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MEAN ACTIVITY COEFFICIENTS FOR THE SIMPLE ELECTROLYTE IN AQUEOUS MIXTURES OF POLYELECTROLYTE AND SIMPLE ELECTROLYTE. V. COMMON COUNTERION MIXTURES OF ALKALI-METAL DEXTRANSULFATES WITH ALKALI METAL CHLORIDES

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Mean molal activity coefficients of simple electrolyte in aqueous solutions of Li, Na, K or Cs salts of dextransulfate (DS) with added LiCl, NaCl, KCl or CsCl are reported. The measurements were carried out by means of an electrochemical cell method using a cation exchange membrane as cation selective electrode and Ag/AgCl electrodes. For LiDS–LiCl, NaDS–NaCl and CsDS–CsCl systems the polymer concentration, m_p, was varied from 0.0088 to 0.113 m and at a given m_p the ratio X of the polymer to salt concentration was varied from 0.5 to 16. Due to the insolubility of KDS in high concentration of KCl, the measurements on KDS–KCl system were performed in the m_p range of 0.0088–0.089 m and some of the smaller X values were omitted. The activity coefficient results are compared to Manning's limiting laws, the additivity rule, and to new limiting laws. The additivity rule can give an excellent representation of the data for all m_p values when γ_p is used as an adjustable parameter.

1. Introduction

The mean activity coefficient of the added salt in polyelectrolyte-simple electrolyte mixtures is a thermodynamically well defined and experimentally unambiguous parameter which has proven particularly useful in the investigation of interactions in polyelectrolyte solutions and in the verification of theoretical descriptions of such systems. Excellent reviews by Ise [1] and Manning [2,3] refer to a number of mean activity measurements of added salts as well as to numerous single ion activity determinations. Some recent papers on single counterion systems attest to the reproducibility of the data and to the usefulness of the mean activity coefficient for comparisons to theory [4–10]. The number of polyelectrolytes studied, and especially the number of added electrolytes is still very limited. Indications from single ion activity measurements that differences in binding occur e.g. between different alkali metal ions, and between polyions with different functional groups would have to show up in mean activity measurements as well, especially in systems with an excess of polyelectrolyte. Refined theoretical descriptions of polyion-small ion interactions need to be checked against data of higher accuracy than single ion activity measurements can provide. In this paper we report mean activity data for LiCl, NaCl, KCl and CsCl in mixtures of the corresponding alkali dextransulfate and chloride mixtures. The choice of dextransulfate (DS) was made for a number of reasons. High quality data from another research group exist for the mean activity coefficient of NaCl in NaDS [4], which enables us to compare our data to these measurements for accuracy checks. Some single ion activity data seem to indicate differences in alkali metal binding by DS [11,12] even though such a difference had not been reported in polystyrenesulfonate mixtures.

It has been known for a long time that the strong interaction between polyion and counterion forces a large fraction of the counterions to be in the immediate vicinity of the polyion. The concept of counter-

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ion condensation, introduced by Oosawa, Imai and Kagawa [13–15], was combined by Manning with the Debye-Hückel approximation for the electrostatic polyion-small ion interactions to arrive at the Manning limiting laws [16]. Both condensation and Debye-Hückel type interactions are non-specific in that counterions of the same charge will have the same interactions with the polyion. Thus the many reported cases of differences in "binding" between univalent counterions, if they are correct, must be accounted for by different theoretical treatments. However, the reports on the specificity of polyion-alkali-metal counterion are often contradictory. As early as 1954 Wall and Doremus [17] found the polyion mobility and the fraction of bound counterions in sodium and potassium polyacrylates, as determined from transport number and conductance measurements, to be independent of the counterion, although a weak concentration dependence was observed. Eisenberg from conductance measurements on alkali metal polyacrylates also concluded that the interactions were non-specific [18]. Other reports of non-specificity based on conductance measurements are for arabates [19], and carboxymethylcellulose [20]. Tondre and Zana [21], on the basis of ultrasonic absorption measurements, find non-specific interactions in alkalimetal polystyrene sulfonates. On the other hand, a number of workers have reported the existence of specific interactions. Hen and Strauss [22], from Donnan exclusion and density measurements concluded that the polyvinylsulfonate-counterion interactions increase in the order $Li^+ < Na^+ < K^+$. Tondre and Zana [21] find the binding sequence $Li^+ < Cs^+ < Rb^+ < Na^+ < K^+$ for polyethylenesulfonate. For Heparin, a highly charged polysaccharide with both sulfonate and carboxyl groups on the glucoside unit, Salminess and Luomanmaki's ultrafiltration experiments [23] show a preference for K^+ over Na^+, in agreement with Dunstone's ion exchange measurements [24]. For dextransulfate, single ion activity measurements [11,12] indicate a preference for K^+ over Na^+, but for another sulfonated polysaccharide, carrageenan, the results are contradictory. Podlas and Ander [25] report a preference of Na^+ over K^+, but Pass and co-workers using two different techniques [26,27] report the sequence $Na^+ < K^+$, similar to the dextransulfate results.

For the description of the activity of the small ions a number of semi-empirical descriptions and theoretical calculations exist. The additivity rule originally proposed by Mock and Marshall [28] can be formulated as an additivity of the counterion activities in the mixture [15]:

$$a_+ = a_p + a_+^0, \tag{1}$$

where a_+ is the counterion activity in the mixture, a_p the counterion activity in the pure polyelectrolyte and a_+^0 the counterion activity in the pure simple electrolyte. Often it is also assumed that $\gamma_- = \gamma_-^0$, the activity coefficient of the co-ion in the pure simple electrolyte. With the Bates convention for the single ion activities in the simple electrolyte this leads, for 1:1 added electrolytes, to:

$$\gamma_\pm/\gamma_\pm^0 = \{((\gamma_p/\gamma_\pm^0) + X^{-1})\,(1 + X^{-1})^{-1}\}^{1/2}, \tag{2}$$

where $\gamma_\pm$ is the activity coefficient of the added electrolyte in the mixture, $\gamma_\pm^0$ the activity coefficient of the pure electrolyte at the same concentration m_s as in the mixture, γ_p the counterion activity coefficient in the pure polyelectrolyte at m_p, and X the polyion to co-ion molality ratio, $X = m_p/m_s$. We should again point out the purely empirical character of eq. (2). Although γ_p is often equated to ϕ_p, the osmotic coefficient of the pure polyelectrolyte, the experimental evidence for this equality is far from clear, and theoretical considerations lead to a different relationship [16,29]. The direct determination of γ_p *via* single ion activity measurements can be questioned [1], and certainly suffers from a lack of reproducibility. For this reason, and in line with the now well understood empirical character of the additivity rule, it may be quite justified to use γ_p as an adjustable parameter which should conform to the fairly wide constraints given by the uncertainty in direct ϕ_p or γ_p determinations.

Manning's limiting law [16] for the mean activity coefficient of an added 1:1 electrolyte, with $\xi > 1$ and corrected for the interactions between the small ions [4,31] is given by:

$$\gamma_\pm/\gamma_\pm^0 = \{(\xi^{-1} + X^{-1})(1 + X^{-1})^{-1}\}^{1/2} \times \exp\{-(\tfrac{1}{2}\xi^{-1})(\xi^{-1} + 2X^{-1})^{-1}\}, \tag{3}$$

where $\xi = e^2/DkTb$, e is the proton charge, D the dielectric constant, k Bolzmann's constant and T the temperature. When the charge density parameter ξ is smaller than unity the condensation term on the right hand side of eq. (3) disappears and only the Debye-Hückel type interactions remain:

$$\gamma_{\pm}/\gamma_{\pm}^{0} = \exp\{-(\tfrac{1}{2}\xi^{-1})(\xi^{-1}+2X^{-1})^{-1}\}. \tag{4}$$

In both eqs. (3) and (4) $\gamma_{\pm}^{0}$ is the activity coefficient of the pure added electrolyte at m_s. One of the surprising outcomes of the experimental work sofar has been that in the case of added 1:1 electrolytes eq. (3) gives a poorer representation of the experimental data in the region of high excess of polyelectrolyte than does the analogous equation in the case of an added 2:1 electrolyte [4–8,30]. It has been suggested that the discrepancy between eq. (3) and the experimental results at high X is due to theoretical problems with the calculation of the co-ion activity [7,32]. Recent calculations of small ion activities based on a first higher term or a summed higher term approximation of the cluster expansion method [33] indicate that there may be a large difference in co-ion and counterion activities even for polyions with a charge density parameter lower than unity. Recent experimental work by Ander seems to support this finding [34]. If this is indeed the case it would mean that the Debye-Hückel approximation is not sufficiently accurate to describe the polyion-small ion interactions. The summed up cluster calculations are not valid for charge densities higher than one, however by assuming that for such polyions condensation will indeed occur, and the first higher cluster term can then be used to describe the interactions between the small ions and the polyion with and effective charge density of unity, Iwasa was able to derive the following "new limiting law" for the mean activity coefficient [29]:

$$\begin{aligned}\gamma_{\pm}/\gamma_{\pm}^{0} = {} & [(\xi^{-1}+X^{-1})(1+X^{-1})^{-1}]^{1/2} \\ & \times \exp[\xi^{-1}(\xi^{-1}+2X^{-1})^{-1} \\ & \times \{-0.5+0.39\,\xi^{-1}(\xi^{-1}+2X^{-1})^{-1}\}],\end{aligned} \tag{5}$$

where we clearly recognize the small ion-small ion interaction correction, the condensation term, the Debye-Hückel term, and the limiting case (for $m_p \rightarrow 0$ and X not too large) of the first higher cluster term correction.

The mean activity coefficient determinations of the added alkali chloride in mixtures LiCl + LiDS, NaCl + NaDS, KCl + KDS, and CsCl + CsDS were carried out by a galvanic cell technique using an ion-exchange membrane in the appropriate ionic form as alkali ion "electrode" together with a Ag/AgCl electrode [6,7]. 5 Polymer concentrations between 0.0088 and 0.113 monomolal were used for the Li, Na and Cs salts. For the potassium salt 4 polymer concentrations between 0.0088 and 0.089 monomolal were used. In this case measurements at $m_p = 0.113$ were avoided due to solubility problems when the KCl concentration reaches 0.05 m [12]. At a given polymer concentration 5 ratios of the polyion to co-ion monomolality between 0.5 and 16 were measured. Because eqs. (3) and (5) contain the same small ion-small ion correction factor $\gamma_{\pm}^{0}$, we will compare these theoretical predictions for $\gamma_{\pm}/\gamma_{\pm}^{0}$ directly to the corrected mean activity coefficient, $\gamma_{\pm}^{c}$, given by:

$$\gamma_{\pm}^{c} = \gamma_{\pm}(\exp)/\gamma_{\pm}^{0}, \tag{6}$$

where $\gamma_{\pm}(\exp)$ is the experimentally measured activity. We will also discuss our results in terms of specifity in the interactions between the dextransulfate polyion and the various alkali ions.

2. Experimental

Sodium dextransulfate, average molecular weight 500,000 was obtained from Pharmacia, Uppsala, Sweden. The main impurities, chloride, sulfate and phosphate buffer, were removed by diafiltration with a CH3 hollow fiber ultrafiltration unit (Amicon Corp., Lexington, Mass.) using a hollow fiber cartridge with a molecular weight cut-off of 10,000. Lithium and cesium dextransulfate were obtained from the sodium salt by salt exchange in a 65 ml stirred ultrafiltration cell. A 2% dextransulfate solution and a 0.1 M LiCl or CsCl washing solution were used. When all sodium had been replaced the LiCl or CsCl was removed by diafiltration. In the case of the potassium salt a different procedure was used. NaDS was dialysed against 0.2 M KCl, which caused KDS to precipitate in the dialysis bag. When conversion was complete after repeated KCl changes, the outside KCl concentration was lowered to 0.01 M to allow the KDS to dissolve. The final solution was again purified by diafiltration. The purified solutions were concentrated to the desired concentration by ultrafiltration in the hollow fiber cell. Concentrations of the stock solution were determined by ion exchange on a cation exchange column (Dowex 50W-X8) followed

Table 1
Activity coefficients of the added salt in alkalichloride-alkalidextransulfate mixtires, m_p: dextransulfate molality in equivalents/kg H_2O. m_s: chloride molality. $\gamma_\pm$: experimental mean molal activity coefficient. For uncertainty in $\gamma_\pm$, see text

LiCl–LiDS			NaCl–NaDS			KCl–KDS			CsCl–CsDS		
m_p	m_s	$\gamma_\pm$	m_p	m_s	$\gamma_\pm$	m_p	m_s	$\gamma_\pm$	m_p	m_s	$\gamma_\pm$
0.113	0.007031	0.501	0.113	0.00700	0.470				0.113	0.006961	0.422
0.113	0.01245	0.530	0.113	0.01245	0.492				0.113	0.01228	0.438
0.113	0.02805	0.554	0.113	0.02803	0.530				0.113	0.02767	0.484
0.113	0.1100	0.639	0.113	0.1091	0.605				0.112	0.1047	0.569
0.112	0.2196	0.674	0.113	0.2185	0.623				0.112	0.2092	0.582
0.0880	0.005492	0.484	0.0894	0.005557	0.448	0.0896	0.005550	0.425	0.0873	0.005360	0.422
0.0879	0.009714	0.505	0.0879	0.009717	0.501	0.0896	0.009876	0.440	0.0872	0.009515	0.440
0.0878	0.02186	0.544	0.0878	0.02186	0.540	0.0896	0.02224	0.494	0.0869	0.02137	0.488
0.0876	0.08556	0.633	0.0892	0.08631	0.618				0.0856	0.07977	0.575
0.0872	0.1702	0.662	0.0868	0.1684	0.661				0.0839	0.1564	0.593
0.0589	0.003679	0.491	0.0589	0.003660	0.458	0.0590	0.003656	0.423	0.0584	0.003586	0.425
0.0589	0.006511	0.505	0.0587	0.006494	0.493	0.0590	0.006504	0.449	0.0584	0.006376	0.449
0.0589	0.01466	0.543	0.0588	0.01464	0.538	0.0589	0.01463	0.501	0.0583	0.01433	0.499
0.0586	0.05730	0.650	0.0585	0.05667	0.630				0.0573	0.05340	0.604
0.0584	0.1140	0.688	0.0582	0.1128	0.669				0.0563	0.1049	0.640
0.0295	0.001839	0.492	0.0294	0.001827	0.445	0.0295	0.001828	0.443	0.0293	0.001796	0.430
0.0295	0.003255	0.502	0.0294	0.003255	0.485	0.0295	0.003253	0.462	0.0292	0.003188	0.453
0.0294	0.007367	0.546	0.0296	0.007360	0.541	0.0295	0.007316	0.520	0.0291	0.007167	0.521
0.0293	0.02866	0.661	0.0293	0.02834	0.661	0.0300	0.02973	0.646	0.0287	0.02675	0.637
0.0292	0.05705	0.707	0.0291	0.05642	0.702				0.0282	0.05252	0.683
0.00884	0.0005519	0.474	0.00883	0.0005488	0.476	0.00885	0.0005484	0.461	0.00877	0.0005384	0.429
0.00899	0.0009934	0.487	0.00883	0.0009767	0.497	0.00882	0.0009726	0.474	0.00877	0.0009567	0.452
0.00912	0.002270	0.552	0.00882	0.002196	0.553	0.00884	0.002195	0.549	0.00874	0.002150	0.519
0.00880	0.008599	0.693	0.00878	0.008500	0.702	0.00916	0.009806	0.677	0.00862	0.008027	0.671
0.00859	0.01696	0.735	0.00873	0.01693	0.744	0.00900	0.01788	0.734	0.00847	0.01578	0.739

by titration with NaOH. Accuracy of the concentrations of the stock solutions is estimated at ± 0.3%. These rather elaborate purification and conversion procedures, as opposed to the much simpler ion-exchange method used e.g. for polystyrenesulfonates [6,7] are necessary because glycoside linkages in dextransulfate hydrolyse rapidly in acidic medium. The sulfur content of dextransulfate reported by Pharmacia is 17%, which corresponds to an average of 1.9 sulfonate groups per glycoside unit. Determination of the equivalent weight of LiDS, NaDS, and KDS by drying a sample of known concentration to dryness under vacuum at 50–70°C resulted in rather large uncertainties. In the case of LiDS an apparently very low degree of substitution was obtained (1.6), probably due to incomplete water removal at the relatively low drying temperature. The values obtained for NaDS and KDS were 1.9 and 2.1 respectively and we will use the value 2.0 ± 0.2 in our calculation of the average charge density parameter of the dextransulfate polyanion. The same value was used by Wells [4] based on sulfur analysis of a dried sample.

Analytical grade LiCl, NaCl, and KCl were used without further purification. CsCl was "ultrapure" (Ventron Co., Beverly, Mass.). All solutions were prepared by weight from the alkali dextransulfate and alkalichloride stock solution in double distilled water. All concentrations are given as molalities.

Ag/AgCl electrodes were prepared following the method of Ives and Janz [35]. The cation exchange membrane, the membrane cell, and the potential measurements were described earlier [6,7]. The membrane was brought in the desired ionic form by soaking in a alkalimetal chloride + hydroxide solution. Calibration curves were made in the usual way, activity coefficients of the reference solutions were taken from Robinson and Stokes [36] and Harned and Owen [37] by suitable interpolations. Potentials were reproducible to ± 0.2 mV. The estimated accuracy of the $\gamma_\pm$ values is ± 0.005 at $m_p = 0.11$ m to ± 0.008 at $m_p = 0.009$ m.

3. Results and discussion

Mean molal activity coefficients, $\gamma_\pm$, of the added salt in mixtures of alkalimetal dextransulfate with alkalimetal chloride are listed in table 1. In figs. 1–5 the corrected activity coefficients $\gamma_\pm^c$ [eq. (6)] are plotted as a function of $X^{1/2}$.

In order to estimate the repeatability of the results, measurements in LiCl and CsCl mixtures were performed with two independently prepared series of solutions (table 2). A number of repeated measurements on the other systems indicate a similar repeat-

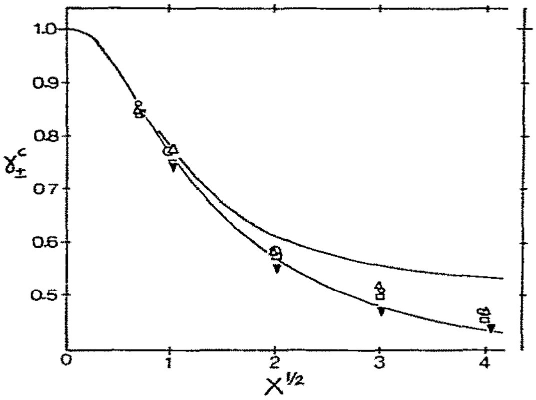

Fig. 1. Corrected mean activity coefficients $\gamma_\pm^c$ of LiCl (○), NaCl (△), KCl (□), and CsCl (▾) in alkalichloride–alkalidextransulfate mixtures. $m_p = 0.0089$ mole/kg. $X = m_p/m_{Cl}$. Full lines: eq. (3) (lower line) and eq. (5) (upper line).

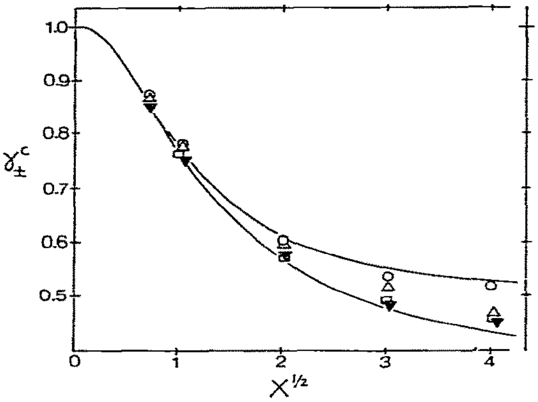

Fig. 2. Corrected mean activity coefficients $\gamma_\pm^c$ of LiCl (○), NaCl (△), KCl (□), and CsCl (▾) in alkalichloride–alkalidextransulfate mixtures. $m_p = 0.029$ mole/kg. $X = m_p/m_{Cl}$. Full lines: eq. (3) (lower line) and eq. (5) (upper line).

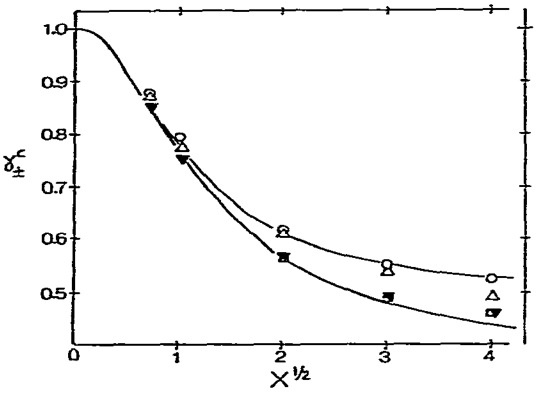

Fig. 3. Corrected mean activity coefficients $\gamma_\pm^c$ of LiCl (○), NaCl (△), KCl (□), and CsCl (▼) in alkalichloride–alkalidextransulfate mixtures. m_p = 0.059 mole/kg. $X = m_p/m_{Cl}$. Full lines: eq. (3) (lower line) and eq. (5) (upper line).

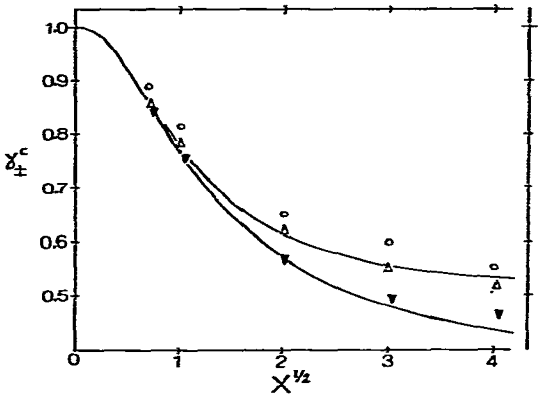

Fig. 5. Corrected mean activity coefficients $\gamma_\pm^c$ of LiCl (○), NaCl (△), and CsCl (▼) in alkalichloride–alkalidextransulfate mixtures. m_p = 0.113 mole/kg. $X = m_p/m_{Cl}$. Full lines: eq. (3) (lower line) and eq. (5) (upper line).

ability pattern, i.e. a slightly better reproducibility as m_p increases. In figs. 6 and 7 our results for the NaCl–NaDS system are compared to those of Wells [4]. A direct comparison could only be made for a limited number of mixtures because Wells' concentration series were at constant added salt concentration, whereas ours are at constant polyion concentration. For this reason, only the first three points of Wells in fig. 6 (up to $X^{1/2} = 1.6$) and the first two points in fig. 7 (up to $X^{1/2} = 0.9$) are direct data points, the other points are extrapolated to the lower m_p values used by us assuming $\gamma_\pm^c$ to be independent of m_p. It should be mentioned that Wells measured $\gamma_\pm$ by the galvanic cell method and with a Donnan exclusion technique and observed good agreement between the two methods. It is of some importance to stress the excellent agreement between Wells' and our results for the mean activity coefficient of the added salt, also in the light of the very poor agreement obtained between the single ion activity coefficients reported by different groups [11,12,38]. The good internal consistency of our data can also be judged from figs. 1–5, where only 2 out of the 93 data points shown seem to fall significantly outside the smoothed curves which can be drawn through the data for all salts.

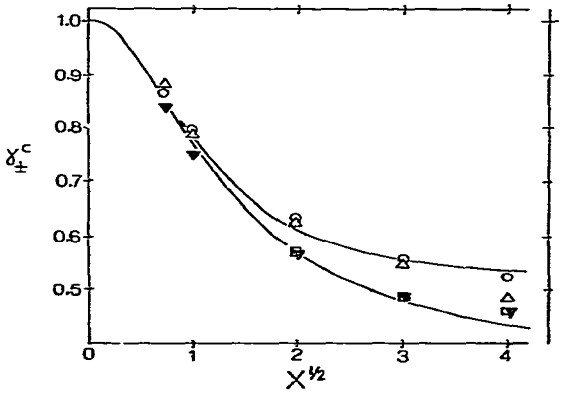

Fig. 4. Corrected mean activity coefficients $\gamma_\pm^c$ of LiCl (○), NaCl (△), KCl (□), and CsCl (▼) in alkalichloride–alkalidextransulfate mixtures. m_p = 0.088 mole/kg. $X = m_p/m_{Cl}$. Full lines: eq. (3) (lower line) and eq. (5) (upper line).

Also plotted in figs. 1–5 are the values of $\gamma_\pm^c$ as predicted by Manning's limiting law (MLL, eq. (3)), and by the limiting version of the first higher cluster term + condensation approximation [eq. (5)]. The experimental curves of $\gamma_\pm^c$ versus X for LiCl and NaCl show a clear dependence on the polyion concentration m_p, a dependence which was not noticed in our study of polystyrenesulfonate mixtures [6,7], although a barely significant dependence could be in-

Table 2

$\gamma_\pm^c$ values obtained from independently prepared solution series (1) and (2). m_p in monomolal/kg H_2O, $X = m_p/m_s$, $\gamma_\pm^c$ is corrected molal activity coefficient

LiCl + LiDS			CsCl + CsDS					
$m_p = 0.113$			$m_p = 0.0293$			$m_p = 0.0088$		
X	$(\gamma_\pm^c)_1$	$(\gamma_\pm^c)_2$	X	$(\gamma_\pm^c)_1$	$(\gamma_\pm^c)_2$	X	$(\gamma_\pm^c)_1$	$(\gamma_\pm^c)_2$
16.0	0.549	0.548	16.0	0.452	0.458	16.0	0.440	0.447
9.0	0.595	0.578	9.0	0.484	0.495	9.0	0.469	0.472
4.0	0.648	0.645	4.0	0.572	0.572	4.0	0.548	0.540
1.0	0.813	0.808	1.0	0.750	0.758	1.0	0.741	0.752
0.5	0.889	0.890	0.5	0.847	0.856	0.5	0.841	0.849

ferred from the NaPSA–NaCl results [6]. As X increases, $\gamma_\pm^c$ is seen to go up with increasing m_p as we go from Cs^+ and K^+ to Na^+ and Li^+. Thus, for the lowest polyion concentration the increase in $\gamma_\pm^c$ as we go from Cs^+ to Li^+ is only marginally significant, but as the polyion concentration increases a clear trend $\gamma_{CsCl}^c < \gamma_{KCl}^c < \gamma_{NaCl}^c < \gamma_{LiCl}^c$ develops, although the CsCl and KCl coefficients are not very different.

Neither Manning's limiting law nor the first higher term corrected limiting law predict such a dependence. Manning's limiting law is seen to be in very reasonable agreement with the data points at the lowest polymer concentration. The zero ionic strength limit of the first higher term correction increases the predicted values of $\gamma_\pm^c$ from the MLL values. Although both a polyion concentration dependence and a counterion dependence are predicted by the full, non-limiting first higher cluster term + condensation calculations via the κa terms [33], the difference with the $\kappa a \rightarrow 0$ limiting curves plotted in figs. 1–5 is small at the actual concentrations of our data, as can be seen from the non-limiting cases plotted in refs. [29] and [33]. Certainly the non-limiting cluster expression cannot predict the difference between the LiCl and the CsCl data, and any κa dependence predicted would be much smaller than what is experimentally observed at high X. The validity of the cluster term calculations is of course limited to the region where X is not too large.

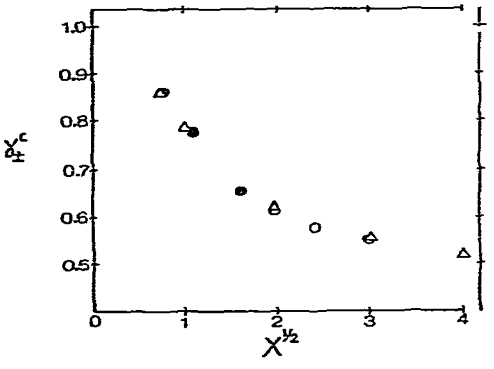

Fig. 6. Corrected mean activity coefficients $\gamma_\pm^c$ of NaCl in NaCl–NaDS mixtures at m_p = 0.089 mole/kg. △: our values. ●: ref. [4]. ○: ref. [4] (extrapolated to m_p = 0.089).

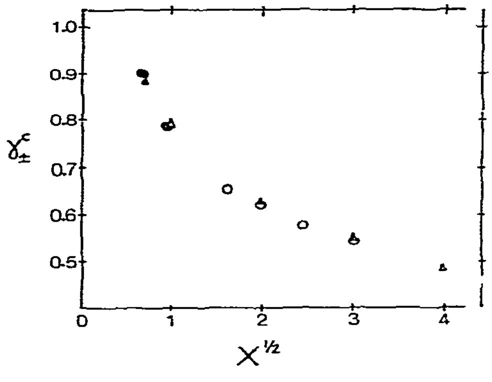

Fig. 7. Corrected mean activity coefficients $\gamma_\pm^c$ of NaCl in NaCl–NaDS mixtures at m_p = 0.113 mole/kg △: our values. ●: ref. [4]. ○: ref. [4] (extrapolated to m_p = 0.113).

Up to $X = 2$ the difference in the $\gamma_\pm^c$ prediction of the Manning limiting law and the new limiting law is minor, and in the high X region we should treat this difference as plotted with some reservation, although there is no doubt that the higher cluster terms will increase $\gamma_\pm^c$ (in fact, at $X = \infty$ the counterion activity predictions of the two theories would be the same and the difference would only be caused by the difference in the co-ion activity). Finally, in comparing the data to eqs. (3) and (5) it should be kept in mind that there is an appreciable uncertainty in our experimental determination of the equivalent weight of the polymer, and thus in the calculation of ξ. For instance if the degree of substitution was 2.2 instead of the 2.0 value used, this would decrease both theoretical values at $X = 16$ in figs. 1–5 by about 5%.

In the light of these theoretical and experimental uncertainties, the agreement between the data and theory is probably as good as we can expect it to be. The points at the lowest m_p values are very close indeed to Manning's limiting law, and in this the results deviate from the polystyrenesulfonate case. Since neither Manning's limiting law, the new limiting law, or the full version of the first higher cluster term + condensation equation predicts the increase in $\gamma_\pm$ at high X as m_p increases for LiCl and NaCl, it seems reasonable to conclude that this increase is not caused by long range polyion-small ion interactions. *However, neither does it seem reasonable to attribute this to an increase of the "degree of binding" as we go from lithium to cesium,* since after all the cesium curves are virtually identical to the completely nonspecific limiting laws! We will return to this point later in the discussion.

A semi-empirical representation of the data can be given by the "additivity rule", which in various forms has been applied by a number of authors [15, 28,39–43]. As we have said before, the value chosen for γ_p in eq. (2) can be rather arbitrary even if single ion activity or osmotic coefficient data are available. For instance, due to the rather wide divergence between existing single ion activity data for Na^+ in NaDS or K^+ in KDS [11,12,38] we could choose values for γ_p anywhere between 0.12 and 0.22 for K^+ and between 0.18 and 0.28 for Na^+, which would of course make a large difference in the high X region. Wells' determinations [4] of the osmotic coefficient are, at the lowest polyion concentration, in good agreement with the Manning limiting law value ($\phi_p = (2\xi)^{-1} = 0.18$), but increase as m_p increases. The first higher cluster term + condensation approximation yields the same value for ϕ_p as Manning's limiting law, and, in its limiting version, also the same value for γ_p, i.e. 0.217. Using $\gamma_p = 0.217$ in eq. (2) yields values for the predicted mean activity coefficients as compared to the observed ones which are too high at all m_p's for CsCl and KCl, and which are too high for the 2 lower m_p series in the NaCl and LiCl cases (figs. 8–11). The appearance of $\gamma_\pm^0$ in the square root term on the right hand side of eq. (2) is not sufficient to describe the different curves for LiCl at various m_p's, or for NaCl at various m_p's, with one single γ_p value for LiDS and one for NaDS.

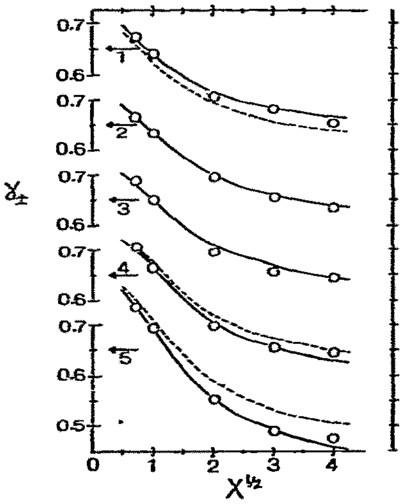

Fig. 8. Mean activity coefficients $\gamma_\pm$ of LiCl in LiCl–LiDS mixtures. $m_p = 0.113$ (curve 1), 0.088 (curve 2), 0.059 (curve 3), 0.029 (curve 4), and 0.0089 (curve 5). Broken lines: eq. (2) with $\gamma_p = 0.218$. Full lines: eq. (2) with variable γ_p (table 3).

If we view the additivity rule as an empirical mixture rule in which the properties of the mixture ($\gamma_\pm$) are calculated from the properties of the pure components ($\gamma_\pm^0$ and γ_p), of which only $\gamma_\pm^0$ is experimentally accessible, we can find the values for γ_p which give the best fit of eq. (2) to each experimental $\gamma_\pm$ versus X curve. This has also been done in figs. 8–11, and the best fit values of γ_p are given in table 3. We notice that the γ_p values so obtained are certainly

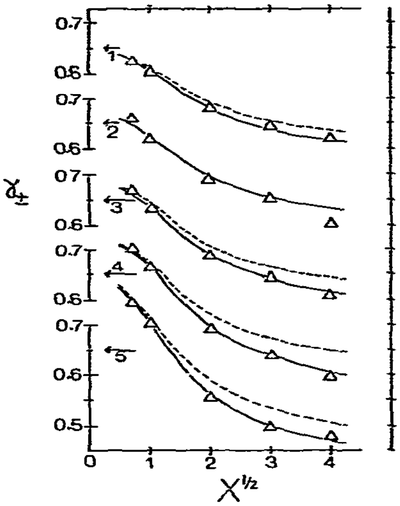

Fig. 9. Mean activity coefficients $\gamma_\pm$ of NaCl in NaCl–NaDS mixtures. m_p = 0.113 (curve 1), 0.088 (curve 2), 0.059 (curve 3), 0.029 (curve 4), and 0.0088 (curve 5). Broken lines: eq. (2) with γ_p = 0.218. Full lines: eq. (2) with variable γ_p (table 3).

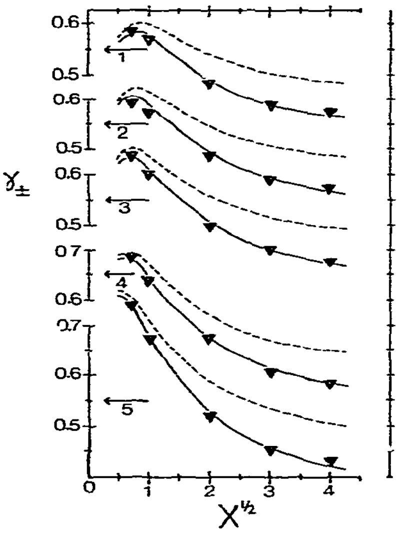

Fig. 11. Mean activity coefficients $\gamma_\pm$ of CsCl in CsCl–CsDS mixtures. m_p = 0.113 (curve 1), 0.087 (curve 2), 0.058 (curve 3), 0.029 (curve 4), and 0.0087 (curve 5). Broken lines: eq. (2) with γ_p = 0.218. Full lines: eq. (2) with variable γ_p (table 3).

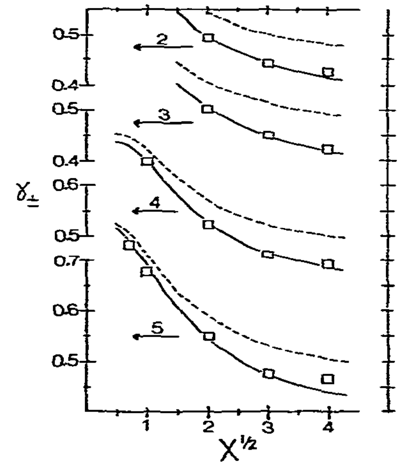

Fig. 10. Mean activity coefficients of $\gamma_\pm$ of KCl in KCl–KDS mixtures. m_p = 0.089 (curve 2), 0.059 (curve 3), 0.029 (curve 4), and 0.0088 (curve 5). Broken lines: eq. (2) with γ_p = 0.218. Full lines: eq. (2) with variable γ_p (table 3).

within the margin of error allowed by the direct γ_p or ϕ_p determinations. As is already clear from the experimental data themselves, they increase from CsCl to LiCl at a given m_p. They are virtually independent of m_p for CsCl and KCl, and increase with m_p for NaCl and LiCl. The increase with m_p in the case of the NaDS system is not inconsistent with the increase in ϕ_p in the same system [4]. It is also clear from the experimental data that all theoretical and semi-empirical equations fit the data well in the low X range ($X < 2$), and therefore sensitive comparisons of $\gamma_\pm$ data to theory can only be made in the range where

Table 3
"Best fit" γ_p values from additivity rule (eq. (2))

m_p	LiCl	NaCl	KCl	CsCl
0.1126	0.252	0.217		0.140
0.089	0.217	0.195	0.140	0.140
0.058	0.217	0.185	0.140	0.143
0.0294	0.194	0.175	0.150	0.147
0 0088	0.165	0.177	0.150	0.130

$X > 2$. As far as the additivity rule is concerned, the fit in this range is largely determined by the choice for γ_p.

We will now present a brief discussion of our results in terms of specificity in counterion–polyion interactions. Two earlier reports on dextransufate, based on single ion activity measurements, indicate a preference sequence $Na^+ < K^+$ for dextransulfate with a degree of substitution of 2.54 and 1.46 [12], and $Li^+ < Na^+ < Cs^+ < K^+$ for dextransulfate with a degree of substitution of 1.35 [11]. As was pointed out earlier, there is a wide discrepancy between the actual activity coefficient values reported by these two groups. Other reports of single ion activity measurements on sulfonated polysaccharides are also interpreted as indicative of specific binding [25,26], but again the experimental data are rather contradictory. No such experimental uncertainty exists in the case of mean activity coefficients, as can be judged from the comparison of our data with those of Wells. From our results as presented in figs. 1–5 it is tempting to conclude that the preference sequence $Li^+ < Na^+ < K^+ \leqslant Cs^+$ at $m_p = 0.113$ vanishes at the lowest polymer concentrations used. In our opinion the data do not support such a claim. First of all, if Cs^+ was "bound" stronger than Li^+, we would expect the LiCl activity curve to approximate the completely non-specific limiting law, with the CsCl activity curve being lower. Yet, the contrary is the case: the CsCl activity curve is very close to the limiting law at all concentrations, it is rather the LiCl curve which is higher! Secondly, there is no reason to assume that would such a difference in binding occur it would tend to vanish at low polyion concentrations. However this is what is experimentally observed for the difference in mean activity coefficients values. The differences in the activity coefficients of the pure alkalihalides at higher concentrations can be adequately described by a model taking into account the difference in hydration of the alkali ions [36]. This difference rapidly vanishes below 0.1 m. The mean activity coefficient of the alkalihalide in large excess alkali dextransulfate is largely determined by the counterion activity coefficient, the contribution of the co-ion can reasonably be assumed small and fairly independent of m_p. In comparison with the pure alkalihalides, a much more likely conclusion seems to be that there is no specific interaction between the dextransulfate ion and alkali counterions, the difference at higher polyion concentrations being due to a difference in hydration number similar to what is observed in pure alkalihalide solutions. A similar explanation has been proposed by Marinsky [42] for selectivity differences in crosslinked polystyrenesulfonates.

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