Published in final edited form as:

J Chem Eng Data. 2019 ; 64: . doi:10.1021/acs.jced.8b01106.

Bubble Point Measurements of Neopentane + Ethane Mixtures

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Abstract

Bubble point measurements have been taken on three compositions of the neopentane + ethane system. The results are modeled with a Peng-Robinson equation with symmetrical mixing rule and a Helmholtz-energy-based 4-parameter model. Interaction parameters for all fits are provided. The results are consistent with other similar mixture systems (neopentane + propane and ethane + pentane) and demonstrate near ideal mixing.

Graphical abstract

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Keywords

Bubble point pressure; Vapor-liquid equilibrium

INTRODUCTION

Neopentane, or 2,2-dimethylpropane, is known to be a component of natural gas,¹ although there are few vapor-liquid equilibrium (VLE) measurements of neopentane with linear alkanes. As a pentane isomer, it is expected to have similar properties to *n*-pentane and isopentane but is the only one of the three to be a gas at room temperature and atmospheric pressure, indicating the quarternary carbon and tetrahedral symmetry may influence its properties. VLE measurements have previously been done for methane²⁻⁴ + and propane⁵ + neopentane mixtures, as well as with *n*-pentane⁶ (which is heavier than the other *n*-alkanes), but no data exist for the neopentane + ethane system.

The first bubble-point measurements of the binary system neopentane + ethane are presented here. These measurements are modeled with a Peng-Robinson equation with a symmetrical mixing rule, as well as a 4-parameter Helmholtz-energy based model. Comparisons to the similar systems of propane + neopentane and ethane + pentane were examined for consistency of the model. These measurements are important for the accurate modeling of natural gas systems.

MATERIALS AND METHODS

Materials.

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose. Neopentane (2,2-dimethylpropane) obtained from General Air and ethane (Sigma-Aldrich) included in each mixture were used without further purification. The manufacturer did not state a purity for the neopentane and reported purity for ethane was 99.9%. The purity of each mixture component is provided (Table 1) and the NIST/EPA/NIH Mass Spectral Database was used for peak identification.⁷ No distinguishable impurities were seen for ethane, even when the sample was purposefully overloaded to observe this. The neopentane showed one impurity of 2-butyne. The lower purity of the neopentane dominates the uncertainty of the mixture composition. Uncertainty in the sample composition was determined as previously described.⁸

Mixture preparation.

Mixtures were prepared gravimetrically following the method given in Keulen et al.⁸ The standard deviation of the repeat weighings was around 3.0 mg.

Measurements.

A schematic of the instrument used to make the measurements is shown in Figure 1 and has been previously described in detail.⁸

Uncertainty Analysis.

The expanded uncertainty for our bubble point measurements was previously reported.⁸ The reported overall combined uncertainty for each point was calculated by taking the root sum of squares of the pressure equivalents of the temperature and composition uncertainties, the uncertainty in pressure, and the measurement repeatability. This number was multiplied by two (coverage factor, $k=2$) and is reported as an uncertainty in pressure as well as a percent uncertainty in pressure for each bubble point.

RESULTS AND DISCUSSION

Bubble point pressures for three compositions of neopentane + ethane binary mixtures were measured from 270 K to 370 K (Table 2). In this table, the temperature, pressure and neopentane composition are given as well as uncertainty in the pressure (absolute value and percentage). An initial deviation from the predictions in REFPROP 9.1 is given in the table for comparison. It is clear from the significant deviation from the REFPROP predictions, especially at high neopentane concentrations, that there was an opportunity for these measurements to inform the models for better predictions.

Initial modeling of the system was accomplished through use of the Peng-Robinson equation with a symmetrical mixing rule.⁹ The consistency of the model with the data is shown in Figure 2. From an analysis of the deviations, it became apparent that two measurements significantly deviate from the prediction. These measurements were considered outliers and were not used for modeling. The experimental nature of the outliers was not determined. The interaction parameter was determined to be -0.0035 , which indicates nearly ideal mixing of the components. The uncertainty of that parameter evaluated by the NIST ThermoData Engine software¹⁰ is 0.0026 for 95 % confidence. In order to estimate the significance of that parameter, we performed modeling with Peng-Robinson equation with zero interaction parameters. The maximum deviation increased from 2 % to 3 %, and the deviations acquired a prominent systematic nature at the highest temperature.

Further improvement on the model can be achieved through the use of a Helmholtz energy multi-fluid approximation model as executed in the NIST ThermoData Engine¹⁰ utilizing REFPROP¹¹ engine. By using the KW0 mixing functions from the GERG-2004 monograph¹², the data could be more accurately fit with a 4-parameter model with $\beta_T = 0.987197$, $\gamma_T = 1.04599$, $\beta_v = 1.01588$ and $\gamma_v = 1.01090$. This fit allows for a deviation of $\pm 1\%$ from the equation of state (Figure 3).

Comparison of the results to similar mixtures also shows that Peng-Robinson fits for both propane + neopentane and ethane + pentane systems have interaction parameters close to zero (0.0012 and 0.0179 respectively) indicating near ideal mixing in these systems also (Figure 4). Both systems reinforce the confidence in the results provided here.

CONCLUSIONS

Bubble point measurements were made on three compositions of neopentane + ethane systems. These results were modeled with increasing accuracy with a Peng-Robinson model, a Peng-Robinson fit with symmetrical interaction parameters, and finally a Helmholtz based 4-parameter system. Interaction parameters for all fits are provided. The user may determine the best model for their purpose, but it is advantageous that the simplistic Peng-Robinson model gives a good fit. The results are consistent with similar mixture systems and demonstrate near ideal mixing and it does not appear the tetrahedral symmetry of neopentane plays a role in this mixture.

ACKNOWLEDGEMENTS

The purity analysis of the pure fluids was provided by Dr. Tara Lovestead of NIST.

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Figure 1.

Schematic of the apparatus used to make the bubble point measurements. The SPRT is located in the metal wall of the cell. Valves (V-1, V-5) control access to the pressure transducers (PT_L and PT_V) on the liquid and vapor sides respectively. The valves V-2, V-3 and V-6 are used to load the sample (E-1) from the mixture bottle into the system. A pneumatic valve (PV) is used to control a slight bleed from the system when it is necessary to open up the bubble and allows for it to be placed in the waste container E-2. A vacuum system E-4, with cold trap E-3 is used to evacuate the system prior to sample loading.

Figure 2. Data fit with Peng-Robinson with a symmetrical mixing rule. The interaction parameter was determined to be -0.0034711 . A) Phase boundary pressure for neopentane + ethane system with the original Peng-Robinson fit. B) Deviation from the Peng-Robinson fit for the neopentane + ethane system. Outliers are designated in orange.

Figure 3. Data fit with 4-parameter Helmholtz multi-fluid approximation. A) Phase boundary pressure for the Helmholtz energy multi-fluid approximation model from TDE utilizing REFPROP. B) Deviation from the equation presented in part A. Outliers are designated in orange.

Figure 4: Peng-Robinson models of similar mixtures. A) Literature data⁵ with a Peng-Robinson fit for a neopentane + propane mixture. Interaction parameter = 0.0012. B) Literature data¹³⁻¹⁵ with a Peng-Robinson fit for an ethane + pentane mixture system. Interaction parameter = 0.0179. Points in green are reported as smoothed data from the literature, where points in black are not. Orange data points are rejected because of inconsistencies or because they belong to the dew line, rather than the bubble point.

Table 1.

Measured purity of mixture components.

Chemical	GC-MS	GC-FID
<i>neopentane</i>		99.82 %±0.01 %
<i>ethane</i>	>99.9 %±0.05 %	

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Table 2:

Measured bubble point pressures for the system neopentane (1) + ethane (2) at temperature T , pressure P , and liquid mole fraction x_1 . Standard uncertainties u are $u(T) = 0.03$ K. The values of the expanded uncertainty for $U(x_1)$ and $U(P)$ are given in the table. Comparisons are made to REFPROP 9.1 (P_{REFPROP}). Predicted pressures are given for both the Helmholtz model (P_{KW0}) and Peng-Robinson model (P_{PR}), as well as deviations from the model.

x_1	$U(x)$	T/K	P/kPa	$U(P)/\text{kPa},$ $k = 2$	$(u(P)/P) \times 100$	$(1 - P_{\text{REFPROP}}/P_{\text{exp}}) \times 100$	$P(\text{KW0})$	$(1 - P_{\text{KW0}}/P_{\text{exp}}) \times 100$	$P(\text{PR})$	$(1 - P_{\text{PR}}/P_{\text{exp}}) \times 100$
0.762	0.037	270.37	479.439	4.16	0.87	-35.30	480.887	-0.30	474.571	1.02
0.762	0.037	275.34	537.344	4.25	0.79	-33.53	538.257	-0.17	531.884	1.02
0.762	0.037	280.33	599.863	4.36	0.73	-31.88	600.355	-0.08	593.947	0.99
0.762	0.037	285.29	666.922	4.42	0.66	-30.29	666.701	0.03	660.272	1.00
0.762	0.037	285.29	665.415	4.44	0.67	-30.58	666.701	-0.19	660.272	0.77
0.762	0.037	290.27	737.313	4.47	0.61	-29.08	738.101	-0.11	731.658	0.77
0.762	0.037	295.24	814.672	4.62	0.57	-27.55	814.292	0.05	807.826	0.84
0.762	0.037	300.23	897.821	4.79	0.53	-26.05	895.894	0.21	889.385	0.94
0.762	0.037	300.22	892.703	4.79	0.54	-26.75	895.726	-0.34	889.217	0.39
0.762	0.037	305.19	980.425	4.92	0.50	-25.32	982.219	-0.18	975.627	0.49
0.762	0.037	310.18	1074.351	5.06	0.47	-23.92	1074.45	-0.01	1067.72	0.62
0.762	0.037	315.17	1173.867	5.21	0.44	-22.59	1172.22	0.14	1165.26	0.73
0.762	0.037	320.16	1279.351	5.47	0.43	-21.30	1275.65	0.29	1268.35	0.86
0.762	0.037	325.13	1377.977	5.52	0.40	-21.18	1384.42	-0.47	1376.65	0.10
0.762	0.037	330.12	1494.848	5.75	0.38	-19.97	1499.52	-0.31	1491.1	0.25
0.762	0.037	335.11	1618.291	5.17	0.32	-18.78	1620.64	-0.15	1611.34	0.43
0.762	0.037	335.12	1618.703	5.94	0.37	-18.77	1620.89	-0.14	1611.58	0.44
0.762	0.037	340.11	1746.936	6.24	0.36	-17.73	1748.12	-0.07	1737.67	0.53
0.762	0.037	345.10	1884.778	6.40	0.34	-16.53	1881.54	0.17	1869.61	0.80
0.762	0.037	350.10	2026.941	6.73	0.33	-15.52	2021.51	0.27	2007.69	0.95
0.762	0.037	350.11	2022.479	6.73	0.33	-15.79	2021.8	0.03	2007.97	0.72
0.762	0.037	355.09	2172.415	6.86	0.32	-14.72	2167.5	0.23	2151.31	0.97
0.762	0.037	360.10	2327.440	7.21	0.31	-13.79	2320.44	0.30	2301.27	1.12
0.762	0.037	365.09	2728.941	7.80	0.29	-2.94	2479.08	9.16	2456.22	9.99
0.520	9.36E-04	265.35	824.560	4.57	0.55	-17.88	819.319	0.64	838.949	-1.75
0.520	9.36E-04	270.33	925.490	4.77	0.52	-17.26	919.822	0.61	941.594	-1.74
0.520	9.36E-04	275.31	1031.650	4.93	0.48	-16.93	1027.88	0.37	1051.86	-1.96
0.520	9.36E-04	280.31	1148.530	5.15	0.45	-16.31	1144.1	0.39	1170.33	-1.90
0.520	9.36E-04	285.28	1271.010	5.39	0.42	-15.85	1267.41	0.28	1295.86	-1.96
0.520	9.36E-04	290.28	1403.750	5.59	0.40	-15.26	1399.37	0.31	1429.97	-1.87
0.520	9.36E-04	295.27	1545.020	5.93	0.38	-14.63	1539.03	0.39	1571.63	-1.72
0.520	9.36E-04	300.22	1685.620	5.95	0.35	-14.57	1685.43	0.01	1719.79	-2.03
0.520	9.36E-04	305.19	1841.820	6.24	0.34	-13.98	1840.31	0.08	1876.11	-1.86
0.520	9.36E-04	310.18	2002.570	6.69	0.33	-13.63	2003.71	-0.06	2040.5	-1.89

x1	U(x)	T/K	P/kPa	U(P)/kPa, k = 2	(u(P)/P)×100	(1-P _{REFPROP} /P _{exp})×100	P(KW0)	(1-P _{KW0} /P _{exp})×100	P(PR)	(1-P _{PR} /P _{exp})×100
0.520	9.36E-04	315.16	2176.270	6.83	0.31	-13.01	2174.59	0.08	2211.78	-1.63
0.520	9.36E-04	320.15	2351.670	7.23	0.31	-12.70	2353.52	-0.08	2390.36	-1.65
0.520	9.36E-04	325.14	2542.470	7.60	0.30	-12.03	2539.98	0.10	2575.54	-1.30
0.520	9.36E-04	330.13	2724.290	7.84	0.29	-12.07	2733.75	-0.35	2766.87	-1.56
0.520	9.36E-04	335.12	2930.040	8.24	0.28	-11.38	2934.53	-0.15	2963.81	-1.15
0.261	4.70E-04	265.35	1342.512	5.34	0.40	-3.86	1334.18	0.62	1350.44	-0.59
0.261	4.70E-04	270.32	1509.387	5.58	0.37	-3.76	1500.18	0.61	1518.45	-0.60
0.261	4.70E-04	275.30	1689.529	5.91	0.35	-3.66	1679.3	0.61	1699.6	-0.60
0.261	4.70E-04	280.31	1881.831	6.19	0.33	-3.69	1872.6	0.49	1894.85	-0.69
0.261	4.70E-04	285.29	2088.632	6.57	0.31	-3.57	2077.86	0.52	2101.83	-0.63
0.261	4.70E-04	290.31	2304.896	7.12	0.31	-3.70	2298.03	0.30	2323.32	-0.80
0.261	4.70E-04	295.29	2538.386	7.48	0.29	-3.56	2529.52	0.35	2555.46	-0.67
0.261	4.70E-04	300.22	2778.295	7.94	0.29	-3.58	2771.31	0.25	2796.94	-0.67
0.261	4.70E-04	305.19	3037.882	8.29	0.27	-3.41	3027.45	0.34	3051.4	-0.44
0.261	4.70E-04	310.18	3300.838	9.01	0.27	-3.53	3296.61	0.13	3317.03	-0.49
0.261	4.70E-04	315.17	3587.441	9.64	0.27	-3.27	3577.04	0.29	3591.46	-0.11
0.261	4.70E-04	320.15	3869.803	9.76	0.25	-3.40	3867.16	0.07	3872.36	-0.07
0.261	4.70E-04	325.14	4182.447	10.64	0.25	-2.94	4166.76	0.38	4158.51	0.57
0.261	4.70E-04	330.13	4476.076	11.14	0.25	-3.09	4473.4	0.06	4446.3	0.67
0.261	4.70E-04	335.12	4973.519	12.06	0.24	1.00	4784.51	3.80	4731.62	4.86
0.261	4.70E-04	340.10	5060.384	11.93	0.24	-3.29	5095.83	-0.70	5008.24	1.03