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Solubility of Cyclopropane in Aqueous Solutions of Potassium Chloride

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An experimental apparatus was designed for measuring the solubility of gases in liquids at low pressure and temperatures. Accurate data for the solubility of gaseous cyclopropane in aqueous potassium chloride are reported. The data were taken at 273, 276, and 278 K, at KCl concentrations of 0, 0.5, 1.1, 1.5, and 10 g/L and at pressures up to cyclopropane hydrate formation conditions. Gas solubility followed Henry's law over the entire range of data. Reciprocal Henry's constants were fitted to an empirical relation in temperature and salt content and confidence limits are given for the relation.

Introduction

The solubility of gases in liquids is an area of active interest from both theoretical and practical standpoints. A knowledge of the solubility of gases is of practical importance in various industrial applications. The more important uses are in the gas–liquid separation processes of absorption and stripping. Another more specific application is in the experimental study of gas hydrate dissociation conditions, where reliable solubility data are required; this is the end goal for the present work, which restricts the range of solubility data.

Three previous papers report the solubility of cyclopropane in water; however, only the data of Hafemann and Miller (*1*) are in the temperature and pressure range of the present work. Inga and McKetta (*2*) measured the solubility of cyclopropane in water at pressures of 0.101 to 4.27 MPa and temperatures between 294 and 378 K. Allott and Stewart (*3*) measured the solubility of various anaesthetics, including cyclopropane, in water at 310 K. Satoru (*4*) studied the solubility of cyclopropane at 298 and 311 K at atmospheric pressure. Wilhelm, Battino, and Wilcock (*5*) presented correlations of solubility of many gases including cyclopropane in the temperature range from 298 to 361 K. However, no studies of cyclopropane in aqueous salt solutions have been reported.

This paper briefly describes an experimental apparatus for measuring the solubility of gases in liquids at low pressures. Solubility data for the cyclopropane-KCl-H_2O system are given and the data were fitted to an empirical expression.

Apparatus and Experimental Procedure

Gas solubility was measured by determining the number of moles of cyclopropane which dissolved in a known amount of solvent. Figure 1 shows a schematic of the apparatus.

The equilibrium cell has a length of 12.5 cm and an inside diameter of 5.1 cm for a total volume of 280.98 cm^3. The cell was made of bearing bronze with two windows, each located on opposite sides of the cell. It was designed for a maximum pressure of 3.4 MPa. The liquid contents of the cell were mixed by an ultrasonic transducer placed on the outside of the bottom end plate. The cell was immersed in a constant-temperature bath containing a silicone heat-transfer fluid.

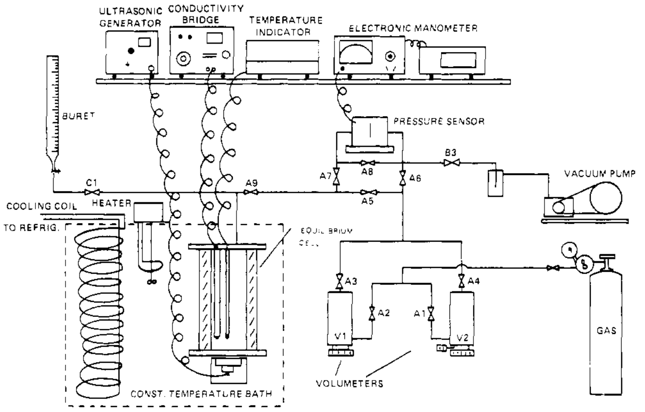

Figure 1. Experimental apparatus for the measurement of cyclopropane, solubility in salt solutions.

Salt solutions were made by placing a weighed amount of salt into a 1-L volumetric flask and filling the remainder of the flask with distilled water. Approximately 200 cm^3 of liquid was introduced into the cell by means of a buret with graduations of 1.0 cm^3. The liquid was deaerated by freezing and pumping; contents of the cold trap weighted before and after pumping indicated a liquid loss of approximately 0.5 cm^3. During liquid filling, valve A9 was closed; the volume of the lines between valves C1 and A9 and the cell was 7.57 cm^3.

The volumeters, V_1 and V_2, the lines to the pressure sensor, and the line to valve A9 were filled and evacuated three times. Once thermal equilibrium was established, the temperature, pressure, and setting of volumeter V_2 were noted. Volumeter V_1 was open during these experiments and had a volume of 196.08 cm^3. Volumeter V_2, which had a resolution of 0.05 cm^3, was calibrated using helium P-V-T measurements.

After measuring the vapor pressure of the solvent, valve A9 was opened and cyclopropane gas was allowed to dissolve into the liquid. The moles of cyclopropane going into solution were computed by knowing the initial and final temperature and pressure and the total gas volume. The moles in the vapor space were computed using the virial equation truncated after the second coefficient. The second virial coefficient for cyclopropane was calculated using the Pitzer–Curl (*6*) correlation.

The initial runs indicated that equilibrium was established in 4 h using ultrasonics or in 7 h without ultrasonics. The initial runs also indicated that a plot of ln $(P - P_{\text{final}})$ vs. time was linear; this observation was used to determine the equilibrium pressure for the remaining runs.

The temperature was measured by a platinum resistance thermometer with a digital readout. Comparing the vapor pressure of pure water in the cell with the data of Wexler (*7*) indicated that the temperature ($IPTS_{68}$) was accurate to within ±0.01 K. The pressure was measured with a differential capacitance monometer with an accuracy to ±0.25% as given by the vendor. Pressure calibration checks made against a mercury manometer verify this accuracy. The conductivity bridge was not used in these experiments.

The analysis of the gas as reported by Matheson Gas Co. was as follows: cyclopropane (99.86%), propylene (<1230 ppm), allene (<100 ppm), air (<50 ppm), and carbon dioxide (<1 ppm),

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Table I. Solubility Data for Cyclopropane KCl Solutions

temp, K	vapor pressure, kPa	salt content, g/L	K', mole fract/kPa	pressure, kPa	cyclopropane concn, mole fract	pressure, kPa	cyclopropane concn, mole fract
273.23	0.6157	0.0000	0.5828E-05	32.86	0.0001915	39.41	0.0002297
273.16	0.6158	0.0000	0.5778E-05	6.07	0.0000350	12.00	0.0000694
273.16	0.6151	0.5100	0.5768E-05	42.00	0.0002422		
273.17	0.6149	1.0980	0.5721E-05	37.90	0.0002168	45.90	0.0002627
273.23	0.6154	1.5180	0.5693E-05	30.73	0.0001749	47.46	0.0002702
273.22	0.5852	10.0900	0.5158E-05	26.90	0.0001386	44.06	0.0002274
276.20	0.7589	0.0000	0.5038E-05	46.66	0.0002351	69.25	0.0003488
276.16	0.7583	0.5080	0.4989E-05	52.04	0.0002598	80.03	0.0003992
276.20	0.7581	1.1250	0.4952E-05	57.24	0.0002835	86.14	0.0004265
276.17	0.7559	1.5050	0.4929E-05	49.26	0.0002431	91.10	0.0004489
276.24	0.7538	10.0200	0.4441E-05	51.92	0.0002306	83.33	0.0003700
278.21	0.8730	0.0000	0.4556E-05	86.53	0.0003939	97.26	0.0004435
278.20	0.8725	0.4860	0.4522E-05	57.26	0.0002590	73.41	0.0003320
278.16	0.8718	1.0850	0.4500E-05	42.72	0.0001921	73.06	0.0003288
278.17	0.8697	1.5080	0.4477E-05	53.13	0.0002377	89.58	0.0004011
278.16	0.8673	10.0120	0.4012E-05	62.06	0.0002492	99.00	0.0003971
274.16	0.6110	0.5000	0.5507E-05	71.42	0.0003933		
274.15	0.6109	0.000	0.5590E-05	68.81	0.0003794	76.55	0.0004215
274.15	0.6110	0.5000	0.5509E-05	78.75	0.0004336	76.73	0.0004229
280.15		0.000	0.4033E-05	51.00	0.0002560	85.20	0.0004288
283.15		0.000	0.3585E-05	45.20	0.0002257	01.20	0.0004560

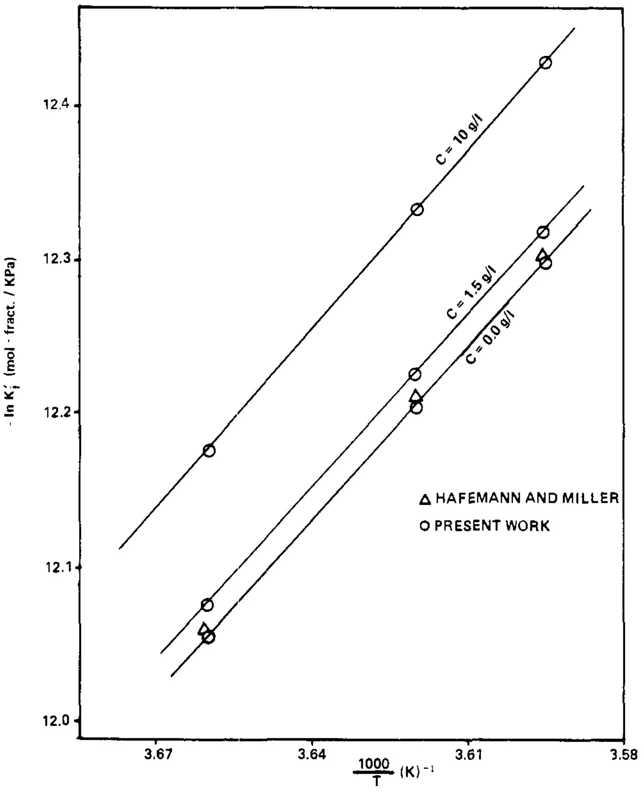

Figure 2. Inverted Henry's constants of cyclopropane in KCl solutions, as a function of temperature.

No further purification was made.

Results

Table I gives the solubility data for the cyclopropane-salt solutions. Reciprocal Henry's constants (x_i/p_i) were determined from a least-squares fit of the data, using an intercept of the solvent vapor pressure. Representative values of reciprocal Henry's constants vs. temperature and salt concentration are given in Figures 2 and 3.

The reciprocal Henry's constants were least-squares fitted to the following equation of Rice, Gale, and Barduhn (*8*), with constants and confidence limits given in Table II.

$$\ln K = a + \frac{b}{T} + \left(c + \frac{d}{T}\right)C \tag{1}$$

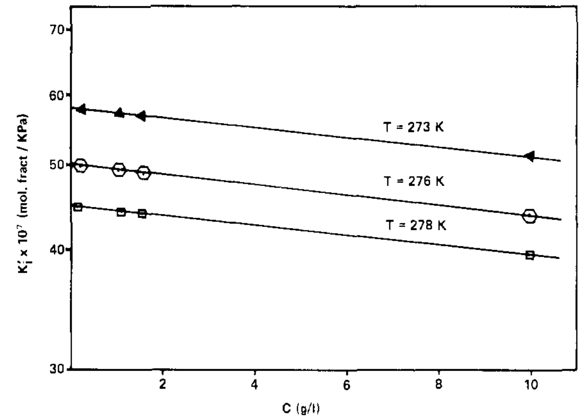

Figure 3. Inverted Henry's constants of cyclopropane as a function of salt concentration.

Table II. Coefficient and Confidence Intervals in Equation 1 $\ln K = a + b/T + (c + d/T)C$

coefficient	value	99% confidence interval[a]
a	−22.422	1.34
b	2811.090	0.87
c	−0.379	0.26
d	102.320	0.54

[a] Based upon 15 degrees of freedom.

with K in mole fraction/kPa, T in K, and C in g/L.

Analysis and Discussion of Results

An error analysis indicated that the maximum uncertainty in the reciprocal Henry's constant was ±1.02%. The maximum error in the moles of solute was estimated to be ±0.11%. The maximum error in the mole fraction of cyclopropane was ±0.43% and the remainder of the error was in the pressure and temperature measurements. The low-pressure data points of run 7 in Table I were corrected for the presence of water vapor in the lines and volumeters; this correction was negligible for all higher pressure data.

Activity coefficients of KCl solutions were computed from vapor pressure data and found to agree with the measurements of Robinson (*9*) to within ±0.11% average deviations.

Figure 2 shows the data of this work compared to those of Hafemann and Miller for cyclopropane in pure water. The results are slightly below those of Hafemann but agreement was within

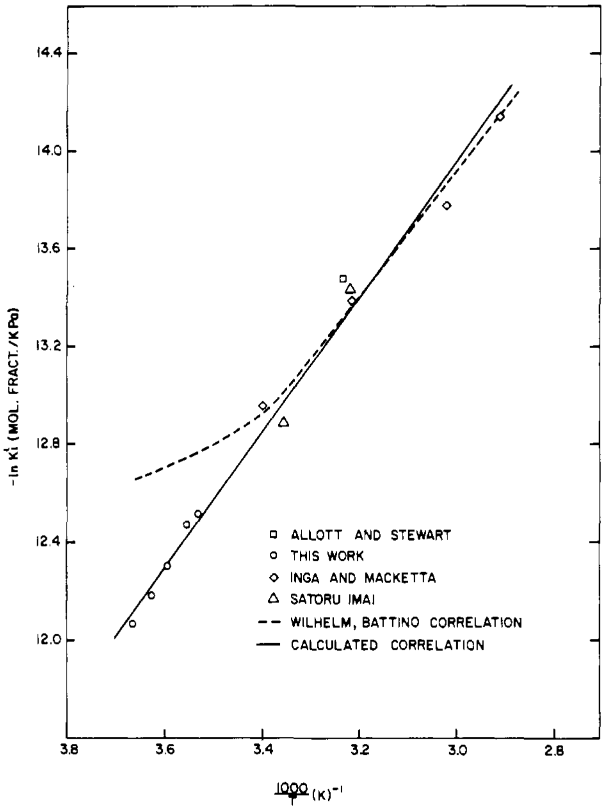

Figure 4. Comparison of experimental data and correlations at zero salt concentration.

1.6%, well within the accuracy stated by Miller (*10*). When the data of the present study were extrapolated to the temperature range of Inga and McKetta, the data were above those of Inga by 2.6%. A further extrapolation (over 30 K) to the temperature range of Allot and Stewart showed agreement to within 6%. A comparison with the data of Saturu shows agreement within 4%. As shown in Figure 4 the correlation of Wilhelm et al. (*5*) for cyclopropane solubility fit the data between 298 and 344 K acceptably; however, there is a significant deviation for the low-temperature data of this work.

Glossary

a, b, c, d	constants in eq 1 and Table II
C	KCl concentration in solution, g/L
K_i	reciprocal Henry's constant, kPa^{-1}
P	pressure, kPa
P_{final}	equilibrium pressure, kPa
P_i	partial pressure, kPa
x_i	mole fraction of component i in solution

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Activity Coefficient of Hydrochloric Acid in the System HCl–NH_4Cl–KCl–H_2O at Constant Total Molality 0.5 mol kg^{-1} at 298.15 K

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The activity coefficients of hydrochloric acid in aqueous mixed solutions with ammonium and potassium chlorides at a constant total molality of 0.5 mol kg^{-1} have been determined at 298.15 K from electromotive force measurements of the cell, Pt,H_2(g, 1 atm)|HCl(m_1), NH_4Cl(m_2), KCl(m_3)|AgCl|Ag, with $m_1 + m_2 + m_3 = 0.5$ mol kg^{-1} and $m_3/(m_2 + m_3) = 0.25$, 0.50, and 0.75. A simple additive scheme based on Harned's rule for the composing binary electrolyte solutions of the acid permits an accurate prediction of the experimental activity coefficients of the acid.

There exist abundant data for activity and osmotic coefficients in binary salt mixtures in aqueous solutions but those concerning mixtures of three or more salts, such as are representative of natural brines, are scarce. For such mixtures, it should be feasible to predict their properties from experimental data for binary solutions of the component salts, using equations such as those of Wood and co-workers (*1–3*) or the more recent equations of Pitzer (*4*). However, it could be more convenient in many cases to resort to simpler empirical means of estimating them. Gieskes (*5*) has proposed a simple additive scheme for representing the activity coefficient of an electrolyte in a multicomponent electrolyte solution. He wrote, for the activity coefficient of component 1 in the presence of other salts, 2, 3, ..., N,

$$\log \gamma_1 = \log \gamma_1^0 - \sum_{i=2}^{N} \alpha_{1i} y_i I \qquad (1)$$

where I is the total ionic strength of the solution, y_i is the ionic strength fraction of component i, and γ_1^0 is the activity coefficient of component 1 in its own solution to which I refers. α_{1i} is the Harned coefficient for component 1 in binary solutions with component i; it is assumed to vary only with I and not with

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