A STUDY OF HYDROGEN-BONDED SPECIES OF ACETIC ACID IN WATER

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ABSTRACT

Hydrogen-bonded species in aqueous solutions of acetic acid have been quantitatively studied in the concentration range of 0 to 85 % w/w. Their presence has been indirectly determined from equilibrium constants by a non-linear least squares treatment of proton chemical shifts. The results suggest that monomers and dimers predominantly exist within the range of 1.6×10^{-3} to 8.0×10^{-3} % w/w and 6.0 to 20.0 % w/w respectively, whereas cyclic dimers and linear dimers coexist within the range of 10.0 to 25.0 % w/w, and oligomeric species are formed above 50.0 % w/w.

INTRODUCTION

The quantitative species distribution of hydrogen-bonded species of acetic acid in aqueous solution is still not well known, the reason being that their concentrations cannot directly be measured by experiment. However, when a simulation technique was introduced over a decade ago, it provided a means for tackling the above mentioned problems. For example, Goldman[1-3] has succeeded in applying this technique in the study of complex mixtures of hydrogen-bonded species of acetic acid in carbon tetrachloride. He determined corresponding equilibrium constants by simulation based on the so-called "least squares treatment" of the non-linear relation of proton chemical shifts of that solution to the species concentrations. Although information about hydrogen-bonded species of aqueous acetic acid cannot be regarded as abundant, it is sufficient to be useful for the simulation method. Such information is available in the literature, for example, the postulation of monomeric and linear dimeric species by Beckmann,[4] and several subsequent papers.[5-9] Karle and Brockway[10] used the electron diffraction method to study the structure of acetic acid in the gas phase and concluded that it exists mainly as cyclic dimers and hence they assumed a mixture of monomers, cyclic dimers and oligomer in the liquid state of acetic acid.

In this paper, we have adopted the Goldman simulation approach to the study of quantitative distribution of hydrogen-bonded species present in an aqueous acetic acid solution at various concentrations. Not only is a wider range of concentrations covered, but also more varieties of species are taken into account in addition to those proposed by previous workers.[1,5-9,10] The inclusion of ionic species has required some modifications of the Goldman treatment represented by equation 4.

EXPERIMENTS

All chemicals used in this work were of analytical grade. Deionized water was used throughout. The nmr and conductivity measurement were performed at 32 °C, 1 atm and the uncertainties of the results were estimated to be less than ± 0.02 % for the nmr work and ± 0.05 % for the conductivity measurement.

The fractions of proton of hydrogen ions at various concentrations were derived and computed from the conductivity data. The proton chemical shifts of the aqueous acetic acid solutions were measured in D_2O using DSS(2,2- Dimethyl -2- silapantane -5- sulfonate) as external reference.

COMPUTATIONAL METHOD

The equilibrium constants K_c, K_1 and K are related to the mole fraction of various species as follows :

$$K_c = X_c / X_1^2 \qquad .....(1)$$

$$K_1 = X_2 / X_1^2 \qquad .....(2)$$

and

$$K = X_{i+1} / X_i X_1 \qquad .....(3)$$

where X_c, X_1, X_2 and X_i are the mol fractions of cyclic dimer, monomer, linear dimer and oligomer units, respectively. These equilibria were simulated by fitting the experimental and calculated hydroxyl proton chemical shifts at various concentrations. The calculated chemical shift was determined from eq. (4) :

$$\delta^{calc.} = f(E)\delta(E) + f(I)\delta(I) + f(C)\delta(C) + f(H^+)\delta(H^+) + f(H_2O)\delta(H_2O) \qquad .....(4)$$

where f(E), f(I), f(C), $f(H^+)$, and $f(H_2O)$ are the fractions of acid protons of the end proton, internal hydrogen bonding proton, hydrogen-bonded proton in cyclic dimer, hydrogen ion and water proton, respectively, while $\delta(x)$ represents an individual proton of the type x as mentioned above.

The last two terms of eq.(4) are determinable variables since they can be obtained from the measurements. Other terms are unknown. However, by following Ruangpornvisuti's work,[11] we derived the fractions of protons namely f(E), f(I) and f(C) from the mass balance relationship for total acetic acid in the solution, and with the aid of eqs. (1), (2) and (3), the unknown parameters in terms of the equilibrium constants K, K_1 and K_c were obtained. Finally six parameters i.e., K, K_1 and K_c and proton chemical shifts δ(E), δ(I) and δ(C) were refined by scanning for their magnitude within a certain range of the values taken from ref. (1).

According to the non-linear relation between the observed chemical shifts and their concentrations, the non-linear least squares fit method was used in terms of standard deviation minimizing :

$$\sigma = \sqrt{\frac{\sum_{j=1}^{N} (\delta^{obsd.j} - \delta^{calc.j})^2}{N - 1}}$$

RESULTS AND DISCUSSION

The equilibrium constants obtained from the simulation, K, K_1 and K_c, are equal to 54.4, 141.7 and 262.5 respectively. These values are significantly acceptable within the concentration range of 0 to 85 % w/w shown by a very small discrepancy between the calculated and observed chemical shifts. Fig. 1 shows that at high concentrations (above 85 % w/w), the calculated chemical shifts increasingly deviate, as a function of concentration, from the observed chemical shifts. This may be attributed to the fact that in the model used in this work every acetic acid species is considered to be solvated with water molecules. Although this consideration is reasonable for a fairly dilute solution, at a higher concentration some of the acetic acid species may be left unsolvated, implying a need for a different model. The alternative argument is that in this work we assumed the independence of K, K_1 and K_c on the apparent concentration of (monomeric) acetic acid. This assumption may be valid for each narrow range of concentration but becomes uncertain if applied to the extreme situation i.e. from a very dilute to a very high concentration. If this is the case, anomalous results at high concentrations can be expected. This argument is supported by the work of Jose B. Ng and H.F. Shurvell[12] who have applied factor analysis and band contour resolution techniques to the Raman spectra of acetic acid in aqueous solution and found a drastic increase in acid concentration above 14 M. It is, therefore, interesting to look more closely into the tendency of changes in the values of the equilibrium constant, especially of K_c, as a function of concentration at above 85 % w/w.

Although some more work is required in order to refine the results, it suffices, in the present work, to illustrate the application of the simulation technique in a study of a complex system like acetic acid in water. Here we show that once the equilibrium constants are found, the mole percent of existing species are readily obtainable. From Fig. 2 it is read that monomers and dimers predominantly co-exist within the concentration range 1.6×10^{-3} to 8.0×10^{-3} and 6.0 to 20.0 % w/w, respectively, whereas cyclic dimers and linear oligomeric species are formed above 50.0 % w/w. It is interesting to note that Semmler *et al.*,[13] in the most recent paper, have shown similar findings to our species distribution although using a different approach.

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บทคัดย่อ

งานวิจัยที่รายงานนี้เป็นการศึกษาหาปริมาณของสปีชีส์ต่าง ๆ ที่มีพันธะไฮโดรเจน (hydrogen bonded species) ที่เกิดในกรดอะซีติกผสมน้ำ ในช่วงความเข้มข้น 0-85 % w/w การมีสปีชีส์เหล่านี้ในสารละลายดังกล่าวทราบโดยทางอ้อมจากการคำนวณค่าคงที่สมดุลย์ ซึ่งได้จากการนำวิธีการทางคณิตศาสตร์ที่เรียกว่า non-linear least square มาใช้กับค่าโปรตอนเคมีคัลชิฟท์ (proton chemical shifts) ผลที่ได้ทำให้สามารถสรุปได้ว่าโมโนเมอร์และไดเมอร์ จะปรากฏอยู่ในช่วงความเข้มข้น $1.6\times10^{-3}-8.0\times10^{-3}$ % w/w และ 6.0 – 20.0 % w/w ตามลำดับ ในขณะที่ไซคลิกไดเมอร์และลิเนียร์ไดเมอร์จะอยู่ด้วยกันในช่วงความเข้มข้น 10.0-25.0 % w/w ส่วนที่ความเข้มข้นเหนือ 50% ไปนั้น จะพบว่า ส่วนใหญ่เป็นโอลิโกเมอร์สปีชีส์

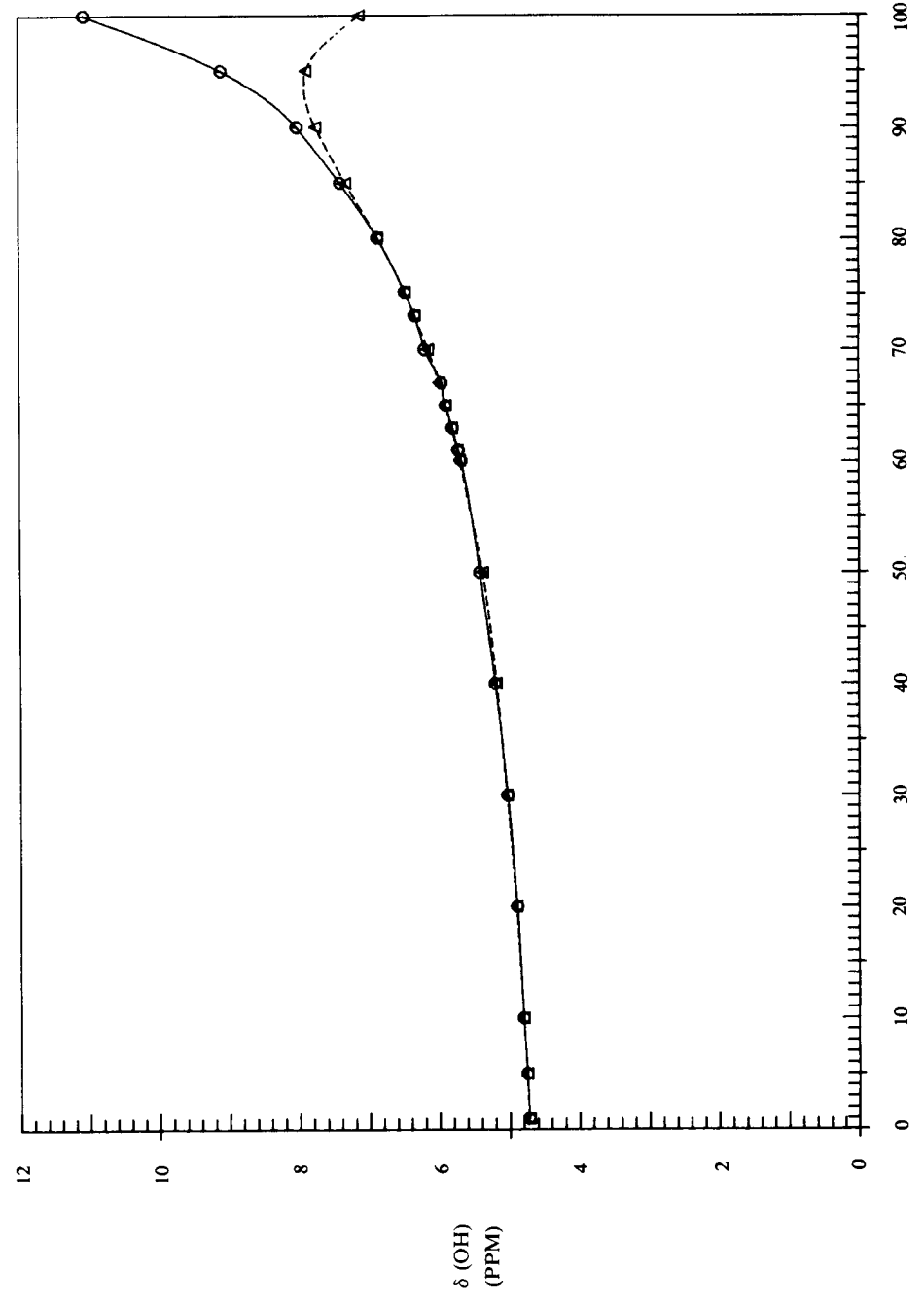

Fig. 1 Calculated —△—△—△— and observed —●—●—●— chemical shifts at various concentrations (32°c)

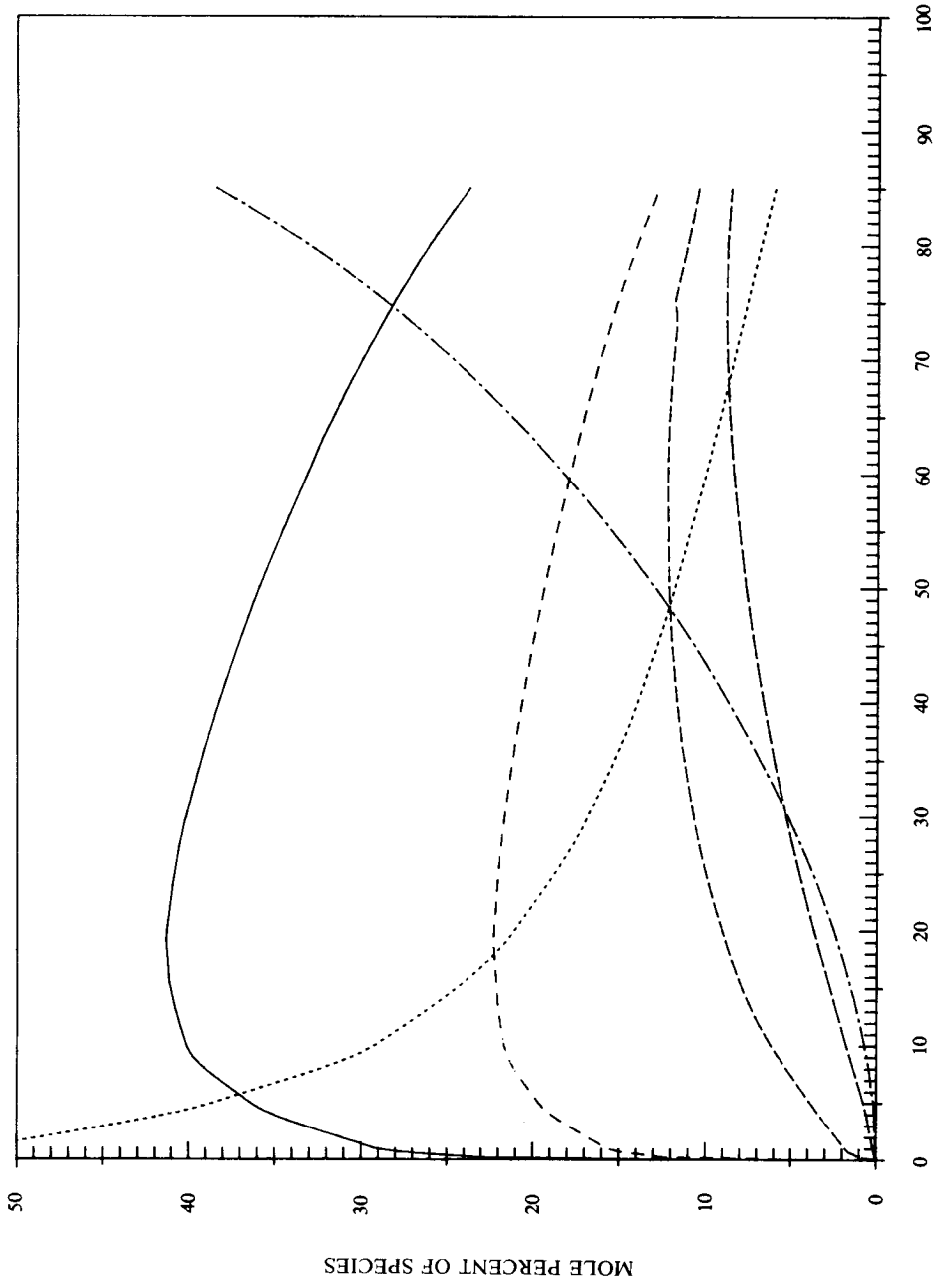

Fig. 2 Mole percent of cyclic dimer_____, monomer.....,linear dimer_ _ _ _,trimer_ _ _ _, tetramer_ _ _ _ and the sum of species greater than tetramer_____._____._____., at various concentrations.