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STUDIES ON ELECTROLYTE–NONELECTROLYTE INTERACTIONS: VISCOSITY BEHAVIOR OF ALKALI HALIDES IN AQUEOUS SUCROSE SOLUTIONS

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ABSTRACT

The effect of various added electrolytes (sodium and potassium halides of progressively increasing molecular volume) on the viscosity behavior of aqueous sucrose solution (292mM) has been investigated. Data are presented for the concentration range 0.125–3M of the electrolytes over the temperature range of 25 to 40°. The data have been found to satisfy Moulik's equation, $(\eta/\eta_0)^2 = M + K'C^2$, for concentrated solutions of electrolytes beyond the Einstein region. The "effective", rigid, molar volume (V_e) and apparent, Jones–Dole B-coefficient (in sucrose solution) have been computed by employing the Breslau–Miller treatment. The change in the viscosity behavior is attributed to structuring effects in solution.

INTRODUCTION

Thermodynamic and transport properties of multicomponent systems having water as one of the components are now under active investigation in various laboratories. In recent years, a number of review articles[1–6] have appeared stressing the importance of structural changes induced by the solutes. Effects of the simple alkali-metal halides and large tetraalkylammonium ions on these properties have been widely studied[7–11]. These effects have been detected experimentally by observing the changes brought about by the solutes in the various properties of water, such as viscosity, conductance, and heat capacity. It has been shown by these methods that ions of such small, simple electrolytes as LiF and $MgCl_2$, having high charge-density, act as net structure-makers, whereas comparatively large ions of simple electrolytes having low charge-density, such as of CsI and KBr, behave as net structure-breakers. In this respect, solutions of nonelectrolytes and of many organic salts are of special interest, as many of these solutes are known to increase the structure of water[7].

Studies on ternary systems of aqueous solutions are relevant, because it is sometimes difficult to arrive at any definite conclusion from a study of binary systems alone. In a ternary system, the properties of a model compound are usually studied in an aqueous system, in order to determine the response of the modified water-structure caused by the co-solutes. It is well known that polyhydroxy compounds interact with electrolytes in solutions[12,13]. Definite adducts of various carbohydrates with salts and hydrated oxides of alkali and alkaline-earth metals have been reported in recent years[14–16]. Studies have also been undertaken in this laboratory to investigate the interaction of electrolytes with water in the presence of sucrose, employing conductance measurements[17].

Very few workers[18–20] have examined the viscosity behavior of concentrated electrolyte solutions comprising ternary systems. However, in recent years, the viscosities of electrolyte solutions comprising binary systems have been used as an indication of the amount of structure existing within a solution[8,21,22]. It is well known that the Jones–Dole equation[23] *1*,

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC, \tag{1}$$

is limited in its application (only to 0.1–0.2M solutions), and no comparable treatment has so far been reported for concentrated solutions of electrolytes. However, M. L. Miller and Doran[24] and Nightingale[6] have utilized the Eyring treatment of the viscosity[25], based on the theory of rate processes, to investigate the viscosity of electrolyte solutions up to concentrations of the order of 10M. Breslau and I. F. Miller[18] noted the similarity in concentration between concentrated electrolyte solutions and high-volume fraction-dispersion, and utilized the equation obtained by Thomas[26] for volume fractions $\leqslant 0.25$, namely,

$$\eta/\eta_0 = 1 + 2.5\phi + 10.05\phi^2, \tag{2}$$

where η and η_0 are the viscosities of the nonelectrolyte solution containing electrolyte, and the nonelectrolyte solution, respectively, and ϕ is the measured volume-fraction. Using the substitution $\phi = CV_e$, where C is the molar concentration of electrolyte, and V_e is the "effective", rigid, molar volume, an expression for V_e was obtained from the foregoing, namely,

$$V_e = \frac{-2.5C + [(2.5C)^2 - 4(10.05C^2)(1 - \eta/\eta_0)]^{1/2}}{2(10.5)C^2} \ . \tag{3}$$

The B coefficient for concentrated solutions of univalent electrolytes is also obtained from the expression evolved by Breslau and Miller[18], namely,

$$B = 2.90\bar{V}_e - 0.018, \tag{4}$$

where $\bar{V}_e$ is the average, "effective", rigid, molar volume.

Moulik[19] suggested an alternative equation that successfully correlates viscosity data in the field of concentrated dispersions; it was given as

$$(\eta/\eta_0)^2 = M + K'C^2, \tag{5}$$

where M and K' are constants.

The main aspect of the investigation now reported is that studies have been made on the viscosity behavior of concentrated solutions of electrolytes in the presence of a co-solute (*e.g.*, sucrose). We report viscosity and density data obtained for sodium and potassium halides in aqueous sucrose solution (292mM), in the concentration range of 0.125–3M over the temperature range of 25–40°. Equations *3*, *4*, and *5* have been used for the analysis of the present data.

EXPERIMENTAL

Materials. — All of the chemical compounds employed in the present investigation were of Analytical Reagent Grade, and were obtained from B.D.H. or E. Merck. They were used as such, without any further purification.

Preparation of solutions. — Double-distilled, conductivity water having a conductivity of <1 μmho was used to prepare all of the solutions. A stock solution (292mM) of sucrose in conductivity water was prepared. Solutions of electrolytes were prepared on a molar basis; as pointed out by Nightingale[6], the molar scale of concentrations is satisfactory for most of the common inorganic salts, because the density of a 1M solution is such that one liter of the solutions contain very close to 54 moles of water. For measurements, a 3M solution of the electrolyte was first prepared in the sucrose solution, and then other concentrations were obtained by diluting the 3M solution with a suitable volume of the stock solution of sucrose. Solutions were always kept in stoppered, Pyrex-glass vessels, so as to prevent evaporation.

Measurement of density and viscosity. — The density of each solution was determined at 25, 30, 35, and 40° with a pycnometer in the conventional way.

Viscosity measurements at the specified temperatures were made with a modified Tuan–Fuoss viscometer[2,7]. A slight modification of this viscometer was

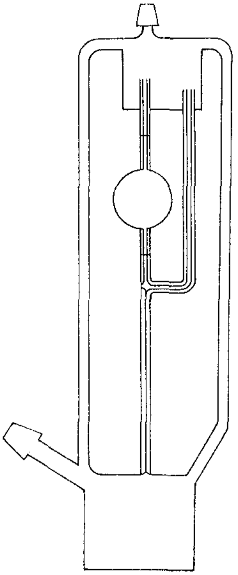

Fig. 1. Modified Tuan–Fuoss viscometer.

made, as shown in Fig. 1. This viscometer is so designed that a series of dilutions can be made on a sample of solute without opening the viscometer between check runs at a given concentration. In this way, evaporation errors are eliminated, and contamination of the contents of the viscometer by dust or moisture is minimized. The viscometer was fitted on to a wooden base by means of clips, which helped to keep the viscometer exactly vertical in the thermostat bath. Before each experiment, the viscometer was thoroughly cleaned with chromic acid, washed with distilled water, and dried in an oven for ~2 h.

Methods. — Experimental solutions were filtered before use. The flow time of the viscometer for conductivity water was determined to be 220 sec at 25°; the reproducibility was found to be better than ±0.1 sec, the time measurements being made with a stopwatch having ±0.1 sec as the least count. All of the viscosity and density measurements were conducted in a constant-temperature bath controlled to within ±0.05° of the temperature specified. Viscosities were measured at a series of concentrations, the lowest concentration being 125mM, and the highest, 3M. Densities were measured over the same range of concentrations.

RESULTS

From the flow times and the density values, the relative viscosities (η/η_0) were calculated. The value of η/η_0 was computed for each value of concentration of an alkali halide in aqueous sucrose solution. These values are given in Tables I and II. From the data reported in these Tables, the values of $(\eta/\eta_0)^2$ and C^2 were obtained. The plot of $(\eta/\eta_0)^2$ *versus* C^2 are given in Figs. 2 and 3. As the plot of $(\eta/\eta_0)^2$ against C^2 showed the same trend at all four temperatures, the plots for all six salts employed are given for 25° only. The "effective", rigid, molar volume (V_e) was computed from these data by employing the Breslau–Miller equation *3* for all six salts in aqueous sucrose solution at the various concentrations and temperatures. The data are given in Tables III and IV. The values of the average, "effective", rigid, molar volume, $\bar{V}_e$, were calculated for each salt in aqueous sucrose solution over the concentration range of 3–0.125M, the total number of data employed being 10; on the basis of the average, "effective", rigid, molar volume, the value of the apparent B coefficient for all of the salts in aqueous sucrose solution were calculated by employing Eq. *4*. The values of the B coefficient are given in Table V, and Tables VI and VII give the values of the B coefficient for the potassium salts in aqueous sucrose solution over the concentration range of 3–0.75M, the total number of data being 6, and over the concentration range of 0.5–0.125M, the total number of data being 4.

DISCUSSION

A plot of $(\eta/\eta_0)^2$ *versus* C^2 obtained from equation *5* (given by Moulik[19]), Figs. 2 and 3, shows a straight line within a limited region. In the region of lower concentration, a curve is obtained; this is known as the Einstein region. The results show that Moulik's equation is also valid for our system. In the case of sodium salts in aqueous sucrose solution, the trend of the curve in the Einstein region is downward

TABLE I

RELATIVE VISCOSITY (η/η_0) AT VARIOUS CONCENTRATIONS OF ELECTROLYTE IN AQUEOUS SUCROSE SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*NaCl* *Temperature (°C)*				*NaBr* *Temperature (°C)*				*NaI* *Temperature (°)C*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	1.399	1.380	1.378	1.368	1.303	1.300	1.298	1.296	1.223	1.222	1.221	1.220
2.50	1.317	1.316	1.295	1.286	1.240	1.232	1.228	1.226	1.166	1.165	1.164	1.163
2.00	1.242	1.241	1.221	1.210	1.177	1.176	1.173	1.169	1.117	1.116	1.114	1.112
1.50	1.184	1.176	1.154	1.144	1.124	1.122	1.120	1.116	1.077	1.074	1.071	1.067
1.00	1.118	1.111	1.091	1.089	1.077	1.074	1.073	1.069	1.044	1.039	1.036	1.030
0.75	1.089	1.083	1.066	1.064	1.057	1.054	1.052	1.044	1.031	1.026	1.024	1.022
0.50	1.064	1.055	1.039	1.039	1.044	1.033	1.030	1.023	1.021	1.015	1.011	1.010
0.375	1.055	1.043	1.027	1.026	1.035	1.031	1.021	1.014	1.018	1.013	1.005	1.004
0.250	1.041	1.029	1.015	1.014	1.026	1.022	1.012	1.004	1.013	1.009	1.001	0.999
0.125	1.024	1.017	1.005	1.004	1.016	1.013	1.001	0.993	1.007	1.005	0.993	0.992

TABLE II

RELATIVE VISCOSITY (η/η_0) AT VARIOUS CONCENTRATIONS OF ELECTROLYTE IN AQUEOUS SUCROSE SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*KCl* *Temperature (°C)*				*KBr* *Temperature (°C)*				*KI* *Temperature (°C)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	1.025	1.033	1.047	1.059	0.966	0.980	0.997	1.012	0.919	0.935	0.956	0.974
2.50	1.010	1.022	1.031	1.041	0.957	0.969	0.985	1.007	0.912	0.927	0.943	0.958
2.00	0.998	1.012	1.017	1.021	0.953	0.961	0.976	0.984	0.911	0.923	0.936	0.947
1.50	0.996	0.998	1.003	1.008	0.955	0.963	0.970	0.978	0.920	0.926	0.935	0.944
1.00	0.995	0.996	0.996	0.997	0.962	0.964	0.966	0.971	0.932	0.937	0.943	0.947
0.75	0.994	0.993	0.993	0.992	0.967	0.968	0.969	0.972	0.943	0.944	0.946	0.949
0.50	0.994	0.993	0.992	0.989	0.976	0.974	0.973	0.972	0.959	0.956	0.955	0.954
0.375	0.993	0.992	0.991	0.987	0.980	0.978	0.977	0.973	0.968	0.975	0.962	0.959
0.250	0.993	0.991	0.990	0.985	0.984	0.980	0.978	0.973	0.970	0.969	0.967	0.963
0.125	0.992	0.990	0.987	0.982	0.990	0.983	0.979	0.974	0.980	0.975	0.971	0.966

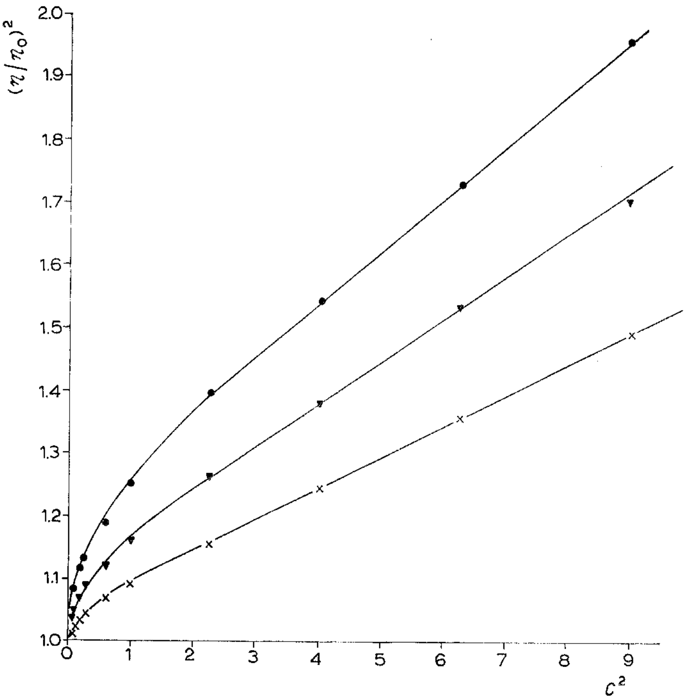

Fig. 2. Plot of $(\eta/\eta_0)^2$ against C^2 in aqueous sucrose solution at 25°. (● NaCl, ▲ NaBr, and × NaI.)

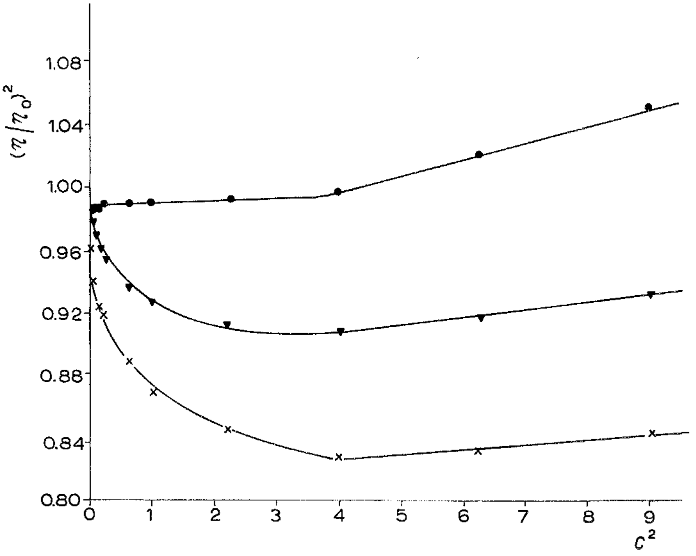

Fig. 3. Plot of $(\eta/\eta_0)^2$ against C^2 in aqueous sucrose solution at 25°. (● KCl, ▲ KBr, and × KI.)

TABLE III

"EFFECTIVE", RIGID, MOLAR VOLUME (V_e) AT VARIOUS CONCENTRATIONS OF ELECTROLYTE IN AQUEOUS SUCROSE SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*NaCl* *Temperature (°C)*				*NaBr* *Temperature (°C)*				*NaI* *Temperature (°C)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	0.0368	0.0354	0.0353	0.0346	0.0297	0.0295	0.0293	0.0291	0.0232	0.0231	0.0230	0.0229
2.50	0.0369	0.0368	0.0349	0.0340	0.0295	0.0287	0.0283	0.0281	0.0217	0.0216	0.0215	0.0214
2.00	0.0372	0.0371	0.0345	0.0331	0.0287	0.0286	0.0282	0.0276	0.0201	0.0199	0.0196	0.0193
1.50	0.0396	0.0381	0.0340	0.0321	0.0282	0.0278	0.0274	0.0266	0.0184	0.0178	0.0171	0.0162
1.00	0.0405	0.0384	0.0322	0.0315	0.0277	0.0267	0.0263	0.0250	0.0165	0.0147	0.0136	0.0114
0.75	0.0421	0.0395	0.0320	0.0311	0.0280	0.0266	0.0257	0.0220	0.0157	0.0133	0.0123	0.0113
0.50	0.0467	0.0406	0.0294	0.0294	0.0330	0.0251	0.0229	0.0177	0.0162	0.0117	0.0086	0.0078
0.375	0.0542	0.0430	0.0276	0.0266	0.0354	0.0315	0.0216	0.0146	0.0186	0.0135	0.0052	0.0042
0.250	0.0617	0.0444	0.0234	0.0219	0.0399	0.0340	0.0188	0.0063	0.0203	0.0141	0.0015	−0.0062
0.125	0.0737	0.0527	0.0155	0.0124	0.0496	0.0404	0.0029	−0.0226	0.0218	0.0155	−0.0226	−0.0261

TABLE IV

"EFFECTIVE", RIGID, MOLAR VOLUME (V_e) AT DIFFERENT CONCENTRATIONS OF ELECTROLYTE IN AQUEOUS SUCROSE SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*KCl* *Temperature (°C)*				*KBr* *Temperature (°C)*				*KI* *Temperature (°C)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	0.0032	0.0041	0.0058	0.0072	−0.0048	−0.0027	−0.0004	0.0027	−0.0127	−0.0098	−0.0063	−0.0036
2.50	0.0015	0.0034	0.0047	0.0061	−0.0074	−0.0052	−0.0024	0.0011	−0.0169	−0.0135	−0.0101	−0.0072
2.00	−0.0004	0.0023	0.0033	0.0040	−0.0102	−0.0083	−0.0050	−0.0032	−0.0215	−0.0180	−0.0144	−0.0117
1.50	−0.0010	−0.0005	0.0007	0.0021	−0.0130	−0.0105	−0.0084	−0.0060	−0.0251	−0.0228	−0.0196	−0.0165
1.00	−0.0020	−0.0016	−0.0016	−0.0012	−0.0162	−0.0153	−0.0144	−0.0121	−0.0310	−0.0284	−0.0253	−0.0234
0.75	−0.0032	−0.0037	−0.0037	−0.0043	−0.0186	−0.0180	−0.0174	−0.0156	−0.0338	−0.0331	−0.0318	−0.0298
0.50	−0.0048	−0.0056	−0.0064	−0.0089	−0.0200	−0.0217	−0.0226	−0.0235	−0.0359	−0.0381	−0.0390	−0.0400
0.375	−0.0075	−0.0086	−0.0097	−0.0141	−0.0220	−0.0243	−0.0255	−0.0301	−0.0360	−0.0397	−0.0433	−0.0470
0.250	−0.0113	−0.0146	−0.0162	−0.0246	−0.0263	−0.0331	−0.0365	−0.0452	−0.0505	−0.0523	−0.0559	−0.0632
0.125	−0.0262	−0.0328	−0.0428	−0.0596	−0.0328	−0.0562	−0.0699	−0.0873	−0.0665	−0.0838	−0.0979	−0.1158

TABLE V

APPARENT JONES–DOLE B COEFFICIENT OF ELECTROLYTES IN AQUEOUS SUCROSE SOLUTION AT DIFFERENT TEMPERATURES[a]

Salt	*Temperature (°C)*			
	25	*30*	*35*	*40*
NaCl	0.118	0.100	0.068	0.065
NaBr	0.077	0.068	0.049	0.032
NaI	0.038	0.030	0.011	0.006
KCl	−0.033	−0.035	−0.037	−0.045
KBr	−0.068	−0.075	−0.077	−0.082
KI	−0.113	−0.116	−0.117	−0.122

[a] Concentration range, 3–0.125M; number of data points employed, 10.

TABLE VI

APPARENT JONES–DOLE B COEFFICIENT OF POTASSIUM HALIDES IN AQUEOUS SUCROSE SOLUTION AT DIFFERENT TEMPERATURES[a]

Salt	*Temperature (°C)*			
	25	*30*	*35*	*40*
KCl	−0.019	−0.016	−0.014	−0.011
KBr	−0.052	−0.047	−0.041	−0.034
KI	−0.086	−0.079	−0.070	−0.062

[a] Concentration range, 3–0.75M; number of data point employed, 6.

TABLE VII

APPARENT JONES–DOLE B COEFFICIENT OF POTASSIUM HALIDES IN AQUEOUS SUCROSE SOLUTION AT DIFFERENT TEMPERATURES[a]

Salt	*Temperature (°C)*			
	25	*30*	*35*	*40*
KCl	−0.054	−0.063	−0.073	−0.096
KBr	−0.075	−0.116	−0.130	−0.153
KI	−0.155	−0.173	−0.189	−0.211

[a] Concentration range, 0.5–0.125M; number of data points employed, 4.

[*i.e.*, as the concentration decreases, the value of $(\eta/\eta_0)^2$ also decreases], but, for potassium chloride in aqueous sucrose solution, the trend of the curve in the Einstein region is slightly downward, and for potassium bromide and iodide, it is upward [*i.e.*, as the concentration decreases, the value of $(\eta/\eta_0)^2$ increases]. This is, perhaps, due to the different behavior of the sodium and potassium ions; with respect to water, sodium halides are known to be structure makers, whereas potassium halides behave as structure breakers.

Interpretation of the B coefficient for the alkali halides in aqueous sucrose solution in terms of the structuring effects of electrolytes upon water has been discussed on the basis of the following view. The B value usually decreases with increasing size of the ion, often to a negative value[21,28], and, in such cases, B increases with increased temperature[8,29,30]. This is in a direction opposite from that for the hydration effects, and, consequently, this behavior has been attributed to the ability of these ions to disrupt the structure of water in their vicinity[28,31]; these ions are termed structure breakers. In the case where the B coefficient decreases with increasing temperature, this is in favor of the hydration effect, and, consequently, this behavior has been attributed to the ability of these ions to produce a water structure in their vicinity; these ions are thus known as structure makers. As a general rule, it is assumed, in all structural-hydration[5,32–35] interactions, that two solutes will attract each other if their structural influences, or their tendency to orient water molecules, are compatible with each other; conversely, an incompatibility in these structural influences or tendencies will result in repulsive forces.

The B coefficients are listed in Table V for the concentration range 3–0.125M (number of data points used, 10) for all of the alkali halides at a fixed concentration of sucrose solution. The value of the B coefficient decreases with increasing temperature; this indicates that all of the alkali halides in aqueous sucrose solution show a structure-making trend. Potassium halides are structure breakers in aqueous solution alone, but, in sucrose solutions, they show a structure-making trend. This is due to the fact that sucrose[35] is a strong structure-maker because of the 8 hydrogen-bonding sites in the molecule (which are closely bound to water molecules by hydrogen bonding). This effect predominates over the structure-breaking properties of potassium halides, resulting in an overall, structure-making effect.

However, examination of the data listed in Table VI for the B coefficient of potassium halides in aqueous sucrose solution for the concentration range 3–0.75M (number of data points, 6 only), shows that the B value computed from the foregoing equation increases with increasing temperature. This indicates that potassium halides in this concentration range exhibit structure-breaking properties in aqueous solution, in conformity with the behavior of potassium halides in aqueous solutions alone. The data listed in Table VII for the lower concentrations of potassium halides (0.5–0.125M) show a structure-making effect due to the appreciable concentration of sucrose in comparison to that of the potassium halides. However, on the whole, it shows a structure-making trend. The structure-breaking effects of potassium salts in the concentration range of 3–0.75M are in the order: KI > KBr > KCl. The overall, structure-making order of potassium salts over the concentration range of 3–0.125M in 292mM sucrose solution is KCl>KBr>KI, and, for the sodium salts in 292mM sucrose solution, the structure-making effects are in the order: NaCl>NaBr>NaI.

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