

Figure 1. NMR spectrum of 1-nitropropene.

reason to suspect that our measurements for the titled material contain any errors above and beyond those associated with the measurement process. We must attribute the difference between our results and those published previously to the fact that the two studies might possibly represent different mixtures of isomers. We know that the composition of the isomeric mixture is temperature dependent. Two samples distilled and collected

at different temperatures will have slightly different compositions. For example, our calculated slope in the vapor pressure equation corresponds to a value of 1935.7 when phrased in terms of logarithms to the base 10, a deviation of 390 parts in 2306 or 17% from the previously reported value of 2306. This deviation is well outside of our experimental error.

#### Acknowledgment

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Registry No. 1-Nitropropene, 3156-70-5.

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## Virial Coefficients of Ethanol from 373.07 to 473.15 K

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Pressure, volume, and temperature were measured for the ethanol system at temperatures of 373.07, 388.17, 398.15, 400.81, 423.15, 448.15, and 473.15 K. The apparatus was a Kay-type PVT tube, in which the sample was compressed by a mercury piston. From the PVT data, second virial coefficients were computed. The apparatus and the calculational procedure were checked with both toluene and tetramethylsilane systems in order to verify the results reported herein. Our second virial coefficients and those from the literature were compared with predictions from the Tsonopoulos correlation. In the course of this investigation, the critical point of ethanol was checked, as well as the normal boiling point.

#### Introduction

Ethanol is an interesting compound as part of a binary system because of its high acentric factor, 0.644 (1), and the many nonideal systems formed (2). This investigation was undertaken in the hopes of preparing mixtures of ethanol with various members of the dimethylsiloxane series for measurements of mixture second virial coefficients. However, our apparatus was found to be unsuitable because of the difficulty of loading a mixture of known composition into our cell with a vacuum line where the molecular weight of one or both of the compounds is small and the compound is a liquid at room temperature. Therefore, this effort was abandoned, and this note reports the ethanol data obtained.

Dymond and Smith (3) present very few data for the second virial coefficients of ethanol, as compared to other compounds. There have been only three previous investigations (4-6), and their data range from 313.15 to 399.4 K. As usual, there is much scatter; in the neighborhood of 333 K, values reported are -1.285 (5), -1.522 (6), and -1.988 (4) m<sup>3</sup> kmol<sup>-1</sup>.

#### Experimental Section

**Materials.** Ethanol was obtained as absolute 200 proof spectrometric grade from AAPER Alcohol and Chemical Co., Louisville, KY 40214. It was dried over activated silica gel.

**Apparatus.** Our PVT apparatus was developed by Kay (7) and has been reported upon in a recent series of papers (8, 9). Briefly, a sample of pure ethanol was loaded from a vacuum line into the experimental tube, which is composed of two precision-bore glass tubes of differing diameters. The volume of this tube was determined by mercury weighings. The ethanol sample was confined by mercury in the experimental tube, which was attached via a compressor block to a pressure measuring system. The tube temperature was maintained constant by condensing vapors inside a vapor jacket; the temperature was measured by a thermocouple. Details of the experimental procedure, the calculational procedure, and the apparatus are well documented in the literature, and the interested reader is referred to the most recent references (10, 11).

#### Results and Discussion

This section discusses in turn the measurements of the normal boiling point of ethanol, critical point, and the PV iso-

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Table I. Critical Constants of Ethanol

ref	$T_c$ , K	$P_c$ , kPa
this work	513.95	6129
1	513.92	6137
13	513.98	6131

therms. The second virial coefficients of ethanol are then presented and discussed. Second virial coefficients for toluene and tetramethylsilane were obtained in this apparatus in order to verify the calculational and experimental procedures involved, and are reported elsewhere (11).

**Normal Boiling Point.** The normal boiling point of ethanol was determined in a Swietoslowski ebulliometer (12), which was calibrated with isooctane just before the determination. Our value of 351.46 K agrees to within 0.02 K of the literature value of 351.44 K (1).

**Critical Point of Ethanol.** The critical point of ethanol was measured as a check on the PVT apparatus, purity of compound, and method of data reduction. Table I presents our determination of the critical point, along with the literature values (1, 13). Agreement is excellent, 0.03 K for the critical temperature and 0.13% or better for the critical pressure.

**Pressure-Volume-Temperature.** The PVT relations of ethanol were determined in our apparatus for seven temperatures, ranging from 373.07 K (99.92 °C) to 473.15 K (200.00 °C). These data are in Table II, along with the value of the compressibility factor  $Z$ , computed as the product  $PV$  divided by the product  $RT$ , with the gas constant  $R$  taken as 8.31441 kPa m<sup>3</sup> kmol<sup>-1</sup> K<sup>-1</sup>. The molecular weight of ethanol is 46.07 kg kmol<sup>-1</sup> (1). All the latest standards and scales were used, e.g., the IPTS-68 for temperatures. The bubble-dew point differences were also measured and were found to be lower than 0.1 bar.

We estimate the precision of our temperature measurements to be  $\pm 0.005$  K, and the accuracy  $\pm 0.1$  K, although our literature checks indicate that this is a conservative number. The precision of our pressure measurements is  $\pm 0.001$  bar; all measurements reported (except the critical pressure and bubble-dew point pressures) were taken with atmospheric manometers. The accuracy of our pressure measurements is estimated at  $\pm 0.007$  bar, however. The greatest error in our pressure determination arises from the expansion of the confining mercury with temperature. The temperature of the mercury in our apparatus varies from the hot sample temperature (Table II) inside the experimental tube to room temperature inside the cylinder block. Note that our critical point pressure checked the literature to 0.13%, another measure of our pressure accuracy.

The volume of the sample was determined from a cathetometer reading of the mercury-sample meniscus. Our cathetometer could be read to  $\pm 0.001$  cm, with  $\pm 0.005$ -cm accuracy, which limited the accuracy of the volume readings to 0.25% in the smaller tube section and 0.05% in the larger section. The mass of the sample was determined from the PVT data by adjusting the number of moles so that the  $Z$  vs.  $1/V$  curve extrapolated to unity at zero pressure (8-10).

**Second Virial Coefficients.** The PVT data in Table II were used to compute the second virial coefficients of ethanol at the temperature of each isotherm, using the volume series

$$Z = 1.0 + B/V \quad (1)$$

The computational procedure is to find the number of moles of sample by adjusting the intercept in eq 1 to unity. Hence, any adsorption effects are negligible. Then  $B$  is found by least squares from eq 1, using only those points that are linear, as determined by standard statistical tests. Further details are in the literature, the most recent references being ref 10 and 11. These second virial coefficients are in Table III; also included are values of the 95% confidence limits. Our virial coefficients

Table II. PVT Relations of Ethanol

$P$ , kPa	$V$ , m <sup>3</sup> kmol <sup>-1</sup>	$Z$	$P$ , kPa	$V$ , m <sup>3</sup> kmol <sup>-1</sup>	$Z$
$T = 373.07$ K (99.92 °C)					
170.71	17.222	0.9478	212.98	13.620	0.9352
180.52	16.206	0.9432	222.14	12.977	0.9294
190.79	15.344	0.9438	231.24	12.418	0.9257
201.80	14.410	0.9375			
$T = 388.17$ K (115.02 °C)					
177.53	17.419	0.9582	246.32	12.382	0.9451
192.24	16.071	0.9573	275.11	11.003	0.9379
205.70	14.964	0.9538	312.60	9.554	0.9253
221.10	13.876	0.9506	363.37	8.065	0.9080
$T = 398.15$ K (125.00 °C)					
55.13	59.343	0.9883	315.79	9.897	0.9442
72.70	44.937	0.9868	326.35	9.543	0.9408
93.45	34.898	0.9851	336.47	9.228	0.9379
114.85	28.248	0.9800	346.86	8.925	0.9352
136.41	23.672	0.9754	374.28	8.209	0.9282
280.83	11.216	0.9515			
$T = 400.81$ K (127.66 °C)					
187.07	17.185	0.9647	283.62	11.136	0.9478
204.38	15.714	0.9638	336.81	9.268	0.9367
227.12	14.079	0.9595	382.35	8.067	0.9255
248.00	12.844	0.9558			
$T = 423.15$ K (150.00 °C)					
75.48	46.255	0.9924	310.95	10.926	0.9657
93.65	37.221	0.9908	322.78	10.533	0.9664
113.30	30.688	0.9883	336.60	10.065	0.9630
132.11	26.242	0.9854	349.46	9.674	0.9609
151.71	22.795	0.9830	361.81	9.329	0.9593
170.99	20.146	0.9791	386.70	8.689	0.9550
297.70	11.445	0.9685			
$T = 448.15$ K (175.00 °C)					
61.43	60.425	0.9962	179.72	20.453	0.9865
83.01	44.623	0.9941	327.49	11.104	0.9760
101.08	36.664	0.9946	352.75	10.291	0.9742
131.12	28.218	0.9930	380.10	9.526	0.9717
155.62	23.666	0.9884			
$T = 473.15$ K (200.00 °C)					
56.81	68.911	0.9951	173.34	22.425	0.9881
77.90	50.406	0.9981	191.66	20.207	0.9845
101.05	38.725	0.9947	323.61	11.970	0.9847
124.77	31.403	0.9959	347.44	11.126	0.9827
148.97	26.216	0.9927	372.10	10.364	0.9803

Table III. Second Virial Coefficients of Ethanol

$T$ , K	$B$ , m <sup>3</sup> kmol <sup>-1</sup>	95% confidence limit,		$T$ , K	$B$ , m <sup>3</sup> kmol <sup>-1</sup>	95% confidence limit,	
		m <sup>3</sup> kmol <sup>-1</sup>	m <sup>3</sup> kmol <sup>-1</sup>			m <sup>3</sup> kmol <sup>-1</sup>	m <sup>3</sup> kmol <sup>-1</sup>
473.15	-0.196	$\pm 0.067$		398.15	-0.569	$\pm 0.027$	
448.15	-0.280	$\pm 0.024$		388.17	-0.625	$\pm 0.086$	
423.15	-0.378	$\pm 0.022$		373.07	-0.965	$\pm 0.202$	
400.81	-0.583	$\pm 0.075$					

are plotted in Figure 1, along with the literature data of the three earlier investigations (3-6). The scatter in the earlier investigations previously alluded to is very evident. Our  $B$  values seem to join closely with those of all three prior investigators in the region 338-401 K (115-128 °C).

Tsonopoulos (14) correlated the second virial coefficients of hydrogen-bonding compounds such as alcohols by adding a third empirical term  $f^{(2)}$  to the standard Pitzer-Curl (15) correlation

$$BP_c/(RT_c) = f^{(0)} + \omega f^{(1)} + f^{(2)} \quad (2)$$

$$f^{(2)} = a/T_r^6 - b/T_r^8 \quad (3)$$

where  $a$  for the alcohols is 0.0878 and  $b$  is a positive constant that is a function of the dipole moment. Tsonopoulos discarded the data of Hanks and Lambert (4) in the course of his corre-

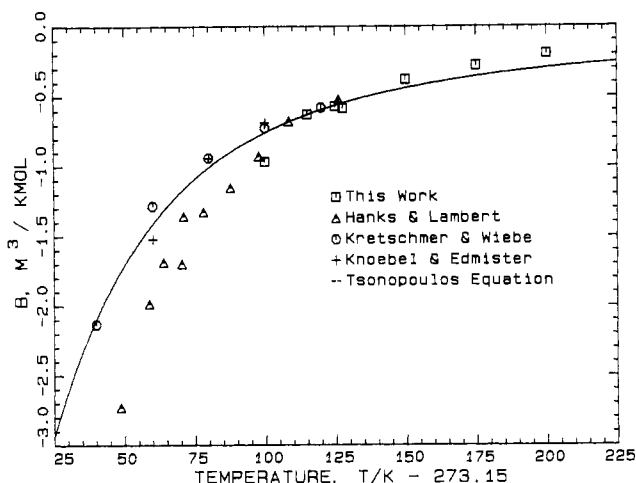


Figure 1. Second virial coefficients of ethanol. Curve is from the Tsonopoulos correlation, eq 2 and 3.

lation. His value of  $b$  for ethanol is 0.0572, and the resulting line is also shown in Figure 1. We reoptimized the constant  $b$  by using the five points of Kretschmer and Wiebe (5), the three points of Knoebel and Edmister (6), and our seven points. We found that with the latest physical constants (1), the value of  $b$  for ethanol should be 0.0532; this shift is not deemed significant in view of the scatter in Figure 1 and in view of the small data base.

#### Glossary

$a$	parameter in eq 3, 0.0878 for ethanol (14)
$b$	parameter in eq 3, 0.0572 for ethanol (14)
$B$	second virial coefficient, $\text{m}^3 \text{kmol}^{-1}$

$f^{(0)}, f^{(1)}, f^{(2)}$	functions of reduced temperature in eq 2 (14)
$P$	pressure, kPa
$P_c$	critical pressure, kPa
$R$	gas constant, $8.31441 \text{ kPa m}^3 \text{kmol}^{-1} \text{K}^{-1}$
$T$	temperature, K
$T_c$	critical temperature, K
$T_r$	reduced temperature, $T/T_c$
$V$	volume, $\text{m}^3 \text{kmol}^{-1}$
$Z$	compressibility factor ( $PV/RT$ )

Registry No. Ethanol, 64-17-5; toluene, 106-88-3; tetramethylsilane, 75-76-3.

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## Viscosity of Molten Sodium Salt Hydrates

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**Viscosity of molten sodium salt hydrates,  $\text{NaOH}\cdot\text{H}_2\text{O}$ ,  $\text{Na}(\text{CH}_3\text{COO})\cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$ , and  $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$ , suitable for energy storage applications has been determined with a modified Ubbelohde viscometer. The temperature dependence shows an Arrhenius behavior which can be represented by an equation  $\eta = A \exp(E_v/RT)$ , above the melting points of the salt hydrates studied. The values of activation energy ( $E_v$ ) of viscous flow are reported.**

Hydrated salts (1-3) have been extensively investigated for thermal energy storage applications due to their high energy storage densities and low cost. Some of the salts recommended for this purpose show great supercooling as well as glass-forming tendencies which are undesirable. In the case of tabular crystals, such as those of sodium acetate trihydrate, supercooling is considerable. Viscosity is an important parameter (4), as it influences the crystallization of such salts. Both the viscosity data as well as a generalized empirical corresponding states relationship which could be used to calculate the viscosities of a given class of melts outside the existing experimental range are lacking in the literature. The present investigation has been designed to determine the viscosity of

the most commonly recommended salt hydrates suitable for energy storage applications, so that the utility of each can be properly assessed.

#### Theoretical and Experimental Section

A modified Ubbelohde viscometer (5) has been used in the present investigation. The salient feature of this design is that the flow of melt through the capillary is caused by its hydrostatic pressure only.

Poiseuille's equation applicable to the capillary flow is

$$v = \eta/\rho = at - b/t \quad (1)$$

Values of the constants  $a$  and  $b$  have been calculated by using standard values of the density and the viscosity of carbon tetrachloride and benzene, available in the literature (6). With the least-squares method of curve fitting, new constants  $A$  and  $B$  for the instrument are calculated. These constants have been used to define a new correlation between viscosity and time, which can be represented as follows:

$$\eta = A + Bt \quad (2)$$

For the viscometer used, the values of constants  $A$  and  $B$  are  $-0.363$  and  $0.0075$ , respectively. The accuracy of this