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STUDIES ON THE VISCOSITY BEHAVIOR OF CONCENTRATED SODIUM AND POTASSIUM HALIDES IN AQUEOUS D-MANNITOL SOLUTION

VISHNU AND VIJAI P. MISRA
Department of Chemistry, University of Gorakhpur, Gorakhpur-273001 (India)

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ABSTRACT

The viscosity behavior of added sodium and potassium halides (in the concentration range 0.125–3M), in aqueous (0.4M) D-mannitol solution, over the temperature range 25–40° has been investigated. It has been found that Moulik's equation holds good for these systems beyond the Einstein region. From the relative viscosity data, the "effective", rigid molar volume, V_e, and apparent B coefficient have been computed by employing the Breslau–Miller treatment. On the basis of the values of the apparent B coefficient of these electrolytes, the change in viscosity behavior is attributed to structure making/breaking effects in solution.

INTRODUCTION

Physicochemical studies of ternary systems comprising water as one of the components have been the subject of active research in recent years. Such studies on ternary systems have also been undertaken from the viewpoint of understanding the change in water structure brought about by the cosolutes. Many workers have studied ternary systems containing two electrolytes[1], two nonelectrolytes[2,3], and an electrolyte and a nonelectrolyte[4–7] in great detail. In earlier communications[8,9], we have described the solute–solvent interaction in alkali halides–sucrose (or D-xylose)–water systems.

In the present communication, D-mannitol has been used as the model cosolute, and its interactions with sodium and potassium halides in aqueous medium have been investigated by employing viscosity measurements. D-Mannitol is a polyhydroxy alcohol that possesses six hydrogen-bonding sites[10], but aqueous solutions of D-mannitol have not been widely investigated. Robinson and his associates[4,5] measured the activity coefficients of alkali halides in aqueous D-mannitol solution, and Dunlop[11] studied the diffusion and frictional coefficients of the NaCl–D-mannitol–water system and obtained the Onsager reciprocal relationship for the system.

In this paper, the relative viscosities have been obtained for sodium and potassium halides in the concentration range 0.125–3M in aqueous D-mannitol (0.4M) solution over a temperature range of 25–40°. The apparent B coefficient values have been calculated by obtaining the "effective" rigid molar volume with the help of relative viscosity data at the corresponding temperatures and concentrations of sodium and potassium halides, in order to express the structuring properties of electrolytes in aqueous D-mannitol solution.

EXPERIMENTAL

Materials and preparation of solutions. — Analytical-reagent grade samples of NaCl, NaBr, NaI, KCl, KBr, KI, and D-mannitol, obtained from B.D.H. and E. Merck, were employed for the present work, and were used, as such, without further purification.

All solutions were prepared in doubly distilled conductivity water having a specific conductance of $\sim 10^{-6}$ ohm^{-1}.cm^{-1}. A D-mannitol solution (0.4M) was prepared in conductivity water, and used as a stock solution. A solution (3M) of the electrolyte was prepared in the D-mannitol solution, and the other concentrations were obtained by diluting this solution with the stock solution.

Density and viscosity measurements. — Viscosity and density values were determined[8] by the method and with the apparatus described previously.

RESULT AND DISCUSSION

The values of relative viscosity (η/η_0) for each of the alkali halides in aqueous D-mannitol solution at different ionic concentration in the temperature range 25–40° were calculated with the help of equation *1*.

$$(\eta/\eta_0) = d.t/d_0 \cdot t_0, \tag{1}$$

where η and η_0 are respectively the viscosities of the electrolyte in aqueous D-mannitol solution, and of aqueous D-mannitol solution alone, d and t are the density and the time of flow of the electrolyte in aqueous D-mannitol solution, and d_0 and t_0 are respectively the density and time-flow of aqueous D-mannitol solution. These values are given in Tables I and II. The viscosity data were tested by using the values in the Moulik equation[12]

$$(\eta/\eta_0)^2 = M + KC^2, \tag{2}$$

where M and K are constants and C is the concentration (molarity). The $(\eta/\eta_0)^2$ values were computed, and plotted against C^2. As similar plots were obtained for all six electrolytes at 25, 30, 35, and 40°, only those obtained at 25° are given in Figs. 1 and 2. From Tables I and II, "effective" rigid molar volumes, V_e, were computed by employing an equation given by Breslau and Miller[13].

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

These values are presented in Tables III and IV. A graph of V_e *versus* C for sodium halides in aqueous D-mannitol solution at 25° is given in Fig. 3, and the plot of V_e

TABLE I

RELATIVE VISCOSITY (η/η_0) AT VARIOUS CONCENTRATIONS OF ELECTROLYTES IN AQUEOUS D-MANNITOL SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*NaCl* *Temperature (degrees)*				*NaBr* *Temperature (degrees)*				*NaI* *Temperature (degrees)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	1.380	1.369	1.362	1.357	1.292	1.283	1.280	1.279	1.203	1.202	1.201	1.200
2.50	1.300	1.290	1.286	1.282	1.227	1.217	1.214	1.212	1.150	1.149	1.147	1.141
2.00	1.226	1.219	1.214	1.209	1.168	1.159	1.157	1.152	1.103	1.101	1.100	1.093
1.50	1.160	1.155	1.148	1.145	1.118	1.109	1.105	1.101	1.066	1.064	1.061	1.053
1.00	1.105	1.097	1.091	1.086	1.075	1.065	1.063	1.055	1.037	1.032	1.028	1.020
0.75	1.078	1.070	1.066	1.059	1.054	1.045	1.042	1.032	1.027	1.019	1.017	1.007
0.50	1.052	1.045	1.039	1.032	1.036	1.028	1.027	1.015	1.018	1.008	1.004	0.997
0.375	1.039	1.033	1.026	1.018	1.032	1.020	1.019	1.006	1.015	1.005	0.998	0.990
0.250	1.032	1.021	1.013	1.005	1.023	1.013	1.010	0.998	1.011	1.001	0.994	0.988
0.125	1.022	1.008	0.998	0.992	1.014	1.002	0.996	0.989	1.006	0.994	0.989	0.984

TABLE II

RELATIVE VISCOSITY (η/η_0) AT VARIOUS CONCENTRATIONS OF ELECTROLYTES IN AQUEOUS D-MANNITOL SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*KCl* *Temperature (degrees)*				*KBr* *Temperature (degrees)*				*KI* *Temperature (degrees)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	1.027	1.036	1.054	1.066	0.975	0.990	1.009	1.020	0.934	0.947	0.971	0.983
2.50	1.015	1.024	1.036	1.045	0.965	0.977	0.993	1.002	0.927	0.935	0.957	0.965
2.00	1.006	1.012	1.019	1.028	0.962	0.971	0.985	0.990	0.932	0.935	0.951	0.955
1.50	1.001	1.002	1.005	1.014	0.963	0.968	0.979	0.979	0.935	0.939	0.947	0.949
1.00	0.997	0.997	0.998	1.001	0.969	0.970	0.972	0.974	0.944	0.945	0.949	0.950
0.75	0.997	0.996	0.994	0.994	0.976	0.973	0.973	0.972	0.952	0.953	0.957	0.958
0.50	0.996	0.995	0.991	0.988	0.983	0.978	0.976	0.973	0.966	0.965	0.963	0.961
0.375	0.996	0.994	0.990	0.986	0.987	0.981	0.978	0.975	0.974	0.970	0.967	0.965
0.250	0.995	0.993	0.989	0.983	0.989	0.981	0.979	0.976	0.982	0.974	0.972	0.967
0.125	0.994	0.989	0.986	0.980	0.993	0.987	0.981	0.978	0.990	0.983	0.977	0.971

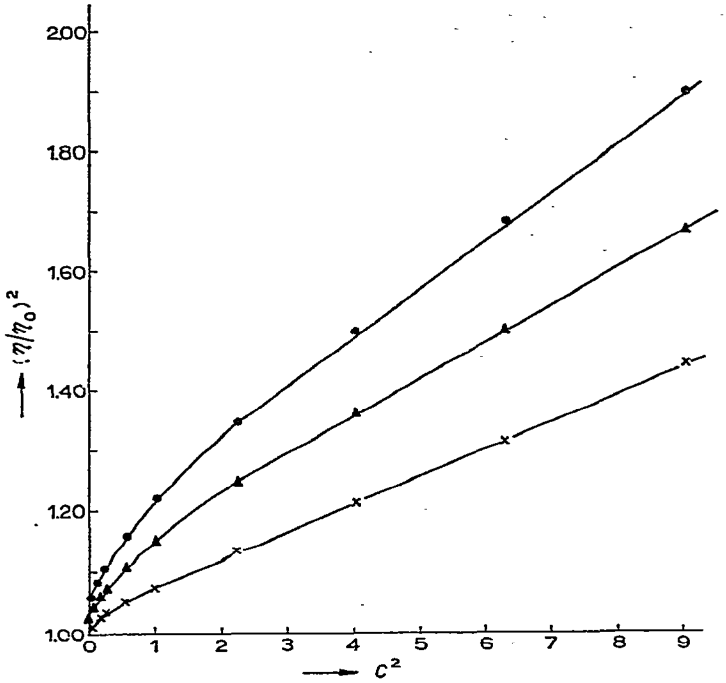


Fig. 1. Plot of $(\eta/\eta_0)^2$ against C^2 at 25°. [●, NaCl; ▲, NaBr; ×, NaI in aqueous D-mannitol solution.]

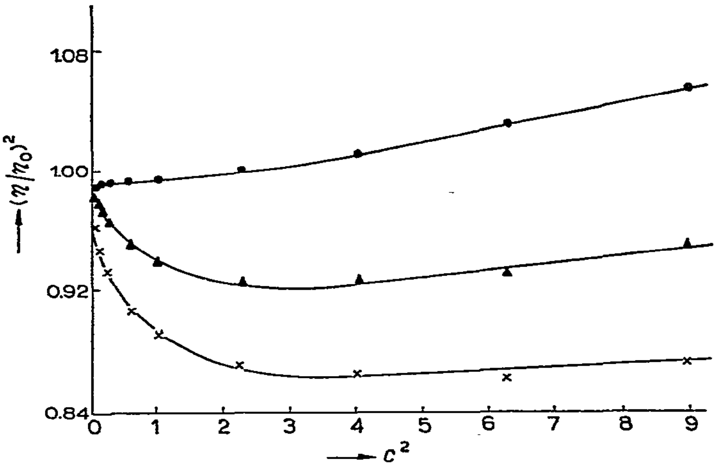


Fig. 2. Plot of $(\eta/\eta_0)^2$ against C^2 at 25°. [●, KCl; ▲, KBr; ×, KI in aqueous D-mannitol solution.]

versus C for sodium halides in aqueous (0.4M) D-xylose[9] solution at 25° is given in Fig. 4. The plots of V_e *versus* C for alkali halides in D-mannitol at 30° are given in Fig. 5. From the V_e values given in Tables III and IV, the average, effective, rigid, molar volumes, $\overline{V}_e$, were calculated, and, with the help of $\overline{V}_e$ values, apparent B

TABLE III

"EFFECTIVE", RIGID, MOLAR VOLUME (V_e) AT VARIOUS CONCENTRATIONS OF ALKALI HALIDES IN AQUEOUS D-MANNITOL SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*NaCl* *Temperature (degrees)*				*NaBr* *Temperature (degrees)*				*NaI* *Temperature (degrees)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	0.0354	0.0346	0.0341	0.0338	0.0288	0.0281	0.0279	0.0278	0.0214	0.0214	0.0213	0.0212
2.50	0.0354	0.0344	0.0340	0.0337	0.0282	0.0272	0.0269	0.0267	0.0199	0.0198	0.0196	0.0189
2.00	0.0352	0.0343	0.0336	0.0330	0.0276	0.0263	0.0259	0.0252	0.0179	0.0176	0.0175	0.0164
1.50	0.0351	0.0342	0.0329	0.0323	0.0270	0.0252	0.0244	0.0235	0.0160	0.0155	0.0149	0.0130
1.00	0.0366	0.0341	0.0322	0.0306	0.0270	0.0237	0.0230	0.0203	0.0140	0.0122	0.0107	0.0077
0.75	0.0373	0.0338	0.0320	0.0289	0.0266	0.0224	0.0210	0.0162	0.0138	0.0098	0.0088	0.0036
0.50	0.0386	0.0337	0.0294	0.0244	0.0273	0.0214	0.0207	0.0112	0.0140	0.0063	0.0031	−0.0024
0.375	0.0392	0.0335	0.0266	0.0186	0.0325	0.0206	0.0196	0.0063	0.0156	0.0052	−0.0021	−0.0108
0.250	0.0487	0.0325	0.0203	0.0079	0.0355	0.0203	0.0157	−0.0032	0.0172	0.0015	−0.0097	−0.0196
0.125	0.0678	0.0250	−0.0067	−0.0262	0.0435	0.0060	−0.0131	−0.0361	0.0187	−0.0196	−0.0361	−0.0529

TABLE IV

"EFFECTIVE", RIGID, MOLAR VOLUME (V_e) AT VARIOUS CONCENTRATIONS OF ALKALI HALIDES IN AQUEOUS D-MANNITOL SOLUTION AT DIFFERENT TEMPERATURES

Molarity	*KCl* *Temperature (degrees)*				*KBr* *Temperatures (degrees)*				*KI* *Temperature (degrees)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.00	0.0034	0.0045	0.0056	0.0080	−0.0034	−0.0013	0.0011	0.0025	−0.0100	−0.0078	−0.0040	−0.0023
2.50	0.0023	0.0037	0.0054	0.0067	−0.0059	−0.0038	−0.0011	0.0003	−0.0135	−0.0117	−0.0074	−0.0059
2.00	0.0011	0.0023	0.0036	0.0053	−0.0081	−0.0060	−0.0030	−0.0020	−0.0155	−0.0147	−0.0107	−0.0097
1.50	0.0002	0.0005	0.0013	0.0036	−0.0105	−0.0090	−0.0058	−0.0058	−0.0196	−0.0182	−0.0156	−0.0149
1.00	−0.0012	−0.0012	−0.0008	0.0003	−0.0130	−0.0126	−0.0117	−0.0108	−0.0248	−0.0243	−0.0224	−0.0219
0.75	−0.0016	−0.0021	−0.0032	−0.0032	−0.0133	−0.0150	−0.0150	−0.0156	−0.0279	−0.0273	−0.0247	−0.0241
0.50	−0.0032	−0.0040	−0.0073	−0.0097	−0.0139	−0.0182	−0.0200	−0.0226	−0.0288	−0.0297	−0.0316	−0.0334
0.375	−0.0042	−0.0064	−0.0097	−0.0152	−0.0141	−0.0209	−0.0243	−0.0278	−0.0290	−0.0337	−0.0372	−0.0397
0.250	−0.0080	−0.0113	−0.0179	−0.0280	−0.0179	−0.0314	−0.0348	−0.0400	−0.0297	−0.0435	−0.0470	−0.0559
0.125	−0.0196	−0.0361	−0.0461	−0.0665	−0.0229	−0.0428	−0.0630	−0.0734	−0.0328	−0.0562	−0.0768	−0.0979

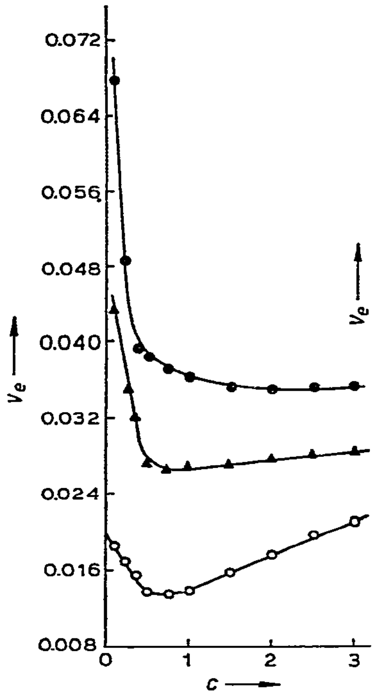
coefficient values were obtained for univalent electrolyte employing equation[13] *4*.

$$B = 2.90\ \bar{V}_e - 0.018 \qquad (4)$$

The apparent B coefficient values are given in Tables V–VII for different concentration of these electrolytes in aqueous D-mannitol solution.

It is evident from the plots of $(\eta/\eta_0)^2$ *versus* C^2, given in Figs. 1 and 2, that a straight-line behavior is shown at the higher concentrations of electrolytes in aqueous D-mannitol solution, whereas, in the region of lower concentrations (Einstein region), curves are obtained for all six salts at 25, 30, 35, and 40°. In the region of lower concentrations, the trend is different for all of these electrolytes in aqueous D-mannitol solution; sodium halides show a downward trend (see Fig. 1), potassium chloride shows a slight downward trend (see Fig. 2), and potassium bromide and iodide show an upward trend (see Fig. 2). This behavior is, perhaps, due to the different structural properties of the sodium and potassium ions in solution; sodium halides in aqueous solution show structure-making, and potassium halides show structure-breaking, behavior. Furthermore, a similar trend has been observed for alkali halides in aqueous solutions of sucrose[8] and D-xylose[9].

Fig. 3 gives a plot of V_e *versus* C for NaCl, NaBr, and NaI in aqueous D-



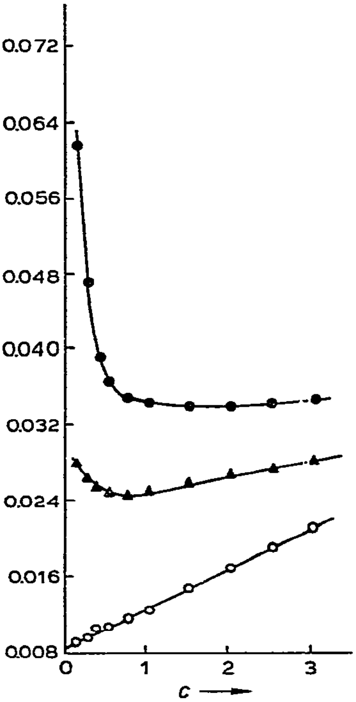


Fig. 3. (left) Plot of V_e against C at 25°. [●, NaCl; ▲, NaBr; ○, NaI in aqueous D-mannitol solution.]

Fig. 4. (right) Plot of V_e against C at 25°. [●, NaCl; ▲, NaBr; ○, NaI in aqueous D-xylose solution.]

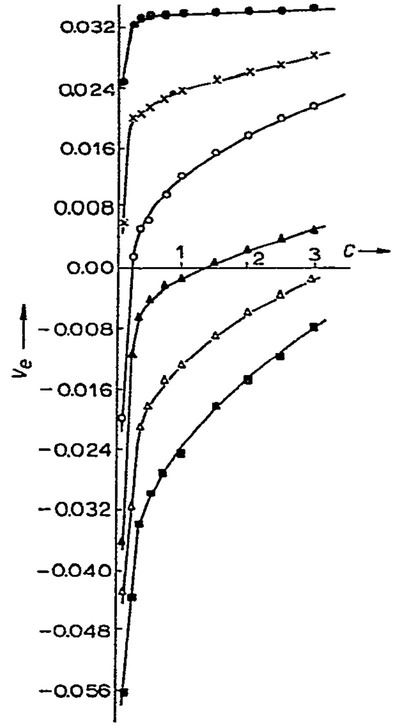


Fig. 5. Plot of V_e against C at 30°. [●, NaCl; ×, NaBr; ⊙, NaI; ▲, KCl; △, KBr; ■, KI in aqueous D-mannitol solution.)

mannitol solution at 25°. It may be seen that V_e decreases with increasing concentration (to attain a minimum), followed by an increase in V_e with further increase in concentration; thus, a systematic curve is obtained. This type of curve is observed only at 25° for sodium halides in aqueous D-mannitol solution. It may also be

TABLE V

APPARENT *B* COEFFICIENT OF ELECTROLYTES[a] IN AQUEOUS D-MANNITOL SOLUTION AT DIFFERENT TEMPERATURES

Salt	*Temperature (degrees)*			
	25	*30*	*35*	*40*
NaCl	0.101	0.078	0.060	0.045
NaBr	0.070	0.046	0.038	0.016
NaI	0.031	0.019	−0.004	−0.019
KCl	−0.027	−0.033	−0.038	−0.046
KBr	−0.053	−0.065	−0.069	−0.075
KI	−0.085	−0.095	−0.098	−0.106

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

TABLE VI

APPARENT *B* COEFFICIENT OF POTASSIUM HALIDES[a] IN AQUEOUS D-MANNITOL SOLUTION AT DIFFERENT TEMPERATURES

Salt	*Temperature (degrees)*			
	25	*30*	*35*	*40*
KCl	−0.016	−0.014	−0.012	−0.008
KBr	−0.044	−0.041	−0.035	−0.033
KI	−0.072	−0.068	−0.059	−0.056

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

TABLE VII

APPARENT *B* COEFFICIENT OF POTASSIUM HALIDES[a] IN AQUEOUS D-MANNITOL SOLUTION AT DIFFERENT TEMPERATURES

Salt	*Temperature (degrees)*			
	25	*30*	*35*	*40*
KCl	−0.043	−0.060	−0.077	−0.104
KBr	−0.068	−0.100	−0.121	−0.137
KI	−0.105	−0.136	−0.157	−0.182

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

noted that the upward trend becomes less pronounced on passing from NaCl to NaI. Similar curves are obtained for sodium halides in aqueous D-xylose[9] (0.4M) solution at the same temperature (shown in Fig. 4 for comparison). In these solutions also, the upward trend diminishes on passing from NaCl to NaI, and the effect is not observed in the water–D-xylose–sodium iodide system at 25°.

Fig. 5 gives plots of V_e *versus* C for alkali halides in aqueous D-mannitol solution at 30°. In these plots, the value of V_e decreases slowly with decrease in concentration, and, at the lower concentrations, the value of V_e decreases abruptly, so that a systematic curve is obtained. This type of curve is obtained for all six of the alkali halides at all of the temperatures used, except for sodium halides at 25° in both aqueous D-mannitol and D-xylose[9] solutions. Similar, systematic curves were reported by Eagland and Pilling[14] for concentrated, aqueous tetraalkylammonium halide solutions, but Breslau and Miller[13] were unable to observe such behavior for aqueous solutions of normal electrolytes; however, they noted that, at the higher concentrations of aqueous sodium and potassium halides, the V_e values were greater than at lower concentrations of these electrolytes.

The unusual, upward trend that is observed at 25° for sodium halides in aqueous D-mannitol and D-xylose solutions (shown in Figs. 3 and 4) could, perhaps, be ascribed to the structure-promotion brought about by D-mannitol and D-xylose. The addition of a structure-making agent that has many hydrogen-bonding sites may enhance the cluster-formation of water, thus leading to the build-up of superstructures. As the temperature is increased, these structures are disrupted. In the network type of model for liquid water, an average of 91 water molecules per cluster exist at 0°, decreasing to ~25 at 70°. It is well known that D-xylose is less structure-making than D-mannitol, and that the structure-breaking order of halide ions is $I^- > Br^- > Cl^-$. All these factors would tend to account for the rising portion of the curves and their subsequent decrease, due to compatibility, or incompatibility, of these structural influences of the solutes, or their tendency to orient water molecules[10,15-17].

The apparent *B* coefficient values for all six alkali halides (3–0.125M) in aqueous D-mannitol solution (0.4M) at 25, 30, 35, and 40° are listed in Table V. The apparent *B* coefficient values decrease with increasing temperature. The *B* coefficient decreases with increasing temperature; this favors the hydration effect, and, consequently, this behavior has been attributed to the ability of these ions to construct water structure in their vicinity, and thus to show a structure-making trend. It may be pointed out that potassium halides, although structure breakers in aqueous solution, behave as slight structure-makers in aqueous D-mannitol solution; this is due to the fact that D-mannitol possesses six hydrogen-bonding sites[10] that are closely bound to water molecules by hydrogen bonding. This effect dominates the structure-breaking properties of potassium halides, resulting in an overall, structure-making trend.

The apparent *B* coefficient values for potassium halides (3–0.75M) in aqueous D-mannitol (0.4M) solution at the four temperatures are listed in Table VI. The apparent *B* coefficient values increase with increased temperature. The *B* value usually decreases, often to a negative value[18,19], with increasing in the size of the ion, and, in such cases, *B* increases with increased temperature[20-22]. This is in the opposite direction for the hydration effects, and, consequently, this behavior has been attributed to the ability of these ions to disrupt water structure in their vicinity[19,23]. This shows that potassium halides in this concentration range show structure-breaking properties in aqueous D-mannitol solution, also in conformity with the behavior of potassium halides in aqueous solution alone. The apparent *B* coefficient value for four lower concentrations (0.5–0.125M) of potassium halides in aqueous D-mannitol solution, given in Table VII, shows a structure-making trend, due to the appreciable concentration of the D-mannitol in comparison to that of the potassium halides. The structure-making trend of alkali halides in aqueous D-mannitol solution is in the order: NaCl > NaBr > NaI > KCl > KBr > KI, and the structure-breaking trend of potassium salts in the concentration range 3–0.75M is in the order: KI > KBr > KCl.

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