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Investigation of the Role of Ionic Liquids in Tuning the pK_a Values of Some Anionic Indicators

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Abstract The effect of imidazolium-based ionic liquids, ([C_{12}mim][Cl] and [C_8mim][Cl]), on the acid-base equilibria of two sulfonated indicators has been studied. The presence of ILs leads to decreased pK_a values because of the stronger electrostatic interaction of cationic ILs with the basic forms of the indicators with more negative charge. The longer alkyl side chain of [C_{12}mim][Cl] compared to [C_8mim][Cl] results in stronger hydrophobic interaction of this IL with the basic forms of the dyes leading to a more effective decrease in the pK_a values. Also, the transition points and transition intervals of the acid-base titration curves of the indicators were affected by the presence of ILs. It was found that the IL interaction with acid-base indicators also results in sharpening the acid-base titration curves of the indicators. From these observations, it is concluded that the presence of ILs can tune the pK_a values of indicators. All the experiments were performed spectrophotometrically and the results were obtained using curve fitting methods.

Keywords Ionic liquids · Imidazolium-based · Acid-base equilibrium · Titration · pK_a

1 Introduction

Micelles of amphiphilic compounds can inhibit or accelerate reaction rates (by up to several orders of magnitude) and also shift the equilibria (acid-base, redox and complexation). These changes are generally due to the hydrophobic and electrostatic interactions of the reactants with micellar aggregates. The proper selection of an ionic surfactant can provide a structure with an interior, an exterior and a charged interface, with an electrical potential at or near the micellar surface that can differ by a few hundred millivolts from that of the bulk. This allows ionic, as well as uncharged, species to interact with micellar aggregates, thus

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greatly influencing equilibria and rates of reactions [1]. The acid-base equilibria of indicators and thus the pK_a values are significantly affected by the presence of micelles [2, 3]. As knowledge of the shifts in the pK_a values of indicators is of great value in analytical chemistry, considerable attention has been paid to understanding the phenomenon [4–9]. This shift can be explained in terms of differences between the properties of the bulk solvent and the interfacial region and perturbation of the acid-base equilibria by the electrostatic field effect of the charged interface. The dissociation equilibria of substituted benzoic acids in cationic and anionic surfactant micelles have been investigated potentiometrically [10]. The acid-base equilibria of a number of phenols, amines, carboxylic acids, dyes, amino acids, medicinal compounds and solvatochromic acid-base indicators in aqueous micellar solutions have been examined [11–16]. The association constants for the interaction of indicators with micelles may be quite informative with regard to the pK_a shifts of such indicators.

Ionic liquids (IL) are a new class of ionic solvents that have gained much attention in many fields of chemistry in the recent years. These compounds have low melting points, negligible vapor pressures, and are stable over a wide range of temperature [17–24]. Recently, ILs based on the 1-alkyl-3-methylimidazolium cation ([$C_n$mim]) have received much attention as green solvents or additives in aqueous solutions. The amphiphilic nature of the [$C_n$mim] cation means that, in many respects, these ILs will act analogously to cationic surfactants [25]. Recently many reports have been published to prove the surfactant-like and aggregation behavior of ILs [26–30], but to the best of our knowledge there is no report on the investigation of the effect of these ILs on acid-base equilibria. As ionic liquids are gaining major importance as green solvents, the study of acid-base behavior in ionic liquid media is important to the understanding of the mechanisms of reactions in analytical and pharmaceutical applications. These studies may also suggest the possibility of analogous pK_a shifts for biologically active compounds induced by their incorporation into membranes, liposomes, or micelles. In the present paper, we focused our attention on studying the effects of some 1-alkyl-3-methylimidazolium ionic liquids on the dissociation constants, transition points and transition intervals of the acid-base titration curves of two sulfonated acid-base indicators, namely, methyl orange (MO) and azocarmine G (AZG).

2 Experimental

2.1 Materials

The ILs were synthesized according to standard methods by the reaction of 1-methylimidazole with an excess of the appropriate haloalkane [17]. The reactants were stirred without any additional solvent at 70 °C for 72 h. The [$C_n$mim][Cl] salt, where n is the carbon number of the alkyl chain, was then purified by repeated washing with ethyl acetate before drying overnight at 70 °C under a vacuum. The purity of the products was assessed by ^{1}H NMR spectroscopy and washing was continued until the characteristic peaks for the starting materials (1-haloalkane and imidazole) were not observed. All ILs should be dried at 70 °C and stored in a dry place before use [26]. KCl that was used to fix the ionic strength was purchased from Merck and used without any purification. At all titration steps the pH was adjusted by the addition of few μL of concentrated HCl and NaOH solutions to be sure that the total volume of the solution was not affected.

2.2 Apparatus

The UV-Vis absorption spectrophotometric measurements were carried out with a Perkin-Elmer (Lambda 2) spectrophotometer using a 1-cm quartz cell. The temperature in all experiments was kept constant at 25 °C using a LO-Temprol 154 thermostat.

3 Results and Discussion

3.1 Study of the Effect of ILs on the pK_a Values of the Indicator

The acid-base equilibrium of a protonated indicator in the experimental pH ranges can be represented as

$$\mathrm{HIn} \overset{K_a}{\rightleftharpoons} \mathrm{In}^- + \mathrm{H}^+ \tag{1}$$

$$K_a = \frac{[\mathrm{In}^-][\mathrm{H}^+]}{[\mathrm{HIn}]} \tag{2}$$

$$C_t = [\mathrm{HIn}] + [\mathrm{In}^-] \tag{3}$$

where HIn, In^- and C_t refer to the acidic and basic forms and total concentration of the indicators, respectively.

The equilibrium concentration of the acidic (HIn) and basic (In^-) forms of indicators can be calculated using Eqs. 2 and 3 as follows:

$$[\mathrm{HIn}] = C_t \frac{[\mathrm{H}^+]}{([\mathrm{H}^+] + K_a)} \tag{4}$$

$$[\mathrm{In}^-] = C_t \frac{K_a}{([\mathrm{H}^+] + K_a)} \tag{5}$$

Beer's law can be expressed as:

$$A_{\mathrm{HIn}} = \varepsilon_{\mathrm{HIn}} b[\mathrm{HIn}] \tag{6}$$

$$A_{\mathrm{In}^-} = \varepsilon_{\mathrm{In}^-} b[\mathrm{In}^-] \tag{7}$$

So at any wavelength:

$$A = A_{\mathrm{HIn}} + A_{\mathrm{In}^-} \tag{8}$$

$\varepsilon_{\mathrm{HIn}}$ and $\varepsilon_{\mathrm{In}^-}$ can be obtained by dividing the absorbance value at a certain wavelength by the total concentration of indicator in completely acidic and basic media, respectively.

A curve-fitting method was applied to calculate the K_a values (and then the pK_a values) of the indicators in aqueous solutions.

In the present work, we are primarily concerned with the effect of different concentrations of two imidazolium-based ionic liquids, 1-octyl-3-methylimidazolium chloride [C_8mim][Cl] and 1-dodecyl-3-methylimidazolium chloride [C_{12}mim][Cl], on the pK_a values of two sulfonated indicators. As mentioned previously, the aggregation behavior of these ILs have been investigated before and their critical aggregation concentrations (CAC) have been reported [26–31]. Azocarmine G (AZG) and methyl orange (MO) were chosen as two sulfonated indicators in this work. The type of dye–IL interaction was investigated in our previous work [31]. It is notable that these sulfonated dyes have negative charges in both acidic and basic pH because of presence of the $-SO_3^-$ group. Therefore, both forms can interact with ILs, but as mentioned previously [31], this interaction is stronger in the case of the basic form, because of the higher negative charge. Figures 1 and 2 show the spectral changes of AZG and MO by varying pH in the presence and absence of [C_{12}mim][Cl]. All the experiments were performed in 1 mol·dm^{-3} KCl to prevent the change in ionic strength upon addition of ILs. However it should be noted that the spectral changes of the indicators in the presence of ILs are the results of IL–dye interaction, not the effect of varying ionic strength [31]. A curve-fitting method was applied to calculate the apparent pK_a values of the indicators in different concentrations of ILs. The fitting procedure is described as follows.

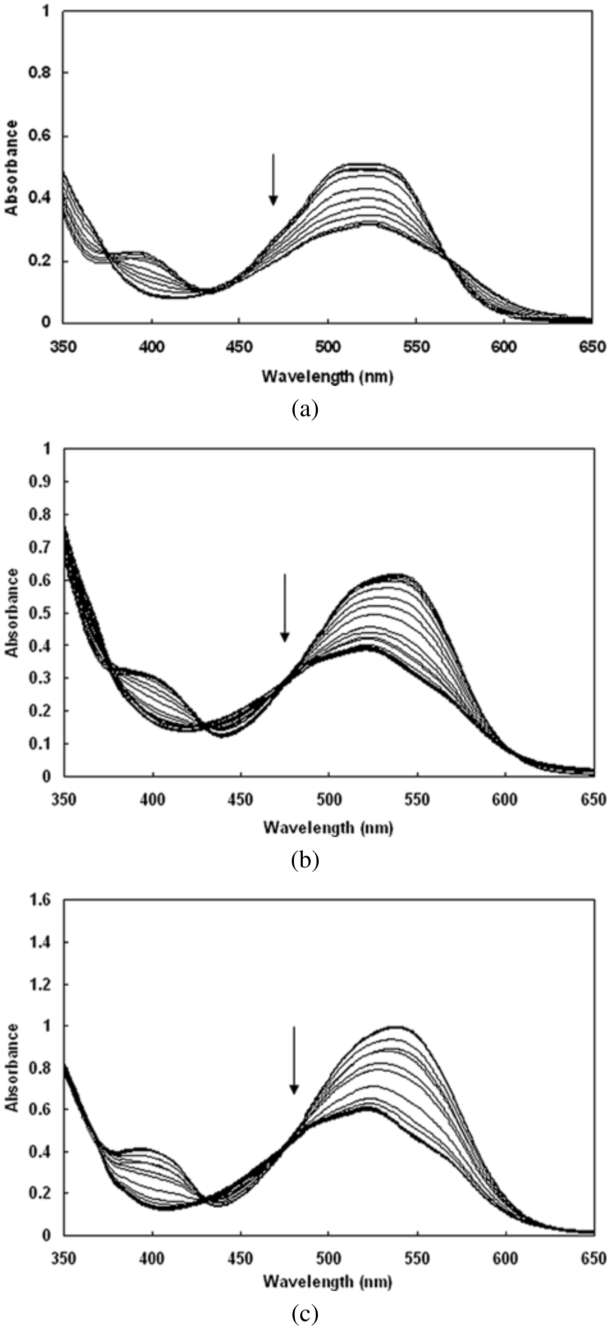
3.1.1 Fitting Procedure

The experimental absorbance values were chosen at the maximum wavelength of the acidic or basic form of the indicators whereas the calculated absorbance values were obtained by Eqs. 4–8. The main goal in every fitting procedure is to approach the best fit or minimum differences between the experimental and calculated absorbance values by changing the fitting parameter(s). The procedure is started by considering an initial estimate for the K_a values (as the fitting parameter) and the best fit is obtained for the minimum difference between experimental and calculated absorbance values (by calculating the sum of the square errors between them). The fitting procedure was carried out in Excel (Solver program). The calculated pK_a values are reported in Table 1. Good agreement between the calculated and experimental absorbance values against pH were observed for both indicators with ILs. As an example, Fig. 3 shows the absorbance variation against pH for Azocarmine G in the presence of different concentrations of [C_8mim][Cl].

As can be seen by increasing the IL concentration the pK_a values decrease. These pK_a variations can be related to the difference between the properties of the bulk solvent and of the interfacial region. These variations in behavior can originate from two different sources. One of them is related to the electrostatic interaction of the ILs and indicators, and the other is the hydrophobic interaction. The anion of the indicator (In$^-$) is strongly attracted to the interfacial layer of the IL with positive charge due to the electrostatic attraction between opposite charges. The stronger electrostatic interaction of In$^-$, compared to HIn, with the positive head group of IL [31] can influence the acid-base equilibrium. In other words, the dissociation equilibrium (Eq. 1) moves towards the right upon addition of IL, causing a decrease in the pK_a^{app} values compared to the pK_a value in water (pK_a^w).

Table 1 The pK_a values of two indicators obtained by curve fitting method in different concentrations of [C_8mim][Cl] and [C_{12}mim][Cl]

	[C_8mim][Cl] (mol·dm^{-3})	pK_a	[C_{12}mim][Cl] (mol·dm^{-3})	pK_a
Azocarmine G	–	7.80	–	7.80
	0.05	7.40	0.011	4.58
	0.27	6.07	0.063	4.28
	0.67	5.50	0.110	4.67
	[C_8mim][Cl]	pK_a	[C_{12}mim][Cl]	pK_a
Methyl orange	–	3.35	–	3.35
	0.18	2.41	0.0011	3.03
	0.34	2.26	0.0032	2.07

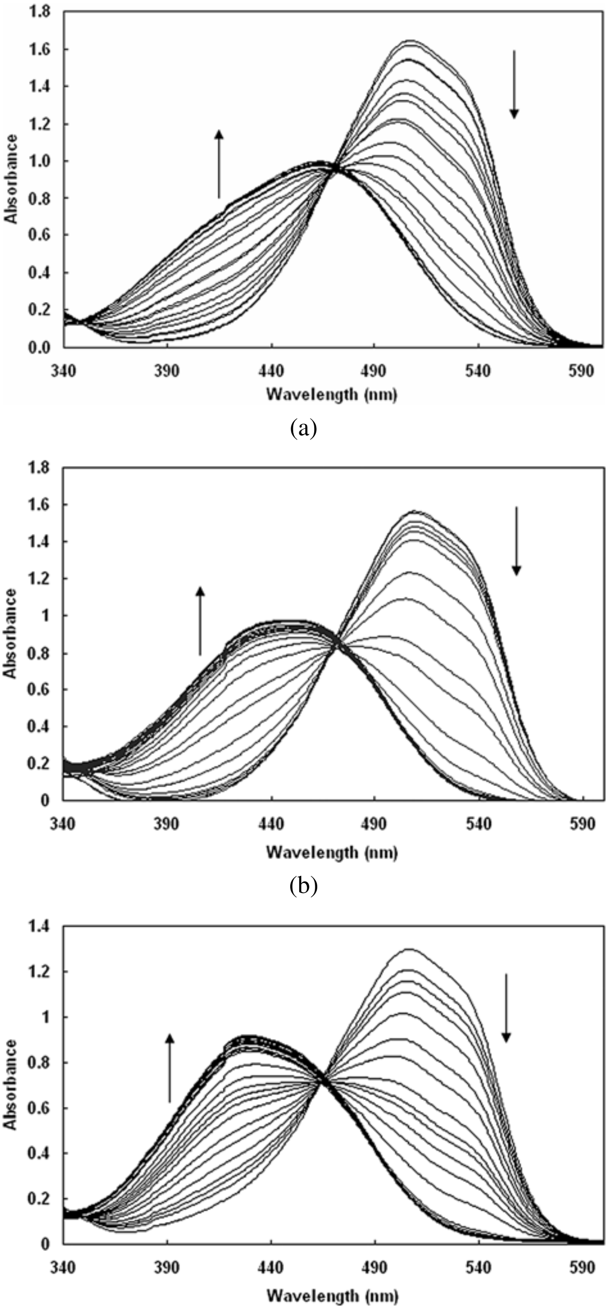


(a)

(b)

(c)

Fig. 1 Absorption spectra of AZG (5.8×10^{-5} mol·dm^{-3}) at different pH values, (**a**) in pure water (pH from 3.1 to 12.1), (**b**) in 0.67 mol·dm^{-3} [C_8mim][Cl] (pH from 1.6 to 11.4), and (**c**) in 0.11 mol·dm^{-3} [C_{12}mim][Cl] (pH from 2.1 to 12.4)



(a)

(b)

(c)

Fig. 2 Absorption spectra of MO (1.46×10^{-5} mol·dm^{-3}) at different pH values, (**a**) in pure water (pH from 1.4 to 12.6), (**b**) in 0.34 mol·dm^{-3} of [C_8mim][Cl] (pH from 0.65 to 12.25), and (**c**) in 0.0032 mol·dm^{-3} [C_{12}mim][Cl] (pH from 1.4 to 12.7)

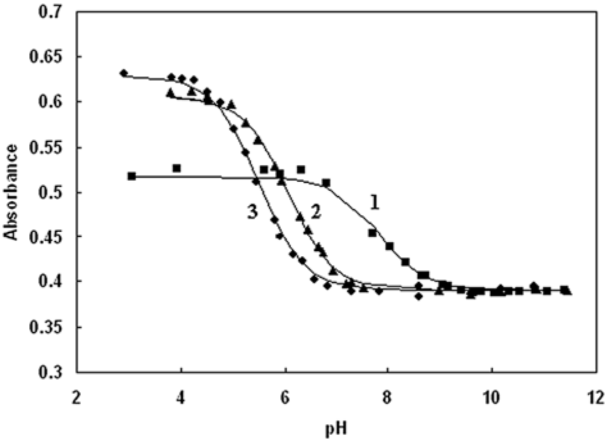


Fig. 3 Plot of calculated (*lines*) and experimental (*dots*) absorbance values versus pH at maximum wavelength of AZG in the concentrations (1) 0 mol·dm^{-3}, (2) 0.27 mol·dm^{-3} and (3) 0.67 mol·dm^{-3} [C_8mim][Cl]

Table 2 The influence of [C_8mim][Cl] and [C_{12}mim][Cl] on the transition points and the transition intervals of acid-base indicators

	Azocarmine G		Methyl orange	
	pH transition interval	ΔpH	pH transition interval	ΔpH
Water	5.90–9.82	3.92	1.39–4.85	3.46
[C_8mim][Cl]	3.82–6.84	3.02	0.97–3.77	2.80
[C_{12}mim][Cl]	3.33–5.76	2.23	1.37–3.43	1.91

As can be seen from Table 1, the decrease in the pK_a values of the two indicators was achieved at a lower concentration of [C_{12}mim][Cl] compared to the [C_8mim][Cl]. This can be related to the longer alkyl chain of [C_{12}mim][Cl] that leads to the formation of IL aggregates at a lower concentration compared to [C_8mim][Cl].

Also, a relatively sharp decrease in the pK_a^{app}values can be observed at IL concentrations near or at the CAC. However, at IL concentrations well above the CAC, the pK_a values decrease slightly and the curve reaches a plateau.

3.2 Study of the Effect of ILs on the Transition Point and Transition Interval of the Indicators

Since the IL solutions have remarkable effects on the dissociation equilibria of acid-base indicators, the transition points and transition intervals of the acid-base titration curves of the indicators should be affected. The effects of [C_8mim][Cl] and [C_{12}mim][Cl] on the transition points and transition intervals of AZG and MO are shown in Table 2. It can be seen that the transition intervals of AZG and MO in [C_8mim][Cl] and [C_{12}mim][Cl] solutions are reduced with respect to the case in pure water, so it results in an increase in the titration curve sharpness. Again, the effect of [C_{12}mim][Cl] is more pronounced compared to that of [C_8mim][Cl] because the longer alkyl side chain in [C_{12}mim][Cl] leads to stronger hydrophobic interactions and its lower CAC value.

Therefore, the acid-base titration accuracy will increase if the titration is carried out in an optimal IL concentration. According to this special characteristic of ILs, it is expected that the pK_a^{app} of a wide range of acid-base indicators can be tuned by changing the ILs' concentration in aqueous solutions.

4 Conclusion

It is evident that ionic liquids, especially imidazolium-based ILs, can form aggregates that have considerable effects on acid-base equilibria. In this work, the influence of two imidazolium-based ILs ($[C_{12}mim][Cl]$ and $[C_8mim][Cl]$) on the acid-base equilibrium of two anionic indicators (azocarmine G and methyl orange) was investigated and the results show the effectiveness of the presence of ILs in tuning the pK_a values of these indicators.

In addition, ILs can influence the transition interval and transition points of the indicators that can be very useful, especially in the case of some weak acid-base indicators like azocarmine G.

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