Viscosity *B*-Coefficient for Sodium Chloride in Aqueous Mixtures of 1,4-Dioxane at Different Temperatures

Renato Tomaš,[1,]* Toni Jovanović[1] and Marija Bešter-Rogač[2]

[1] *Faculty of Chemistry and Technology, University of Split, Nikole Tesle 10, HR-21000 Split, Croatia.*

[2] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia.*

* *Corresponding author: E-mail: rtomas@ktf-split.hr*

Dedicated to prof. Jože Koller on the occasion of his 70th birthday.

Abstract

Viscosities of sodium chloride solutions in water–1,4-dioxane binary mixtures with mole fractions of 1,4-dioxane, x_D = 0.05, 0.10, 0.15 and 0.20, in the temperature range from 278.15 to 318.15 K were determined. The relative viscosity data have been analyzed and interpreted in terms of the rearranged Jones-Dole equation, $(\eta_r - 1) - Ac^{1/2} = Bc$. The viscosity *A*-coefficients were calculated from Falkenhagen and Vernon theory by help of the literature limiting ionic conductivity data and *B*-coefficients were estimated from linear plots. All *B*-coefficients obtained for NaCl water–1,4-dioxane binary mixtures are positive at all temperatures. These data were compared with the data for NaCl in aqueous medium at different temperatures reported in literature. The ion-ion, ion-solvent and solvent -solvent interactions have been discussed.

Keywords: Sodium chloride, water–1,4-dioxane binary mixtures, viscosity data, viscosity *B*-coefficient, ions-solvent interactions

1. Introduction

Viscometric studies of electrolyte solutions have been often used in order to obtain information regarding solute-solvent interactions. Whereas viscosity of electrolyte solutions has been widely studied in water and organic solvents,[1,2] less consideration has been devoted to solutions in solvent mixtures. A survey of the literature on the viscosity data of electrolytes solutions in aqueous mixtures with organic solvents shows that they were determined mostly for 1,1 type of electrolytes and usually at one or only several temperatures in aqueous mixtures of formamide,[3,4] *N,N*-dimethylformamide,[5] dimethylsulfoxide,[6] acetone,[7] dimethylacetamide,[8] 2-ethoxyethanol,[9] methanol,[10,11] ethylene glycol[12,13] and *tert*-butanol.[14]

Among aqueous mixtures water–1,4-dioxane mixtures permit the widest variation of the solvent permittivity ranging from 2.21 to 78.36 in pure 1,4-dioxane and in water at 298.15 K, respectively.[15] Thus, these mixtures have been used as a favourite solvent system to study ion-ion, solvent-ion and solvent-solvent interaction.[16–19] Surpri-

singly, there is a lack of the viscometric studies of electrolyte solutions in these mixtures. To our best knowledge there are only two investigation dealing with viscosity of electrolytes in water–1,4-dioxane mixtures. In 1973 Fuoss and Reynolds reported viscosity data for alkali metal halides and tetraalkylammonium salts in water–1,4-dioxane mixtures containing 0–63 mass % of 1,4-dioxane at 298.15 K.[20] Das and Das investigated viscosities of NaCl, NaBr, NaNO_3, KCl, KBr and KNO_3 solutions in water–1,4-dioxane mixtures with 10, 20 and 30 mass % of 1.4-dioxane, and at four ranging from 303.15 to 328.15 K.[21] Unfortunately in this paper no experimental data are given.

In the present work precise viscometric data for NaCl in water–1,4-dioxane binary mixtures (with mole fraction of 1,4-dioxane, x_D = 0.05, 0.10, 0.15, and 0.20) in the concentration range $0.05 \leq c/$ moldm$^{-3}\leq 0.30$ at nine temperatures (from 278.15 to 318.15 K in step of 5 K) are reported. The relative viscosity data, η_r, have been analysed and interpreted in terms of the rearranged Jones-Dole equation, $(\eta_r - 1) - Ac^{1/2} = Bc$. From the reported limiting ionic conductivity data,[16,17] the viscosity *A*-coefficients

have been calculated from Falkenhagen and Vernon theory.[2,22] Viscosity *B*-coefficient were determined, compared with those reported for NaCl in water[2] and in water-1,4-dioxane mixtures at 298.15 K[20] and discussed in terms of ion-solvent interactions.

2. Experimental

2. 1. Materials

1,4-dioxane (Merck, *p.a.*) was used without further purification. Demineralized water was bi-distilled in a quartz apparatus (DESTAMAT Bi18E, Heraeus). The final product with a specific conductivity of less than 0.5 μS cm⁻¹ was applied. Sodium chloride (NaCl, Merck, *p.a.,* ≥99.5%) was dried before use at 130 °C for 24 h. The mixed solvents were prepared by weighing and stock solutions were prepared by adding of weighed amount of solvent to weighed amount of NaCl. Solutions of definite molality were prepared by weighing the pure mixed solvent and the stock solution of NaCl in a particular mixed solvent. The molarity, *c* can be determined from the molality and density data by means of the relation:

$$c = \frac{1000\,\rho\,m}{(1000 + m\,M)} \quad (1)$$

where *m* is the molality of solution (moles of electrolyte per kilogram of solvent), ρ is the density of solution, and *M* is the molar mass of sodium chloride. Taking into account the sources of errors (impurities, weighing, …), concentrations *c* are accurate ± 0.0001 mol dm⁻³.

2. 2. Viscosity and Density Measurements

The viscosites of solutions were determined with a micro Ubbelohde viscometer (SI Analytics GmbH, Mainz, Germany, type and capillary no. 53610/I) and an automatic flow time measuring system ViscoSystem® AVS 370. The viscometer was immersed in a transparent thermostat bath with the precision of the set temperature better than 0.01 K. Each measurement was automatically repeated at least five times and yielded a reproducibility of the flow time of better than 0.02 %. The kinematic viscosity of solutions, *v* (m² s⁻¹), was calculated from the equation[23] $v = C \cdot t - E/t^2$, where *t* (s) is the flow time, *C* and *E* are constants characteristic for the viscometer and were determined by calibration of the viscometer with water. The values of $C = 1.00772 \times 10^{-8}$ m² s⁻² and $E = -4.9602 \times 10^{-5}$ m² s were determined by using the kinematic viscosity of water (v (293.15 K) = 1.0038 × 10⁻⁶ m² s⁻¹ and v (298.15 K) = 0.8929 × 10⁻⁶ m² s⁻¹))[24] and the flow times at 293.15 K and 298.15 K. The absolute (dynamic) viscosity, η (Pa s = kg m⁻¹ s⁻¹), was obtained from the relation, $\eta = v \rho$, where ρ (kg m⁻³) is the density of investigated solution, which was determined at each tempe-

rature (± 0.005 K) by the method of Kratky *et al.*[25] using Anton Paar density meter DMA 5000 (Anton Paar, Graz, Austria) with a declared reproducibility ~5 × 10⁻³ kg m⁻³. The errors from calibration and temperature control yield an uncertainty of 0.05% of absolute viscosity.

3. Results and Discussion

The measured viscosity, η, and density, ρ, data for the solutions of NaCl at all operating temperatures in water–1,4-dioxane binary mixtures with mole fraction of dioxane, x_D = 0.05, 0.10, 0.15, and 0.20 are presented in Tables 1–4, and in Figures S1 – S4 in Supporting information. It is evident that density and viscosity continually increase with increasing concentration of NaCl and increasing content of 1,4-dioxane in the mixture and decreases with increasing temperature in all investigated systems.

A comparison between densities, ρ_0, and viscosities, η_0, of the solvent mixtures as determined in our work and the literature data[16,26,27] at 293. 15 and 303.15 K shows an excellent agreement (Figure S5 in Supporting information).

The relative viscosity, η_r, of electrolyte solution is related to the molarity, *c*, according to the Jones-Dole equation:

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (2)$$

where η and η_0 are the viscosities of the solution and solvent, respectively. Eq. (1) in this form, is used by the most of authors for processing viscosity data.[22,28] At higher concentration ($c > 0.5$ mol dm⁻³) a quadratic term Dc^2 is added in eq. (2) and that expression is known as Kaminsky relation.[29] Viscosity coefficients *A*, *B*, and *D* depend on the solute, the solvent, and the temperature.

The viscosity *A*-coefficient is a measure of long-range ion-ion interactions, and the viscosity *B*-coefficient depends on ion-solvent interactions.[2,30] The *A* and *B* coefficients can be obtained from the intercept and the slope of the straight line using Eq. (2) in the next form

$$(\eta_r - 1) - A \cdot c^{1/2} = B \cdot c \quad (3)$$

Thus determined *A*-values should be positive, while *B*-values can be positive or negative. Furthermore, if the limiting molar conductivities of the constituent ions are known, *A*-value can be calculated theoretically from the ionic interaction theory by Falkenhagen and Vernon[2,22] by help of the relation[28]

$$A = \frac{0.2577 \Lambda^\infty}{\eta_0 (\varepsilon_r T)^{1/2}\,\lambda_+^\infty \lambda_-^\infty}\left[1 - 0.6863\left(\frac{\lambda_+^\infty - \lambda_-^\infty}{\Lambda^\infty}\right)^2\right] \quad (4)$$

where ε_r is relative permittivity of the solvent and Λ^∞, λ_+^∞, and λ_-^∞ are limiting molar conductivities of the electrolyte, cation, and anion respectively, at temperature *T*.

Table 1. Experimental densities, ρ, and viscosities, η, as function of concentration, c, of NaCl solution in water-1,4-dioxane mixtures with mole fraction of 1,4- dioxane, $x_D = 0.05$ at different temperatures.

c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s
	$T = 278.15$ K			$T = 293.15$ K			$T = 308.15$ K	
0	1.022388	2.3061	0	1.016686	1.4614	0	1.009405	1.0144
0.0511	1.024616	2.3238	0.0508	1.018802	1.4783	0.0504	1.011565	1.0234
0.1021	1.026697	2.3438	0.1015	1.020837	1.4895	0.1008	1.013606	1.0325
0.1530	1.028743	2.3577	0.1521	1.022884	1.4990	0.1510	1.015502	1.0407
0.2038	1.030942	2.3689	0.2026	1.024967	1.5092	0.2012	1.017606	1.0468
0.2545	1.032731	2.3798	0.2531	1.027012	1.5174	0.2512	1.019622	1.0531
0.3052	1.035021	2.4047	0.3034	1.028953	1.5313	0.3012	1.021537	1.0627
	$T = 283.15$ K			$T = 298.15$ K			$T = 313.15$ K	
0	1.020564	1.9555	0	1.014426	1.2848	0	1.006727	0.9131
0.0510	1.022863	1.9799	0.0507	1.016517	1.2971	0.0503	1.008864	0.9207
0.1019	1.024991	1.9921	0.1013	1.018598	1.3026	0.1005	1.010911	0.9297
0.1527	1.027038	2.0046	0.1518	1.020603	1.3153	0.1506	1.012804	0.9355
0.2034	1.029094	2.0156	0.2022	1.022659	1.3216	0.2006	1.014897	0.9400
0.2540	1.031001	2.0252	0.2525	1.024688	1.3335	0.2506	1.016902	0.9484
0.3046	1.033217	2.0433	0.3027	1.026653	1.3369	0.3004	1.018806	0.9554
	$T = 288.15$ K			$T = 303.15$ K			$T = 318.15$ K	
0	1.018775	1.6845	0	1.011946	1.1262	0	1.003919	0.8249
0.0509	1.020893	1.7031	0.0506	1.014158	1.1398	0.0502	1.005910	0.8297
0.1017	1.022998	1.7134	0.1010	1.016174	1.1501	0.1002	1.008089	0.8382
0.1524	1.025043	1.7242	0.1514	1.018116	1.1599	0.1502	1.009981	0.8440
0.2031	1.027130	1.7339	0.2017	1.020186	1.1640	0.2001	1.012063	0.8512
0.2536	1.029192	1.7449	0.2519	1.022259	1.1727	0.2499	1.014060	0.8583
0.3040	1.031190	1.7596	0.3020	1.024156	1.1847	0.2995	1.015851	0.8627

Table 2. Experimental densities, ρ, and viscosities, η, as function of concentration, c, of NaCl solution in water-1,4-dioxane mixtures with mole fraction of 1,4- dioxane, $x_D = 0.10$ at different temperatures.

c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s
	$T = 278.15$ K			$T = 293.15$ K			$T = 308.15$ K	
0	1.036924	2.9318	0	1.028437	1.8370	0	1.019026	1.2476
0.0511	1.039070	2.9642	0.0507	1.030495	1.8539	0.0502	1.021071	1.2641
0.1023	1.041146	2.9823	0.1014	1.032545	1.8703	0.1005	1.023104	1.2771
0.1538	1.043129	3.0018	0.1525	1.034507	1.8814	0.1511	1.025053	1.2828
0.2054	1.045281	3.0288	0.2037	1.036616	1.8963	0.2019	1.027136	1.2991
0.2573	1.047019	3.0554	0.2552	1.038364	1.9189	0.2528	1.028901	1.3112
0.3094	1.049527	3.0873	0.3069	1.040800	1.9395	0.3041	1.031284	1.3189
	$T = 283.15$ K			$T = 298.15$ K			$T = 313.15$ K	
0	1.034227	2.4840	0	1.025398	1.6018	0	1.015692	1.1152
0.0509	1.036303	2.5095	0.0505	1.027450	1.6202	0.0500	1.017737	1.1320
0.1020	1.038374	2.5252	0.1011	1.029495	1.6342	0.1002	1.019766	1.1430
0.1534	1.040348	2.5470	0.1521	1.031450	1.6430	0.1506	1.021713	1.1513
0.2049	1.042483	2.5670	0.2031	1.033548	1.6604	0.2012	1.023790	1.1622
0.2566	1.044226	2.5871	0.2544	1.035301	1.6837	0.2520	1.025561	1.1697
0.3086	1.046706	2.6164	0.3060	1.037716	1.7030	0.3031	1.027932	1.1847
	$T = 288.15$ K			$T = 303.15$ K			$T = 318.15$ K	
0	1.031380	2.1268	0	1.022261	1.4067	0	1.012259	1.0037
0.0508	1.033445	2.1453	0.0504	1.024309	1.4209	0.0499	1.014306	1.0142
0.1017	1.035506	2.1620	0.1008	1.026347	1.4305	0.0998	1.016334	1.0309
0.1529	1.037474	2.1738	0.1516	1.028299	1.4404	0.1501	1.018279	1.0376
0.2043	1.039595	2.1995	0.2025	1.030389	1.4595	0.2005	1.020354	1.0481
0.2559	1.041388	2.2155	0.2536	1.032146	1.4756	0.2512	1.022129	1.0539
0.3077	1.043795	2.2406	0.3050	1.034545	1.4932	0.3021	1.024490	1.0676

Table 3. Experimental densities, ρ, and viscosities, η, as function of concentration, c of NaCl solution in water-1,4-dioxane mixtures with mole fraction of 1,4- dioxane, $x_D = 0.15$ at different temperature.

c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s
	T = 278.15 K			T = 293.15 K			T = 308.15 K	
0	1.045452	3.3327	0	1.035198	2.0895	0	1.024294	1.4125
0.0515	1.047771	3.3636	0.0510	1.037504	2.1082	0.0505	1.026603	1.4288
0.1031	1.049789	3.4111	0.1021	1.039571	2.1364	0.1011	1.028707	1.4524
0.1551	1.051892	3.4473	0.1536	1.041719	2.1605	0.1520	1.030855	1.4803
0.2072	1.054086	3.4884	0.2051	1.043886	2.1890	0.2030	1.033071	1.4990
0.2594	1.056172	3.5226	0.2569	1.045993	2.2078	0.2543	1.035207	1.5090
0.3120	1.058264	3.5661	0.3090	1.048112	2.2496	0.3059	1.037359	1.5338
	T = 283.15 K			T = 298.15 K			T = 313.15 K	
0	1.042102	2.8262	0	1.031640	1.8333	0	1.020403	1.2638
0.0513	1.044417	2.8567	0.0508	1.033946	1.8483	0.0503	1.022270	1.2864
0.1028	1.046451	2.8990	0.1018	1.036027	1.8698	0.1007	1.024834	1.3051
0.1546	1.048599	2.9378	0.1531	1.038175	1.8989	0.1514	1.026982	1.3228
0.2065	1.050751	2.9765	0.2045	1.040356	1.9235	0.2023	1.029218	1.3328
0.2586	1.052845	3.0101	0.2560	1.042247	1.9442	0.2533	1.031359	1.3544
0.3110	1.054945	3.0480	0.3080	1.044601	1.9742	0.3047	1.033520	1.3770
	T = 288.15 K			T = 303.15 K			T = 318.15 K	
0	1.038685	2.4198	0	1.028006	1.6008	0	1.016632	1.1485
0.0512	1.040990	2.4524	0.0507	1.030324	1.6167	0.0501	1.018814	1.1699
0.1025	1.043039	2.4890	0.1014	1.032407	1.6368	0.1003	1.020996	1.1762
0.1541	1.045187	2.5230	0.1525	1.034555	1.6596	0.1508	1.023144	1.1874
0.2058	1.047346	2.5586	0.2037	1.036752	1.6812	0.2015	1.025405	1.2071
0.2578	1.049447	2.6003	0.2552	1.038870	1.7035	0.2524	1.027545	1.2178
0.3100	1.051558	2.6285	0.3069	1.041011	1.7395	0.3036	1.029714	1.2364

Table 4. Experimental densities, ρ, and viscosities, η, as function of concentration, c, of NaCl solution in water-1,4-dioxane mixtures with mole fraction of 1,4- dioxane, $x_D = 0.20$ at different temperatures.

c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s	c / mol dm^{-3}	ρ / g cm^{-3}	η / mPa s
	T = 278.15 K			T = 293.15 K			T = 308.15 K	
0	1.05074	3.5444	0	1.03920	2.2420	0	1.02715	1.5131
0.0518	1.05306	3.6031	0.0512	1.04150	2.2680	0.0506	1.02946	1.5392
0.1036	1.05508	3.6543	0.1025	1.04357	2.3080	0.1013	1.03157	1.5587
0.1559	1.05718	3.7045	0.1542	1.04572	2.3514	0.1524	1.03371	1.5820
0.2082	1.05938	3.7568	0.2059	1.04789	2.3745	0.2036	1.03593	1.5963
0.2608	1.06146	3.8076	0.2580	1.04999	2.3927	0.2551	1.03807	1.6147
0.3136	1.06355	3.8630	0.3102	1.05211	2.4197	0.3067	1.04022	1.6372
	T = 283.15 K			T = 298.15 K			T = 313.15 K	
0	1.04695	3.0064	0	1.03523	1.9552	0	1.02300	1.3537
0.0516	1.04926	3.0570	0.0510	1.03754	1.9783	0.0504	1.02530	1.3799
0.1033	1.05130	3.0984	0.1021	1.03962	2.0019	0.1009	1.02743	1.3936
0.1553	1.05345	3.1401	0.1536	1.04177	2.0258	0.1518	1.02958	1.4099
0.2074	1.05560	3.1823	0.2052	1.04395	2.0552	0.2028	1.03181	1.4269
0.2599	1.05769	3.2230	0.2570	1.04606	2.0740	0.2541	1.03395	1.4398
0.3125	1.05979	3.2673	0.3090	1.04820	2.1205	0.3055	1.03612	1.4551
	T = 288.15 K			T = 303.15 K			T = 318.15 K	
0	1.04311	2.5757	0	1.03122	1.7027	0	1.01876	1.2145
0.0514	1.04541	2.6199	0.0508	1.03354	1.7283	0.0502	1.02104	1.2363
0.1029	1.04746	2.6538	0.1017	1.03562	1.7502	0.1005	1.02323	1.2475
0.1547	1.04961	2.6891	0.1530	1.03777	1.7746	0.1512	1.02537	1.2618
0.2067	1.05177	2.7284	0.2044	1.03997	1.8072	0.2020	1.02763	1.2811
0.2590	1.05387	2.7624	0.2561	1.04208	1.8248	0.2530	1.02977	1.2913
0.3113	1.05598	2.8034	0.3079	1.04423	1.8561	0.3043	1.03194	1.3102

In present study, the rearranged Jones-Dole equation (3) was applied. By help of the values of relative permittivity[16] and viscosity (from present study) of the solvent, and limiting molar conductivities[16] of the NaCl (Λ^∞), Na$^+$ (λ_+^∞), and Cl$^-$ (λ_-^∞) at temperature T, values of A-coefficients were calculated using equation (4). Applied parameters are given in Table 5 and Table S1 in Supporting information, whereas in Table 6 the values of estimated A-coefficients are listed.
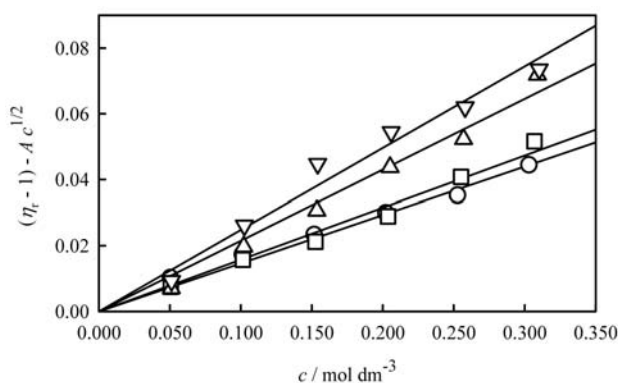
Figure 1. Plots of $(\eta_r - 1) - Ac^{1/2}$ against c for NaCl in water–1,4-dioxane mixtures at 293.15 K. Experimental values: O, $x_D = 0.05$; □, $x_D = 0.10$; △, $x_D = 0.15$; ▽, $x_D = 0.20$. Full lines are linear fits starting from the origin, and from their slopes B-coefficients were determined.
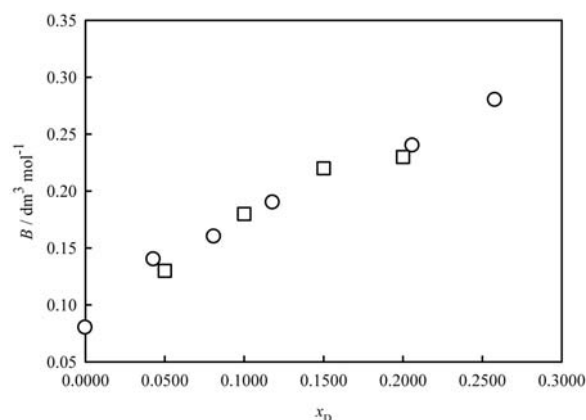

Figure 2. Viscosity B-coefficients for NaCl in water–1,4-dioxane mixtures at 298.15 K: (□), this work; (O), Ref. 20.

Table 5. The parameters of Falkenhagen and Vernon eq. (4) for NaCl in water–1,4-dioxane mixtures at 293.15 K.

Input data in Eq. (4)[a]	$x_D = 0.05$	$x_D = 0.10$	$x_D = 0.15$	$x_D = 0.20$
λ_+^∞/ S cm^2 mol^{-1}	33.07	25.50	21.99	19.35
λ_-^∞/ S cm^2 mol^{-1}	48.19	36.42	31.05	26.97
Λ^∞ / S cm^2 mol^{-1}	81.26	61.92	53.04	46.32
ε_r	63.344	50.271	40.940	32.421

[a]Values are interpolated or extrapolated from literature data.[16]

In Figure 1 the plot of $(\eta_r - 1) - Ac^{1/2}$ (rearranged Jones-Dole eq. (3)) in dependence on concentration, c, at 293.15 K is presented. From the slopes viscosity B-coefficients were estimated by the assumption that the straight line must cross the origin. Obtained B-coefficients are gathered in Table 7 for all investigated systems at all temperatures together with the literature data for NaCl in water.[2]

A comparison between obtained B-coefficients for NaCl in water–1,4-dioxane mixtures at 298.15 K with the literature data[20] shows a reasonable agreement (Figure 2).

Table 6. A-coefficients as calculated from Falkenhagen and Vernon eq. (4) for NaCl in water–1,4-dioxane mixtures at different temperatures.[a]

| T / K | x_D | | | |
	0.05	0.10	0.15	0.20
278.15	0.0061	0.0071	0.0081	0.0098
283.15	0.0062	0.0072	0.0083	0.0100
288.15	0.0063	0.0074	0.0084	0.0101
293.15	0.0064	0.0075	0.0085	0.0102
298.15	0.0065	0.0076	0.0086	0.0104
303.15	0.0067	0.0078	0.0088	0.0106
308.15	0.0067	0.0079	0.0090	0.0108
313.15	0.0068	0.0080	0.0091	0.0110
318.15	0.0069	0.0082	0.0092	0.0112

[a]Unit: A, dm$^{3/2}$ mol$^{-1/2}$

Viscosity A-coefficients, listed in Table 6, are positive at all temperatures. As stated, they depend on the relative permittivity and viscosity of the solvent, but also on the charge and the mobilities of ions and finally on temperature as well. Very small positive A-values suggest the presence of relative weak ion-ion interaction (Coulombic forces). From Table 6 thus it can be concluded that Coulombic forces are stronger in systems with higher content of 1,4-dioxane – as it is expected due to lower permittivity of solvent mixture – and at higher temperatures.

The B-coefficients are positive (Table 7) at all temperatures and bigger than A-coefficients (Table 6), showing the dominance of ions-solvent interaction over ions-ions interaction. This finding can be confirmed by small association constant, K_A, of NaCl in water–1,4-dioxane

Table 7. The viscosity *B*-coefficients for NaCl in water–1,4-dioxane mixtures at different temperatures.[a]

T / K	x_D				
	0.00[b]	0.05	0.10	0.15	0.20
278.15	0.034	0.124	0.151	0.206	0.267
283.15	0.053	0.129	0.152	0.235	0.260
288.15	0.063	0.137	0.155	0.264	0.263
293.15	0.071	0.146	0.158	0.215	0.248
298.15	0.080	0.129	0.174	0.221	0.231
303.15	0.083	0.160	0.181	0.241	0.266
308.15	0.088	0.145	0.181	0.265	0.249
313.15	0.093	0.141	0.190	0.271	0.234
318.15	0.098	0.142	0.196	0.225	0.237

[a]Unit: *B*, dm³ mol⁻¹ [b]Data from Ref. 2.

mixtures with low content of 1,4-dioxane. As reported in[16] K_A (x_D=0.0575) = ~ 5, K_A (x_D=0.1104) = ~ 8 and K_A (x_D=0.2000) = ~ 24 at 298.15 K.

At given temperature, the *B*-coefficients mostly follow the order: *B* (x_D = 0.00) < *B* (x_D = 0.05) < *B* (x_D = 0.10) < *B* (x_D = 0.15) < *B* (x_D = 0.20). This increase in the *B*-coefficient with increasing 1,4-dioxane content in the mixture may be attributed to the stronger ions-solvent interactions.[28]

According to classification in literature for water medium,[2,30] chloride ion is water-structure-breaking ion (*B* < 0), while sodium ion is weak water-structure-making ion (*B* > 0) (or borderline case). Furthermore, it is well known that the NaCl in water has a structure-breaking nature, thus chloride ion exhibits positive temperature coefficient, d*B*/d*T* = 0.0014 dm³ mol⁻¹ K⁻¹, while for sodium ion this value is zero at 298.15 K.[2]

From Table 7 it is evident that viscosity *B*-coefficients for NaCl in solutions with x_D = 0.05, 0.10, and 0.15 show the trend of an increase with the temperature (d*B*/d*T* > 0) what can be attributed to a structure-breaking nature of NaCl in these systems. Namely, with raising temperature hydrogen bonds are breaking and thus less structured water can be influenced by the ionic solute.[20]

Small change of the B-value with temperature for x_D = 0.20 may be ascribed to the weakening of the ions-solvent interactions in comparison to solvent-solvent interactions. It is worth to mention, that water–1,4-dioxane binary mixtures show maximum in viscosity at x_D ≈ 0.25[26,27,31] which can be ascribed to the strong interaction between 1,4-dioxane and water molecules.

4. Conclusions

In present work, the *B*-coefficients of NaCl in water–1,4-dioxane binary mixtures in the temperature range from 278.15 to 318.15 K in four solvent mixtures with mole fraction of 1,4-dioxane, x_D = 0.05, 0.10, 0.15 and 0.20, were determined by help of the rearranged Jones-

Dole equation, $(\eta_r - 1) - Ac^{1/2} = Bc$, and experimental data on viscosity, whereas the viscosity *A*-coefficients have been calculated from Falkenhagen and Vernon theory.

All obtained values of *B*-coefficients are positive and bigger than values of *A* in all solvent mixtures suggesting that ions-solvent are prevailing upon ion-ion interactions, what is agreement with small association constants for NaCl in these mixtures as obtained from conductivity measurement and reported in literature.[16]

Whereas for NaCl in solutions with x_D = 0.05, 0.10, and 0.15 it mainly states that d*B*/d*T* > 0, whereas – due to weak dependence of *B* on the temperature – this can be not assumed for x_D = 0.20. It can be concluded that in solutions with lower content of 1,4-dioxane the structure-breaking nature of NaCl is prevailing and ions-solvent interactions are dominant. With increasing content of 1,4-dioxane the solvent-solvent interactions become more important, resulting finally also in a maximum in viscosity at x_D ≈ 0.25[26,27,31] which can be attributed to the strong interaction between 1,4-dioxane and water molecules.

It would be interesting to carry out this kind of research on the systems with higher content of 1,4-dioxane in the solvent. But according to the literature[16] the association of NaCl increases dramatically with increasing amount of 1,4-dioxane and thus model, assuming negligible ion association applied in this study, can not be used.

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Povzetek

Izmerili smo viskoznosti raztopin NaCl v mešanicah vode in 1,4-dioksana (z molskim deležem 1,4-dioksana, $x_D = 0.05$, 0.10, 0.15 in 0.20) v temperaturnem območju med 278.15 in 318.15 K. Dobljene vrednosti relativnih viskoznosti smo analizirali in razložili s pomočjo Jones-Dolove enačbe $(\eta_r - 1) - Ac^{1/2} = Bc$. Koeficiente A smo pridobili z uporabo Falkenhagenove in Vernonove teorije, koeficiente B pa smo določili z linearno regresijo. Dobljene vrednosti B-koeficientov za NaCl v proučevanih topilih so pozitivne pri vseh temperaturah. Podatke smo primerjali s podatki iz literature za NaCl v vodi pri različnih temperaturah ter v mešanicah vode in 1,4-dioksana pri 298.15 K ter jih interpretirali s pomočjo možnih interakcij v preiskovanih raztopinah.