Volumetric and Viscometric Properties of Some Sulpha Drugs in Aqueous Solutions of Sodium Chloride at $T = (288.15$ to $318.15)$ K

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The partial molar volumes $V_2°$ and viscosity *B*-coefficient have been measured from density and flow time measurements for sulphanilamide, sulphanilic acid, and sulphosalicylic acid dihydrate in water and in aqueous solutions of (0.05, 0.1, 0.3, and 0.5) mol·kg^{-1} sodium chloride at temperatures from (288.15 to 318.15) K, by the use of a vibrating tube digital densimeter and Micro-Ubbelohde type capillary viscometer, respectively. The transfer volumes at infinite dilution calculated from partial molar volumes have both positive and negative values. The overall positive values at higher concentrations of sodium chloride are in the following order: sulphosalicylic acid dihydrate > sulphanilic acid > sulphanilamide, which is also the order of hydrophilicity of these drugs. The interaction coefficients, partial molar expansibilities $V_E°$, and second-order derivative have also been calculated. The transfer *B*-coefficient values, $\Delta_{tr}B$, are calculated from viscosity *B*-coefficient data. Transition state theory has been used to calculate $\Delta\mu^{o\#}$, the activation free energy for the viscous flow of solutions. The related activation parameters like $\Delta H^{o\#}$ and $\Delta S^{o\#}$ have been calculated. Also the excess molecular volume and contribution of various groups of the drug compound to $V_2°$ have been calculated.

Introduction

Most biochemical processes occur in aqueous media; therefore, studies on the physicochemical properties of biomolecules like amino acids, sugars, and drugs in aqueous solution provide useful information which is important to understand the complex mechanism of molecular interactions.[1] Thermodynamic and transport properties are very useful in understanding molecular interactions (hydrophilic, hydrophobic, and ionic interactions) in different solution media, as they provide convenient parameters for the elucidation of solute−solvent and solute−solute interactions in the solution phase.[2]

Sulfonamides are a group of synthetic organic drugs, structurally similar to PABA (*p*-aminobenzoic acid)[3] used against the infection caused by gram positive and negative bacteria, fungi, and certain protozoans. With the advent of antibiotics, the use of sulpha drugs has been diminished,[4] but still they occupy an important place among antibacterial drugs.[5] Some workers have carried out thermodynamic studies on sulpha drugs in different media,[6−8] but data are still lacking on the volumetric and viscometric properties of these drugs in aqueous solutions of electrolytes. As electrolytes influence the stability of biomolecules[9,10] greatly and also play an important role in living cells,[11] seawater,[12] and soils,[13] we therefore planned to carry out the volumetric and viscometric studies on a few sulpha drugs (sulphanilamide, sulphanilic acid) and a medical intermediate, sulphosalicyclic acid dihydrate, in aqueous solutions of sodium chloride at different concentrations [(0.05, 0.1, 0.3, and 0.5) mol·kg^{-1}] and at different temperatures [(288.15 to 318.15) K]. Partial molar volumes, viscosity *B*-coefficients, partial molar expansibilities, activation free energy for viscous flow, and other related parameters have been derived, and these have been discussed in terms of various interactions occurring in these solutions.

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Experimental Section

Sulphanilamide from Loba Chime India, sulphanilic acid, sulposalicyclic acid dihydrate from Spectrochem India, and sodium chloride from Qualigen India were dried for 24 h in a vacuum desiccator before use. All of the chemicals used are of analytical reagent grade, having a purity of 99 % or more. Deionized, doubly distilled degassed water with a specific conductance less than $1.3 \cdot 10^{-6}$ $\Omega^{-1} \cdot cm^{-1}$ was used for the preparation of all of the solutions. The solutions were prepared on a weight basis by using a Mettler balance with a precision of ± 0.01 mg. The densities of the solution were measured by using a vibrating tube digital densimeter with a precision of $\pm 1 \cdot 10^{-3}$ kg·m^{-3} and an accuracy of $\pm 3 \cdot 10^{-3}$ kg·m^{-3}. The temperature of the water around the densimeter cell was controlled within 0.01 K using a thermostat. The densimeter was calibrated using dry air and pure water, and its work was checked by measuring the densities of aqueous sodium chloride solutions, which agree well with the literature values.[14] The maximum uncertainty in the measured densities comes out to be $3.7 \cdot 10^{-3}$ kg·m^{-3}. Viscosity measurements were carried out with a Micro-Ubbelhode viscometer. The viscometer was calibrated with double-distilled deionized water with flow time data collected at four different temperatures, (288.15, 298.15, 308.15, and 318.15) K, and by using viscosity data from literature.[15] Flow time measurements were performed using an automatic viscosity (time) measurement unit (Schott AVS 350) with a resolution of 0.01 s. The temperature around the viscometer was maintained within ± 0.01 K using a constant temperature bath (model: MC 31A Julabo/Germany). The average of at least six readings reproducible within 0.01 s measured as the final efflux time was used for calculations. The calculated viscosities have an uncertainty within ± 0.001 mPa·s.

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Results and Discussion

The apparent molar volume, $V_{2,\phi}$, of sulphanilamide, sulphanilic acid, and sulphosalicylic acid dihydrate in water and in sodium chloride solutions, m_B = (0.05, 0.1, 0.3, and 0.5) mol·kg^{-1}, where m_B is the molality of sodium chloride at temperatures (of 288.15, 298.15, 308.15, and 318.15) K, have been determined from the experimentally measured densities using the following relation.

$$V_{2,\phi} = M/\rho - [(\rho - \rho_o)/m_A\rho\rho_o] \quad (1)$$

where M and m_A are the molar mass and molality of solute, that is, sulpha drugs in solutions, and ρ and ρ_o are the densities of the solution and solvent, respectively. The values of $V_{2,\phi}$ as a function of molality and temperature are given in the Table 1.

Partial molar volumes ($V_2^\circ = V_2^{\circ}{}_{,\phi}$) at infinite dilution were evaluated by least-squares fitting the following equation to the corresponding data as:

$$V_{2,\phi} = V_2^{\circ} + S_v m_A \quad (2)$$

where S_v is the experimental slope. The V_2° and S_v values are given in Table 2. The S_v values are negative in the case of sulphanilamide and sulphanilic acid in water as well as in aqueous sodium chloride solutions at all of the studied temperatures. Plots of $V_{2,\phi}$ versus m_A are shown in the Supporting Information, as Figures SF1 and SF2. Similarly, a decrease has been reported[16,17] for apparent molar volumes with concentration in the case of nicotinamide. This decrease in apparent molar volumes with increasing concentration has been rationalized in terms of self-association of nicotinamide molecules in aqeuous solutions. The presently observed trends in case of sulphanilamide and sulphanilic acid may also be attributed to the self-association of these drugs in aqeuous solutions.

Further, the presence of different groups on aromatic ring also contributes to this difference of S_v. The S_v values for sulphosalicyclic acid dihydrate follow opposite trend, that is, S_v values are positive both in water as well as in aqueous solutions of sodium chloride at all of the studied temperatures. A figure is given in SF3 in the Supporting Information. Moreover, the S_v values in water and in aqueous sodium chloride solutions are comparable. This may be due to the more hydrophilic nature of sulphosalicylic acid dihydrate.

The partial molar volumes of transfer, $\Delta_{tr}V_2^\circ$, at infinite dilution of each sulpha drug from water to aqueous solutions of sodium chloride have been determined as

$$\Delta_{tr}V_2^{o} = V_2^{o}(\text{aqueous solution of NaCl}) - V_2^{o}(\text{water}) \quad (3)$$

The $\Delta_{tr}V_2^\circ$ values are both negative and positive at different concentrations of NaCl for the studied drugs. The $\Delta_{tr}V_2^\circ$ values (Figures 1 and 2) for sulphanilamide and sulphanilic acid after passing through a minimum at about 0.05 m_B starts increasing with concentration of sodium chloride at all of the studied temperatures. It may be noted that the temperature dependence of $\Delta_{tr}V_2^\circ$ values in these cases is not very regular. In the case of sulphanilamide the $\Delta_{tr}V_2^\circ$ values at 288.15 K are lower, and these increase at 298.15 K which again starts decreasing at higher temperatures. Moreover, this is the case only at higher concentrations of sodium chloride, whereas at lower concentrations of sodium chloride, even these changes are not clearly observable. The $\Delta_{tr}V_2^\circ$ values in the case of sulphanilic acid are lower at 318.15 K at all concentrations of sodium chloride studied, whereas at other three temperatures studied the $\Delta_{tr}V_2^\circ$ values are almost overlapping. In the case of sulphosalicyclic acid dihydrate (Figure 3), the $\Delta_{tr}V_2^\circ$ values increase with temperature in the order of (318.15 < 288.19 < 308.15 < 298.15) K. Overall positive $\Delta_{tr}V_2^\circ$ values at higher concentrations of sodium chloride decrease in the following order: sulphosalicyclic acid dihydrate > sulphanilic acid > sulphanilamide. This may be attributed to the hydrophilic groups of these drugs, and the hydrophilicity decreases in the same order (Figure 4).

In the presently studied systems the following types of interactions are possible: (i) hydrophilic−ionic interactions among OH, $-NH_2$, and other groups of sulpha drugs and Na^+ and Cl^- ions of the cosolute, (ii) hydrophobic−ionic interactions between nonpolar parts of the studied drugs and Na^+ and Cl^- ions of sodium chloride. The first type of interactions contributes positively, whereas the second type of interactions contribute negatively, according to the cosphere overlap model.[18] The negative $\Delta_{tr}V_2^\circ$ values (Figures 1 to 3) observed at lower concentrations of sodium chloride suggest that the second type of interactions are dominating, whereas with the increase of concentration of sodium chloride, the first type of interactions starts building up, and at higher concentrations, the $\Delta_{tr}V_2^\circ$ values become positive. Thus, hydrophilic−ionic interactions dominate at higher concentrations of sodium chloride.

The limiting partial molar volume V_2° can also be expressed by using the equation given by Shahidi and Farrell[19] as follows

$$V_2^{o} = V_{vw} + V_{void} - V_{shrinkage} \quad (4)$$

where V_{vw} is the van der Waal's volumes, V_{void} is the volume associated with void or empty space, and $V_{shrinkage}$ is the volume due to shrinkage that arises from the electrostriction of the solvent caused by hydrophilic groups present in the solute. It is assumed that V_{vw} and V_{void} are not significantly affected by the presence of NaCl, so the negative $\Delta_{tr}V_2^\circ$ can therefore be attributed to an increase in the shrinkage volume in the presence of the aqueous solution of NaCl (at lower concentrations), but as the concentration of NaCl increases, the $\Delta_{tr}V_2^\circ$ becomes positive due to a decrease in shrinkage volumes at these concentrations.

The transfer volume $\Delta_{tr}V_2^\circ$ of the studied drugs can also be expressed by McMillan−Mayer equation[20] as follows

$$\Delta_{tr}V_2^{o} = 2V_{AB}\cdot m_B + 3V_{ABB}\cdot m_B{}^2 + \ldots \quad (5)$$

where A stands for solute (drug) and B for NaCl, V_{AB} and V_{ABB} are of volumetric pair and triplet interaction coefficients, respectively. The values for these coefficients are given in Table 3. Negative values for V_{AB} and positive values for V_{ABB} are observed for the three drugs at all of the studied temperatures. Negative values for V_{AB} show the presence of solvophobic−ionic interactions, while positive values for V_{ABB} suggest the presence of solvophilic−ionic interactions between solute and cosolute molecules. Therefore, there is a competition between both kind of interactions and the absence of complete dominance of one kind. These observations are in line with the conclusions drawn from $\Delta_{tr}V_2^\circ$ values as mentioned above.

To study the effect of temperature on the calculated properties, the partial molar expansibilities V_E° ($V_E^\circ = (\partial V_2^\circ/\partial T)_P$) and second derivative $(\partial^2 V_2^\circ/\partial T^2)_P$ have been calculated by fitting the data using the method of least-squares into the following equation

$$V_2^{o} = a + bT + cT^2 \quad (6)$$

where a, b, and c are constants and T is the absolute temperature. The calculated values for these parameters are given in the Table

Table 1. Densities, ρ, and Apparent Molar Volumes, $V_{2,\phi}$, of Some Sulpha Drugs in Water and in Aqueous NaCl Solutions as a Function of Concentrations of Drugs and NaCl from T = (288.15 to 318.15) K[a]

m_A / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ / m^3·mol^{-1}	m_A / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ / m^3·mol^{-1}
T/K = 288.15					
Sulphanilamide in Water					
0.01316	0.999796	121.39 (0.03)	0.03105	1.000725	120.63 (0.01)
0.01579	0.999933	121.20 (0.02)	0.03342	1.000849	120.56 (0.01)
0.02227	1.000266	121.03 (0.02)	0.04091	1.001247	120.22 (0.01)
Sulphanilamide in Aqueous NaCl Solutions					
m_B[b] = 0.05 mol·kg^{-1} (ρ_o[c] = 1001.231 kg·m^{-3})					
0.01025	1.001767	119.80 (0.04)	0.02648	1.002631	119.07 (0.01)
0.01405	1.001967	119.65 (0.03)	0.03192	1.002925	118.85 (0.01)
0.02218	1.002400	119.27 (0.02)	0.03513	1.003101	118.67 (0.01)
m_B = 0.1 mol·kg^{-1} (ρ_o = 1003.334 kg·m^{-3})					
0.00866	1.003779	120.48 (0.04)	0.02419	1.004595	119.69 (0.02)
0.01190	1.003948	120.33 (0.03)	0.02644	1.004715	119.58 (0.01)
0.01968	1.004357	119.89 (0.02)	0.03308	1.005072	119.25 (0.01)
m_B = 0.3 mol·kg^{-1} (ρ_o = 1011.651 kg·m^{-3})					
0.00944	1.012126	120.94 (0.04)	0.02550	1.012954	120.12 (0.01)
0.01283	1.012300	120.76 (0.03)	0.03070	1.013227	119.86 (0.01)
0.01614	1.012468	120.64 (0.02)			
m_B = 0.5 mol·kg^{-1} (ρ_o = 1019.785 kg·m^{-3})					
0.00991	1.020276	121.10 (0.04)	0.02556	1.021077	120.11 (0.01)
0.01824	1.020699	120.58 (0.02)	0.02877	1.021244	119.92 (0.01)
0.02376	1.020983	120.24 (0.02)	0.03442	1.021541	119.61 (0.01)
Sulphanilic Acid in Water					
0.00817	0.999669	106.92 (0.05)	0.03100	1.001201	106.14 (0.01)
0.01529	1.000144	106.70 (0.02)	0.03890	1.001736	105.90 (0.01)
0.02369	1.000706	106.43 (0.02)	0.04164	1.001923	105.81 (0.01)
Sulphanilic Acid in Aqueous NaCl Solutions					
m_B = 0.05 mol·kg^{-1} (ρ_o = 1001.231 kg·m^{-3})					
0.01090	1.001965	105.69 (0.04)	0.03106	1.003331	105.33 (0.01)
0.01783	1.002434	105.55 (0.02)	0.03665	1.003710	105.24 (0.01)
0.02427	1.002870	105.45 (0.02)	0.04040	1.003966	105.17 (0.01)
m_B = 0.1 mol·kg^{-1} (ρ_o = 1003.334 kg·m^{-3})					
0.01159	1.004110	106.00 (0.03)	0.03212	1.005500	105.40 (0.01)
0.01876	1.004594	105.77 (0.02)	0.03862	1.005943	105.24 (0.01)
0.02347	1.004912	105.66 (0.02)	0.04343	1.006272	105.10 (0.01)
m_B = 0.3 mol·kg^{-1} (ρ_o = 1011.651 kg·m^{-3})					
0.01371	1.012550	107.06 (0.03)	0.03103	1.013695	106.62 (0.01)
0.01557	1.012672	107.02 (0.02)	0.03862	1.014201	106.40 (0.01)
0.02347	1.013194	106.82 (0.02)	0.04084	1.014349	106.38 (0.01)
m_B = 0.5 mol·kg^{-1} (ρ_o = 1019.785 kg·m^{-3})					
0.00885	1.020358	107.69 (0.04)	0.02890	1.021663	107.14 (0.01)
0.01371	1.020671	107.58 (0.03)	0.03103	1.021805	107.04 (0.01)
0.02005	1.021084	107.37 (0.02)	0.04045	1.022426	106.78 (0.01)
Sulphosalicylic Acid Dihydrate in Water					
0.00920	1.000035	155.51 (0.04)	0.04474	1.003469	156.35 (0.01)
0.02311	1.001395	155.83 (0.02)	0.05423	1.004382	156.56 (0.01)
0.03359	1.002409	156.07 (0.01)	0.06044	1.004973	156.64 (0.01)
Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions					
m_B = 0.05 mol·kg^{-1} (ρ_o = 1001.231 kg·m^{-3})					
0.01328	1.002550	154.97 (0.03)	0.03600	1.004770	155.38 (0.01)
0.02035	1.003240	155.11 (0.02)	0.04235	1.005380	155.55 (0.01)
0.03141	1.004320	155.28 (0.01)	0.06193	1.007260	155.94 (0.01)
m_B = 0.1 mol·kg^{-1} (ρ_o = 1003.334 kg·m^{-3})					
0.00912	1.004236	154.99 (0.04)	0.03933	1.007166	156.00 (0.01)
0.01725	1.005032	155.31 (0.02)	0.04274	1.007491	156.12 (0.01)
0.02977	1.006248	155.67 (0.01)	0.05307	1.008470	156.43 (0.01)
m_B = 0.3 mol·kg^{-1} (ρ_o = 1011.651 kg·m^{-3})					
0.01593	1.013209	155.47 (0.02)	0.04584	1.016052	156.80 (0.01)
0.02989	1.014550	156.09 (0.01)	0.04860	1.016308	156.94 (0.01)
0.03889	1.015401	156.50 (0.01)	0.06146	1.017494	157.49 (0.01)
m_B = 0.5 mol·kg^{-1} (ρ_o = 1019.785 kg·m^{-3})					
0.01163	1.020902	156.78 (0.03)	0.03880	1.023472	157.34 (0.01)
0.02133	1.021825	157.03 (0.02)	0.04846	1.024374	157.52 (0.01)
0.02709	1.022370	157.13 (0.01)	0.05732	1.025196	157.67 (0.01)
T/K = 298.15					
Sulphanilamide in Water					
0.01316	0.997704	122.38 (0.05)	0.03105	0.998620	121.54 (0.01)
0.01579	0.997837	122.25 (0.02)	0.03342	0.998742	121.47 (0.01)
0.02227	0.998168	121.96 (0.02)	0.04091	0.999135	121.10 (0.01)
Sulphanilamide in Aqueous NaCl Solutions					
m_B = 0.05 mol·kg^{-1} (ρ_o = 0999.114 kg·m^{-3})					
0.01025	0.999634	121.46 (0.03)	0.02648	1.000471	120.86 (0.01)
0.01405	0.999828	121.34 (0.02)	0.03192	1.000757	120.60 (0.01)
0.02218	1.000247	121.03 (0.02)	0.03513	1.000925	120.50 (0.01)
m_B = 0.1 mol·kg^{-1} (ρ_o = 1001.144 kg·m^{-3})					
0.00866	1.001577	122.07 (0.06)	0.02419	1.002370	121.32 (0.01)
0.01190	1.001741	121.92 (0.03)	0.02644	1.002487	121.14 (0.01)
0.01968	1.002137	121.54 (0.02)	0.03308	1.002833	120.86 (0.01)
m_B = 0.3 mol·kg^{-1} (ρ_o = 1009.282 kg·m^{-3})					
0.00944	1.009745	122.41 (0.04)	0.02550	1.010556	121.44 (0.01)
0.01283	1.009913	122.25 (0.03)	0.03070	1.010824	121.13 (0.01)
0.01614	1.010080	121.95 (0.02)			
m_B = 0.5 mol·kg^{-1} (ρ_o = 1017.177 kg·m^{-3})					
0.00991	1.017650	123.11 (0.04)	0.02556	1.018416	122.30 (0.01)
0.01824	1.018055	122.67 (0.02)	0.02877	1.018575	122.14 (0.01)
0.02376	1.018327	122.39 (0.02)	0.03442	1.018859	121.85 (0.01)
Sulphanilic Acid in Water					
0.00817	0.997584	107.60 (0.05)	0.03100	0.999103	106.75 (0.01)
0.01529	0.998054	107.32 (0.02)	0.03890	0.999637	106.45 (0.01)
0.02369	0.998614	107.00 (0.01)	0.04164	0.999824	106.33 (0.01)
Sulphanilic Acid in Aqueous NaCl Solutions					
m_B = 0.05 mol·kg^{-1} (ρ_o = 999.114 kg·m^{-3})					
0.01090	0.999840	106.50 (0.03)	0.03106	1.001190	106.19 (0.01)
0.01783	1.000302	106.43 (0.02)	0.03665	1.001584	106.11 (0.01)
0.02427	1.000734	106.32 (0.02)	0.04040	1.001817	106.04 (0.01)
m_B = 0.1 mol·kg^{-1} (ρ_o = 1001.144 kg·m^{-3})					
0.01159	1.001911	106.91 (0.06)	0.03212	1.003280	106.46 (0.01)
0.01876	1.002390	106.70 (0.03)	0.03862	1.003710	106.34 (0.01)
0.02347	1.002700	106.62 (0.02)	0.04343	1.004030	106.28 (0.01)
m_B = 0.3 mol·kg^{-1} (ρ_o = 1009.282 kg·m^{-3})					
0.01371	1.010169	107.96 (0.03)	0.03103	1.011293	107.78 (0.01)
0.01557	1.010290	107.93 (0.02)	0.03862	1.011786	107.67 (0.01)
0.02347	1.010802	107.86 (0.02)	0.04084	1.011931	107.65 (0.01)
m_B = 0.5 mol·kg^{-1} (ρ_o = 1017.177 kg·m^{-3})					
0.00885	1.017742	108.51 (0.04)	0.02890	1.019036	107.90 (0.01)
0.01371	1.018053	108.38 (0.03)	0.03103	1.019174	107.86 (0.01)
0.02005	1.018462	108.19 (0.02)	0.04045	1.019791	107.52 (0.01)
Sulphosalicylic Acid Dihydrate in Water					
0.00920	0.997937	157.52 (0.04)	0.04474	1.001320	158.24 (0.01)
0.02311	0.999272	157.80 (0.02)	0.05423	1.002207	158.44 (0.01)
0.03359	1.000269	157.98 (0.01)	0.06044	1.002785	158.55 (0.01)
Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions					
m_B = 0.05 mol·kg^{-1} (ρ_o = 999.106 kg·m^{-3})					
0.00920	1.000004	157.22 (0.05)	0.04135	1.003070	157.88 (0.01)
0.01712	1.000766	157.44 (0.03)	0.06283	1.005080	158.420 (0.01)
0.02922	1.001921	157.67 (0.01)	0.06312	1.005100	158.45 (0.01)
m_B = 0.1 mol·kg^{-1} (ρ_o = 1001.144 kg·m^{-3})					
0.00912	1.002030	157.17 (0.04)	0.03933	1.004890	158.20 (0.01)
0.01725	1.002810	157.43 (0.02)	0.04274	1.005209	158.30 (0.01)
0.02977	1.004000	157.85 (0.01)	0.05307	1.006164	158.63 (0.01)
m_B = 0.3 mol·kg^{-1} (ρ_o = 1009.282 kg·m^{-3})					
0.01593	1.010799	158.12 (0.02)	0.04584	1.013556	159.67 (0.01)
0.02989	1.012102	158.81 (0.01)	0.04860	1.013804	159.81 (0.01)
0.03889	1.012927	159.30 (0.01)	0.06146	1.014950	160.44 (0.01)
m_B = 0.5 mol·kg^{-1} (ρ_o = 1017.177 kg·m^{-3})					
0.01162	1.018268	159.04 (0.03)	0.03880	1.020785	159.52 (0.01)
0.02133	1.019173	159.20 (0.02)	0.04846	1.021668	159.64 (0.01)
0.02709	1.019705	159.33 (0.01)	0.05732	1.022473	159.79 (0.01)
T/K = 308.15					
Sulphanilamide in Water					
0.01316	0.994705	123.77 (0.03)	0.03105	0.995604	122.80 (0.01)
0.01579	0.994835	123.64 (0.02)	0.03342	0.995726	122.65 (0.01)
0.02227	0.995159	123.29 (0.02)	0.04091	0.996113	122.26 (0.01)
Sulphanilamide in Aqueous NaCl Solutions					
m_B = 0.05 mol·kg^{-1} (ρ_o = 996.063 kg·m^{-3})					
0.01025	0.996571	122.88 (0.04)	0.02648	0.997392	122.13 (0.01)
0.01405	0.996762	122.66 (0.03)	0.03192	0.997670	121.92 (0.01)
0.02218	0.997172	122.35 (0.02)	0.03513	0.997837	121.76 (0.01)

Table 1. Continued

m_A / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ / m^3·mol^{-1}	m_A / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ / m^3·mol^{-1}
$m_B = 0.1$ mol·kg^{-1} ($\rho_o = 998.053$ kg·m^{-3})					
0.00866	0.998477	123.36 (0.04)	0.02419	0.999260	122.30 (0.01)
0.01190	0.998637	123.18 (0.03)	0.02644	0.999375	122.18 (0.01)
0.01968	0.999029	122.62 (0.02)	0.03308	0.999719	121.77 (0.01)
$m_B = 0.3$ mol·kg^{-1} ($\rho_o = 1006.056$ kg·m^{-3})					
0.00944	1.006507	123.93 (0.04)	0.02550	1.007296	122.98 (0.01)
0.01283	1.006672	123.67 (0.03)	0.03070	1.007558	122.64 (0.01)
0.01614	1.006833	123.50 (0.02)			
$m_B = 0.5$ mol·kg^{-1} ($\rho_o = 1013.841$ kg·m^{-3})					
0.00991	1.014305	124.27 (0.04)	0.02556	1.015055	123.49 (0.01)
0.01824	1.014701	123.90 (0.02)	0.02877	1.015212	123.33 (0.01)
0.02376	1.014968	123.58 (0.02)	0.03442	1.015493	122.96 (0.01)
Sulphanilic Acid in Water					
0.00817	0.994592	108.67 (0.05)	0.03100	0.996100	107.51 (0.01)
0.01529	0.995057	108.35 (0.02)	0.03890	0.996630	107.16 (0.01)
0.02369	0.995612	107.90 (0.02)	0.04164	0.996815	107.04 (0.01)
Sulphanilic Acid in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\rho_o = 996.063$ kg·m^{-3})					
0.01090	0.996777	107.75 (0.03)	0.03106	0.998108	107.30 (0.01)
0.01783	0.997232	107.68 (0.02)	0.03665	0.998475	107.28 (0.01)
0.02427	0.997657	107.52 (0.02)	0.04040	0.998729	107.07 (0.01)
$m_B = 0.1$ mol·kg^{-1} ($\rho_o = 998.053$ kg·m^{-3})					
0.01159	0.998851	108.10 (0.06)	0.03212	1.000150	107.69 (0.01)
0.01876	0.999280	107.97 (0.03)	0.03862	1.000580	107.54 (0.01)
0.02347	0.999580	107.86 (0.02)	0.04343	1.000900	107.43 (0.01)
$m_B = 0.3$ mol·kg^{-1} ($\rho_o = 1006.056$ kg·m^{-3})					
0.01371	1.006931	108.99 (0.03)	0.03103	1.008084	108.51 (0.01)
0.01557	1.007051	108.95 (0.02)	0.03862	1.008542	108.28 (0.01)
0.02347	1.007559	108.71 (0.02)	0.04084	1.008688	108.20 (0.01)
$m_B = 0.5$ mol·kg^{-1} ($\rho_o = 1013.841$ kg·m^{-3})					
0.00885	1.014395	109.85 (0.04)	0.02890	1.015665	109.25 (0.01)
0.01371	1.014701	109.73 (0.03)	0.03103	1.015801	109.16 (0.01)
0.02005	1.015101	109.54 (0.02)	0.04045	1.016406	108.85 (0.01)
Sulphosalicylic Acid Dihydrate in Water					
0.00920	0.994942	158.87 (0.04)	0.04474	0.998278	159.74 (0.01)
0.02311	0.996259	159.25 (0.01)	0.05423	0.999153	159.94 (0.01)
0.03359	0.997242	159.45 (0.01)	0.06044	0.999722	160.07 (0.01)
Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\rho_o = 999.114$ kg·m^{-3})					
0.00920	0.996940	158.52 (0.05)	0.04135	0.999980	159.22 (0.01)
0.01712	0.997700	158.73 (0.03)	0.06283	1.001960	159.70 (0.01)
0.02922	0.998840	158.97 (0.01)	0.06312	1.001990	159.71 (0.01)
$m_B = 0.1$ mol·kg^{-1} ($\rho_o = 998.053$ kg·m^{-3})					
0.00808	0.998830	158.57 (0.06)	0.03425	1.001270	159.78 (0.01)
0.02072	1.000080	159.20 (0.02)	0.04413	1.002180	160.21 (0.01)
0.02678	1.000580	159.47 (0.02)	0.04961	1.002670	160.46 (0.01)
$m_B = 0.3$ mol·kg^{-1} ($\rho_o = 1006.056$ kg·m^{-3})					
0.01593	1.007558	159.28 (0.02)	0.04584	1.010296	160.62 (0.01)
0.02989	1.008850	159.89 (0.01)	0.04860	1.010545	160.71 (0.01)
0.03889	1.009671	160.29 (0.01)	0.06146	1.011687	161.26 (0.01)
$m_B = 0.5$ mol·kg^{-1} ($\rho_o = 1013.841$ kg·m^{-3})					
0.01163	1.014919	160.42 (0.03)	0.03880	1.017389	161.22 (0.01)
0.02133	1.015809	160.69 (0.02)	0.04846	1.018254	161.45 (0.01)
0.02709	1.016332	160.88 (0.01)	0.05732	1.019039	161.70 (0.01)
T/K = 318.15					
Sulphanilamide in Water					
0.01316	0.990877	124.74 (0.03)	0.03105	0.991766	123.71 (0.01)
0.01579	0.991006	124.59 (0.02)	0.03342	0.991885	123.60 (0.01)
0.02227	0.991325	124.24 (0.02)	0.04091	0.992269	123.16 (0.01)
Sulphanilamide in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\rho_o = 992.222$ kg·m^{-3})					
0.01025	0.992725	123.59 (0.04)	0.02648	0.993538	122.90 (0.01)
0.01405	0.992914	123.46 (0.03)	0.03192	0.993814	122.71 (0.01)
0.02218	0.993321	123.09 (0.02)	0.03513	0.993977	122.58 (0.01)
$m_B = 0.1$ mol·kg^{-1} ($\rho_o = 994.181$ kg·m^{-3})					
0.00866	0.994602	123.98 (0.04)	0.02419	0.995378	123.00 (0.01)
0.01190	0.994761	123.82 (0.03)	0.02644	0.995495	122.78 (0.01)
0.01968	0.995150	123.26 (0.02)	0.03308	0.995838	122.35 (0.01)

Table 1. Continued

m_A / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ / m^3·mol^{-1}	m_A / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	$V_{2,\phi} \cdot 10^6$ / m^3·mol^{-1}
$m_B = 0.3$ mol·kg^{-1} ($\rho_o = 1002.152$ kg·m^{-3})					
0.00944	1.002598	124.69 (0.04)	0.02550	1.003380	123.72 (0.01)
0.01283	1.002761	124.53 (0.03)	0.03070	1.003641	123.35 (0.01)
0.01614	1.002920	124.34 (0.02)			
$m_B = 0.5$ mol·kg^{-1} ($\rho_o = 1009.794$ kg·m^{-3})					
0.00991	1.010253	125.02 (0.04)	0.02556	1.010998	124.18 (0.01)
0.01824	1.010646	124.60 (0.02)	0.02877	1.011156	123.93 (0.01)
0.02376	1.010910	124.31 (0.02)	0.03442	1.011433	123.64 (0.01)
Sulphanilic Acid in Water					
0.00817	0.990764	109.94 (0.05)	0.03100	0.992244	108.89 (0.01)
0.01529	0.991221	109.59 (0.02)	0.03890	0.992765	108.52 (0.01)
0.02369	0.991766	109.20 (0.02)	0.04164	0.992949	108.36 (0.01)
Sulphanilic Acid in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\rho_o = 992.222$ kg·m^{-3})					
0.01090	0.992934	108.16 (0.03)	0.03106	0.994262	107.62 (0.01)
0.01783	0.993388	107.97 (0.02)	0.03665	0.994633	107.48 (0.01)
0.02427	0.993812	107.83 (0.02)	0.04040	0.994884	107.34 (0.01)
$m_B = 0.1$ mol·kg^{-1} ($\rho_o = 994.181$ kg·m^{-3})					
0.01159	0.994930	108.76 (0.06)	0.03212	0.996273	108.10 (0.01)
0.01876	0.995397	108.51 (0.03)	0.03862	0.996701	107.90 (0.01)
0.02347	0.995704	108.38 (0.02)	0.04343	0.997020	107.76 (0.01)
$m_B = 0.3$ mol·kg^{-1} ($\rho_o = 1002.152$ kg·m^{-3})					
0.01371	1.003018	109.80 (0.03)	0.03103	1.004124	109.33 (0.01)
0.01557	1.003136	109.78 (0.02)	0.03862	1.004612	109.13 (0.01)
0.02347	1.003639	109.57 (0.02)	0.04084	1.004756	109.05 (0.01)
$m_B = 0.5$ mol·kg^{-1} ($\rho_o = 1009.794$ kg·m^{-3})					
0.00885	1.010342	110.69 (0.04)	0.02890	1.011600	110.08 (0.01)
0.01371	1.010645	110.55 (0.03)	0.03103	1.011734	110.00 (0.01)
0.02005	1.011041	110.37 (0.02)	0.04045	1.012331	109.71 (0.01)
Sulphosalicylic Acid Dihydrate in Water					
0.00920	0.991107	160.92 (0.04)	0.04474	0.994388	161.60 (0.01)
0.02311	0.992401	161.19 (0.01)	0.05423	0.995245	161.86 (0.01)
0.03359	0.993367	161.41 (0.01)	0.06044	0.995806	161.97 (0.01)
Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\rho_o = 992.222$ kg·m^{-3})					
0.01328	0.993470	160.38 (0.02)	0.03600	0.995580	160.99 (0.01)
0.02035	0.994130	160.57 (0.01)	0.04235	0.996161	161.17 (0.01)
0.03141	0.995150	160.89 (0.01)	0.06193	0.997934	160.67 (0.01)
$m_B = 0.1$ mol·kg^{-1} ($\rho_o = 994.181$ kg·m^{-3})					
0.00808	0.994950	159.72 (0.06)	0.03425	0.997360	161.16 (0.01)
0.02072	0.996120	160.52 (0.02)	0.04413	0.998250	161.85 (0.01)
0.02678	0.996686	160.82 (0.02)	0.04961	0.998730	162.17 (0.01)
$m_B = 0.3$ mol·kg^{-1} ($\rho_o = 1002.152$ kg·m^{-3})					
0.01593	1.003643	160.25 (0.02)	0.04584	1.006335	162.13 (0.01)
0.02989	1.004917	161.12 (0.01)	0.04860	1.006574	162.35 (0.01)
0.03889	1.005723	161.69 (0.01)	0.06146	1.007687	163.10 (0.01)
$m_B = 0.5$ mol·kg^{-1} ($\rho_o = 1009.794$ kg·m^{-3})					
0.01163	1.010860	161.69 (0.03)	0.03880	1.013310	162.31 (0.03)
0.02133	1.011742	161.91 (0.02)	0.04846	1.014169	162.50 (0.02)
0.02709	1.012262	162.06 (0.01)	0.05732	1.014950	162.70 (0.01)

[a] In m_A, A represents sulpha drugs, and in m_B, B represents NaCl. Uncertainties in apparent molar volumes (m^3·mol^{-1}) are also given in parentheses. [b] m_B is the molality of NaCl in water. [c] ρ_o is the density of aqueous NaCl solutions.

4. The values of expansibilities in the case of sulphanilamide and sulphosalicylic acid dihydrate decrease regularly with temperature in water as well as in sodium chloride solutions but do not follow any regular trend with the increasing concentration of sodium chloride. In sulphanilic acid, these values increase regularly with temperature in water, but in sodium chloride solutions, these values decrease regularly with the increase in temperature.

Table 2. Partial Molar Volumes, V_2^o, of Some Sulpha Drugs in Water and in Aqueous NaCl Solutions from T = (288.15 to 318.15) K[a]

	$V_2^o \cdot 10^6/m^3 \cdot mol^{-1}$				
sulpha drugs	m_B[b] = 0.0 mol·kg^{-1}	m_B = 0.05 mol·kg^{-1}	m_B = 0.1 mol·kg^{-1}	m_B = 0.3 mol·kg^{-1}	m_B = 0.5 mol·kg^{-1}
			T/K = 288.15		
sulphanilamide	121.90 ± 0.04 (−40.67)	120.27 ± 0.01 (−45.23)	120.92 ± 0.02 (−50.69)	121.43 ± 0.02 (−51.09)	121.70 ± 0.02 (−61.33)
sulphanilic acid	107.20 ± 0.02 (−33.58)	105.87 ± 0.01 (−17.33)	106.31 ± 0.01 (−27.57)	107.42 ± 0.01 (−23.78)	107.96 ± 0.02 (−29.29)
sulphosalicylic acid dihydrate	155.31 ± 0.03 (22.64)	154.69 ± 0.03 (20.00)	154.72 ± 0.02 (32.52)	154.76 ± 0.01 (44.50)	156.59 ± 0.03 (19.04)
			T/K = 298.15		
sulphanilamide	122.97 ± 0.01 (−45.54)	121.88 ± 0.02 (−39.42)	122.51 ± 0.03 (−50.31)	122.98 ± 0.04 (−60.62)	123.61 ± 0.01 (−51.28)
sulphanilic acid	107.90 ± 0.01 (−37.47)	106.69 ± 0.02 (−16.04)	107.09 ± 0.03 (−17.16)	108.12 ± 0.01 (−13.61)	108.80 ± 0.02 (−32.01)
sulphosalicylic acid dihydrate	157.32 ± 0.02 (20.31)	157.03 ± 0.02 (22.36)	156.86 ± 0.01 (33.59)	157.30 ± 0.02 (51.41)	158.86 ± 0.02 (16.30)
			T/K = 308.15		
sulphanilamide	124.50 ± 0.01 (−54.94)	123.31 ± 0.03 (−43.94)	123.94 ± 0.03 (−66.42)	124.46 ± 0.03 (−58.92)	124.83 ± 0.04 (−53.15)
sulphanilic acid	109.08 ± 0.02 (−49.44)	108.04 ± 0.06 (−21.51)	108.36 ± 0.01 (−21.67)	109.39 ± 0.01 (−27.54)	110.16 ± 0.02 (−31.41)
sulphosalicylic acid dihydrate	158.68 ± 0.02 (23.26)	158.33 ± 0.01 (21.72)	158.24 ± 0.03 (44.94)	158.59 ± 0.02 (43.70)	160.10 ± 0.02 (28.01)
			T/K = 318.15		
sulphanilamide	125.49 ± 0.01 (−56.98)	124.02 ± 0.02 (−41.23)	124.60 ± 0.03 (−67.66)	125.33 ± 0.04 (−63.82)	125.62 ± 0.04 (57.12)
sulphanilic acid	110.31 ± 0.02 (−46.42)	108.47 ± 0.02 (−27.32)	109.11 ± 0.01 (−30.77)	110.21 ± 0.02 (−27.91)	110.98 ± 0.01 (−31.92)
sulphosalicylic acid dihydrate	160.72 ± 0.02 (20.60)	160.04 ± 0.01 (26.55)	159.26 ± 0.06 (58.26)	159.24 ± 0.02 (63.03)	161.45 ± 0.01 (21.94)

[a] Parentheses contain the value of S_v ($S_v \cdot 10^6/m^3 \cdot mol^{-2} \cdot kg$). The variation in the correlation coefficient (R) is 0.996 to 0.999. [b] m_B is the molality of NaCl in water.

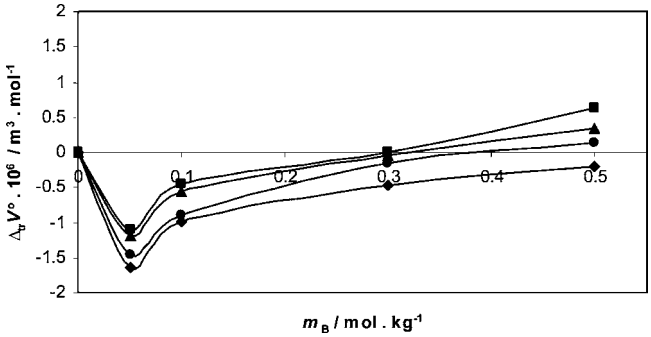

Figure 1. Partial molar volume of transfer ($\Delta_{tr}V_2°$) vs m_B for sulphanilamide at the following temperatures: ♦, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

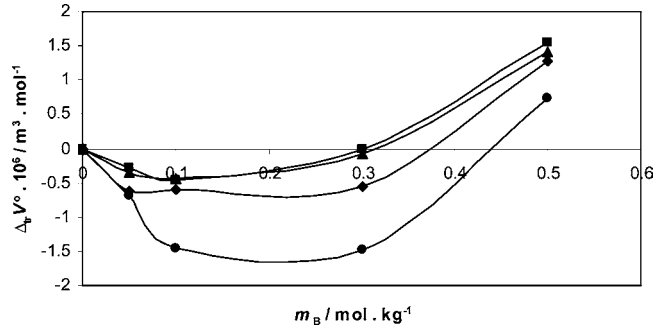

Figure 3. Partial molar volume of transfer ($\Delta_{tr}V_2°$) vs m_B for sulphosalicylic acid dihydrate at the following temperatures: ♦, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

Having qualitative information regarding the hydration of solute from thermal expansion, Hepler[21] used the following thermodynamic relation.

$$(\partial C^o_{p,2}/\partial T)_P = -T(\partial^2 V_2^o/\partial T^2)_P \quad (7)$$

It has been suggested that $(\partial^2 V_2°/\partial T^2)_P$ should be negative for the structure-breaking and positive for the structure-making solute. For sulphanilamide and sulphosalicylic acid dihydrate, the negative values for $(\partial^2 V_2°/\partial T^2)_P$ in water as well as in aqueous solutions of sodium chloride suggest that these solutes act as structure breakers. However, the $(\partial^2 V_2°/\partial T^2)_P$ value for sulphanilic acid is positive in water, and it is negative in sodium chloride solutions (except at 0.3 mol·kg^{-1} for sulphanilic acid), showing that it acts as a structure maker in water but a structure breaker in sodium chloride solutions.

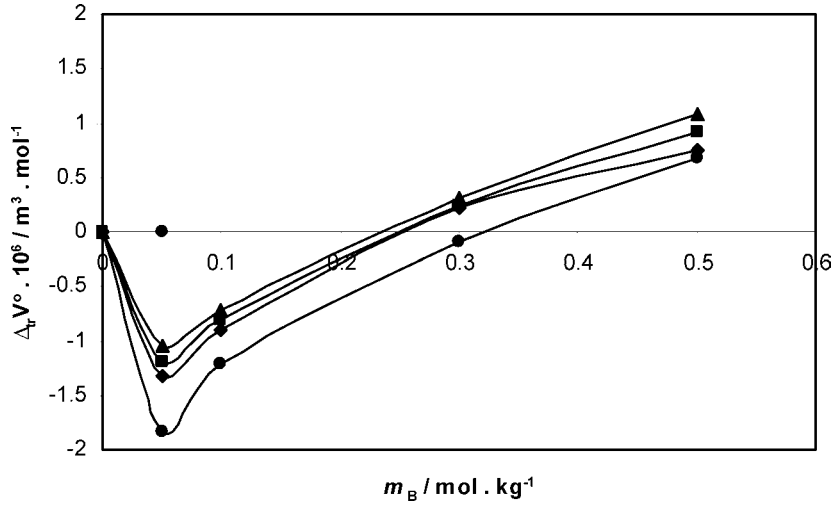

Figure 2. Partial molar volume of transfer ($\Delta_{tr}V_2°$) vs m_B for sulphanilic acid at the following temperatures: ♦, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

Table 3. Pair, V_{AB}, and Triplet, V_{ABB}, Interaction Coefficients of Studied Sulpha Drugs in Aqueous NaCl Solutions from T = (288.15 to 318.15) K

sulpha drugs	$V_{AB}\cdot10^6$ / $m^3\cdot mol^{-2}\cdot kg$	$V_{ABB}\cdot10^6$ / $m^3\cdot mol^{-2}\cdot kg^2$	$V_{AB}\cdot10^6$ / $m^3\cdot mol^{-2}\cdot kg$	$V_{ABB}\cdot10^6$ / $m^3\cdot mol^{-2}\cdot kg^2$
	T/K = 288.15		T/K = 298.15	
sulphanilamide	−4.562 ± 3.442	6.086 ± 5.124	−2.856 ± 2.315	4.503 ± 3.446
sulphanilic acid	−3.289 ± 3.219	5.680 ± 4.792	−3.131 ± 2.864	5.622 ± 4.263
sulphosalicylic acid dehydrate	−4.421 ± 0.608	7.624 ± 0.905	−2.749 ± 0.316	5.751 ± 0.470
	T/K = 308.15		T/K = 318.15	
sulphanilamide	−2.748 ± 2.611	4.299 ± 3.887	−3.770 ± 3.289	5.469 ± 4.896
sulphanilic acid	−2.751 ± 2.514	5.333 ± 3.743	−5.149 ± 4.100	8.103 ± 6.103
sulphosalicylic acid dihydrate	−2.833 ± 0.341	5.701 ± 0.508	−7.912 ± 0.660	11.578 ± 0.983

Table 4. Partial Molar Expansibilities, V_E^o, of Some Sulpha Drugs in Water and in Aqueous NaCl Solutions from T = (288.15 to 318.15) K

m_B[a] / mol·kg^{-1}	$V_E^o\cdot10^6$ / $m^3\cdot mol^{-1}\cdot K^{-1}$ 288.15 K	298.15 K	308.15 K	318.15 K	SD[b]	$(\partial^2V_2^o/\partial T^2)_P\cdot10^6$ / $m^3\cdot mol^{-1}\cdot K^{-2}$
			Sulphanilamide in Aqueous NaCl Solutions			
0.0	0.129	0.125	0.121	0.117	0.224	−0.0004
0.05	0.194	0.149	0.104	0.059	0.121	−0.0045
0.1	0.191	0.145	0.098	0.052	0.136	−0.0047
0.3	0.183	0.149	0.115	0.081	0.121	−0.0034
0.5	0.214	0.158	0.102	0.046	0.058	−0.0056
			Sulphanilic Acid in Aqueous NaCl Solutions			
0.0	0.068	0.095	0.121	0.148	0.096	0.0027
0.05	0.121	0.101	0.082	0.062	0.297	−0.0020
0.1	0.099	0.097	0.096	0.094	0.226	−0.0001
0.3	0.087	0.093	0.099	0.105	0.228	0.0006
0.5	0.106	0.105	0.104	0.103	0.237	−0.0001
			Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions			
0.0	0.087	0.086	0.084	0.083	0.297	−0.0001
0.05	0.218	0.186	0.155	0.123	0.324	−0.0032
0.1	0.234	0.178	0.122	0.066	0.089	−0.0056
0.3	0.288	0.192	0.097	0.002	0.136	−0.0094
0.5	0.227	0.181	0.135	0.089	0.252	−0.0046

[a] m_B is the molality of NaCl in water. [b] SD is the standard deviation.

A similar kind of results for the second derivative has been reported for structurally similar nicotinamide by Kundu and Kishore[16] and Sinha et al.[17]

The volumetric effect of solute−solvent interactions may be estimated from the partial molecular volume $V_{2,m}^\circ$ and the corresponding molecular volume (V°) in the solid state.[16] The excess partial molecular volume $V_{2,ex}^\circ$ per molecule can be calculated as:

$$V_{2,ex}^{\ o} = V_{2,m}^{\ o} - V^o \tag{8}$$

where $V_{2,m}^\circ = V_{2,\phi}^\circ/N_A$ and $V^\circ = M_2/d_2^\circ N_A$. Here N_A is the Avogadro constant ($6.023\cdot10^{23}$), and d_2° is the density of pure solid sulpha drugs [sulphanilamide (1.08 g·cm^{-3}) and sulphanilic acid (1.49 g·cm^{-3})]. The calculated values for $V_{2,ex}^\circ$ for both of the above drugs (Table 5) are negative in water as well as in the presence of sodium chloride solutions, suggesting that these drug molecules are tightly packed in water and in sodium chloride solution, and this is in line with the fact discussed earlier for these two drugs in terms of their self-association. These drugs also show a structure-breaking property. Similar results have been reported for pyridine.[16] Kundu and Kishore[16] got the positive value for nicotinamide and concluded that the $-CONH_2$ group is a structure promoter. However, for sulpha drugs, the presently observed results suggest that the presence of $-SO_2NH_2$ group adds to the structure-breaking property.

On applying the group additivity scheme, from the V_2° values of sulpha drugs in the present study and aniline and hydroxybenzoic acid from literature,[22,23] the contributions of $-SO_2NH_2$ and $-SO_3H$ groups to V_2° in water are ($33.49\cdot10^{-6}$, $18.40\cdot10^{-6}$, and $19.88\cdot10^{-6}$) m^3·mol^{-1}, for sulphanilamide, sulphanilic acid, and sulphosalicylic acid dihydrate, respectively, at 298.15 K. However, the difference in the contribution values for the $-SO_3H$ group in sulphanilic acid and sulphosalicylic acid dihydrate may be due to the difference in the surrounding groups in the two drugs. Moreover, no reports for V_2° of these drug compounds are available in literature for comparison.

The viscosities η of solution were calculated by using the following expression.

$$\eta/\rho = at - b/t \tag{9}$$

where ρ is the density of solution, t is the flow time, and a and b are viscometer constants. The relative viscosities η_r ($\eta_r = \eta/\eta_o$, where η_o and η are the viscosities of solvent and solution, respectively) are given in the Table 6. The value of uncertainty calculated in η_r on the average comes out to be ± 0.001. The viscosity data have been fitted using the Jones−Dole empirical equation,[24] which describes the relative viscosities of electrolyte solution as a function of concentration.

$$\eta/\eta_o = 1 + Ac^{1/2} + Bc \tag{10}$$

where c is the molarity (calculated from molality), A is a constant arising from the interactions between the ions, and B is the viscosity B-coefficient.

The above equation upon rearrangement becomes

$$(\eta/\eta_o - 1)/c^{1/2} = A + Bc^{1/2} \tag{11}$$

The plot of $(\eta/\eta_o - 1)/c^{1/2}$ versus $c^{1/2}$ has been found to be linear at all studied temperatures in accordance with the

Table 5. Partial Molecular Volume ($V_{2,m}^{\circ}$), Molecular Volume (V°), and Excess Molecular Volume ($V_{2,ex}^{\circ}$) of Sulphanilamide and Sulphanilic Acid in Water and in Aqueous NaCl Solutions

	sulphanilamide			sulphanilic acid		
m_B[a]	$V_{2,m}^{\circ} \cdot 10^{29}$	$V^{\circ} \cdot 10^{29}$	$V_{2,ex}^{\circ} \cdot 10^{29}$	$V_{2,m}^{\circ} \cdot 10^{29}$	$V^{\circ} \cdot 10^{29}$	$V_{2,ex}^{\circ} \cdot 10^{29}$
mol·kg^{-1}	m^3·molecule^{-1}	m^3·molecule^{-1}	m^3·molecule^{-1}	m^3·molecule^{-1}	m^3·molecule^{-1}	m^3·molecule^{-1}
0.0	20.42	26.47	−6.05	17.91	19.30	−1.39
0.05	20.23		−6.24	17.71		−1.59
0.1	20.34		−6.13	17.78		−1.52
0.3	20.42		−6.05	17.95		−1.35
0.5	20.42		−6.05	17.95		−1.35

[a] m_B is the molality of NaCl in water.

Jones−Dole equation. The values of the *A* and *B*-coefficients along with their standard deviations are summarized in the Supporting Information as Table ST1. The *A*-coefficient reflects the solute−solute interactions, and the *B*-coefficient reflects the solute−solvent interactions. At a given concentration, the *B*-coefficient can be interpreted in terms of competition between the specialized viscosity effect [Coulombic interactions, size and shape effect or Einstein effect, alignment or orientation of polar molecules by the ionic field and distortion of the solvent structure].[25]

The *B*-coefficients of transfer, $\Delta_{tr}B$, have been evaluated as follows,

$$\Delta_{tr}B = B\text{-coefficient (aqueous solution of NaCl)} - B\text{-coefficient in water} \quad (12)$$

The plots between $\Delta_{tr}B$ and molality of sodium chloride are given in the Figures 5 to 7. Both negative and positive values of $\Delta_{tr}B$ for sulphanilamide and sulphosalicyclic acid dihydrate have been observed at lower and at higher concentrations of NaCl, respectively. The values of $\Delta_{tr}B$ first decrease, and after passing through the minima, the values start increasing as the concentration of NaCl increases. It becomes positive for sulphosalicyclic acid dihydrate at a molality (m_B) of about 0.39 mol·kg^{-1} at 298.15 K, 0.32 mol·kg^{-1} at 308.15 K, 0.22 mol·kg^{-1} at 288.15 K, and 0.26 mol·kg^{-1} at 318.15 K. For sulphanilamide, the $\Delta_{tr}B$ values first decrease and then start increasing with the concentration of NaCl. The $\Delta_{tr}B$ values are negative at the three temperatures, (288.15 to 308.15) K, over the whole concentration range of NaCl studied, whereas at 318.15 K the $\Delta_{tr}B$ values become positive above $m_B \approx 0.1$ mol·kg^{-1}. Moreover, $\Delta_{tr}B$ values in this case increase with the temperature.

Similarly, for sulphanilic acid, the values of $\Delta_{tr}B$ first decrease up to $m_B \approx 0.05$ mol·kg^{-1} and then progressively increase with the increase in concentration of NaCl at all studied temperatures (except at concentrations above $m_B \approx 0.3$ mol·kg^{-1} at 318.15 K). In general, the $\Delta_{tr}B$ values decrease with temperature in this case.

The solvation[26] can be judged from the B/V_2° ratio given in Table ST2 of Supporting Information. These values are an important indicator of solvated and unsolvated drug molecules. The B/V_2° ratio lies between (0 and 2.5) for an unsolvated spherical species. A higher value is an indicator of solvated spherical species. For sulphanilamide and sulphanilic acid, the B/V_2° ratio is more in water than in aqueous sodium chloride solution, which means that these drugs are more solvated in water than in aqueous sodium chloride solutions. Similarly, the data in the case of sulphosalicyclic acid dihydrate show that this compound is more solvated at higher concentrations of sodium chloride. It can be said that sodium chloride enhances the solvation of sulphosalicyclic acid dihydrate but diminishes the solvation of sulphanilamide and sulphanilic acid.

According to Erying's simple model,[27] the average activation free energy of a single solute in a pure solvent can be calculated from the following equation.

$$\eta_o = (hN_A/V_1^{o})\exp(\Delta\mu_1^{o\#}/RT) \quad (13)$$

where *h*, N_A, *T*, and *R* are Planck's constant, Avogadro's number, the temperature, and universal gas constant, respectively, and V_1° is the average molar volume of aqueous sodium chloride solution at temperatures of (288.15 to 318.15) K, calculated from density data. The $\Delta\mu_1^{o\#}$ and V_1° values are given in Table ST2 of Supporting Information.

The activation free energy, $\Delta\mu_2^{o\#}$, for the viscous flow of sulpha drugs in aqueous and mixed aqueous solution is related to *B*-coefficients as reported by Feakins et al.,[28,29] as follows.

$$B = (V_1^{o} - V_2^{o}) + V_1^{o}(\Delta\mu_2^{o\#} - \Delta\mu_1^{o\#}/RT) \quad (14)$$

This can be rearranged as

$$\Delta\mu_2^{o\#} = \Delta\mu_1^{o\#} + (RT/V_1^{o})[B - (V_1^{o} - V_2^{o})] \quad (15)$$

The $\Delta\mu_2^{o\#}$ values are given in Table ST2 of Supporting Information.

The Gibbs energy of activation or Gibbs energy of transfer, $\Delta G_2^{\circ}(1\rightarrow1')$, is the difference between the solvation energy of the solute in the ground state solvent and the transition state solvent. The movement of solute through its own viscous transition state $\Delta G_2^{\circ}(2\rightarrow2')$ is the second contributor to $\Delta\mu_2^{o\#}$. The $\Delta G_2^{\circ}(1\rightarrow1')$ values given in the Supporting Information as Table ST2 have been obtained from $\Delta\mu_2^{o\#}$ values and $\Delta G_2^{\circ}(2\rightarrow2')$, which is equal to $\Delta\mu_1^{o\#}$. The positive $\Delta\mu_2^{o\#}$ and $\Delta G_2^{\circ}(1\rightarrow1')$ values are much larger in comparison to $\Delta\mu_1^{o\#}$, suggesting that the formation of the transition state is less favored in the presence of sulpha drugs at all studied temperatures. This may be because of the breaking and distortion of intramolecular bonds. The $\Delta G_2^{\circ}(1\rightarrow1')$ values increase as the concentration of sodium chloride increases, for all three drugs, with temperature. However, $\Delta G_2^{\circ}(1\rightarrow1')$ values for sulphanilamide and sulphanilic acid are higher in water than in the sodium chloride solutions. Thus, the increased concentration of NaCl retards the transfer of solute from the ground-state solvent to the transition-state solvent.

The values of activation entropy, $\Delta S_2^{o\#}$, and enthalpy, $\Delta H_2^{o\#}$, for the viscous flow of sulpha drug in water and in aqueous NaCl solution have been calculated by using the following relation.

$$\Delta S_2^{o\#} = -d(\Delta\mu_2^{o\#}/dT) \quad (16)$$

$$\Delta H_2^{o\#} = \Delta\mu_2^{o\#} + T\Delta S_2^{o\#} \quad (17)$$

The calculated activation parameters are given in Table ST2 of Supporting Information. The values for $\Delta H_2^{o\#}$ and $\Delta S_2^{o\#}$ for the studied drugs are concentration-specific, which may be due

Table 6. Relative Viscosities (η_r) of Some Sulpha Drugs in Water and Aqueous NaCl Solutions as a Function of Concentration of Sulpha Drugs and NaCl from T = (288.15 to 318.15) K

m_A / mol·kg^{-1}	η_r	m_A / mol·kg^{-1}	η_r	m_A / mol·kg^{-1}	η_r
		T/K = 288.15			
		Sulphanilamide in Water			
		(η_o[a] = 1.1382 mPa·s)			
0.01075	1.0038	0.01834	1.0061	0.02431	1.0074
0.02530	1.0079	0.03290	1.0100	0.03964	1.0119
		Sulphanilamide in Aqueous NaCl Solutions			
		m_B[b] = 0.05 mol·kg^{-1} (η_o = 1.1460 mPa·s)			
0.02032	1.0000	0.02245	1.0024	0.03130	1.0058
0.03783	1.0080				
		m_B = 0.1 mol·kg^{-1} (η_o = 1.1506 mPa·s)			
0.01146	1.0000	0.01584	1.0008	0.01697	1.0013
0.01980	1.0039	0.02915	1.0087		
		m_B = 0.3 mol·kg^{-1} (η_o = 1.1648 mPa·s)			
0.00541	1.0011	0.01089	1.0027	0.01427	1.0052
0.02284	1.0087	0.02890	1.0117		
		m_B = 0.5 mol·kg^{-1} (η_o = 1.1785 mPa·s)			
0.01132	1.0024	0.01913	1.0042	0.02165	1.0054
0.02805	1.0071	0.03503	1.0088		
		Sulphanilic Acid in Water			
0.01062	1.0044	0.01687	1.0060	0.02132	1.0075
0.03025	1.0103	0.03888	1.0133		
		Sulphanilic Acid in Aqueous NaCl Solutions			
		m_B = 0.05 mol·kg^{-1} (η_o = 1.1460 mPa·s)			
0.01005	1.0053	0.01394	1.0028	0.01944	1.0045
0.02225	1.0057	0.02762	1.0071	0.03738	1.0101
		m_B = 0.1 mol·kg^{-1} (η_o = 1.1506 mPa·s)			
0.00634	1.0012	0.01596	1.0050	0.02273	1.0072
0.03420	1.0119	0.03616	1.0121	0.04459	1.0154
		m_B = 0.3 mol·kg^{-1} (η_o = 1.1648 mPa·s)			
0.01572	1.0055	0.02235	1.0073	0.02715	1.0091
0.03258	1.0107	0.03725	1.0129		
		m_B = 0.5 mol·kg^{-1} (η_o = 1.1785 mPa·s)			
0.00817	1.0036	0.01315	1.0055	0.01945	1.0081
0.02199	1.0088	0.02800	1.0110	0.03112	1.0122
		Sulphosalicylic Acid Dihydrate in Water			
0.02287	1.0121	0.03321	1.0174	0.04266	1.0219
0.05981	1.0307				
		Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions			
		m_B = 0.05 mol·kg^{-1} (η_o = 1.1460 mPa·s)			
0.01046	1.0009	0.01846	1.0048	0.02689	1.0083
0.03631	1.0143	0.05138	1.0201		
		m_B = 0.1 mol·kg^{-1} (η_o = 1.1506 mPa·s)			
0.01133	0.9992	0.02465	1.0062	0.03089	1.0099
0.04301	1.0173	0.05364	1.0240		
		m_B = 0.3 mol·kg^{-1} (η_o = 1.1648 mPa·s)			
0.00921	1.0031	0.01558	1.0058	0.02249	1.0079
0.04368	1.0162	0.04812	1.0180	0.06164	1.0232
		m_B = 0.5 mol·kg^{-1} (η_o = 1.1785 mPa·s)			
0.01171	1.0074	0.02781	1.0139	0.03626	1.0177
0.04095	1.0192	0.05381	1.0259		
		T/K = 298.15			
		Sulphanilamide in Water			
		(η_o = 0.8904 mPa·s)			
0.01076	1.0032	0.01838	1.0053	0.02431	1.0070
0.02530	1.0075	0.03290	1.0098	0.03964	1.0118
		Sulphanilamide in Aqueous NaCl Solutions			
		m_B = 0.05 mol·kg^{-1} (η_o = 0.8978 mPa·s)			
0.01361	1.0059	0.01772	1.0088	0.02032	1.0100
0.02246	1.0115	0.03130	1.0174	0.03783	1.0213
		m_B = 0.1 mol·kg^{-1} (η_o = 0.9012 mPa·s)			
0.01146	1.0015	0.01584	1.0038	0.01697	1.0057
0.01980	1.0083	0.02915	1.0145		
		m_B = 0.3 mol·kg^{-1} (η_o = 0.9173 mPa·s)			
0.00541	0.9984	0.01089	0.9994	0.01427	1.0008
0.02284	1.0030	0.02890	1.0041		
		m_B = 0.5 mol·kg^{-1} (η_o = 0.9320 mPa·s)			
0.01913	1.0026	0.02196	1.0033	0.02805	1.0051
0.03503	1.0073				
		Sulphanilic Acid in Water			
0.01062	1.0052	0.01687	1.0074	0.02337	1.0098
0.03025	1.0108	0.03888	1.0144		
		Sulphanilic Acid in Aqueous NaCl Solutions			
		m_B = 0.05 mol·kg^{-1} (η_o = 0.8978 mPa·s)			
0.01161	1.0017	0.01339	1.0025	0.02361	1.0050
0.02722	1.0063	0.03062	1.0077	0.03704	1.0089
		m_B = 0.1 mol·kg^{-1} (η_o = 0.9012 mPa·s)			
0.00634	1.0016	0.01600	1.0045	0.02273	1.0070
0.03420	1.0110	0.03616	1.0115	0.04459	1.0142
		m_B = 0.3 mol·kg^{-1} (η_o = 0.9173 mPa·s)			
0.00873	1.0024	0.01572	1.0043	0.02235	1.0066
0.02715	1.0081	0.03258	1.0090	0.03725	1.0109
		m_B = 0.5 mol·kg^{-1} (η_o = 0.9320 mPa·s)			
0.00904	1.0032	0.01303	1.0039	0.01935	1.0067
0.02385	1.0074	0.03017	1.0092	0.03887	1.0120
		Sulphosalicylic Acid Dihydrate in Water			
0.02287	1.0107	0.03321	1.0145	0.04266	1.0188
0.05981	1.0260				
		Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions			
		m_B = 0.05 mol·kg^{-1} (η_o = 0.8978 mPa·s)			
0.01046	0.9989	0.01846	1.0038	0.02689	1.0084
0.03631	1.0133	0.05138	1.0206	0.05704	1.0233
		m_B = 0.1 mol·kg^{-1} (η_o = 0.9012 mPa·s)			
0.01133	0.9952	0.02466	1.0032	0.03089	1.0069
0.04301	1.0139	0.05365	1.0217		
		m_B = 0.3 mol·kg^{-1} (η_o = 0.9173 mPa·s)			
0.01558	1.0046	0.02249	1.0063	0.04368	1.0154
0.04812	1.0178	0.06164	1.0218		
		m_B = 0.5 mol·kg^{-1} (η_o = 0.9320 mPa·s)			
0.01171	1.0076	0.02781	1.0137	0.03626	1.0182
0.04095	1.0208	0.05381	1.0271		
		T/K = 308.15			
		Sulphanilamide in Water			
		(η_o = 0.7194 mPa·s)			
0.01076	1.0017	0.01838	1.0041	0.02431	1.0054
0.02530	1.0062	0.03290	1.0082		
		Sulphanilamide in Aqueous NaCl Solutions			
		m_B = 0.05 mol·kg^{-1} (η_o = 0.7251 mPa·s)			
0.01361	1.0002	0.01772	1.0012	0.02032	1.0017
0.02246	1.0020	0.03130	1.0047	0.03783	1.0079
		m_B = 0.1 mol·kg^{-1} (η_o = 0.7280 mPa·s)			
0.01697	0.9981	0.01980	0.9990	0.02915	1.0015
		m_B = 0.3 mol·kg^{-1} (η_o = 0.7433 mPa·s)			
0.00541	0.9986	0.01089	0.9998	0.01427	1.0010
0.02284	1.0033	0.02890	1.0046		
		m_B = 0.5 mol·kg^{-1} (η_o = 0.7564 mPa·s)			
0.01132	0.9988	0.01913	0.9999	0.02196	1.0012
0.02805	1.0024	0.03503	1.0048		
		Sulphanilic Acid in Water			
0.00618	1.0028	0.01062	1.0036	0.01687	1.0063
0.02132	1.0079	0.02337	1.0084	0.03888	1.0119
		Sulphanilic Acid in Aqueous NaCl Solutions			
		m_B = 0.05 mol·kg^{-1} (η_o = 0.7251 mPa·s)			
0.01339	1.0028	0.02360	1.0057	0.02722	1.0071
0.03062	1.0080	0.03704	1.0097		
		m_B = 0.1 mol·kg^{-1} (η_o = 0.7280 mPa·s)			
0.00634	1.0020	0.01596	1.0051	0.02273	1.0069
0.03420	1.0112	0.04459	1.0147		
		m_B = 0.3 mol·kg^{-1} (η_o = 0.7433 mPa·s)			
0.00873	1.0026	0.01572	1.0048	0.02235	1.0064
0.02715	1.0077	0.03258	1.0096	0.03746	1.0113
		m_B = 0.5 mol·kg^{-1} (η_o = 0.7564 mPa·s)			
0.01315	1.0017	0.01945	1.0030	0.02199	1.0035
0.02800	1.0048	0.03112	1.0055		

Table 6. Continued

m_A / mol·kg^{-1}	η_r	m_A / mol·kg^{-1}	η_r	m_A / mol·kg^{-1}	η_r
Sulphosalicylic Acid Dihydrate in Water					
0.02287	1.0102	0.03321	1.0151	0.04266	1.0191
0.05981	1.0265				
Sulphosalicylic Acid Dihydrate in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\eta_o = 0.7251$ mPa·s)					
0.01046	0.9992	0.01846	1.0037	0.02689	1.0085
0.03631	1.0137	0.05138	1.0215		
$m_B = 0.1$ mol·kg^{-1} ($\eta_o = 0.7280$ mPa·s)					
0.01133	0.9997	0.02466	1.0054	0.03089	1.0094
0.04301	1.0185	0.05365	1.0272		
$m_B = 0.3$ mol·kg^{-1} ($\eta_o = 0.7433$ mPa·s)					
0.01558	1.0039	0.02249	1.0060	0.04368	1.0147
0.04812	1.0163	0.06164	1.0211		
$m_B = 0.5$ mol·kg^{-1} ($\eta_o = 0.7564$ mPa·s)					
0.01171	1.0083	0.02781	1.0155	0.03626	1.0203
0.04095	1.0228	0.05381	1.0287		
T/K = 318.15					
Sulphanilamide in Water					
($\eta_o = 0.5963$ mPa·s)					
0.01076	1.0003	0.01838	1.0027	0.02431	1.0049
0.02530	1.0051	0.03290	1.0073	0.03964	1.0088
Sulphanilamide in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\eta_o = 0.6022$ mPa·s)					
0.02032	0.9981	0.02246	0.9986	0.03130	1.0003
0.03783	1.0029				
$m_B = 0.1$ mol·kg^{-1} ($\eta_o = 0.6056$ mPa·s)					
0.00597	0.9975	0.01146	0.9981	0.01584	0.9987
0.01980	0.9993	0.02915	1.0007		
$m_B = 0.3$ mol·kg^{-1} ($\eta_o = 0.6189$ mPa·s)					
0.00541	0.9996	0.01089	1.0001	0.01427	1.0007
0.02284	1.0026	0.02890	1.0034		
$m_B = 0.5$ mol·kg^{-1} ($\eta_o = 0.6296$ mPa·s)					
0.01132	1.0021	0.01913	1.0041	0.02196	1.0047
0.02805	1.0060	0.03503	1.0077		
Sulphanilic Acid in Water					
0.01136	1.0060	0.02046	1.0079	0.02864	1.0117
0.03381	1.0130	0.03759	1.0144	0.04297	1.0155
Sulphanilic Acid in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\eta_o = 0.6022$ mPa·s)					
0.01161	1.0023	0.01339	1.0029	0.02361	1.0058
0.02721	1.0068	0.03062	1.0082	0.03704	1.0098
$m_B = 0.1$ mol·kg^{-1} ($\eta_o = 0.6056$ mPa·s)					
0.00634	1.0011	0.01596	1.0039	0.02273	1.0062
0.03420	1.0107	0.03616	1.0113	0.04459	1.0134
$m_B = 0.3$ mol·kg^{-1} ($\eta_o = 0.6189$ mPa·s)					
0.00873	1.0024	0.01572	1.0049	0.02235	1.0066
0.02715	1.0079	0.03258	1.0096	0.03725	1.0109
$m_B = 0.5$ mol·kg^{-1} ($\eta_o = 0.6296$ mPa·s)					
0.01315	1.0034	0.01945	1.0050	0.02199	1.0056
0.02800	1.0073	0.03112	1.0082		
Sulphosalicylic Acid Dihydrate in Water					
0.02287	1.0115	0.03321	1.0167	0.04266	1.0208
0.05981	1.0277				
Sulphosalicylic Acid in Aqueous NaCl Solutions					
$m_B = 0.05$ mol·kg^{-1} ($\eta_o = 0.6022$ mPa·s)					
0.01046	1.0016	0.01846	1.0044	0.02689	1.0077
0.03631	1.0112	0.05138	1.0191		
$m_B = 0.1$ mol·kg^{-1} ($\eta_o = 0.6056$ mPa·s)					
0.02466	1.0047	0.03089	1.0084	0.04301	1.0138
0.05365	1.0205				
$m_B = 0.3$ mol·kg^{-1} ($\eta_o = 0.6189$ mPa·s)					
0.00921	1.0021	0.01557	1.0041	0.04368	1.0127
0.04812	1.0150	0.06164	1.0197		
$m_B = 0.5$ mol·kg^{-1} ($\eta_o = 0.6296$ mPa·s)					
0.01171	1.0117	0.02781	1.0184	0.03626	1.0219
0.04095	1.0242	0.05381	1.0306		

[a] η_o is the viscosity of aqueous NaCl solutions. [b] m_B is the molality of NaCl in water.

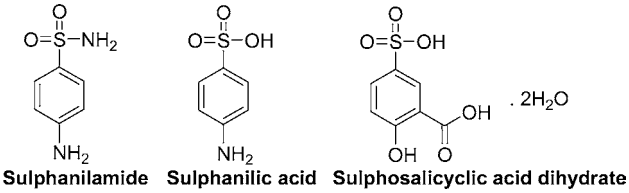

Figure 4. Structure of sulpha drugs.

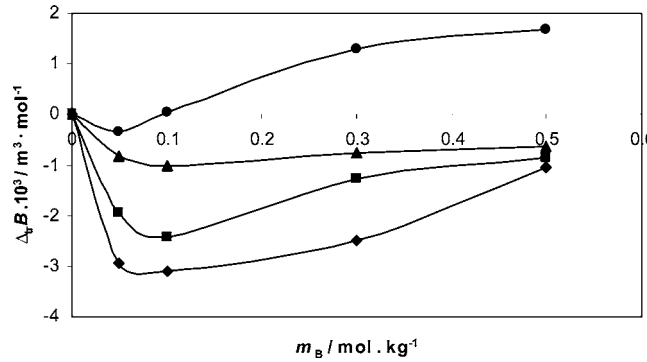

Figure 5. Viscosity B: coefficient transfer ($\Delta_{tr}B$) vs m_B for sulphanilamide at the following temperatures: ♦, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

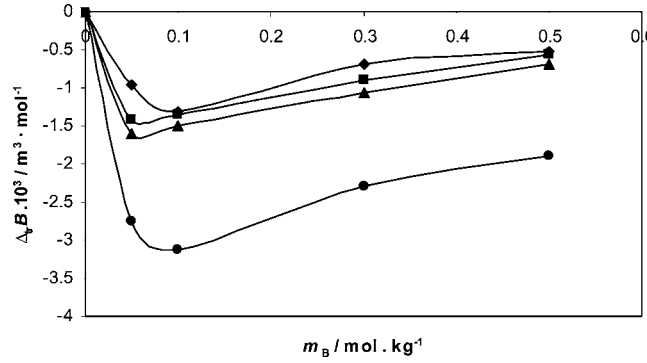

Figure 6. Viscosity B: coefficient transfer ($\Delta_{tr}B$) vs m_B for sulphanilic acid at the following temperatures: ♦, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

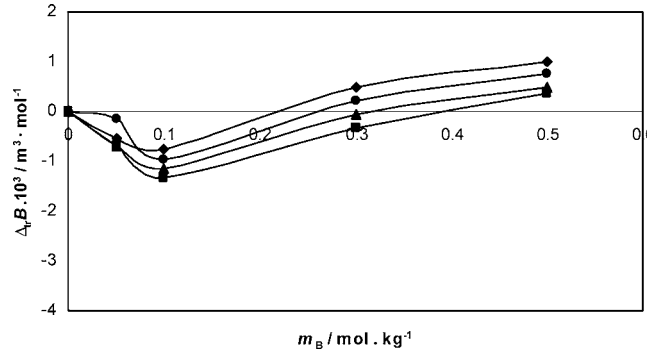

Figure 7. Viscosity B: coefficient transfer ($\Delta_{tr}B$) vs m_B for sulphosalicylic acid at the following temperatures: ♦, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

to the competition between various interactions occurring in these solutions.

Conclusion

The partial molar volumes and viscosity B-coefficients for sulphanilamide, sulphanilic acid, and sulphosalicylic acid dihydrate in water and in aqueous (0.05, 0.1, 0.3, and 0.5) mol·kg^{-1} sodium chloride solutions have been determined at

temperatures from (288.15 to 318.15) K. The negative S_v values in the case of sulphanilamide and sulphanilic acid in water as well as in aqueous sodium chloride solutions have been attributed to the self-association of these molecules. The transfer volumes at infinite dilution have both negative and positive values. The overall positive values at a higher concentration of sodium chloride are in the following order: sulphosalicylic acid dihydrate > sulphanilic acid > sulphanilamide, which is also the order of hydrophilicity of these drugs. The $(\partial^2 V_2°/\partial T^2)_P$ values suggest that sulphanilamide and sulphosalicylic acid dihydrate are structure breakers in both water and aqueous sodium chloride solutions, but sulphanilic acid is a structure maker in water and a structure breaker in sodium chloride solutions. Negative values of excess molecular volume also justify the self-association of sulphanilamide and sulphanilic acid. The results of activation free energy for the viscous flow of solutions suggest the formation of transition state is less favored in the presence of studied sulpha drugs.

Supporting Information Available:

Figures and tables of the viscosities, *B*-coefficients, average molar volume, and activation free energy of water and aqueous NaCl solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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