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BHABHA ATOMIC RESEARCH CENTRE

**PREFERENTIAL SOLVATION OF SINGLE IONS IN
MIXED SOLVENTS**

**PART 1 : NEW EXPERIMENTAL APPROACH AND SOLVATION OF
MONOVALENT IONS IN METHANOL-WATER AND
ACETONITRILE-WATER MIXTURES)**

**PART 2 : THEORETICAL COMPUTATION AND COMPARISON
WITH EXPERIMENTAL DATA)**

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ATOMIC ENERGY COMMISSION

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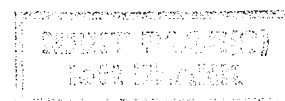
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60	<i>Abstract :</i>	<p>Preferential solvation of single ion solutions has been studied with Li⁺, Na⁺, K⁺ and Ag⁺- forms of Dowex 50 W resins of different cross-linkings in methanol-water and acetonitrile (AN)- water mixtures. The solvent uptake by this alkali metal ionic forms of Dowex 50W resins was studied in an isopiestic set-up using 2,4,6 and 8 m LiCl solutions in 11.0, 20.8, 44.3 and 70.2% (w/w) methanol-water mixtures and that of Na⁺- and Ag⁺- forms using 14.6 to 94.3% (w/w) AN - water mixtures. The solvent sorbed in the resin phase was extracted by Rayleigh-type distillation and analysed gas chromatographically. The data were analysed by the N_o (mole fraction of the organic solvent in the resin phase) vs n_T (total solvent content in the resin phase) plots and separation factor, α (ratio of mole fraction of the solvents in the resin and solution phases) or N_o vs m (molality in the resin phase) plots. The limiting values of these plots gave the composition of the solvent in the primary solvation shell around the single ion. The compositions of the primary solvation shell around Li⁺, Na⁺ and K⁺ in methanol-water mixtures and Na⁺ and Ag⁺ in acetonitrile (AN) - water mixtures have been computed using Frank's equation and the approach of Marcus and compared with the experimental results obtained with the above mentioned ionic forms of Dowex 50W resins in different mixed solvents. The experimental results for Li⁺ showed good agreement with the values computed using Frank's equation for all methanol-water composition. However, in the case of Na⁺ and K⁺ in methanol-water mixtures and Na⁺ in AN-water mixtures, there was agreement only at lower organic solvent content and the Frank's equation predicted higher values for the organic solvent in the primary solvation shell around the cation at higher organic solvent content as compared to experimental results.</p>
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PART 1

NEW EXPERIMENTAL APPROACH AND SOLVATION OF

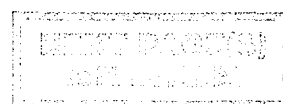
MONOVALENT IONS IN METHANOL-WATER AND ACETONITRILE-

WATER MIXTURE



ABSTRACT

Preferential solvation of single ion solutions has been studied with Li^+ , Na^+ , K^+ and Ag^+ - forms of Dowex 50W resins of different cross-linkings in methanol-water and acetonitrile (AN)- water mixtures. The solvent uptake by this alkali metal ionic forms of Dowex 50W resins was studied in an isopiestic set-up using 2,4,6 and 8 m LiCl solutions in 11.0, 20.8, 44.3 and 70.2 % (w/w) methanol-water mixtures and that of Na^+ - and Ag^+ - forms using 14.6 to 94.3 % (w/w) AN- water mixtures. The solvent sorbed in the resin phase was extracted by Rayleigh-type distillation and analysed gas chromatographically. The data were analysed by the N_s (mole fraction of the organic solvent in the resin phase) vs n_T (total solvent content in the resin phase) plots and separation factor, α (ratio of mole fraction of the solvents in the resin and solution phases) or N_s vs m (molality in the resin phase) plots. The limiting values of these plots gave the composition of the solvent in the primary solvation shell around the single ion. At low molalities and low methanol contents, water was preferentially sorbed by the Li^+ in the resin. Comparison between the Li^+ - form of the resin and LiCl solution in methanol-water mixtures indicated the role of Cl^- in the formation of solvation shell around Li^+ in solution. The solvent uptake characteristics of Ag^+ - form of the resin and the solubility of Ag_2SO_4 in AN-water mixtures were similar indicating the specific interaction between Ag^+ and AN and between Ag^+ and SO_4^{2-} (in solution) and SO_3^- group (in the resin). Ag^+ -form of the resin behaves as a single ion solution only at low AN content. The study has also established that Li^+ , Na^+ and K^+ form of resin in methanol-water mixtures at low methanol content and Na^+ -form in AN-water mixtures of low AN content behave as single ion solutions. At higher composition of the organic solvent, ion pair formation in the resin phase occurs and the resin phase does not behave like a single ion solution.



PART 1

**NEW EXPERIMENTAL APPROACH AND SOLVATION OF
MONOVALENT IONS IN METHANOL-WATER AND ACETONITRILE-
WATER MIXTURE**

Ion-ion, ion-solvent and solvent-solvent interactions determine the behaviour of electrolyte in solutions.¹ When the ion-solvent interaction is stronger than the ion-ion and solvent-solvent interactions, the ion is solvated.¹ Solvation of ions has been studied much more frequently in pure aqueous and non-aqueous solvents than in mixed solvents.¹⁻⁶ In binary solvent systems, complication arises in the sense that the composition of the solvation shell of either one or both the ions differs from the bulk composition; that is, ions tend to prefer one of the solvents over the other for their solvation. Thus, in mixed solvents, containing a binary electrolyte, both the ions can be preferentially solvated by the same solvent or with more interesting consequence, one ion is bound more strongly by one component and the other prefers the second solvent component. The former is called the homoselective solvation and the latter the heteroselective solvation.⁶

The preferential solvation of ions in mixed solvents has been experimentally studied using solvent transference number by Hittorf method by Strelhow and Koepp for AgNO_3 in water-acetonitrile (AN) mixtures, NMR chemical shift measurements in the case of Ag^+ -water-AN, free energy of transfer of Ag^+ from water to AN or DMSO and from methanol to DMSO and solubility measurements in the case of AgCl in water-AN mixtures and others.²⁻¹¹ From NMR chemical shift studies solvation numbers for Ag^+ have been obtained; solvent transference number studies indicated that Ag^+ is more strongly solvated by AN and SO_4 by water. However, these studies do not give reliable data about the composition of primary solvation shell around the ion, Ag^+ , for example, as a function of bulk solvent composition.

Preferential solvation in mixed solvents has been studied theoretically in greater detail. The treatment of Debye¹², later extended by Frank¹³, is based entirely on electrostatic consideration. Padova¹⁴ introduced the excess free energy of transfer of an ion from one solvent to the other to analyse the preferential solvation phenomenon. Recently, Marcus¹⁵ has developed a quasi-lattice quasi-chemical theory of preferential solvation which takes into account both ion-solvent and solvent-solvent interactions. Specific interactions of solvents with cations are also taken into consideration in this approach via the free energy of transfer of the cation and the solvent-solvent interactions via excess free energies of mixing of the two solvents. As the experimental studies reported so far do not give a complete and reliable picture about the solvation shell around an ion in mixed solvent media, the theoretical treatment and the equation developed have not so far been tested with experimental data.

As electrolyte solutions invariably contain cation and anion, the experimental techniques described above suffer from the drawback, in that the ion-ion interactions are superimposed on ion-solvent interactions. These techniques also require concentrated solution in order to get information about solvent molecules in the solvation shell and bulk solvent, where ion-ion interaction become more predominant and are also limited by solubility considerations.

Recently,¹⁶ studies on single ion solvation in aqueous media have been carried out using strong acid cation exchangers and strong base anion exchangers. This approach has made possible the study of single ion hydration in a wider range of concentration and temperature. These studies have been extended to look into the possibility of ion exchange matrix for studying the phenomenon of preferential solvation of simple ion in mixed solvent system. Hopefully, the information thus obtained will also provide a means to test and verify the theoretical treatment on preferential solvation.

For studies of those systems, in which there are essentially electrostatic interactions between the ion and the two solvents, methanol-water system and Li^+ , Na^+ and K^+ forms of Dowex 50W resin with different crosslinkings have been chosen and Ag^+ and AN-water system as a case having specific interactions (between Ag^+ and AN).

The results of these studies are presented in two parts. Part 1 deals with the experimental details and the results obtained therein. In Part 2, the solvation shell compositions for the univalent cation in methanol-water and AN-water mixtures are computed on the basis of the theoretical treatment and are compared with the experimental results.

Experimental

Preparation of the resin: Li^+ , Na^+ , K^+ and Ag^+ - forms of Dowex 50 W resins of 4, 8 and 12 % cross-linkings were prepared from their respective salts by the conventional method. They were vacuum dried and stored in well-stoppered bottles.

Preparation of solvents and solutions : Stock solutions of methanol-water and AN-water mixtures of various compositions were prepared from GR grade methanol and acetonitrile (AN) and by mixing them with distilled water in the desired volume proportion at 298 K. Their weight by weight (w/w) composition were calculated from their densities and volumes and were verified by the gas chromatographic analysis. The composition used in the present study are : 11.0, 20.8, 44.3 and 70.2 % (w/w) methanol-water mixtures and 14.6, 32.7, 43.3, 54.3, 71.7 and 94.3 % (w/w) AN-water mixtures. 2,4,6 and 8 m LiCl solutions were prepared in the 11.0, 20.8, 44.3 and 70.2 % (w/w) methanol-water mixtures for use in the isopiestic experiments.

Maximum solvent uptake studies : The total maximum solvent uptake in the methanol-water and AN-water mixed solvents by the resin in different ionic forms

was estimated by contacting a known weight of the vacuum dried resin (VDR) with 70 cm³ of the mixed solvent (of a particular solvent composition) in a conical flask. The mixture was shaken for 2 h in a mechanical shaker and later the resin samples were separated and surface dried (SDR). A known weight of the SDR sample was heated to 383 K to constant weight and the total solvent uptake by the resin was determined from the weight loss on drying. Another known weight of the SDR sample was taken in a conical flask connected to a distillation unit, similar to the Rayleigh distillation described earlier.¹⁷ The entire solvent was distilled from the resin at 423 K under running vacuum for nearly 2 h into a weighed U-tube kept in liquid nitrogen. The gain in the weight of the U-tube corresponds to the loss of solvent from the resin. This value coincided with the value obtained by drying the resin at 383 K. The distillate was analysed gas chromatographically to determine the solvent composition in the resin phase.

Solvent uptake at lower methanol-water activities : The resin samples with lower n_w , n_s values (n_w , n_s represent the number of moles of water and solvent, respectively, per equivalent of the resin) for a particular methanol-water composition was prepared by equilibrating the resin in LiCl solutions of varying concentrations in different methanol-water mixtures isopiesticly in the set up described in earlier publication.¹⁸ The methanol and water content in the isopiesticly equilibrated resins were estimated as described above.

Determination of vapour phase composition : For knowing the water and methanol activities in various LiCl solutions the vapour phase composition is required. It was determined using about 25 cm³ of solvent (or solution) in a 100 cm³ conical flask connected to the Rayleigh distillation set up. The liquid was desorbed of all the air or gas by subjecting it to freeze-thaw cycle in liquid nitrogen, a few times. The flask was then immersed in a thermostat at 298 ± 1 K and was allowed to attain thermal equilibrium. The total vapour pressure was measured using mercury manometer. The vapour in the flask was slowly distilled into an U-tube kept in

liquid nitrogen, in the distillation set up. The unit was cut-off from the vacuum pump and the distillation was carried out only under the temperature gradient between the flask and the U-tube. The slow rate of distillation was maintained in order not to disturb the equilibrium between the vapour and the liquid in the flask, thereby ensuring no appreciable change in vapour pressure. Nearly 0.1 g of the vapour was collected which was analysed for the solvent composition by gas chromatography.

Analysis of the water-solvent (methanol or AN) mixture : The composition of the mixed solvent was analysed either by gas chromatographic technique or chemical analysis.

Gas chromatographic analysis : A gas chromatograph with thermal detector fabricated in Chemistry Division, BARC, was used for the analysis. A parapak-T column maintained at 373 K (for methanol-water) or at 423 K (for AN-water) was used. Hydrogen at a flow rate of 40 ml/min was the carrier gas. The column was first calibrated with 10 different standard solutions of the mixed solvents of known composition covering the entire range of solvent composition employed in the studies with 3 to 4 injections of about 1.6 μ of the sample. Both water and solvent peaks were measured and correlated with absolute amount of water of solvent by using densities of various solvent and water compositions available in literature. The calibration curves were recorded every time before starting the actual analysis. Representative chromatograph and calibration curves for methanol-water and AN-water mixtures are given in Figs. 1 and 2.

Chemical analysis : For analysing very low concentrations of methanol (~2-3% methanol) Nanji-Narman method,¹⁹ described in an earlier publication²⁰, was used.

Results and discussion

Methanol-Water system : Fig. 3 shows the partial vapour pressure of methanol as a function of composition of the methanol-water mixtures obtained in the present

study. These values compare well with the data reported by Butler et al²¹, which are also plotted in Fig.3.

Results of the vapour phase composition of LiCl solutions (2,4,6 and 8 m) prepared in different methanol-water mixtures were analysed in terms of the activity ratios a_m/a_w (m and w represent, respectively, methanol and water) of the two components and separation factor, α . They are defined as :

$$a = \frac{N \times \text{total pressure}}{\text{Vapour pressure of pure solvent}}$$

$$\alpha = \frac{N'_s / (1 - N'_s)_{\text{vapour}}}{N_s / (1 - N_s)_{\text{solvent}}}$$

where N is the mole fraction of solvent in vapour phase and N_s 's are the mole fraction in solution and N'_s 's are the mole fraction in the vapour phases.

Fig. 4 shows the variation of a_m/a_w as a function of molality of LiCl in the methanol-water mixtures. The activity ratios for salt solutions remain more or less the same as for pure solvent mixtures upto ~ 4m concentration in all solvent mixtures. At higher salt concentrations this is valid only for solution of low methanol content [11.0, 20.8 % (w/w)]. Significant deviation in a_m/a_w from pure solvent mixtures are observed for solvent mixtures with higher methanol content (Fig.4).

Isopiestic solvent uptake studies were carried out with Li^+ - form (in 2, 8 and 12 % cross-linked Dowex 50W resins), Na^+ - and K^+ -forms (in 4 % cross-linked Dowex 50W resin) using LiCl solutions of varying concentrations in different methanol-water mixtures. Li^+ being the smallest alkali metal ion, the electrostatic interactions with the solvents will be the strongest. Hence, Li^+ -methanol-water system has been studied in greater detail.

The data have been presented and analysed in terms of $\bar{n}_T (= \bar{n}_s + \bar{n}_w)$, the total solvent content in the resin, \bar{N}_s , the mole fraction of methanol in the resin phase and the separation factor, α , defined as

$$\alpha = \frac{\bar{N}_s / (1 - \bar{N}_s)_{\text{resin}}}{N_s / (1 - N_s)_{\text{solution}}}$$

Typical data obtained are given in Table 1, for Li^+ -form of the resin using LiCl solution in 70.2 % (w/w) methanol-water mixture.

Solvent uptake studies by variously cross-linked Li^+ , Na^+ - and K^+ - form of Dowex 50W resin in methanol-water mixtures have been reported by Nandan et al.²⁰ There is a good agreement between the data obtained in the present study and those reported by Nandan et al.

Fig. 5 shows the variation of \bar{N}_s with molality, \bar{m} , in the resin phase for Li^+ -form of the resin for different composition of methanol-water mixtures. In the case of 11% (w/w) methanol-water mixture, \bar{N}_s increases with molality and reaches a constant value at higher molalities. In other methanol-water mixtures, \bar{N}_s decreases with molality and approaches a constant value at higher molalities. This indicates that at low molalities and low methanol content water is absorbed more preferentially than it would be from the primary solvation shell considerations.

The effect of secondary solvation shell can be seen more clearly in the plot of \bar{N}_s or $\bar{n}_T (= \bar{n}_s + \bar{n}_w)$, shown in Fig.6. The plots show that \bar{N}_s remains constant for all solvent compositions when \bar{n}_T is less than 6, that is, in the region where only the primary solvation shell is present. In the methanol-water mixtures, the solvation number of Li^+ is expected to be 4 to 6. The limiting composition in the region of 0-6 \bar{n}_T can be taken as primary shell composition in various methanol-

water mixtures. The values of \bar{N}_s in these limiting compositions for Li^+ -form of the resin in different methanol-water mixtures are given in Table 2.

Figs. 7 to 10 show the variation of α with m for LiCl solutions and Li^+ -form of the resin for different methanol-water mixtures. In the case of LiCl solutions (Figs. 7 to 10), α always increases with m which implies that the solvation is mainly by water than by methanol in LiCl solutions.

A comparison between the variation of α (Li^+ -resin) and α (LiCl solution) with m (Figs.7 to 10) shows the effect of Cl^- . In 11% and 20.8 (w/w) methanol-water mixtures, the absence of Cl^- is seen from the larger variation in α with m for Li^+ -resin and LiCl solutions. At higher methanol compositions, α for Li^+ -resin and LiCl solution are more or less the same. α for Li^+ -resin at high molality in the resin in all methanol-water composition reaches a limiting value. The limiting values can be associated with primary solvation shell. In the case of LiCl solution, this region cannot be explored due to solubility limitations. Variation of α at low molalities can be attributed to secondary solvation shell.

In low methanol concentrations secondary solvation shell could be formed in the case of Li^+ (in the resin). In the case of LiCl solutions, due to anion - cation interactions and to lower dielectric constants, secondary solvation shell is not likely to be formed. Hence, the larger differences in the α vs m plots for Li^+ -resin and LiCl solution (Figs. 7 to 10). At higher methanol concentrations, the secondary solvation shells for both Li^+ (in the resin) and LiCl are not properly formed and so the variation of α with m are nearly the same for both Li^+ -resin and LiCl solutions (Figs.7 to 10). These effects of solvation of Li^+ in the resin phase are clearly demonstrated in the \bar{N}_s vs \bar{m} and \bar{N}_s vs \bar{n}_T plots (Figs. 5 and 6).

Figs. 11 and 12 show the variation of \bar{N}_s with \bar{n}_T for Na^+ - and K^+ - forms of Dowex 50W x 4, respectively, for all compositions of methanol-water mixtures. At low \bar{n}_T values \bar{N}_s remains constant and then increases at higher \bar{n}_T values, similar to

that observed in the case of Li^+ -resin. The constant value corresponds to the composition of the primary solvation shell around these ions. These limiting values are given in Table 2.

Acetonitrile-Water System

In these systems the Ag^+ , having strong interactions with AN and the Na^+ , which does not have any specific interactions, have been studied, covering the whole range of composition of AN-water mixture and using Ag^+ - and Na^+ - forms of Dowex 50W x 8 and Dowex 50W x 12 resins. The solvent imbibed by the resin at different composition of AN-water mixture were estimated. Fig. 13 shows the variation of N_s with n_T for Ag^+ - and Na^+ - forms of the resin, respectively.

At very low concentration of AN, about 7 moles of total solvent are taken up per equivalent of Ag^+ -resin [Fig. 13(A)] and much less at higher AN concentrations. Data available in literature on Ag^+ in aqueous and AN-water mixtures indicate that the maximum solvation number of Ag^+ is 4 or 6 in these solvents.³ Thus, in Ag^+ -AN-water systems only the primary solvation shell of Ag^+ is likely to exist.

It is known that Ag^+ has specific interactions with sulphonic acid groups in the resin.²² That is why Ag^+ - form of the resin swells much less in aqueous medium as compared to other univalent metal ionic forms of the resins of the same cross-linking. This implies that the resin phase in Ag^+ - form cannot be strictly considered as single ion solution (as was the case for other monovalent cationic forms). When the AN concentration in the solvent mixture increases, because of the lowering of dielectric constant in the resin due to the presence of AN, the situation becomes worse. Such effects are expected to be least in solvent mixtures of low AN content. It is obvious from the data that Ag^+ - resin absorbs AN preferentially from AN-water mixture with composition 14.6% and 32.7% (w/w) (with AN mole fractions, 0.0698 and 0.1756, respectively). At high AN

concentration, resin absorbs water preferentially which increases with increase in AN concentration in the solvent mixture.

Resin prefers water in order to overcome specific interaction between Ag^+ and sulphonic acid groups and ensure complete dissociation of Ag^+ in the resin phase. This situation is similar to the solubility of Ag_2SO_4 in AN-water mixtures. In mixtures of low AN content, solubility of Ag_2SO_4 increases compared to aqueous system. Because of the specific interactions between Ag^+ and AN, Ag^+ is solvated to a greater extent in solvent mixtures having low AN content and more of Ag_2SO_4 dissolves. Water is needed to overcome the strong interaction between Ag^+ and SO_4^{2-} . At high AN concentrations in the solvent mixtures, Ag^+ - SO_4^{2-} interactions cannot be overcome and the solubility decreases, though whatever Ag^+ are present in those solution (of high AN content) are preferentially solvated by AN. In Fig. 14, the solubility of Ag_2SO_4 in AN-water mixture⁶ are plotted along with the data for the separation factor, α , for the Ag^+ - form of the resin as a function of mole fraction of AN in the AN-water mixture. The similarity in the variation of α and solubility with mole fraction of AN is a strong evidence that both processes (that is, solvent fractionation by Ag^+ - form of the resin and solubility of Ag_2SO_4) in AN-water mixtures are governed by similar interactions, namely, strong affinity of Ag^+ for AN and strong electrostatic interaction between Ag^+ and SO_4^{2-} (in solution) or SO_3^- group (in the resin phase).

As discussed in the case of methanol-water mixtures, the limiting values of solvent composition in the resin phase (where $\bar{n}_r < \text{primary solvation number}$) can be taken as the solvent composition in the primary solvation shell of the ions in the resin. Moreover, Ag^+ can be considered as single ion solution only for AN-water mixtures of low AN content; at high AN concentrations, these limiting values would be the composition of the primary solvation of Ag^+ in resin only. These limiting values for various AN-water mixtures are given in Table 2.

As Na^+ does not have any specific interaction with either AN or sulphonic acid groups, Na^+ -form of the resin should behave as a single ion solution in AN-water mixtures as in methanol-water system. From the \bar{N}_s vs \bar{n}_T plots [Fig. 13 (B)], it is seen that between 2 to 9 moles of total solvent (\bar{n}_T) are taken up by the resin in the various AN-water composition. At low AN-concentration, \bar{N}_s is slightly larger for Dowex 50W x 8 [Fig. 13 (B)], where some contributions from secondary solvation shell could come ($\bar{n}_T >$ primary hydration number of Na^+). The limiting values of \bar{N}_s for different compositions of AN-water mixtures given in Table 2 are the average of Na^+ -form of Dowex 50W x 8 and Dowex 50W x 12 resins.

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Table 1

Solvent fractionation by Li⁺ form of Dowex 50 W resins in 70.2 % methanol-water mixture.

LiCl m	Resin cross linking	Solvent uptake g/eq	Conc. in resin \bar{m}	n_s	\bar{N}_s	\bar{n}_T	α
0 m	x2	489.3	2.04	7.88	0.441	17.86	7.54
	x8	179.5	5.57	2.63	0.389	6.76	9.65
	x12	136.8	7.30	1.72	0.313	5.50	13.50
2 m	x2	143.5	6.97	2.53	0.421	6.01	9.29
	x8	102.4	9.76	1.53	0.341	4.49	13.07
	x12	81.3	12.29	1.09	0.297	3.67	15.98
4 m	x2	77.1	12.97	1.23	0.371	3.32	12.69
	x8	66.9	14.95	0.96	0.324	2.97	15.60
	x12	64.0	15.60	0.87	0.304	2.87	17.37
6 m	x2	49.2	20.30	0.78	0.368	2.13	15.96
	x8	47.7	20.94	0.70	0.334	2.10	18.79
	x12	46.8	21.36	0.70	0.337	2.06	18.32

Table 2

Limiting values of N_s for different ions in methanol-water and acetonitrile-water mixtures

methanol-water system					
methanol % (w/w)	mole fraction of methanol in solu	limiting values of \bar{N}_s			
		N_s	Li^+	Na^+	K^+
11.0	0.069		0.06	-	-
20.8	0.129		0.09	0.08	0.07
44.3	0.309		0.20	0.14	0.13
70.2	0.570		0.33	0.22	0.22

acetonitrile-water system				
acetonitrile % (w/w)	mole fraction of AN in solu.	limiting values of \bar{N}_s		
		N_s	Na^+	Ag^+
14.6	0.0698		0.0331	0.1219
32.7	0.1756		0.0450	0.1753
43.3	0.2508		0.0681	0.1840
54.3	0.3425		0.0787	0.1990
71.7	0.5263		0.1017	0.2479
94.3	0.8787		0.1444	0.3997

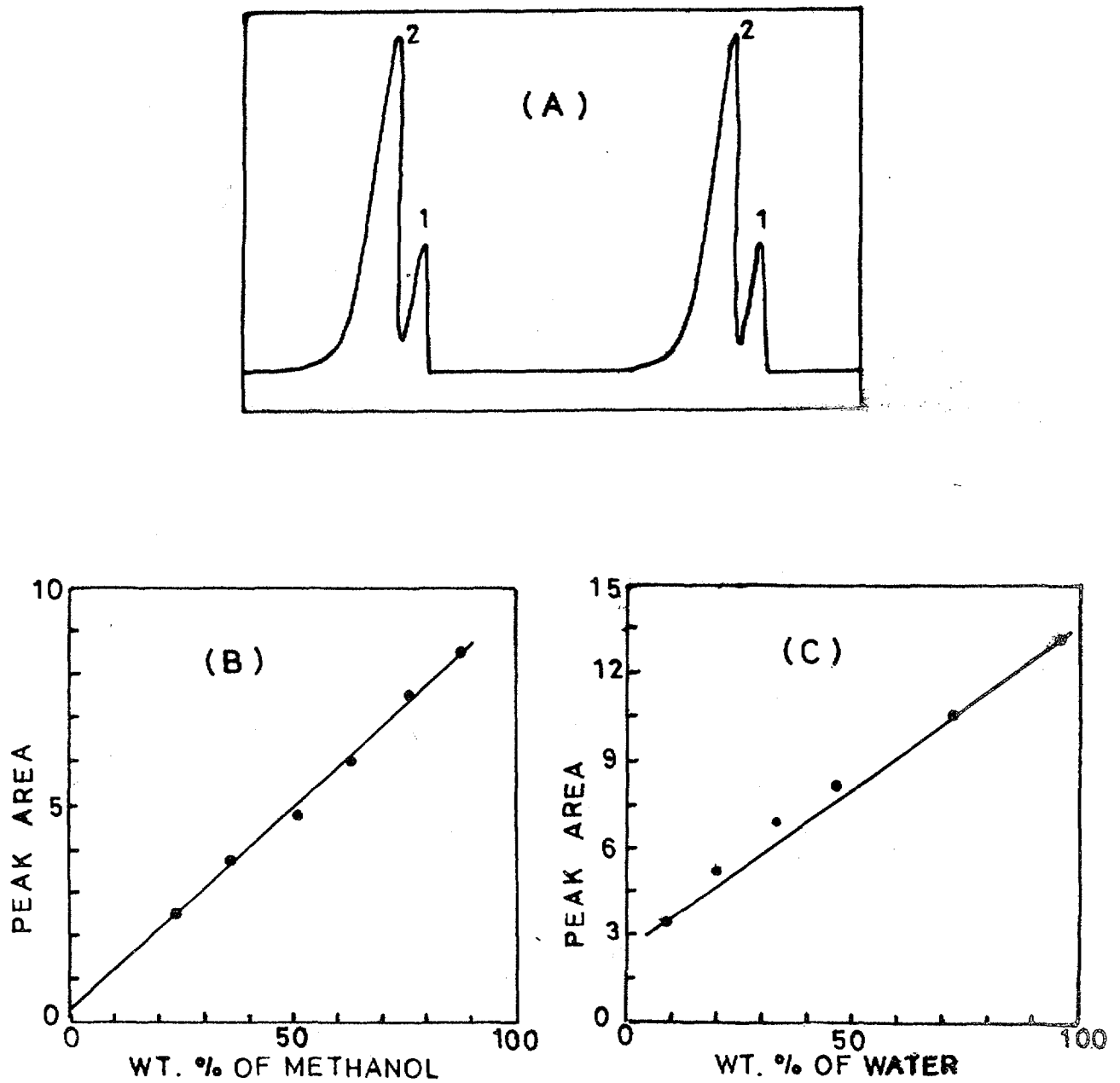


Fig. 1. Typical chromatogram and calibration curve for methanol-water mixtures. (A) Chromatogram of 44 % (w/w) methanol-water mixture; 1. water; 2. methanol; (B) variation of peak area with wt.% of methanol; (C) variation of peak area with wt.% of water

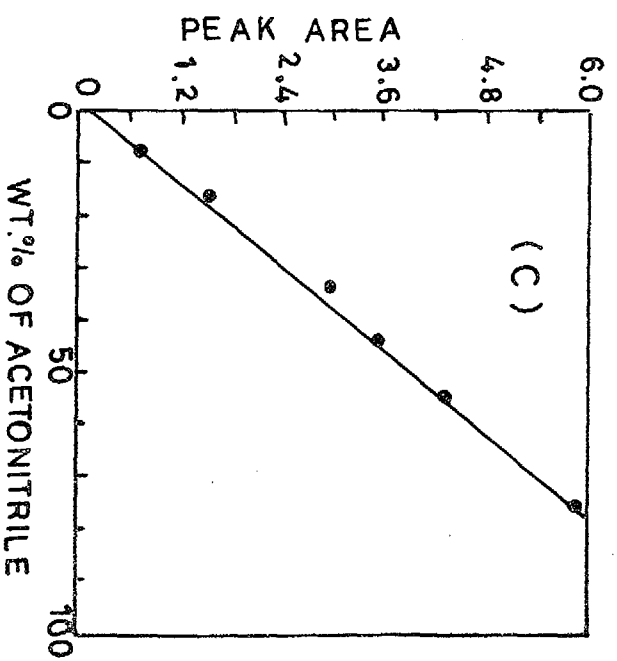
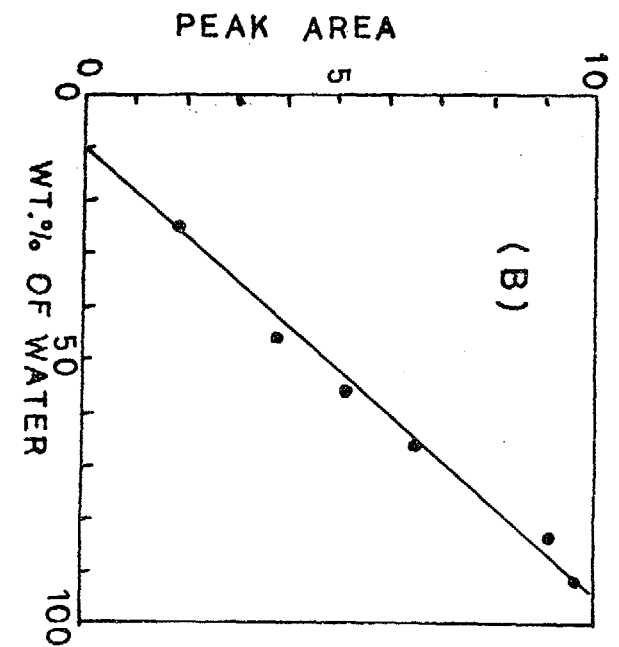
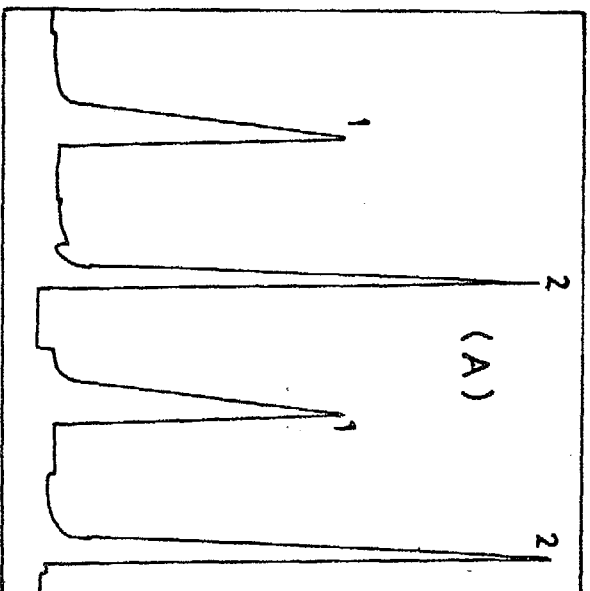


Fig. 2. Typical chromatogram and calibration curve for acetonitrile-water mixtures.

(A) Chromatogram of AN-water mixture. 1. acetonitrile 2. water; (b) variation of peak area with wt. % of water; (C) variation of peak area with wt. % of AN.

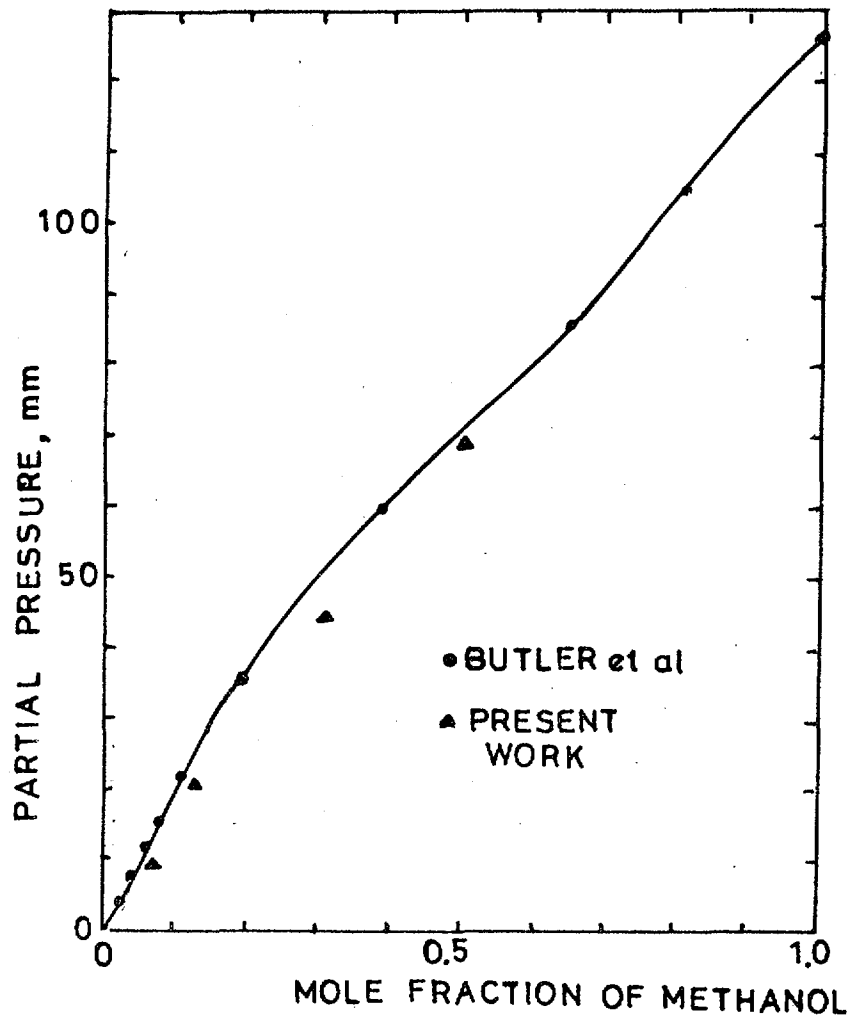


Fig.3. Partial vapour pressure of methanol as a function of composition of methanol-water mixtures.

(●) data of Butler et al (Ref.21); (▲) present work

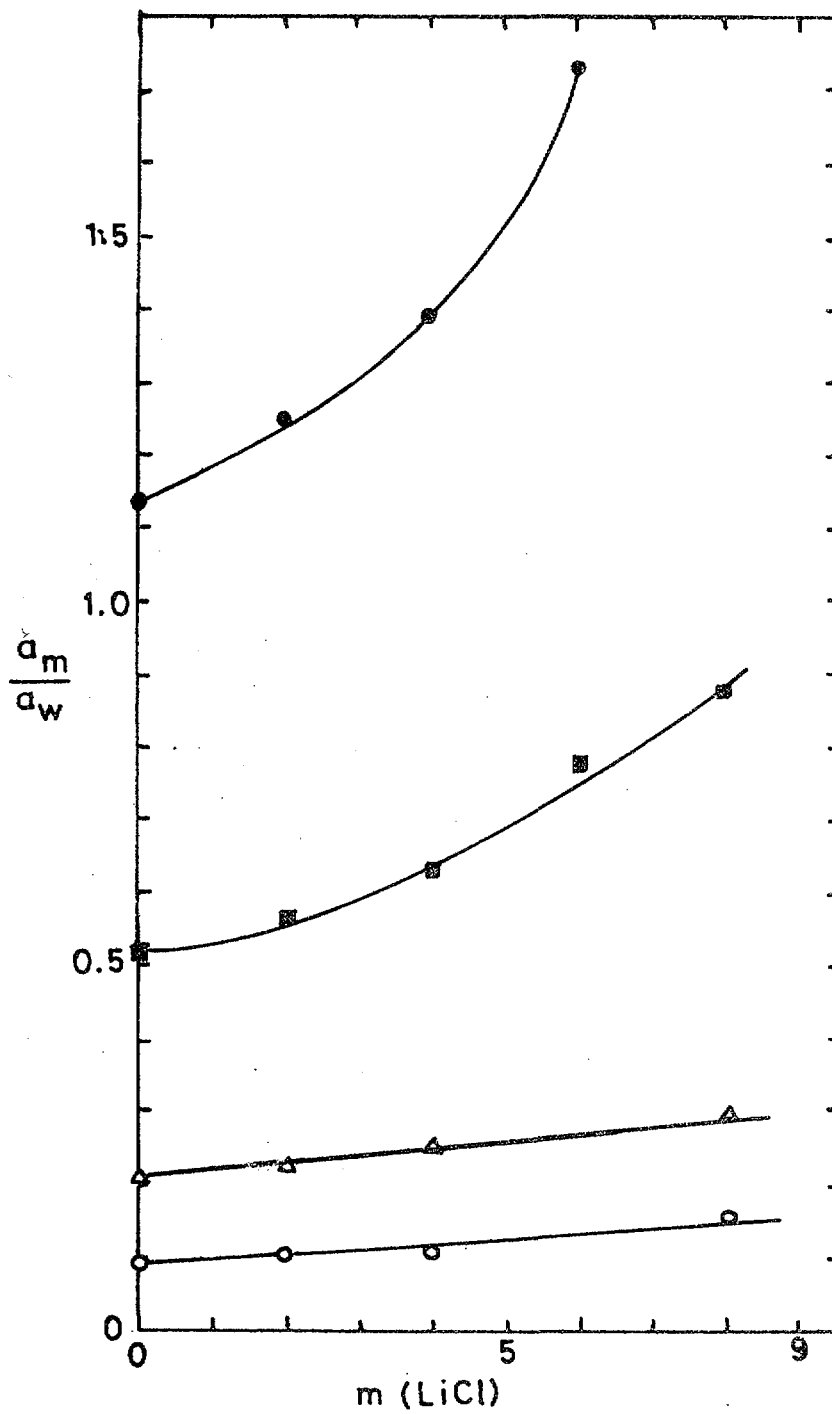


Fig.4. Variation of a_m/a_w (activity ratio) with molality of LiCl solution
(\circ) 11.0% (w/w); (\triangle) 20.8% (w/w); (\blacksquare) 44.3% (w/w); (\diamond) 70.2% (w/w).

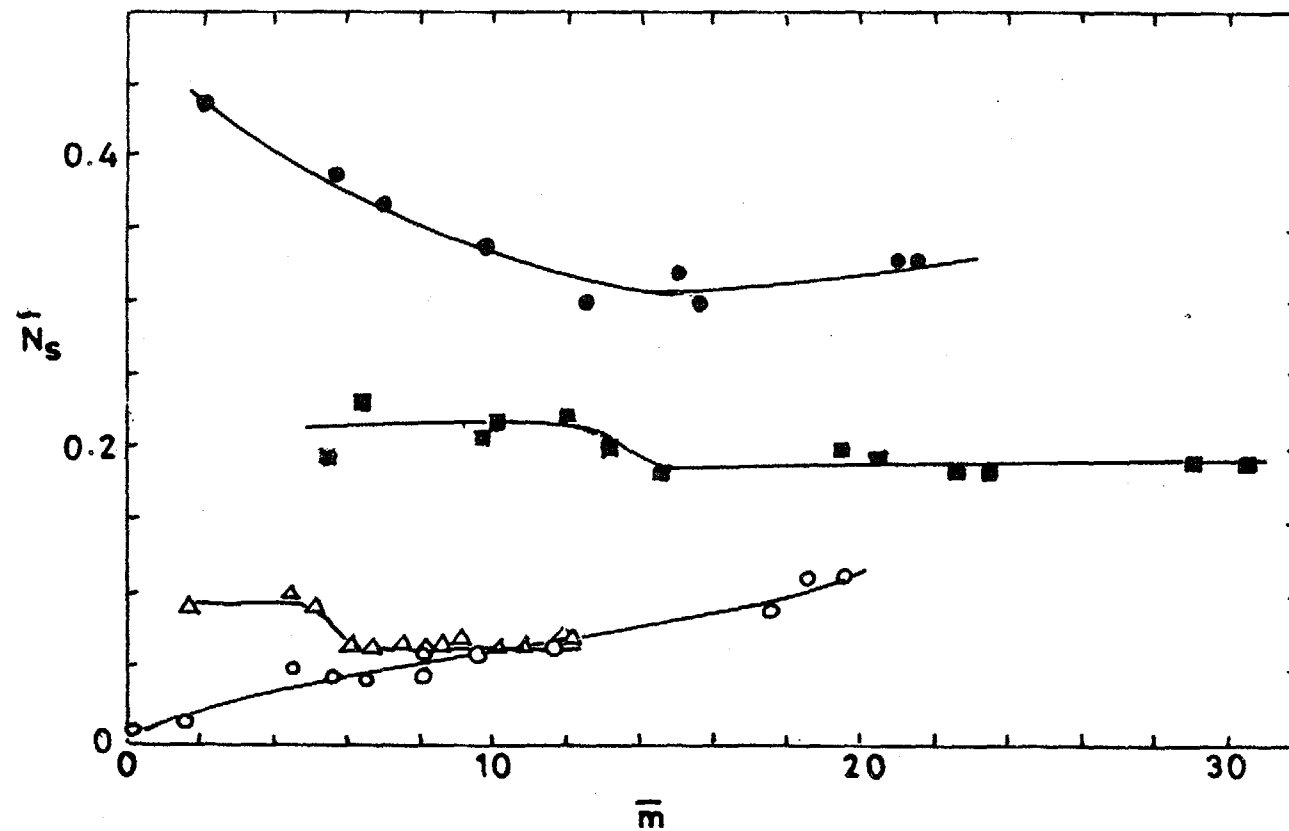


Fig.5. Variation of \bar{N}_s with \bar{m} (molality in resin phase) for the Li^+ form of the resin in methanol-water mixtures.

(o) 11.0% (w/w); (Δ) 20.8% (w/w); (\blacksquare) 44.3% (w/w); (\blacklozenge) 70.2% (w/w).

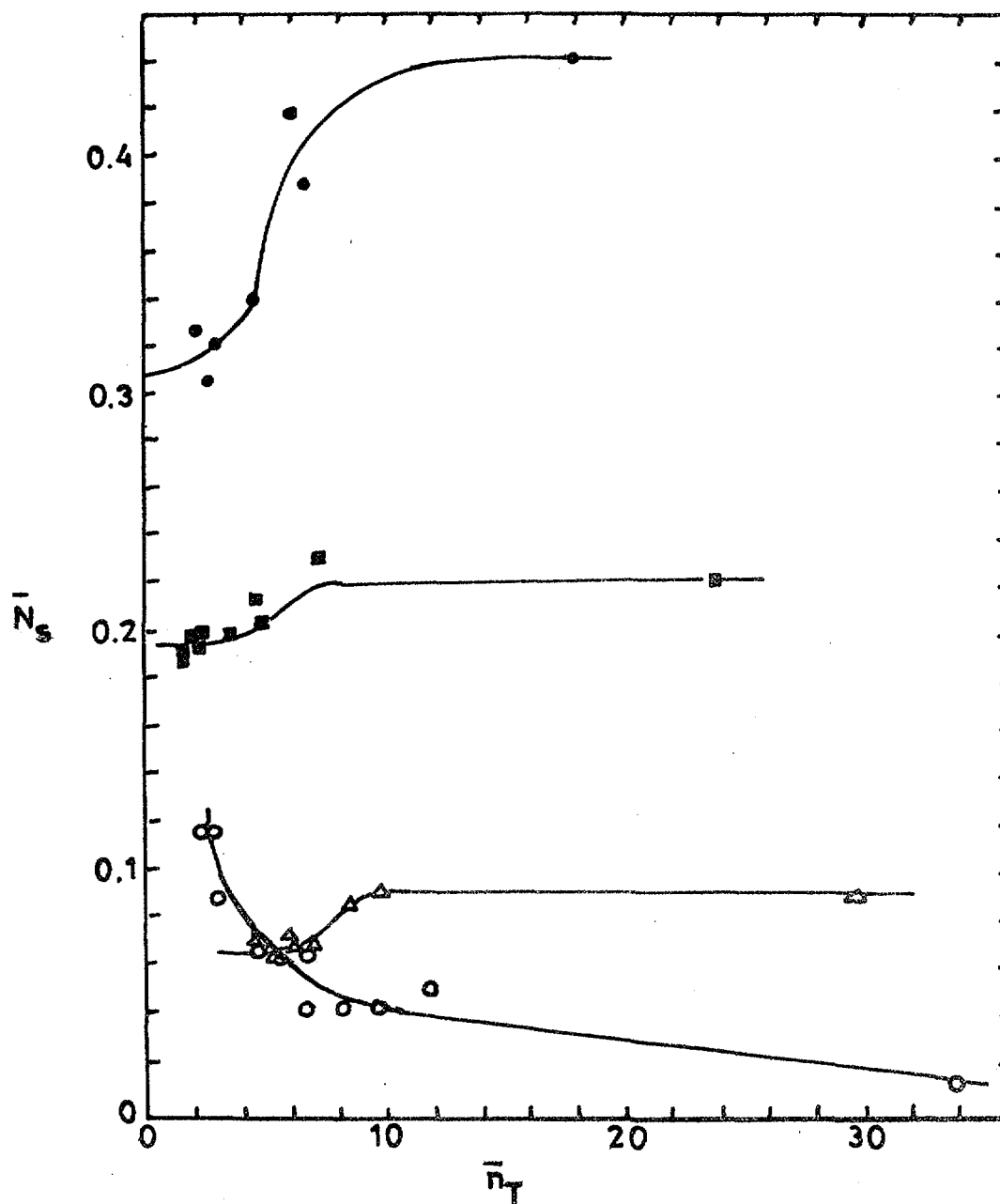


Fig.6. Variation of \bar{N}_s with \bar{n}_T ($= \bar{n}_s + \bar{n}_w$) for the Li^+ form of the resin in methanol-water mixtures.

(o) 11.0% (w/w); (Δ) 20.8% (w/w); (\blacksquare) 44.3% (w/w); (\bullet) 70.2% (w/w).

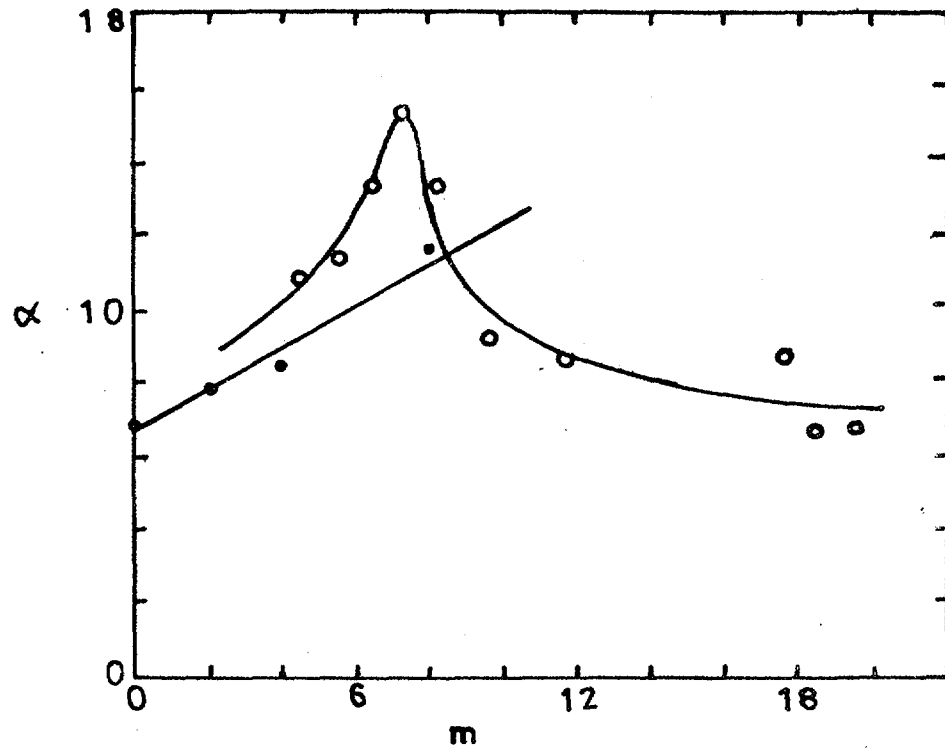


Fig.7. Variation of α with m for 11.0 % (w/w) methanol-water mixtures.
(o) LiCl solution; (•) Li⁺-form of the resin

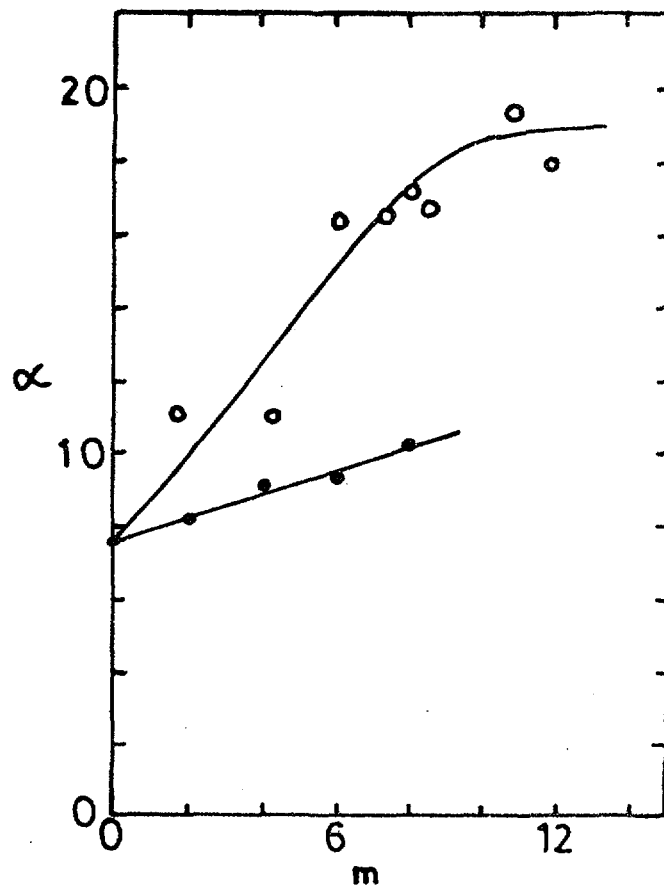


Fig.8. Variation of α with m for 20.8 % (w/w) methanol-water mixtures.
(o) LiCl solution; (•) Li⁺-form of the resin

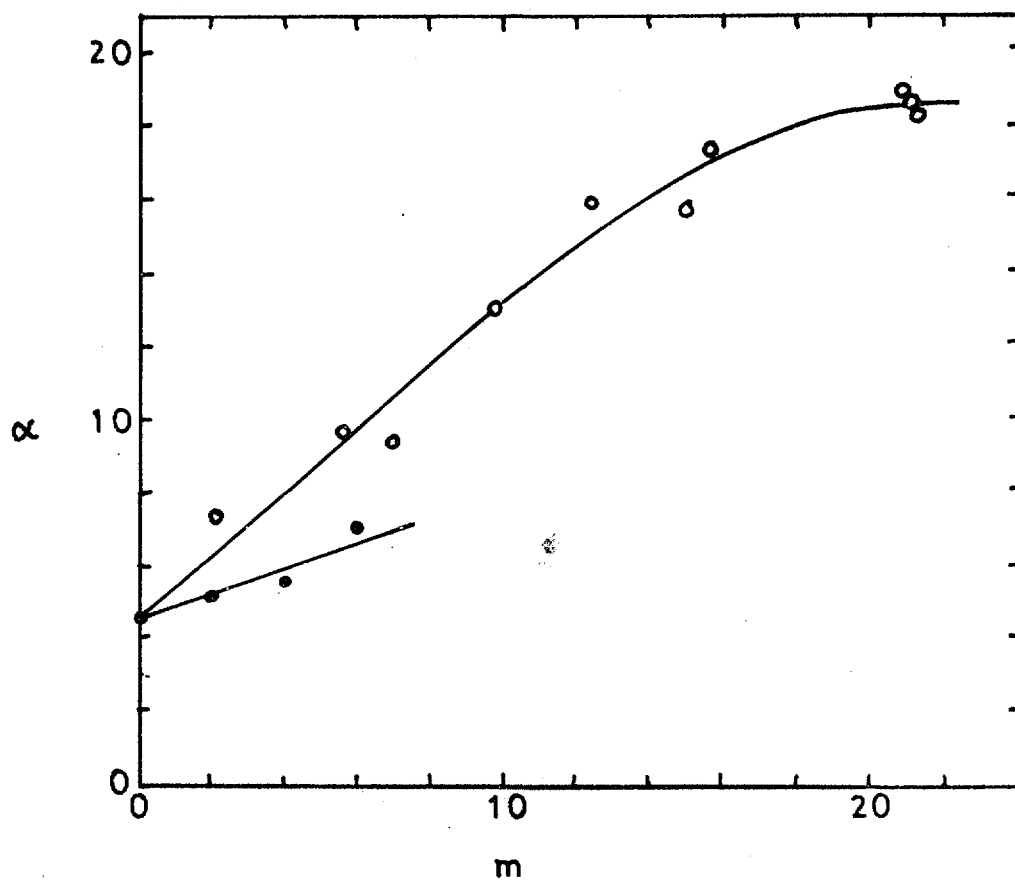


Fig.9. Variation of α with m for 44.3 % (w/w) methanol-water mixtures.
(o) LiCl solution; (•) Li⁺-form of the resin

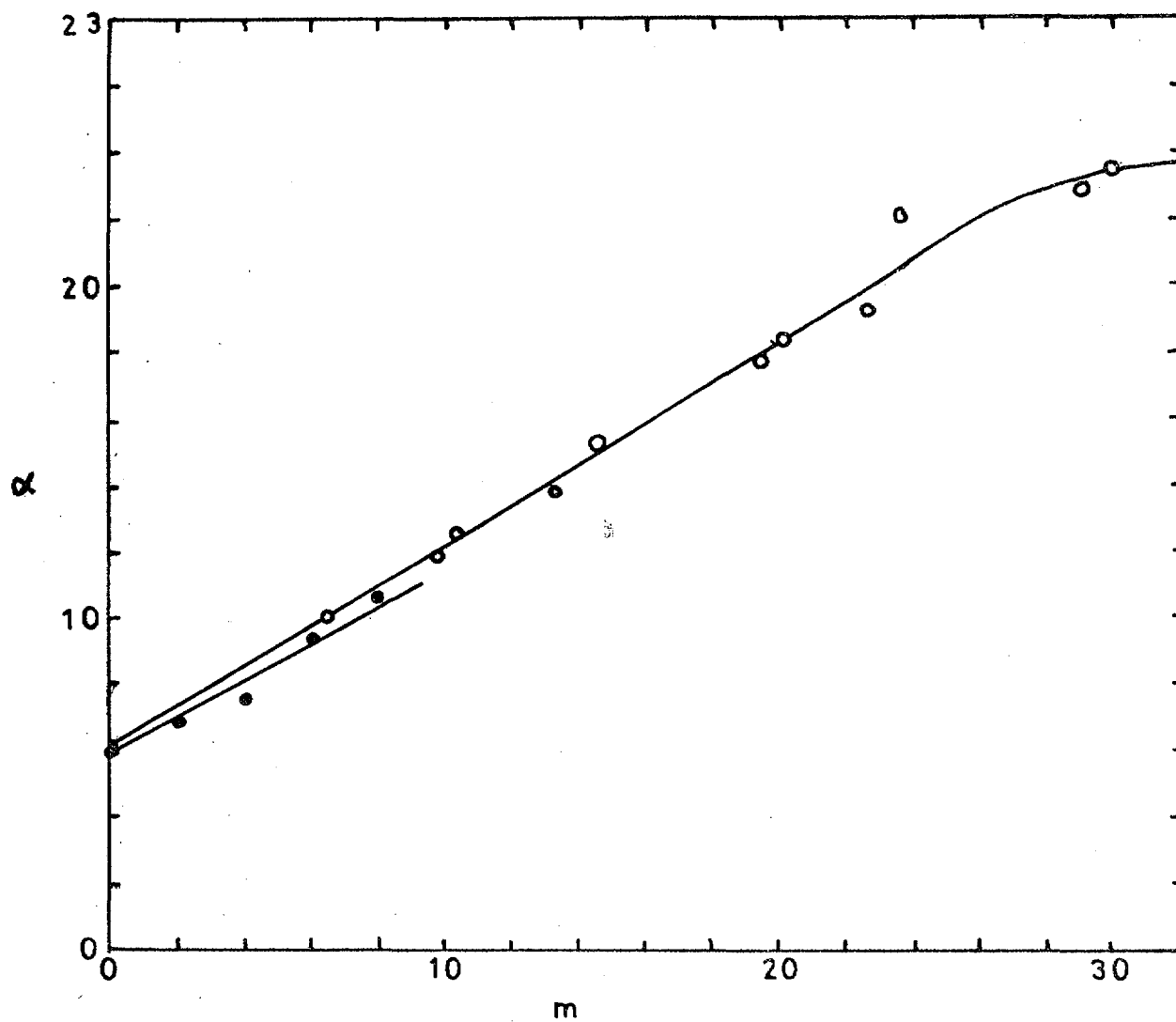


Fig.10. Variation of α with m for 70.2 % (w/w) methanol-water mixtures.
(o) LiCl solution; (•) Li⁺-form of the resin

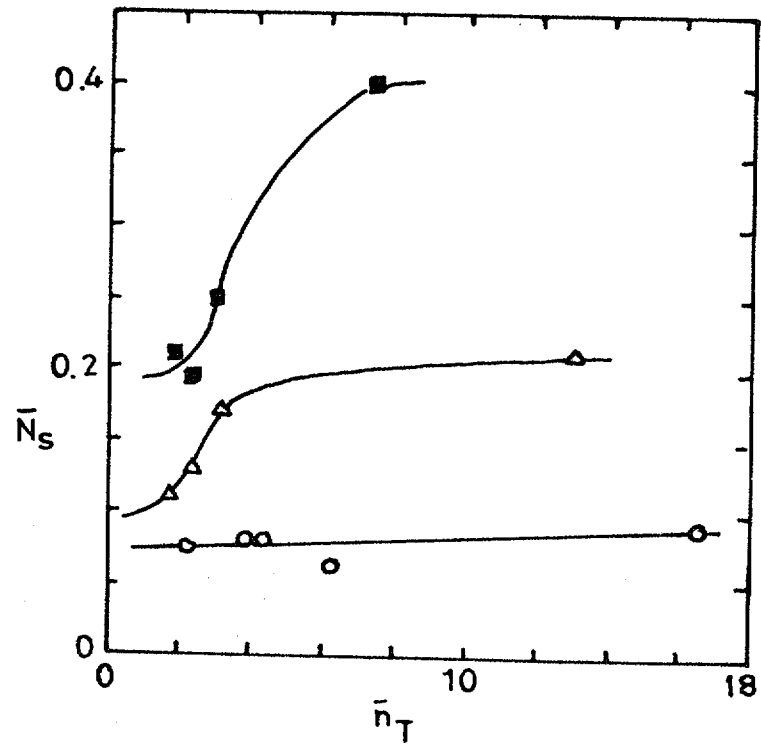


Fig.11. Variation of \bar{N}_s with \bar{n}_T for the Na^+ form of the resin in methanol-water mixtures.

(o) 20.8 % (w/w); (Δ) 44.3 % (w/w); (\blacksquare) 70.2 % (w/w).

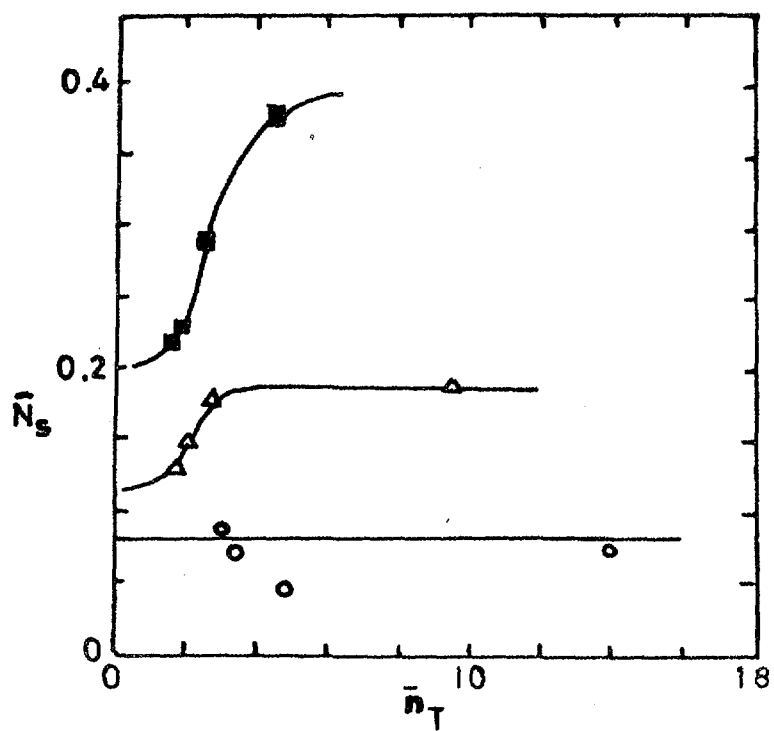


Fig.12. Variation of \bar{N}_s with \bar{n}_T for the K^+ form of the resin in methanol-water mixtures.

(o) 20.8 % (w/w); (Δ) 44.3 % (w/w); (\blacksquare) 70.2 % (w/w).

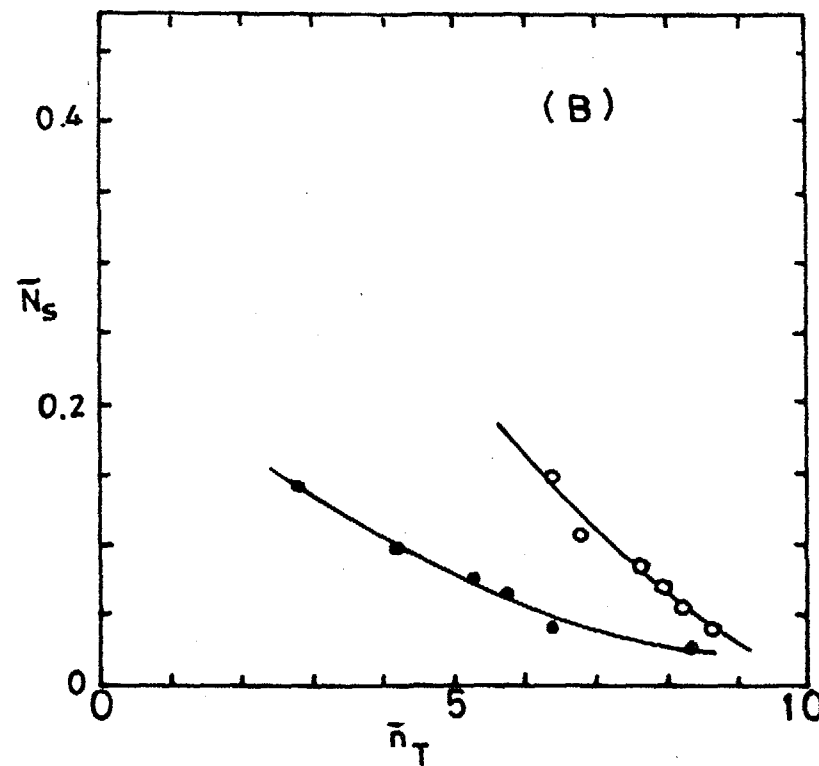
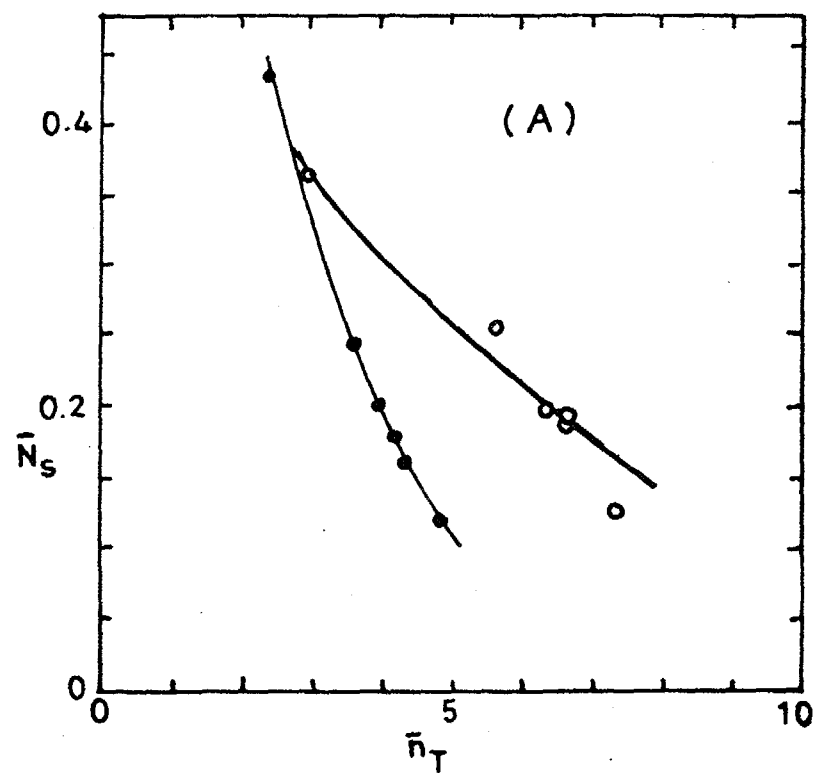


Fig.13. Variation of \bar{N}_s with \bar{n}_T for the Ag^+ and Na^+ -forms of Dowex 50W x 8 and Dowex 50 W x 12 in acetonitrile-water mixtures
 (A) Ag^+ -form of the resin ; (B) Na^+ -form of the resin ;
 (o) Dowex 50W x 8 ; (•) Dowex 50W x 12

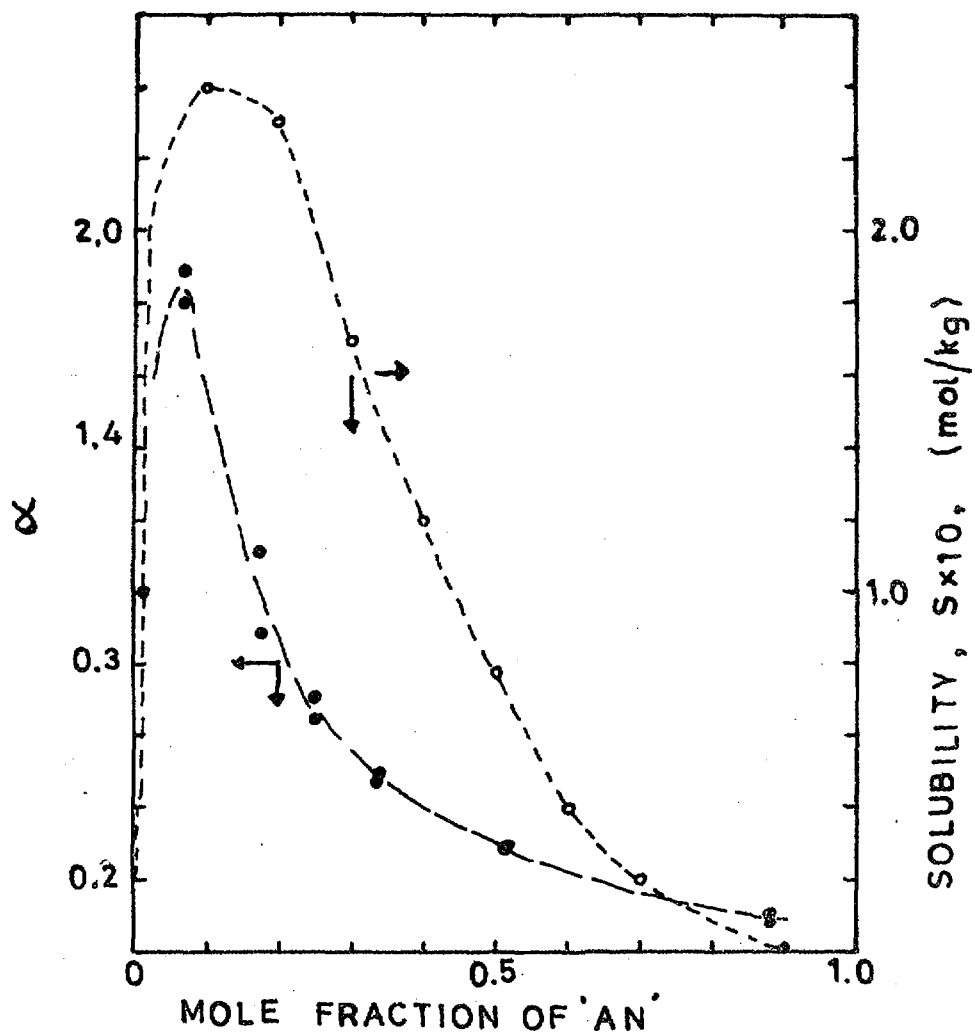
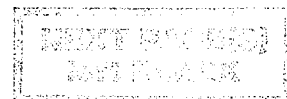


Fig.14. Separation factor for Ag⁺ resin and solubility of Ag₂SO₄ as a function of mole fraction of acetonitrile in acetonitrile-water mixtures
 (o) solubility of Ag₂SO₄ (Ref.6); (•) separation factor, α

PART 2
THEORETICAL COMPUTATION AND COMPARISON WITH
EXPERIMENTAL DATA



ABSTRACT

The compositions of the primary solvation shell around Li^+ , Na^+ and K^+ in methanol-water mixtures and Na^+ and Ag^+ in acetonitrile (AN) - water mixtures have been computed using Frank's equation and the approach of Marcus and compared with the experimental results obtained with the above mentioned ionic forms of Dowex 50W resins in different mixed solvents and reported in Part 1. The experimental results for Li^+ showed good agreement with the values computed using Frank's equation for all methanol-water composition. However, in the case of Na^+ and K^+ in methanol-water mixtures and Na^+ in AN-water mixtures, there was agreement only at lower organic solvent content and the Frank's equation predicted higher values for the organic solvent in the primary solvation shell around the cation at higher organic solvent content as compared to experimental results. This could be attributed to the ion pairs formation at higher solvent composition in methanol-water mixtures and the exclusion of AN by the resin, due to its lower dielectric constant. Frank's equation predicted preferential solvation of Ag^+ by water in the AN-water mixture, contrary to the experimentally obtained data. The values for the composition in the primary solvation shell obtained by the approach of Marcus agreed with the experimental data of alkali metal ions in methanol-water and AN-water systems only at low content of the organic solvent. Marcus' approach predicted the preferential solvation of Ag^+ by AN as observed experimentally, but gave a higher values for AN in the solvation shell than the experimental data. These comparisons bring out the emphasis of the theoretical approach like electrostatic interactions in Frank's equation and specific interaction (through free energy of transfer) in the approach of Marcus in predicting the composition of primary solvation shell composition and the practical difficulty in getting experimental data for a truly single ion solution.

PART 2

THEORETICAL COMPUTATION AND COMPARISON WITH EXPERIMENTAL DATA

As mentioned in Part 1¹, preferential solvation in mixed solvents has been studied in greater detail theoretically. In this paper (Part 2), the primary solvation shell composition of different cations in methanol-water and acetonitrile (AN)-water mixtures computed from the theoretical approaches of Debye, Frank and Marcus will be compared with the experimental results reported in Part 1¹ and discussed.

Theory of Debye-Frank

Debye² analysed the preferential solvation from an electrostatic consideration in terms of "solvent sorting" in the immediate neighborhood of an ion. The restriction in this approach was that the total volume of solvent was held constant with respect to changes in field strength or composition. The resultant equation is

$$v_2 \ln \frac{N_1}{N_1^0} - v_1 \ln \frac{N_2}{N_2^0} = \frac{Z^2 e^2}{8\pi kT\epsilon^2 r^4} \left(v_2 \frac{\partial \epsilon}{\partial n_1} - v_1 \frac{\partial \epsilon}{\partial n_2} \right) \quad (1)$$

where Z is the valence of the ion, e the electrostatic charge and r the distance from the ion to the site where the composition is considered. n_1 and n_2 are number of molecules per unit volume of the two solvents making up the solution, v_1 and v_2 are molecular volumes satisfying the identity for ideal solution, namely, $n_1 v_1 + n_2 v_2 = 1$. $N_1 = n_1/(n_1 + n_2)$ and $N_2 = n_2/(n_1 + n_2)$ are the mole fractions of solvent 1 and 2 in the immediate vicinity of the ion (primary solvation shell) and N_1^0 and N_2^0 are

the mole fractions of solvent 1 and 2 in the bulk solution, so that $N_1 + N_2 = 1$ and $N_1^0 N_2^0 = 1$, ϵ is the dielectric constant, k is Boltzmann's constant.

Frank³ formulated a more general equation, in which the restriction of keeping the total volume constant, in Debye's approach, was removed and is:

$$\ln \frac{N_1}{N_1^0} - \ln \frac{N_1^0}{N_2^0} = \frac{VZ^2 e^2}{(n_1 + n_2) 8\pi RT \epsilon^2 Y^4} \left(\frac{\partial \epsilon}{\partial N_1} \right)_{P,T,E} \quad (2)$$

where V is the volume of the mixture, $[V/(n_1 + n_2)]$ is the molar volume of the mixture, $\partial \epsilon / \partial N_1$ is the composition dependence of dielectric constant, ϵ , of solvent mixture at a given pressure, temperature and electric field. In this derivation, since ϵ is assumed to be independent of the electric field strength, $(\partial \epsilon / \partial N_1)_{P,T}$ becomes an experimentally accessible quantity. The right hand side of eq. 2, is analogous to the separation factor between the primary solvation shell and bulk solution and thus, can be compared with the corresponding separation factor determined and reported in Part 1. The primary solvation shell composition, N_1 , were computed for the methanol-water and AN- water mixtures using eq.2 in the following way: ϵ vs mole fraction of methanol or AN were plotted and the slopes at various compositions give $(\partial \epsilon / \partial N_1)$; molar volumes were calculated from densities and mole fractions of the organic solvent; values of solvated radii, r , were taken from literature⁴⁻⁶, Tables 1 to 3 give the various quantities for methanol-water and AN-water mixtures used for the calculations. Values of N_1 and separation factor, α , for various methanol-water and AN-water mixtures were computed using Frank's equation (eq.2) with the help of lotus spread sheet on personal computer. The local mole fraction around cations in various composition of methanol-water and AN-water mixtures evaluated using Frank's equation are plotted in Figs. 1 to 5.

Theory of Marcus

Marcus⁷ has developed a quasi-lattice quasi-chemical theory of preferential solvation which yields the actual amount of the preferential solvation of ion via Gibbs free energy of transfer of ions from a reference solvent to a mixture of solvents. This is defined as $dx_i = x_i^L - x_i$, the excess of the local mole fraction of the solvent, S, in the vicinity of ion X over its mole fraction in bulk in very dilute solution of X in the mixture of solvents S₁ and S₂.

The theory results in an expression for the preferential solvation parameter,

$$g(x) = \Delta G_t^{oE} / x(1-x) RT \quad (3)$$

where x is the mole fraction of one of the solvents and R is the gas constant. The excess standard Gibbs free energy of transfer, ΔG_t^{oE} , is the difference between the standard molar Gibbs free energy of transfer of the ion X from the reference solvent W(water) to mixture or solvents S₁ and S₂, $\Delta G^{oE} [X, W \rightarrow (S_1 + S_2)]_E$ and the sum of the corresponding quantities for transfer into pure solvents S₁ and S₂,

$$g(x) = -[G_{12}^E(x) / x(1-x)RT] - f(x, y, \Delta) \quad (4)$$

The expression shows that the preferential solvation depends on excess free energy of mixing of the two solvents $G_{12}^E(x)$ and the function $f(x, y, \Delta)$, where

$$\Delta = [\Delta G_t^o(X, W \rightarrow S_2) - \Delta G_t^o(X, W \rightarrow S)] / zRT \quad (5)$$

where z is the lattice parameter, and y is (with $x = x_2$) defined as,

$$y = (1-x)x^{-1} (N_{22}/N_{11})^{1/2} \quad (6)$$

and N_{ij} are the numbers of (i, j) neighbours.

The preferential solvation of X by one of the two solvents in a mixture, say, S₁, can be defined as the difference between the local mole fraction x_i^L and the bulk mole fraction x_i ,

$$dx_1 = x_1^L - x_1 = \{(1-x_1) [1 - ye^{\Delta/2}] \} / [1 + (1-x_1) yx_1^{-1} \exp(\Delta/2)] \quad (7)$$

the evaluation of Δ and y from certain data pertaining to the system is necessary in order to calculate dx_1 . The quantity Δ requires the standard molar Gibbs free energies of transfer to the ion X from the reference solvent W into pure solvent S_1 and S_2 . These are experimentally accessible quantities, based on the TATB assumption and the lattice parameter, z , is a fitting parameter (that is, primary solvation number). y is independent of the nature of X, but depends on the composition of the solvent mixture. This parameter is defined in eq.6 and is computed as follows:

Let N_1 be the number of particles in the system and $S=(Z/2)(N_1 + N_2)$ be the total number of nearest neighbour pairs. Then, $ZN_1 = 2N_{11} + N_{12}$ or $N_{11} = (ZN_1 - N_{12})/2$ and similarly for N_{22} and $ZN_2 = 2x_1S$ and similarly for ZN_2 .

$$(N_{22}/N_{11})^{1/2} = [(1-x_1 - N_{12}/2S)/(x_1 - N_{22}/2S)]^{1/2} \quad (8)$$

and y can, thus be obtained from eq.6 and $N_{12}/2S$, where

$$N_{12}/2S = (1 - \{1 - 4x_1(1-x_1) [1 - \exp(-\Delta e_{12}/kT)]\}^{1/2}) / 2 [1 - \exp(-\Delta e_{12}/kT)] \quad (9)$$

and

$$\exp(-\Delta e_{12}/kT) = \{2 \exp[-2G_{12}^E(x=0.5)/zRT] - 1\}^{-2} \quad (10)$$

that is, the exponent is the excess molar Gibbs free energy of mixing of the two solvents at the equimolar composition.

Thus, using the values of Δ and y , the dx_1 was calculated for Li^+ , Na^+ and K^+ in methanol-water mixtures and Ag^+ and Na^+ in acetonitrile-water mixtures using a computer program, [eqs.5,6,7,8 and 9], which then gives value of x_1^L [eq.7], the local organic component mole fraction around the ion. The Marcus equation was solved for various methanol or acetonitrile-water compositions using

different values of z (that is, assumed solvation number in the primary solvation shell).

Parameters used in Marcus' equation: Free energies of transfer for Li^+ , Na^+ and K^+ for methanol-water mixtures were taken from the data reported by Popovych⁸, where the transfer activity coefficients of ions Ph_4As^+ , Ph_4P^+ , BPh_4^- , Li^+ , Na^+ , K^+ , Cs^+ and H^+ have been determined using the average value of $m \gamma_{\text{BP}}$ derived from the assumption $m \gamma_{\text{Ph}} = m \gamma_{\text{PhAs}}$. The values of $\log m \gamma_{\text{H}}$ of KCl , NaCl and LiCl are calculated from E° values of AgCl electrodes. Using the free energy of transfer of Cl^- , the free energies of transfer of various cations for methanol-water mixtures were calculated with TATB assumption. The values, thus, obtained are: 3.76 KJ mole^{-1} for Li^+ , 8.96 KJ mole^{-1} for Na^+ , and 10.22 KJ mole^{-1} for K^+ . The excess Gibbs free energy of mixing has been reported for methanol-water mixtures by Westmeier⁹ and the value for the equimolar mixture, $G_{\text{ws}}^E (x=0.5)$, is 0.299 KJ mole^{-1} .

The standard molar Gibbs energy of transfer from water into acetonitrile for Ag^+ and Na^+ are -23.2 KJ mole^{-1} and 15.1 KJ mole^{-1} , respectively, as evaluated from recent review by Marcus¹⁰ using TATB assumption. According to Treiner et al¹¹, the excess Gibbs free energy of mixing for equimolar mixture of AN-water, $G_{\text{ws}}^E (x = 0.5)$, is 1.32 KJ mole^{-1} .

The local mole fraction around cations in various composition of methanol-water and AN-water mixtures evaluated from the above parameters and Marcus equation are plotted in Figs.1 to 5.

Comparison of experimental data with theoretical results

For a direct comparison, experimentally obtained values of x_1^L for methanol-water and AN-water systems [available Part 1 of the paper] are also plotted in Figs.1 to 5. As the values of x_1^L obtained from Marcus equation, with $z=6$ are in closer agreement with values obtained in resin phase data, the Marcus equation is discussed only for $z=6$.

Methanol-water system: It can be seen from Fig.1 that Frank's equation and the experimental values are in close agreement for Li^+ for all methanol composition. On the other hand, Marcus approach gives reasonable values only for low methanol content and at higher methanol content the values are very much higher for all the cations (Figs.1 to 3).

In the case of K^+ and Na^+ , for higher methanol compositions, Frank's equation predicts increasingly higher values of x_i^L compared to what are obtained from resin phase data as seen in Figs. 2 and 3. However, the experimentally obtained values from resin phase data may also suffer from the incomplete dissociation of K^+ and Na^+ in resin phase at higher methanol content. This is supported by the existence of ion-pairs in the solution of KCl and NaCl mixtures of higher methanol contents¹². Marcus equation gives consistently much higher values than those of experimental ones, for all the three cations as methanol concentration increases. As mentioned in Part 1, the fractionation of solvent in solution phase for Ag^+ -AN system is much more favourable towards water due to the specific interaction of Ag^+ and ionogenic group. From this one can conclude that Frank's equation, which is based entirely on electrostatic consideration predicts the preferential solvation phenomenon in those systems where no other effect, like specific interaction or ion-pair formation, is present. Marcus equation, on the other hand, introduces specific interactions, via free energies of transfer, consistently over estimates the solvent fractionation. Further, this emphasizes that the resin phase studies of single ion can give realistic values for x_i^L , where ions do not have any specific interactions with the ionogenic group as in alkali metal ions in low methanol content.

Acetonitrile-water Systems:

Na^+ -AN-water system: Frank's equation gives much higher values for x_i^L for all the AN composition compared to resin phase data. In this system only electrostatic interactions between ions and solvents and ion and ionogenic group are present and

the discrepancy may be due to lower dielectric constant (35) of AN, which makes the resin phase exclude the solvent much more than that required by the solvation phenomenon of ions (that is, just to keep the ions dissociated in the resin phase AN is excluded). At low AN content, the agreement between the resin phase and Frank's data is good. Marcus equation on the other hand, predicts much higher value than Frank's as discussed in methanol-water system. These are illustrated in the plots of x_i^L vs x_i for Na^+ AN- water system (Fig.4).

Ag⁺ - AN-water system: Fig.5 clearly shows that at low concentration, Ag^+ is preferentially solvated by AN, whereas Frank's data predicts preferential solvation of Ag^+ by water. As the emphasis in Frank's equation is based on electrostatic ground, ion is always solvated by solvents of higher dielectric constant and solvent with lower dielectric constant will always be excluded. On the other hand, Marcus equation shows that the values with $z=6$ predicts preferential solvation of Ag^+ by AN to a large extent than observed in the resin phase. Thus, Marcus equation is able to predict preferential solvation by Ag^+ by AN because of its emphasis on specific interactions via free energy of transfer. At higher AN concentration, resin phase data suffers from the requirement of dissociation of Ag^+ in resin phase (as discussed in Part I) and preferentially takes water to a much greater extent.

Acknowledgments

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Table 1 Density, molar volume and dielectric constant of various methanol-water mixtures (Ref.4)

mole fraction of methanol	density	molar volume	dielectric constant ϵ
0.1	0.972	19.90	70.0
0.2	0.951	21.85	65.0
0.3	0.929	23.89	59.5
0.4	0.907	26.01	54.0
0.5	0.886	28.23	49.5
0.6	0.867	30.45	46.0
0.7	0.847	32.83	42.0
0.8	0.820	35.60	39.0
0.9	0.809	37.10	36.0

Table 2 Density, molar volume and dielectric constant of various acetonitrile-water mixtures (Ref.5)

mole fraction of AN	density	molar volume	dielectric constant ϵ
0.1	0.954	20.78	69.5
0.2	0.918	23.69	61.5
0.3	0.880	26.99	55.0
0.4	0.854	30.29	50.0
0.5	0.836	33.59	46.0
0.6	0.820	36.79	43.0
0.7	0.808	40.67	41.0
0.8	0.796	49.57	39.0
0.9	0.784	48.63	37.5

Table 3 Solvated radii of different cations (Ref.6)

ion	radius \AA
Li^+	2.00
Na^+	2.28
K^+	2.17
Ag^+	1.97

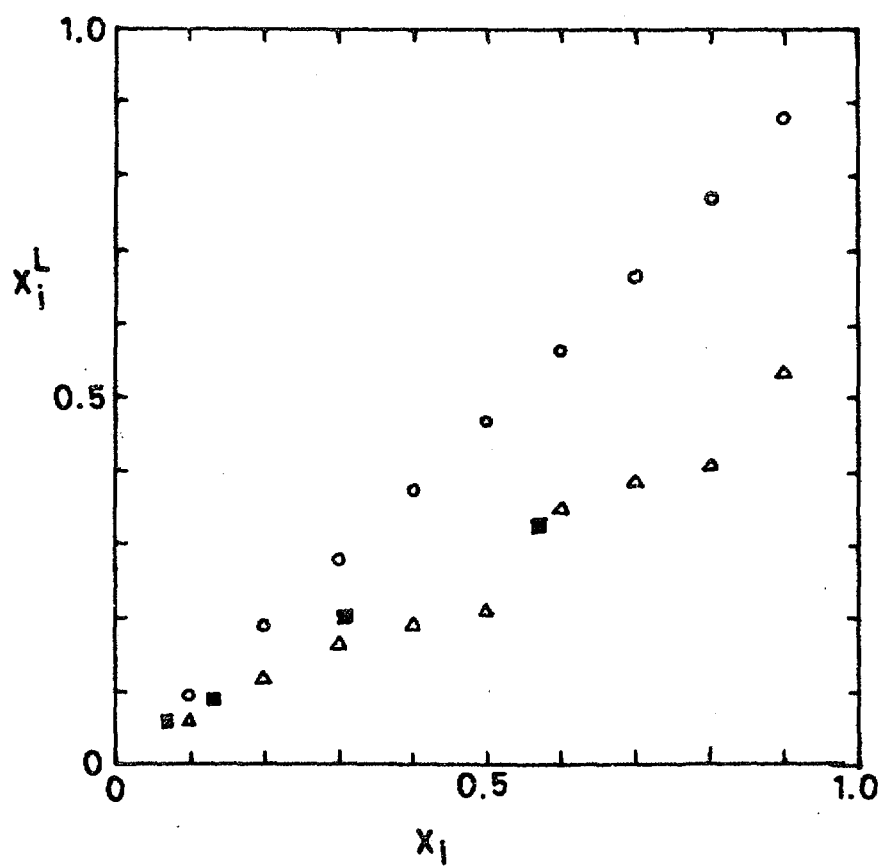


Fig. 1. Variation of x_i^L with x_i for Li^+ -form of the resin in methanol-water mixture.
(O) Marcus' equation; (Δ) Frank's equation; (■) experimental data.

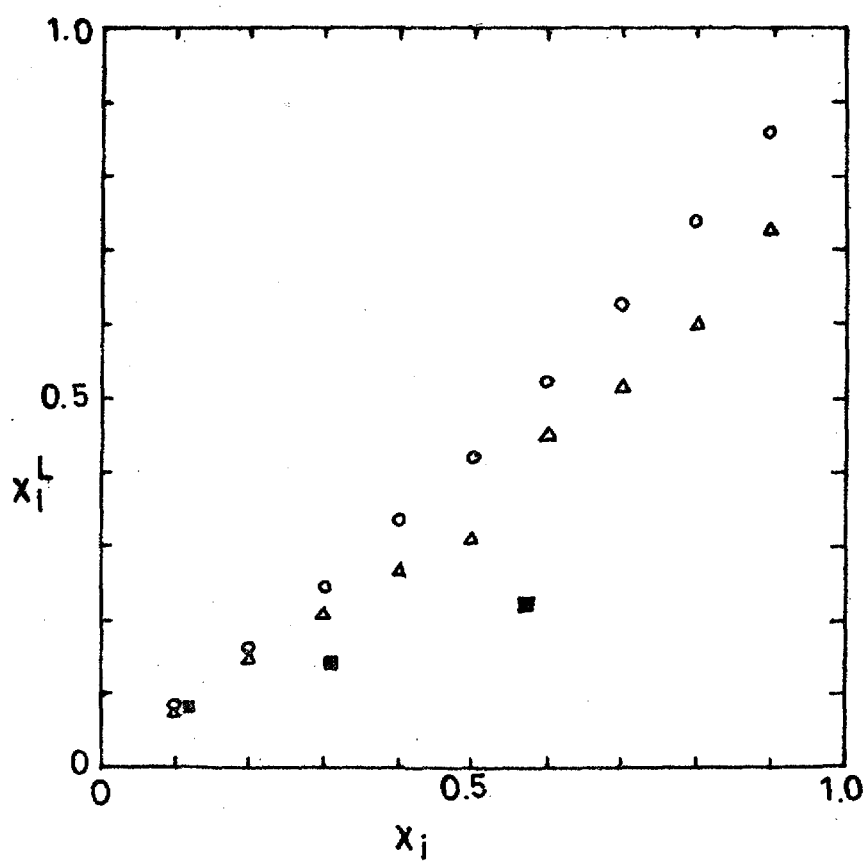


Fig.2. Variation of x_i^L with x_i for Na^+ -form of the resin in methanol-water mixture. (O) Marcus' equation; (Δ) Frank's equation; (\blacksquare) experimental data.

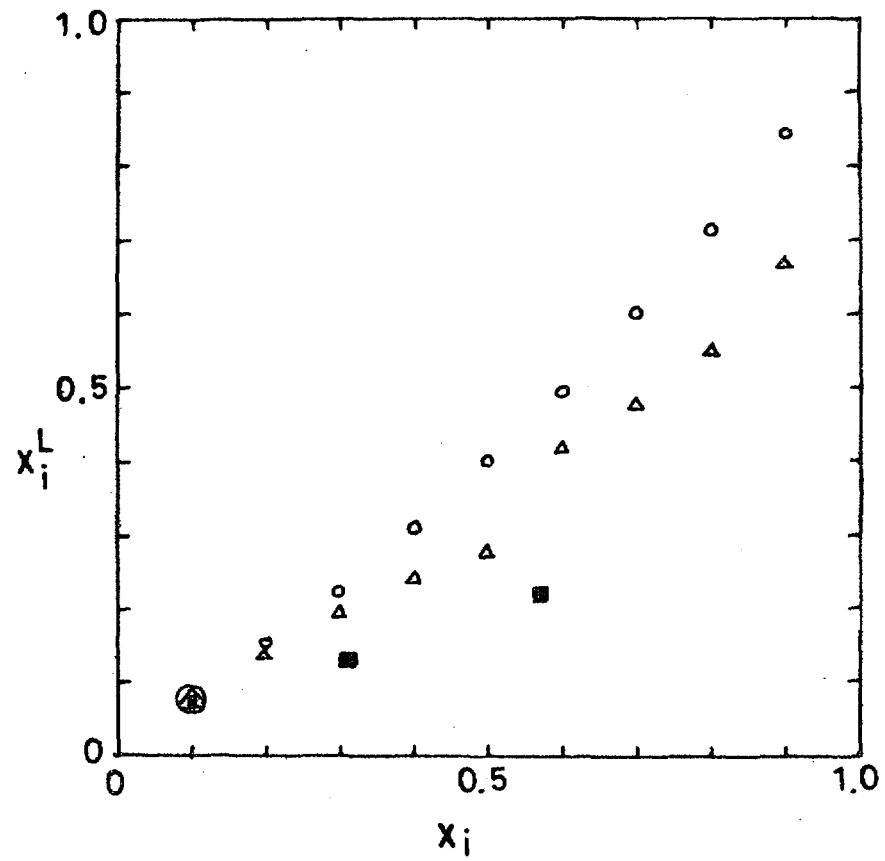


Fig.3. Variation of x_i^L with x_i for K^+ -form of the resin in methanol-water mixture. (O) Marcus' equation ; (Δ) Frank's equation; (\blacksquare) experimental data.

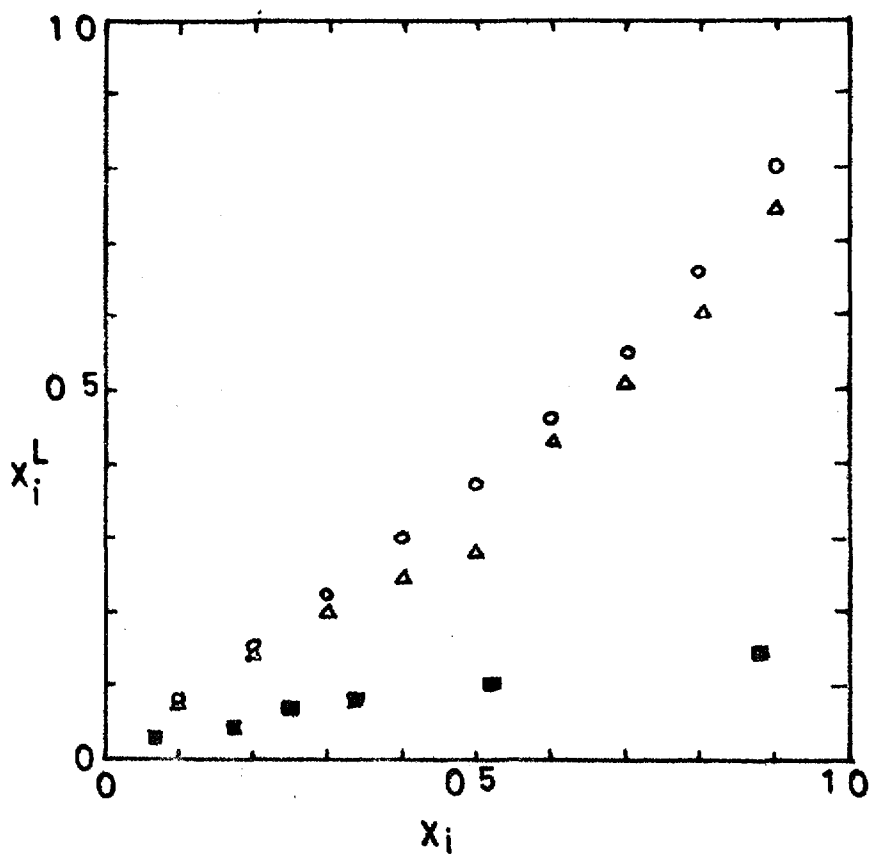


Fig.4. Variation of x_i^L with x_i for Na^+ -form of the resin in methanol-water mixture. (O) Marcus' equation ; (Δ) Frank's equation; (■) experimental data.

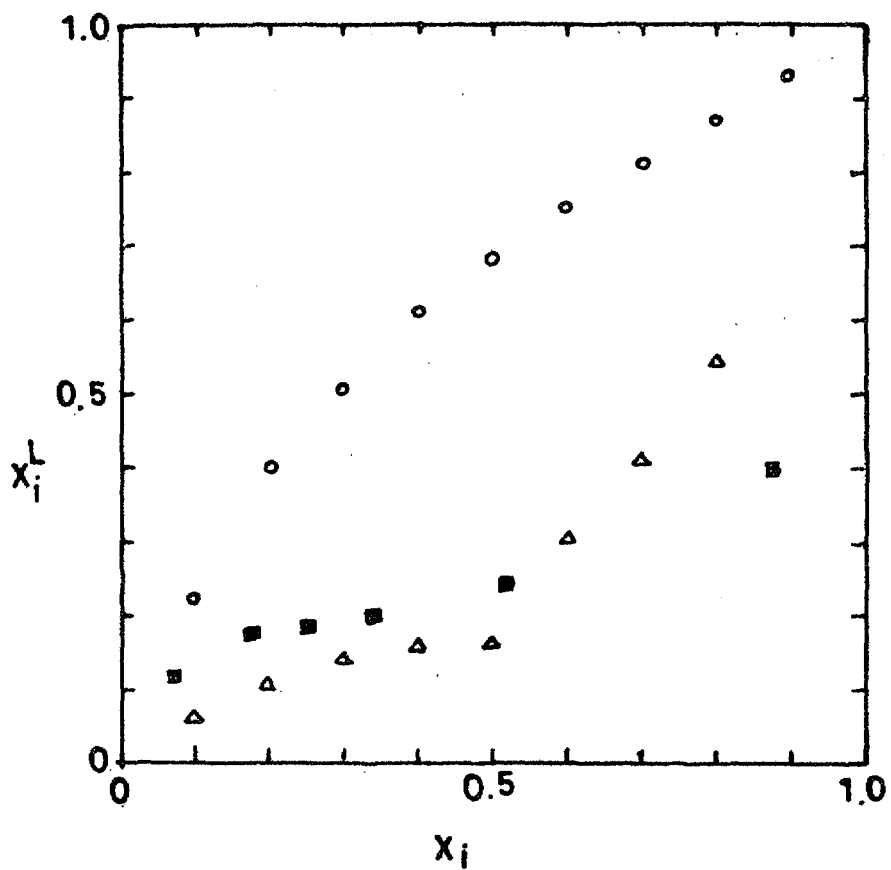


Fig.5. Variation of x_i^L with x_i for Ag^+ -form of the resin in methanol-water mixture. (O) Marcus' equation; (Δ) Frank's equation; (\blacksquare) experimental data.

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