

## Acidity function of calcium nitrate tetrahydrate melt

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Visible spectra of methyl red, methyl orange, *p*-nitrophenol, *p*-nitroaniline, and bromophenol blue in calcium nitrate tetrahydrate melt have been recorded at 25°C. All the indicators react with the acidic calcium nitrate tetrahydrate melt. It is found that indicators having high  $pK_a$  value in the range  $\leq 4$  can be used as probes if the spectra of acidic and basic forms of such indicators in the hydrate melt are well separated. Acidity function of calcium nitrate tetrahydrate melt has been determined from the spectral data of *p*-nitroaniline and bromophenol blue only and its values, 1.8 and 2.6 respectively are estimated from their respective spectra.

Room-temperature molten salts are now emerging as potential solvents for synthetic work<sup>1</sup>. Hydrate melts are one kind of room-temperature ionic liquids<sup>2</sup>, which possess remarkable chemical properties. Due to the presence of aquometal complexes hydrate melts and highly concentrated aqueous solutions of certain metal salts have high acidic behaviour<sup>3-6</sup>, which can be controlled by the addition of a second salt<sup>4</sup>. The acidic behaviour of hydrate melts is attributed to the equilibrium of the type



where M represents a metal ion of oxidation number, n. In the recent past structure and dynamics of hydrated metal ions have drawn the attention of both theoretical and experimental chemists<sup>7</sup>.

Different attempts have been made to find a suitable scale for expressing the acidity of hydrate melts or concentrated aqueous solutions. The application of optical basicity scale suggested by Duffy and Ingram<sup>3</sup> is, however, restricted to oxide-containing systems only. The commonly used *pH* scale also cannot be employed to hydrate melts. Instead, acidity of hydrate melts has to be viewed in terms of the tendency of the aquometal complex to donate protons to some suitable acceptors, which are normally organic indicators. A spectrophotometric

method can therefore be used to estimate the acidity of hydrate melts in terms of the Hammett acidity function,  $H_0$ , which is given by the relation<sup>8</sup>,

$$H_0 = pK_a + \log[c_B / c_{BH^+}] \quad \dots (2)$$

In Eq. (2)  $c_B$  and  $c_{BH^+}$  are the concentrations of the organic base B and its protonated form  $BH^+$ , respectively.  $K_a$  denotes the equilibrium constant for the dissociation equilibrium of  $BH^+$ . The method of determining the value of  $c_B/c_{BH^+}$  for an indicator from its absorbance values in either aqueous or non-aqueous media is well known.<sup>8</sup> However, difficulties are faced while applying the spectrophotometric method to hydrate melts containing nitrate ions due to (i) reaction of melts with organic indicators and (ii) melts not having good UV transparency.

In this work we have recorded visible spectra of molten systems containing calcium nitrate tetrahydrate (CNTH) and various organic indicators with a view to employ the spectrophotometric technique for the determination of  $H_0$  value of CNTH melt by overcoming the above mentioned difficulties.

### Experimental

The indicators used for spectral study are *p*-nitrophenol (PNP) (CDH, analytical reagent), *p*-nitroaniline (PNA) (SISCO, extrapure), methyl red (MR) (E. Merck), methyl orange (MO) (E. Merck), and bromophenol blue (BPB) (BDH, analytical reagent). MO, PNP and PNA were recrystallized from their solutions in double distilled water. MR and BPB were recrystallized from their solutions in toluene (BDH) and benzene (BDH), respectively. The solutions of MR in toluene and BPB in benzene were prepared by refluxing. CNTH (E. Merck) was used without additional purification.

CNTH melt was prepared by heating the hydrated salt in a water bath (INSREF make) around 50°C and then allowing it to cool slowly to form the supercooled melt. Stock acidic CNTH melt was prepared by adding known amount of acetic acid (SD, AR grade) to a weighed amount of the melt. To prepare stock basic CNTH melt, excess of NaOH pellets (SD, AR grade) were added to the melt (~3g of pellets to ~10g of melt) and heated at about 50°C in the thermostat for about an hour. The undissolved

NaOH was removed from the melt by vacuum filtration using a sintered crucible. Stock solutions of PNP, PNA, and MO of known concentrations were prepared in doubly distilled water, whereas stock solutions of BPB and MR were prepared in 1:1 ethanol and water mixture. Spectra were taken immediately after the addition of weighed amounts of indicator solutions to the melt (neat, acidic or basic) of known weight using a Beckmann DU-650 spectrophotometer. The temperature of the samples was maintained at 25°C by circulating thermostated water around the cell (quartz cell of path length 1 cm) holder.

### Results and discussion

The  $\lambda_{\max}$  values of acidic and basic forms of PNP, PNA, BPB, MR and MO in CNTH melt determined from their respective absorption spectra are given in Table 1. The literature<sup>3,9-11</sup> values of  $\lambda_{\max}$  for the above indicators in aqueous medium are given in Table 1, with respect to which the  $\lambda_{\max}$  values in the melt are either in close agreement or red shifted. Red shifting of  $\lambda_{\max}$  in hydrate melt compared to its position in water, which was also observed by others<sup>4</sup>, may be attributed to the stabilization of the  $\pi^*$  state of the indicators in the ionic melt due to ion-ion and ion-dipole interactions. In case of PNA, the  $\lambda_{\max}$  for the acidic form could not be located accurately due to non-transparency of the pure melt below ~330 nm<sup>4</sup>. In Table 1 the literature<sup>3,12</sup> values of  $pK_a$  of the indicators in water are also listed. It may be noted that for the calculation of  $H_0$  of hydrate melts  $pK_a$  values of indicators in water are generally used since  $pK_a$  values in hydrate melts are not known.

In acidic CNTH melt, the absorbance of the indicators is found to vary with time which is attributed to the nitration of the organic indicators.<sup>13</sup> Owing to this problem, experimental determination of meaningful values of  $H_0$  of CNTH melt using Eq. (2) has been considered to be difficult. To overcome this problem attempts have been made to determine the value of the ratio  $c_B/c_{BH^+}$  using the spectral data of an indicator in neat and basic CNTH melt only. For this purpose, it is considered that an indicator exists completely in the deprotonated form in basic CNTH melt. After evaluating the extinction coefficients for the basic form of the indicators, the values of  $c_B$  and  $c_{BH^+}$  were easily determined from the absorbance and concentration of an indicator in the neat melt. An almost similar approach was used by Duffy and Ingram<sup>3</sup> to estimate  $c_B/c_{BH^+}$  in concentrated aqueous

Table 1—Spectral data and parameters of Eq. (2) for different indicators in calcium nitrate tetrahydrate melt at 25°C ( $\lambda_{\max}$  in aqueous medium are given in the parentheses)

Indicator	$\lambda_{\max} \pm 2/\text{nm}$		$\log[c_B/c_{BH^+}]$	$H_0 \pm 0.2$
	Acidic	Basic		
MR	520	462	—	—
( $pK_a=5.0$ ) <sup>a</sup>	(522) <sup>b</sup>	(423) <sup>b</sup>	—	—
PNP	333	408	—	—
( $pK_a=7.1$ ) <sup>a</sup>	(317) <sup>c</sup>	(407) <sup>c</sup>	—	—
MO	510	470	—	—
( $pK_a=3.7$ ) <sup>a</sup>	(507) <sup>a</sup>	(462) <sup>a</sup>	—	—
PNA	-	394	0.8	1.8
( $pK_a=0.99$ ) <sup>d</sup>	-	(380) <sup>d</sup>	—	—
BPB	447	590	-1.5	2.6
( $pK_a=4.1$ ) <sup>a</sup>	(440) <sup>c</sup>	(595) <sup>c</sup>	—	—

<sup>a</sup> ref. 12, <sup>b</sup> ref. 9, <sup>c</sup> ref. 10, <sup>d</sup> ref. 3, <sup>e</sup> ref. 11

solutions of  $ZnCl_2$ . We, however, observed that the above method adopted by us for estimating  $c_B/c_{BH^+}$  could not be satisfactorily applied using MR, MO, and PNP indicators because of two reasons. Firstly, these indicators exist in the neat melt predominantly in the protonated forms thereby rendering the amount of basic forms very small. Secondly, part of the spectra of the acidic forms of these indicators overlap with the spectra of the basic forms. Therefore, for employing the present method of estimating  $c_B/c_{BH^+}$  in hydrate melts containing nitrate ion, the indicator to be used must have a low  $pK_a$  value. An attempt has been made below to evaluate  $H_0$  of CNTH melt from the spectral data of PNA and BPB only.

The  $pK_a$  value of PNA is 0.99, which is the lowest among the  $pK_a$  values of the indicators used in this study. This indicator was used by other workers for determining  $H_0$  of similar type of systems<sup>3,4</sup>. A low value of  $pK_a$  of PNA ensures, as mentioned above, a high amount of basic form of the indicator in the neat hydrate melt. As expected, in the neat melt a clear and intense band at 394 nm due to the basic form of PNA was observed. Thus, using PNA the value of  $c_B$  was evaluated accurately and the value of  $H_0$  obtained for CNTH melt is equal to 1.8 (Table 1).

In the case of BPB, although its  $pK_a$  is more than that of MO, the value of  $c_B$  was estimated accurately in spite of the fact that the amount of the basic form of the indicator in neat melt is low. This was possible because in BPB the difference between the  $\lambda_{\max}$  values of its acidic and basic forms is 143 nm whereas in MO this difference is only 40 nm. The well separated spectra due to acidic ( $\lambda_{\max} = 447$  nm) and basic ( $\lambda_{\max} = 590$  nm) forms of BPB in neat CNTH melt were obtained. The value of  $H_0$  for CNTH melt calculated using BPB is found to be 2.6 (Table 1).

The values of  $H_0$  obtained for CNTH melt using PNA and BPB indicators are different by 0.8 unit. Based on the uncertainties involved in concentration values of the indicators the error limit of  $H_0$  values was estimated to be nearly  $\pm 0.2$ . Thus, it appears that  $H_0$  value of a melt determined using indicator probes depends on the  $pK_a$  values of the indicators. From the reported data<sup>3</sup> such a dependence of  $H_0$  value on the  $pK_a$  of indicator can be noticed in concentrated  $ZnCl_2$  solutions. For example, using 4-chloro-2-nitroaniline ( $pK_a = -1.03$ ), 4-nitrodiphenylamine ( $pK_a = -2.38$ ), and 2,5-dichloro-4-nitroaniline ( $pK_a = -1.82$ ) indicators, the reported  $H_0$  values for zinc chloride tetrahydrate are  $-2.35$ ,  $-2.10$ , and  $-1.86$ , respectively and those for zinc chloride hexahydrate are  $-1.45$ ,  $-0.83$ , and  $-0.78$ , respectively. This virtual dependence of  $H_0$  on  $pK_a$  is because of using in Eq. (2) the  $pK_a$  values of indicators in water instead of those in the melt.  $pK_a$  values of all acidic species vary differentially by changing the solvent. It has been shown<sup>8</sup> that the difference between the  $pK_a$  values of an acid in water and another solvent is governed by the transfer activity coefficients of all the species involved in the dissociation equilibrium. Therefore, the  $H_0$  of melt obtained by using  $pK_a$  of indicators in water are not the true  $H_0$  and can be called as apparent  $H_0$  of CNTH melt with water as reference medium.

The correctness of the  $H_0$  value of CNTH melt obtained cannot be tested directly as the literature value of  $H_0$  of pure CNTH melt is not available for comparison. Therefore, an attempt has been made to check the correctness of the  $H_0$  value of CNTH melt by an indirect manner. For instance, Duffy and Ingram<sup>3</sup> predicted a value of  $-4.1$  for the  $pK_a$  of  $Zn(H_2O)_4^{2+}$  based on its optical basicity value whereas the measured  $H_0$  value of zinc chloride tetrahydrate melt is in the range  $-2.35$  to  $-1.86$  as given above. In the light of this, an empirical relation is presumed to exist between the  $H_0$  of a hydrate melt and the  $pK_a$  of the corresponding aquometal ion. Applying this empirical relation to CNTH melt,  $H_0$  value in the range  $1.5$  to  $1.2$  may be anticipated for this melt since the value predicted by Duffy and Ingram<sup>3</sup> for  $pK_a$  of  $Ca(H_2O)_4^{2+}$  is equal to  $2.6$ . Secondly, using the predicted value of  $pK_a$  of  $Ca(H_2O)_4^{2+}$ , the degree of dissociation,  $\alpha$ , of this aquometal ion was estimated by solving the quadratic equation in  $\alpha$  for the dissociation equilibrium given in Eq. (1) which then provides a value of  $1.3$  for  $H_0$  by ignoring the activity coefficient terms. Thirdly, on extrapolating separately the  $H_0$  values reported<sup>4</sup> for the binary molten mixtures

CNTH +  $Al(NO_3)_3 \cdot 9H_2O$  and CNTH +  $Cd(NO_3)_2 \cdot 4H_2O$ , we obtained the  $H_0$  value of CNTH melt as  $1.5 \pm 0.1$  and  $2.6 \pm 0.1$ , respectively. It is worthwhile to note that the  $H_0$  values of CNTH melt estimated thus are comparable with the present measured values using PNA and BPB.

It may, therefore, be concluded that spectrophotometric technique using organic indicators can be employed for the determination of  $H_0$  function of hydrate melts containing metal nitrates even if the indicator undergoes nitration in the acidic melt and the melt has no UV transparency. However, the indicators to be used must have low  $pK_a$  value, preferably  $\leq 1$ . Indicators having high  $pK_a$  value in the range  $\leq 4$  can also be used as probes for the determination of  $H_0$  provided such indicators have well separated absorption bands for their acidic and basic forms in neat hydrate melt.

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