

## Relationship between Ion Exchange, Eluent Concentration & Volume Fraction of Water in Water-Ethanol, Water-Methanol & Water-Acetone Solvent Systems

(Mrs) V. A. BHUMRALKAR & D. S. DATAR

Maharashtra Association for the Cultivation of Science, Pune 411004

Received 6 February 1978; revised 23 May 1978; accepted 20 June 1978

Ion exchange equilibria using eluent solutions in water, water-methanol, water-ethanol and water-acetone have been studied. The ion exchange is controlled by ionic mobilities and ionic interactions taking place in the sorbed layer on the resin. With dilute solutions of eluent, square root relationship is found between the concentration of electrolyte in the sorbed layer and the amount of exchange. The greater exchange in water-alcohol and water-acetone systems is due to both the electrolyte and the resin having preference for water resulting in the enhanced concentration of the electrolyte in the sorbed layer. The enhanced concentration corresponds to the reciprocal of the volume fraction of water in the solvent mixture.

**A**QUEOUS organic solvent mixtures are being increasingly used for metal separation. This has given impetus to the studies on the behaviour of ion exchange resins in mixed solvent media. Considerable information is now available, nevertheless the phenomenon of ion exchange in mixed solvent solution is less understood from the theoretical point of view than that in pure aqueous systems.

The present study has been undertaken for the purpose of obtaining data useful in nickel and cobalt recovery in aqueous and mixed solvent systems. Investigations on the metal uptake and the metal elution from Agrion C-100 cation exchange resin in aqueous system have been made and compared with the findings in aqueous organic solvent medium under similar conditions. An attempt is made to find explanations for the semiquantitative relationships obtained.

### Materials and Methods

Agrion C-100, a polystyrene base sulphonic acid type cation exchange resin in sodium form (IAEC, Bombay) having a total exchange capacity 4.8 meq/g resin was used. Analytical grade chemicals were used. The solvents employed in this investigation were purified<sup>1</sup>. The required solutions were prepared and standardized<sup>2,3</sup>.

Known amount of the resin in the required form and the eluting solutions in the given quantities were taken in glass stoppered flasks. These were shaken well from time to time, kept for 48 hr and aliquots of the supernatant liquid analysed<sup>3</sup>, and the extent of the ion exchange calculated per gram of the dry resin.

### Results and Discussion

The exchange of sodium by nickel and cobalt is faster as compared to the reverse reaction of

elution of nickel and cobalt by sodium. The concentration of the surrounding electrolyte determines the position of the equilibrium which is almost independent of the anion of the salt<sup>4</sup>. The presence of organic solvent has synergistic effect and the values in aqueous organic solvent are higher than the corresponding values in aqueous solution<sup>5,6</sup>.

Ion exchange equilibria were investigated for (i) uptake of nickel (cobalt) by Agrion C-100 resin in sodium form from aqueous solution of nickel (cobalt) chloride, (ii) elution of nickel (cobalt) from Agrion C-100 in nickel (cobalt) form by aqueous solutions of three sodium salts, sodium chloride, sodium formate and sodium acetate and by three acids, hydrochloric, sulphuric and acetic acids varying the concentrations and keeping the volume of the electrolyte solution (50 ml) and weight of the resin (0.5 g) same in each case, (iii) elution of nickel (cobalt) by aqueous sodium chloride, hydrochloric acid and sulphuric acid, varying the volume of the eluent, (iv) uptake of nickel (cobalt) in aqueous organic solvents employing only four compositions of water organic solvent mixtures owing to the limitation of solubility and (v) elution of nickel (cobalt) using 0.1N sodium chloride solution in water-methanol, water-ethanol and water-acetone (ten compositions with regular increasing organic component) and 100 ml of solution and 0.5 g resin in each case.

*Nickel (cobalt) uptake* — Nickel (cobalt) uptake by the resin from dilute aqueous solution is fast and complete. The maximum uptake values (3.91 meq/g resin) are lower (Table 1) than the total ion exchange capacity (4.8 meq/g resin) because some of the sites on the resin are occupied by the complex ion pairs,  $\text{Ni}^{2+}\text{Cl}^-$  and  $\text{Co}^{2+}\text{Cl}^-$  instead of the simple nickel (cobalt) ions<sup>7</sup>.

Nickel (cobalt) uptake is adversely affected in water organic solvent mixtures (Table 2). This

TABLE 1 — NICKEL (COBALT) UPTAKE BY AGRION C-100 IN SODIUM FORM FROM AQUEOUS SOLUTION OF NICKEL (COBALT) SALT

(Volume of the salt solution: 50 ml weight of resin, ~ 0.5 g)

Conc. of salt solution meq/litre	Uptake (meq/g resin)	
	Nickel	Cobalt
20.0	2.00	2.00
56.4	3.81	3.76
90.2	3.91	3.89
224.8	3.91	3.88
282.0	3.91	3.87
564.0	3.72	3.87

TABLE 2 — SODIUM TO NICKEL/COBALT EXCHANGE IN AGRION C-100 Na USING NICKEL/COBALT CHLORIDE IN AQUEOUS ORGANIC SOLVENT MEDIA

(Conc. of nickel chloride, 56.4 meq/litre; conc. of cobalt chloride, 51.6 meq/litre; vol. of nickel/cobalt chloride, 50 ml; weight of resin, 0.5 g)

% (v/v) water	Sodium to nickel/cobalt exchange (meq/g resin) in mixture of					
	Water + ethanol		Water + methanol		Water + acetone*	
	Nickel	Cobalt	Nickel	Cobalt	Nickel*	Cobalt
100	3.81	3.76	3.82	3.76	3.78	3.76
80	3.63	3.73	3.40	3.66	3.48	3.59
60	2.86	3.70	3.24	3.46	2.91	3.45
50	2.80	3.49	3.28	3.22		3.28
40		2.76	3.22	2.94		3.17
20		2.75		2.89		2.97
10		2.70		2.85		2.84

\*Concentration of nickel chloride used for nickel uptake in water-acetone media is 49 meq/litre.

is attributed by the previous workers to the uptake of salt as a whole<sup>8</sup>. Nickel (cobalt) chloride is not soluble in high organic compositions; for example, nickel chloride is insoluble in 30:70 water-methanol and 50:50 water-ethanol and water-acetone. It is noteworthy that the magnitude of decrease in cobalt uptake is relatively less than that of nickel, possibly due to higher solubility of cobalt salt than nickel salt in alcohols. Cobalt salt shows complex formation in solutions with more than 60 volume percent acetone in water-acetone mixture, as indicated by the intensification of colour, e.g. violet colour with 20:80 water-acetone and blue colour in 10:90 water-acetone. The decrease in nickel (cobalt) uptake thus appears to be due to the complex formation between metal salt and organic solvent.

*Nickel (cobalt) elution in aqueous solution* — The elution in aqueous medium by the three sodium salts is nearly same. The eluting capacity of sodium acetate is about 3-12% less than that of sodium chloride, and sodium formate occupies the middle place. The elution by acetic acid is negligible evidently because of the insignificant dissociation of acetic acid. Between hydrochloric acid and sulphuric acid, the former is a better eluent. This is due to greater dissociation of hydrochloric acid. In all the cases the elution by sodium salts is higher than by acids (Fig. 1). This may be due to the reverse exchange process being more in the presence of acids.

Further the magnitude of exchange increases with the increase in the volume of eluent in contact with the resin. Elutions of nickel and cobalt are approximately equal within experimental error for the same eluent concentration when larger volume of eluent (200 ml) are used. Comparing the elution values, it is seen that when the exchange is less as

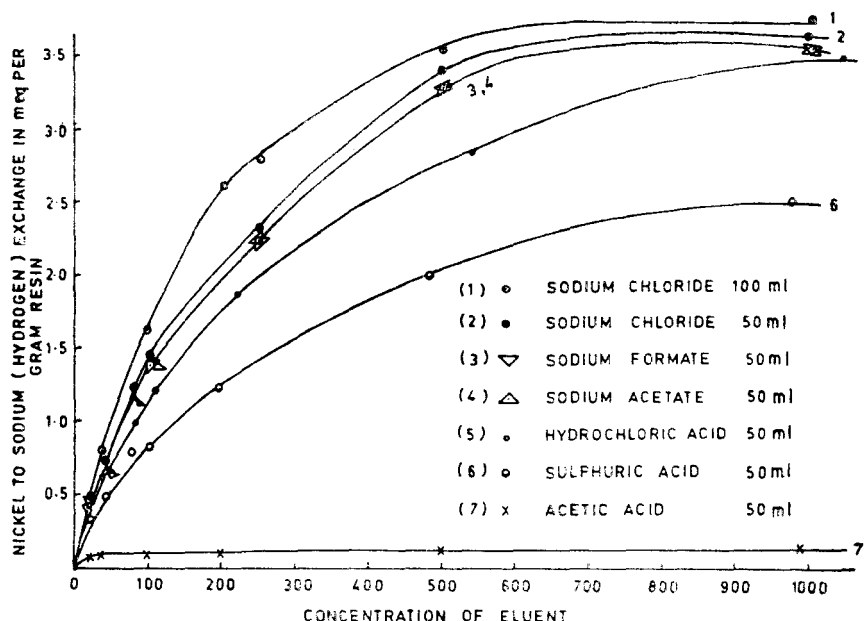


Fig. 1 — Plot of nickel to sodium (hydrogen) exchange in Agrion C-100 Ni against concentration of eluent solution in water

in case of sulphuric acid, the increment with the increase in volume is faster than in the case of sodium chloride eluent and is proportional to the volume increase (Tables 3 and 4).

*Nickel (cobalt) elution in mixed solvent solutions* — The amount of nickel to sodium exchange increases with the increase in the ethanol content in the solvent mixture (Fig. 2). There is gradual increase up to 40 volume per cent of ethanol and more rapid increase for higher ethanol compositions. This is in accordance with the observations of Okuno *et al.*<sup>9</sup> and Gable and Strobel<sup>10</sup>.

The exchange in 50:50 composition is one and a half times that in aqueous medium. The exchange reaction is still higher in the solutions with greater alcohol content; for water-ethanol (10:90) compositions the extent of exchange is twice as much as in aqueous medium. The nickel to sodium and cobalt to sodium exchange are same in different compositions of water-ethanol.

The behaviour in water-methanol and water-ethanol in respect of nickel to sodium exchange is similar but the elution values in water-methanol are lower than in water-ethanol in the case of nickel to sodium exchange but similar in the case of cobalt to sodium exchange. The results can be compared with those of Sakaki and Kakihana<sup>11</sup> who found that selectivity is greater in water-ethanol system than in water-methanol system of the same alcohol content. The elution values both in the case of nickel and cobalt are one and a half times for 50:50 water-methanol and two times for 10:90 water-methanol of the exchange value in water solution.

Behaviour in aqueous acetone is similar to that in aqueous alcohol. The increase in nickel to sodium exchange varies more regularly with the increase in acetone than in the case of alcohols. Similar observations have been made by Kakihana and Sekiguchi<sup>12</sup> and Bafna<sup>13</sup>, while studying the alkali metal ion to hydrogen exchange. The increase in elution values with the organic component is

TABLE 3 — EFFECT OF VARIATION IN VOLUME OF ELUENT ON NICKEL (COBALT) ELUTION FROM AGRION C-100 USING AQUEOUS SODIUM CHLORIDE

(Weight of resin, ~ 0.5 g)

Vol. of eluent ml	Elution of nickel (cobalt) (meq/g resin) by sodium chloride having concentration (meq/litre)					
	40		100		200	
	Nickel	Cobalt	Nickel	Cobalt	Nickel	Cobalt
50	0.71	0.70	1.27	1.25	2.19	2.03
100	0.81 (14)	0.78 (12)	1.62 (28)	1.59 (24)	2.44 (12)	2.36 (16)
150	0.93 (31)	0.91 (30)	1.85 (46)	1.85 (48)	2.67 (22)	2.57 (27)
200	—	1.08	1.89 (49)	1.88 (50)	2.68 (22)	2.69 (31)

Values in parentheses show per cent increase of the elution value over that with 50 ml volume of eluent.

TABLE 4 — EFFECT OF VARIATION IN VOLUME OF ELUENT ON NICKEL (COBALT) ELUTION FROM AGRION C-100 USING AQUEOUS HYDROCHLORIC ACID AND SULPHURIC ACID

(Weight of resin, ~ 0.5 g)

Vol. of eluent ml	Elution of nickel (cobalt) (meq/g resin) by hydrochloric and sulphuric acids having concentration (meq/litre)					
	55*		45†		97.3†	
	Nickel	Cobalt	Nickel	Cobalt	Nickel	Cobalt
50	0.78	0.75	0.56	0.47	0.83	0.72
100	0.89	0.84	0.73 (31)	0.64 (36)	1.09 (31)	1.09 (50)
150	1.02	0.90	0.79 (41)	0.69 (47)	1.25 (51)	1.20 (62)
200	1.16	1.01	0.91 (63)	0.89 (87)	1.40 (68)	1.39 (93)

Values in parentheses show per cent increase of the elution value over that with 50 ml volume of eluent.

\*By hydrochloric acid.

†By sulphuric acid.

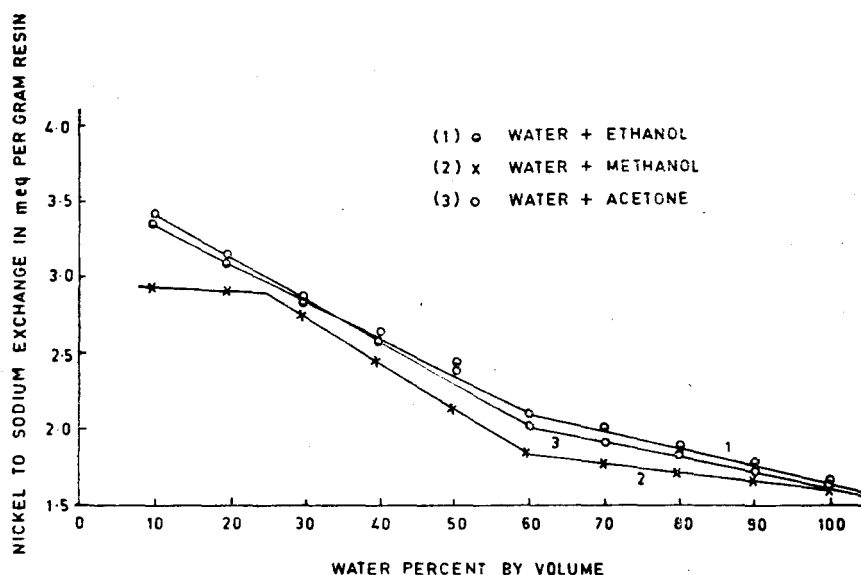


Fig. 2 — Plot of nickel to sodium exchange in Agrion C-100 ( $Ni^{2+}$  form) against water per cent by volume in aqueous organic solvents employing 0.1N sodium chloride as eluent

not so regular for cobalt to sodium exchange. Another observation made is that when the resin in cobalt form is immersed in sodium chloride solution of high acetone composition (containing 30:70, 20:80 and 15:85 water-acetone), the solution becomes blue, the intensity of blue colour being more with the increase in the acetone content.

It will be seen that the elution composition curves consist of two linear portions with a point of transition between 45 and 55% organic solvent composition.

**Square root relationship between exchange and eluent concentration** — A charged sponge model<sup>14</sup> is found useful in explaining the mechanism of the various ion exchange processes taking place. The cation exchange resin consists of a polyanion and positive counter ion. When the resin is in contact with an electrolyte solution, the exchangeable cations in the resin are exchanged for cations in the solution. The first step in the process is the uptake or sorption of the solute and solvent from the solution into the pores of the resin. The replacement of the counter ion in the resin by the cation in solution is then determined by the concentration of the cation in the sorbed layer.

Another factor that influences the exchange is mobility of the cations in the sorbed liquid. Following the same reasoning that led to the Debye and Huckel theory<sup>15</sup> and Onsagar equation<sup>16</sup>, it can be assumed that in the sorbed layer, mobility of the cations is proportional to the square root of the concentration of the electrolyte in the case of strong electrolytes in dilute solution. It may be seen from the results graphically shown in Figs. 3 and 4 that the elution of nickel and cobalt from Agrion C-100 resin in nickel or cobalt form

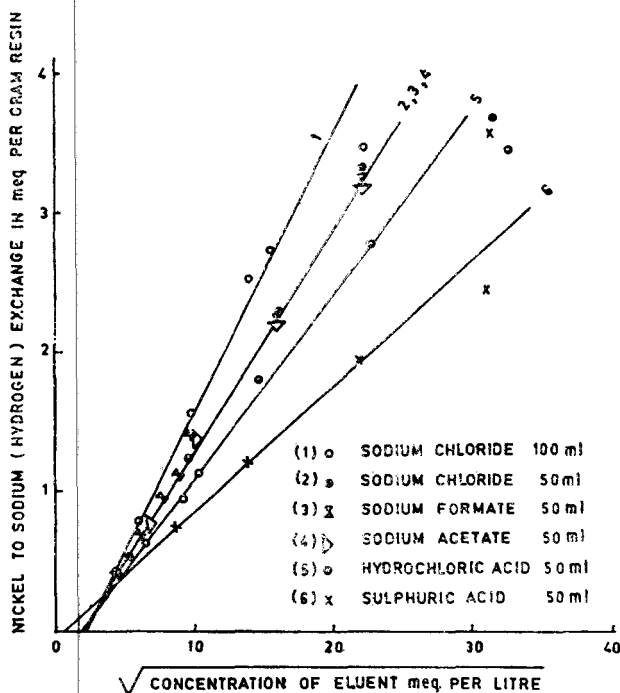


Fig. 3 — Plot of nickel to sodium (hydrogen) exchange in Agrion C-100 ( $\text{Ni}^{2+}$  form) against square root of concentration of eluent solution in water

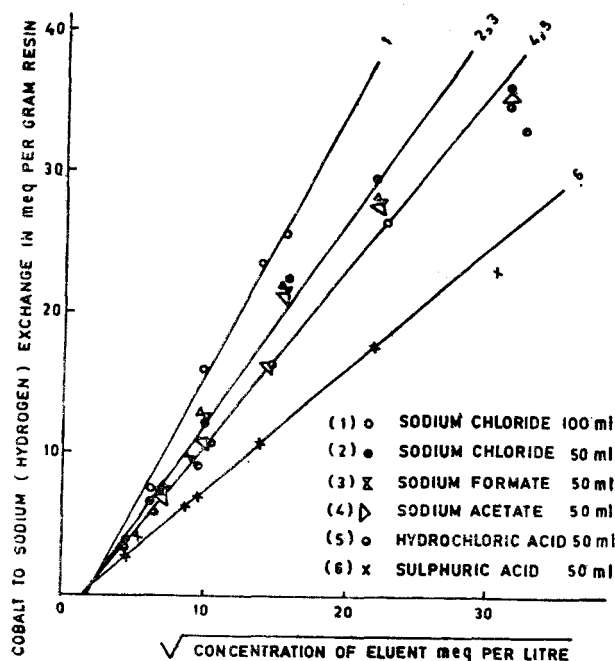


Fig. 4 — Plot of cobalt to sodium (hydrogen) exchange in Agrion C-100 ( $\text{Co}^{2+}$  form) against square root of concentration of eluent solution in water

by acids and sodium salts is proportional to the square root of the concentration of these strong electrolytes.

The square root law is obeyed in the range 20-500 meq/litre electrolyte concentration. The elution readings taken using more volume of sodium chloride (or sulphuric acid), generally show closer agreement with the square root relationship. At higher concentration, the relationship does not hold good obviously because the mobility of the cations is decreased owing to the retarding effect of the interionic attraction.

**Enhanced concentration effect in resin phase** — The replacement of water by a nonaqueous solvent in an ion exchange system influences the solvent uptake by the resin phase. More polar the solvent the greater is the amount of solvent taken up, while the solvents of low polarity are as a rule taken up to a less extent<sup>10,17-21</sup>.

It is reported that in aqueous organic solvent, water is concentrated in the resinous phase<sup>20,22,23</sup> while the solution is richer in the organic solvent. This effect is more pronounced with mixed solvent<sup>24,25</sup> having low water content. The selective sorption of solvent is influenced by the cation to a marked degree<sup>26,27</sup>. In aqueous methanol or aqueous acetone the solvation shell around the cations consists of water molecules<sup>28</sup>.

A study in progress at this Institute has revealed that in aqueous organic solvents, clusters containing both water and organic solvent molecules exist and that the ions which have a preference for water can displace organic molecules from the clusters. As a result of this rearrangement, counter ions in the resin in water organic solvent mixtures are solvated entirely by the water molecules. The electrolyte has also preference for water and

TABLE 5 — ENHANCED CONCENTRATION TERMS DETERMINED FROM SOLVENT COMPOSITION AND ELUTION VALUES IN AQUEOUS ORGANIC SOLVENTS

% (v/v) water*	Enhanced concentration terms (meq/litre) from elution values in mixture of					
	Water + ethanol		Water + methanol		Water + acetone	
	Nickel	Cobalt	Nickel	Cobalt	Nickel	Cobalt
100 (1.00)	100	100	100	100	100	100
90 (1.11)	110	110	105	130	120	120
80 (1.25)	125	120	105	135	130	120
70 (1.43)	145	140	110	140	140	150
60 (1.66)	160	145	125	140	170	180
50 (2.00)	200	200	200	190	205	185
40 (2.50)	240	215	200	215	255	240
30 (3.33)	280	240	270	220	300	280
20 (5.00)	360	440	300	290	430	380
15 (6.66)	450	440	310	410	500	500

\*Values in parentheses refer to reciprocal of volume fraction of water in solvent mixture.

accumulates in water medium in the neighbourhood of the resin. As amount of water goes on diminishing with the increase in the organic component in the mixture, the system behaves as if there is enhancement of the concentration<sup>17,20</sup> of the sorbed solution. The enhanced concentration term corresponds to the reciprocal of the volume fraction of water in the solvent mixture and is the same for the three aqueous organic solvents employed in this study. These are calculated for the ten solvent compositions and are given in Table 5.

The enhanced concentration terms thus calculated are compared (Table 5) with the concentration terms, corresponding to the elution values experimentally observed for nickel (cobalt) elution in water-ethanol, water-methanol and water-acetone read from the elution curves for nickel (cobalt) under otherwise similar conditions in pure aqueous systems.

The enhanced concentration terms obtained by the two methods show close agreement for all the three aqueous organic solvents up to 70 volume per cent of the organic solvent. At higher organic compositions, the concentration values determined from the experimental data are lower than the calculated enhanced concentration terms. This may be due to the interference on account of the formation of polymeric species by the interaction of water and organic solvent. The exchange reaction in the aqueous organic solvents is 1.2 to 2.2 times that of the corresponding value in pure aqueous medium. Considering the square root relationship, this means that the concentration of the electrolyte in the sorbed layer is enhanced 2 to 5 times its con-

centration in the eluting solution. The non-uniform distribution of the electrolyte and its enhanced concentration in the sorbed layer is the cause of the synergistic behaviour in the mixed solvent medium.

### Acknowledgement

Thanks of the authors are due to the Director, Maharashtra Association for the Cultivation of Science, Pune, for facilities and to the CSIR, New Delhi, for financial assistance.

### References

1. VOGEL, A. I., *Text book of practical organic chemistry* (Longmans, Green, London), 1957.
2. VOGEL, A. I., *Text book of quantitative inorganic analysis* (Longmans, Green, London), 1962.
3. FLASCHKA, H. A., *EDTA titrations — An introduction to theory and practice* (Pergamon Press, New York), 1959.
4. KITCHNER, J. A., *Paper presented at conference on ion exchange and its application held at London*, 1955.
5. MOODY, G. J. & THOMAS, J. D. R., *Analyst*, **93** (1968), 557.
6. KORKISCH, J., *Progress in nuclear energy series: IX, Analytical chemistry*, Vol. 6 (Pergamon Press, New York), 1966.
7. GHATE, M. R., GUPTA, A. R. & SHANKAR, J., *Indian J. Chem.*, **4** (1966), 64.
8. KATZIN, L. I. & GEBERT, E., *J. Am. chem. Soc.*, **75** (1953), 801.
9. OKUNO, H., HONDA, H. & ISHIMORI, T., *Japan Analyst*, **2** (1953), 4281.
10. GABLE, R. W. & STROBEL, H. A., *J. phys. Chem.*, **60** (1956), 513.
11. SAKAKI, T. & KAKIHANA, H., *Chem. Abstr.*, **47** (1953), 10951.
12. KAKIHANA, H. & SEKIGUCHI, K., *J. Pharm. Soc. Japan*, **75** (1955), 111.
13. BAFNA, S. L., *J. scient. ind. Res.*, **B12** (1953), 613.
14. HELFFERICH, F., *Ion exchange* (McGraw-Hill, New York), 1962, 6.
15. DEBYE, P. & HUCKEL, E., *Physik Z.*, **24** (1923), 185, 305.
16. ONSAGAR, L., *Physik Z.*, **27** (1926), 388; **28** (1927), 277.
17. BODAMER, G. W. & KUNIN, R., *Ind. Engng Chem.*, **45** (1953), 2577.
18. BONNER, O. D. & MOORFIELD, J. C., *J. phys. Chem.*, **58** (1954), 555.
19. SUNDHEIM, B. R., WAXMAN, M. H. & GREGOR, H. P., *J. phys. Chem.*, **57** (1953), 974.
20. DAVIES, C. W. & OWEN, B. D. R., *J. chem. Soc.*, 1956, 1676; 1681.
21. GARBER, H. J., *Ind. Engng Chem.*, **45** (1953), 1671.
22. DAVIES, G. W. & THOMAS, J. J., *J. chem. Soc.*, 1952, 1607.
23. KEMBER, N. F., MACDONALD, P. J. & WELLS, R. A., *J. chem. Soc.*, 1955, 2273.
24. BONNER, O. D., *J. phys. Chem.*, **58** (1954), 318; **59** (1955), 719.
25. GREGOR, H. P., NOBEL, D. & GOTTLIB, M. H., *J. phys. Chem.*, **59** (1955), 10.
26. NANDAN, D., GUPTA, A. R. & SHANKAR, J., *Indian J. Chem.*, **10** (1972), 285; **11** (1973), 655.
27. NANDAN, D. & GUPTA, A. R., *Indian J. Chem.*, **10** (1972), 83.
28. WILSON, J. R., *Deminevalization by electrodialysis* (Butterworths, London), 1960.
29. BONNER, O. D., *J. chem. Educn.*, **34** (1957), 174.