

Potentiometric Titrations of Para and Nitro Substituted Aromatic Acids and their Mixtures in Methylenechloride

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(Received on 30th June 2010, accepted in revised form 1st January 2011)

Summary: In this study, it was the purpose to examine the potentiometric titrations of para and nitro substituted aromatic acids in methylenechloride (MEK) as a non-aqueous solvent. Good analytical results were obtained in determining the amount of each acid and the amounts of acids in their ternary mixtures by using 0.0964 N tetrabutylammoniumhydroxyde (TBAH) as a standard titrant. Methylenechloride (MEK) which is a good solvent for many organic compounds and has a convenient liquid range of -86 to 80 °C was used for titration of the para and nitro substituted aromatic acids. A linear relationship has been found between pK_a values of the para and nitro substituted aromatic acids in water and the half neutralization potential (HNP) values determined by potentiometric titration curves of the same acids in MEK.

Introduction

Potentiometric titrations are primarily concerned with phenomena that occur at the electrode surfaces in a solution and with applied reactions that are going to be completed in order to indicate the end point [1-8].

When an acid is dissolved in a solvent, it has some tendency to transfer a proton to a solvent molecule. The simplest reaction that may run is the following;



Titrimetry in nonaqueous solvents is a powerful tool in analytical chemistry and provides detailed information about the ion-pair formation, reaction rates and the equilibria for many solute-solvent systems at low concentrations [9-17].

Solvent and structural effects are the biggest factors influencing the acidity or basicity of a molecule and it is very difficult to evaluate the extent of such an effect [16, 18-20]. Ideally, a consideration of the effect of substituents should be based upon the effect of substituent on the potential energies of the acids and ion. Unfortunately, the potential energies are largely inaccessible. For this reason, the free energies containing contributions from kinetic energies of vibration and rotation are determined. Because, the changes in kinetic energies can be assumed parallel to the changes in potential energies in determination of the free energies. According to this approach, a substituent which stabilizes the ion more than acid or base will favor ionization, whereas a substituent which stabilizes the parent compound more than ion will cause a decrease in ionization. Somewhat less rigorously, but more conveniently, the

effect of a given substituent on the ionization may be considered from the viewpoint of electrostatics. If the electron charge density in the vicinity of the ionizable proton is decreased by the action of a substituent, it is easier to remove the proton and hence the dissociation constant increases (pK_a decreases). Because of the difficulties encountered in estimating the effect of substituents on relative stabilities of the acid or base and its ion, the electrostatic approach is generally easier to apply and has been adopted in the present discussion [21].

It is also necessary to consider the resonance and inductive effects in order to account for the effect of substituents in aromatic rings, particularly a substituent located at ortho and para to the reaction center [22]. The effect of ortho substituents depends not only on their resonance characteristics under consideration here, but also on their steric requirements [23]. Inductive effects decrease with increasing distance from the acid center [18, 21].

MEK used in this study has a convenient liquid range of -86 ° to 80 °C, dissolves many substances and is used as a solvent in processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films. For this reason it finds use in the manufacture of plastics, textiles, in the production of paraffin wax, and in household products such as lacquer and, varnishes. MEK is used in dry erase markers as the solvent of the erasable dye. MEK is also an important solvent to determine the amounts of organic compounds which are soluble in this solvent by titrimetric method [24-26].

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This paper is a preliminary account of the experience joined with the potentiometric measurement of para and nitro substituted aromatic acids in MEK by using TBAH as primary standard titrant [9-11, 19, 27-31]. The effects of substitutes on the half neutralization potentials (HNP values) determined by potentiometric titration in MEK solvent and the relationship between the HNP values determined by potentiometric titration in MEK and the pKa values (in water) of these compounds were investigated. As the half neutralization potentials of acids are slightly concentration dependent, the titrations were carried out with identical concentration and also on dilute solution.

Results and Discussions

Because of associations between ion pairs and molecules, half neutralization potential can be concentration dependent and leads to differences in the slope of titration curves for various aromatic acids. The shape of curves is believed to be due to near-neighbor effects, ion sizes and the dielectric constant of the solvent.

A group of organic para and nitro substituted aromatic acids with known pKa values in water was titrated potentiometrically by using TBAH as titrant in MEK solvent. The titration curves of benzoic and nitro substituted aromatic acids in MEK by using 0.0964 N TBAH is given in Fig. 1. Nitro groups having inductive effect in the aromatic ring of benzoic acid increase the acid strength. With increasing distance from acid center for nitro groups in the aromatic ring, the acid strength of benzoic acid decreases (pKa increases). The pKa of values of benzoic acid, 4-nitrobenzoic acid, 3-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 2,5-dinitrobenzoic acid, 2,4-dinitrobenzoic acid and picric acid in water are 4.20, 3.44, 3.45, 2.82, 1.62, 1.43 and 0.38, respectively. Similar observations have been determined for HNP values of benzoic acid (HNP=-376 mV) and nitro substituted aromatic acids such as 4-nitrobenzoic acid (HNP=-310 mV), 3-nitrobenzoic acid (HNP=-310 mV), 3,5-dinitrobenzoic acid (HNP=-280 mV), 2,5-dinitrobenzoic acid (HNP=-268 mV), 2,4-dinitrobenzoic acid (HNP=-254 mV) and picric acid (HNP=-106 mV). It is also necessary to consider resonance in order to account for the effect of substituents in aromatic ring. However, the electronegative substituents in meta and para positions in aromatic ring have almost similar effect for ionization of carboxyl groups and for the pKa values of 3-nitrobenzoic acid (pKa=3.45) and 4-nitrobenzoic acid (pKa=3.44), respectively. For this

reason, the HNP values of 3-nitrobenzoic acid and 4-nitrobenzoic acid determined by potentiometric titration were found to have the same potential values (HNP=-310 mV). A relationship was observed between the pKa values of nitro substituted aromatic acids in water and the HNP values of the same acids determined by potentiometric titration curves in MEK. This relation is shown in Fig. 2. As can be seen, the HNP values determined by potentiometric titration curves decreased with increasing pKa values of nitro substituted aromatic acids in water.

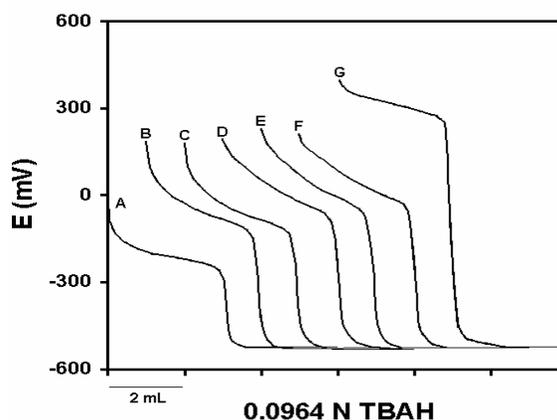


Fig. 1: The potentiometric titration curves of nitro substituted aromatic acids in MEK by using 0.0964 N TBAH as titrant.

A: Benzoic acid, B: 3-nitrobenzoic acid, C: 4-nitrobenzoic acid, D: 3,5-dinitrobenzoic acid, E: 2,5-dinitrobenzoic acid, F: 2,4-dinitrobenzoic acid, G: Picric acid.

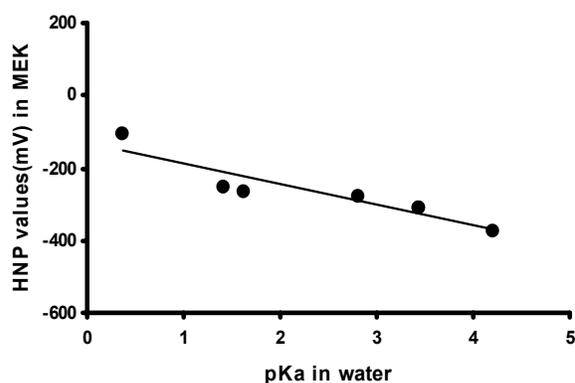


Fig. 2: The relation between HNP values measured by potentiometric titration curves of nitro substituted aromatic acids in MEK by using 0.0964 N TBAH as titrant and pKa values of the same acids in water.

Fig. 3 shows the potentiometric titration curves of para substituted aromatic acids in MEK solvent using 0.0964 N TBAH as titrant. The HNP values were determined from the potentiometric titration curves of para substituted aromatic acids titrated by 0.0964 N TBAH. The pKa value of para amino benzoic acid in para substituted aromatic acids containing amino (pKa=4.97), methoxyl (pKa=4.44), fluorine (pKa=4.14), chlorine (pKa=3.98) and bromine (pKa=3.97) functional groups has higher value than others due to its more electropositive characterization. The electronegative substituents such as bromine, chlorine and fluorine groups reduce pKa values of para substituted aromatic acids. It is known that the decrease in the pKa value observed for the substituent in para position is larger for benzoic acid containing chlorine groups in para position than that of fluorine functional group in para position. This is agreement with the conclusion that second row elements presumably because of their larger size are less able to form stable double bonds than first row element. Therefore, resonance structures involving double bonds to second row element such as chlorine are less important than the corresponding resonance structures to first low element such as fluorine. For this reason, pKa value of 4-fluorobenzoic acid is higher than those of 4-chlorobenzoic acid and 4-bromobenzoic acid. Similar observations have been determined in the titration of para substituted aromatic acids in MEK solvent by using TBAH as titrant and the HNP values of para substituted aromatic acids containing amino (HNP=-405) and methoxyl functional groups in para positions were determined lower than those of para substituted aromatic acid containing fluorine (HNP=-376 mV), chlorine (HNP=-373 mV) and bromine (HNP=-361 mV). The relation between the pKa values of para substituted aromatic acids in water and the HNP values of the same acids determined by potentiometric titration curves in MEK solvent was found for para substituted aromatic acids. The increase in the pKa values of para substituted aromatic acids in water resulted in a decrease in the HNP values determined by potentiometric titration curves of para substituted aromatic acids which were titrated using 0.0964 N TBAH (Fig. 4).

Solvent, structure, resonance and inductive effects are important to consider the experimental results. The effect of a given substitute on the ionization should be also considered [18, 21, 32]. The differences in the HNP values of aromatic acids in non-aqueous media provide the titration possibilities of acid mixtures together. Fig. 5 and 6 indicate the titration curves of the mixture of possible three acids

in MEK solvent using 0.0964 N TBAH as titrant. Good analytical results were obtained in determining each acid in their mixture. The experimental results for the titration of possible acid mixtures are given in Table-1.

Table-1: The potentiometric titrations of the mixtures of aromatic acids in MEK by using 0,0964 N TBAH as standard titrant.

Acid mixtures	pK _a	Taken (mg)	Found (mg)	Recovery (%)
Picric	0.38	44.10	44.17	100.16
4-nitrobenzoic	3.44	23.50	23.36	99.40
4-aminobenzoic	4.97	23.20	23.13	99.70
Picric	0.38	45.70	45.53	99.12
3,5-dinitrobenzoic	2.82	28.70	28.63	99.76
4-aminobenzoic	4.97	21.10	21.15	100.24
Picric	0.38	45.00	45.30	100.67
2,5-dinitrobenzoic	1.62	27.70	27.58	99.57
4-aminobenzoic	4.97	22.30	22.47	100.76
Picric	0.38	45.40	45.30	99.98
2,4-dinitrobenzoic	1.43	27.70	28.63	99.76
4-aminobenzoic	4.97	22.50	22.47	99.87
Picric	0.38	45.10	44.17	97.94
3,5-dinitrobenzoic	2.82	27.20	26.60	101.47
4-methoxybenzoic	4.44	24.70	24.20	97.97
Picric	0.38	44.90	44.17	98.37
2,5-dinitrobenzoic	1.62	27.35	27.60	100.91
4-methoxybenzoic	4.44	25.30	25.56	101.42
Picric	0.38	41.80	41.91	100.26
2,5-dinitrobenzoic	1.62	25.90	25.60	98.68
Benzoic	4.20	22.50	22.36	99.41

* Norbert Adolp Lange, Handbook of Chemistry, (Mc Graw – Hill Book Company, Inc.) New York, 1961.
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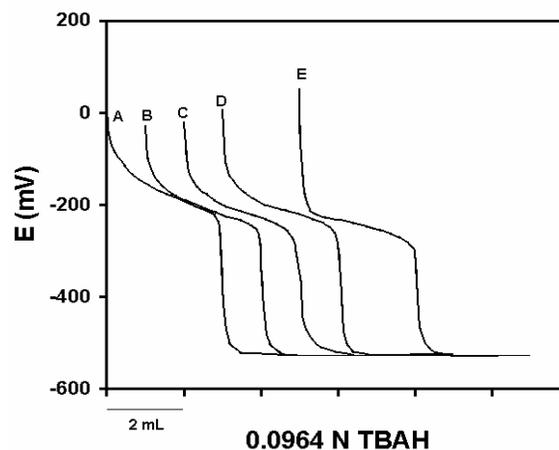


Fig. 3: The potentiometric titration curves of para substituted aromatic acids in methanol by using 0.0964N TBAH as titrant. A: 4-bromobenzoic acid, B: 4-clorobenzoic acid, C: 4- fluorobenzoic acid, D: 4-methoxybenzoic acid, E: 4-aminobenzoic acid.

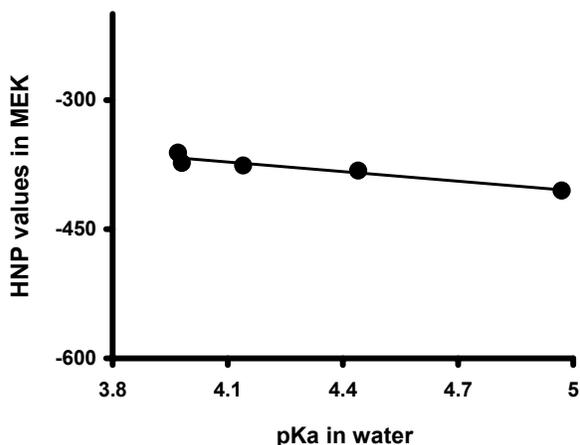


Fig. 4: The relation between the HNP values determined by potentiometric titration curves of para substituted aromatic acids in MEK by using 0.0964 N TBAH as titrant and pKa values of the same acids in water.

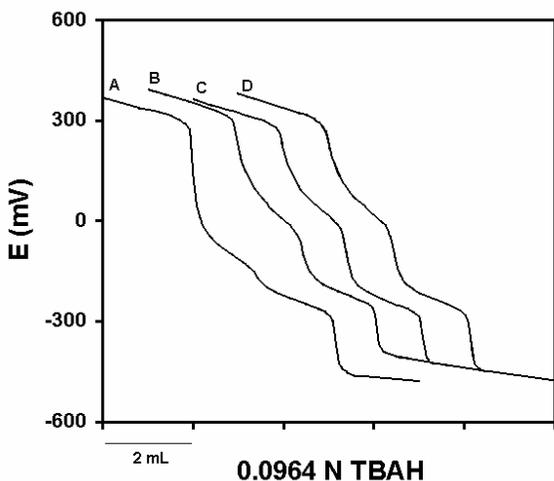


Fig. 5: The potentiometric titration curves of the ternary mixtures of aromatic acids in MEK.

A: Picric acid; 4-nitrobenzoic acid; 4-aminobenzoic acid, B: Picric acid; 3,5-dinitrobenzoic acid; 4-aminobenzoic acid, C: Picric acid; 2,5-dinitrobenzoic acid; 4-aminobenzoic acid, D: Picric acid; 2,4-dinitrobenzoic acid; 4-aminobenzoic acid,

Water is known as amphiprotic solvent and it can act as a base or an acid. However, it has a limited range of acid or base strengths. Organic solvents generally provide the largest pH change at the equivalent points for the titrations of acids or bases. For this reason, the solvent selected will be to a large extent determine the success of the titration. Fig. 7 is given to indicate the effects of MEK and methanol solvents for the titration mixture of picric,

2,4-dinitrobenzoic and glutaric acids using 0.0964 N TBAH as titrant. The potentials at half neutralization points of picric ($pK_a=0.38$), 2,4-dinitrobenzoic ($pK_{a1}=1.43$) and glutaric ($pK_{a1}=4.34$, $pK_{a2}=5.42$) acids were found to be -106 mV, -254 mV, -316 mV and -526 mV in MEK solvent and -28 mV, -102 mV and -216 mV in methanol. As can be seen from results and Fig. 7, the second neutralization point and its potential of glutaric acid in methanol were not observed for the titration of these acid mixtures, because the mV range of MEK solvent is higher than that of methanol.

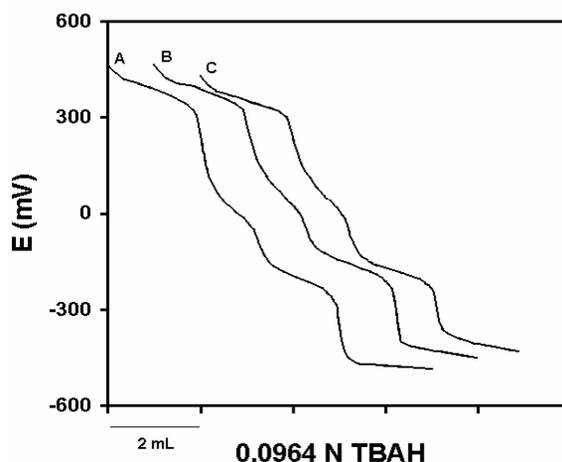


Fig. 6: The potentiometric titration curves of the ternary mixtures of aromatic acids in MEK solvent.

A: Picric acid; 3,5-nitrobenzoic acid; 4-methoxybenzoic acid, B: Picric acid; 2,5-dinitrobenzoic acid; 4-methoxybenzoic acid, C: Picric acid; 2,5-dinitrobenzoic acid; benzoic acid.

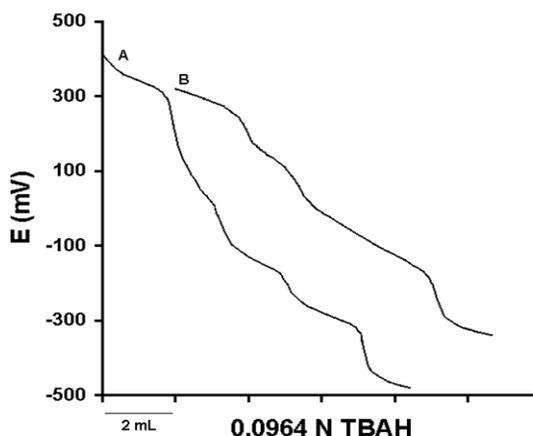


Fig. 7: The effect of solvent type on the titration of the mixture of picric, 2,4-dinitrobenzoic and glutaric acids. A: in MEK; B: in methanol.

Experimental

Reagents

Benzoic, 2-nitrobenzoic, 3-nitrobenzoic, 4-nitrobenzoic, 2,4-dinitrobenzoic, 3,5-dinitrobenzoic, 2,5-dinitrobenzoic, 4-aminobenzoic, 4-methoxybenzoic, 4-fluorobenzoic, 4-bromobenzoic, 4-chlorobenzoic and picric acids in high purity a.g. were purchased by Fluka, 0.1 N TBAH (p.a) and the solvent of methylethylketone (MEK) were supplied by Merck.

Apparatus

Autometric potentiometric titrations were carried out with a semi-automatic Metrohm E-336A potentiograph, E-436D titrating set and Metrohm universal titration vessel. Conventional glass electrode (Backman 4990-80 type) was used as indicator electrode and fiber-type calomel electrode was employed as a reference electrode. Calomel electrode was modified by replacing concentrated solution of LiCl in methanol. Electrodes were equilibrated in the solvent when not in use.

Procedure

The potentiometric measurements have been described previously [9-13, 27-31]. Accurately weighted acid samples were dissolved in 25 ml of solvent and then were titrated 0.0964 N TBAH. The titrant was added automatically and the reaction mixture was stirred with a magnetic bar during titration.

Conclusion

In this study, the titration of para and nitro substituted aromatic acids and their possible ternary mixtures in MEK and methanol was investigated by using 0.0964 N TBAH as standard titrant. The relationship between pK_a values of the para and nitro substituted aromatic acids in water and the half neutralization potential (HNP) values determined by potentiometric titration curves of the same acids in MEK were examined. Water is an amphiprotic solvent which acts as a base or an acid. However, it has a very limited range of acid or base strength. For this reason, nonaqueous titrations are frequently desirable or required because of the increased sensitivity, improved selectivity or greater solubility achieved with non-aqueous solvents. Moreover organic compounds in industrial wastes cause serious hazardous effects to human health and environment.

Most of aromatic acids can dissolve in organic solvents and to determine the amount of substituted aromatic acids in organic solvent is important for analytical research and applications using potentiometric titration method.

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