Viscosity and Compression of Ethanol–Water Mixtures for Pressures up to 40 000 psig

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Viscosity and compression data have been obtained for ethanol–water mixtures at 25, 35, 45, and 55 °C and for pressures up to 40 000 psig. Viscosity data are observed to exhibit a maximum with composition while the compression data exhibit a minimum. For the higher temperatures (45 and 55 °C) several new complicating features such as points of inflection and second maxima or minima, are indicated. Six equations of state have been tested and compared for their ability to predict volumes under different conditions of pressure, temperature, and composition.

Viscosity and PVT behavior of liquids under atmospheric pressure has been a subject of numerous investigations, but relatively few works have been reported on liquid behavior under high pressure. Furthermore, most high pressure data that have been reported deal with pure components (*2, 4, 9*) and liquid mixtures have not received wide attention (*1, 6, 11*).

The present investigation was undertaken to obtain viscosity and compression data for ethanol–water mixtures under high pressure. The existing state of knowledge on these properties of ethanol–water mixtures under pressure may be summarized as follows: (a) density data (i) Moesveld (*11*) at 500, 1000, and 1500 atm and at 25 °C, (ii) Stutchbury (*15*) at 1000 atm and 30 °C, (iii) Hamann and Smith (*6*) at 1000 atm and 30 °C; (b) viscosity data, Abaszade et al. (*1*) for pressures up to 1200 bars and temperatures 0–200 °C.

The data reported in this paper have been obtained in a visco-compression meter that permits concurrent measurement of the properties of interest. Data have been obtained for a full range of compositions at four tempertures and for pressures up to 40 000 psig.

Experimental Method

The details of the experimental setup are reported elsewhere (*5, 17*). The equipment used was a refinement of the setup used previously in our laboratory for high pressure measurements (*5*). Compression was measured by piston displacement and viscosity by the falling cylinder technique.

The compression meter consisted of a stainless steel tube, 61.625 in. long, 0.25 in. nominal o.d. and 0.083 in. i.d. A 1 in. long, 0.0625 in. diameter magnet was positioned on top of the rubber piston that separated oil from the test liquid. The position of the magnet was determined by a magnetically sensitive reed switch.

The viscometer consisted of a stainless steel tube, 57.56 in. long, 0.5625 in. o.d. and 0.1875 in i.d. The plummet used was an Alnico magnet, 1.246 in. long with 0.1711 in. diameter. A digital counter coupled with two reed switches was used to determine the time of fall.

To determine density and viscosity values under atmospheric pressure, a double capillary pycnometer (*16*) and a Cannon–Fenske viscometer were utilized.

Calibration Procedure

The pycnometer was calibrated at the four temperature levels by using freshly distilled water as the standard. The standard density values were obtained from the International Critical Tables (*8*). In the compression setup, the occupied volume of the system under atmospheric pressure, V_0, was established directly through mercury displacement.

The Cannon–Fenske viscometer was calibrated by using the viscosities of water taken from the International Critical Tables (*8*) and of alcohol taken from Bingham (*3*). A two constant viscosity equation was employed,

$$\eta = C_1 t - C_2/t \qquad (1)$$

where t is the time of fall. The constants C_1 and C_2 are obtained by calibration.

The instrument constant K in the viscometer equation

$$\eta = K(\sigma - \rho)t \qquad (2)$$

where σ and ρ are densities of the plummet and test fluid, respectively, was determined separately for each temperature and composition level under investigation. The values of K for mixtures were calculated by using previously established Cannon–Fenske viscosities as the standards. The value of K was assumed to be independent of pressure since high pressure viscosity standards are not available.

In all experimental work, distilled water from a still manufactured by the Baumstead Sybron Corporation was used. The ethanol used was obtained from Consolidated Alcohol Limited and had a quaranteed purity of 99.90%. The mixtures of ethanol and water were prepared by taking appropriate weights of the two materials.

Error Estimates

High pressure compression measurements can have errors resulting from (i) difficulties in establishing basic vessel dimensions, (ii) changes in vessel dimensions due to changes in pressure and temperature, (iii) difficulties in locating the precise position of the rubber piston. While the first and the third error sources can only be minimized, as has been attempted in the present work, the second source of error can be essentially eliminated. This was accomplished by using thick-walled cylinder deformation formulas for estimating correct equipment size for each temperature and pressure. High pressure viscosity values have potential sources of errors in determination of the calibration constant, fluid and plummet density, and the fall time. These errors can only be minimized but not eliminated. Table I summarizes relevant accuracy and error information.

Table I. Error Estimates

Temperature of the bath	±0.5 °C
Pressure gauge	±50 psi
Composition of mixture	±0.1%
Time of fall	±0.01 s
Density by pycnometer	±0.01%
Viscosity by Cannon–Fenske viscometer	±0.37%
Compression	±1.20%
Viscosity by falling cylinder method	±1.25%

Table II

Pressure, psig	Compression $-\Delta V/V_0 \times 100$	Viscosity, cP
$T = 25$ $v_0 = 1.0029$		
$X = 0.00$ $\eta_0 = 0.895$		
5 000	1.57	0.855
9 900	2.89	0.849
15 100	4.18	0.811
19 900	5.27	0.814
25 200	6.39	0.787
30 600	7.41	0.814
35 600	8.29	0.840
40 400	9.17	0.853
$T = 25$ $v_0 = 1.0233$		
$X = 0.05$ $\eta_0 = 1.426$		
5 400	1.36	1.403
10 200	2.60	1.388
15 300	3.82	1.490
20 400	4.93	1.502
25 050	5.85	1.421
30 450	6.85	1.407
34 800	7.60	1.337
40 100	8.47	1.407
$T = 25$ $v_0 = 1.0389$		
$X = 0.10$ $\eta_0 = 1.973$		
5 300	1.43	1.976
9 850	2.68	2.024
15 000	3.79	2.021
19 950	4.84	2.063
25 150	5.84	2.077
30 600	6.75	2.111
35 250	7.56	2.130
40 600	8.37	2.152
$T = 25$ $v_0 = 1.0542$		
$X = 0.15$ $\eta_0 = 2.310$		
5 400	1.60	2.432
10 250	2.88	2.513
15 050	3.99	2.605
20 100	5.12	2.666
25 000	6.12	2.742
30 100	7.13	2.826
35 200	8.01	2.903
40 800	9.22	2.975
$T = 25$ $v_0 = 1.0711$		
$X = 0.20$ $\eta_0 = 2.453$		
5 300	1.60	2.604
10 000	2.88	2.766
14 750	4.05	2.892
19 650	5.13	3.038
25 100	6.24	3.194
30 100	7.15	3.317
35 000	8.01	3.454
40 750	8.89	3.610
$T = 25$ $v_0 = 1.1058$		
$X = 0.30$ $\eta_0 = 2.467$		
5 250	1.49	2.702
9 900	2.84	2.941
14 700	4.12	3.183
19 550	5.30	3.419
25 150	6.51	3.709
30 100	7.46	3.961
34 850	8.34	4.246
39 650	9.17	4.506
$T = 25$ $v_0 = 1.1370$		
$X = 0.40$ $\eta_0 = 2.250$		
5 100	2.14	2.537
10 000	3.85	2.836
14 600	5.21	3.110
19 700	6.52	3.403
25 050	7.73	3.730
31 000	8.95	4.080
35 000	9.70	4.338
40 000	10.55	4.685
$T = 25$ $v_0 = 1.1644$		
$X = 0.50$ $\eta_0 = 2.025$		
5 400	2.53	2.332
10 550	4.42	2.624
15 000	5.79	2.928
20 250	7.20	3.206
25 000	8.33	3.510
30 100	9.47	3.846
34 950	10.41	4.219
$T = 25$ $v_0 = 1.1896$		
$X = 0.60$ $\eta_0 = 1.823$		
5 300	3.05	2.114
10 000	4.93	2.379
14 850	6.52	2.672
20 000	17.97	2.997
24 950	9.20	3.284
30 200	10.34	3.623
36 300	11.58	4.066
$T = 25$ $v_0 = 1.2364$		
$X = 0.80$ $\eta_0 = 1.438$		
5 700	3.19	1.723
10 050	5.46	1.990
14 950	7.19	2.187
19 600	8.66	2.440
24 650	10.04	2.740
29 650	11.28	3.042
33 050	12.04	3.217
$T = 25$ $v_0 = 1.2742$		
$X = 1.00$ $\eta_0 = 1.099$		
5 350	3.27	1.196
9 900	5.54	1.128
15 100	7.60	1.281
19 800	9.14	1.307
24 700	10.60	1.567
29 550	11.81	1.715

Experimental Results

Compression and viscosity of 11 ethanol–water mixtures were measured at six to eight different pressures (up to 40 000 psig) for temperatures of 25, 35, 45, and 55 °C. In all, 334 data points were established. Table II presents data for 25 °C only. The complete table of data has been deposited on microfilm with the Journal of Chemical and Engineering Data. See paragraph at end of paper regarding supplementary material.

The data obtained in this investigation were checked for external consistency against available literature, as follows.

A. Compression Data. The density of alcohol–water mixtures under atmospheric pressure, as obtained by the pycnometer, agreed within ±0.3% with the data reported in Perry's Chemical Engineers' Handbook (*14*). High pressure density data were compared to existing literature sources (*6, 9, 11, 15*) and found to agree well. Typical comparisons are shown in Figures 1 and 2. As seen from Figure 1, pure water data agree extremely well

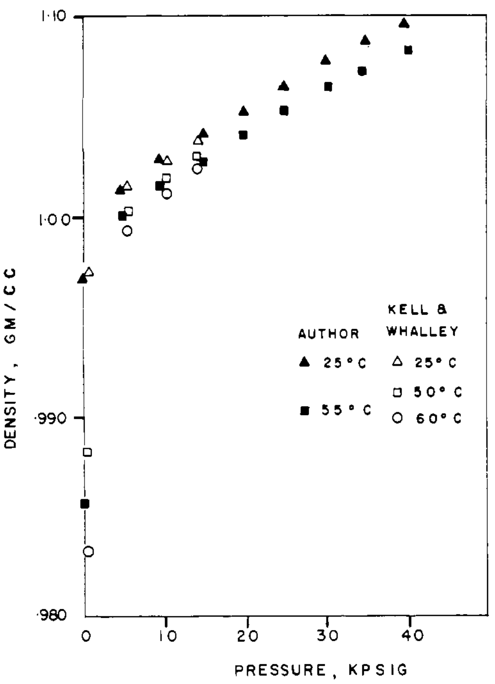

Figure 1. Comparison of high pressure density data for pure water.

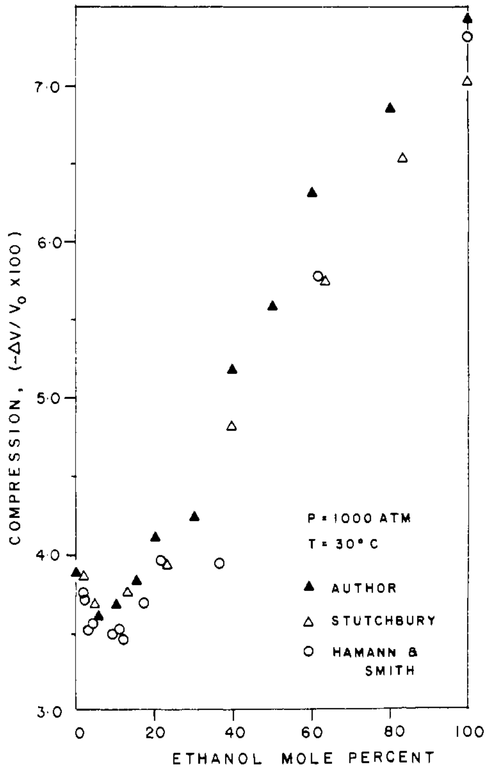

Figure 2. Comparison of compression data for ethanol-water mixtures at 1000 atm.

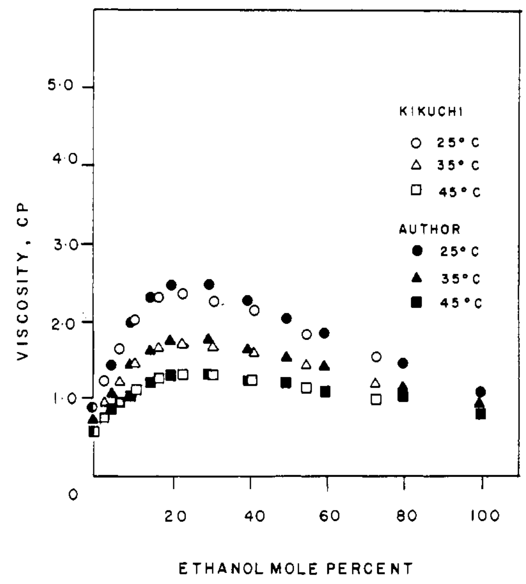

Figure 3. Comparison of viscosity data for ethanol-water mixtures at atmospheric pressure.

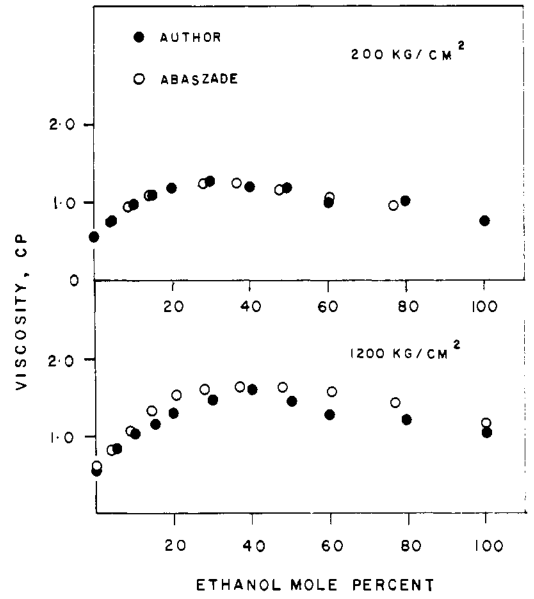

Figure 4. Comparison of viscosity data for ethanol-water mixtures at 50 °C.

with those of Kell and Whalley (*9*). Previous data on mixtures under pressure are rather limited. Figure 2 indicates that good agreement with previously reported data is obtained in the low ethanol fraction range.

B. Viscosity Data. The viscosity of alcohol-water mixtures under atmospheric pressure was compared to the data of Bingham (*3*) and Kikuchi and Oikawa (*10*). Good agreement was observed, as shown for Kikuchi and Oikawa comparison in Figure 3. Abaszade et al. (*1*) seem to be the only researchers who have measured viscosity of alcohol-water mixtures under pressures comparable to those applied in the present work. Figure 4 displays a comparison at two pressure levels. Agreement between the two data sets is good at lower pressures, and only satisfactory at higher pressures.

Discussion of Results

A. Compression Data. The compression data for ethanol-water mixtures display a minimum at from 5 to 10 mole % alcohol. This kind of behavior has been reported for many other binary systems involving water (*13*). Newitt and Weale (*12*) have attempted to correlate existence of the compression minimum to other mixture properties such as ultrasonic velocity and partial molar volume. Hamann and Smith (*6*) have tried to relate the minima to excess volume. The present data seem to indicate the presence of other features at higher mole percent alcohol. These include points of inflection and a second minimum in certain cases.

Table III. Equations of State

Name	Form of the equation	Average absolute error[a]
Tait	$PV_0/(V_0 - V) = A + BP$	5.75×10^{-4}
Bridgman	$V_0 - V = A + B \ln P$	41.0×10^{-4}
Hudleston	$\ln [V^{2/3}P/(V_0^{1/3} - V^{1/3})] = A + B(V_0^{1/3} - V^{1/3})$	4.13×10^{-4}
Chaudhuri	$P = A[(V_0/V)^4 - (V_0/V)^2]^B$	4.52×10^{-4}
Modified Chaudhuri I	$P = A[(V_0/V)^4 - (V_0/V)^2]$	15.1×10^{-4}
Modified Chaudhuri II	$P = A + B[(V_0/V)^4 - (V_0/V)^2]$	6.26×10^{-4}

[a] Defined as $\sum_{T,X}\{\sum_P|(V/V_0) - (\bar{V}/V_0)|\}/n$ where V_0 is the initial sample volume, V is the experimental volume, $\bar{V}$ is the predicted volume, and n is the total number of data points; $n = 334$.

For each temperature and composition, the compression data were correlated against pressure. Six equations of state, shown in Table III, were tested for their goodness of fit. Four of the equations tested were from the literature, while the other two were empirical variations of the Chaudhuri equation. The constants for each of the equations were determined by linear least-squares method. All six equations were found to yield acceptable fits judged on the basis of criterion such as correlation coefficient and F-ratio. To compare the ability of these equations to predict volumes under different pressures, the regression constants for each equation were used to predict volumes for each experimental data point. The basis for comparison was an average absolute error defined in Table III. The method used to obtain predicted volumes was direct iteration. This method failed for the Hudleston equation. However, a decreasing step size trial-and-error procedure was successful.

Results presented in Table III show that there are obvious differences in the ability of various equations to predict volume. Either the Hudleston or Chaudhuri equation is to be recommended. Both of these are two constant equations though Chaudhuri's equation has a simpler form. The Bridgman equation, while simple in form, gives poor predictions.

B. Viscosity Data. Viscosity data for ethanol–water mixtures exhibit a maximum with composition. The maximum shifts to higher ethanol fractions with pressure and does not shift significantly with temperature. As with compression data, the viscosity behavior starts to exhibit additional features for 45 and 55 °C. Existence of a second maximum at higher compositions is indicated, particularly for high pressure values.

The present data confirm the existence of a viscosity minimum with pressure for pure water as has been reported by previous investigators (*7*).

Glossary

A, B	constants in equations of state
C_1, C_2	instrument constants, eq 1
K	instrument constant, eq 2
P	pressure, psig
t	falling time of the cylinder, s
T	temperature, °C
v	specific volume, cm g^{-1}
V	volume of the liquid, cm^3
X	mole fraction of ethanol
η	viscosity of the liquid, cP
ρ	density of the liquid, g cm^{-3}
σ	density of the falling cylinder, g cm^{-3}

Subscript

0	at atmospheric pressure

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Supplementary Material Available: Compression and viscosity measurements (24 pages). Ordering information is given on any current masthead page.