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Ethanol Densities Between -50 And 20 °C

Mark R. Schroeder

Bruce E. Poling

Missouri University of Science and Technology, bruce.poling@utoledo.edu

David B. Manley

Missouri University of Science and Technology

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Table III. Comparison of Experimental and Calculated Values of $(D_{ij})_v^a$

	exptl	LN	LNI
$10^5(D_{11})_v$	1.45	1.48	1.47
$10^5(D_{12})_v$	0.09	0.19	0.15
$10^5(D_{21})_v$	0.09	0.04	0.40
$10^5(D_{22})_v$	1.66	1.71	1.85

^a Units: cm²/s.

the primary data in Table I. The density at the prefixed mean concentration, $d(\bar{C}_1, \bar{C}_2)$ and the density derivatives, H_i , are calculated by fitting the density data in Table I to an expansion about $d(\bar{C}_1, \bar{C}_2)$ by the method of least squares using the expression

$$d_{\text{calcd}} = d(\bar{C}_1, \bar{C}_2) + H_1(C_1 - 1.9) + H_2(C_2 - 0.1)$$

The average deviation between d_{calcd} and the experimental values was found to be ± 0.000005 . The Fortran program for this calculation was prepared by Dr. M. A. Loewenstein, formerly of this laboratory. Table II also contains the partial molal volumes, \bar{V}_i , and the refractive index derivatives, R_i . In this table, C_0 and \bar{V}_0 denote the concentration and the partial molal volume of water, respectively.

The results of the experiments were examined to determine whether the system had been gravitationally stable throughout the duration of diffusion. Values for gravitational criteria I and II (6, 8) were calculated for each experiment, and all experiments were found to satisfy these criteria.

Table III gives the comparison of experimental and calculated diffusion coefficients. For these calculations the activity coefficients were obtained (9) by assuming that the Harned relationship holds for this system. Both LN and LNI approximations give less satisfactory estimates for the cross-term diffusion coefficients compared to the case where the concentrations of two electrolytes are not too different. However, as in the cases of the H₂O-KCl-HCl and H₂O-NaCl-HCl systems, the LN approximation gives overall better values for the $(D_{ij})_v$'s. Thus, it appears that, for strong electrolyte systems, the LN approximation generally gives better estimates of diffusion coefficients than the LNI method.

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Ethanol Densities between -50 and 20 °C

Mark R. Schroeder, Bruce E. Poling,* and David B. Manley

Chemical Engineering Department, University of Missouri—Rolla, Rolla, Missouri 65401

The density of ethanol was measured between -50 and 20 °C to $\pm 0.01\%$. The measurements were made by using a procedure similar to ASTM D1217-54, "Standard Method of Test of Density and Specific Gravity of Liquids by Bingham Pycnometer". The results were correlated by the equation in $D = -0.215231 - (1.05037 \times 10^{-3})T - (7.837 \times 10^{-7})T^2 - (7.47 \times 10^{-9})T^3$ (D in g/cm³, T in °C).

Introduction

In order to measure densities with a vibrating tube densimeter, one must first calibrate the densimeter with a fluid for which densities are known to the desired accuracy. Above 0 °C, water is a suitable calibration fluid. Below 0 °C, water is not suitable and densities of the desired accuracy could not be found for any other common fluid. Thus, ethanol densities between -50 and 20 °C were measured to $\pm 0.01\%$ with a pycnometer technique. These new data will be useful for calibrating devices such as the vibrating tube densimeter.

Experimental Section

The experimental procedure was similar to ASTM D1217-54 (7). In this procedure a pycnometer (see Figure 1) is filled to the mark with water at a known temperature. The weight of the pycnometer thus filled minus the weight of the empty pycnometer allows calculation of the pycnometer volume. Ethanol densities can then be obtained by determining the weight of

ethanol required to fill the pycnometer to the mark at the desired temperature. In this work, the water used in the calibration was distilled in stainless steel, boiled, and then allowed to cool to room temperature before injection into the pycnometer. Ethanol was obtained as absolute ethanol and further purified by distillation over sodium metal and ethyl phthalate in water-free air (2). This purification method gave ethanol with a water content of 0.003 wt % as determined by a Karl Fischer analysis. For the water calibrations and ethanol measurements, temperature was measured with a Rosemount Model 162 platinum resistance thermometer with a calibration traceable to the NBS. The thermometer and the Mueller resistance bridge used were tested by measuring the triple point of water to ± 0.02 °C. Between -20 and 30 °C, a Neslab-RTE-8 circulating bath with a Bayley proportional band controller, Model 123, was used. At -30, -40, and -50 °C, a Neslab Endocal LT 50 bath was used. All measurements were made at least once in each of two different pycnometers.

Several modifications were required to extend the ASTM D1217-54 procedure to low temperatures. First, the volume of the bulb above the mark on the pycnometer was increased from <1 to 3.8 cm³. This allowed for expansion of the ethanol from -50 °C to room temperature. One problem that arose at the low temperatures was condensation of water on the inside of the pycnometer. This problem was eliminated by using a rubber serum stopper on the pycnometer during part of the procedure. In this procedure, a syringe was used to fill the pycnometer bulb with ethanol at room temperature. A serum stopper was placed in the pycnometer neck, a syringe needle

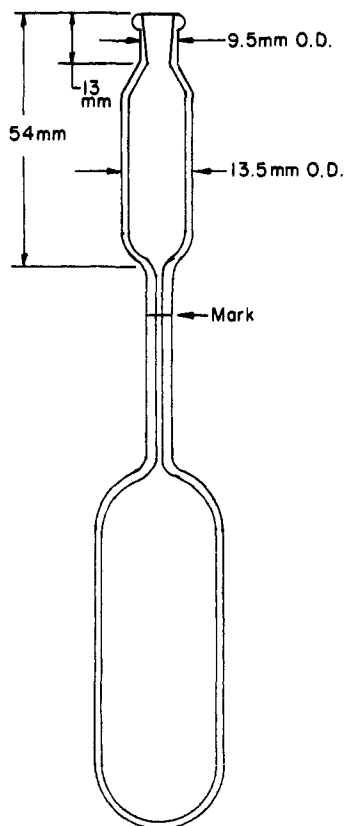


Figure 1. Pycnometer showing dimensions that deviate from ASTM D1217-54.

was inserted through the stopper, and the entire pycnometer was submerged in the low-temperature bath. This setup allowed for a series of ethanol injections as temperature equilibrium was approached without removing the stopper. When both temperature equilibrium was reached and the liquid level was at the mark, the rubber stopper was removed, the bulb above the mark was wiped dry, and the glass stopper was replaced. The pycnometer was then allowed to come to ambient temperature. Just before being weighed, the pycnometer was quickly opened and closed to equilibrate the pressure inside the pycnometer with the atmosphere. The pycnometer was then weighed.

A third modification in the ASTM D1217 procedure had to do with the method for correcting the volume change of the pycnometers due to thermal expansion of glass. The recommended value in the ASTM procedure for the cubical coefficient of thermal expansion of glass is 9.6×10^{-6} . Because the low temperatures used were far removed from the calibration temperatures, it seemed prudent to check this value experimentally. Water calibrations were done at least 6 times at three different temperatures (4, 10, and 20 °C) for both pycnometers. The resulting values of the thermal expansion coefficient were 9.2×10^{-6} and 10.4×10^{-6} . Thus, when the pycnometer volumes were correlated linearly with temperature, the experimental volumes generally deviated from the calculated values by about $\pm 0.001\%$. All else was the same as the ASTM D1217 procedure. In the calculations, the weight of the pycnometer, its contents, and the weights were corrected for buoyancy due to air.

Results and Discussion

Experimental densities are shown in Table I. These values were correlated by eq 1, where D is the density in g/cm^3 and

$$\ln D = -0.215231 - (1.05037 \times 10^{-3})T - (7.837 \times 10^{-7})T^2 - (7.47 \times 10^{-9})T^3 \quad (1)$$

Table I. Density of Ethanol as a Function of Temperature

temp, °C	density, g/cm ³	temp, °C	density, g/cm ³
20.03	0.789 26	-20.01	0.823 26
20.02	0.789 28	-20.01	0.823 28
10.00	0.797 89	-30.00	0.831 73
10.00	0.797 88	-30.00	0.831 71
-0.00	0.806 32	-30.00	0.831 79
-0.01	0.806 30	-30.02	0.831 74
-5.00	0.810 60	-40.00	0.840 28
-5.00	0.810 62	-40.00	0.840 39
-10.00	0.814 82	-40.00	0.840 31
-10.00	0.814 83	-40.00	0.840 29
-15.00	0.819 04	-49.98	0.848 99
-15.00	0.819 03	-50.00	0.848 91
-19.97	0.823 25		

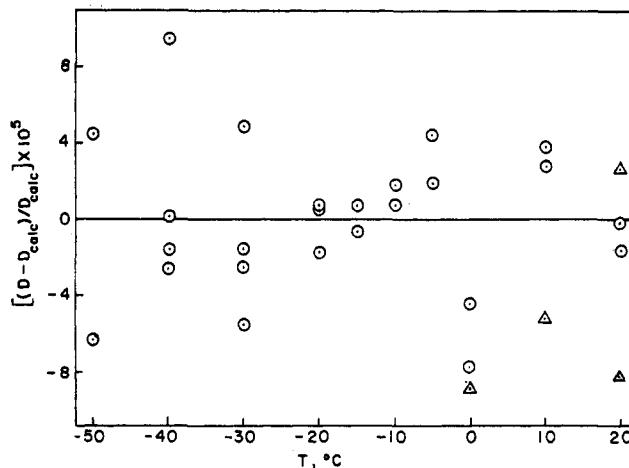


Figure 2. Deviations of densities from eq 1. Circles are experimental points in Table I; triangles are literature values at 0 °C (4), 10 °C (5), and 20 °C (3, 5).

T is in °C. Deviations of the experimental values from this correlation are shown in Figure 2. The variation of replicate points at -20 °C and above is less than $\pm 0.002\%$. For temperatures less than -20 °C, this variation increases to about $\pm 0.005\%$. Considering these variations, the temperature variations, calibration uncertainties, and probable purity, the experimental ethanol densities have an estimated uncertainty of $\pm 0.01\%$. This estimate is based on a value of $2 \times 10^{-5} \text{ g}/\text{cm}^3$ for 3 times the standard deviation of the data points about the correlation. Literature values are also shown in Figure 2 at 0 °C (4), 10 °C (5), and 20 °C (3, 5). For temperatures of 20 °C and less, the values in ref 4 and 5 seem to be the most reliable of the data that were reported before 1970. This conclusion is supported by ref 6. The value reported by ref 3 in 1980 appears to be of comparable, if not higher, accuracy. The only ethanol densities reported in the literature for temperatures below 0 °C are 0.856 and 0.872 g/cm^3 at -59 and -78 °C, respectively (7). A linear extrapolation of the data in Table I gives densities of 0.856 47 g/cm^3 at -59 °C and 0.872 62 g/cm^3 at -78 °C.

Conclusion

Ethanol densities have been measured for temperatures between 20 and -50 °C. The uncertainty in these density values is thought to be about $\pm 0.01\%$ based on a 3σ value of $2 \times 10^{-5} \text{ g}/\text{cm}^3$. This information will allow ethanol to be used for calibration purposes in future low-temperature density measurements.

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Direct Determination of Enthalpy of Mixing for the Binary Gaseous System Methane–Carbon Dioxide by an Isothermal Flow Calorimeter

Alpha O. Barry, Serge C. Kallaguine,* and Rubens S. Ramalho

Department of Chemical Engineering, Laval University, Quebec, Quebec G1K 7P4, Canada

Enthalpies of mixing for the binary gaseous system methane–carbon dioxide were measured by an isothermal flow calorimeter at temperatures of 293.15, 305.15, and 313.15 K, with mole fractions of methane ranging from approximately 0.2 to 0.8. For the first two isotherms, the measurements were made at pressures of 0.507, 1.115, and 1.520 MPa (5, 11, and 15 atm, respectively). For the third isotherm, measurements were made at pressures of 0.507, 1.013, 1.520, 2.533, 3.546, and 4.600 MPa (5, 10, 15, 25, 35, and 45.4 atm, respectively). The experimental results were compared with those already available in the literature, as well as with predictions based upon the following equations of state: Benedict–Webb–Rubin (BWR), Redlich–Kwong, and the Redlich–Kwong equation with the modifications proposed by Jacoby and Robinson.

Introduction

Enthalpy data for pure compounds and mixtures are of fundamental importance in process design. They are also particularly important from a scientific point of view, owing to their utilization in verifying predictive methods for thermodynamic properties of mixtures. Such methods are based upon theories of molecular interaction.

It is necessary to determine data for the enthalpies of mixtures in the gaseous phase as functions of temperature, pressure, and mixture composition. The most direct method to obtain this network of data consists of the direct determination of heats of mixing, henceforth designated as excess enthalpies and denoted as H^E . The excess enthalpy of a mixture at constant temperature and pressure is defined as

$$H^E = \Delta H_m - \Delta H_m^{id} = [H_m - \sum_i x_i H_i]_{P,T} \quad (1)$$

Since for an ideal solution the heat of mixing is zero, i.e., $\Delta H_m^{id} = 0$, the excess enthalpy of a mixture is numerically equal to the heat of mixing of the pure components, i.e., $H^E = \Delta H_m$.

Although many calorimetric determinations of enthalpies of mixing for liquids are reported in the literature, relatively few data for gas mixtures are available. The experimental difficulties involved in the determinations in the gas phase, as well as the high cost of the pure components, are the reasons for this scarcity of data. The investigations of excess enthalpies in the gas phase are summarized as follows. The first determinations by Beenakker et al. (1–4) comprised the following

systems: CH₄–H₂, CH₄–Ar, H₂–N₂, H₂–Ar, Ar–N₂, He–CH₄, and He–Ar. Klein (5, 6) studied the system CH₄–N₂. Hejmadi et al. (7, 8) investigated the systems N₂–O₂, N₂–CO₂, and N₂–C₂H₆. Lee and Mather (9, 10) studied the systems N₂–CO₂ and CH₄–CO₂, and Altunin et al. (11) the system N₂–CO₂. In our laboratories, Ba et al. (12–14) obtained data for the systems N₂–O₂, N₂–C₂H₄, and C₂H₄–CO₂. This paper presents data for the system CH₄–CO₂ at temperatures of 293.15, 305.15, and 313.15 K, with mole fractions of methane ranging from approximately 0.2 to 0.8. For the first two isotherms, the measurements were made at pressures of 0.507, 1.115, and 1.520 MPa (5, 11, and 15 atm, respectively). For the third isotherm, measurements were made at pressures of 0.507, 1.013, 1.520, 2.533, 3.546, and 4.600 MPa (5, 10, 15, 25, 35, and 45.4 atm, respectively).

Experimental Procedure

The experimental procedure, as well as a detailed description of the equipment utilized in this investigation, has been reported in previous articles (7, 12–14). The two pure gases, CH₄ and CO₂, flow independently inside tubings of identical dimensions, arriving at the calorimeter at essentially the same temperature and pressure. The mixing of the two gases is accompanied by a temperature drop. To compensate for this temperature drop, a measured quantity of energy is supplied to the system by a Kepco Model SM-325-2A(M) power supply, with regulation to 0.01%. In this manner, the temperature difference between the two pure gases at the calorimeter inlet and the exit gas mixture is essentially brought to zero. The energy supplied is determined by measuring potential drops across standard calibrated resistors, utilizing a Leeds and Northrup K-5 potentiometer. Mole fractions of the gaseous constituents in the mixture were calculated from the measured values of individual flow rates.

Some improvements were performed with respect to the equipment described in the previous articles, including a forced-draft system for the calorimeter assembly and a disposal system for safe elimination of the gas mixtures to the atmosphere. The methane and the carbon dioxide were supplied by Lynde Co. of Canada and Air Liquid of Canada, respectively. The methane has a certified purity of 99%, containing 0.1% CO₂, 0.2% O₂, 0.2% N₂, 0.3% C₂H₆, and 0.2% C₃H₈. The carbon dioxide has a certified purity of 99.8%, containing 100 ppm of CO, 50 ppm of H₂, 100 ppm of H₂O, and approximately 0.2% N₂. The effect of the impurities in the gases was evaluated by utilizing Hejmadi's methods (7, 8) and found to be negligible.