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First observation of clusters for solvated tropylium ions

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We have first observed clusters for solvated tropylium ions ($Tr^+(ROH)_n$) which were isolated from ROH–CH_3CN (1:1 by vol.; R = Me, Et, and Pr^n) solutions by using a specially designed mass spectrometer and found the clear-cut essential features concerning the solvation structure around Tr^+.

The solvation structure around a carbocation has not thoroughly been clarified in spite of so many investigations from various aspects for a long time[1] owing to few practically available methods for direct observation.[2] Earlier than a decade ago, a specially designed mass spectrometer was devised[3] and utilized to examine the composition of clusters which were isolated from a liquid phase[3,4] and an electrospray source[3a] was introduced to the special mass spectrometer to result in direct observation of species of clusters with a positive charge.[5] Our instruments have the advantage of a splendid isolation of clusters and a hermetic way of working. Then, by using the mass spectrometer and tropylium ion as a stable carbocation, we have examined the compositions of clusters for solvated tropylium ions ($Tr^+(ROH)_n$) to find clear-cut essential features for the solvated carbocation clusters.

The Tr^+–solvent clusters were obtained from a solution containing tropylium ions, by electrospray interface. Since the experimental details on the mass spectrometric analysis of clusters including an ion isolated from solutions containing ionic species has already been reported elsewhere,[5] it is briefly explained here. A sample solution containing ionic species is injected into a five-stage differentially pumped vacuum chamber through the electrospray interface, which leads to the formation of multi-charged liquid droplet flow. The resulting multi-charged liguid droplets fly from the first room to the fifth room through the pressure difference and the electric field in the vacuum chamber. During the flight, the multi-charged liquid droplets are fragmented into the clusters and molecules through the expansion due to the decrease of pressure and the electric repulsion among the ions providing the multi-charge. After the fragmentation of the multi-charged liquid droplets, the strongly interacting cation(s)-molecules were isolated as clusters. However, weakly interacting molecules were vapourized as monomeric molecules. Herein, the clusters with positive charge, by Tr^+, were analyzed by the quadrupole mass spectrometer.

The positively charged clusters were analyzed for a solution of tropylium tetrafluoroborate ($Tr^+BF_4^-$; 4.5×10^{-3} M) in ethanol–acetonitrile (1:1 by vol.). Signals corresponded to clusters containing Tr^+, *e.g.* $Tr^+(EtOH)_2$ to $Tr^+(EtOH)_{17}$, though only up to eight solvent molecules were shown in Fig. 1. No complexes of Tr^+ with CH_3CN were detected. The signal intensity generally decreased with an increase in the number of EtOH molecules which formed clusters with Tr^+, with an exception of those from $Tr^+(EtOH)_4$ to $Tr^+(EtOH)_6$ (Fig. 1). The signals from $Tr^+(EtOH)_4$ to $Tr^+(EtOH)_6$ were somewhat larger than their neighbouring ones. Four to six are 'magic number clusters'.[6] An analogous tendency was observed for $Tr^+(MeOH)_n$, from a solution of Tr^+ ions in MeOH–CH_3CN, and $Tr^+(Pr^nOH)_n$, from a solution of Tr^+ ions in Pr^nOH–CH_3CN. The same feature in cluster compositions could be observed for neutral clusters which were isolated from EtOH–CH_3CN (1:1 by vol.) solutions.[7] Theoretical calculation by $b_3$lyp/6-31G** indicated that the binding constant between Tr^+ and five MeOH molecules was larger compared to that for the less or more MeOH molecules.[8]

The relative signal intensities for a solution of Tr^+ in MeOH–EtOH–CH_3CN (1:1:2, by vol.) indicated that the cluster forming ability for Tr^+ was apparently MeOH:EtOH = 1.0:5.2.[9] Similarly, the solution of Tr^+ in EtOH–Pr^nOH–CH_3CN was analyzed to show that the cluster forming ability for Tr^+ is EtOH:Pr^nOH = 1.0:14.[9] Consequently, the ability for Tr^+ should be MeOH:EtOH:Pr*n*OH = 1.0:5.2:70. The longer the alkyl chain of alcohol molecules, the stronger the cluster forming ability, *i.e.* the solvation ability for Tr^+. Such a tendency might be related to the clustering of the alcohols in acetonitrile, that is, the clustering of alcohols was promoted with an increase in the size of the alkyl group. The binding energy for Tr^+ with an alcohol molecule from theoretical calculations (by $b_3$lyp/6-31G**)[10] was consistent with the observed sequence of cluster forming ability mentioned above. Also, the calculations are in line with the work of Meot-Ner (Mautner) for other ions.[11] The binding energy has a linear relationship with donor numbers[12] for EtOH, MeOH, and CH_3CN suggesting that the Lewis basicity of the alcohol molecule might play a significant role for the carbocation.

In conclusion, we have first observed the solvated cluster compositions for Tr^+ and found that the cluster forming ability (solvation ability) increased with increasing alkyl chain length

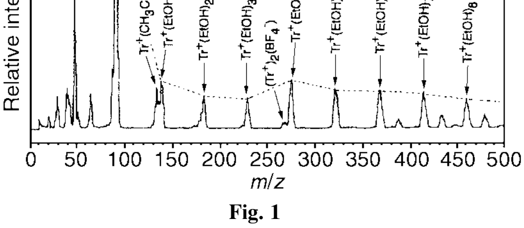

Fig. 1

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of alcohols. Further elaboration and application of the present methodology are now in progress.

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7 Another specially designed mass spectrometer for analysis of neutral clusters (see ref. 4) was used.

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9 The ratios of relative signal intensities were estimated from the ones of summations of height of all detected signals corresponding to the respective alcohol molecule.

10 Binding energy calculated by b$_3$lyp/6-31G** is 9.652, 17.067, 17.331, and 17.541 kcal mol^{-1} for Tr$^+$–CH$_3$CN, Tr$^+$–MeOH, Tr$^+$–EtOH, and Tr$^+$–Pr^{n}OH, respectively.

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