Binary Vapor-Liquid Equilibrium for C₃ Hydrocarbons*

by Toshikatsu Hakuta**, Kunio Nagahama**, and Mitsuho Hirata**

Summary: High-purity propylene feedstock is required for manufacture of polypropylene. Accurate vapor-liquid equilibrium data of C₃ hydrocarbons are essential for the determination of fractionation requirements to obtain high-purity propylene from a C₃ hydrocarbon mixture.

The apparatus used in this investigation was a modification of the forced-circulation type. It has been stated by Ruhemann¹⁾ that this type of apparatus is the most accurate and reliable of all low temperature method.

Binary vapor-liquid equilibrium relationships for the propylene-propane, propylene-propadiene(allene) and propane-propadiene systems were determined at isothermal conditions of 0°C and 20.1°C.

In these three binary mixtures, the propane-propadiene system forms a minimum boiling azeotropic mixture. Azeotropic conditions were determined using a smoothing method proposed by Suda²⁾ which was based on a simple relation in vapor-liquid equilibrium ratio of the constituents.

1 Introduction

The equilibrium data for the propylene-propane system have been reported by Reamer and Sage³⁾, by Hanson et al.⁴⁾, by Mann, Pardee and Smyth⁵⁾ and by Hirata, Hakuta and Onoda⁶⁾. But data for propylene-propadiene and propane-propadiene systems have not been published. Hill et al.⁷⁾ suggested that greater deviation from ideality might be expected for the system such as the propane-propadiene, with greater differences in the degree of saturation of molecular structure. It is reported in "Azeotropic Data-II"⁸⁾ that the propane-propadiene system formed a minimum boiling azeotropic mixture, but vapor-liquid equilibrium data are not unpublished. So the authors investigated equilibrium relationships for propylene-propane, propylene-propadiene and propane-propadiene systems, and determined azeotropic points of the propane-propadiene system at 0°C and 20.1°C.

2 Materials

The propylene and propane samples were furnished by Takachiho Chemical Industry Co.. The propylene sample was specified to contain 99.32% propylene, 0.05% ethane, 0.15% propane and 0.49% air, and the propane sample was specified to contain 99.85% propane, 0.05% ethane and 0.10% air. The propadiene(allene) sample was furnished by The Matheson Co. Inc. and had

a minimum purity of 99%.

3 Experimental Apparatus and Experimental Method

3.1 Apparatus

The experimental apparatus used in this investigation is illustrated in Figure 1. This apparatus for measuring the vapor-liquid equilibrium is one of the types of forced circulation of the vapor phase. This is entirely made of stainless steel designed for operating conditions; temperatures as low as -200°C and pressures up to 100 atm.. The equilibrium cell has a capacity of 150 ml. with glass windows for inspection from outside.

Both the vapor and liquid phase sampling cells have a capacity of 10 ml., detailed descriptions of which were made previously⁹⁾. The sampling vessel, in which the liquid sample is allowed to vaporize, has a capacity of about 100 ml..

The circulation of the vapor phase is carried out by means of a magnetic pump provided with two check valves. The magnetic pump is shown in Figure 2. The rate of circulation can be adjusted at will between 0 ml/min and 300 ml/min.

The measurement of temperature in this investigation was carried out by a mercury thermometer. The pressure was read with a differential pressure gauge and a dead weight pressure tester.

3.2 Experimental Method

First, V in Figure 1, is connected to a vacuum pump for evacuation the system completely. A high-boiling component is introduced into the

* Received November 18, 1968.

** Faculty of Engineering, Tokyo Metropolitan University (2-1-1, Fukazawa, Setagaya-ku, Tokyo, Japan).

Fig. 1 Schematic Diagram of V-L Equilibrium Apparatus

① Magnetic coil	⑤ Valve stopper
② Piston	⑥ Check valve
③ Piston ring	⑦ Sleeve
④ Piston stopper	⑧ Fitting

Fig. 2 Magnetic Piston Pump

system from a sample cylinder.

The equilibrium cell is maintained at a desired temperature. The 0°C run was taken with ice and water in cooling bath and the 20.1°C run was done in the constant temperature bath which was controlled by means of temperature controller.

After the temperature desired was obtained, the magnetic pump is operated to circulate the vapor phase, and high and/or low boiling components are fed into the system. When the liquid surface in equilibrium cell was adjusted and pressure was reached to a desired level, the feed valve is closed.

When a steady state was established for about half an hour, the pressure is read to an accuracy

Fig. 3 Pressure-Composition Diagram of Propylene-Propane System

of 0.01 kg/cm^2 and the valves of the vapor phase sampling cell are closed in order to sample the vapor-phase. As vapor phase is circulated through the by-pass in vapor phase sampling cell at this time, the equilibrium condition is not broken. Immediately thereafter, the liquid sample is collected in the evacuated liquid phase sampling vessel and the sampling cell.

The sample is subjected to gas chromatographic analysis by valve operation.

The analysis was carried out by Yanagimoto GCG-3DH Gas Chromatograph equipped with 4

Table 1 Vapor-Liquid Equilibrium Original Data System: Propylene (1)-Propane (2) at 0°C

P Kg/cm ² -abs.	x_1	y_1	$y_1 - x_1$	K_1	K_2	α	γ_1	γ_2
4.85	0.0000	0.0000						
4.89	0.0141	0.0184	0.0043	1.305	0.9956	1.311	1.072	1.004
5.04	0.1234	0.1533	0.0299	1.242	0.9659	1.286	1.051	1.004
5.07	0.1487	0.1849	0.0362	1.243	0.9575	1.298	1.057	1.000
5.09	0.1616	0.1988	0.0372	1.230	0.9556	1.287	1.051	1.002
5.14	0.1980	0.2385	0.0405	1.210	0.9495	1.274	1.044	1.006
5.17	0.2140	0.2572	0.0432	1.202	0.9450	1.272	1.043	1.007
5.23	0.2618	0.3086	0.0468	1.179	0.9366	1.259	1.035	1.009
5.27	0.2956	0.3454	0.0498	1.168	0.9293	1.257	1.034	1.010
5.29	0.2972	0.3488	0.0516	1.174	0.9266	1.267	1.042	1.009
5.31	0.3144	0.3649	0.0505	1.161	0.9263	1.253	1.034	1.013
5.32	0.3275	0.3792	0.0517	1.158	0.9231	1.254	1.035	1.012
5.33	0.3321	0.3839	0.0518	1.156	0.9224	1.253	1.034	1.012
5.35	0.3535	0.4047	0.0512	1.145	0.9208	1.243	1.029	1.015
5.36	0.3567	0.4079	0.0512	1.144	0.9204	1.243	1.029	1.016
5.39	0.3779	0.4288	0.0509	1.135	0.9182	1.236	1.028	1.020
5.51	0.4875	0.5343	0.0468	1.096	0.9087	1.206	1.014	1.031
5.57	0.5437	0.5872	0.0435	1.080	0.9047	1.194	1.011	1.038
5.64	0.6159	0.6534	0.0375	1.061	0.9024	1.176	1.004	1.048
5.71	0.6882	0.7187	0.0315	1.044	0.9022	1.157	1.001	1.062
5.76	0.7392	0.7667	0.0275	1.037	0.8946	1.159	1.003	1.061
5.85	0.8499	0.8662	0.0163	1.019	0.8914	1.143	1.001	1.075
5.90	0.9224	0.9304	0.0085	1.009	0.8905	1.133	1.000	1.083
5.96	1.0000	1.0000						

at 20.1°C

8.58	0.0000	0.0000						
8.79	0.0766	0.0989	0.0223	1.289	0.9758	1.321	1.084	1.000
9.19	0.2253	0.2702	0.0449	1.199	0.9420	1.273	1.055	1.009
9.40	0.3473	0.3911	0.0432	1.126	0.9328	1.208	1.013	1.022
9.64	0.4406	0.4873	0.0467	1.106	0.9165	1.207	1.020	1.030
9.82	0.5630	0.6086	0.0456	1.081	0.8955	1.207	1.016	1.025
9.97	0.6358	0.6740	0.0382	1.060	0.8951	1.184	1.011	1.040
10.06	0.6967	0.7258	0.0291	1.042	0.9041	1.152	1.003	1.060
10.24	0.8311	0.8571	0.0260	1.031	0.8462	1.218	1.011	1.010
10.34	0.8974	0.9103	0.0129	1.014	0.8741	1.161	1.004	1.053
10.45	1.0000	1.0000						

Table 2 Vapor-Liquid Equilibrium Original Data System: Propylene (1)-Propadiene (2) at 0°C

P	x_1	y_1	$y_1 - x_1$	K_1	K_2	α	γ_1	γ_2
3.92	0.0000	0.0000						
4.10	0.0790	0.1300	0.0510	1.646	0.9446	1.742	1.133	0.988
4.36	0.1439	0.2551	0.1112	1.783	0.8701	2.037	1.305	0.968
4.58	0.2330	0.3511	0.1181	1.507	0.8460	1.781	1.159	0.988
4.74	0.3129	0.4525	0.1396	1.447	0.7968	1.816	1.151	0.963
4.89	0.3972	0.5388	0.1416	1.357	0.7651	1.773	1.114	0.954
5.23	0.5818	0.6928	0.1110	1.191	0.7346	1.621	1.046	0.922
5.37	0.6910	0.7642	0.0732	1.106	0.7631	1.449	0.997	1.045
5.48	0.7223	0.7847	0.0624	1.086	0.7753	1.401	1.000	1.084
5.67	0.8085	0.8510	0.0425	1.053	0.7781	1.353	1.002	1.125
5.67	0.8065	0.8582	0.0517	1.064	0.7328	1.452	1.013	1.060
5.83	0.9009	0.9278	0.0269	1.030	0.7286	1.413	1.008	1.083
5.83	0.9038	0.9282	0.0244	1.027	0.7464	1.376	1.005	1.110
5.96	1.0000	1.0000						

at 20.1°C

7.00	0.0000	0.0000						
7.36	0.1155	0.1559	0.0404	1.351	0.9542	1.415	0.951	1.033
7.52	0.1490	0.2003	0.0513	1.344	0.9397	1.430	0.967	1.010
8.00	0.2735	0.3409	0.0674	1.247	0.9072	1.374	0.954	1.037
8.49	0.3923	0.4794	0.0871	1.222	0.8568	1.426	0.993	1.039
8.69	0.4635	0.5450	0.0815	1.176	0.8462	1.390	0.978	1.051
9.06	0.5642	0.6315	0.0673	1.119	0.8456	1.323	0.970	1.094
9.50	0.6936	0.7426	0.0490	1.071	0.8401	1.274	0.973	1.140
9.94	0.8195	0.8536	0.0339	1.042	0.8111	1.284	0.991	1.152
10.08	0.8817	0.9042	0.0225	1.026	0.8098	1.266	0.989	1.166
10.17	0.8963	0.9114	0.0151	1.017	0.8544	1.190	0.990	1.241
10.21	0.9210	0.9375	0.0165	1.018	0.7911	1.287	0.995	1.154
10.45	1.0000	1.0000						

Table 3 Vapor-Liquid Equilibrium Original Data System: Propane (1)-Propadiene (2) at 0°C

P	x_1	y_1	$y_1 - x_1$	K_1	K_2	α	γ_1	γ_2
3.92	0.0000	0.0000						
3.97	0.0149	0.0320	0.0171	2.148	0.9826	2.186	1.756	0.994
4.09	0.0426	0.1021	0.0595	2.397	0.9379	2.556	2.022	0.979
4.28	0.1104	0.2123	0.1019	1.923	0.8855	2.172	1.694	0.966
4.43	0.1785	0.3257	0.1472	1.825	0.8208	2.223	1.665	0.927
4.55	0.2561	0.4029	0.1468	1.573	0.8027	1.960	1.473	0.930
4.59	0.2875	0.4301	0.1426	1.496	0.7999	1.870	1.413	0.935
4.77	0.5100	0.6286	0.1186	1.233	0.7580	1.627	1.212	0.922
4.84	0.6319	0.6894	0.0575	1.091	0.8438	1.293	1.088	1.042
4.87	0.7291	0.7536	0.0245	1.034	0.9096	1.137	1.037	1.129
4.88	0.7632	0.7791	0.0159	1.021	0.9329	1.094	1.026	1.161
4.89	0.7974	0.8055	0.0081	1.010	0.9600	1.052	1.017	1.197
4.88	0.8612	0.8394	-0.0218	0.9747	1.157	0.9424	0.979	1.439
4.87	0.9233	0.8863	-0.0370	0.9599	1.482	0.6475	0.963	1.841
4.87	0.9336	0.8938	-0.0398	0.9574	1.599	0.5986	0.960	1.985
4.86	0.9738	0.9619	-0.0119	0.9878	1.454	0.6793	0.990	1.804
4.85	1.0000	1.0000						

at 20.1°C

7.00	0.0000	0.0000						
7.27	0.0739	0.1035	0.0296	1.401	0.9680	1.447	1.187	1.005
7.62	0.1904	0.2567	0.0663	1.401	0.9058	1.546	1.244	0.986
7.87	0.2835	0.3445	0.0620	1.215	0.9149	1.328	1.115	1.029
8.18	0.3915	0.4528	0.0613	1.157	0.8993	1.286	1.103	1.052
8.45	0.5270	0.5650	0.0380	1.072	0.9197	1.166	1.056	1.110
8.65	0.6352	0.6570	0.0220	1.034	0.9402	1.100	1.043	1.162
8.66	0.7120	0.7300	0.0180	1.025	0.9375	1.094	1.035	1.160
8.71	0.7424	0.7411	-0.0013	0.9982	1.005	0.9982	1.013	1.251
8.70	0.8183	0.8076	-0.0107	0.9869	1.059	0.9320	1.001	1.316
8.68	0.9214	0.8906	-0.0308	0.9666	1.319	0.7326	0.978	1.636
8.65	0.9632	0.9407	-0.0225	0.9766	1.611	0.6061	0.985	1.991
8.58	1.0000	1.0000

Fig. 4 Pressure-Composition Diagram of Propylene-Propadiene System

m. Activated Aluminum/Squalane column. Hydrogen was used as a carrier gas and the flow rate was 80 ml/min. The column temperature was about 60°C and the filament current was 200 mA.

Fig. 5 Pressure-Composition Diagram of Propane-Propadiene System

Fig. 6 $\alpha-x_1$ Diagram of Propylene-Propane System Fig. 7 $\alpha-x_1$ Diagram of Propylene-Propadiene System Fig. 8 $\alpha-x_1$ Diagram of Propane-Propadiene System

4 Experimental Results and Discussion

Experimental results of vapor-liquid equilibrium measurements for the propylene-propane, propylene-propadiene and propane-propadiene

Table 4 Azeotropic Data for Propane-Propadiene System

Condition	x_1, y_1	
0°C	0.8045	4.89 kg/cm ² ·abs.
20.1°C	0.7407	8.71 kg/cm ² ·abs.
760 mmHg	88.3 vol%	-42°C (Lit. 8)

Fig. 9 γ_1, γ_2-x_1 Diagram of Propylene-Propane System at 20.1°C Fig. 10 γ_1, γ_2-x_1 Diagram of Propylene-Propadiene System at 0°C Fig. 11 γ_1, γ_2-x_1 Diagram of Propane-Propadiene System at 20.1°C

system were tabulated in Table 1, Table 2 and Table 3, respectively. In these tables, K_i , α and γ_i were calculated in the following equations.

$$K_i = \frac{y_i}{x_i} \quad (1)$$

$$\alpha_{ij} = \frac{y_i}{x_i} \cdot \frac{(1-x_i)}{(1-y_i)} \quad (2)$$

$$\gamma_i = \frac{\pi y_i}{P_i x_i} \quad (3)$$

Figure 3, 4 and 5 show the pressure-composition diagram for the above systems. Figure 6, 7 and 8 show the relative volatility (α)-liquid composition diagrams. As shown in Figure 6, 7 and 8, relative volatility of the propylene-propane system is not affected by the variation of temperature. On the other hand, the relative volatility for the propylene-propadiene and propane-propadiene systems is considerably affected.

In these systems the propane-propadiene system formed a minimum boiling azeotropic mixture. Azeotropic points at 0°C and 20.1°C are shown in Table 4. Figure 9, 10 and 11 show the activity coefficients-liquid composition diagrams for each system. These systems have a crosspoint in activity coefficients, but the propylene-propadiene system at 20.1°C has not. In this system the activity coefficients for propylene (γ_1) are scattered around unity. So it is impossible to test the soundness of the data for the propylene-propadiene system at 20.1°C with Redlich-Kister's¹⁰⁾ formula.

$$\int_{x_1=0}^{x_1=1} \log \gamma_1/\gamma_2 = 0 \quad (4)$$

The solid lines in all figures and the determination of azeotropic points are based on a simple smoothing method using K values of the constituents.

5 Conclusion

The isothermal vapor-liquid equilibrium data for the propylene-propane, propylene-propadiene and propane-propadiene systems were obtained in this investigation. The variation of the relative

volatility with temperatures was small in the propylene-propane system, but was considerably large in the propylene-propadiene and propane-propadiene systems. The propane-propadiene system formed a minimum boiling azeotropic mixture and the azeotropic points were determined.

Acknowledgement

The author's thanks are due to Y. Misaki, N. Tanaka and T. Mori who helped us in the experimental work of this investigation, and also to Chisso Co., Ltd. for the supply of high-purity C₃ hydrocarbons used in this work.

Nomenclature

K	Vapor-liquid equilibrium ratio
P	Pressure, kg/cm ² ·abs.
P°	Vapor pressure of pure component, kg/cm ² ·abs.
T	Temperature, °C
x	Mole fraction in liquid phase
y	Mole fraction in vapor phase
α	Relative volatility
γ	Activity coefficient
π	System pressure, kg/cm ² ·abs. Subscripts

Subscripts

- 1 Low boiling component
- 2 High boiling component
- i i component

Literature Cited

- 1) Ruhemann, M., "The Separation of Gases", 2nd., Oxford Univ. Press, England (1949).
- 2) Suda, S., Thesis of Dr. Eng., Tokyo Metropolitan University (Dec. 1966).
- 3) Reamer, H. H., Sage, B. H., *Ind. Eng. Chem.*, **43**, 1628 (1951).
- 4) Hanson, G. H., Hogan, R. J., Nelson, W. T., Cines, M. R. *ibid.*, **44**, 604 (1952).
- 5) Mann, A. N., Pardee, W. A., Smyth, R. W., *J. Chem. Eng. Data*, **8**, 499 (1963).
- 6) Hirata, M., Hakuta, T., Onoda, T., *J. Petrol. Inst.*, **10**, 440 (7), (1967).
- 7) Hill, A. B., McCormick, R. H., Barton, P., Fenske, M. R., *A. I. Ch. E. Journal*, **8**, 681 (1962).
- 8) Horsley, L., "Azeotropic Data-II", 32 (1962) *Am. Chem. Soc.*, Washington.
- 9) Hirata, M., Suda, S., *Kagaku Kogaku*, **31**, 759 (1967).
- 10) Redlich, O., Kister, T., *Ind. Eng., Chem.* **40**, 345 (1948).