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STUDIES ON THE VISCOSITY BEHAVIOR OF ALKALI HALIDES IN AQUEOUS D-XYLOSE SOLUTION

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ABSTRACT

The viscosity behavior of ternary systems comprising sodium or potassium halides (concentration range 0.125–3M) in aqueous D-xylose solution (0.4M) at 25, 30, 35, and 40° has been determined. It is found that Moulik's equation holds for such concentrated solutions beyond the Einstein region. Furthermore, the "effective" rigid molar volume and the apparent *B* coefficient have been computed from the relative viscosity data by employing the Breslau–Miller treatment. The results are explained in terms of the structure-making or -breaking effects in solution by analyzing the values of the apparent *B* coefficient obtained for different temperatures.

INTRODUCTION

The ion–solvent interaction in aqueous solution has been widely studied by various physicochemical techniques; however, the study of ternary systems comprising electrolyte–solvent–nonelectrolyte molecules has been the subject of only recent interest. A few ternary systems had been studied by Robinson and associates[1–4], but a clear understanding of ion–solvent, as well as electrolyte–nonelectrolyte, interaction has not yet emerged. Work by Vishnu and Misra[5,6] on the viscosity behavior of a few common electrolytes (*e.g.*, sodium and potassium halides) in aqueous sucrose and D-mannitol solutions has provided a new approach to the study, for ternary systems, of the structural changes produced by electrolytes in the presence of nonelectrolytes in aqueous solution.

In the present work, D-xylose was used as the nonelectrolyte, and its interactions with sodium and potassium halides in aqueous medium were investigated by employing viscosity measurements. It was already known that water molecules are bound around the D-xylose molecules, and that the D-xylose molecule acts as a structure maker[7]. However, relatively very few investigations have been made on aqueous D-xylose solutions. The Uedairas[7,8] measured the osmotic and activity coefficients of sodium benzenesulfonate and sodium *p*-toluenesulfonate in aqueous D-xylose solutions by the isopiestic, vapor-pressure method in order to study the interaction of the organic electrolyte with the solvent.

We here report data on the "effective" rigid molar volume and apparent *B* coefficient values obtained, for sodium and potassium halides in aqueous D-xylose solution, from the viscosity data by employing the following equations[9] (which have been used for concentrated solutions).

$$Ve = \frac{-2.5C + [(2.5C)^2 - 4(10.05C^2)(1 - \eta/\eta_0)]^{1/2}}{2(10.05)C^2} \qquad (1)$$

and

$$B = 2.90\ \overline{Ve} - 0.018, \qquad (2)$$

where Ve = "effective" rigid molar volume, $\overline{Ve}$ = average "effective" rigid molar volume, η = viscosity of the electrolyte-containing, nonelectrolyte solution, η_0 = viscosity of the nonelectrolyte solution, and C = the molar concentration.

The apparent B coefficient values have been used to interpret the structuring effect of ions and molecules in water. The viscosity data have been tested by using Moulik's equation[10], namely,

$$(\eta/\eta_0)^2 = M + KC^2 \qquad (3)$$

where M and K are constants, which holds good beyond the Einstein region.

Relative viscosity data have been obtained for NaX and KX (where X = Cl^-, Br^-, and I^-) in aqueous D-xylose (0.4M) solution in the concentration range of 0.125–3M over a temperature range of 25–40°. Equations *1* and *2* were employed for obtaining data on the "effective" rigid molar volume and apparent B coefficient for sodium and potassium halides in aqueous D-xylose solution, and the results used to express the structuring properties of ions in aqueous D-xylose solution.

EXPERIMENTAL

Materials, and preparation of solutions. — The salts (NaCl, NaBr, NaI, KCl, KBr, and KI) used in the present investigation were of analytical-reagent grade, obtained from B.D.H. and E. Merck. All of the salts were used as such, without further purification. The D-xylose used was of B.D.H. (Analar) grade, and was recrystallized from water–ethanol, and dried *in vacuo* over phosphorus pentaoxide at 100°.

All of the solutions were prepared, on a molar basis, in doubly distilled, demineralized, conductivity water (sp. cond. ~10^{-6} $ohm^{-1}.cm^{-1}$). A solution (0.4M) of D-xylose in conductivity water was used as a stock solution. By use of this stock solution of D-xylose, a 3M solution of the electrolyte was first prepared, and, by diluting this solution with the stock solution, other concentrations were obtained for measurements. To prevent evaporation, solutions were always kept in stoppered, Pyrex-glass vessels.

Density and viscosity measurements. — Viscosity and density values were determined at specified temperatures with the apparatus described previously[5].

TABLE I

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

Molarity	*NaCl Temperature*				*NaBr Temperature*				*NaI Temperature*			
	25°	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*
3.00	1.368	1.366	1.360	1.356	1.283	1.280	1.253	1.230	1.203	1.201	1.197	1.196
2.50	1.291	1.288	1.283	1.279	1.220	1.212	1.195	1.179	1.146	1.144	1.143	1.140
2.00	1.218	1.214	1.211	1.208	1.163	1.158	1.145	1.132	1.099	1.098	1.097	1.092
1.50	1.154	1.151	1.148	1.142	1.113	1.106	1.099	1.087	1.062	1.061	1.058	1.054
1.00	1.099	1.094	1.090	1.084	1.069	1.063	1.057	1.049	1.033	1.031	1.025	1.020
0.75	1.073	1.068	1.065	1.057	1.049	1.044	1.040	1.031	1.023	1.020	1.012	1.006
0.50	1.049	1.043	1.038	1.030	1.033	1.026	1.022	1.014	1.014	1.009	0.999	0.994
0.375	1.039	1.030	1.026	1.019	1.025	1.018	1.013	1.005	1.010	1.004	0.994	0.988
0.250	1.031	1.018	1.012	1.004	1.017	1.009	1.005	0.996	1.006	1.001	0.992	0.985
0.125	1.020	1.005	0.998	0.990	1.009	1.001	0.996	0.987	1.003	0.995	0.988	0.983

TABLE II

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

Molarity	*KCl Temperature*				*KBr Temperature*				*KI Temperature*			
	25°	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*
3.00	1.037	1.053	1.063	1.073	0.987	1.006	1.025	1.040	0.944	0.965	0.984	1.004
2.50	1.022	1.035	1.045	1.051	0.974	0.992	1.010	1.020	0.933	0.950	0.968	0.985
2.00	1.011	1.021	1.030	1.033	0.971	0.984	0.998	1.005	0.930	0.944	0.958	0.972
1.50	1.002	1.010	1.016	1.017	0.970	0.977	0.989	0.992	0.931	0.944	0.956	0.965
1.00	0.999	1.001	1.002	1.003	0.974	0.977	0.983	0.984	0.946	0.955	0.957	0.962
0.75	0.998	0.997	0.996	0.995	0.979	0.981	0.982	0.983	0.957	0.958	0.961	0.966
0.50	0.997	0.996	0.994	0.990	0.984	0.983	0.982	0.979	0.966	0.967	0.969	0.969
0.375	0.997	0.995	0.992	0.987	0.987	0.985	0.984	0.979	0.974	0.972	0.971	0.970
0.250	0.996	0.994	0.991	0.984	0.991	0.987	0.985	0.980	0.982	0.979	0.975	0.972
0.125	0.996	0.994	0.987	0.982	0.993	0.989	0.986	0.981	0.990	0.985	0.980	0.976

RESULTS AND DISCUSSION

The relative viscosity values (η/η_0) at 25, 30, 35, and 40° were calculated, for each of the sodium and potassium halides in aqueous D-xylose solution at different concentrations of electrolytes, from the respective measurements of flow time and density. These values are given in Tables I and II. The values of $(\eta/\eta_0)^2$ were computed from Tables I and II, and plotted against C^2. As these plots for all six salts under investigation showed similar trends at all four temperatures, only the plots

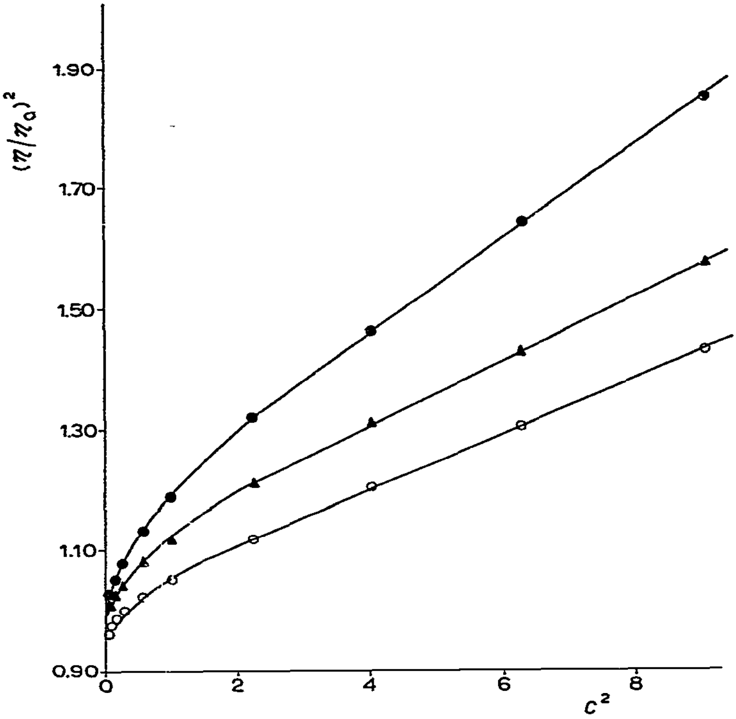

Fig. 1. Plot of $(\eta/\eta_0)^2$ *versus* C^2 at 35°.
[Key: (●) NaCl, (▲) NaBr, and (⊙) NaI, in aqueous D-xylose solution.]

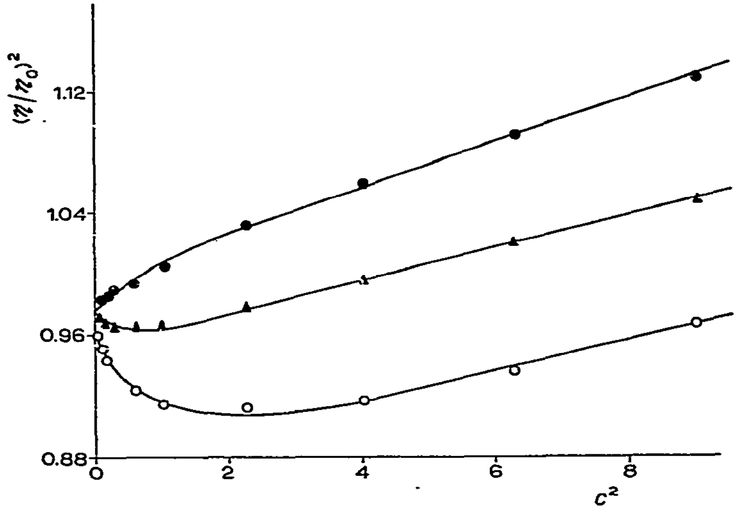

Fig. 2. Plot of $(\eta/\eta_0)^2$ *versus* C^2 at 35°.
[Key: (●) KCl, (▲) KBr, and (⊙) KI, in aqueous D-xylose solution.]

TABLE III

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

Molarity	*NaCl* *Temperature*				*NaBr* *Temperature*				*NaI* *Temperature*			
	25°	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*
3.00	0.0346	0.0344	0.0340	0.0337	0.0281	0.0279	0.0257	0.0238	0.0214	0.0213	0.0209	0.0208
2.50	0.0345	0.0342	0.0337	0.0334	0.0275	0.0267	0.0249	0.0232	0.0195	0.0192	0.0191	0.0188
2.00	0.0341	0.0336	0.0332	0.0328	0.0268	0.0261	0.0242	0.0223	0.0173	0.0172	0.0170	0.0162
1.50	0.0340	0.0334	0.0329	0.0317	0.0260	0.0246	0.0231	0.0206	0.0151	0.0149	0.0142	0.0133
1.00	0.0347	0.0331	0.0319	0.0299	0.0250	0.0230	0.0210	0.0182	0.0125	0.0118	0.0096	0.0077
0.75	0.0351	0.0329	0.0316	0.0280	0.0243	0.0220	0.0201	0.0157	0.0118	0.0103	0.0062	0.0031
0.50	0.0365	0.0323	0.0287	0.0229	0.0251	0.0199	0.0170	0.0109	0.0109	0.0070	−0.0008	−0.0048
0.375	0.0392	0.0305	0.0266	0.0196	0.0256	0.0186	0.0135	0.0052	0.0108	0.0042	−0.0064	−0.0130
0.250	0.0473	0.0279	0.0188	0.0063	0.0264	0.0141	0.0079	−0.0064	0.0094	0.0015	−0.0130	−0.0246
0.125	0.0618	0.0155	−0.0067	−0.0312	0.0281	0.0029	−0.0131	−0.0428	0.0092	−0.0164	−0.0395	−0.0562

TABLE IV

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

Molarity	*KCl* *Temperature*				*KBr* *Temperature*				*KI* *Temperature*			
	25°	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*	*25°*	*30°*	*35°*	*40°*
3.00	0.0046	0.0065	0.0076	0.0087	−0.0017	0.0007	0.0032	0.0050	−0.0082	−0.0049	−0.0021	0.0005
2.50	0.0034	0.0053	0.0067	0.0075	−0.0043	−0.0012	0.0015	0.0031	−0.0122	−0.0087	−0.0054	−0.0024
2.00	0.0021	0.0040	0.0057	0.0062	−0.0060	−0.0032	−0.0004	0.0009	−0.0160	−0.0124	−0.0090	−0.0058
1.50	0.0005	0.0026	0.0041	0.0044	−0.0084	−0.0063	−0.0029	−0.0021	−0.0210	−0.0165	−0.0127	−0.0099
1.00	−0.0004	0.0003	0.0007	0.0011	−0.0108	−0.0095	−0.0069	−0.0065	−0.0238	−0.0195	−0.0185	−0.0162
0.75	−0.0010	−0.0016	−0.0021	−0.0026	−0.0116	−0.0104	−0.0098	−0.0093	−0.0247	−0.0241	−0.0223	−0.0168
0.50	−0.0024	−0.0032	−0.0048	−0.0081	−0.0131	−0.0139	−0.0148	−0.0174	−0.0288	−0.0279	−0.0261	−0.0261
0.375	−0.0032	−0.0053	−0.0086	−0.0141	−0.0141	−0.0164	−0.0175	−0.0232	−0.0290	−0.0313	−0.0325	−0.0337
0.250	−0.0064	−0.0097	−0.0146	−0.0263	−0.0146	−0.0212	−0.0246	−0.0331	−0.0297	−0.0348	−0.0417	−0.0470
0.125	−0.0131	−0.0196	−0.0428	−0.0596	−0.0229	−0.0361	−0.0461	−0.0630	−0.0312	−0.0495	−0.0665	−0.0803

TABLE V

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

Salt	*Temperature*			
	25°	*30°*	*35°*	*40°*
NaCl	0.095	0.071	0.058	0.042
NaBr	0.058	0.041	0.029	0.008
NaI	0.022	0.008	−0.010	−0.023
KCl	−0.022	−0.023	−0.032	−0.042
KBr	−0.049	−0.051	−0.052	−0.060
KI	−0.083	−0.084	−0.086	−0.087

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

TABLE VI

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

Salt	*Temperature*			
	25°	*30°*	*35°*	*40°*
KCl	−0.014	−0.010	−0.007	−0.006
KBr	−0.039	−0.033	−0.026	−0.022
KI	−0.069	−0.060	−0.052	−0.042

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

TABLE VII

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

Salt	*Temperature*			
	25°	*30°*	*35°*	*40°*
KCl	−0.036	−0.046	−0.069	−0.096
KBr	−0.065	−0.082	−0.093	−0.117
KI	−0.104	−0.122	−0.139	−0.154

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

obtained at 35° are given (in Figs. 1 and 2). From the relative viscosity values, which are summarized in Tables I and II, values of the "effective" rigid molar volume, Ve, were obtained by employing equation I; the values of Ve are presented in Tables III and IV. By use of the Ve values, the average "effective" rigid molar volumes,

$\overline{Ve}$, were calculated. The apparent *B* coefficient values were obtained from the $\overline{Ve}$ values by employing equation *2*. The values of the apparent *B* coefficients for these salts are given in Tables V, VI, and VII.

The plots of $(\eta/\eta_0)^2$ *versus* C^2 given in Figs. 1 and 2 show a trend to a straight line at higher concentrations of the electrolytes, whereas, in the region of lower concentrations (Einstein region), a curve is obtained. This proves the validity of Moulik's equation for all six salts at all four temperatures. Examination of the plots within the Einstein region revealed that the behavior differs for all of these salts in the presence of aqueous D-xylose solution: sodium halides show a downward trend (Fig. 1), potassium chloride shows only a slight, downward trend (Fig. 2), and for potassium bromide and iodide, there is an upward trend (Fig. 2). This difference in behavior may, perhaps, be due to different structural properties of sodium and potassium ions in solution. In aqueous solution, sodium halides behave as structure makers, whereas potassium halides behave as structure breakers (with respect to water). A similar trend has been observed by us for aqueous sucrose and D-mannitol solutions[5,6].

It has been observed that the apparent *B* values for sodium halides in aqueous sucrose and D-mannitol solutions decrease with increasing temperatures, whereas the apparent *B* coefficient values obtained for potassium halides (in the higher ranges of concentration) increase with rise in temperature, an observation in conformity with the results of Kay and co-workers[11]. However, it is interesting that, in all structural-hydration interactions[12], two solutes will attract each other if their structural influences are similar in nature, resulting in an increase of viscosity and an overall, structure-making effect, but will repel one another if their influences are opposite in nature, thereby showing an overall, structure-breaking effect.

The values of the *B* coefficient are listed in Table V for the concentration range of 3–0.125M (number of data points used, 10) for all six alkali halides at a fixed concentration (0.4M) of aqueous D-xylose solution; the values of the *B* coefficient decrease with increasing temperature, thus showing a structure-making trend. It is interesting that potassium chloride, although a structure breaker in aqueous solution, shows a slight, structure-making trend in aqueous D-xylose solution, owing to the fact that D-xylose possesses many hydrogen-bonding sites (but fewer than sucrose and D-mannitol), that are closely bound to water molecules by hydrogen bonding. This effect dominates the structure-breaking properties of potassium halides, resulting in a overall, structure-making trend.

However, examination of the data listed in Table VI for the apparent *B* coefficients of potassium halides in aqueous D-xylose solution for the concentration range 3–0.75M (number of data points, 6 only) reveals that the values of the *B* coefficients increase with increasing temperature; this shows that, in this concentration range, potassium halides have structure-breaking properties in aqueous D-xylose solution, a result also in conformity with the behavior of potassium halides in aqueous solution alone. Table VII gives the data for four lower concentrations (0.5–0.125M) of potassium halides in aqueous D-xylose solution; if these data, only, are examined, a structure-making trend, due to the appreciable concentration of D-xylose in comparison to that of the potassium halide, is seen.

The structure-breaking effect of potassium salts in the concentration range of 3–0.75M is in the order: KI > KBr > KCl. The over-all, structure-making order of potassium salts over the concentration range of 3–0.125M in aqueous D-xylose solution is KCl > KBr > KI, and the structure-making trend of sodium salts in aqueous D-xylose solution are in the order: NaCl > NaBr > NaI.

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