High-Pressure Phase Behavior of the System Propane−Boltorn H3200[†]

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High-pressure phase equilibrium data have been measured for the system propane + Boltorn H3200 at temperatures of (300 to 470) K and at pressures up to 14 MPa. Boltorn H3200 is a hydroxyl-functional hyperbranched polyester whose OH-end groups are functionalized with a mixture of eicosanoic and docosanoic acid leading to $C_{20/22}$ alkane chains as end groups. The phase equilibrium measurements were performed according to the synthetic method using the Cailletet apparatus. Besides two-phase fluid phase equilibria, a three-phase curve liquid−liquid−vapor, a three-phase curve solid polymer−liquid−liquid, and a three-phase curve solid polymer−liquid−vapor were measured also.

Introduction

Hyperbranched polymers are a relatively new class of polymers that can be easily synthesized via one-step reactions and represent economically promising products for large-scale industrial applications. Hyperbranched polymers belong to the class of dendritic polymers,[1] together with the dendrigrafts and the dendrimers. However, the synthesis of these latter two types of dendritic polymers is much more complicated.

The properties of hyperbranched polymers can be adjusted by controlled functionalization of the end groups. In this way, selective solvents can be tailored that can be an alternative for ionic liquids in some applications. Seiler et al.[2] have shown the applicability of hyperbranched polymers as new selective solvents for extractive distillation and solvent extraction. Not much information is available on the phase behavior of systems with hyperbranched polymers. Seiler et al.[3] have studied the influence of hyperbranched polyesteramide and hyperbranched polygycerol on vapor−liquid equilibria of aqueous azeotropic systems, liquid−liquid equilibria in the system THF + water + hyperbranched polyester, and liquid−liquid and liquid−liquid−vapor equilibria in CO_2 + water or ethanol + hyperbranched polyester systems. Kozlowska et al.[4] studied the phase behavior of carbon dioxide with mixtures of methanol and a fatty acid modified dendritic polyester.

In this contribution, the results are presented of an experimental investigation on the high-pressure phase behavior of propane + hyperbranched Boltorn H3200. These results include experimental bubble points, cloud points, solid solubility data, and data on three-phase equilibria liquid−liquid−vapor, solid polymer−liquid−vapor, and solid polymer−liquid−liquid. These multiphase equilibria are important because they represent the boundaries of the different two-phase regions.

Experimental Section

Materials and Sample Preparation. The propane used (Scott specialty gases) had a minimum purity of 99.95%. Perstop AB (Sweden) produces a series of hydroxyl-functional hyperbranched polyesters based on 2,2-bis-methylpropionic acid with an ethoxylated pentaeytriol core, designated as Boltorn H20, H30, and so forth. Boltorn H3200, the hyperbranched polymer used in this work ($M_w = 10\,500\ \mathrm{g\cdot mol^{-1}}$, $M_w/M_n = 1.6$, melting temperature of 333 K) is synthesized from Boltorn H30 whose OH-end groups are functionalized with a mixture of eicosanoic and docosanoic acid leading to $C_{20/22}$ alkane chains as end groups. Approximately (0.003 to 0.1) g of solid Boltorn H3200 was introduced in the Cailletet tube. The mass of the polymer was determined by weighing on an analytical balance. The polymer sample is degassed by repeatedly melting and freezing under vacuum. After this, propane is added to the sample using a gas-volumetric method. The mass of propane was determined from the virial equation of state truncated after the term containing the second virial coefficient. The values of the second virial coefficient of propane were calculated from a correlation.[5] The mixture of propane and the polymer was prepared with an uncertainty in the mass fraction of less than ± 0.001.

Experimental Procedure. The experiments were carried out according to the synthetic method using the Cailletet apparatus that was described in detail by de Loos et al.,[6] which can be used at pressures up to 15 MPa.

The sample is kept at constant temperature with a thermostat liquid flowing through a thermostat jacket. At low temperature, water is used as a thermostat liquid, but at high temperature the thermostat liquid used is silicone oil. The temperature of the thermostat liquid is controlled using a PID controller. The temperature is measured using a calibrated platinum resistance thermometer. The accuracy of the temperature measurements is 0.02 K. The total uncertainty in the temperature is estimated to be 0.02 K at low temperature and 0.05 K at high temperature.

Phase boundaries were determined visually by changing the pressure at constant temperature. The pressure is measured using a dead weight gauge (uncertainty ± 0.002 MPa at pressures below 5 MPa and ± 0.01 MPa at pressures above 5 MPa).

Results and Discussion

In Table 1 to 11, the experimental data for the system propane + Boltorn H3200 are given. These tables represent the results of isoplethic measurements at 11 constant Boltorn mass fractions ranging from 0.025 to 0.90.

Figure 1 shows the P,T-section for a mixture of propane and Boltorn H3200 with a Boltorn mass fraction of 0.501. The

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[†] Part of the “William A. Wakeham Festschrift”.

10.1021/je900130y CCC: $40.75

Table 1. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.025$

S_BLV		$S_BL \rightarrow L$		$L_2L_1 \rightarrow L$		L_2L_1V		$S_BL_2L_1$		$S_BL_2L_1V$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
299.01	0.98	312.98	6.05	313.43	4.06	312.06	1.34	311.95	2.05	312.06	1.34
303.71	1.10	313.01	8.05	315.36	4.45	313.42	1.38	311.95	3.05		
307.29	1.20	312.69	10.05	318.28	5.31	323.22	1.72				
308.62	1.24	312.61	12.05	320.22	5.71	333.05	2.12				
				323.17	6.50	343.04	2.59				
				325.12	6.85	352.96	3.13				
				328.10	7.27	362.90	3.75				
				333.03	8.28	370.04[a]	4.25				
				337.98	9.03						
				342.95	9.94						
				347.88	10.78						
				352.86	11.43						
				357.77	11.75						

[a] Critical end point $L_2(L_1 = V)$.

Table 2. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.050$

L_2L_1V		$S_BL \rightarrow L$		$L_2L_1 \rightarrow L$		S_BLV		$S_BL_2L_1$		$S_BL_2L_1V$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
307.34	1.22	312.49	5.05	312.96	5.15	303.31	1.12	310.54	2.05	310.84	1.32
308.48	1.25	312.80	6.05	315.00	5.30			310.49	3.05		
310.84	1.32	313.43	7.05	316.50	5.75						
313.30	1.40	313.17	8.05	317.91	5.76						
314.16	1.42	313.13	10.05	320.96	6.75						
322.99	1.73	312.57	12.05	322.70	6.83						
331.59	2.04			327.50	7.86						
341.84	2.54			332.11	8.64						
351.62	3.06			336.96	9.59						
361.35	3.66			341.90	10.60						
369.98[a]	4.30			346.85	11.65						
				351.71	12.57						

[a] Critical end point $L_2(L_1 = V)$.

Table 3. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.099$

S_BLV		$S_BL \rightarrow L$		$L_2L_1 \rightarrow L$		L_2L_1V		$S_BL_2L_1$		$S_BL_2L_1V$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
288.73	0.78	312.29	6.05	308.51	4.50	303.70	1.14	304.71	1.55	306.25	1.21
293.64	0.89	312.28	8.05	313.21	5.72	306.25	1.21	305.29	2.05		
298.68	1.01	311.94	10.05	317.91	6.82	308.67	1.27	305.95	2.55		
303.63	1.13	312.19	12.05	322.67	7.89	313.21	1.41	306.20	3.05		
				327.41	8.93	322.77	1.75	306.79	3.55		
				332.21	9.97	332.21	2.12	308.25	4.05		
				337.13	11.00	341.97	2.58	309.70	4.55		
				342.04	11.99	351.72	3.09	311.80	5.05		
				346.93	13.00	361.51	3.70				
						369.99	4.27				
						369.82[a]	4.27				

[a] Critical end point $L_2(L_1 = V)$.

Table 4. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.200$

L_2L_1V		$S_BL \rightarrow L$		$L_2L_1 \rightarrow L$		S_BLV		$S_BL_2L_1$		$S_BL_2L_1V$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
308.65	1.25	315.65	7.05	313.57	5.83	304.27	1.11	309.51	2.05	309.43	1.27
309.43	1.27	315.46	8.05	318.37	6.93			309.70	3.05		
313.52	1.40	315.38	10.06	323.30	8.02			310.94	4.05		
318.36	1.55	315.44	12.06	328.19	9.08			312.61	5.05		
323.26	1.73	315.51	13.06	333.09	10.10			315.05	6.05		
333.08	2.13			337.97	11.09						
343.03	2.60			342.86	12.06						
352.79	3.12			347.77	13.01						
362.58	3.73			352.67	13.92						
369.99[a]	4.25										

[a] Critical end point $L_2(L_1 = V)$.

diagram shows at high temperature a two-phase region L_2L_1 with lower solution temperatures and upper solution pressures. The low-pressure boundary of this two-phase region is a three-phase equilibrium L_2L_1V which practically coincides with the vapor pressure curve of pure propane. Below this curve a two-phase region L_2V is found. Above the high-pressure boundary (the cloud point curve) of the L_2L_1region a homogeneous L_2 region is found. At low temperature, the solid hyperbranched polymer precipitates, which results in a two-phase region S_BL_2. The boundary between the L_2L_1 region and the S_BL_2 region is a three-phase curve $S_BL_2L_1$. The point of intersection of this curve and the L_2L_1V curve is a quadradruple point $S_BL_1L_2V$.

Table 5. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.301$

L_2L_1V		$S_BL \rightarrow L$		$L_2L_1 \rightarrow L$		S_BLV		$S_BL_2L_1$		$S_BL_2L_1V$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
308.52	1.24	311.74	5.55	308.54	4.45	298.19	0.95	309.02	2.05	308.52	1.24
308.66	1.24	312.22	6.05	313.38	5.57	304.24	1.11	309.60	3.05		
313.42	1.38	312.13	8.05	318.29	6.69			310.29	4.05		
323.20	1.72	312.02	10.05	323.22	7.77			311.43	5.05		
333.12	2.12	311.49	12.06	328.18	8.83						
343.19	2.59	311.22	13.06	333.08	9.87						
353.05	3.13			338.11	10.87						
362.92	3.75			343.07	11.84						
370.00	4.23			348.06	12.79						
369.99[a]	4.25										

[a] Critical end point $L_2(L_1 = V)$.

Table 6. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.401$

L_2L_1V		$S_BL \rightarrow L$		$L_2L_1 \rightarrow L$		$S_BL_2L_1$		$S_BL_2L_1V$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
308.48	1.25	313.47	6.05	313.17	5.27	309.01	2.05	308.89	1.26
308.89	1.26	313.35	7.05	317.64	6.30	309.56	3.05		
312.93	1.38	313.25	8.05	322.10	7.35	310.45	4.05		
322.19	1.71	313.45	9.05	326.34	8.32	312.42	5.05		
331.20	2.08	313.14	10.05	330.85	9.34				
340.63	2.53	313.67	11.05	336.12	10.32				
350.04	3.02	313.50	12.05	340.94	11.27				
359.81	3.62	313.68	13.06	345.77	12.19				
369.15	4.25			350.74	13.08				
369.34[a]	4.25								

[a] Critical end point $L_2(L_1 = V)$.

Table 7. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.501$

L_2L_1V		$S_BL \rightarrow L$		$L_2L_1 \rightarrow L$		S_BLV		$S_BL_2L_1$		$S_BL_2L_1V$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
311.42	1.37	310.78	4.05	308.61	3.15	303.65	1.14	310.50	2.05	311.42	1.37
313.41	1.43	310.07	4.55	310.57	3.55	308.59	1.28	310.91	2.55		
323.28	1.77	310.37	5.05	312.62	4.05			310.79	3.05		
333.11	2.17	310.80	5.55	318.73	5.39			309.89	3.55		
342.99	2.63	310.63	6.05	323.28	6.46						
352.78	3.16	310.91	7.55	328.17	7.52						
362.63	3.78	310.89	8.05	333.12	8.55						
369.85[a]	4.27	310.81	10.06	338.04	9.55						
		310.63	12.06	342.94	10.52						
		310.54	13.06	347.88	11.46						
				352.79	12.38						
				357.62	13.24						

[a] Critical end point $L_2(L_1 = V)$.

Table 8. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.603$

L_1L_2V		$S_BL \rightarrow L$		$L_1L_2 \rightarrow L$	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
308.58	1.25	313.67	1.75	315.94	1.75
313.17	1.39	313.54	2.05	318.38	2.32
312.52	1.40	313.68	2.55	323.33	3.43
323.31	1.74	314.17	2.80	328.33	4.51
333.20	2.13	314.45	3.05	333.24	5.55
343.07	2.60	314.56	4.05	338.15	6.55
352.90	3.13	314.30	5.05	343.02	7.53
362.70	3.74	314.52	6.05	347.90	8.48
369.91[a]	4.26	314.63	8.05	352.80	9.41
		314.59	10.05	357.74	10.32
		314.51	12.06	362.67	11.20
		314.31	13.06	367.63	12.06

[a] Critical end point $L_2(L_1 = V)$.

Table 9. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.701$

$L_2V \rightarrow L$		$S_BL \rightarrow L$		$L_1L_2 \rightarrow L$		S_BLV		L_2L_1V	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P /MPa
314.33	1.41	313.90	2.05	345.27	2.78	309.92	1.29	351.99	3.10
313.23	1.37	313.78	3.05	346.76	3.00			361.62	3.69
322.71	1.70	313.96	4.05	347.69	3.21			369.93[a]	4.29
332.31	2.09	314.11	6.05	348.76	3.39				
342.02	2.55	313.81	8.05	350.10	3.65				
345.92	2.76	314.02	10.05	351.88	4.02				
		314.15	12.05	353.94	4.47				
		314.35	13.56	356.79	4.96				
				358.82	5.29				
				361.64	5.90				
				363.60	6.23				
				366.20	6.65				
				370.92	7.47				
				380.62	9.08				
				390.73	10.66				
				400.82	12.13				
				410.66	13.48				

[a] Critical end point $L_2(L_1 = V)$.

The three-phase curve L_2L_1V ends at higher temperature in an upper critical end point $L_2(L_1 = V)$, where the propane rich liquid phase and the vapor phase become critical. The phase diagrams for Boltorn mass fractions of 0.025, 0.050, 0.099, 0.200, 0.301, and 0.401 are similar to Figure 1. Because of polydispersity of the polymer, the system does not really behave as a real binary system, for example, the coordinates of the quadruple point and the upper critical end point slightly vary with composition.

Table 10. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.801$

LV → L		S_BL → L	
T/K	*P*/MPa	*T*/K	*P*/MPa
316.32	1.32	316.55	2.05
322.69	1.52	316.25	3.05
332.34	1.89	316.59	4.05
341.98	2.24	316.87	6.05
351.51	2.69	316.78	8.05
361.07	3.21	316.96	10.06
366.72	3.56	316.60	12.06
370.58	3.83	316.77	13.06
380.60	4.54		
390.15	5.37		
400.16	6.36		
410.28	7.44		
420.27	8.46		
430.38	9.54		
440.29	10.52		
450.24	11.45		
460.28	12.34		

Table 11. Experimental Phase Equilibrium Data for the System Propane + Boltorn H3200 at a Constant Boltorn Mass Fraction $w = 0.901$

LV → L		S_BL → L	
T/K	*P*/MPa	*T*/K	*P*/MPa
322.77	1.06	319.97	1.20
332.23	1.27	320.85	2.40
341.92	1.51	320.74	4.40
351.82	1.78	320.75	6.40
361.54	2.08	320.83	8.40
371.30	2.40	321.26	10.40
380.90	2.75		
390.62	3.12		
400.63	3.52		
410.61	3.95		
420.55	4.40		
430.53	4.85		
440.50	5.31		
450.33	5.76		
460.16	6.22		
470.07	6.70		

Going from low Boltorn mass fraction to high mass fraction of Boltorn the point of intersection of the three-phase curve $S_BL_2L_1$, the cloud point curve and the solid + liquid/liquid boundary curve moves toward the quadruple point $S_BL_1L_2V$ and the accessible part of the three-phase curve $S_BL_2L_1$ becomes smaller. At a Boltorn mass fraction of 0.603, the three-phase curve $S_BL_2L_1$ has disappeared from the diagram and the cloud point curve now intersects with the three-phase curve L_2L_1V, see Figure 2. With increasing Boltorn mass fraction this latter point of intersection moves along the three-phase curve to higher temperature and pressure as can be seen in Figure 3, which

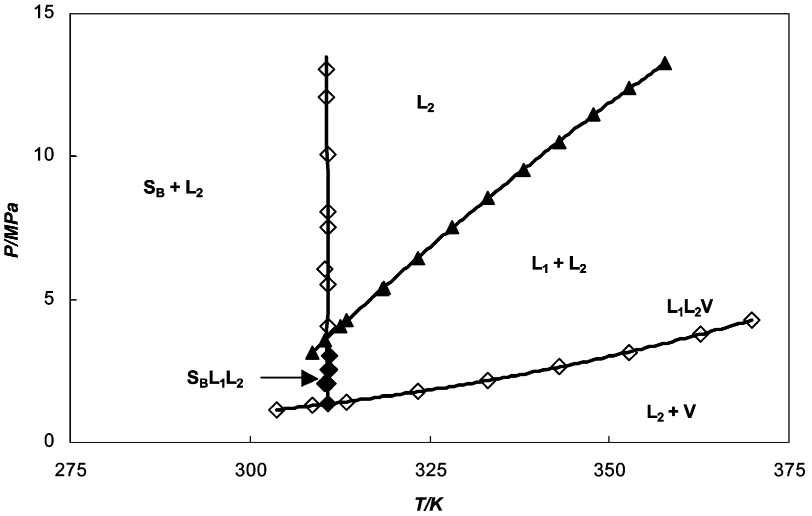

Figure 1. Phase diagram of propane + Boltorn H3200 at a mass fraction of Boltorn of 0.501.

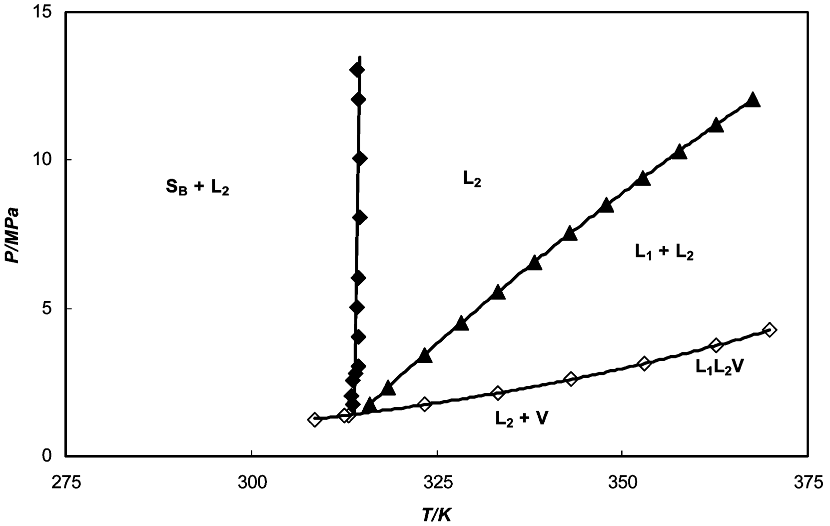

Figure 2. Phase diagram of propane + Boltorn H3200 at a mass fraction of Boltorn of 0.603.

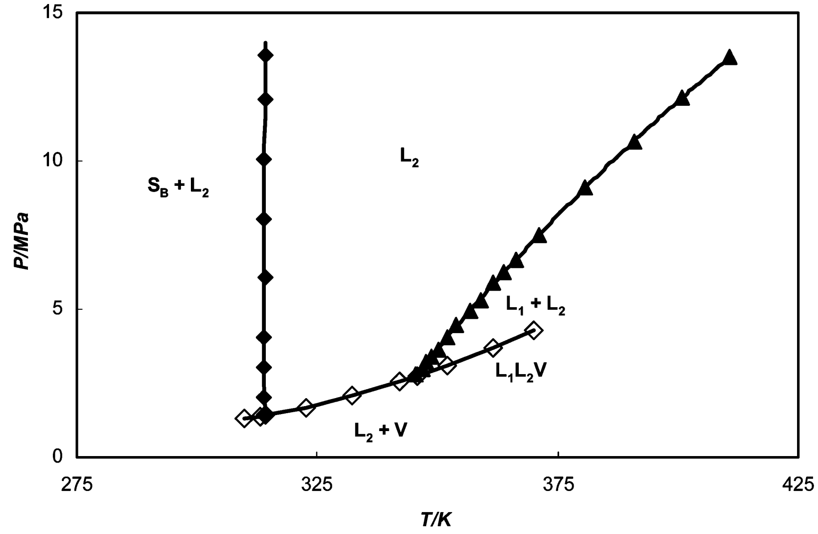

Figure 3. Phase diagram of propane + Boltorn H3200 at a mass fraction of Boltorn of 0.701.

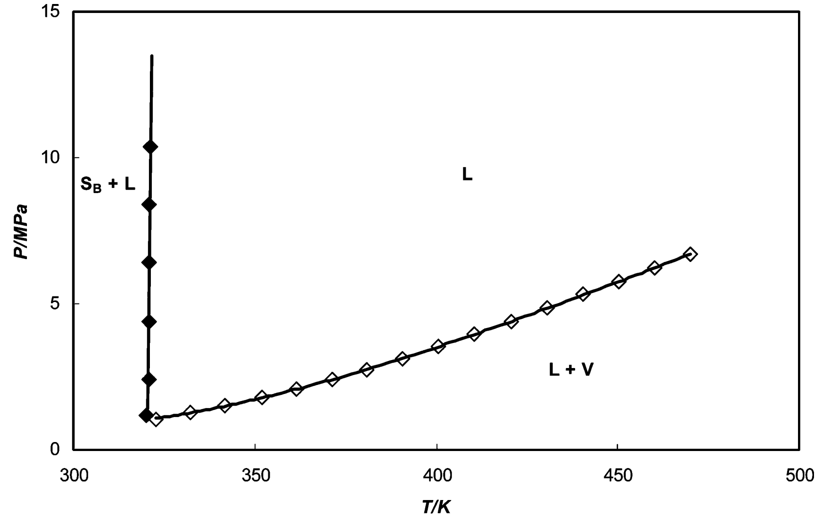

Figure 4. Phase diagram of propane + Boltorn H3200 at a mass fraction of Boltorn of 0.901.

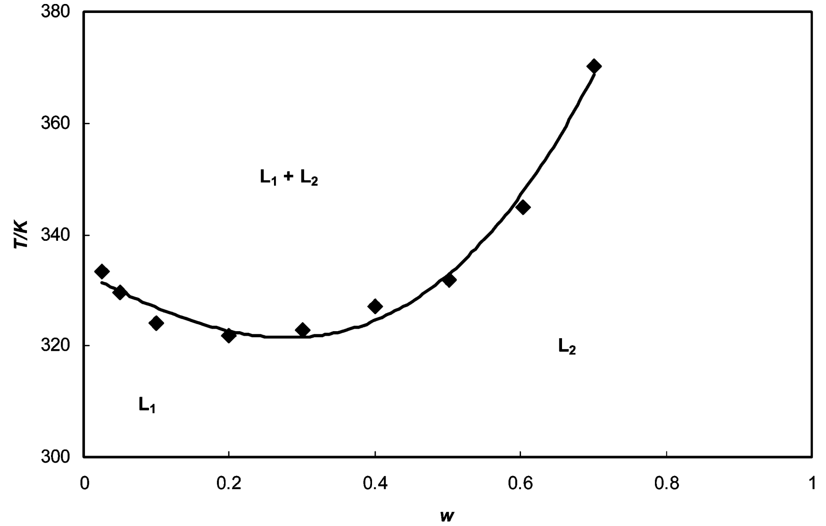

Figure 5. Isobaric liquid−liquid equilibria of propane + Boltorn H3200 at P = 8 MPa. w is the mass fraction of Boltorn.

shows the P,T-diagram for a mixture with a Boltorn mass fraction of 0.701. The accessible part of the L_2L_1V curve is now from the point of intersection with the cloud point curve up to the critical end point.

At a certain Boltorn mass fraction this point of intersection coincides with the critical end point and the length of the L_2L_1V curve becomes zero. When the polymer mass fraction is higher no longer a liquid−liquid phase split is found, as can be seen in Figure 4, which shows a P,T-diagram for a mixture with a Boltorn mass fraction of 0.901.

In Figure 5 interpolated cloud point temperatures are plotted as function of composition at a constant pressure of 8.00 MPa. The figure shows that a broad region of liquid−liquid equilibria is found; the system shows a liquid−liquid phase split at Boltorn mass fractions from 0.025 up to 0.70. The isobaric cloud point curve shows a temperature minimum at a Boltorn mass fraction of about 0.20, which again is proof of lower critical solution temperature behavior.

From Figures 1−5, it can be concluded that the system propane + Boltorn H3200 shows a liquid−liquid phase split with lower critical solution temperatures that interferes with the solidification surface of Boltorn H3200. Therefore it is unknown if the three-phase curve L_2L_1V has a lower critical end point or not. In the first case the system is a type IV system in the classification of fluid phase behavior of Van Konynenburg and Scott;[7] in the second case, propane + Boltorn H3200 shows type III fluid phase behavior.

Literature Cited

(1) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and other Dendritic polymers*; John Wiley & Sons, Ltd.: West Sussex, UK, 2001.

(2) Seiler, M.; Köhler, D.; Arlt, W. Hyperbranched polymers: new selective solvents for extractive distillation and solvent extraction. *Sep. Purif. Technol.* **2003**, *30*, 179–197.

(3) Seiler, M.; Rolker, J.; Arlt, W. Phase behaviour and thermodynamic phenomena of hyperbranched polymer solutions. *Macromolecules* **2003**, *36*, 2085–2092.

(4) Kozlowska, M. K.; Jurgens, B. F.; Schacht, C. S.; Gross, J.; De Loos, Th. W. Phase Behavior of Hyperbranched Polymer Systems: Experiments and Application of the Perturbed-Chain Polar SAFT Equation of State. *J. Phys. Chem. B* **2009**, *113*, 1022–1029.

(5) Lide, D.; Kehiaian, H. *Handbook of Thermophysical and Thermochemical Data*; CRC Press: Boca Raton, FL, 1994.

(6) De Loos, Th.W.; Van der Kooi, H. J.; Ott, P. L. Vapor-Liquid Critical Curve of the System Ethane + 2-Methylpropane. *J. Chem. Eng. Data* **1986**, *31*, 166–168.

(7) Van Konynenburg, P. H.; Scott, R. L. Critical curves and phase equilibria in binary van der Waals mixtures. *Philos. Trans. R. Soc., A* **1980**, *298*, 495–540.

Received for review January 30, 2009. Accepted March 23, 2009.

JE900130Y