amine group in the 4 position (para) increases the basicity of the ring nitrogen by 10 000-fold ($pK_b = 4.9$), probably through resonance stabilization of the cation rather than the free base itself (*17*). Increased density of charge on the ring nitrogen, together with a residual positive charge on the amino nitrogen, allows for the greatly enhanced basicity that is observed. This effect is present in reduced intensity in 2-AMP ($pK_b = 7.3$), with the result that the basicity of 2-AMP is intermediate between that of 4-AMP and the parent pyridine.

The thermodynamic quantities for the dissociation of 2-aminopyridinium ion and 4-aminopyridinium ion are similar, suggesting that the differences in the dissociation processes are largely matters of degree rather than of kind. In both instances, the entropy changes are small, which is characteristic of isoelectric dissociation processes in general. The differences in basic strength are thus attributable to enthalpy contributions.

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Critical Constants, Vapor Pressure, and Saturated Volumes of Hexafluoroacetylacetone

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The critical temperature, pressure, and volume were determined for hexafluoroacetylacetone. The vapor–ligand equilibrium was determined from the temperature of 422.8 K to the critical temperature. Vapor–pressure equations were suggested to correlate the data. The densities of saturated liquid and saturated vapor were determined in the above temperature range.

Introduction

In recent years, fluoro compounds have found increasing use on an industrial scale. Banks (*1*) gives many examples of the increasing industrial use of fluoro compounds. Accurate vapor–liquid equilibrium data and accurate correlations are very important for the design of the industrial equipment that will handle the liquid and the vapor. Very little research has been done on the vapor–liquid equilibrium of fluoro compounds. The purpose of this study is to find the critical properties and the vapor–liquid equilibrium of hexafluoroacetylacetone. No previous study of the vapor–liquid equilibrium of hexafluoroacetylacetone has been found in the literature. The vapor–liquid equilibrium was studied from 422.8 K to the critical point. Many equations have been suggested in the literature to correlate the vapor–liquid equilibrium as given by Nieto and Thodos (*2*). In this work the data were correlated by two equations of the form

$$\log P = A + B/T \qquad (1)$$

$$\log P = A + B/T + CT \qquad (2)$$

The least-squares method and Gaussian elimination were used to find the constants in eq 1 and 2. The percentage deviation defined as 100 × [(calculated pressure) – (measured pressure)]/(measured pressure) was calculated for the two equations. Also, the specific volumes of the saturated vapor and the saturated liquid were measured.

Experimental Section

The hexafluoroacetylacetone used in this study was supplied by Koch-light Laboratores Ltd., England, with a stated purity of 98%. The hexafluoroacetylacetone was further purified by placing it in contact with activated molecular sieves to absorb traces of moisture and was then degassed.

Liquid samples may contain small amounts of dissolved air. If accurate vapor–liquid equilibrium is to be obtained, the sample must be degassed. Ronc and Ratcliff (*3*) discussed three ways of degassing. The degassing method used in this work is different from their methods. The hexafluoroacetylacetone was degassed by subjecting it to a cycle of freezing, pumping, melting, and freezing. The degassed sample was kept in a flask attached to a high-vacuum train and surrounded by a mixture of dry ice and acetone.

Apparatus and Procedure

The apparatus and the methods for the measurements have been described in previous publications (*4*). The temperature was measured by the platinum resistance type 385. The platinum resistance with its electronic digital indicator, type 2180A, was supplied by Fluke. It can read to 0.01 K and has a maximum error of ±0.02 K.

The pressure was measured by a pressure gauge manufactured by Matheson with an absolute accuracy of ±0.025%. The experimental tube was constructed from precision-bore

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Table I. Temperature, Pressure, and Specific Volumes of Saturated Liquid and Vapor of Hexafluoroacetylacetone and Percentage Deviations Using Eq 1 and 2

		specific vol, cm^3/g		eq 1		eq 2	
temp, K	press., kPa	saturated vapor	saturated liquid	P(calcd), kPa	% dev	P(calcd), kPa	% dev
422.8	1028.05	10.61	0.73	995.0	−3.2	994.99	−3.22
428.5	1088.03	10.32	0.73	1104.23	1.5	1104.21	1.49
434.1	1227.82	8.45	0.74	1219.96	−0.64	1219.94	−0.64
438.8	1327.68	7.12	0.75	1323.80	−0.29	1323.78	−0.29
445.7	1487.55	5.87	0.77	1487.82	0.02	1487 81	+0.02
450.7	1587.53	5.67	0.78	1615.62	1.77	1615.61	1.77
454.8	1687.50	5.32	0.79	1726.23	2.30	1726.22	2.30
464.7	1987.39	4.27	0.81	2015.81	1.43	2015.81	1.43
470.1	2137.34	3.72	0.90	2187.72	2.36	2187.72	2.36
472.6	2237.31	3.55	0.91	2270.76	1.50	2270.76	1.5
475.8	2427.31	3.28	0.96	2380.30	−1.94	2380.31	−1.9
478.8	2527.27	2.96	0.97	2486.37	−1.62	2486.38	−1.62
480.8	2587.26	2.76	0.99	2558.92	−1.10	2558.94	−1.1
485.0	2767.16	1.39	1.39	2716.15	−1.84	2716.17	−1.84

glass tubing of 0.003-m i.d. The inside volume of the tube at any height from the sealed end was determined by the mercury displacement method. Appropriate corrections for thermal expansion of Pyrex glass and variation of internal radius with pressure were introduced as approximated by Perry (*5*).

Results

The critical properties were found to have the following values: critical temperature, 485.10 K; critical pressure, 2767.16 kPa; critical volume, 1.39 cm^3/g.

The measured temperature, pressure, and specific volume at the dew point and the bubble point are shown in Table I. Two different equations have been used to correlate the pressure–temperature data. These equations were of the form

$$\log (P/\text{kPa}) = A + B/(T/\text{K}) \qquad (1)$$

$$\log (P/\text{kPa}) = A + B/(T/\text{K}) + C(T/\text{K}) \qquad (2)$$

Using the data in Table I and applying the least-squares method, I found the constants in eq 1 to be

$$\log (P/\text{kPa}) = 6.398524 - 1437.81649/(T/\text{K}) \qquad (3)$$

Also, the percentage deviations defined as

$$\frac{P(\text{calcd}) - P(\text{measured})}{P(\text{measured})} \times 100$$

were calculated. The results of these calculations are shown in Table I.

Equation 2 contains three constants. The least-squares method and the Gauss–Jordan elimination method were used to find these constants. Equation 2 becomes

$$\log (P/\text{kPa}) =$$
$$6.39863 - 1437.861509/(T/\text{K}) - (1.9476676 \times 10^{-8})(T/\text{K})$$

Using this equation, I calculated the pressures and percentage deviations and tabulated them in Table I.

Conclusion

Unfortunately no vapor-pressure data have been found in the literature to compare this work with. But from our previous experience and works (*4*, *6*, *7*) great confidence can be attached to these results. The measuring instruments used were of very high accuracy. The temperature could be read to within 0.01 K with a maximum error of ±0.02 K. The Matheson pressure gauge used has an accuracy of ±0.025%.

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