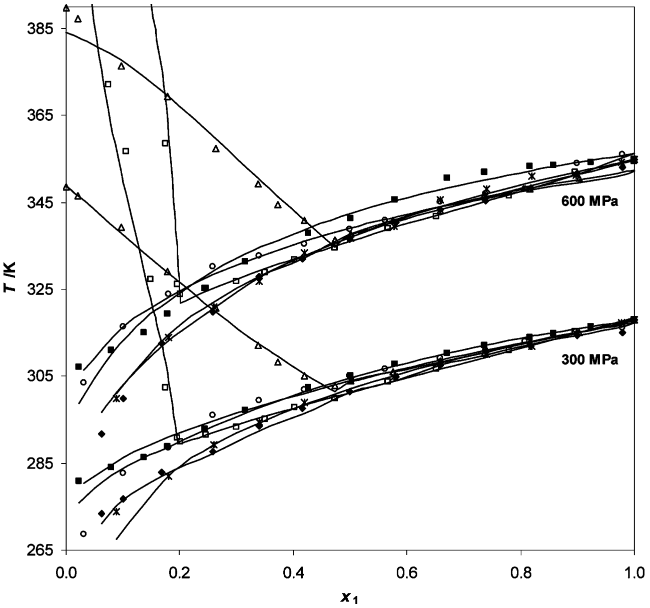

Figure 8. (Solid + liquid) equilibrium of {tridecane (1) + solvent (2)} at pressures of 300 MPa and 600 MPa: ♦, 3-methylpentane; *, 2,2-dimethylbutane; ○, 1-hexyne; △, benzene; ■, hexane;[22] □, cyclohexane.[21] Solid lines were calculated with eq 19.

The solubilities of tetradecane in two branched-chain hydrocarbons are very similar, with a slightly higher result in 2,2-dimethylbutane. The lower solubility is observed for hexane[22] and benzene (in the concentration range x_1 from 1 to 0.5). In the (tetradecane + benzene) binary solution, the eutectic point was observed at $x_{1,\text{e}} = 0.476$ and $T_{1,\text{e}} = 255.7$ K. The solubility of tetradecane in benzene is lower than that in hexane and in branched-chain hydrocarbons. The lowest solubility of tetradecane in this work was observed in 1-hexyne. The values of the solute mole fraction for the (solid + liquid) equilibria in saturated solutions at $T = 255$ K are 0.50, 0.49, 0.47, 0.46, 0.41, and 0.099 for 2,2-dimethylbutane, 3-methylpentane, hexane, benzene, 1-hexyne, and cyclohexane, respectively. For the lower concentration of tridecane ($x_1 < 0.5$), better solubility of the solute was observed in hexane than in 3-methylpentane.

Correlation at High Pressure. The SLE correlation at high pressure was proposed earlier on the basis of eq 2.[11,21] It was shows that the activity coefficient, γ_1, at high pressure can be expressed as

$$\ln \gamma_1 = \sum_{i=0}^{3} a_i\left(\frac{1}{T} - \frac{1}{T_{\text{fus},1}}\right)^i + a'\left(\ln \frac{T}{T_{\text{fus},1}} + \frac{T_{\text{fus},1}}{T} - 1\right) \tag{17}$$

and after substituting eq 17 into eq 2 for binary systems

Table 8. Parameters and Standard Deviations of the Wilson, NRTL ($\alpha = 0.75$), and UNIQUAC Equations for the (Tridecane (1) + 3-Methylpentane or 2,2- Dimethylbutane or 1-Hexyne or Benzene (2)} Systems under Atmospheric Pressure

solvent	parameters			deviations^a		
	Wilson	NRTL	UNIQUAC	Wilson	NRTL	UNIQUAC
	$g_{21} - g_{11}$ $g_{12} - g_{22}$	Δg_{21} Δg_{12}	Δu_{21} Δu_{12}	δ_T/K	δ_T/K	δ_T/K
	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}			
3-methylpentane	1929.33	−816.62	−708.90	0.28	0.30	0.29
	−131.49	2125.35	1125.84			
2,2-dimethylbutane	649.15	−827.33	−290.04	0.58	0.57	0.58
	78.86	1515.05	444.46			
1-hexyne	−2242.77	1330.09	990.31	0.45	0.45	0.46
	2738.73	−788.39	−703.48			
benzene	−3662.80	2183.91	2976.90	0.18	0.18	0.17
	4983.35	−1076.38	−1664.21			

and simplifications, we obtain

$$\ln x_1 = \sum_{i=0}^{3} b_i \left(\frac{1}{T} - \frac{1}{T_{\text{fus},1}}\right)^i + b' \left(\ln \frac{T}{T_{\text{fus},1}} + \frac{T_{\text{fus},1}}{T} - 1\right) \qquad (18)$$

where $b_0 = -a_0$, $b_1 = -a_1 - \Delta_{\text{fus}}H_1/R$, $b_2 = -a_2$, $b_3 = -a_3$, $b' = -a' + \Delta_l^s C_{p_{m},1}/R$.

The value of the second term on the right-hand side of eq 18 is small and can be neglected. Thus, eq 18 may be rewritten in a simple form:

$$\ln x_1 = \sum_{i=0}^{3} b_i \left(\frac{1}{T} - \frac{1}{T_{\text{fus},1}}\right)^i \qquad (19)$$

(Solid + liquid) phase equilibrium curves are dependent on pressure. With increasing pressure, the SLE curves shift to higher temperature. In eq 19, the b_i terms were found to be pressure-dependent. This dependence can be expressed as follows:

$$b_i = \sum_{j=0}^{2} D_{ji} P^j \qquad (20)$$

Objective function OF used in the fit of the parameters of eqs 19 and 20 is as follows

$$\text{OF} = \sum_{i=1}^{n} \omega_i^{-2} (\ln x_{1i}^{\text{calcd}}(T_i, P_i, D_{ji}) - \ln x_{1i}) \qquad (21)$$

where $\ln x_{1i}^{\text{calcd.}}$ denotes values of the logarithm of the solute mole fraction calculated from eq 19, $\ln x_{1i}$ denotes the logarithm of the experimental solute mole fraction, and the symbols T_i, P_i, and D_{ji} express temperature, pressure, and coefficients from eq 20, respectively. ω_i is the weight of the calculated values, described by means of the error propagation formula.

Table 9. Parameters D_{ji} of Equation 20 for the Measured {Tridecane (1) + 3-Methylpentane or 2,2-Dimethylbutane or 1-Hexyne (2)} Systems

	3-methylpentane	2,2-dimethylbutane	1-hexyne
D_{00}	-3.2458×10^{-1}	3.4334×10^{-2}	2.9963×10^{2}
D_{10}	-4.1116×10^{-3}	-8.5326×10^{-3}	-5.2219×10^{-1}
D_{20}	-8.2874×10^{-6}	-7.2899×10^{-7}	-1.4234×10^{-3}
D_{01}	-4.4048×10^{3}	-3.1733×10^{3}	2.3293×10^{5}
D_{11}	1.0244×10^{1}	1.9558×10^{0}	-4.4552×10^{2}
D_{21}	-3.4604×10^{-2}	-2.0832×10^{-2}	-7.8815×10^{-1}
D_{02}	-3.9285×10^{6}	-1.2609×10^{6}	5.9556×10^{7}
D_{12}	1.5669×10^{4}	1.8601×10^{4}	-1.2460×10^{5}
D_{22}	-3.6708×10^{1}	-4.7602×10^{1}	-1.3296×10^{2}
D_{03}	-4.8093×10^{9}	-1.6943×10^{9}	4.9862×10^{9}
D_{13}	1.0738×10^{7}	1.6031×10^{7}	-1.1402×10^{7}
D_{23}	-1.3275×10^{4}	-3.1890×10^{4}	-6.1741×10^{3}
σ^a	0.0258	0.0178	0.0299

[a] The standard deviation $\sigma = (\sum_{i=1}^{n} (\ln x_i^{\text{calcd}} - \ln x_i)^2/n)^{1/2}$.

Table 10. Parameters D_{ji} of Equation 15 for the Measured {Tridecane (1) + Benzene (2)} System

	$0 < x_1 < x_e$	$x_e < x_1 < 1$
D_{00}	8.4342×10^{-2}	-4.4895×10^{-1}
D_{10}	-3.8330×10^{-3}	1.4470×10^{-3}
D_{20}	-6.1719×10^{-6}	-7.6016×10^{-5}
D_{01}	-1.6158×10^{2}	-4.0212×10^{3}
D_{11}	-1.0361×10^{1}	-5.1717×10^{0}
D_{21}	-2.0682×10^{-2}	-2.0937×10^{-1}
D_{02}	1.2604×10^{6}	-9.9318×10^{6}
D_{12}	-2.1260×10^{4}	-1.1544×10^{3}
D_{22}	-1.7009×10^{1}	-2.1971×10^{2}
D_{03}	8.7573×10^{8}	-1.0645×10^{10}
D_{13}	-1.4762×10^{7}	1.6289×10^{7}
D_{23}	-1.5295×10^{3}	-9.4311×10^{4}
σ^a	0.0121	0.0116

[a] The standard deviation $\sigma = (\sum_{i=1}^{n} (\ln x_i^{\text{calcd}} - \ln x_i)^2/n)^{1/2}$.

Table 9 contains coefficients D_{ji} of eq 20 for the systems with no eutectic points observed. For the system (tridecane + benzene), where a eutectic point was observed, coefficients D_{ji} of eq 20 are listed in Table 10 for two different liquidus curves. Direct experimental points and their correlation and prediction for a few constant compositions are shown in Figures 1 and 2 for the (tridecane + 3-methylpentane) system and for a few constant temperatures for the (tridecane + 2,2-dimethylbutane) system, respectively. During the experiment, pressure was measured under constant composition−temperature conditions. The relation between the temperature T and pressure p of the SLE at constant x_1 can be satisfactorily described with a simple quadratic equation, so the $p-x$ diagram can be transformed into the $T-x$ diagram. The conversion of the pressure−mole fraction diagram into the traditional temperature−mole fraction diagram can be made, and the results are shown in Figures 3−5. The experimental results shown in these Figures are presented at 300 MPa or 500 MPa and at atmospheric pressure (0.1 MPa). The dashed lines represent the prediction with eq 11. Figure 6 shows full experimental data, correlation, and prediction on a 3D diagram (with no solid−solid transition temperature) for the (tridecane + benzene) system.

The values of α of eq 5[31] were fitted to the pure compounds' melting temperatures for a wide range of pressure. As expected, the value is related to the solid-phase crystalline behavior. A value of 0.043 was used for tridecane. To keep a purely predictive approach for mix-

Table 11. Standard Deviations of the Correlation and Prediction of the (Solid + Liquid) Phase Equilibria for Tridecane Systems with Specified Hydrocarbons

	EOS − G^E	correlation
	$\sigma_T{}^a$	$\sigma_T{}^a$
system	K	K
tridecane + 3-methylpentane	7.62	1.10
tridecane + 2,2-dimethylbutane	5.96	1.01
tridecane + 1-hexyne	7.73	1.42
tridecane + benzene	4.60	0.95
tridecane + hexane[b]	1.78	1.17
tridecane + cyclohexane[b]	10.03	2.69

[a] The standard deviation $\sigma_T = (\sum_{i=1}^{n} (T_i^{calcd} - T_i)^2/n)^{1/2}$. [b] From ref 22.

tures, the k_{ij}'s were estimated from a group contribution model.[39] A comparison of correlation and prediction is shown for all of the systems in all Figures and in Table 11. The description of the experimental data is quite good, particularly if one takes into account that the model used is purely predictive and only pure component data are used to predict the mixture behavior at extremely large pressures, far above the pressure range to which cubic equations of state were normally applied.

The limitations on the description of the 3-methylpentane, 2,2-dimethylbutane, 1-hexyne, and benzene crystallization close to the eutectic point must be related to a variation of the volume of phase change, ($V^L - V^S$), with pressure[43] that will make the β parameter pressure-dependent and cannot be considered within the framework of the adopted model. Such a dependence is not apparent for the alkanes, whose larger value of α makes them less sensitive to pressure effects.

Sometimes an inflection point on the liquidus was observed, which is characteristic of a solid−solid phase transition as discussed for (alkane + ether) binary mixtures.[20] According to literature data[23] at normal pressure, tridecane shows a solid−solid first-order transition close to the melting point. For tridecane, the rotational transition is observed up to 300 MPa when the transition and melting points converge.[44] Only a slight increase of 10% was observed in the total enthalpy of the solid−solid phase transition and fusion with increasing pressure up to 300 MPa.[45] Unfortunately, from the results presented in this work under high pressure (see Figures), it is not easy to find new information on the transition forms and on the influence of pressure on the transition temperatures because the effects of the solid−solid phase transition are too small to be noticed in these measurements.

Conclusions

(Solid + liquid) phase equilibria for four systems of binary (tridecane + 3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene) mixtures have been investigated at atmospheric pressure and at pressure up to 1.0 GPa. With increasing pressure, the freezing curves shift to higher temperatures monotonically.

At a pressure of 0.1 MPa, the solubility of the solute in the tested solvents increases in the order 2,2-dimethylbytane > 3-methylpentane > hexane[22] > benzene > 1-hexyne > cyclohexane,[21] especially at higher concentrations of alkane. These results are shown in Figure 7. The addition of a short hydrocarbon solvent or an aromatic compound to an ordered long-chain paraffin leads to the destruction of the conformational order of the long-chain alkane through the Patterson effect. This order/disorder phenomenon is greater in the systems where the solubility is higher (2,2-dimethylbutane or 3-methylpentane) and reveals almost ideal solubility, owing to a larger destruction of alkane order. From our previous discussion,[27,46] one may conclude that positive contributions from the Patterson effect must be considered. These destructions increase with the solute (hydrocarbon) chain length. Also, the solubilities at normal pressure are changing for longer-chain hydrocarbons, and the lowest solubility is observed in hexane.[27] For benzene and 1-hexyne, the additional packing effect connected with the expected high enthalpy of mixing of these compounds and interactional effect has to exist. The shape of the solvent and the triple carbon bond as well as the aromatic property have an influence on the solute−solvent interaction and the hydrocarbon solubility. It was shown earlier that globular or spherical solvents destroy the conformational order in liquid long-chain hydrocarbons, giving high positive values for the enthalpy and entropy of mixing.[47] According to an early study of Patterson et al.,[48] the thermodynamic properties of alkane mixtures are made up of combinatorial, free volume, and interactional (field forces + order destruction) contributions.

The influence of high pressure is much greater for the (tridecane + hexane) binary mixture. The packing effects give a lower solubility of tridecane at pressures higher than 300 MPa in short-chain hydrocarbons (hexane) than in 2,2-dimethylbutane or 3-methylpentane. At high pressure equal to 600 MPa, the solubility increases in the order 2,2-dimethylbutane > 3-methylpentane > cyclohexane[21] > benzene > 1-hexyne > hexane.[22] The general conclusion is that the increase in pressure decrease the order/disorder phenomenon of long-chain hydrocarbons in short alkanes to a much greater extent than in globular solvents (branched-chain hydrocarbons) and spherical (cyclohexane) and aromatic hydrocarbons (benzene).

The prediction of (solid + liquid) phase equilibria under high pressure (higher than 300 MPa) was presented. The proposed model provides a good representation of the complete set of binary mixtures measured. Until now, 11 systems with (tridecane or hexadecane or octadecane or eicosane + 3-methylpentane or 2,2-dimethylbutane or 1-hexyne or benzene or cyclohexane or hexane) have been tested, and the accuracy was very good excluding compositions close to the eutectic points.[21,22] The proposed model uses only pure component data for the prediction of binary mixture behavior, and the result seems to be very satisfactory along the liquidus curve and moderately good close to the eutectic points. These calculations may be very useful for practical purposes.

Acknowledgment

We gratefully acknowledge Professor J. A. P. Coutinho for cooperation and software for the high-pressure prediction.

List of Symbols

a, b = parameters calculated from mixing rules
a_i, b_i = parameters of the high-pressure correlation with the Yang equation
C_i = volume correction
$\Delta_s^l C_{p_m}$ = change in the heat capacity at melting temperature, J·mol^{-1}K^{-1}
f_i^{α} = fugacity in the α phase for component i
ϕ_i^{α} fugacity coefficient in the phase α for the component i
$\Delta_{fus}H_i$ = enthalpy of fusion for component i, J·mol^{-1}

$\Delta_{\mathrm{tr}}H_i$ = enthalpy of the solid−solid phase transition for component i, J·mol^{-1}
k_{ij} = interaction parameter obtained from a group contribution method (Jaubert, Mutelet)
K_i^{s} = equilibrium constant
P = pressure in the system, MPa
P_{o} = pressure under standard conditions (equal to 1 bar)
R = gas constant, J·mol^{-1}K^{-1}
r_i, q_i = parameters of the UNIQUAC model
T = temperature in the system, K
$T_{\mathrm{fus},i}$ = melting temperature, K
$T_{\mathrm{tr},i}$ = temperature of the solid−solid phase transition of component i, K
x_i^{α} = molar fraction of component i in the α phase
$V_i^{\alpha_{\mathrm{o}}}$ = molar volume of component i in the α phase under standard conditions, m^3·mol^{-1}
V_i^{α} = molar volume of the component i in the α phase, m^3·mol^{-1}
α, β = parameters
γ_i = activity coeffitient of component i in the liquid phase

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