

# The System Propane + Elcosane: $P$ , $T$ , and $x$ Measurements in the Temperature Range 288–358 K

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Bubble points for binary mixtures of propane + elcosane have been measured for eight isopleths in the temperature interval 288–358 K and in the pressure interval 0.35–3.5 MPa. From the experimental data  $P$ - $x$  sections have been obtained by interpolation. The isothermal data were correlated with the Peng-Robinson equation of state.

## Introduction

In the system ethane + propane + elcosane retrograde condensation of a heavy liquid has been found experimentally (1). To obtain a better quantitative understanding of this phenomena, calculations using an equation of state (EOS) are needed. Since engineering EOSs contain at least one adjustable parameter for each binary subsystem, experimental information on the binary subsystems is needed. For the binary mixture propane + elcosane such data are not available.

In this paper experimental bubble points are presented for the system propane + elcosane in the temperature range where the ternary system shows liquid-liquid-vapor equilibria. Isothermal data obtained from the original measurements have been fitted to the Peng-Robinson equation of state (2). Binary interaction parameters for six isotherms are given.

The binary system propane + elcosane system exhibits type I or type II phase behavior according to the classification of Scott and van Konynenburg (3). In the  $P$ - $T$  projection the critical line is continuous and extends from the critical point of propane to the critical point of elcosane. No three-phase line  $L_2$ - $L_1$ -V has been observed (4). Since the temperature interval of interest is below the critical point of propane, no critical points for the mixture have been measured.

## Experimental Section

The experiments were performed using a so-called Cailletet apparatus. A mixture of known composition is contained in a glass measuring cell. At a fixed temperature the pressure where the last bubble disappears is obtained visually. This procedure allows the determination of the boundary between the homogeneous liquid region and the two-phase vapor-liquid region.

The pressure was measured using a dead weight pressure gauge with an accuracy within  $\pm 0.0015$  MPa. A platinum resistant thermometer with an accuracy of  $\pm 0.005$  K was used to measure the temperature. During the experiments the temperature in the water thermostat was maintained constant within  $\pm 0.015$  K. A more detailed description of the apparatus and the experimental procedure can be found elsewhere (5).

**Materials.** The elcosane used in this work was obtained from Shell Research in Houston. A minimum purity of 98.0 mol % was ascertained by the producer.

Propane was delivered by Air Products Co. with a minimum purity of 99.95%. To check the purity, the vapor pressure curve was measured. The mean deviation in the vapor pres-

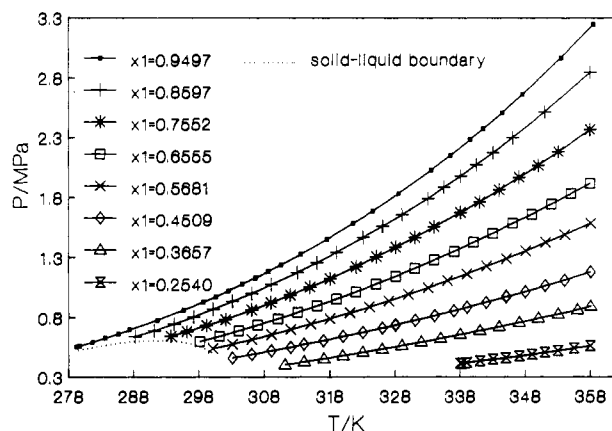


Figure 1. Vapor-liquid equilibria in the system propane + elcosane: experimental bubble-point pressure as a function of temperature for mixtures of given composition.

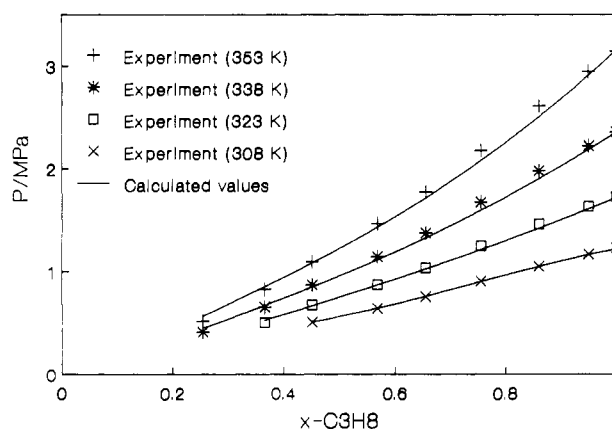


Figure 2. Vapor-liquid equilibria in the system propane + elcosane: isothermal  $P$ - $x$  sections (—, calculated using the Peng-Robinson equation of state).

sure between our experiment and the literature (6) in the temperature range 303–363 K was 0.005 MPa.

The elcosane and propane were used without further purification.

## Results

In Table I the experimental bubble-point pressure as a function of temperature is given for eight isopleths. These data are plotted in Figure 1. The dotted line represents the solid-liquid boundary for propane mole fractions greater than 0.56. This line has been established within an accuracy of  $\pm 0.5$  K. At lower propane concentrations the bubble-point measurements were started at the lowest pressure possible to be measured by the pressure gauge.

All curves for constant composition can be approximated by third-order polynomials. From these polynomials  $P$ - $x$  sections can be calculated at any temperature in the investigated temperature range. Some of the calculated isotherms are presented in Figure 2.

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**Table I. Vapor-Liquid Equilibria in the System Propane (1) + Eicosane (2): Bubble-Point Pressure as a Function of Temperature for a Given Mole Fraction  $x_1$** 

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
$x_1 = 0.9497$									
279.29	0.552	291.65	0.777	306.68	1.132	321.61	1.582	341.56	2.372
279.75	0.562	295.64	0.862	306.65	1.127	324.58	1.682	344.47	2.507
281.71	0.592	298.67	0.927	308.64	1.182	328.57	1.832	347.60	2.662
283.68	0.627	300.63	0.972	310.61	1.237	333.51	2.027	353.56	2.967
285.70	0.662	302.54	1.022	313.59	1.322	336.55	2.152	358.56	3.247
287.38	0.697	304.61	1.077	317.57	1.447	339.54	2.282		
$x_1 = 0.8597$									
288.24	0.639	303.15	0.934	319.04	1.338	335.54	1.883	351.03	2.513
291.16	0.689	306.14	0.999	323.10	1.463	338.09	1.979	358.06	2.848
294.19	0.744	309.09	1.074	326.10	1.556	340.53	2.073		
297.17	0.804	313.08	1.173	329.08	1.653	343.07	2.174		
300.16	0.869	316.06	1.253	333.07	1.789	346.09	2.298		
$x_1 = 0.7552$									
293.70	0.642	306.09	0.862	322.05	1.222	338.08	1.672	350.02	2.067
296.13	0.682	309.05	0.922	325.13	1.302	338.09	1.672	353.12	2.182
299.13	0.732	312.02	0.987	328.09	1.382	341.05	1.762	358.02	2.367
302.07	0.782	314.99	1.052	331.06	1.462	344.02	1.862		
306.08	0.862	318.06	1.122	334.03	1.552	347.04	1.967		
$x_1 = 0.6555$									
298.11	0.597	313.10	0.842	328.09	1.142	343.04	1.497	357.99	1.917
301.12	0.642	316.07	0.897	331.04	1.207	346.07	1.582		
304.09	0.687	319.06	0.952	334.02	1.277	349.03	1.657		
307.00	0.737	321.99	1.012	337.11	1.347	352.07	1.742		
310.12	0.787	325.07	1.077	340.04	1.442	355.06	1.832		
$x_1 = 0.5681$									
300.11	0.539	315.12	0.744	327.03	0.936	342.07	1.226	358.07	1.581
303.11	0.574	318.05	0.789	330.05	0.991	345.10	1.286		
306.10	0.614	321.08	0.839	333.08	1.046	348.07	1.351		
309.14	0.654	321.09	0.836	336.06	1.106	351.09	1.421		
312.06	0.699	324.06	0.886	339.04	1.161	354.07	1.486		
$x_1 = 0.4509$									
303.10	0.460	317.07	0.605	331.10	0.774	345.11	0.974	358.05	1.179
306.08	0.490	320.05	0.640	334.08	0.814	345.11	0.969		
309.11	0.520	323.08	0.675	337.05	0.854	348.03	1.014		
312.08	0.550	326.05	0.710	339.08	0.884	351.06	1.064		
314.09	0.574	328.07	0.735	342.03	0.924	354.04	1.109		
$x_1 = 0.3657$									
311.13	0.403	323.06	0.508	335.04	0.623	347.11	0.757	358.07	0.892
314.05	0.428	326.04	0.533	338.05	0.657	350.03	0.792		
317.09	0.453	329.06	0.563	341.08	0.687	353.06	0.827		
320.00	0.478	332.05	0.593	344.03	0.722	356.04	0.862		
$x_1 = 0.2540$									
338.00	0.415	341.04	0.435	347.10	0.475	353.05	0.520		
338.19	0.414	343.04	0.450	349.06	0.490	355.53	0.540		
339.00	0.420	345.03	0.460	351.03	0.505	358.06	0.560		

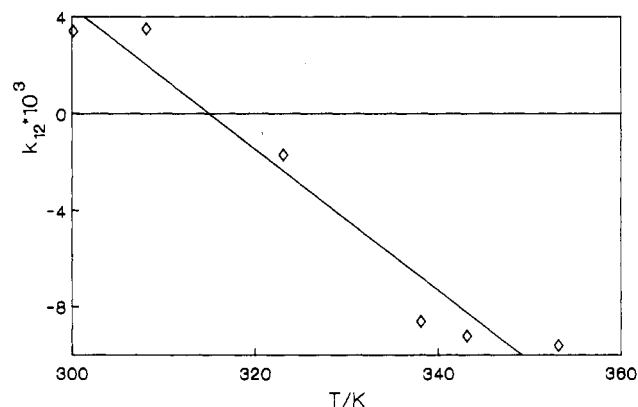
**Table II. Binary Interaction Parameters and Root Mean Square Relative Deviation of Pressure (RMSD(P)) for the System Propane + Eicosane for Six Temperatures Fitted with the Peng-Robinson EOS**

T/K	$k_{12}$	RMSD-(P)/%	T/K	$k_{12}$	RMSD-(P)/%
300.15	0.0034	1.5	338.15	-0.0086	4.1
308.15	0.0035	1.4	343.15	-0.0092	4.1
323.15	-0.0017	2.4	353.15	-0.0096	3.8

**Correlations.** Isothermal data for six temperatures have been fitted using the Peng-Robinson equation of state (2) with one adjustable binary interaction parameter,  $k_y$ . Each isotherm was fitted separately. The objective function for the optimization has been defined as follows:

$$OF = \sum \left( \frac{P_i^{\text{calcd}} - P_i^{\text{exptl}}}{P_i^{\text{exptl}}} \right)^2 \quad (1)$$

where  $P_i^{\text{exptl}}$  and  $P_i^{\text{calcd}}$  are the experimental and calculated pressure for a given temperature and liquid composition, respectively.

**Figure 3. Temperature dependence of the binary interaction parameter  $k_y$ .**

The results of the correlation for six isotherms are given in Table II. The values of the binary interaction parameters are small and change slightly with temperature. Figure 2 shows that deviations between calculation and experiment are bigger for

higher temperatures and higher propane concentration. The dependence of  $k_{12}$  on temperature can be seen in Figure 3.

Registry No. Eicosane, 112-95-8; propane, 74-98-6.

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## Partial Molar Volumes for Acetonitrile + Water

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The densities of acetonitrile + water were measured over the whole composition range at 5, 15, 25, 35, and 45 °C. The apparent and partial molar volumes and partial molar expansibilities were evaluated for both components as a function of mole fraction. In the aqueous-rich region, the partial molar volume of acetonitrile increases abruptly with the mole fraction. Only a small minimum of the partial molar volume was observed at very dilute solutions at lower temperatures, although a marked maximum was recognized in the partial molar expansibility curve. The partial molar volume of water vs composition curve, on the other hand, passes through a pronounced minimum in the organic-rich region, that is, in contrast with most alcohols + water.

#### Introduction

The present work is part of a systematic study on the volumetric behavior of aqueous organic mixtures. There have been reliable partial molar volume data for many nonelectrolytes in dilute aqueous solutions at 25 °C. However, relatively little data are available at other temperatures, and little attention has been given to the aqueous mixtures in which the mole fraction of water is small.

It is well known that the partial molar quantities vs composition curves have a characteristic minimum or maximum in the water-rich region for a number of aqueous solutions, typically alcohols + water (1). Previously we have reported that a pronounced minimum is also observed for the partial molar volume of water in organic regions for tetrahydrofuran (2) or *tert*-butyl alcohol (3) solutions, but not for the other alcohol solutions (2, 4-7). A similar minimum has been reported for acetonitrile solutions at 25 °C by Armitage et al. (8) and de Visser et al. (9). This paper describes the more precise density data for water (W) + acetonitrile (A) at various temperatures.

#### Experimental Section

Densities of the solutions were measured relative to densities of the pure solvents with an oscillating-tube densimeter (Anton Paar, DMA 60) operated in a phase-locked loop mode using two measuring cells (DMA 601). Details of the apparatus and procedure have been described elsewhere (3, 10). The temper-

ature of the cells was maintained within  $\pm 0.002$  °C by using a quartz temperature controller constructed in our laboratory. The densimeter was calibrated at each temperature with water (11) and dry air.

The acetonitrile was fractionally distilled and stored over molecular sieves 3A. The water content, determined by the Karl-Fischer method, was less than 0.002 wt %. The water was distilled using a quartz still and degassed before using. All solutions were prepared by successive addition of a stock solution or a pure component to a known quantity of another component up to about 50 wt %. The addition was carried out by weight in a mixing chamber connected to the density measuring cell with a Teflon tube and a flow pump.

#### Results and Discussion

The density differences between solution and pure water ( $\rho - \rho_w$ ) are summarized in Table I.

For the binary solution of components 1 and 2, the apparent molar volume  $V_{\phi_2}$  of component 2 is given by

$$V_{\phi_2} = x_1 M_1 (\rho_1 - \rho) / x_2 \rho_1 \rho + M_2 / \rho \quad (1)$$

where  $x$  and  $M$  are the mole fraction and the molar mass of the components and  $\rho_1$  and  $\rho$  are the densities of component 1 and the solution.

For dilute solutions the variation of  $V_{\phi_2}$  with molality  $m$  can be fitted with a linear equation:

$$V_{\phi_2} = V_2^\infty + A_2 m \quad (2)$$

where  $V_2^\infty$  is the limiting partial molar volume. The linear relation was found to hold up to about 0.5 and 1.2 mol kg<sup>-1</sup> for  $V_{\phi_A}$  in water and  $V_{\phi_w}$  in acetonitrile, respectively, at all temperatures studied. The parameters of eq 2, determined by the method of weighted least squares, are summarized in Table II. In general the limiting partial molar volumes are in good agreement with those from the literature. In the table are also reported the values of the excess limiting partial molar volume  $V_2^E$ , calculated by

$$V_2^E = V_2^\infty - V_2^* \quad (3)$$

where  $V_2^*$  is the molar volume of the pure solute. Both values of  $V_A^E$  and  $V_w^E$  are negative as well as those for aqueous solutions of polar nonelectrolytes. The characteristic feature of acetonitrile + water is that the deviation constants  $A_A$  and