TABLE 1 — POLAROGRAPHIC HALF-WAVE OXIDATION AND REDUCTION POTENTIALS OF SOME HYDROCARBONS AND TRANSITION ENERGIES OF THEIR COMPLEXES WITH IODINE

Molecule	I (eV)	A (eV)	$E_{\frac{1}{2}}$ (ox) (V) Calc.	Exp.	$-E_{\frac{1}{2}}$ (red) (V) Calc.	Exp.	ΔE_{CT} (eV) Calc.	Exp.
Benzene	9·03	—	2·25	2·30	—	—	4·221	4·184
Naphthalene	8·26	0·27	1·55	1·54	1·84	1·98	3·426	3·452
Anthracene	7·81	0·78	1·15	1·09	1·40	1·46	2·962	2·890
Phenanthrene	8·19	0·28	1·49	1·50	1·83	1·94	3·354	3·288
Chrysene	7·96	0·45	1·28	1·35	1·68	1·81	3·117	3·154
Triphenylene	8·18	0·05	1·48	1·55	2·03	1·97	3·344	3·154
Pyrene	7·86	0·63	1·19	1·16	1·53	1·61	3·014	2·959
Biphenyl	8·29	0·01	—	—	2·06	2·08	3·457	3·654
Stilbene	8·01	—	—	—	—	—	3·168	3·331
Naphthacene	7·52	1·10	0·89	0·77	1·12	1·14	—	—
3,4-Benzphenanthrene	—	0·34	—	—	1·78	1·75	—	—
1,2-Benzanthracene	7·79	0·56	1·13	1·18	1·59	1·53	—	—
Pentacene	—	1·32	—	—	0·93	0·86	—	—
Dibenz-(1,2:5,6)-anthracene	7·87	0·57	1·20	1·19	1·58	1·55	—	—
Dibenz(1,2:7,8)anthracene	7·93	0·61	1·26	1·26	1·55	1·57	—	—
Dibenz(1,2:3,4)anthracene	7·94	0·48	1·27	1·33	1·66	1·54	—	—
Pentaphene	—	0·69	—	—	1·48	1·53	—	—
Perylene	7·55	0·89	0·92	0·85	1·31	1·25	—	—
Benz(4,5)pyrene	7·87	0·51	1·20	1·27	1·63	1·67	—	—
Benz(1,2)pyrene	7·64	0·84	1·00	0·94	1·35	1·36	—	—
Benz(1,12)pyrelene	7·71	—	1·06	1·01	—	—	—	—
Coronene	7·88	0·40	1·21	1·23	1·73	1·64	—	—
Anthanthrene	—	1·08	—	—	1·14	1·19	—	—
Benz(1,2:4,5)pyrene	7·69	0·69	1·04	1·01	1·58	1·45	—	—
Dibenz(1,2:6,7)pyrene	—	1·01	—	—	1·20	1·16	—	—
Dibenz(1,2:7,8)pyrene	—	0·90	—	—	1·30	1·32	—	—
Dibenz(4,5:9,10)pyrene	—	0·34	—	—	1·78	1·69	—	—
p-Terphenyl	—	0·23	—	—	1·87	1·91	—	—
p,p-Diphenyl-biphenyl	—	0·35	—	—	1·77	1·77	—	—
Azulene	7·31	—	0·70	0·71	—	—	—	—
Fluoranthene	8·15	0·87	1·46	1·45	1·32	1·35	—	—
Benz(8,9)fluoranthene	—	0·73	—	—	1·44	1·39	—	—

reduction potentials, etc. seem to be same in different solvents, their absolute values vary[13]. From the table it is clear that our calculated values are in excellent agreement with experimental values.

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Exchange of Metal Ions on Dowex A-1(H⁺)

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Distribution of about forty metal ions between Dowex A-1(H⁺) and aqueous solutions (pH 1·0 to 6·0) in the presence and absence of 1,10-phenanthroline is reported. The data are compared with the results of similar experiments with a carboxylic acid exchanger (Zeo-Karb- 226, H⁺).

SORPTION characteristics of metal ions on Dowex A-1 as a function of pH have been reported[1-4], employing the exchanger in acid or salt form and adjusting the pH with or without buffers. The pH of decomplexation of some metal ions from the exchanger is also available[5-7].

Recently, sorption characteristics of about forty cations on a carboxylic acid exchanger (ZeoKarb-226, H⁺) as a function of pH (1·0 to 6·0 without buffers) have been studied in our laboratory[8]. For comparison, the study of sorption of metal ions on Dowex A-1 as a function of pH (ref. 4) has been extended to other cations and the results are reported
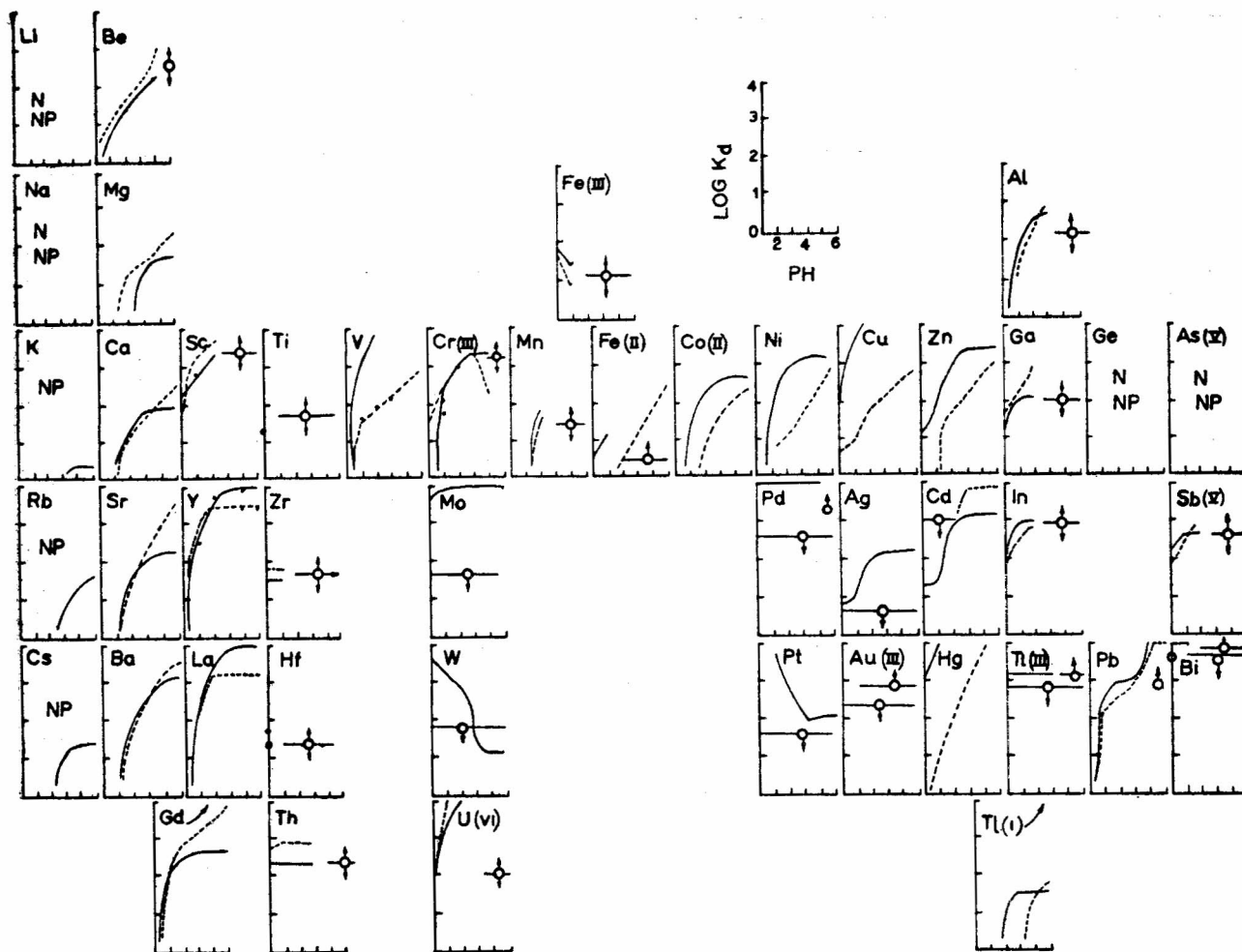
Fig.1—Kd VALUES OF METAL IONS ON DOWEX A-1(H$^+$)
[N= NO ADSORPTION, NP=NO ADSORPTION IN PRESENCE OF PHEN
—○— PRECIPITATION, —○— PRECIPITATION IN PRESENCE OF PHEN]

in this paper. Sorption of 1,10-phenanthroline (phen) by this exchanger in acid form was observed as in the case of ZeoKarb- 226 (ref. 8, 9). Hence, sorption characteristics of the same cations in presence of phen are also studied and the results reported in this note.

Ion exchanger and reagents employed in the present studies were the same as described earlier[4,9]. Kd values of metal ions were determined following the same procedure as described earlier[4] ($\sim$1 mg metal ion, 25 ml aqueous phase, 50·0 mg phen and 0·25 g exchanger).

The variation of Kd values of metal ions as a function of initial pH of the aqueous phase is shown by the continuous lines in Fig. 1 (data in ref. 4 is included). Generally, Kd of a metal ion increases with pH (till there is precipitation in the aqueous phase), which may be attributed to greater ionization of protons of the functional group. In the case of Tl^{3+} and Th^{4+} the values remain steady while those of Fe^{3+}, W and Pt(IV) decrease.

It is known that metal ions are sorbed by this exchanger by electrostatic interaction, chelation and anion exchange[10]. Kd values of alkali ions on resin having imino-diacetic acid functional group are nearly the same as those on carboxylic acid exchanger. In view of the negligible complex forming tendencies, these may be sorbed by electrostatic interaction. Generally higher Kd values of many metal ions (e.g. Co, Ni, Cu, Zn, Sc and La) than those on carboxylic acid exchanger appear to reveal the chelating properties of the functional group. It may be noted that Kd of UO$_2^{2+}$ is higher than that of Th^{4+} (except at pH 1·0) though the latter forms more stable complexes with aminopolycarboxylic acids than the former. The strong sorption of Pd, Au and Bi at pH 1·0 may involve anion exchange.

Variation of Kd values of metal ions in the presence of phen as a function of pH is represented by dotted lines in Fig. 1. In this case also Kd values generally increase with pH as in the absence of phen. In the case of Cr^{3+}, there is an increase up to pH 4·0 and a decrease thereafter, while that of Fe^{3+} decreases with increase of pH. Kd values are not determined in the presence of phen in the case of Pd, Pt, Ag, Au, Mn, W, Tl^{3+}, due to precipitation in the aqueous phase.

The lower Kd values of metal ions like Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+} and In^{3+} in the presence of phen than in its absence, can easily be explained that phen competes for metal ions with the chelating group in the resin. It is surprising to find the Kd values of Be^{2+}, Mg^{2+}, Cd^{2+}, Ga^{3+}, Th^{4+} and UO_2^{2+} to be higher in the presence of phen. It will be interesting to investigate if mixed complex formation is occurring in the resin phase. In the case of metal ions like Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+} and Y^{3+} the two curves cross each other, which is suggestive of sorption of the metal ion by different mechanisms at different pH values.

Though the sorption of many metal ions is higher on Dowex A-1 than on the ZeoKarb-226 in absence of phen, the same is lower in the presence of phen in the case of ions like Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Hg^{2+} (but not La^{3+}). This lends further support that phen competes with iminodiacetic acid group and with carboxylic acid group of the ZeoKarb-226.

The data in Fig. 1 reveal the possibility of some analytical separations of interest. Work is in progress on these and also to elucidate the mechanism and nature of species sorbed in the presence and absence of phen on Dowex A-1.

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Electrochemically Initiated Copolymerization of Acrylamide with Acrylic Acid & Methacrylic Acid

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Electrochemically initiated copolymerization of acrylamide with acrylic acid or methacrylic acid has been carried out in aqueous medium using sodium acetate as the electrolyte. Monomer reactivity ratios (r_1) have been calculated from the copolymer composition data following approximation method and are found to be in agreement with the values obtained by using conventional chemical initiation method.

ELECTROCHEMICALLY initiated copolymerization reactions in aqueous medium have not been studied much. Though there are a few reports on non-homogeneous copolymerization systems[1], apparently there seems to be no published data on the values of reactivity ratios in electrochemically initiated aqueous homogeneous systems.

In the present work, we report the results of electrochemically initiated copolymerization of acrylamide (AM) with acrylic acid (AA) and methacrylic acid (MAA) in aqueous medium using sodium acetate as electrolyte.

AM was recrystallized twice from chloroform solutions and dried *in vacuo*. AA was purified by distillation under reduced pressure (b.p. 35° 12 mm) and the middle fraction was collected. MAA was purified by fractional crystallization following the method of Paxton[2]. Water used was doubly distilled and boiled for 1 hr and cooled in an atmosphere of purified nitrogen before each experiment.

Polymerization was carried out with sodium acetate ($0.5M$) as electrolyte in a conventional electrolytic cell with platinum electrodes. A constant current of 50 mA was allowed to pass through the cell. The conversions were kept below 5%. The products were precipitated in ≈ 20 volumes of acetone, washed several times in dry acetone and dried. The copolymers were purified by reprecipitation from aqueous solutions and the final products dried *in vacuo*.

The composition of the copolymer was determined from carboxyl group analysis applying reverse dye partition technique[3] (RDP) and used disulfine blue (VN 150) as the dye.

The electrochemical initiation method was adopted for the preparation of copolymers of AM with AA or MAA under limiting conditions where the concentration of AM (M_1) was much higher than that of AA or MAA (M_2). In an attempt to prepare a copolymer using higher acid concentration in the feed it was observed that the rate of polymerization was extremely slow and also the resulting copolymer became insoluble in water when the (MAA) exceeded 10%. This led us to carry out experiments under limiting conditions and to calculate the reactivity ratios following approximation method[4]. Results of the copolymer composition by the application of RDP technique are presented in Table 1. The plot of $(M_2/M_1)_{polymer}$ versus $(M_2/M_1)_{feed}$ is linear passing through the origin (except scattering of a few points), the slope of which give the reciprocal of r_1 (Fig. 1)[5].

TABLE 1 — DETERMINATION OF r_1 VALUE IN THE COPOLYMERIZATION OF AM(M_1) WITH AA OR MAA(M_2) UNDER DIFFERENT CONDITIONS

Condition of copolymerization	M_2	r_1	Ref.
Electrochemical initiation [Electrolyte, NaOAc ($0.5M$), temp. = 30°C]	AA	1·54	Present work
do	MAA	1·17	do
Thermal initiation [0·5% $K_2S_2O_8$; temp. = 60°]	AA	0·48 ± 0·06 to 1·32 ± 0·12 (at different pH)	5
Redox initiation [($K_2S_2O_8$ + $KHSO_3$); temp. = 25°]	AA	0·60	7