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EPOXY BASED ANION EXCHANGE MEMBRANE *

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THE use of ion exchange resin for electrolytic processes is relatively becoming more popular day by day. The more important of these processes use ion exchange membranes (e.g., electrodialysis, preparation of chemicals, etc.). These membranes act as selective barriers and to some extent as "ionic sieves". Commercial ion exchange membranes are either of the homogeneous or heterogeneous type. Heterogeneous membranes consist of finely powdered ion exchange resin, held together by inert plastic binding materials. A large number of binding materials may be used in the preparation of the membranes. Polystyrene, polyethylene, phenolic resins, methyl methacrylate, selectron, synthetic and natural rubber, and many other binders have been used¹. The present work deals with the preparation of anion exchange membrane with the use of epoxy resin as a binder to the anion exchange resin, the membrane being cast during the polymerisation of epoxy resin brought about by a crosslinking agent. Similar type of epoxy based cation exchange membrane has been reported². Out of several epoxy resins (adhesives and the hardeners) tried, it was found that the mixture of Araldite (AY 103) and Lancast (both products

of CIBA Ltd.) used as binding agent for the exchange resin powder gave satisfactory membranes as far as flexibility, toughness and other mechanical properties are concerned.

EXPERIMENTAL

Preparation of Membrane

(a) About 200 g Amberlite IRA 400, strongly basic anion exchange resin was treated in the conventional way till it was completely in chloride form. The dried resin was ground till the desired mesh size was obtained (-240, +400).

(b) *Preparing Binding Mixture*.—(Six different mixtures having different ratios of epoxy resin (Araldite AY 103) and the crosslinking agent (Lancast) were prepared. These were used as the binding agent for the anion exchange resin powder.

(c) To 10 g of the dried resin powder was added the mixture of (b) dropwise till on proper mixing the mass was transformed into a dough like form. The dough was passed through rubber rollers several times till a sufficiently tough sheet was obtained.

(d) The sheet so obtained was cured at 50-60°C in an oven for one hour, rolled again, and was left in a glass cabinet at room temperature for 5-6 days for complete curing.

The well cured membranes were immersed in distilled water for several hours and then dried between filter-paper folds. This process of hydration and drying was repeated six

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times. Thus, six samples of fully cured membranes with different proportions of Araldite and Lancast were obtained.

Physical Properties: Tensile strength and percentage elongation.—Both these properties were studied on "Wire tensile testing machine" (range of capacity used — 0.50 kg). Membrane sheet was cut into strips measuring 20 × 100 mm. Strip was clamped uniformly between the two holders of the machine and the stretching process started. Reading was taken when the strip gave way. The average of four readings of each type of sample was recorded. The results are given in Table I.

TABLE I

Data showing the variation in tensile strength and percentage elongation of the membranes having different ratios of the binding components. Average percentage of binder in membrane—16-22

Sl. No.	Composition of the binder		Tensile strength kg/cm ²	Per cent elongation
	Araldite AY 103	Lancast		
A	1.00	0.50	42.0	2-3
B	1.00	0.55	40.0	5-6
C	1.00	0.60	36.0	6-8
D	1.00	0.65	34.5	12-16
E	1.00	0.70	22.5	1-18
F	1.00	0.75	18.0	20-22

in the machine "Paper burst resistance tester" made in U.S.S.R. When the machine was operated reading was taken when the sample burst. Average of four readings were recorded.

Per cent Swelling and Per cent Water.—About one square centimeter of the membrane sample was dried to constant weight. Its thickness at 16 different places was measured. The sample was then immersed in distilled water for complete swelling (about 8 days). It was weighed accurately and its thickness measured as before. From the difference in the weights and the thickness, the percentage swelling and per cent water was calculated.

Exchange Capacity.—The exchange capacity of the membrane in the chloride form was determined by liberating Cl⁻ ions by means of 1 M Na₂SO₄ and analysing Cl⁻ ions by Mohr's method.

The physical and chemical properties of this membrane and those of Amberplex A-1 are given in Table II for comparison.

Conductivity.—The conductivity of the membrane was determined with the help of the cell having construction similar to that used by Scatchard³. Membrane was rigidly held in an inert perspex frame having a circular opening of one square centimeter.

The membrane after equilibrating in the electrolyte was clamped rigidly between two half glass cells, with provision for introducing

TABLE II

Physical and Chemical properties of the hydrated Amberplex A-1 and epoxy based anion exchange membrane

Sl. No.	Property	Amberplex A-1	Our sample
1	Type of resin	.. Anion exchange amberlite type	Amberlite IRA 400
2	Physical form	.. Flexible sheet	Flexible sheet
3	Colour	.. Yellow	Yellow
4	Thickness	.. 7-10 mm	10-11 mm
5	Film weight (lb/sq.ft)	.. About 0.14	About 0.19
6	Moisture %	.. 25-35	33.00
7	Tensile strength lb/sq.ft	.. 350	480
8	Elongation (%) at rupture	.. 15-20	16
9	Bursting strength Mullen lb/sq.inch	.. 12-16	16.47
10	% swelling from dry to hydrated state	.. 42	16.8
11	Exchange capacity meq/dry gram	.. 1.5	2.24

If the graph of stress-strain is plotted it can be concluded that the sample D has a maximum area under the curve which measures the toughness and flexibility. As our requirements were of mechanically stable membrane, the sample D membrane only was selected for further studies.

Bursting Strength.—Membrane square of 70 × 70 mm was cut and was clamped uniformly

electrodes. Platinized platinum electrodes were used for measuring the resistance of the solution with and without the membrane in the cell. The resistance was measured by means of a conductance bridge, (Philips PR 9500) at 1000 cycles.

Conductance of the membrane was calculated from the values obtained from the difference between the two resistance measurements.

TABLE III
Specific conductivity of membrane in NaCl solutions

(Membrane thickness 1.5 mm)

Sl. No.	Solution concentration (N)	Resistance of solution Rs ohms	Resistance of solution + membrane R ohms	Membrane resistance (R-Rs) ohms	Sp. conductivity of membrane ohm ⁻¹ cm ⁻¹
A	2.00	20	37	17	0.0166
B	1.00	35	58	23	0.0120
C	0.50	58	87	29	0.0097
D	0.10	210	270	60	0.0047
E	0.05	490	557.8	67.8	0.0042

Cell constant = 1.88

Temperature = 30° C

The results obtained for five different concentrations of sodium chloride are given in Table III.

True Transport Number by Electrolysis Through the Membrane

The method used for finding out the transport number of the membrane was based on that employed by Winger⁴.

The cell system used was

Ag⁻/AgCl/NaCl/Anion Exchange Membrane/NaCl/AgCl/Ag⁺

The membrane was first equilibrated in the electrolyte solution and was then introduced between two half glass cells. NaCl solution (known volume) was filled in the cells and a small current of about 3-4 milliamperes was passed through the cell, with a silver coulometer connected in series. After electrolysis for four hours, the anolyte and catholyte were analysed for their chloride concentration. From the change in Cl⁻ concentration of the catholyte the true transport number was calculated. Five concentrations of NaCl were studied. The results are given in Table IV.

TABLE IV

True transport number measurements Electrolyte NaCl

Cell system: Ag⁻/AgCl/NaCl/M/NaCl/AgCl/Ag⁺

Sl. No.	Concentration of electrolyte (N)	¹ Na ⁺	¹ Cl ⁻
1	2	0.360	0.630
2	1	0.269	0.709
3	0.5	0.206	0.810
4	0.1	0.108	0.892
5	0.05	0.0898	0.910

Discussion.—The aim of the present investigation was to develop a heterogeneous membrane comparable to those reported in the literature with respect to general physical and electrochemical properties. Epoxy based cation ex-

change membranes are found suitable in these respect². However, similar types of anion exchange membranes are developed here. Amberlite strongly basic anion exchange resin having mesh size (-240 + 400) was incorporated with epoxy resin. It is found that membranes with desired mechanical stability could be obtained with Amberlite percentage as high as 84. Membranes with percentage of Amberlite higher than 90 cracked while curing. Membrane with Amberlite percentage between 80 to 84 received no damage even after repeated desiccation and hydration. Moreover, it has sufficiently low resistance (< 70 Ω) in wide range of NaCl concentration (0.05 N and above), which permits, therefore, the potential measurements even with a students' potentiometer. Higher flexibility of this membrane is rather a disadvantage, as higher flexibility results in poorer electrochemical characteristics⁵. Higher flexibility might be due to the flexible nature of Lancast, which due to its property stretches itself over the ion exchanger, thus offering greater time and resistance to the contact between electrolyte and ion exchanger. This might also be the reason for the long period required for reaching equilibrium (60 hours). On comparing this membrane with Amberplex A-1, manufactured by Rohm and Haas Co., U.S.A., with respect to their properties (Table II), it can be seen that both membranes have almost the same properties in case of per cent water, per cent elongation, bursting strength and general nature. However, they differ in tensile strength, per cent swelling and exchange capacity. Most probably the difference in tensile strength is due to the incorporation of the type of binder used. The difference in per cent swelling can be attributed to the possibility of a larger inter-molecular distance or to what is known as crosslinking of copolymers in the case of our sample. Since highly

crosslinked resins have a reduced ability to swell, the matrix formed by epoxy resin in this case is a rigid matrix and offers more resistance to water. According to Pepper *et al.*¹¹, membrane exhibiting high swelling in water is at a disadvantage.

In conductivity measurements it is demonstrated that the conductivity of the membrane approaches a minimum value at low concentrations of external solution. On comparing the specific conductance of this membrane with those of commercial ion exchange membranes in equilibrium with sodium chloride (Fig. 1), it is seen that the specific conductivity of our membrane and that of Nepton AR 111 have nearly the same values upto the concentration of 0.2 N NaCl. Above 0.2 N of NaCl, our membrane has relatively high conductivity. The specific conductance of commercial heterogeneous anion exchange membrane and our membrane are plotted as a function of the concentration of the sodium chloride solution with which the membranes are in equilibrium (Fig. 1).

To decide whether this membrane can be evaluated for industrial electro dialysis, its transport number is directly measured in a test cell rather than calculated from potential measurements.

The transport number seems to decrease with increasing solution concentration. That may be due to the fact that the quantity of mobile ions in the resin with sign opposite to that

of the exchange ion increases with increase in solution concentration.

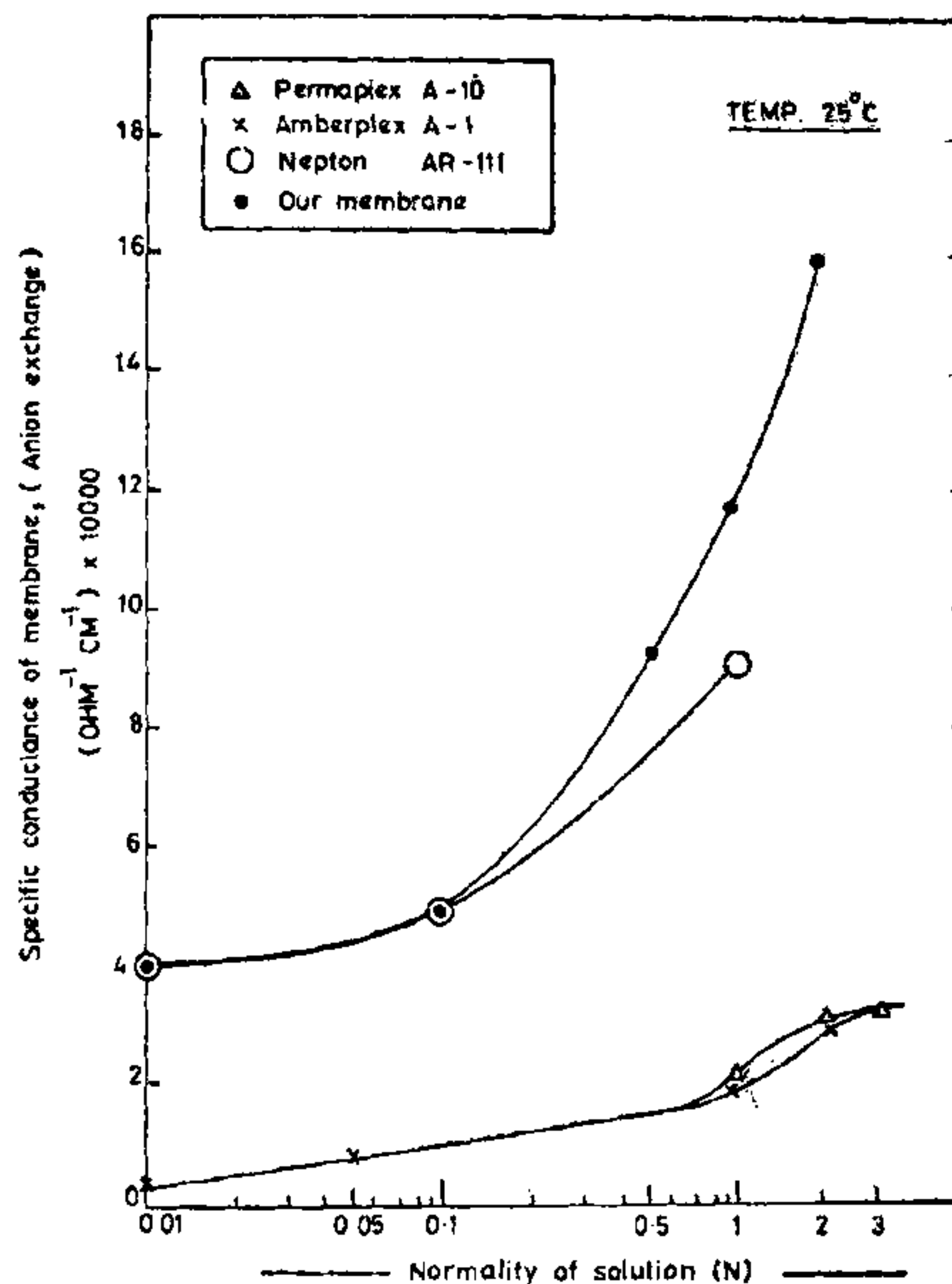


FIG. 1. Specific conductance of commercial and epoxy based anion exchange membranes in equilibrium with NaCl solution.

Like conductivity, transport number is a very important property of membranes for

TABLE V

Properties of Anion Exchange Membranes

Description	Amberplex A-1	Nepton AR-111	Permutit A-1374	Permapiex A-10	Our membrane (epoxy based anion)
Manufacturer	.. Rohm & Haas Co., Philadelphia, Penn.	Ionics, Inc., Cambridge, Mass.	Permutit Co., Inc., New York	Permutit Co. Ltd., London	
Thickness (in)	.. 0.030	0.024	0.009	0.020	0.040
Specific gravity	.. 1.07	..	1.7	..	0.7
Moisture %	.. 25-35	47	About 20	30-40	33
Exchange capacity (meq/g wet membrane)	About 1.1	1.6	..	1.3	1.65
Specific conductance ($\text{ohm}^{-1} \text{cm}^{-1} \times 10^3$)					
0.01 N NaCl	0.511	4	4.0
0.1 N NaCl	0.844	5	2.5-3.1	0.80	4.7
1.0 N NaCl	1.90	9	..	2.08	12
Resistance of unit area in 0.1 N NaCl (ohm ft.^2)	0.064-0.095	0.013	0.008-0.01	0.068	0.068
Effect of drying and re-wetting.	No harm unless clamped to rigid frame	..	Rapid and uneven drying damages membrane	No harm unless clamped to rigid frame	Cracks only when rigidly clamped

electrodialysis processes. Low transport number reduces the efficiency of the desalting process.

Some of the important electrical and chemical properties of commercial anion exchange membranes and our membranes are summarized in Table V.

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GEOHYDROLOGICAL STUDY IN PARTS OF SHOLAPUR DISTRICT AND ITS BEARING ON THE FEASIBILITY OF TUBEWELLS IN THE DECCAN TRAP *

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ABSTRACT

Systematic geohydrological studies in parts of Sholapur District of Maharashtra have brought to light a succession of massive and vesicular trap units between the elevations of 411.48 and 472.44 m above M.S.L. Here the traps show a gentle dip towards east. Based on the studies so far carried out, the authors discuss the feasibility of tubewells in the traps of this area. Taking particular advantage of the high permeability of the vesicular traps, the paper emphasizes the need of exploratory drilling in the area in the downdip direction of the trappean units, tapping the cumulative thickness of the vesicular units thereof.

INTRODUCTION

SYSTEMATIC groundwater studies in Akalkot *tahsil* of Sholapur District of Maharashtra were undertaken at the instance of the Government of Maharashtra to investigate the possibility of locating the water bearing zones at economic depths below the existing ones with scope for purposes of irrigation.

While investigating for groundwater geological mapping of the area was undertaken to delineate different units of the Deccan Trap. To collect adequate information on the occurrence, movement and development of groundwater in different trap units, large number of wells in them were examined. Yield tests were conducted on select irrigation wells to study the yield characteristics of the wells tapping different units. Samples of water were collected from select wells to study the chemical quality of groundwater in them.

LOCATION AND EXTENT

Akalkot *tahsil* lies in the south-eastern part of Sholapur District. An area of about

800 sq.km lying in parts of toposheet Nos. 56-C/3 and 7, and 47-0/15 was covered during the field season 1963-64.

PHYSIOGRAPHY AND RAINFALL

Located in the middle of the Deccan trap terrain the area examined forms the northern part of the Bhima basin. It is marked by its undulating relief ranging in elevation from 411.48 to 472.44 m (*i.e.*, 1350 to 1550 ft) above M.S.L. The general slope of the country is towards south. The region is typically characterised by the morphology of the Deccan trap flows. A glance at the geological map of the area will bring out the role of geology in the evolution of the morphology of the terrain. The massive hard basalt constitutes the high ground while the soft vesicular basalts form the depressions in the area (Fig. 1).

The Bhima form the chief drainage of the area with a tortuous course. It flows along the southern margin of the area. The numerous streams that drain the area are but the tributaries of the Bhima. The major tributaries are the Dhubdhabi and the Bori river.

The south-west monsoon contributes maximum rainfall annually between July and

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