Table V. Comparison of Measured Viscosity Data with Data Reported in the Literature

system	D, %	S, %	temp, °C	ref
acetone-water	0.65	0.88	25	4
	0.91	1.20	25	5
ethanol-water	0.38	0.51	40	6
	0.70	0.81	40	4
methanol-water	0.80	0.87	40	7

recommended $Z = -1.10$, while Dizechi (*2*), using an optimization technique, determined Z values for various polar liquids, some of which are listed in Table I. Even though Z is actually dependent upon temperature, this dependency is so weak that selection of only one value of Z for each polar liquid is sufficient.

For $C_1 = C_2 = C_2 = ... = 273.15$ K, eq 2 reduces to the equation proposed by McAllister (*1*).

Results of both correlations are compiled in Table IV. In Table IV the first column provides a count; the second column identifies the mixture whereby the sequence of components corresponds to 1, 2, 3. The mean percentage deviation and the standard percentage error for McAllister's equation (eq 1) and eq 2 are listed in columns three and four, respectively. Mean deviation and standard error on a percentage basis are calculated from the following definitions:

mean percentage deviation

$$D = \frac{1}{m}\sum_{i=1}^{m}\frac{100|\text{viscosity}_{i,\text{exptl}} - \text{viscosity}_{i,\text{calcd}}|}{\text{viscosity}_{i,\text{exptl}}} \tag{3}$$

standard percentage error

$$S = \left\{\frac{1}{m}\sum_{i=1}^{m}\left[\frac{100(\text{viscosity}_{i,\text{exptl}} - \text{viscosity}_{i,\text{calcd}})}{\text{viscosity}_{i,\text{exptl}}}\right]^2\right\}^{1/2} \tag{4}$$

where m is the number of data points.

Inspection of Table IV shows that eq 2 is superior to eq 1 when applied to mixtures of polar liquids, one of them being water. Thus, eq 2 provides for a much better correlation technique.

A comparison of experimental viscosity data obtained in this study with some data reported in the literature is provided in Table V. This comparison is based on mean percentage deviation and standard percentage error as defined in eq 3 and 4 except that reported viscosity values are used in place of the calculated viscosity values. Mean percentage deviations and standard percentage errors were found generally to be smaller than 1%. Sufficient data for comparison of viscosities of ternary mixtures could not be found.

Glossary

C	constant in eq 2
D	mean percentage deviation
m	number of experimental data points at a fixed temperature
M	molar mass
S	standard percentage error
t	temperature, °C
t_b	boiling temperature at atmospheric pressure, °C
x_i	mole fraction of component i
Z	constant in eq 2
ρ	density
ν	kinematic viscosity, m^2/s
ν_m	kinematic viscosity of the mixture

Subscripts

1, 2, 3	components 1, 2, and 3, respectively
ij	refer to interaction of type $i-i-j$, etc.
123	refer to interaction between three molecules; one of component 1, one of component 2, and one of component 3
av	average
calcd	calculated
exptl	experimental

Literature Cited

(1) McAllister, R. A. *AIChE J.* **1960**, *6*, 427.
(2) Dizechi, M. Doctoral Dissertation, University of California at Santa Barbara, Santa Barbara, CA, 1980.
(3) Goletz, E.; Tassios, D. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 75.
(4) Barry, Guy; Bircumshaw, L. L. *International Critical Tables* **1929**, *5*, 22.
(5) Howard, K. S.; McAllister, R. A. *AIChE J.* **1958**, *4*, 362.
(6) Bingham, E. C.; Hatfield, J. E.; Jackson, R. F. *Bur. Stand. J. Res. Sci.* **1917**, 298.
(7) Mikhail, S. A.; Kimel, W. R. *J. Chem. Eng. Data* **1961**, *6*, 533.

Received for review September 10, 1981. Accepted April 27, 1982.

Vapor Pressures of Some Isotopic Hydrogen Cyanides

Gerry T. Appleton and W. Alexander Van Hook*
Chemistry Department, University of Tennessee, Knoxville, Tennessee 37996

Vapor pressures are reported for solid and liquid phases (approximately 230–300 K) of HCN, DCN, and $HC^{15}N$ with a precision of about 0.8% for the solid and 0.2% for the liquids. The data are discussed in the context of the theory of isotope effects in condensed phases.

Introduction

The vapor pressure of hydrogen cyanide has been measured only a few times in the past 50 years. A review of the literature prior to 1934 has been compiled by Kelley (*1*). Agreement between early workers is poor. In 1934 Lewis and Schutz (*2*) made measurements of the vapor pressures of HCN and DCN between 235 and 294 K by mercury manometry. Giauque and Ruehrwein (*3*) made more careful measurements from the triple point, 259.91 K, to 298.8 K, and also published results on the heat capacity and the heats of fusion and vaporization for HCN. Since their 1939 report, no further studies on the vapor pressure or related thermodynamic properties of HCN or its isotopic isomers have been indexed in *Chemical Abstracts*.

HCN is a simple molecule, and we concluded that new data on the vapor pressure isotope effects for isotopic cyanides would be of interest in determining details of the motions of the

0021-9568/82/1727-0363$01.25/0 © 1982 American Chemical Society

Table I. Least-Squares Parameters of Fit to ln (P(torr)) = $A + B/T + CT^a$: Liquids

compd	ref	no. of points	temp range, K	σ^b	A	B	C
HCN	*2*	7	259–294	7×10^{-3}	17.9932 ± 0.063	−3389.16 ± 17.3	
HCN	*3*[c]	10	260–299	3×10^{-4}	20.1987 ± 0.109	−3687.25 ± 15.2	$-4.1067 \times 10^{-3} \pm 0.19 \times 10^{-3}$
HCN	present work	40	260–297	1.1×10^{-3}	19.7777 ± 0.239	−3624.28 ± 33.1	$-3.4169 \times 10^{-3} \pm 0.43 \times 10^{-3}$
DCN	*2*	7	265–294	1.8×10^{-3}	17.8185 ± 0.021	−3344.18 ± 5.9	
DCN	present work	85	261–304	1.1×10^{-3}	21.5607 ± 0.130	−3885.10 ± 18.3	$-6.4797 \times 10^{-3} \pm 0.23 \times 10^{-3}$
$HC^{15}N$	present work	29	260–275	2.3×10^{-3}	34.8783 ± 3.371	−5664.22 ± 450.0	$-31.371 \times 10^{-3} \pm 6.31 \times 10^{-3}$

[a] 760 torr = 0.986923×10^5 Pa. [b] Root mean square error. [c] Temperature scale corrected to $T = 273.15 + t$

Table II. Least-Squares Parameters of Fit to ln (P(torr)) = $A + B/T^a$: Solids

compd	ref	no. of points	temp range, K	σ^b	A	B
HCN	*2*	6	236–258	6×10^{-3}	21.5061 ± 0.076	−4302.96 ± 19.0
HCN	present work	26	237–256	8×10^{-3}	22.5361 ± 0.054	−4558.69 ± 13.4
HCN[c]	present work	26	237–256	2×10^{-2}	21.6703	−4347.01 ± 32.0
DCN	*2*	6	236–260	1.5×10^{-2}	22.1634 ± 0.176	−4478.61 ± 43.4
DCN	present work	31	227–259	4.8×10^{-3}	21.6205 ± 0.016	−4342.41 ± 3.9
$HC^{15}N$	present work	27	227–259	5.7×10^{-3}	22.2661 ± 0.023	−4504.12 ± 5.8

[a] 760 torr = 0.986923×10^5 Pa. [b] Root mean square error. [c] Result upon forcing the fit through the triple point $T_t = 259.91, P_t = 140.51$.

molecules in the condensed phases (*4*) especially because extensive spectroscopic information is available for this molecule (*5*) to aid in the interpretation of the thermodynamic data. Unfortunately, we were unable to obtain the desired experimental precision because of severe problems associated with polymerization of the molecules followed by dissolution of polymer in the condensed phase. Even so, the results (*6*) are of a precision which is at least comparable with published data. Therefore, after considerable delay, they are reported here.

Experimental Section

HCN, DCN, or $HC^{15}N$ was prepared by the action of H_2SO_4 or D_2SO_4 on NaCN or $NaC^{15}N$, respectively, and purified by low-temperature column distillation. Purities were checked by chromatographic and IR spectroscopic techniques. Vapor pressures were measured in the absolute mode using a Texas Instruments quartz Bourdon manometer. While it would have been desirable to make differential measurements with equipment described previously (*7*), this was impossible because of a buildup of polymer impurity in the gas phase above 20 °C. We were concerned that polymer deposits on the walls of our differential capacitance manometer might cause permanent damage and therefore avoided the use of this equipment. The refrigeration system used in the present experiments was limited to temperatures greater than −16 °C. Measurements below that temperature were obtained with the use of baths of various organic reagents at their melting points (slushes). Temperature control in the slush baths was not as good as at higher temperatures. In addition, equilibrium between solid and vapor was obtained more sluggishly than between the liquid and vapor. These two factors account for the major part of the decrease in precision for the solid/vapor as compared to the liquid/vapor data. The greatest source of systematic error is the buildup of polymeric material in the sample chamber. The amount was found to be a function of time and thermal history of the sample. For brief periods of time below 20 °C the rate of polymerization is small. For this reason low-temperature measurements were taken first to keep the effect of polymerization to a minimum. Care was taken to avoid warming/cooling/warming cycles. A principle difference in experimental design between the best previous measurements (*3*) and the present data is sample size. Giauque and Ruehrwein employed about 50 mL of liquid while the present experiment was designed for about 0.25 mL because of the expense in preparing large amounts of isotopically labeled isomers. Therefore, dissolution of a given quantity of polymeric impurity into the liquid sample is a relatively more acute problem in the present experiments. Previous authors, notably Pezolet and Savoie (*5*) have also commented on the difficulty of preparing both chemically and isotopically pure HCN and DCN.

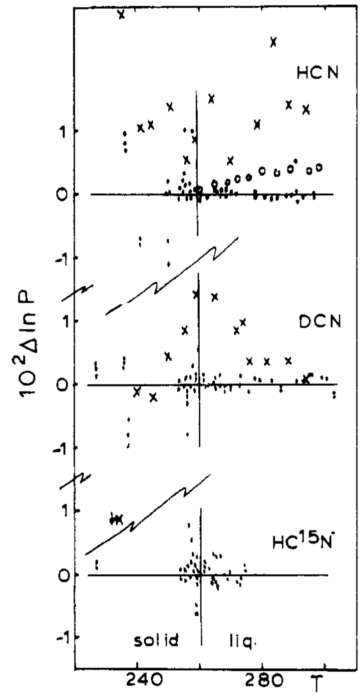

Figure 1. Deviation plots; points are experimental data, $\Delta \ln P = \ln (P_{exptl}/P_{calcd})$. P_{calcd} in each case is taken from the equations for least-squares fits to the present data as reported in Table II: (●) present, (○) ref *3*, (×) ref *2*.

Results

The results of the measurements are summarized in Tables I and II, where they are compared with our fits to the earlier results (*2*, *3*). Deviation plots from least-squares fits to the present data are shown in Figure 1.

It is clear from Tables I and II or Figure 1 that the data for the solid/vapor equilibrium are much less reliable than those for liquid/vapor. We do not regard them as reliable enough to do more than establish the sign of the vapor pressure isotope effects, ln $[P(HCN)/P(DCN)]_{solid}$ and ln $[P(HCN)/P(HC^{15}N)]_{solid}$,

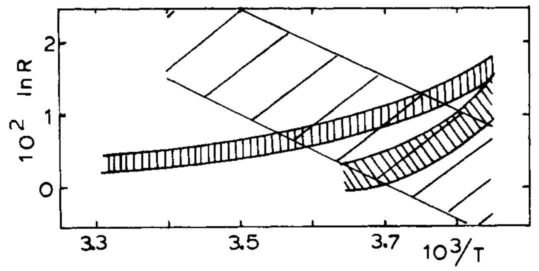

Figure 2. Vapor pressure isotope effects for liquid hydrogen cyanides: (▥) ln [*P*(HCN)/*P*(DCN)], present work; (▨) ln [*P*(HCN)/*P*(DCN] ref *2*; (▧) ln [*P*(HC^{14}N)/*P*(HC^{15}N)], present work.

as positive. For HCN, the triple point is well established (*3*) and the liquid vapor pressure near T_t as measured in two laboratories is in agreement to better than 0.1%. For the solid we therefore recommend the alternate fit (designated as *c* in Table II) forced through the triple point to approximately describe the HCN solid data. That particular fit is also in better agreement with the data of Lewis and Schutz (*2*) than is the unconstrained fit. The reasons for the comparative imprecision of the solid-phase data have been discussed in the previous section.

For HCN the liquid-phase vapor pressure determined in this work is established with a precision of about 0.1% and is in good agreement with the earlier measurements of Giauque and Ruehrwein (*3*) (within 0.1% at the triple point increasing to a maximum deviation of 0.4% near the boiling point). In view of the major experimental problems connected with the growth of polymeric impurity, the agreement is considered satisfactory. The earlier result (*3*) is probably more reliable because the significantly larger liquid volume in that experiment implies a slower buildup of polymeric impurity in the liquid phase. The maximum probable differences that we estimate in the temperature scales used by the two laboratories are not large enough to account for the average pressure difference of 0.2%. The precision of the DCN and HC^{15}N results obtained in the present study is comparable with that for HCN. For DCN and HCN the present results are considerably more precise than those of Lewis and Schutz (*2*) and are to be preferred. The HC^{15}N results only extend up to 275 K because of the limited sample size for this isotopic isomer.

Vapor pressure isotope effects, ln [*P*(HCN)/*P*(DCN)] and ln [*P*(HCN)/*P*(HC^{15}N)], as calculated from the equations in Table I for liquid/vapor equilibrium lines are shown in Figure 2. The hatched-in areas which show the logarithmic vapor pressure ratios as a function of temperature are two standard deviations wide. The results of Lewis and Schutz for HCN/DCN are also shown in the figure. The effects are positive across the entire temperature range decreasing from a maximum value of about 1.5% (for HCN/DCN, around 1% for HC^{14}N/HC^{15}N) at the melting point less than 0.5% near the boiling point. The agreement between the presently reported isotope effect for HCN/DCN and ref *2* is not good, but for reasons discussed above we feel the present results are to be preferred.

Table III. Correlation of VPIE's[a] with Spectroscopic Information

A. Observed and Calculated Frequency Shifts at 261 K (*5*)[b]

frequency		$\Delta\upsilon$(calcd)	$\Delta\upsilon$(observed)
υ_1	HCN	−0.4	−0.1
	DCN	23.0	20.0
$\upsilon_{2,3}$	HCN	−86.0	−86.0
	DCN	−69.0	−53.0
υ_4	HCN	104.5	104.0
	DCN	50.2	55.0

B. Gas- and Liquid-Phase Force Constants at 261 K (*6*)

		gas	liquid
H–C stretch	$(f_1)^c$	6.22731	5.81508
C–N stretch	$(f_2)^c$	18.76485	18.90302
H–C–N bend	$(f_3)^d$	0.259637	0.324726
interaction	$(f_{12})^c$	−0.21873	−0.256
translation	$(f_t)^d$		0.662011
libration	$(f_r)^d$		0.171172
interaction	$(f_{3r})^d$		−0.0056

C. Calculated and Observed Isotope Effects at 261 K

	ln [*P*(HCN)/ *P*(DCN)]	ln [*P*(HC^{14}N)/ *P*(HC^{15}N)]
calcd	0.013	0.008
observed	0.015 ± 0.002	0.013 ± 0.004

[a] VPIE = vapor pressure isotope effect. [b] Units: cm^{-1}. $\Delta\upsilon = \upsilon_{gas} - \upsilon_{liq}$. [c] Units: 10^5 dyn/cm. [d] Units: 10^{-11} dyn cm.

Biegeleisen (*8*) has presented a formalism correlating spectral frequency shifts on condensation with thermodynamic isotope effects, and Jancso and Van Hook (*4*) have reviewed a large literature detailing quantitative calculations in the context of this theory. Such calculations are useful in systematizing data on different isotopic isomers and in performing consistency checks. Spectral frequency shifts on condensation for the important internal modes are available for liquid HCN and DCN at 261 and 292 K and for the gas phase (*5*). The spectral frequency shifts are large and temperature dependent. Using well-established techniques (*4*, *8*), we have succeeded in obtaining an isotope-independent but temperature-dependent set of force constants which satisfactorily describes both the spectral frequency shifts on condensation and the isotopic vapor pressure ratios. The relevant information at 261 K is presented in Table III. Agreement is reasonable. Within the precision of the calculation it is clear that the isotope effects are consistent with the spectroscopic results.

Literature Cited

(1) Kelley, K. K. *U.S., Bur. Mines, Bull.* **1935**, *No. 383*.
(2) Lewis, G. N.; Schutz, P. W. *J. Am. Chem. Soc.* **1934**, *56*, 1002.
(3) Giauque, W. F.; Ruehrwein, R. A. *J. Am. Chem. Soc.* **1939**, *61*, 2626.
(4) Jancso, G.; Van Hook, W. A. *Chem. Rev.* **1974**, *74*, 689.
(5) Pezolet, M.; Savoie, R. *Can. J. Chem.* **1969**, *47*, 3041.
(6) Appelton, G. T. Thesis, University of Tennessee, Knoxville, TN, 1969.
(7) Van Hook, W. A. *J. Chem. Phys.* **1966**, *44*, 234.
(8) Bigeleisen, J. *J. Chem. Phys.* **1961**, *34*, 1485.

Received for review January 8, 1982. Accepted May 10, 1982. This work was supported in part by the National Science Foundation under Grant 81-12965.