

Viscosity of silicate solutions

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Viscosity of Silicate Solutions

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High precision viscosity measurements of electrolyte solutions were used to obtain information about interionic interactions. In solutions of tetramethylammonium (TMA) silicates values for the A and D coefficient in the Jones–Dole equation were found to be significantly higher than for sodium and potassium silicate solutions. Ion association between cations and anions in the silicate solutions investigated is excluded by EMF measurements. The A and D coefficients of solutions which contain both alkali metal and TMA silicate were in the range of the values of alkali metal silicate solutions. As an explanation for this behavior we suggest that hydrophilic and hydrophobic structured solvent regions are present around respectively the silicate and the TMA which cannot overlap. This causes a repulsion between these ions superimposed on the electrostatic attraction.

Introduction

In zeolite syntheses organic cations (for instance quarternary ammonium ions) play an important role as structure determining agents. The type of zeolite formed is dependent on the organic cation. At present it is not clear what processes are involved in the syntheses and how organic cations influence those processes. The influence of tetraalkylammonium (TAA) ions on silicate ions is also present in homogeneous solutions of TAA silicates. Hoebbel et al.^{1,2} found that TAA ions influence the structure of the silicate ions. The silicate structures are quite characteristic for the particular TAA ion present. The TMA ion induces formation of the cubic octameric silicate ion ($\text{Si}_8\text{O}_{20}^{8-}$), while in the presence of tetraethylammonium ions mainly the hexagonal prismatic silicate ions ($\text{Si}_6\text{O}_{15}^{6-}$) is found. The fact, that the type of cation determines the kind of silicate ion present indicates that interactions between cation and silicate ion are very important for the structure formation. In order to obtain basic information on these interactions, we studied silicate solutions rather than the systems encountered in zeolite syntheses because of the more complicated composition of the latter.

In 1929 Jones and Dole^{3,4} described viscosities of electrolyte solutions in terms of interaction parameters, using the equation

$$\mu_r = 1 + A\sqrt{c} + Bc \quad (1)$$

With this equation it is possible to determine interactions in solutions. Kaminsky⁵ extended the equation with a c^2 term

$$\mu_r = 1 + Ac^{1/2} + Bc + Dc^2 \quad (2)$$

In these equations μ_r is the relative viscosity, c is the molar concentration, and A , B , and D are the Jones–Dole coefficients.

The A coefficient describes the long range electrostatic interactions. Shortly after the papers by Jones and Dole, Falkenhagen⁶⁻⁸ and Onsager⁹ developed a theory for

calculating the A coefficient of solutions of strong electrolytes. Falkenhagen starts from an ionic distribution (according to the Debye–Hückel theory) which becomes distorted by simple shear. The movement of the ions toward their equilibrium position causes an increase in viscosity. The A coefficient can be calculated by taking the space integral of the product of the ion concentration with the shear-induced disturbed potential.

The variables in the Falkenhagen equation are the mobility and the charge of the ions. For mixtures of electrolytes, no theoretical equation is available.

According to Quintana¹⁰ the A coefficient of weak electrolytes is smaller than calculated with Falkenhagen's equation. The contribution of the long range electrostatic forces to the viscosity becomes

$$A_{\text{observed}} = A_{\text{Falkenhagen}} [(1 - \alpha)c]^{1/2} \quad (3)$$

Where A_{observed} is the experimental A coefficient, $A_{\text{Falkenhagen}}$ is the A coefficient of the electrolyte calculated by the Falkenhagen equation, α is the degree of association, and c is the concentration.

In 1965 Stokes and Mills¹¹ gave a semiquantitative theory for the B coefficient, taking into account hydrodynamic effects as well as ion–solvent interactions

$$B = B_h + B_{\text{orient}} + B_{\text{str}} + B_{\text{reinf}} \quad (4)$$

B_h is the hydrodynamic contribution which can be compared with the Einstein coefficient for viscosities of suspensions, B_{orient} is the contribution by changes in orientation of the solvent molecules, and B_{str} is the contribution of the structure building or breaking effect of the ions. B_{reinf} is a term added by Krumgalz¹² caused by the hydrophobic hydration.

The B coefficient describes single ion contributions. According to Dordick¹³ it is possible to calculate the B coefficient of mixtures of electrolytes by summation of the B coefficients of the pure electrolytes.

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(4) Jones, G.; Talley, S. K. *J. Am. Chem. Soc.* 1932, 55, 4124.

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For high concentrations Kaminsky⁵ added the Dc^2 term to the Jones–Dole equation. Desnoyers et al.¹⁴ interpreted this term as a result of ion–ion interactions. Palma and Morel¹⁵ found a correlation of the D -coefficient with the entropic parameter S_{EE} , characteristic of the electrolyte–electrolyte pair interactions. High D coefficients correspond to low S_{EE} values. Solutions with low S_{EE} parameters are thought to have a certain degree of order. Ordering by Coulombic forces (Debye–Hückel ion cloud) gives rise to small D coefficients. Out¹⁶ found for sodium chloride $D = 0.013 \text{ L}^2 \text{ mol}^{-2}$. Large D coefficients can be thought of as due to other interactions than Coulombic forces.

At present it is not clear what processes are involved in the syntheses and how organic cations influence those processes; but in closely related systems coacervation (separation into two liquid phases) has been reported.^{1–6} Such coacervation may indicate complex formation between silicate and tetraalkylammonium (TAA) ions based on special interactions. The supposition that such special interactions exist is corroborated by the fact that there is an influence of TAA ions on silicate ions in homogeneous solutions of TAA silicates.

In the present investigation A , B , and D coefficients were obtained for solutions of TMA silicate, sodium silicate, potassium silicate, and mixtures of TMA and alkali silicate solutions. These values were compared with each other and with the coefficients of other electrolytes. Equation 3 brings into account the influence of association on the A coefficient. McCormick et al.¹⁷ has recently shown that in solutions of sodium silicates, ion association takes place. Therefore deviation from Nernstian behavior was investigated by means of ion selective electrodes for sodium and potassium ions.

Experimental Section

Determination of Nernstian Behavior. Materials used were as follows: sodium hydroxide, ex Merck Titrisol; sodium chloride, PA., ex Merck; potassium hydroxide, ex Merck Titrisol; potassium bromide, PA., ex Merck; precipitated silica, ultra pure, ex Merck; twice distilled water.

The procedure used was as follows. The emf as function of the concentration for the bromide, hydroxide, and silicate salts of sodium and potassium was determined with the Orion Autochemistry System 940/960 (i.e. an Orion EA 940 pH/ISE meter, combined with a microprocessor, a disperser, and an electrode tower holding two standard sized electrodes), using the “serial calibration” standard option permitting measurement of emf concentration curves. For the silicate solutions the alkali metal/silicate molar ratio was 2:1. The potentials were measured with a Corning sodium selective electrode for the sodium salts and a Philips potassium selective electrode for the potassium salts against an Orion double junction reference electrode.

Viscosity Measurements. High-precision viscosity measurements were carried out with an Ubbelohde capillary viscometer. The flow time of pure water in the viscometer used was about 185 s. A correction factor for the kinetic energy was applied, using values supplied by the manufacturer; such corrections always were <0.5%. The corrections for the surface tension were included by using the formula²⁰

$$C_t = C_c \left[1 + \left(\frac{4}{gh} \right) \left(\frac{1}{d_u} - \frac{1}{d_l} \right) \left(\frac{\gamma_c}{\rho_c} - \frac{\gamma_t}{\rho_t} \right) \right] \quad (5)$$

where C is the calibration constant for the viscometer, subscripts c and t refer to calibrating liquid and test sample, respectively,

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g is the acceleration of gravity, h is the average driving head, d_u is the average diameter of the upper meniscus in the working capillary, and d_l is the average diameter of the lower meniscus in the working capillary, sample and water, respectively, corrected for loss of kinetic energy.^{18,19}

Materials used were as follows: tetramethylammonium hydroxide pentahydrate (TMAH), 97%, ex Janssen Chimica; sodium hydroxide, ex Merck Titrisol; potassium hydroxide, ex Merck Titrisol; precipitated silica, ultra pure, ex Merck; twice distilled water.

The procedure used was as follows. Stock solutions were made with a base to silica ratio of 2:1. The cation composition was expressed as the molar fraction TMA of all cations. For mixtures of sodium and TMA silicate, TMA fractions of 0, 0.25, 0.5, 0.7, and 1 were used and for mixtures of TMA and potassium silicate, TMA fractions of 0, 0.25, 0.5, 0.75, and 1. Eight samples of each stock solution were prepared in the concentration range $0.02 \leq c \leq 0.7 \text{ M}$ based on the cation concentration. At the highest concentration silicate composition was determined by a method described by Groenen.²¹ No significant differences in silicate composition were found for sodium and TMA silicate solutions. Before measurements the solutions were filtered through a glass filter. Viscosities were measured using a Schott Ubbelohde viscometer Oa and a Schott viscosity measuring unit, AVS 310 ($\pm 0.01 \text{ s}$). The temperature was fixed on $25 \text{ }^\circ\text{C}$ with a LKB 7600 A precision thermostat ($\pm 0.001 \text{ }^\circ\text{C}$). Densities were measured with an Anton Paar DMA calculating precision density meter ($\pm 0.00001 \text{ g/mL}$). Measurements of the surface tensions were carried out with the Krüss tensiometer KT 10 ($\pm 0.1 \text{ mN/m}$) using the Wilhelmy plate method. Surface tensions were found to be dependent of time. This is thought to be due to a slow approach to equilibrium. As liquid in the Ubbelohde viscometer is moving, the surface is not in equilibrium. Therefore the initial surface tension was used for the surface tension correction.

Results

Figure 1 gives the electrode calibration curves of the sodium salts (Figure 1a) and of the potassium salts (Figure 1b). The curves are shifted in a vertical direction, by approximately 20 and 40 mV, to emphasize the Nernstian behavior. If any association of silicate and alkali metal ions takes place, this will be visible as a decrease in slope with increasing concentration.

In Table I all measured relative viscosities of the silicate solutions are presented as function of the molar concentration. Table II gives the coefficients of the extended Jones–Dole equation, for the five ratios of TMA silicate and Na silicate. Table III gives the Jones–Dole coefficients for the mixtures of TMA and potassium silicate. These coefficients were obtained, by fitting the experimental data with a method provided by Press et al.,²² to the extended Jones–Dole equation (eq 2). The viscosities are listed in Table I. The total cation concentration was used in the fitting procedure instead of the silica concentration. As a result of this we have to divide literature A coefficients of bivalent electrolytes by $2^{1/2}$ to adjust them to the concentration scale we used. Because of the additivity rule for the B coefficients, literature values of the B coefficient can be used. The concentration scale we used

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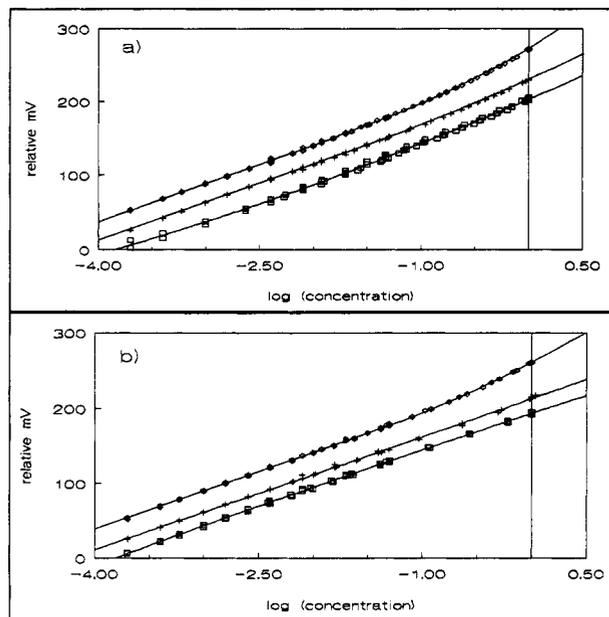


Figure 1. Emf as function of log(molar concentration) of (a) sodium salts (b) potassium salts: \square , halogenide salt; $+$, silicate salt; \circ , hydroxide salt.

is particularly convenient for comparison of the *A*, *B*, and *D* coefficients of the silicate solutions with those of sodium chloride and TMA bromide. The influence of the silicate ions on the coefficients is shown most clearly by keeping all other variables constant while the bromide is replaced by the silicate.

The uncertainties in the viscosities are less than 0.01%. The uncertainties in the fitting parameter can be calculated with the procedures provided by Press et al.²² as well. These uncertainties are about 5% for the *A* coefficients and approximately 1% for the *B* and *D* coefficients. The straight lines through the *B* coefficients are the theoretical lines based on Dordick's¹³ additivity rule calculated with data provided by Out¹⁶ (eq 5).

Discussion

The precision of the coefficients permits us to conclude that in Figure 2 the curves of the *A* and *D* coefficients are significantly convex toward the *X* axis. For ratios up to 0.7 the *B* coefficients can be described as straight lines.

The *B* Coefficient. The *B* coefficients were in the range of 0.24–0.32 dm³ mol⁻¹ for mixtures of sodium and TMA silicate, and for mixtures of potassium and TMA silicate they were in the range of 0.18–0.29 dm³ mol⁻¹. Out¹⁶ found for sodium chloride 0.078 dm³ mol⁻¹, for potassium bromide -0.0468 dm³ mol⁻¹, and for TMA bromide 0.076 dm³ mol⁻¹. The difference in *B* coefficients between the halogenides and the silicates indicates that the contribution of the silicates to the *B* coefficient is large. As silicate ions have a hydrophilic hydration, the large *B* coefficient is most probably due to a large *B*_{str} in eq 4. This means that silicate ions have large structured hydration regions and can therefore be considered as structure builder.

According to the additivity of the *B* coefficients, the curve for sodium TMA mixtures should have been a straight line, described by

$$B(X) = B(X=0) + X(B_{\text{TMA}} - B_{\text{Na}}) \quad (6)$$

where *B*_{TMA} and *B*_{Na} are the ionic *B* coefficients of the TMA and sodium ions and *X* is the fraction of TMA of all cations. The slope can be calculated from *B* coefficients

Table I. Relative Viscosity of Silicate Solutions

concentration	η_r ($\pm 0.01\%$)	concentration	η_r ($\pm 0.01\%$)
TMA Silicate			
0.0296	1.0115	0.2806	1.1031
0.0694	1.0246	0.4250	1.1620
0.0995	1.0351	0.5645	1.2297
0.1403	1.0502	0.6969	1.3037
TMA:Na Silicate 138:62			
0.0311	1.0124	0.2802	1.1040
0.0511	1.0196	0.3963	1.1515
0.0993	1.0364	0.5377	1.2152
0.1817	1.0665	0.6992	1.2925
TMA:Na Silicate 1:1			
0.0300	1.0111	0.2836	1.1059
0.0700	1.0231	0.3455	1.1300
0.1006	1.0362	0.5189	1.2053
0.1398	1.0508	0.6998	1.2917
TMA:Na Silicate 54:146			
0.0189	1.0074	0.2653	1.0882
0.0197	1.0167	0.3822	1.1299
0.1023	1.0334	0.5192	1.1815
0.1806	1.0597	0.6732	1.2448
Na silicate			
0.0349	1.0121	0.4534	1.1494
0.1050	1.0327	0.6336	1.2151
0.1494	1.0461	0.9751	1.3562
0.2235	1.0684	1.3016	1.5124
TMA:K Silicate 3:1			
0.0299	1.0066	0.2900	1.0974
0.0512	1.0110	0.3945	1.1341
0.1003	1.0210	0.5495	1.1923
0.1808	1.0376	0.6845	1.2510
TMA:K Silicate 1:1			
0.0301	1.0089	0.3050	1.0864
0.0701	1.0199	0.3715	1.1065
0.1404	1.0406	0.5489	1.1624
0.2173	1.0606	0.6951	1.2123
TMA:K Silicate 1:3			
0.0297	1.0073	0.2756	1.0690
0.0502	1.0119	0.3820	1.0974
0.1087	1.0262	0.5156	1.1373
0.1759	1.0425	0.6523	1.1808
K Silicate			
0.0300	1.0066	0.2767	1.0593
0.0513	1.0110	0.3825	1.0843
0.1005	1.0210	0.4871	1.1087
0.1793	1.0376	0.6485	1.1519

Table II. Jones-Dole Coefficient of the System (TMA₂ Sil)_x(Na₂Sil)_(1-x)

<i>X</i>	<i>A</i> , (L/mol) ^{0.5}	<i>B</i> , L/mol	<i>D</i> , (L/mol) ²
0	0.0094	0.27	0.088
0.25	0.0119	0.283	0.098
0.5	0.0089	0.32	0.123
0.69	0.0168	0.305	0.14
1	0.0266	0.237	0.227

Table III. Jones-Dole Coefficient of the System (TMA₂ Sil)_x(K₂ Sil)_(1-x)

<i>X</i>	<i>A</i> , (L/mol) ^{0.5}	<i>B</i> , L/mol	<i>D</i> , (L/mol) ²
0	0.0056	0.185	0.064
0.25	0.0052	0.217	0.082
0.5	0.0125	0.2347	0.073
0.75	0.0097	0.285	0.1
1	0.0266	0.237	0.227

found by Out,¹⁶ and from these data is expected to be 0.044 dm³ mol⁻¹. This was found for ratios up to 0.7.

For mixtures of potassium and TMA silicates a slope can be calculated in a similar way and is expected to be 0.123 dm³ mol⁻¹. Similarly for sodium-TMA mixtures the slope does agree with the experimental *B* values for ratios up to 0.75. The exceptionally small *B* coefficient

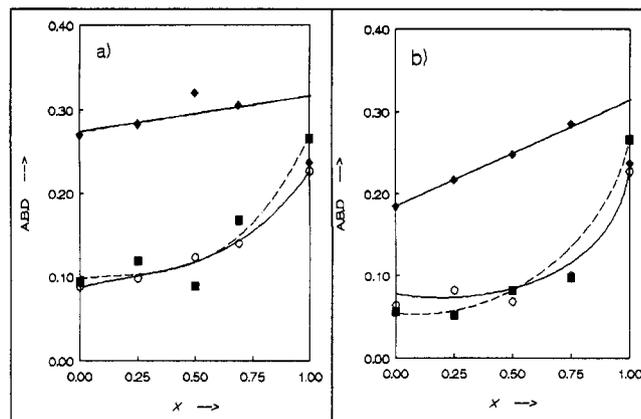


Figure 2. Jones-Dole coefficients of silicate solutions as function of the TMA fraction of all cations, (a) sodium-TMA and (b) potassium-TMA: ■, $10^4 A$ coefficient; ●, B coefficient, ○, D coefficient.

found for TMA silicate, does not conform with the additivity rule.

An explanation for the small B coefficient of TMA silicate is the difference in hydration of the ions. Silicate ions are hydrophilic structure builders and TMA is a hydrophobic structure builder. Frank and Evans²³ suggested that these two hydration types are of a different origin. Therefore these different structured regions do not overlap. The small B coefficient of TMA silicate can then be explained by the assumption that at points of contact of hydrophilically induced and hydrophobically induced solvent regions structure breakdown occurs.

The A Coefficient. The A coefficients of TMA, sodium, and potassium silicate found in this investigation were 0.0266, 0.0099, and 0.0056 $L^{0.5} mol^{-0.5}$, respectively. According to the Falkenhagen theory the A coefficients of TMA and sodium silicate should not differ more than 10%, as the mobility of TMA is less than 10% larger than that of sodium. However the A coefficients of TMA silicate is $2^{1/2}$ times higher than that of sodium silicate. This can be explained by two possible ways: Either the A coefficient of sodium silicate is small because of association or the A coefficient of TMA silicate is exceptionally large.

If association takes place, the degree of association can be calculated with eq 3. This leads to a degree of association of 86%. Association of sodium silicate would strongly influence the emf-concentration curves of Figure 1. A degree of association of 86% would lead to a potential drop of 51 mV with respect to the value observed in completely dissociated salt solutions. For the hydroxide solutions the slope of the emf-concentration curves increases at high concentration. This is most probably due to deviations of the ion selective electrodes at high pH. This takes place at $pH > 13.3$. The pH of the silicate solutions in the concentration range of the viscosity measurements is always lower than that of the critical pH value. Therefore it does not effect the results. As the emf-concentration curve of sodium silicate does not have a slope different from the slopes of sodium chloride and hydroxide (at low concentrations), the degree of association in sodium silicate solutions is less than 5% in the concentration range investigated. Association of potassium silicate can be excluded on the same ground. The A coefficient of sodium silicate is not small because of association.

This leaves an exceptional large A coefficient for TMA silicate. According to Frank and Evans²³ the presence of

large structured solvent regions around ions can cause a deformation of the Debye-Hückel ion cloud. The hydration shell will hinder the approach of the counterions. In fact the result of the deformation of the ion cloud, caused by the structured region, is an increase in average ion-counterion distance. This means that the attraction between TMA and silicate ions is, on the average, less than would be expected on the basis of the charge and dimensions of the ions themselves. The influence of this enlarged ion-counterion distance on the A coefficient is large. As the distance between ion and counterion is large, the shielding will be diminished. A consequence of this is that the potential does not drop as fast with the distance as for the Debye-Hückel ion cloud in the absence of structured regions around the ions. At large distances from the ion, the deformation of the ion cloud in a shear field is more pronounced. As the potential is large, compared to the Debye-Hückel ion cloud, the disturbed potential is also large. In solutions of TMA silicate the counterions are present at a larger distance from the central ion than for sodium silicate. At large distances from the central ion the disturbance of the potential is larger than close to the central ion; thus the space integral of the product of counter ion concentration with the disturbed potential is larger as well.

Thus the large A coefficient of TMA silicate can be explained by an increased TMA-silicate distance because of the different hydration regions of TMA and silicate which do not overlap. This is supported by the form of the curve in Figure 2a. The curve, convex to the X axis, shows a large influence of sodium on the A coefficient. The average TMA-silicate distance is larger than the average sodium-silicate distance. In mixtures of TMA and sodium, the effect of the TMA is small because sodium can approach the silicate closer than TMA. The mean ionic distribution does not differ much from sodium silicate and gives rise to an A coefficient which is in the same range as the A coefficient of sodium silicate.

The A coefficient of potassium silicate is distinctly smaller than the A coefficient of sodium silicate. The electrode calibration curve for potassium silicate, as shown in Figure 1b, is perfectly parallel with the curves of potassium bromide and potassium hydroxide. Ionic association would have been visible as a decrease in slope. The Nernstian behavior for potassium silicate excludes significant association. As potassium has a higher mobility than sodium, the difference in A coefficient between potassium and sodium silicate conforms to the Falkenhagen equation. The curve of the A coefficients in Figure 2b can be explained with the same mechanism as for mixtures of sodium and TMA silicate. The curvature is more pronounced for potassium-TMA silicate mixtures than for sodium-TMA silicate mixtures. Very mobile potassium ions will have more influence on the A coefficient than ions with lower mobility in decreasing the A coefficient.

The D Coefficient. For the curve of the D coefficient as a function of the cation composition we find the same general form as for the curve of the A coefficient. The D coefficients of sodium silicate and potassium silicate (0.087 and 0.064 $L^2 mol^{-2}$) are comparable with those of TMA bromide (0.059 $L^2 mol^{-2}$), sodium chloride (0.013 $L^2 mol^{-2}$), potassium bromide (0.01 $L^2 mol^{-2}$), and other common electrolytes found by Out.¹⁶ The D coefficient of TMA silicate is much higher (0.220 $L^2 mol^{-2}$), and a curve convex toward the X axis is found for the mixed compositions.

The high value of the D coefficient for TMA silicate indicates the presence of additional interionic interactions.

As the D coefficients of TMA bromide are quite small, it is not likely that this interaction occurs between two TMA ions. Nor does it take place between two silicate ions because of the small D coefficients of sodium and potassium silicate. Therefore the additional interaction in TMA silicate solutions occurs between TMA and silicate ions. Because of the electrostatic interactions TMA and silicate ions attract each other. At a certain distance the hydration shells touch. As the hydration layers have a different structure, they cannot overlap. This causes a repulsion between TMA and silicate ions which has its effect on the D coefficient. The form of the curve in Figure 2 can be explained by the difference in equilibrium distance of the cation with the silicate ions. The sodium ions can move closer to the silicate than TMA. The electrical attraction between TMA and silicate ions diminishes because the silicate is shielded by the sodium ions. This causes a diminished interaction between TMA and silicate ions.

Conclusions

By comparing A , B , and D coefficients with each other and with literature data, information is obtained about

interactions between ions in solutions containing TMA ions and silicate ions. The large B coefficients indicate that silicate ions are structure builders. For mixtures of TMA and alkali metal silicates the B coefficients are additive for TMA fractions up to 0.75. The large D coefficient found for TMA silicate, compared to the D coefficients of TMA bromide, sodium silicate, and potassium silicate, shows the presence of strong solute-solute interactions between TMA and silicate ions. The analyses of the B and D coefficients support the explanation for the large A coefficient found for TMA silicate. In the absence of specific hydration effects the A coefficient of TMA silicate should have been the same for TMA and sodium silicate. The large A coefficient can be ascribed to the deformation of the Debye-Hückel ion cloud as a result of strong hydration shells around the silicate and the TMA which do not overlap.

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