Table XIII. Average Percentage Deviation between Theory and Experiment[a]

model	$\|\Delta\rho\|$/%	$\|\Delta U^c\|$/%	$\|\Delta S^c\|$/%
A	0.64	4.90	16.0
B	0.59	1.30	4.7
C	0.45	0.61	4.7
D	0.40	0.63	4.3
M	0.11	0.40	5.0

[a] Range 190-280 K, $P \simeq$ 5-1300 bar.

in Figures 6-8. The average percentage difference between theory and experiment over the whole range of temperature and pressure studied (roughly 190-280 K, for pressures 0.5-130.0 MPa) was evaluated for each model, as shown in Table XIII. This table clearly shows that, as the various anisotropic interactions were included in the potential model, from model A to model D, the discrepancy between theory and experiment is diminished, suggesting that the successive changes in the potential model constitute an improving refinement toward the effective potential of the real fluid. The biggest improvement overall was found between models A and B, especially for the entropy and internal energy; this is not unexpected as the addition of multipolar forces commonly provides an order of magnitude larger contribution to the free energy than either the overlap or dispersion forces. However, these latter forces are shown to provide a nonnegligible improvement to the thermodynamic properties, in contrast to that found for the supercritical region. This may indicate that the subcritical dense-fluid region is more sensitive than either the saturation curve or the supercritical dense-fluid region to more subtle interactions, represented here by the overlap and dispersion forces. The overall generally poor behavior of the isotropic model (A) indicates the importance of the angle-dependent forces as represented by models B-D.

The results for model M (potential model D with a methane reference system) given in Table XIII show this to be the overall most successful model in predicting one-phase properties for ethylene, especially for the density. It is perhaps not surprising that methane should be a better model than argon for the isotropic part of the potential for ethylene, and this is borne out by the results.

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Received for review December 14, 1981. Accepted June 1, 1982. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Additional support was provided under contract DE-AC02-79ER10422 A001 from the Division of Chemical Sciences of the Department of Energy. A.H. acknowledges a fellowship from the Deutsche Forschungsgemeinschaft.

Solubility of Cobalt Anthranilate in Water at Various Temperatures

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The solubility of cobalt anthranilate in water has been determined at 5 K intervals over the temperature range 273-328 K by using radioactive cobalt-57 as a tracer. The solubility results are indicative of a phase change in solid cobalt anthranilate at ~288 K.

Introduction

A large number of bivalent metal ions including Co^{2+} can be precipitated quantitatively by anthranilic acid (*1-4*). In the literature, the solubility product, K_s, of cobalt anthranilate (CA) in water has been reported at 298.15 K by two different schools (*2*, *5*). Yatsimirskii and Kharitonov (*2*) estimated $K_s = 1.2 \times 10^{-12}$ from the solubilities of CA in aqueous ammonia and acetate buffers. Lumme (*5*) reported $_{p}K_{s} = 0.90$ (which corresponds to $K_s = 0.13$) from potentiometric studies. Since the

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two values are in considerable disagreement, we considered it worthwhile to reevaluate the data using a more precise technique.

In this paper, we report the solubilities of CA in water at 5 K intervals over the temperature range 273–328 K. The data reported were obtained by using radioactive cobalt-57 as a tracer.

Experimental Section

All chemicals used were of "analytical reagent" grade. The water used in the experiments was double distilled.

Measurements were made in a thermostat controlled to ±0.01 °C. The temperature fluctuations of the thermostat were observed with a 5 °C Beckman thermometer graduated to 0.01 °C, and the absolute temperature was measured with a precalibrated precision thermometer to ±0.05 °C.

Preparation of Cobalt Anthranilate. Carrier-free radioisotope cobalt-57 obtained as cobalt chloride solution from BARC, India, was added to ~50 mL of aqueous (~0.5 M) cobalt chloride solution acidified with hydrochloric acid (pH ~4). The mixture was boiled for 1 h to bring about complete isotopic exchange, cooled to room temperature, and diluted to ~300 mL with distilled water. CA was precipitated from this solution by adding to it gradually and with constant stirring a slight excess of (~0.2 M) sodium anthranilate solution. The precipitate was washed with water until free from chloride ions and then with ethanol. It was dried initially under suction and finally in an oven at 110 °C. The results of the chemical analysis of the sample (C = 50.82%, H = 3.61%, and N = 8.55%) agreed closely with the stoichiometric ratios (C = 50.77%, H = 3.65%, and N = 8.46%) in CO $(C_7H_6O_2N)_2$.

The activity of the CA sample was determined by dissolving 92 mg of the compound in ~5 mL of dilute hydrochloric acid (~5 N) and diluting the solution to 1 L. The number of counts for 3-mL aliquots was determined by using a single-channel γ-ray spectrometer (BARC, India) provided with a 1-in. thick crystal of sodium iodide activated with thallium. The following observations were made: average background counts = 65 counts/5 min; counts/mL of aliquot = 4518 counts/5 min (average of five determinations); thus, 1 count/min = 3.12×10^{-7} g-ion/L of Co^{2+}.

Preparation of Saturated Solutions. The saturated solutions were prepared by continuous stirring of CA with water under thermostated conditions for periods of 6–8 h, sometimes starting with unsaturated water and other times with solutions which had been saturated at higher temperatures. Replicate experiments showed practically no difference in the final solute concentrations. The saturated solution at 273.15 K was obtained by equilibrating CA with distilled and deionized water and the crushed ice made from distilled and deionized water for an extended period of time. The technique and the saturator used in the present investigations are similar to those of Glew and Hildebrand (*6*) except that the end of the outlet tube of the saturator dipping in the saturated solution was made of sintered glass. The saturator was thermally insulated by glass wool. The temperature of the circulating water was controlled to ±0.05 °C, and the difference between inlet and outlet temperatures was not greater than 0.08 °C at the highest temperature of determination. After the attainment of saturation, the stirrer was temporarily stopped and samples of saturated solution were taken for analysis from the bottom stopcock.

The solubilities were determined by taking a known weight (approximately 3 mL) of the saturated solution and estimating CA in it by counting the radioactive cobalt-57 using a single-channel γ-ray spectrometer with the setting and geometry conditions identical with the ones used for determining the specific activity of CA. Backgrounds for all solutions were measured separately, and an average of three readings of counts/min was used for calculations. The maximum error in the solubility data reported by us is estimated to be around 2%.

Table I. Solubility and Solubility Product (K_S) of Cobalt Anthranilate in Water at Various Temperatures

temp, K	$X_{CA(satd)}$	K_s
273.15	$(4.99 \pm 0.09) \times 10^{-8}$	$(8.52 \pm 0.51) \times 10^{-17}$
278.15	$(5.07 \pm 0.11) \times 10^{-8}$	$(8.89 \pm 0.54) \times 10^{-17}$
283.15	$(5.58 \pm 0.18) \times 10^{-8}$	$(1.18 \pm 0.05) \times 10^{-16}$
288.15	$(6.68 \pm 0.11) \times 10^{-8}$	$(2.03 \pm 0.10) \times 10^{-16}$
293.15	$(8.68 \pm 0.07) \times 10^{-8}$	$(4.44 \pm 0.09) \times 10^{-16}$
298.15	$(1.26 \pm 0.02) \times 10^{-7}$	$(1.35 \pm 0.07) \times 10^{-15}$
303.15	$(2.01 \pm 0.03) \times 10^{-7}$	$(5.42 \pm 0.29) \times 10^{-15}$
308.15	$(3.01 \pm 0.02) \times 10^{-7}$	$(1.82 \pm 0.04) \times 10^{-14}$
313.15	$(4.76 \pm 0.07) \times 10^{-7}$	$(7.22 \pm 0.38) \times 10^{-14}$
318.15	$(7.17 \pm 0.07) \times 10^{-7}$	$(2.45 \pm 0.07) \times 10^{-13}$
323.15	$(1.09 \pm 0.01) \times 10^{-6}$	$(8.48 \pm 0.33) \times 10^{-13}$
328.15	$(1.61 \pm 0.02) \times 10^{-6}$	$(2.76 \pm 0.13) \times 10^{-12}$

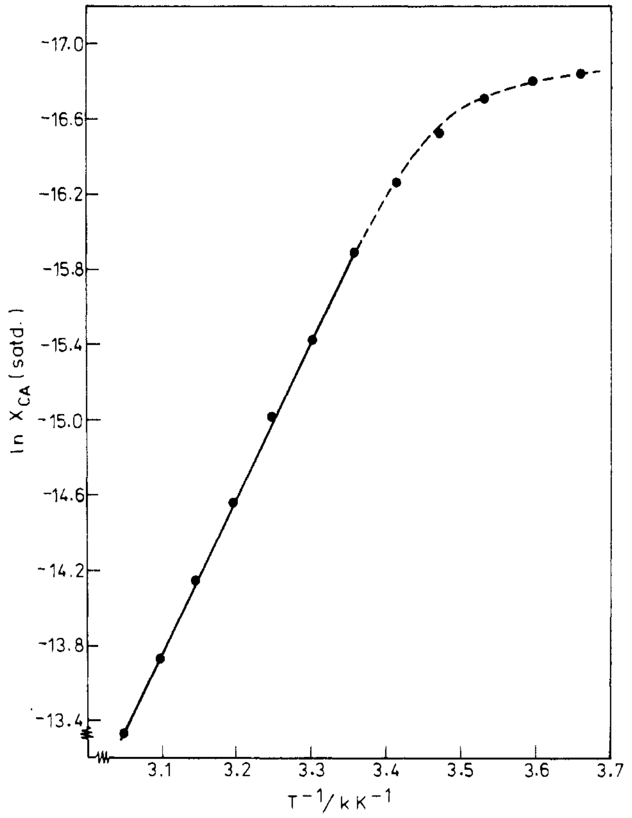

Figure 1. Solubility of cobalt anthranilate in water as a function of temperature.

Results and Discussion

The experimental data for the solubilities of CA in water over the temperature range 273–328 K are recorded in Table I as $X_{CA(satd)}$, the mole fraction of CA in the saturated solution. Each data value reported by us is the mean of at least three replicates. A plot of ln $X_{CA(satd)}$ as a function of T^{-1} records a deviation from linearity around 288 K (see Figure 1). This is indicative of a change in composition or structure of the solid phase.

The solubility products of CA at different temperatures are tabulated in Table I. It is observed that at 298.15 K we obtained a K_s value of 1.35×10^{-15}, which is not in agreement with either of the two values reported in the literature (*2*, *5*). We are unable to explain the surprisingly high value reported by Lumme (*5*). Our results are more precise than the results of indirect determination reported by Yatsimirskii and Kharitonov (*2*). The difference may be due to the small quantity of colloidally dispersed CA in their saturated solution samples. The molar heat of solution for CA in water at 298.15 K obtained from solubility data is 145.4 ± 3.0 kJ/mol.

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Received for review June 30, 1981. Revised manuscript received May 3, 1982. Accepted May 17, 1982.

Viscosity of Molten Alkaline-Earth Chlorides

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Precision determinations of the viscosities of four molten alkaline-earth chlorides are reported. The following equations express the results in mPa s with 0.06–0.19% standard deviation: $MgCl_2$, $\eta = 0.17985 \exp(2470.1/T)$; $CaCl_2$, $\eta = 0.28498 \exp[1373.5/T + (1.258 \times 10^6)/T^2]$; $SrCl_2$, $\eta = 0.36396 \exp[917.0/T + (2.024 \times 10^6)/T^2]$; $BaCl_2$, $\eta = 0.23452 \exp[1946.8/T + (1.828 \times 10^6)/T^2]$. The accuracy estimate is 0.3% on the 68% confidence level. Present data for $CaCl_2$, $SrCl_2$, and $BaCl_2$ deviate 7–12% from previous recommendations. Some comments on the responses of oscillational viscometers are given together with a brief discussion of the results.

Introduction

When one reviews theories for the molten state proposed from observations of transport properties, it becomes apparent that these properties are disappointingly insensitive to differences in liquid structure and that quite accurate data are needed if they are to reveal even major structural changes. It follows that abrupt and dramatic fluctuations in, for instance, the viscosity as a function of temperature and/or composition should not be expected, the continuing appearance of reports to the contrary notwithstanding.

Even today, only a few high-temperature fluids have been investigated with an accuracy that permits the attention to be focused squarely on liquid characteristics rather than experimental artifacts. The present work is part of a program at this laboratory to establish accurate values for the viscosity of molten alkali-metal halides and alkaline-earth halides.

Experimental Section

The viscometer operates by measuring the damping and the time-of-swing of an oscillating noble-metal cylinder. Absolute viscosities are obtained from both types of data without the need of calibration against reference liquids, as described elsewhere (*1*). The method is considered superior to other techniques that we know have been applied to high-temperature liquids, oscillating sphere viscometers included. A similar hollow-cylinder (cup) version, which is useful for very volatile or corrosive liquids although less accurate because of the meniscus effect, is discussed in ref *2*. We have recently commented upon both cylinder and cup oscillational viscometers and high-temperature viscometry in general (*3*). That comment also refers to our available computer programs developed and used in this laboratory for obtaining accurate logarithmic decrements and time-of-swings from a very simple experimental setup, involving two permanently fixed photodetectors and a nonadjustable laser.

Chemicals used were $MgCl_2 \cdot 6H_2O$ (Baker, analytical reagent), $CaCl_2 \cdot 2H_2O$ (Merck, p.a.), $SrCl_2 \cdot 6H_2O$ (BHD analytical) and $BaCl_2 \cdot 2H_2O$ (Merck, p.a.). All salts were purified by passing HCl gas through the samples at temperatures rising from 25 to 400 °C. They were later heated at 400 °C for 0.5 h under 0.01–0.05 Pa in the viscometer furnace immediately before runs. In addition, $MgCl_2$ was melted after the initial treatment with HCl, again treated with HCl, and then filtered and distilled twice on a vacuum line.

After purification, the samples were prepared and handled as previously described for the alkali-metal chlorides (*4*). A low bulk density of the $BaCl_2$ sample made it necessary to premelt part of the charge. Drybox techniques were used in all stages, and the viscometer was purged with highly purified nitrogen.

Gas bubbles, a potential source of serious errors (*4*), did not form on the oscillating cylinder surfaces according to the following criteria: moving the sample-containing crucible repeatedly up and down did not change the viscosity as calculated from either the oscillation period or the damping constant; "period" viscosities agreed with "damping" viscosities within the normal experimental uncertainty; results did not show any correlation with the temperature history of the sample. A quasi-random selection of experimental temperatures could thus be made in contrast to the alkali-metal chloride work. The same measuring procedure was otherwise followed with a few exceptions: the number of oscillations had to be reduced to the 15–30 range because of the high damping, experiments were not repeated with other, independently prepared samples, and the upper temperature limit was that for which recommended density data exist.

Evaporation losses were less than 1% for $CaCl_2$, $SrCl_2$, and $BaCl_2$. It was not determined for $MgCl_2$ as this salt was recovered for later use. Approximate melting points were measured upon completion of the experiments by observing freezing plateaus in situ (no stirring was possible). A pH determination was performed on one salt—$SrCl_2$—after the experiment.

As usual, the investigation was preceded by a series of control experiments in water. Temperatures were measured with a mercury-in-glass thermometer calibrated at the National Physical Laboratory, England. Readability and calibration was 0.002 °C.

Results

The damping of a body oscillating in a fluid depends upon the density of the fluid as well as its viscosity, and the density must

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0021-9568/82/1727-0387$01.25/0