in the N-substituted compounds IV*a–i*. In the IR spectra of IV*a–i* in addition to the band around 1640 cm^{-1} (chromone carbonyl) another band around 1700 cm^{-1} (ester carbonyl) is present. The NMR spectra of III*b–d* recorded in DMSO-D_6 exhibit a signal around 12.6δ due to (−NH) while this signal disappeared in IV*a–i*. The UV data of these compounds (IV*a–i*) are found to be similar to those of parent diazepinones (III*b–d*)[8].

Experimental

*Preparation of dihydrobenzopyrano-benzodiazepinones (II*a–d*)*

Method A.—Chromone-3-carboxaldehydes (I*a–d*) (0·005 mol) were separately mixed with o-phenylenediamine (0·005 mol) in acetic acid (30 ml). The coloured products II*a–d*, separated immediately, were filtered and recrystallised from chloroform-acetone mixture as orange red needles.

Method B.—Orthophenylenediamine (0·005 mol) was separately refluxed with the chromone-3-carboxaldehydes (I*a–d*) (0·005 mol) in methanol for three hours. The coloured products II*a–d* separated during reflux were filtered and recrystallised from chloroform-acetone mixture as orange red needles.

*Preparation of benzopyrano-benzodiazepinones (III*a–d*)*

Method A.—Chromone-3-carboxaldehydes (I*a–d*) (0·005 mol) in acetic acid (15 ml) were added separately to a solution of *o*-phenylenediamine (0·005 mol) in acetic acid (15 ml) at room temperature. The coloured products were separated out immediately. The reaction was allowed to continue on water bath until a clear solution obtained. The solution was cooled and poured into cold water. Neutralization of the above reaction mixture with ammonia solution gave III*a–d*, and were recrystallised from a mixture of benzene-chloroform as shining crystals.

Method B.—The dihydro compounds II*a–d* (0·005 mol) were separately dissolved in nitrobenzene (15 ml) and refluxed for 30 minutes. The excess of nitrobenzene was removed by steam distillation. The residual mixture was cooled. The products III*a–d* separated were filtered and recrystallisation from chloroform-benzene mixture furnished shining crystals. The compounds were found to be identical with those obtained directly from acetic acid.

*Preparation of N-acyl and N-benzyl compounds (IV*a–i*)*

A solution of benzopyrano-benzodiazepinone (III*b*) (0·005 mol) and triethylbenzyl ammonium chloride (TEBAC) (0·002 mol) in benzene was added to aqueous sodium hydroxide solution (40 ml, 20%), and benzoyl chloride (0·005 mol) in benzene (10 ml) was added dropwise over a period of 30 minutes. Then the reaction mixture was stirred well for two hours. The benzene layer was separated, washed with water and dried over anhydrous sodium sulphate. Removal of the solvent yielded IV*a* and was recrystallised from benzene-petroleum ether mixture as colourless crystals.

Similarly benzodiazepinones (III*b–d*) when reacted separately with benzoyl chloride, acetyl chloride and benzyl chloride yielded respective N-substituted products IV*b–i*.

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1. Garattin, S., Mussinie, E. and Randall, L. O., *The Benzodiazopines*, Raven Press, New York, 1973.
2. Randall, L. O. and Kappell, B., *Biochem. Pharm.*, 1961, **6**, 16.
3. Sternbach, L. H. and Reeder, E., *J. Org. Chem.*, 1961, **26**, 4936.
4. Jick, H., *Curr. Therap. Res.*, 1967, **9**, 355.
5. Fitton, A. O., Houghton, P. G. and Suschitzky, H., *Synthesis*, 1979, **5**, 337.
6. Nohara, A., Umetani, T. and Sanno, Y., *Tetrahedron*, 1974, **30**, 3553.
7. Dockx, *Synthesis*, 1973, **8**, 441.

CHLOROSULPHONIC ACID AS DIFFERENTIATING TITRANT IN NON-AQUEOUS MEDIUM

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Chlorosulphonic acid has been used as a titrant in acetic acid and acetic acid-methyl ethyl ketone media for the determination of number of individual bases[1–4]. The acid has certain advantages over perchloric acid[3]. However, no attempt has been made to use the acid as a differentiating titrant. The present work has been undertaken to study the use of chlorosulphonic acid as differentiating titrant. Differentiation of *n*-butylamine from aniline, N-methylaniline and N, N-dimethylaniline was investigated.

Materials and Methods

All the chemicals used were of analytical grade. The purity of the samples was checked by comparing the measured densities with those reported in the

TABLE I

Potentiometric determination of bases in mixtures

Mixture	Base	Amount (mg) Taken	Found	Difference (mg)
n-Butylamine + aniline	*n*-Butylamine	36·6	36·3	−0·3
	Aniline	46·6	46·5	−0·1
	n-Butylamine	18·3	18·2	−0·1
	Aniline	23·3	23·4	+0·1
n-Butylamine + N-methyl aniline	*n*-Butylamine	36·6	36·3	−0·3
	N-methylaniline	53·6	53·7	+0·1
	n-Butylamine	18·3	18·2	−0·1
	N-Methylaniline	26·8	26·9	+0·1
n-Butylamine + N-dimethyl aniline	*n*-Butylamine	36·6	36·3	−0·3
	N-Dimethylaniline	60·6	60·5	−0·1
	n-Butylamine	18·3	18·2	−0·1
	N-Dimethylaniline	30·3	30·4	+0·1

literature. The densities were determined using the bicapillary pyknometer described by Naidu and Krishnan[5]. The stock solutions of the acid and the bases were prepared in dioxane and chloroform respectively. Aliquots of these were successively diluted with respective solvents to get the required concentrations. Potentiometric titrations were performed with Elico Digital pH meter employing glass and calomel electrodes.

Results and Discussion

The end-point in the titration was determined by calculation method[6]. Typical potentiometric curves concerning the titrations of *n*-butylamine, aniline and a mixture of *n*-butylamine with aniline are given in Fig. 1. The titration results are presented in Table I. The results and the curve (*c*) in the figure show that *n*-butylamine can be successfully differentiated from aniline, N-methylaniline and N, N-dimethylaniline using chlorosulphonic acid as titrant. The results also show that semimicro-quantities of bases can be determined with an error less than 1%. Hence it is concluded that chlorosulphonic acid in dioxane can be successfully employed as a titrant not only for the determination of individual bases but also for the determination of mixtures of bases taken in chloroform medium.

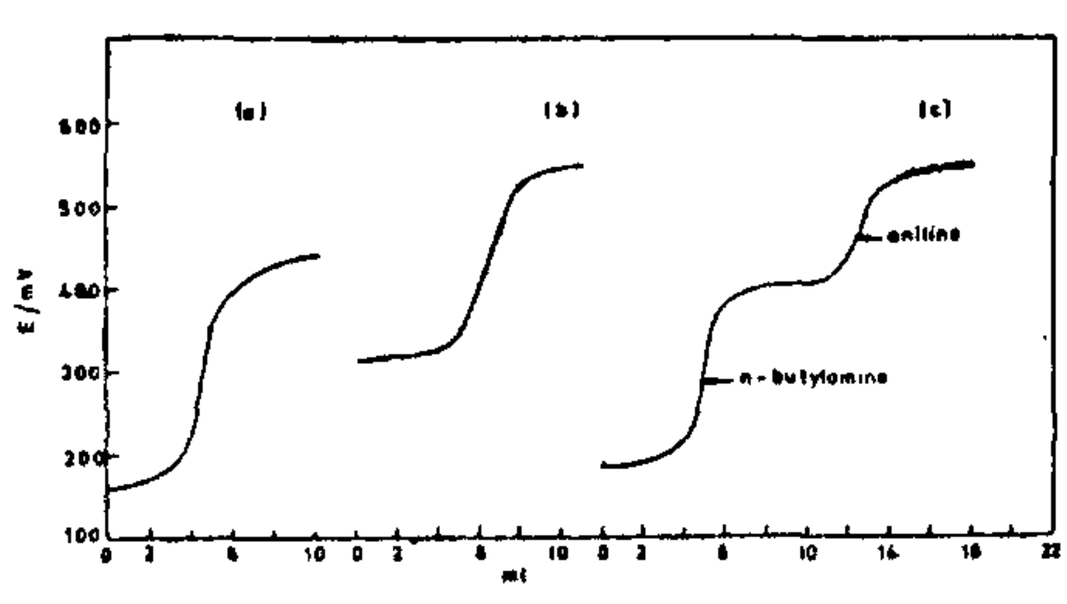

FIG. 1. Potentiometric titrations of (*a*) *n*-butylamine, (*b*) aniline and (*c*) aniline in the presence of *n*-butyl amine with 0·1 M chlorosulphonic acid solution in dioxane using glass and calomel electrodes.

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1. Paul, R. C., Vasisht, S. K., Malhotra, K. C. and Pahil, S. S., *J. Sci. Ind. Res.*, 1962, **21B**, 528.
2. Mohan Rao, K. C. and Naidu, P. R., *Talanta*, 1972, **19**, 1465.
3. — and —, *J. Electroanal. Chem.*, 1972, **35**, 429.
4. Naidu, P. B., *Ph.D. Thesis*, Sri Venkateswara University, Tirupati, 1978.
5. Naidu, P. R. and Krishnan, V. R., *Trans. Faraday Soc.*, 1965, **61**, 1347.
6. Lingane, J. J., *Electro Analytical Chemistry*, Interscience Publishers, New York, 1966.