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Potentiometric and Conductometric Measurements of Dicarboxylic Acids in Non-Aqueous Solvents

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The potentiometric and conductometric measurements have been reported for the titration of aliphatic and aromatic acids in methanol, 1-propanol, pyridine, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK). Good analytical results were obtained by using tetrabutylammonium hydroxide (TBAH) as a standard titrant. A linear relationship has been found between pK_a values in water and half neutralization potential (HNP) values measured by potentiometric titration of dicarboxylic acids in the solvents such as methanol, 1-propanol, pyridine, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK). It has been shown that equivalent conductivities of dicarboxylic acids resulted in a decrease with increase in the pK_a values in the same solvents.

Key Words: Potentiometry, Conductometry, Dicarboxylic acids, Titration.

INTRODUCTION

Potentiometric titrations are primarily concerned with the phenomena that occur at the electrode surfaces in a solution and applied to the reactions that go to completion in order to indicate the end-point. Conductometry is mainly based on the measurements of the electrical conductance of a solution from which the analytical concentration can be derived by previous calibration[1–12]. When an acid is dissolved in a solvent, it has some tendency to transfer a proton to a solvent molecule. The simplest reaction which may be written is as follows:

$$HA + S \rightleftharpoons [HS^+][A^-] \rightleftharpoons HS^+ + A^-$$

Here HA and S represent an acid and a solvent respectively.

Titrimetry in non-aqueous solvents is a powerful tool in analytical chemistry and provides detailed information about the ion-pair formation, reaction rates and the equilibrium for many solvent systems at low concentrations[3–4].

Solvents 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[5].

This paper is a preliminary account of the experience gained with potentiometric and conductometric measurements of dicarboxylic acids in nonaqueous solvents using TBAH as primary standard titrant. Tetraalkylammonium hydroxide, potassium metoxide and diphenylguanidine have been used in earlier studies as titrants in nonaqueous solvents[3, 6, 7]. In this study, potentiometric titrations of dicarboxylic acids in nonaqueous solvents were investigated to show a relationship between the HNP values obtained in potentiometric titration curves of dicarboxylic acids in

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nonaqueous solvents using TBAH as a standard titrant and pK_a values of the same acids in water. As the half neutralization potentials of the acids are slightly concentration dependent, titrations were carried out with identical concentrations and also in dilute solution.

EXPERIMENTAL

The solvents of 1-propanol(Riedel de Haen) and methanol, pyridine, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) in the Merck reagents in high purity grade were used without further purification. Adipic, glutaric, malic, phthalic, pimelic and succinic acids in high purity analytical grade were purchased from Fluka. Malonic, oxalic and 0.096 N TBAH were supplied by Merck.

All potentiometric titrations were carried out with a semi-automatic Metrohm E-336A potentiograph containing E-436D titration set and Metrohm universal titration vessel.

Conventional glass electrode (Beckman 4990-80 type) was used as indicator electrode and fibre-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.

Conductometric titrations in 1-propanol and MIBK were performed by using Metrohm E518 conductometer and platinized platinium electrodes (cell constant equal to 0.665 cm^{-1}), operating at 25°C in the range from 100 mS to 1 μS with a sensitivity of ± 1.0%.

Procedure

The potentiometric measurements have been described previously[8-9, 12]. Accurately weighed acid samples were dissolved in 25 mL of solvents and then were titrated with 0.096 N TBAH. The titrant was added automatically and reaction mixture was stirred with a magnetic bar during titration. The above mentioned procedure has been used for specific conductance measurements. The values of equivalent conductivities were calculated by the following equation:

$$\Lambda = \frac{1000X}{C}$$

where X represents the conductivity of solution of concentration C in g-equiv./L. Λ is equivalent conductivity expressed in $ohm^{-1}\,cm^{2}\,equiv^{-1}$.

RESULTS AND DISCUSSION

A group of organic dicarboxylic acids with known pK_a values in water were titrated potentiometrically by using 0.096 N TBAH as titrant in different solvents. Because of associations between ion pairs and molecules, half neutralization potential can be concentration dependent and leads to differences in the slope of titration curve from those observed in aqueous solutions.

The shape of curves for various dibasic acids is believed to be due to near-neighbour effects, ion sizes, dielectric constant of solvent and temperature. List of dicarboxylic acids and measured HNP values in different solvents are summarized in Table-1. The linear relation between the half neutralization potentials of these acids in methanol, 1-propanol, pyridine, MEK and MIBK and the first pKa values of these acids in water was observed, except for oxalic acid as shown in Fig. 1. The linearity of results obtained from titration of dicarboxylic acids in previously mentioned solvents is found by using least square method.

Potentiometric titration is best suited for solvents with medium or high dielectric strength even if low dielectric solvents as dioxane ($\varepsilon = 2.21$) and dielectric constant of the solvent is a very important factor in determining the shape of the acid-base titration curve.

TABLE-1
THE HNP VALUES OF SOME ORGANIC ACIDS IN METHANOL, 1-PROPANOL, MEK, PYRIDINE AND MIBK

Acids	pK_a* values	HNP values (mV)				
		In methanol	In 1-propanol	In MEK	In pyridine	In MIBK
Oxalic	1.19	474	532	810	572	840
Maleic	1.92	588	688	911	756	962
Malonic	2.83	474	572	810	614	828
Phthalic	2.95	507	578	756	646	807
Malic	3.40	444	462	666	568	756
Succinic	4.19	360	400	594	438	630
Glutaric	4.34	338	368	558	368	594
Adipic	4.42	332	348	534	350	552
Pimelic	4.48	318	328	510	420	540

*pK_a values were obtained from Nobert Adolp Lange, Ph.D., Handbook of Chemistry, Mc Graw-Hill Book Company, Inc., New York (1961) and E. Martell and R.M. Smith, Critical Stability Constants, Plenum Press, New York (1977).

Now let us consider the equation HNP = a · pK_a + b, where a and b represent slope and intercept respectively and r is correlation coefficient of the equation. Because of associations between ion pairs and molecules, half neutralization potential may be concentration dependent. Association of ions and molecules leads to differences in the slope of titration curves from those observed in aqueous solutions. The slopes in the lines of data obtained from Fig. 1 and the values of above mentioned equation are shown in Table-2.

TABLE-2
THE VALES OF SLOPE (a), INTERCEPT (b) AND CORRELATION COEFFICIENT (r) OF LINEAR EQUATIONS SHOWN IN Fig. 1

Solvent	Dielectric (*) constant	Slope (a)	Intercept (b)	Correlation coefficient (r)
Methanol	32.60	–103.54	789.39	0.992
1-propanol	19.70	–137.76	959.31	0.991
MEK	18.45	–152.11	1211.99	0.991
Pyridine	13.24	–161.27	1087.80	0.984
MIBK	12.30	–160.84	1282.24	0.994

*Dielectric constants are obtained from Allen Y. Bard (Ed.), Electroanalytical Chemistry, New York and Donald T. Sawer and Julian L. Roberts (Jr.) (Eds.), Experimental Chemistry for Chemists, a Wiley-Interscience Publication, John Wiley & Sons Inc., New York (1974).

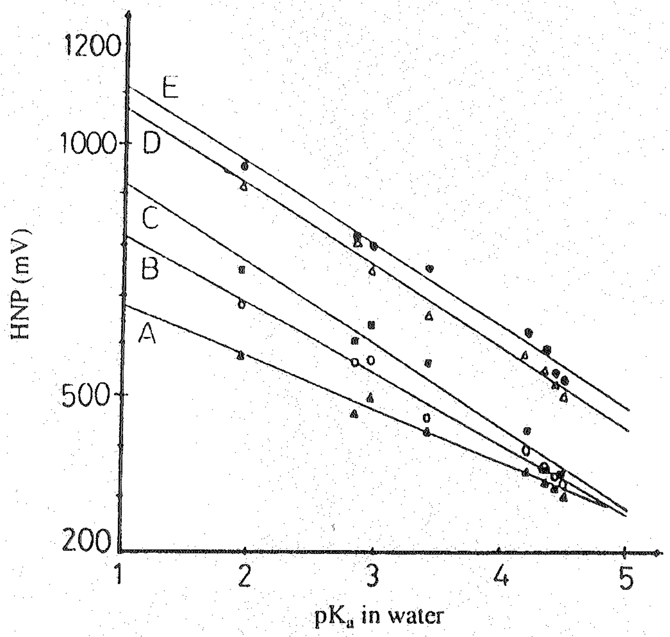

Fig. 1. The titration of some dicarboxylic acids in different solvents by using 0.096 N TBAH as titrant: (A) in methanol, (B) in 1-propanol, (C) in MEK, (D) in MIBK

We also observed that the slope of equations shown in Table-2 decreases with the increase in the dielectric constants of the solutions. This approximation is quite a new one and provides an approximate choice of solvents before titration. The relations between dielectric constants of the solvents and the slope of equations is

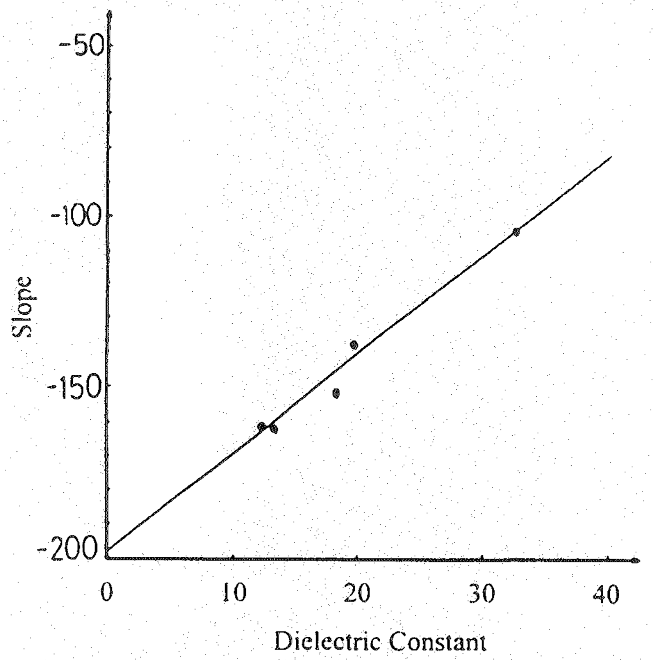

Fig. 2. The relation between dielectric constants for the solvents and the slope of equations

shown in Fig. 2. As can be seen from Fig. 2, there is a linear relation between the dielectric constants and slopes. The obtained linear equation is

$$Y = 2.92X - 199.43 \qquad (r = 0.985)$$

where Y, X and r represent slope, dielectric constant and correlation coefficient respectively.

As shown in Fig. 3, a relationship between the initial potentials of dicarboxylic acids in methanol and MIBK and their pK_a values in water is found as linear. We have obtained the following equations, where Y represents measured potential before titration, X is the pK_a value of the acids and r is correlation coefficient of equation.

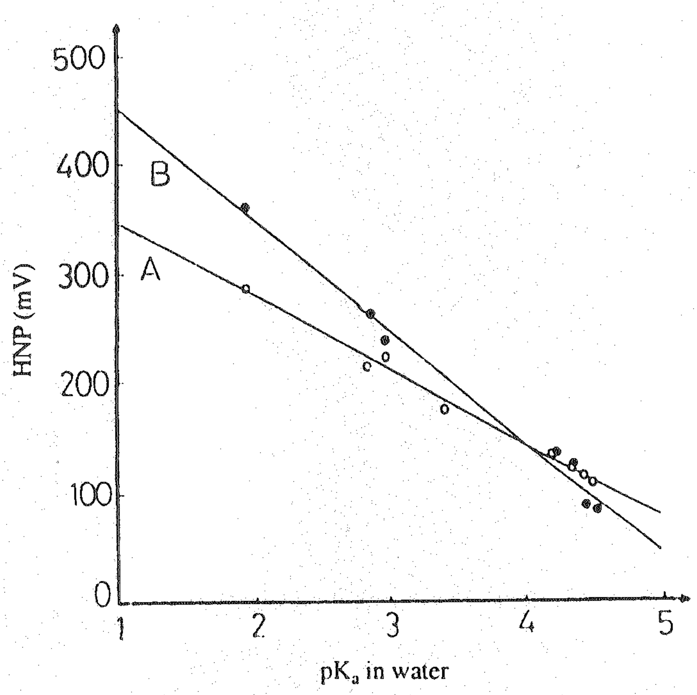

Fig. 3. The relation between the initial potentials of some dicarboxylic acids in nonaqueous media and their pKa values in water: (A) in methanol, (B) in MIBK

$$Y = -101.26X + 548.25 \qquad (r = 0.992 \text{ in methanol})$$
$$Y = -67.06X + 412.42 \qquad (r = 0.996 \text{ in MIBK})$$

Most carboxylic acids are not levelled in pyridine and neutral solvents such as ketone. The order of acidic strength in the nonlevelling solvent is dependent on charge type, molecular species, solvency, intra- and intermolecular hydrogen bonding and the titration species[10].

The potentials at half neutralization points of picric acids (pKa = 0.38), 2,2-dinitrobanzoic acids ($pK_a = 1.43$), and glutaric acid ($pK_{a_1} = 4.34$, $pK_{a_2} = 5.42$) were found to be –106 mV, –254 mV, –316 mV and –526 mV in MEK and –28 mV, –102 mV and –216 mV in methanol respectively[12]. By using neutralization potential of these acids in methanol and MEK and their pK_a values in water, we titrated the mixture of three acids together in both solvents (Fig. 4). As seen from Fig. 4, we did not observe the second neutralization potential of glutaric acid in methanol, because the mV scale of MEK is higher than that of methanol which is not also observed in the titration pure compound.

Equivalent conductivities were calculated from the conductance values of dicarboxylic acids which were measured in 1-propanol and MIBK. As could be

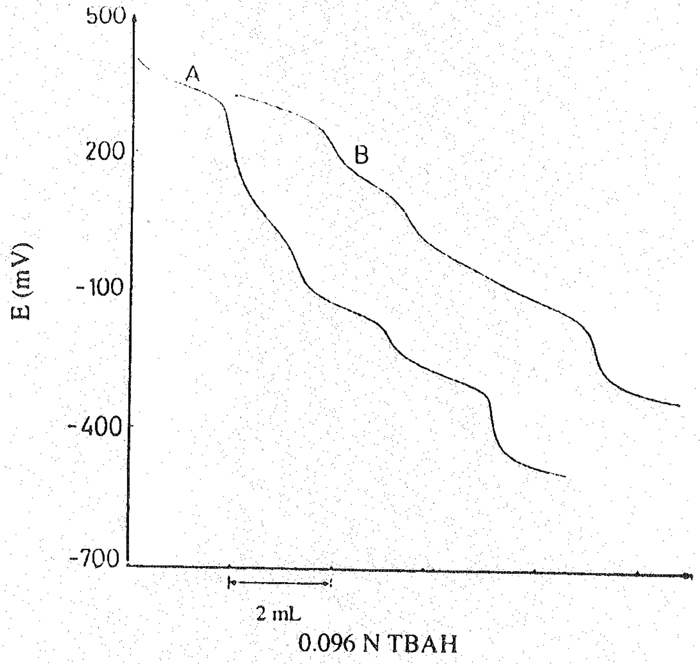

Fig. 4. The titration curves of the mixtures of picric acid (pKa = 0.38), 2,4-dinitrobenzoic acid (pKa = 1.43) and glutaric acid (pKa_1 = 4.34, pKa_2 = 5.42) in MEK(A) and methanol(B) using TBAH as titrant

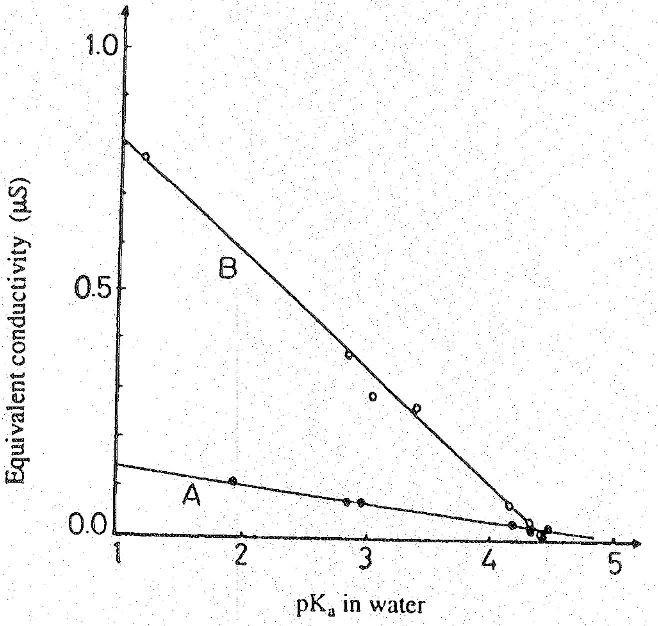

Fig. 5. The relation between the equivalent conductivities of some dicarboxylic acids in non-aqueous medium and their pK_a values in water

seen from Fig. 5, the equivalent conductivities of dicarboxylic acids decrease with the increase in the first pKa values of these acids.

As a conclusion, the conductometric and potentiometric titration measurements can be used in determining the physical parameters and analytical results in the titration of organic acids by using TBAH as titrant in nonaqueous media.

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