On the Dissociation of Hydrogen Cyanide in Aqueous Solutions Containing Different Ionic Media. A Combined Potentiometric and Carbon-13 NMR Study

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The dissociation constant of hydrogen cyanide in aqueous solutions containing three ionic media at 25 °C has been determined by a combination of potentiometry and ^{13}C NMR. The dissociation constants obtained are (in molar units): $pK_a = 9.09$ (in 1.00 M $NaClO_4$); 10.00 (in 3.00 M $LiClO_4$) and 10.11 (in 1.00 M $NaClO_4 - 3.00$ M $LiClO_4$). The advantage of the combination of potentiometry and NMR as compared to potentiometry alone is discussed. It is suggested that in many cases the former method is superior to the latter, since some possible error sources are eliminated. The constants obtained were used to calculate pK_a values for HCN in aqueous solutions containing several other ionic media by means of the specific interaction theory. The calculations showed that the majority of the dissociation constants reported in the literature can be predicted. Some of the recently reported values, however, are not in concordance with our calculations and are probably erroneous. The specific interaction coefficients, $\varepsilon(Na^+, CN^-) = 0.07(1)$ and $\varepsilon(Li^+, CN^-) = 0.22(2)$ (2σ in parentheses), obtained in this work can be used to predict the value of the dissociation constant for HCN in water in other ionic media.

During the last 40–50 years solution chemists have determined a large number of equilibrium constants. These studies have contributed to an improved and a more quantitative understanding of solution chemistry, which in turn has led to many industrial and environmental applications.

Several methods have been used for determining the constants: solubility studies, potentiometry, spectrophotometry etc. In the era of multinuclear NMR a new tool has been added to the chemist's arsenal. With NMR, we can study several chemical problems which were impossible to study before, e.g. microscopic equilibrium constants, structures of species in dilute solution, fast kinetics. In particular, the combination of NMR and potentiometry seems to be the method of choice for the determination of accurate equilibrium constants. This combined approach is in many cases superior to potentiometry (EMF) alone, a method which has for a long time been, and still is, considered as the most accurate.

The semi-empirical specific interaction theory (SIT) has previously been shown to have good predictive capability. In this work we have confirmed the validity of SIT and have shown that some of the literature values of K_a for this simple chemical system are incorrect. Moreover, the inter-

action coefficients obtained in this work can be used in order to predict the values of K_a in other ionic media, thus eliminating the need for tedious experimental work.

The cyanide ion forms complexes with most metal ions. During the last century the chemistry of these complexes has received considerable attention (cf. e.g. Refs. 1 and 2). Several industrial applications of the complexes have been developed, for example in the field of recovery of noble metals and metal coating of surfaces.[2] They also play an important role in organic synthesis.[1,2] Therefore, the parent acid of the complexes, hydrogen cyanide, has been extensively studied.[1,2] The thermodynamic investigations of HCN have recently been reviewed by Beck.[3] In this review Beck has selected certain values of the dissociation constant which deserve significant credit.

During our studies of cyano complexes of thallium(III)[4–6] in different ionic media (1 [$NaClO_4$] = 1.00 M; 2 [$LiClO_4$] = 3.00 M and 3 {[ClO_4^-] = 4.00 M, [Na^+] = 1.00 M, [Li^+] = 3.00 M}) by means of a combination of potentiometry and NMR, we also obtained the dissociation constant, $K_a = [H^+][CN^-]/[HCN]$, for hydrogen cyanide in these media. From these experimental values of the dissociation constant one can calculate the value of K_a in aqueous solutions containing other ionic media by means of the so-called specific interaction theory (SIT).[7] The calculations can also show if the literature values of K_a are correct.

In the following, the experimental determination of the dissociation constant of HCN by means of the combined potentiometry–NMR method is presented. The advantage

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of this method compared to the 'traditional' potentiometric method alone is discussed. Finally, the predicted values of K_a in various ionic media (by means of the specific interaction theory) are compared with the corresponding values reported in the literature.

Experimental

In order to determine the equilibrium constant, small amounts of 1 M $HClO_4$ in an ionic medium were gradually added to an aqueous solution of $Na^{13}CN$ (50–100 mM) in the ionic medium. After each addition, the pH was measured and the ^{13}C NMR spectrum recorded. Because of the fast chemical exchange between HCN and CN^- only one ^{13}C NMR peak was observed. [In acidic solutions the spectra show a doublet which originates from the spin–spin coupling between ^{13}C and ^1H in the HCN molecule ($^1J_{^{13}C-^1H} = 270.6$ Hz).[4] This shows that the proton exchange is slow on this time scale, which is remarkable for an inorganic acid in aqueous solution. This will be further discussed in a forthcoming paper.]

The chemical shift of this peak, δ_{obs}, is a direct function of the individual chemical shifts of HCN (δ_{HCN}) and CN^- (δ_{CN^-}) and the molar fractions of these species (p_{HCN} and p_{CN^-}) [eqn. (1)]. δ_{HCN} and δ_{CN^-} were obtained from

$$\delta_{obs} = \delta_{HCN}p_{HCN} + \delta_{CN^-}p_{CN^-} \tag{1}$$

spectra recorded for extremely acidic and alkaline solutions, respectively. Substituting eqn. (1) into the expression for the dissociation constant (based on concentrations) one obtains eqn. (2). The pH was measured by means of a

$$pK_a = -\log[H^+] + \log[(\delta_{CN^-} - \delta_{obs}) / (\delta_{obs} - \delta_{HCN})] \tag{2}$$

combined glass electrode (Radiometer GK2401B; the inner solution of KCl was replaced by a solution of the ionic medium and a small amount of ionic chloride) connected to a pH meter (Radiometer PHM62). The readings of the electrode were calibrated to pH values using the method of Irving.[8] This leads to the so called 'stoichiometric' equilibrium constant (i.e. based on concentrations).

^{13}C NMR spectra were recorded at 100.6 MHz at a probe temperature of $25 \pm 0.5\,°C$ using a Bruker AM400 spectrometer. The chemical shifts are reported toward higher frequency from TMS and are generally accurate within ± 0.02 ppm. (Some NMR parameters are as follows: flip angle $\approx 20°$; spectral window = 17 kHz; pulse repetition time = 1 s; 2.1 Hz/point.)

The resulting dissociation constants of HCN in different ionic media were calculated by fitting eqn. (2) to the experimental pH and δ_{obs} values and are presented in Table 1.

Table 1. Experimental and calculated[a] values of the dissociation constant of HCN in various ionic media ($K_a = [H^+][CN^-]/[HCN]$; in molar units).

Ionic media	pK_a		Difference	Ref.
	Measured	Calculated		
3.0 M LiClO_4	10.00	9.91	0.09	This work[a]
3.0 M LiClO_4–1 M NaClO_4	10.11	10.19	0.08	4
1.0 M NaClO_4	9.09	9.00	0.09	This work
3.0 M NaClO_4	9.48	9.39	0.09	9
0.1 M NaClO_4	9.06	9.01	0.05	10
1.0 M NaClO_4	8.88	9.00	0.12	10
3.0 M NaClO_4	8.81	9.39	0.58	10
5.0 M NaClO_4	8.78	9.96	1.18	10
0.1 M NaClO_4	9.03	9.01	0.02	11a
0.5 M NaClO_4	9.01	8.95	0.06	11a
1.0 M NaClO_4	9.01	9.00	0.01	11a
3.0 M NaClO_4	9.45	9.39	0.06	11a
5.0 M NaClO_4	10.01	9.96	0.05	11a
0.1 M NaCl	9.04_0	9.01	0.03	11b
0.5 M NaCl	8.94_9	8.95	0.00	11b
1.0 M NaCl	8.94_6	8.99	0.04	11b
3.0 M NaCl	9.22_0	9.30	0.08	11b
5.0 M NaCl	9.66_0	9.71	0.05	11b
0.1 M NaNO_3	8.99^b	9.00	0.01	12
2.0 M NaNO_3	8.62^b	9.02	0.40	13

[a]Using specific interaction theory, see text. [b]Extrapolated to 25 °C using the temperature dependence of pK_a as determined by Izatt et al.[17]

Discussion

Advantage of the combined NMR-potentiometric method as compared to potentiometry alone. The combination of NMR and EMF has some disadvantages; for example, expensive and care-demanding equipment (NMR spectrometer) is needed. On the other hand, when the latter is available, several potential sources of experimental error can be eliminated: (1) In eqn. (2), there is no dependence on the total concentration of cyanide. In the case of potentiometry alone, an error in the total concentration may lead to a severe systematic error in the determined equilibrium constant. This is especially true for chemical systems involving decomposing or volatile species such as HCN. (2) Impurities may be introduced into the dilute solution of the investigated species owing to the presence of the high concentration of the ionic medium (see below). (3) Traces of carbon dioxide may be present. Generally, for the EMF method acid–base impurities act as buffers and can easily affect the readings of the electrode. These readings constitute the only measured parameter, and accordingly, such effects cannot be separated from the investigated equilibria. This situation occurs, since the presence of impurities influences the mass-balance equations used.

For the combined EMF–NMR method, the presence and the concentrations of the impurities do not disturb the measurements, since mass-balance equations are not used here, cf. eqn. (2). In NMR, non-paramagnetic impurities have no direct influence on the chemical shifts, unless they participate in fast (on the NMR timescale of the measured nucleus) chemical exchange reactions with the investigated species.

In the case of pK_a values of HCN, the standard deviation determined in this work is 0.02 units (for one titration including about 20 experimental points), and can be compared to the error of ± 0.03 given in Ref. 10 (potentiometric determination). Hence, the precision of the two methods is comparable. This fact does not, however, say anything about the accuracy of the methods.

In the present case, the chemical shift difference, $\delta_{CN^-} - \delta_{HCN} = 53$ ppm, is very large compared to the experimental uncertainty of the chemical shifts (0.02 ppm). This leads to a good resolution of the ^{13}C measurements. Moreover, no knowledge of the absolute values of the chemical shifts is required. Hence, the whole titration curve can be used without introducing a significant error into eqn. (2). Accordingly, the most uncertain part of the determination of the stability constant will be the measurement of pH. On the contrary, when potentiometry alone is used, the pH measurement is considered to be very accurate.

Inexpensive equipment favours the traditional method. On the other hand, in favourable cases the NMR method gives not only the equilibrium constants but also structural and/or kinetic information. The kinetics of proton exchange in the HCN–water system will be presented in a forthcoming paper.

Calculations by means of the specific interaction theory. The so-called constant ionic medium method,[14] i.e. the use of a concentrated solution of an inert salt (often an alkali perchlorate), proves to be a necessary condition for the study of complicated ionic equilibria. The method is based on the fact that in an inert electrolyte solution of high and constant concentration the variations of activity coefficients are kept to a minimum provided the concentration of the ionic medium far exceeds that of the reagent species. Equilibrium constants in different ionic media are often necessary for specific investigations. The measurement of these constants in several media is often quite a time-consuming task. In many cases this can be avoided by using some method for recalculation of constants from one ionic medium to another. One such method is the semi-empirical 'specific interaction theory' (SIT).[7,15]

In order to use this method, interaction coefficients for the interaction between the various charged species in the solution must be known. Unfortunately, to the best of our knowledge no such constants for the cyanide ion have been reported in the literature. These coefficients can be determined from our experimental equilibrium constants in the following way.

For the thermodynamic (based on activities) dissociation constant of HCN (in SIT calculations, all concentrations are in *molal* units), we have eqn. (3). Taking the logarithm

$$K_a^\circ = \{H^+\}\{CN^-\} / \{HCN\}$$

$$= (\gamma_{H^+}\gamma_{CN^-} / \gamma_{HCN})([H^+][CN^-]/[HCN])$$

$$= (\gamma_{H^+}\gamma_{CN^-} / \gamma_{HCN})K_a \qquad (3)$$

and assuming the activity coefficient $\gamma_{HCN} = 1$ (no charge and low concentration) leads to eqn. (4). From the specific

$$pK_a = pK_a^\circ + \log \gamma_{H^+} + \log \gamma_{CN^-} \qquad (4)$$

interaction theory, we can write eqn. (5) for species i

$$\log \gamma_i = -z_i^2 D + \sum_k \epsilon(i,k)m_k \qquad (5)$$

having charge z_i, where k denotes a species with charge opposite to that of species i, $\epsilon(i,k)$ is the interaction coefficient for ions i and k, and m_k is the molal concentration of the species k. Since the concentration of the medium is normally much higher than those of the measured species, the interactions between the measured species can be neglected. (In the present case this means that the interaction between H^+ and CN^- can be neglected.) D is the Debye–Hückel term, $D = a\sqrt{I_m}/(1 + \varrho\sqrt{I_m})$, where $a = 0.5109$ and $\varrho = 1.5$, and I_m is the ionic strength, $I_m = \frac{1}{2}\Sigma(z_i^2 m_i)$.

In the case of HCN the value of pK_a° has been reported by three independent groups using different experimental methods: 9.22 ± 0.02, spectrophotometry;[16] 9.21 ± 0.01,

potentiometry (glass electrode);[17] and 9.21 ± 0.02, potentiometry (glass electrode*).[18] The agreement between these values is excellent. Hence, the value 9.21 can be used in the calculations. This value has also been recommended in the recent review by Beck.[3]

For the three ionic media discussed in this work (cf. the first three rows of Table 1), the following specific interaction coefficients are involved: $\varepsilon(H^+,ClO_4^-)$, $\varepsilon(Na^+,CN^-)$ and $\varepsilon(Li^+,CN^-)$. Of these, only the first can be found in the literature, $\varepsilon(H^+,ClO_4^-) = 0.14$.[19]

This leaves us with two unknown parameters and three equations [i.e. one equation similar to eqn. (4) for each ionic medium]. A least-squares fit of the two coefficients leads to: $\varepsilon(Na^+,CN^-) = 0.07(3)$ and $\varepsilon(Li^+,CN^-) = 0.23(2)$ (2σ in parentheses). These specific interaction coefficients can be used to calculate pK_a in a wide range of ionic media. There are a number of determinations of $pK_a(HCN)$ in different ionic media reported in the literature. In order to arrive at a conclusion as to which of the experimentally determined values are to be considered reliable, we have calculated pK_a (using SIT) and then compared it to the measured pK_a values. [For the NaCl medium the interaction coefficient $\varepsilon(H^+,Cl^-) = 0.12$ was used[19] and for the $NaNO_3$ medium, $\varepsilon(H^+,NO_3^-) = 0.07$.[19]] For most of the media the difference between the experimental and calculated values was smaller than 0.1. This agreement is quite satisfactory, considering the uncertainty in our interaction coefficients (vide supra).

Specifically, this difference was ≤ 0.08 for the recently determined values in $NaClO_4$[11a] and $NaCl$[11b] ($I = 0.1–5$ M) by Hefter. Hence, in order to use more experimental data and thus to obtain more precise ε-values, in the final calculations we have used our experimental data together with the data of Hefter. A least-squares fit of the two coefficients gave: $\varepsilon(Na^+,CN^-) = 0.07(1)$ and $\varepsilon(Li^+,CN^-) = 0.22(2)$ (2σ in parentheses). Based upon these coefficients various pK_a values in other ionic media have been calculated. The results, together with the literature values, are given in Table 1. In cases where the difference between the calculated and the experimental value is larger than 0.2, we have reason to suggest that the measured values may not be reliable. This suggestion is based on the numerous successful applications of the specific interaction theory[15] and on the excellent agreement between the calculated values of $pK_a(HCN)$ (based on our data only) and the experimental constants determined by Hefter[11] (vide supra).

Supplementary material. A listing of primary experimental data in the form: pH_{exp}, pH_{calc}, $p_{HCN} = [HCN]/[CN]_{tot}$, p_{CN}, ^{13}C linewidth, ^{13}C chemical shift and ($pH_{exp}-pH_{calc}$) in various ionic media, 4 pp, is available from one of the authors (J.G.) on request.

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* Extrapolated to 25 °C using the temperature dependence of pK_a as determined by Izatt et al.[17]