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Propylene–Propane Phase Equilibrium from 230 to 350 K

A. Harmens

Costain Petrocarbon Ltd., Manchester M22 4TB, England

Coherent tables are presented for the vapor–liquid equilibrium of propylene–propane for temperatures from 230 to 350 K. The tables were calculated with a perturbed hard sphere equation of state, adapted specially to the saturation properties of the two substances. Measured equilibrium data from the literature were used for fitting the binary interaction coefficient. Details of the calculation procedure are given. The accuracy of the equilibrium compositions is estimated at about 2% of the smaller of the two mole fractions. It is shown that for production of pure propylene by distillation, lower pressures (but not lower than about 6 bar) have some advantage over higher pressures.

Introduction

The literature on the propylene–propane vapor–liquid equilibrium offers a somewhat disjointed picture, with the various publications being as a rule unsuitable for direct application in process design. At the same time, because of the industrial importance of the system and its small relative volatilities, there is a demand for reliable equilibrium data. In the design of a C_3 distillation column the process engineer may wish to employ a water-cooled overhead condenser, which will fix his operating temperatures at around 320 K. The proximity of the critical points sets a practical limit at about 350 K. Alternatively, he may wish to operate at substantially lower temperatures in order to exploit the larger relative volatilities. In that case the practical limit lies at around 230 K, below which the column pressure would become subatmospheric. It has been the objective of this study to represent the available equilibrium data of this system with a single continuous calculation procedure, covering the temperatures from 230 to 350 K.

Most of the empirical equilibrium data are at elevated pressures. Thermodynamic consistency analysis of such data remains somewhat controversial, because of the uncertain precision with which equations of state or generalized correlations calculate the necessary thermodynamic functions. Smith et al. (*1*) have analyzed this and have used the propylene–propane system as an example. Therefore, no thermodynamic consistency analysis was attempted. A hard-sphere cubic equation of state was used, adapted to the saturation properties of the pure constituents. A single binary interaction coefficient was fitted to empirical equilibrium data, covering the entire temperature range. The calculation procedure thus obtained was used to generate the equilibrium tables.

Equation of State and Mixing Rules

A cubic equation of state as described by Ishikawa et al. (*2*, *3*) was used

$$p = \frac{RT}{v}\left(\frac{2v+b}{2v-b}\right) - \frac{a}{v(v+b)} \tag{1}$$

A factor of $T^{-0.5}$ appearing in the original attraction term was incorporated into the parameter a. Ishikawa et al. (*2*, *3*) could show that in the calculation of phase equilibrium this equation was superior to other two-parameter equations.

Table I. Analysis of Calculated Equilibria

ref	points	AAD, %	bias, %	rmsd
Comparison with Underlying Empirical Data				
7	23	3.08	0.95	0.0158
8	9	6.18	−0.96	0.0199
11	23	3.09	1.19	0.0138
12	19	1.97	1.03	0.0079
total	74	3.17	0.81	0.0136
Comparison with Partly Calculated Empirical Data				
13	45	6.37	1.75	0.0228
14	63	4.24	−0.48	0.0188
total	108	5.13	0.45	0.0206

The parameters a and b are related to the critical constants by

$$a = \Omega_a R^2 T_c^2/p_c \qquad b = \Omega_b R T_c/p_c \tag{2}$$

with Ω_a and Ω_b numerical factors. Pure-component data were taken from Angus et al. (*4*) for propylene and from Goodwin (*5*) for propane. The critical constants are as follows: propylene, T_c = 365.57 K, p_c = 46.646 bar; propane, T_c = 369.80, p_c = 42.42. Since eq 1 should reproduce the saturation behavior of the pure components correctly, the Ω_a and Ω_b were fitted simultaneously to vapor pressure and saturated-liquid volume data. The Ω's thus obtained as functions of temperature could accurately be described by

propylene

$$\Omega_a = 1.10110 - 1.95859t + 0.15929t^2 + 0.81806t^3$$

$$\Omega_b = 0.12818 + 0.28830t - 1.36975t^2 + 1.04981t^3$$

propane

$$\Omega_a = 1.11032 - 2.00671t + 0.17630t^2 + 0.95922t^3$$

$$\Omega_b = 0.12205 + 0.33897t - 1.55702t^2 + 1.29853t^3 \tag{3}$$

with $t = 0.001T$. Equations 1 and 2 with these Ω functions (3) reproduce the underlying vapor pressures virtually exactly. For fugacity formulas, see the Appendix.

For mixtures the equations were used together with the following general mixing rules:

$$a_M = \sum_i\sum_j x_i x_j a_{ij} \qquad b_M = \sum_i\sum_j x_i x_j b_{ij} \tag{4}$$

(analogously with mole fractions y for vapor) with

$$b_{ij} = \tfrac{1}{8}(b_i^{1/3} + b_j^{1/3})^3 \qquad a_{ij} = \left(\frac{a_i a_j}{b_i b_j}\right)^{1/2} b_{ij} k_{ij} \tag{5}$$

As shown by Mollerup (*6*), these expressions have a better foundation in the statistical theory of corresponding states than the conventional arithmetical and geometrical averages. It was found that a second interaction coefficient, in the expression for b_{ij}, could be set equal to 1.0. This stands to reason in view of the great similarity of the two molecular species.

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Table II. Propylene–Propane Phase Equilibrium

p, bar	x_1	y_1	α_1	p, bar	x_1	y_1	α_1	p, bar	x_1	y_1	α_1
	Temperature = 230.0 K				Temperature = 270.0 K				Temperature = 310.0 K		
0.97	0.0000	0.0000		4.31	0.0000	0.0000		12.75	0.0000	0.0000	
1.01	0.1000	0.1378	1.4390	4.45	0.1000	0.1241	1.2755	13.07	0.1000	0.1157	1.1770
1.05	0.2000	0.2591	1.3986	4.58	0.2000	0.2392	1.2578	13.37	0.2000	0.2262	1.1690
1.09	0.3000	0.3672	1.3542	4.70	0.3000	0.3470	1.2399	13.66	0.3000	0.3322	1.1609
1.12	0.4000	0.4674	1.3164	4.82	0.4000	0.4489	1.2219	13.94	0.4000	0.4346	1.1529
1.15	0.5000	0.5608	1.2767	4.92	0.5000	0.5462	1.2038	14.21	0.5000	0.5337	1.1446
1.17	0.6000	0.6497	1.2362	5.02	0.6000	0.6401	1.1856	14.47	0.6000	0.6302	1.1363
1.20	0.7000	0.7357	1.1931	5.11	0.7000	0.7314	1.1670	14.72	0.7000	0.7246	1.1277
1.21	0.8000	0.8223	1.1569	5.19	0.8000	0.8212	1.1483	14.95	0.8000	0.8174	1.1194
1.23	0.9000	0.9089	1.1088	5.26	0.9000	0.9104	1.1294	15.17	0.9000	0.9091	1.1108
1.24	1.0000	1.0000		5.33	1.0000	1.0000		15.38	1.0000	1.0000	
	Temperature = 240.0 K				Temperature = 280.0 K				Temperature = 320.0 K		
1.48	0.0000	0.0000		5.83	0.0000	0.0000		16.02	0.0000	0.0000	
1.54	0.1000	0.1337	1.3884	6.00	0.1000	0.1217	1.2470	16.40	0.1000	0.1139	1.1567
1.60	0.2000	0.2531	1.3556	6.17	0.2000	0.2356	1.2326	16.77	0.2000	0.2233	1.1501
1.65	0.3000	0.3616	1.3218	6.32	0.3000	0.3430	1.2180	17.12	0.3000	0.3289	1.1434
1.70	0.4000	0.4625	1.2905	6.47	0.4000	0.4451	1.2033	17.46	0.4000	0.4311	1.1366
1.74	0.5000	0.5567	1.2556	6.60	0.5000	0.5431	1.1885	17.79	0.5000	0.5305	1.1299
1.78	0.6000	0.6471	1.2223	6.73	0.6000	0.6377	1.1735	18.11	0.6000	0.6275	1.1230
1.81	0.7000	0.7351	1.1893	6.85	0.7000	0.7300	1.1585	18.41	0.7000	0.7225	1.1161
1.84	0.8000	0.8224	1.1580	6.96	0.8000	0.8205	1.1429	18.70	0.8000	0.8160	1.1091
1.86	0.9000	0.9099	1.1224	7.06	0.9000	0.9103	1.1274	18.98	0.9000	0.9084	1.1020
1.88	1.0000	1.0000		7.15	1.0000	1.0000		19.24	1.0000	1.0000	
	Temperature = 250.0 K				Temperature = 290.0 K				Temperature = 330.0 K		
2.18	0.0000	0.0000		7.70	0.0000	0.0000		19.87	0.0000	0.0000	
2.27	0.1000	0.1300	1.3452	7.92	0.1000	0.1195	1.2215	20.32	0.1000	0.1122	1.1372
2.34	0.2000	0.2479	1.3183	8.12	0.2000	0.2322	1.2097	20.76	0.2000	0.2205	1.1316
2.41	0.3000	0.3563	1.2913	8.32	0.3000	0.3392	1.1978	21.18	0.3000	0.3255	1.1260
2.48	0.4000	0.4573	1.2641	8.50	0.4000	0.4415	1.1859	21.59	0.4000	0.4276	1.1204
2.54	0.5000	0.5529	1.2367	8.68	0.5000	0.5399	1.1736	21.99	0.5000	0.5271	1.1147
2.59	0.6000	0.6447	1.2097	8.84	0.6000	0.6353	1.1614	22.38	0.6000	0.6245	1.1089
2.63	0.7000	0.7340	1.1825	8.99	0.7000	0.7283	1.1490	22.75	0.7000	0.7202	1.1032
2.68	0.8000	0.8220	1.1548	9.14	0.8000	0.8196	1.1361	23.10	0.8000	0.8145	1.0974
2.71	0.9000	0.9103	1.1277	9.27	0.9000	0.9100	1.1239	23.44	0.9000	0.9076	1.0916
2.74	1.0000	1.0000		9.39	1.0000	1.0000		23.77	1.0000	1.0000	
	Temperature = 260.0 K				Temperature = 300.0				Temperature = 340.0 K		
3.11	0.0000	0.0000		9.99	0.0000	0.0000		24.36	0.0000	0.0000	
3.22	0.1000	0.1269	1.3079	10.26	0.1000	0.1175	1.1984	24.89	0.1000	0.1105	1.1177
3.32	0.2000	0.2433	1.2861	10.51	0.2000	0.2291	1.1887	25.41	0.2000	0.2177	1.1130
3.42	0.3000	0.3514	1.2642	10.75	0.3000	0.3357	1.1790	25.91	0.3000	0.3220	1.1082
3.50	0.4000	0.4530	1.2420	10.98	0.4000	0.4380	1.1691	26.40	0.4000	0.4238	1.1034
3.58	0.5000	0.5495	1.2199	11.19	0.5000	0.5368	1.1591	26.88	0.5000	0.5235	1.0986
3.65	0.6000	0.6424	1.1976	11.40	0.6000	0.6328	1.1489	27.34	0.6000	0.6213	1.0938
3.72	0.7000	0.7327	1.1750	11.60	0.7000	0.7266	1.1388	27.79	0.7000	0.7176	1.0890
3.78	0.8000	0.8218	1.1526	11.78	0.8000	0.8186	1.1285	28.22	0.8000	0.8126	1.0843
3.83	0.9000	0.9105	1.1301	11.95	0.9000	0.9096	1.1180	28.63	0.9000	0.9067	1.0794
3.87	1.0000	1.0000		12.11	1.0000	1.0000		29.03	1.0000	1.0000	
									Temperature = 350.0 K		
								29.56	0.0000	0.0000	
								30.18	0.1000	0.1087	1.0975
								30.79	0.2000	0.2147	1.0933
								31.38	0.3000	0.3182	1.0892
								31.96	0.4000	0.4197	1.0850
								32.52	0.5000	0.5195	1.0811
								33.07	0.6000	0.6176	1.0769
								33.60	0.7000	0.7146	1.0731
								34.12	0.8000	0.8104	1.0688
								34.62	0.9000	0.9055	1.0651
								35.10	1.0000	1.0000	

Binary Interaction Coefficient k_{ij}

Propylene–propane equilibrium data have been published in a number of places (*7–14*). The data by Hill et al. (*9*) (only three points) had to be rejected as being inconsistent among themselves. Mann et al. (*10*) reported isobaric data, without temperatures, which could not be used. Manley and Swift (*13*) and Laurance and Swift (*14*) measured only total pressure and specific volume of given liquid mixtures and calculated the vapor compositions. That is not without risk, as Smith et al. (*1*) have demonstrated. Suspicion was raised by the fact that at 310.93 K the two papers give quite different bubble point pressures. Therefore, these data were disallowed for the fitting of k_{ij}, but they were used later for comparison.

So four papers remained, giving actually measured isothermal sets of equilibrium data for a number of temperatures. The reported pure-component vapor pressures in general compared well with the vapor pressures used in this work: average absolute deviation 0.22% (maximum 0.40%) for propylene and 0.19% (maximum 1.12%) for propane.

A computer program fitted k_{ij} values to the isothermal sets of empirical equilibrium data. For a given temperature it read

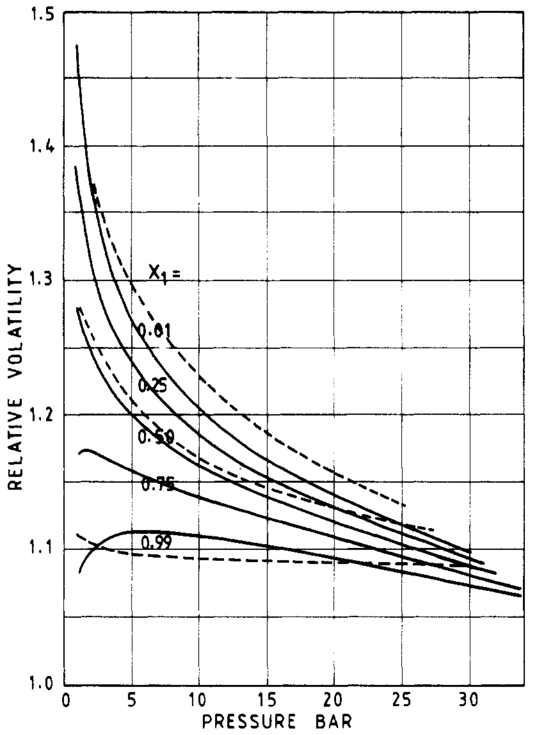

Figure 1. Relative volatility α_1 as function of pressure: (—) this work, (- - -) Funk and Prausnitz.

in all (p,x_1,y_1) data points and adjusted k_{ij} so as to minimize the sum of the relative discrepancies between empirical x_1, x_2, y_1, y_2, and the corresponding calculated values, at each (T,p) point. So a single optimized k_{ij} was returned for each isothermal set of data.

The k_{ij} thus obtained for the data by Hanson et al. (*8*) at 269.54 K and by Hakuta et al. (*12*) at 293.25 K had to be rejected as being clearly incompatible with the other results from the same source and far outside the general trend of k_{ij} values. The remaining nine k_{ij} between 228.65 and 344.26 K could be described by

$$k_{ij} = 0.9340 + 0.3397t - 0.4734t^2 \qquad (6)$$

These k_{ij} lie between 0.987 and 0.995, close to 1, as should be expected.

Testing Calculated Equilibria and Accuracy

The equilibria which could now be calculated were first tested against the underlying data. At each empirical (T,p) point the four calculated equilibrium mole fractions were compared with the corresponding empirical values. The upper part of Table I shows the results of these comparisons. They are expressed as average absolute deviation on a percentage basis (AAD, %), bias or average deviation on a percentage basis (bias, %), and root mean square deviation (rmsd) in mole fraction. "Deviation" here means calculated minus empirical mole fraction.

The deviations are of course partly of experimental origin. AAD contains a few large individual errors (up to 19%) at the extremities of the isothermal data sets, where the small propylene or propane mole fractions have magnified the percentage deviations. Since errors in the middle of the concentration range do not contribute materially to the bias (contributions for propylene and propane largely cancel out), the slightly positive bias indicates that the smaller concentrations tend to be calculated slightly too high.

The lower part of Table I shows comparisons with the partly calculated empirical data by Swift and co-workers (*13*, *14*). As was to be expected, the AAD and rmsd are somewhat larger than in the previous comparison. It is interesting to note that the biases for the two sets of data have opposite signs: the calculated equilibria follow an intermediate course in between the two sets.

An answer to the question as to how accurately the calculated mole fractions actually represent the true equilibrium should embody three aspects: (1) the limiting pure-component phase equilibrium is presumably represented without error; (2) the inaccuracy in the calculated mole fractions is likely to be smaller than the deviations disclosed by the tests; (3) the preponderance of the smaller mole fractions in determining the inaccuracy should be manifested. In view of this, it is estimated that the average absolute error in a calculated equilibrium composition is about 2% of the smaller of the two mole fractions.

The results of the tests against the 74 underlying data points also showed that almost without exception calculated x_1 and y_1 were either both too large or both too small. This being so, the numerator and the denominator of the relative volatility α_1 are both affected to about the same degree by the inaccuracy in the calculated mole fractions. This makes the α_1 largely insensitive to those inaccuracies.

Tabulated Equilibria and the (α,p) Diagram

The computation procedure was incorporated into a bubble point program to generate the equilibrium data and relative volatilities α_1 shown in Table II.

The propylene–propane equilibrium has been analyzed before, by Funk and Prausnitz (*15*), using the composite thermodynamic treatment of Prausnitz and Chueh (*16*). They presented their results in an (α,p) diagram showing lines for constant x_1. A similar diagram was prepared on the basis of our equation of state procedure (Figure 1). It shows curves for five x_1 values, and three corresponding curves from ref *15*. At low pressures there is a measure of agreement, but toward higher pressures the Funk–Prausnitz curves run increasingly too high. This is probably caused by insufficient refinement of the Prausnitz–Chueh procedure, which uses constant Ω_a and Ω_b and (for this system) a $k_{ij} = 1.0$.

The present $x_1 = 0.99$ curve shows a maximum at about 6 bar. At low pressures it falls toward $\alpha_1 = 1.0$. The reason for this is that propane has only a slightly lower vapor pressure than propylene while the liquid mixtures are almost ideal: at constant T the total pressure at the propylene end is almost constant. Table II confirms this. Since at the propylene end Raoult's law approximately holds for propylene, y_1/x_1 equals about 1 and consequently α_1 approaches 1. Toward higher pressures the present curve is noticeably steeper than the Funk–Prausnitz curve. This indicates that for producing pure propylene by distillation it is advantageous to operate at lower pressures, but not below about 6 bar.

Appendix

Fugacity Formulas for Eq 1.

For a single substance

$$\ln \varphi = 2 \ln \left(\frac{2v}{2v - b}\right) + \frac{a}{bRT} \ln \left(\frac{v}{v + b}\right) + Z - 1 - \ln Z \quad (7)$$

For a component i in a mixture

$$\ln \varphi_i = 2 \ln \left(\frac{2v}{2v - b}\right) + \frac{1}{bRT}\left(a + \frac{\partial a}{\partial x_i} - \frac{a}{b}\frac{\partial b}{\partial x_i}\right) \ln \left(\frac{v}{v + b}\right) - \left(\frac{2}{2v - b} - \frac{1}{bRT}\frac{a}{v + b}\right)\left(b - \frac{\partial b}{\partial x_i}\right) - \ln Z \quad (8)$$

In this formula a and b equal a_M and b_M of eq 4.

Glossary

a, b	parameters in equation of state (1)
k	binary interaction coefficient
p	total pressure, bar
R	gas constant (83.1448 bar·cm^3/mol·K)
T	absolute temperature, K
t	0.001T
v	molal volume, cm^3/mol
x	mole fraction in liquid
y	mole fraction in vapor
Z	compressibility factor pv/RT
α_1	relative volatility y_1x_2/x_1y_2
φ	fugacity coefficient
Ω_a, Ω_b	numerical factors in a and b, eq 2 and 3

Subscripts

1, 2	refer to propylene and propane, respectively
i, j	refer to any of the components
c	critical
M	mixture

Registry No. Propylene, 115-07-1; propane, 74-98-6.

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Vapor–Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 3. Poly(ethylene glycols)

Mordechay Herskowitz and Moshe Gottlieb*

Chemical Engineering Department, Ben-Gurion University of the Negev, Beer Sheva, 84105 Israel

The activity of water in solutions of poly(ethylene glycols) (PEGs, molecular weights 200, 600, 1500, 6000) was measured over a wide range of weight fractions at 293.1, 313.1, and 333.1 K. The data were obtained by an isopiestic method. A comparison between the measured activities and predicted values by the UNIFAC method gives a good agreement for PEG 200 solutions only.

Introduction

Poly(ethylene glycols) are polymers that find a wide range of industrial applications due to their high solubility in water. They are commonly used in the pharmaceutical industry as excipients in drug formulation, as surface-active agents in water treatment, as fiber-forming aids in the textile industry, in the manufacture of lubricants and mold release agents, and recently as reactive moieties in the preparation of hydrophilic polyurethane networks for medical purposes (*1*, *2*). The properties of the aqueous solutions of poly(ethylene glycols) have been extensively studied by various methods (*3*–*6*).

Malcolm and Rowlinson (*7*) measured the vapor pressures of aqueous solutions of poly(ethylene glycol) of molecular weights 300, 3000, and 5000 at 303–338 K. The water activity was calculated from the data. Adamcova (*8*) employed an isopiestic method to measure the water activity in aqueous solutions of poly(ethylene glycols) (molecular weights 200–20 000) at 298 K. This study was limited to relatively dilute solutions (polymer weight fraction less than 0.5).

In this work we have enlarged the body of available data on the activity of aqueous PEG solutions by obtaining data for polymers in the molecular weight range of 200–6000 over the entire concentration range.

Experimental Section

The isopiestic apparatus employed in this study is described in detail elsewhere (*9*). The reference solute was lithium chloride, manufactured by Merck Co. Its purity analyzed by atomic absorption and titration was better than 99.8%. The poly(ethylene glycols), manufactured by BDH, were used as supplied. After the salt and the polymers were dried at 120 °C, their water content measured by Karl Fischer analysis was less than 0.3% and 0.7%, respectively.

Results and Discussion

The water activity was calculated from the expression

$$\ln a_w = -\nu_r m_r \phi_r / 55.51 \quad (1)$$

where ν_r, m_r, and ϕ_r are the number of ions, the molality, and

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