

## Lithium Isotope Effects & Ion Exchange Studies in Monoethanolamine-Water Systems

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The ion exchange selectivities of  $\text{Li}^+$  ion versus monoethanolammonium ( $\text{MEA}^+$ ) ion have been studied as a function of resin composition on 1%, 4% and 8% crosslinked Dowex 50W resins in aqueous, 20%, 40% and 60% (w/w) monoethanolamine (MEA)-water mixtures and apparent equilibrium constants computed for various systems. There is a reversal in selectivity of resins in favour of  $\text{Li}^+$  ion in solvents containing more than 40% (w/w) amine. Swelling and solvent fractionation studies carried out for  $\text{Li}^+$  and  $\text{MEA}^+$  forms of resins of various crosslinkings indicate that all the resins have slight preference for water. Lithium isotope effects have also been investigated in the range of 0-55% (w/w)  $\text{MEA-H}_2\text{O}$  on Dowex 50 WX8 resin by the breakthrough technique. Single stage separation factors for  ${}^6\text{Li}/{}^7\text{Li}$  isotopes ( $\alpha_7^6$ ) in amine-water mixtures are close to the value of  $\alpha_7^6$  in aqueous medium (1.0013). The lack of any appreciable change in the swelling of  $\text{Li}^+$ -form in amine-water mixtures vis a vis aqueous ones and small solvent fractionation effects appear to be responsible for insignificant deviation of  $\alpha_7^6$  in  $\text{MEA-H}_2\text{O}$  media as compared to aqueous medium.

RECENTLY lithium isotope effects in ion exchange equilibria in aqueous and a few mixed solvent systems have been reported<sup>1</sup>. An enhancement in the single stage separation factor ( $\alpha_7^6$ ) for the exchange  ${}^6\text{Li}^+ + {}^7\text{LiR} \rightleftharpoons {}^6\text{LiR} + {}^7\text{Li}^+$  was observed in methanol-water mixtures. However these isotope effect studies in mixed solvents have been confined to solvents which solvate  $\text{Li}^+$  ion through the oxygen atom. The present study in amine-water mixtures was undertaken to see the effect of the solvation of  $\text{Li}^+$  ion by amine on lithium isotope effects.

Monoethanolamine (MEA) - water systems are good solvents for many electrolytes being mixtures of solvents of high dielectric constants and exhibit low vapour pressures. A few ion exchange studies<sup>2-4</sup> have been reported in  $\text{MEA-H}_2\text{O}$  mixtures as solvents. Arnold and Churms<sup>2</sup> studied ion exchange equilibria in  $\text{MEA-H}_2\text{O}$  mixtures involving alkali metal ions and monoethanolammonium ( $\text{MEA}^+$ ) ions on three exchange resins (two of them being sulphonic acid type while the third was of a carboxylic acid type) at one resin composition. These authors also investigated swelling and solvent fractionation behaviour of these resins in  $\text{MEA-H}_2\text{O}$  mixtures. In this only study of  $\text{Li}^+$ - $\text{MEA}^+$  exchange in these solvents, a reversal of selectivity for  $\text{Li}^+$  ions was observed in solvents containing > 20 mol % MEA. Devynck and Tremillon<sup>3</sup> investigated the exchanges of  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{MEA}^+$  ions on sulphonic acid, phenolsulphonate and carboxylate type resins in  $\text{MEA-H}_2\text{O}$  mixtures and the swelling behaviour of these resins in these media.

Vaezy *et al*<sup>4</sup> studied the cation exchange equilibria involving alkali metals (K, Rb, Cs), Cu and Hg against  $\text{Na}^+$  and  $\text{MEA}^+$  forms on Amberlite CG-120 resin using radioisotopes  ${}^{24}\text{Na}$ ,  ${}^{42}\text{K}$ ,  ${}^{86}\text{Rb}$ ,  ${}^{134}\text{Cs}$ ,

${}^{64}\text{Cu}$  and  ${}^{203}\text{Hg}$ . The selectivities were determined only as a function of solvent composition.

In the present study,  $\text{Li}^+/\text{MEA}^+$  exchange selectivities in aqueous, 20%, 40% and 60% (w/w)  $\text{MEA-H}_2\text{O}$  mixtures on Dowex 50 WX1, WX4 and WX8 resins have been investigated as a function of resin composition. The swelling and solvent fractionation behaviour of  $\text{Li}^+$  and  $\text{MEA}^+$  forms of these resins has also been investigated using both surface drying as well as centrifuge techniques. The investigations have been limited upto 60% (w/w)  $\text{MEA-H}_2\text{O}$  due to high viscosity of mixtures having higher amine content. Lithium isotope effect experiments in cation exchange equilibria in  $\text{MEA-H}_2\text{O}$  mixtures in the range 0-55% (w/w) amine have been studied using the break through technique and single stage separation factors ( $\alpha_7^6$ ) for the systems computed. The isotope effects experiments have been carried out only with Dowex 50 WX8 resin in  $\text{MEA}^+$  form. Though  $\text{Li}^+$  ion is the preferred cation vis a vis  $\text{MEA}^+$  in solutions containing 40% (w/w) MEA, sharp boundaries on the column could not be obtained with  $\text{LiCl}$  solutions.  $\text{LiOH}$  feed solutions were therefore used. All experiments have been carried out at a temperature of  $298 \pm 1\text{K}$ .

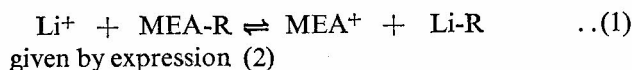
### Materials and Methods

Monoethanolamine (Sarabhai-Merck) was distilled under reduced pressure (5 mm, 333K). The water content obtained by acidimetry was less than 0.2%. Distilled water was used to prepare mixtures yielding 20%, 40%, 55% and 60% (w/w) amine. Other chemicals used were of AR grade.

In the case of  $\text{Li}^+/\text{MEA}^+$  exchange experiments, solutions of  $\text{LiCl}$  and monoethanolammonium chloride (0.1M) in 0%, 20%, 40% and 60% (w/w) amine were prepared from stock solutions

of these salts by adding desired amounts of amine. Monoethanolammonium chloride was prepared in aqueous solution by neutralising MEA with HCl. Dowex 50 W resins of 1% DVB (50-100 mesh) 4% DVB (20-50 mesh) and 8% DVB (20-50 mesh) in Li<sup>+</sup> and MEA<sup>+</sup> forms were air-dried and stored. Parts of these resins were dried in vacuo over P<sub>2</sub>O<sub>5</sub> in an oven at 353 K for swelling and solvent fractionation studies. Li<sup>+</sup> resin capacities were determined by eluting with acid and estimating lithium gravimetrically as Li<sub>2</sub>SO<sub>4</sub>. Capacities of MEA<sup>+</sup> form of resins were determined indirectly by converting them to H<sup>+</sup>-form and determining the capacities of H<sup>+</sup> form in the usual way. The resins dried in vacuo had the following capacities: 1% DVB, MEA<sup>+</sup> = 4.08, Li<sup>+</sup> = 4.98; 4% DVB, MEA<sup>+</sup> = 4.00, Li<sup>+</sup> = 4.92; 8% DVB, MEA<sup>+</sup> = 4.01, Li<sup>+</sup> = 4.90 meq/gm.

*Ion exchange equilibria* — The exchange equilibrium experiments were conducted by batch technique. Air-dried resin (0.5 g each) and solution (50 ml each containing 0.1 M LiCl and 0.1 M monoethanolammonium chloride in varying proportions) were used. A week's time was sufficient to attain equilibrium in all the systems. After equilibration, solutions were carefully decanted and analysed for lithium content by flamephotometry. The concentration of MEA<sup>+</sup> was obtained from the total electrolyte content added and the concentration of Li<sup>+</sup> present in solution. The composition of the equilibrium exchanger was derived from the knowledge of the total capacity of the resin and initial and equilibrium compositions of the solution. The selectivity coefficients (*K<sub>D</sub>*) for the exchange equilibrium (1)



$$K_D = \frac{m_{\text{MEA}^+}}{m_{\text{Li}^+}} / \frac{N_{\text{MEA-R}}}{N_{\text{Li-R}}} \quad \dots(2)$$

were computed and plotted as a function of *N<sub>Li-R</sub>*. As the solution phase activity coefficients of the electrolytes in the various media were not available, only apparent equilibrium constants (*K'*) of Li<sup>+</sup>/MEA<sup>+</sup> exchange, defined by Eq. (3) have calculated.

$$\text{Log } K' = \int_0^1 \text{log } k_D \, dN_{\text{Li-R}} \quad \dots(3)$$

As air-dried 1% DVB resin were expected to take up somewhat significant amount of solvent from the external solution, samples (0.5g each) were first equilibrated with 100% humidity in an isopiestic unit<sup>6</sup> and then used for equilibrium studies. Though correction for change in external solution volumes were thus not required, the percentage of MEA in solution changes slightly due to small amount of amine going into the resin. However, no significant effects on selectivity were expected due to this.

*Swelling and solvent fractionation studies* — About 2g aliquots of Li<sup>+</sup> and MEA<sup>+</sup> form of variously

crosslinked resins dried in vacuo were equilibrated each with 100 ml of 0%, 20%, 40% or 60% (w/w) MEA-H<sub>2</sub>O mixtures for 4 days. One part of each resin was surface-dried and the second part centrifuged for 30 min at 3000 rpm. These wet aliquots were weighed and MEA present in resin eluted with water. Amine was estimated titrimetrically using 0.1 M HCl and a mixed bromocresol green and methyl red indicator. The resin aliquots were then dried in an oven at 388K to obtain the weights of dry resins. The agreement between the surface drying and the centrifuge method for the solvent content and the solvent composition of the resins obtained was very good. In these experiments, care was taken to protect the solvent mixture from atmospheric CO<sub>2</sub> and moisture.

*Isotope effects* — Ion exchange column with H<sup>+</sup> resin [bed height = 120 cm; internal diam. = 12 mm; capacity = 340(meq)] was used. The resin was converted to MEA<sup>+</sup> form by passing an excess of a respective mixed solution of MEA-H<sub>2</sub>O. In the process, the column was also conditioned with respect to the mixed solvent used. LiOH solutions of 0.35 ± 0.05 M were passed through the column at fixed flow rates. Due to increased viscosities of MEA-H<sub>2</sub>O solutions<sup>3</sup> with increasing MEA content, flow rates decreased from 30 ml/hr in aqueous medium to 10 ml/hr in 55% (w/w) MEA. As the flow rates were too small beyond this composition, these studies at higher MEA contents could not be carried out. MEA in the effluent samples was oxidised by carefully heating with conc. HNO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> medium and lithium estimated as Li<sub>2</sub>SO<sub>4</sub>. For mass spectrometric analysis, these Li<sub>2</sub>SO<sub>4</sub> samples were converted to LiNO<sub>3</sub> by adsorbing Li<sup>+</sup> ions on a strong acid cation exchange resin and then eluting with conc. nitric acid.

### Results and Discussion

*Ion exchange and swelling studies* — Log *K<sub>D</sub>* vs *N<sub>Li-R</sub>* plots in Figs. 1 and 2 show that log *K<sub>D</sub>* varies regularly as a function of resin composition for the systems. With increasing crosslinking, Log *K<sub>D</sub>* varies only to a small extent for all solvent compositions. *K'* values (Eq. 3) obtained from these plots are summarised in Table 1. *K<sub>D</sub>* values for 2% DVB resin at *N<sub>Li-R</sub>* = 0.5 reported by Arnold and Churms<sup>2</sup> (included in Table 1) are consistent with the present *K'* values at other crosslinked resins. This is due to the fact that log *K<sub>D</sub>* at 0.5 *N<sub>Li-R</sub>* is close to log *K'* for those systems where Log *K<sub>D</sub>* vs *N<sub>Li-R</sub>* plots exhibit linear variations. The data in Table 1 clearly show that Li<sup>+</sup> ion becomes the preferred ion in solutions containing 40% (or more) amine for all crosslinkings.

The data on the swelling and solvent fractionation on various resins in MEA-H<sub>2</sub>O mixtures are presented in Tables 2-4. These data include the solvent selectivity coefficients, *K<sub>MEA</sub><sup>H<sub>2</sub>O</sup>* for the resin. *K<sub>MEA</sub><sup>H<sub>2</sub>O</sup>* is defined by the expression (4)

$$K_{\text{MEA}}^{\text{H}_2\text{O}} = \frac{\bar{N}_{\text{H}_2\text{O}}}{\bar{N}_{\text{MEA}}} \cdot \frac{N_{\text{MEA}}}{N_{\text{H}_2\text{O}}} \quad \dots(4)$$

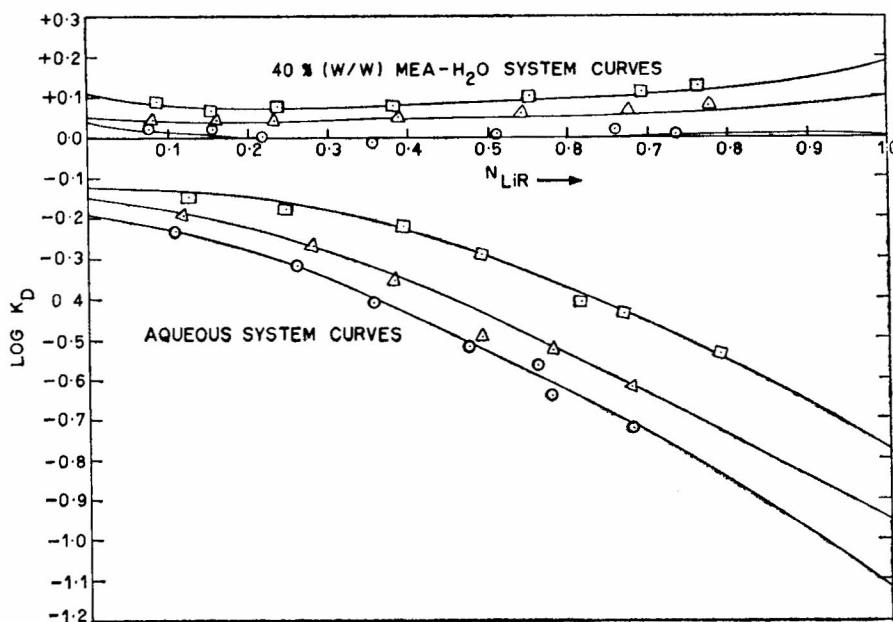


Fig. 1 — Log  $K_D$  vs  $N_{Li-R}$  plots for  $Li^+/MEA^+$  exchange on Dowex 50W resins in aqueous and 40% (w/w) monoethanolamine-water media at  $298 \pm 1$  K [—○—○— (1% DVB); —△—△— (4% DVB); and —□—□— (8% DVB)]

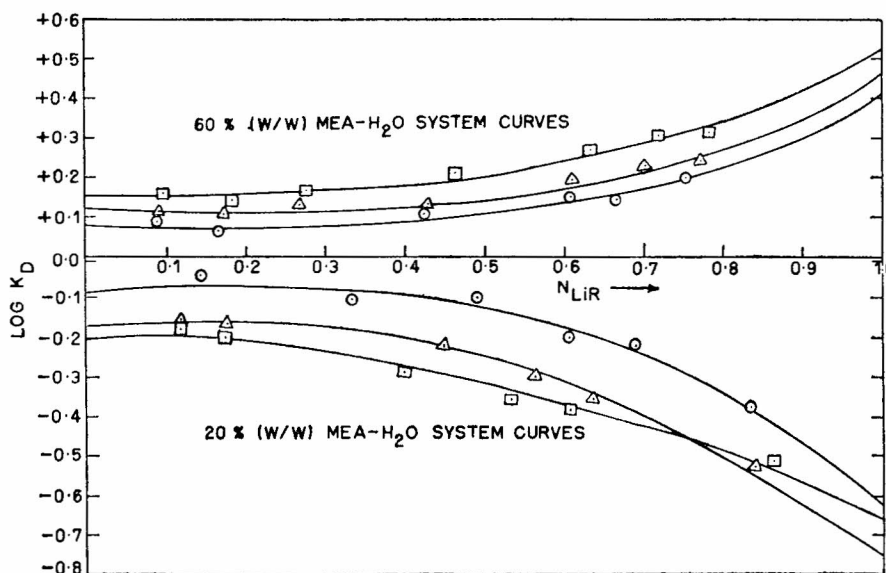


Fig. 2 — Log  $K_D$  vs  $N_{Li-R}$  plots for  $Li^+/MEA^+$  exchange on Dowex 50W resins in 20% (w/w) and 60% (w/w) monoethanolamine water media at  $298 \pm 1$  K [—○—○— (1% DVB); —△—△— (4% DVB); —□—□— (8% DVB)]

where  $\bar{N}$ 's are mole fractions of solvents in the resin phase and  $N$ 's are in the outside mixture.  $K_{MEA}^{H_2O}$  obviously represents the selective sorption of water over MEA by the resin.

It is seen from Tables 2-4 that  $MEA^+$  form resin of a particular crosslinking absorbs almost same quantity of solvent for all solvent compositions. The amount of solvent absorbed diminishes with increase in crosslinking. Devynck and Tremillon<sup>3</sup> also observed a constant amount of sorption of MEA-H<sub>2</sub>O mixture by  $H^+$  resins of 4% and 8% DVB resins over the entire range of solvent

composition.  $Li^+$  forms of resins absorb greater quantity of solvent compared to  $MEA^+$  forms in all the cases though there is some decrease in the quantity sorbed as MEA content in solution increases.  $K_{MEA}^{H_2O}$  values show little preference for water over MEA both for  $Li^+$  and  $MEA^+$  forms for low crosslinked resins. However,  $MEA^+$  form of 8% DVB exhibits greater fractionation than  $Li^+$  form. From the data of Devynck and Tremillon<sup>3</sup> on the solvent fractionation by  $H^+$  form of 4% and 8% DVB resins, solvent composition in the  $MEA^+$  form has been calculated (assuming a  $H^+$  resin capacity

of 5 meq/g). These estimated values show fair agreement with the present data. However Arnold and Churms<sup>2</sup> reported much higher solvent fractionation by MEA<sup>+</sup> form of 2% DVB resin. Con-

sidering the polar nature of MEA, it is difficult to understand such large effects in a low crosslinked resin.

Total solvent uptake by MEA<sup>+</sup> form in aqueous medium, e. g. 8% DVB Dowex-50W resin is 159 g compared to 218 g by Li<sup>+</sup> form and 172 g by NH<sub>4</sub><sup>+</sup> form<sup>7</sup>. This is consistent with the smaller hydration of MEA<sup>+</sup> than NH<sub>4</sub><sup>+</sup> or Li<sup>+</sup> due to its large size. This is further supported by the greater preference of the resin for MEA<sup>+</sup> compared to NH<sub>4</sub><sup>+</sup> (ref. 7) or Li<sup>+</sup> ions.

On addition of amine to the extent of 20% (w/w), the situation does not change appreciably but the selectivity for MEA<sup>+</sup> diminishes. This process continues on further addition of MEA and around 40% (w/w) amine (~17 mol%) the preference for Li<sup>+</sup> and MEA<sup>+</sup> ions becomes more or less same. Due to the addition of amine, the total solvation of Li<sup>+</sup> decreases and that of MEA<sup>+</sup> increases due to

TABLE 1 — APPARENT EQUILIBRIUM CONSTANTS (K') OF Li<sup>+</sup>/MEA<sup>+</sup> EXCHANGE ON DOWEX 50W RESINS IN AQUEOUS AND MEA-H<sub>2</sub>O MIXTURES

[Ionic strength = 0.1 M; temp. = 298K]

Solvent medium	K'			
	1% DVB	2% DVB*	4% DVB	8% DVB
Aqueous	0.46	0.40	0.32	0.26
20% (w/w) MEA-H <sub>2</sub> O	0.65	0.50	0.48	0.44
40% (w/w) MEA-H <sub>2</sub> O	1.01	1.00	1.14	1.23
60% (w/w) MEA-H <sub>2</sub> O	1.35	1.50	1.52	1.73

\*Values of Arnold and Churms<sup>3</sup> at N<sub>Li-R</sub> = 0.5 (resin, Zeokarb 225).

TABLE 2 — SWELLING AND SOLVENT FRACTIONATION DATA FOR DOWEX 50 WX1 RESINS OF MEA<sup>+</sup> AND Li<sup>+</sup> FORMS IN 0-60% (w/w) MEA-H<sub>2</sub>O MIXTURES AT 298±1K

	X1 (MEA <sup>+</sup> -form)				X1 (Li <sup>+</sup> -form)			
	0%	20%	40%	60%	0%	20%	40%	50%
Grams solvent/g dry resin	3.487	3.481	3.138	3.089	5.877	5.501	4.834	4.818
Per cent MEA in pore solvent	—	18.7	38.3	58.5	—	19.2	39.6	58.8
No. of mol MEA/equiv. resin :(n <sub>MEA</sub> )	—	2.60	4.82	7.24	—	3.47	6.29	9.31
No. of mol H <sub>2</sub> O/equiv. resin :(n <sub>H<sub>2</sub>O</sub> )	47.4	38.6	26.4	17.26	66.1	49.6	32.6	22.15
Selective water absorption coefficient (K <sub>MEA</sub> <sup>H<sub>2</sub>O</sup> )	—	1.10	1.13	1.06	—	1.07	1.02	1.06

TABLE 3 — SWELLING AND SOLVENT FRACTIONATION DATA FOR DOWEX 50WX4 RESINS OF MEA<sup>+</sup> AND Li<sup>+</sup> FORMS IN 0-60% (w/w) MEA-H<sub>2</sub>O MIXTURES AT 298±1K

	X4 (MEA <sup>+</sup> -form)				X4 (Li <sup>+</sup> -form)			
	0%	20%	40%	60%	0%	20%	40%	60%
Grams solvent/g dry resin	1.324	1.292	1.283	1.305	2.127	1.838	1.785	1.776
Per cent MEA in pore solvent	—	17.6	36.9	56.9	—	18.7	38.6	58.9
		(19.5)*	(39.0)*	(59.1)*				
No. of mol MEA/equiv. resin: (n <sub>MEA</sub> )	—	0.93	1.94	3.04	—	1.14	2.29	3.48
No. of mol H <sub>2</sub> O/equiv. resin :(n <sub>H<sub>2</sub>O</sub> )	18.38	14.80	11.25	7.82	24.17	16.88	12.39	8.25
Selective water absorption coefficient (K <sub>MEA</sub> <sup>H<sub>2</sub>O</sup> )	—	1.12	1.14	1.14	—	1.10	1.06	1.05

\*From Devynck and Tremillion's data<sup>3</sup>

TABLE 4 — SWELLING AND SOLVENT FRACTIONATION DATA FOR DOWEX 50WX8 RESINS OF MEA<sup>+</sup> AND Li<sup>+</sup> FORMS IN 0-60% (w/w) MEA-H<sub>2</sub>O MIXTURES AT 298 ± 1K

	X8 (MEA <sup>+</sup> -form)				X8 (Li <sup>+</sup> -form)			
	0%	20%	40%	60%	0%	20%	40%	60%
Grams solvent/g dry resin	0.637	0.669	0.695	0.726	1.066	1.068	1.004	1.000
Per cent MEA in pore solvent	—	15.3	33.8	55.2	—	16.2	37.0	58.0
		(12.5)*	(34.4)*	(56.3)*				
No. of mol MEA/equiv. resin:(n <sub>MEA</sub> )	—	0.42	0.96	1.64	—	0.58	1.24	1.92
No. of mol H <sub>2</sub> O/equiv. resin :(n <sub>H<sub>2</sub>O</sub> )	8.60	7.81	6.37	4.51	11.96	10.15	7.17	4.72
Selective water absorption coefficient (K <sub>MEA</sub> <sup>H<sub>2</sub>O</sup> )	—	1.38	1.11	1.22	—	1.30	1.13	1.09

\*From Devynck and Tremillion's data<sup>3</sup>

greater MEA<sup>+</sup>-MEA interactions and two ions start competing more or less equally. As more amine is added, solvated size of Li<sup>+</sup> becomes smaller than that of MEA<sup>+</sup> and there is clear selectivity reversal. Since the thermodynamic data relating to free energies of transfer of the electrolytes and resinates from water to MEA-H<sub>2</sub>O mixtures involved in the present study, are not available in literature, it is not possible to discuss these systems in terms of thermodynamic theory<sup>8</sup>.

*Lithium isotope effects in cation exchange equilibria in MEA-H<sub>2</sub>O mixtures*—The single stage separation factor for the two isotopes of lithium ( $\alpha_7^6$ ), defined as<sup>1</sup>

$$\alpha_7^6 = \left[ \frac{{}^6\text{Li}}{{}^7\text{Li}} \right]_{\text{Resin}} \cdot \left[ \frac{{}^7\text{Li}}{{}^6\text{Li}} \right]_{\text{solution}} \quad \dots (5)$$

has been evaluated by the method described in literature<sup>1</sup> and these values are: aqueous, 1.0013; 20% (w/w) MEA-H<sub>2</sub>O, 1.0012; 40% (w/w) MEA-H<sub>2</sub>O, 1.0014 and 55% (w/w) MEA-H<sub>2</sub>O, 1.0018. As slight changes in solution concentration<sup>9,10</sup> or flow rate have little effect on  $\alpha_7^6$ , these values can be compared with those given in literature<sup>1</sup>.

The values for  $\alpha_7^6$  in 20%, 40% and 55% (w/w) MEA-H<sub>2</sub>O are very close to that in aqueous medium within the experimental accuracy of  $\pm 0.0004$ . Again,  $\alpha_7^6$  values for all other mixed solvents with the exception of MeOH-H<sub>2</sub>O and *i*-PrOH-H<sub>2</sub>O systems given in ref. 1 do not show any significant deviation from that in aqueous medium. MeOH-H<sub>2</sub>O as well as DMSO-H<sub>2</sub>O system have been explained earlier<sup>1</sup> on the basis of (i) swelling, (ii) solvent fractionation behaviour of the Li<sup>+</sup> form of resin and (iii) the magnitude and sign of the free energy of transfer of Li<sup>+</sup> ion [ $\Delta G_i^0(\text{Li}^+)$ ] from water to the desired mixed solvent. In the case of MeOH-H<sub>2</sub>O systems [76% (w/w)], the pore solvent composition and relevant  $\Delta G_i^0(\text{Li}^+)$  values indicate<sup>1</sup> greater solvation of Li<sup>+</sup> ion in the outside solution over and above the existing difference due to the

concentration differences in the two phases which exists in aqueous (as well as mixed solvent even if there is no solvent fractionation) medium. In the case of DMSO-H<sub>2</sub>O mixture, Li<sup>+</sup> form resin shows very little changes<sup>11</sup> in the swelling or solvent composition and  $\alpha_7^6$  value is close to the value for aqueous medium.

The total swelling and the solvent fractionation data in Tables 2-4 for MEA-H<sub>2</sub>O mixtures show swelling changes of less than 7% for Li<sup>+</sup> resin in going from aqueous to 60% MEA and little solvent fractionation (2-4%). Thus these MEA-H<sub>2</sub>O systems behave very much like 52.5% DMSO-H<sub>2</sub>O system and no significant deviations in  $\alpha_7^6$  are expected in these solvents compared to aqueous medium.

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#### References

1. NANDAN, D. & GUPTA, A. R., *Indian J. Chem.*, **16A** (1978), 256.
2. ARNOLD, R. & CHURMS, S. C., *J. chem. Soc.*, (1965), 325.
3. DEVYNCK, J. & TREMILLON, B., *Bull. Soc. chim. Fr.*, (1967), 685.
4. VAEZY, F., RENAULT, N. & DESCHAMPS, N., *Radiochem. radional. Lett.*, **17** (1974), 381.
5. GLUECKAUF, E., in *Separation of isotopes*, edited by H. London (George Newnes Ltd. London), 1961.
6. NANDAN, D. & GUPTA, A. R., *Indian J. Chem.*, **12** (1974), 808.
7. BONNER, O. D. & PAYNE, W. H., *J. phys. Chem.*, **58** (1954), 183.
8. GUPTA, A. R., *J. phys. Chem.*, **75** (1971), 1152.
9. HAGIWARA, J. & TAKAKURA, Y., *J. nucl. Sci. Technol.*, **6** (1969), 279.
10. LEE, D. A. & DRURY, J. S., *J. inorg. nucl. Chem.*, **27** (1965), 1405.
11. VAN WART, H. E. & JANAUER, G. E., *J. phys. Chem.*, **78** (1974), 411.

