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ELECTROLYTE SYSTEMS RELATING TO MILK

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at Massey University.

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A pH titration method using a glass electrode/saturated calomel electrode cell has been applied to the determination of acidity and stability constants in dilute aqueous solutions at 25°C. Two computer programs in FORTRAN have been written and used to calculate the constants from the titration data.

Acidity constants for the homologous series of aliphatic dicarboxylic acids (succinic acid to sebacic acid inclusive) have been determined. Acidity constants for tricarballylic, citric and a number of other carboxylic acids have also been determined and the values obtained are in good agreement with values reported by other workers. A new set of micro acidity constants, differing from those reported by other workers, has been obtained for citric acid from a pH titration study of various methyl esters of citric acid. The stability constants for the magnesium and calcium complexes of citric acid have been redetermined.

The method of calculating acidity constants from substituent effects has been refined to distinguish between macro and micro acidity constants and has been used with some success in the prediction of both micro and macro acidity constants. Good values have been obtained for the first and second but not the third acidity constants for citric acid using this technique. An analogous method for calculating stability constants from substituent effects has been tested and found promising but its application is
hampered by the lack of suitable experimental data.

The thermodynamic basis of the cation exchange resin method of determining cation activities in solution has been described and a new method of resin calibration using two parameter equations developed. The ion exchange resin method has been applied to studies of the seasonal variation of milk composition and to brief studies of the effects of milk pH adjustment, the factors affecting the renneting time of milk and the determination of cation activities in non bovine milks.

Some of the problems associated with calculating cation activities in milk have been briefly discussed. In a preliminary study of synthetic whey, comparisons have been made between cation activities determined experimentally and those calculated from a knowledge of composition and of the relevant acidity and stability constants.
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