

# Viscosities of tetrabutylammonium bromide, sodium tetraphenylborate and sodium bromide in 2-ethoxyethanol+water mixed solvent media at 308.15, 313.15, 318.15 and 323.15 K

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## Abstract

The viscosities of the solutions of tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ), sodium tetraphenylborate ( $\text{NaBPh}_4$ ), sodium bromide ( $\text{NaBr}$ ) in 2-ethoxyethanol+water mixed solvent media containing 0.25, 0.50 and 0.75 mass fractions of 2-ethoxyethanol ( $w_1$ ) have been reported at 308.15, 313.15, 318.15, and 323.15 K. The viscosity data have been analyzed by the Jones–Dole equation for the associated electrolytes to evaluate the viscosity B-coefficients of the electrolytes. These data have also been analyzed by the transition-state treatment to obtain contribution of the solutes to the free energy of activation for viscous flow of the solution. The viscosity of the solvent is found to be greatly modified by the presence of the tetrabutylammonium, tetraphenylborate and bromide ions; sodium ion, on the other hand, is not such efficient in modifying the viscosity of the media investigated. Moreover, these ions behave neither as structure-breaker nor as structure-maker and the formation of the transition-state is made less favorable in their presence in aqueous 2-ethoxyethanol solutions.

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## 1. Introduction

Recently, we have initiated a comprehensive program to study the solvation and association behavior of several 1:1 electrolytes in different nonaqueous solvents from the measurements of various transport, thermodynamic and spectroscopic properties [1–8]. As a part of this series of investigations, we have, very recently, reported [9–11] the results of viscosity measurements on a number of tetraalkylammonium and alkali metal salts in 2-ethoxyethanol+water mixtures at 308.15, 313.15, 318.15, and 323.15 K. We have now extended this work to study the viscometric behavior of tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ), sodium tetraphenylborate ( $\text{NaBPh}_4$ ), sodium bromide ( $\text{NaBr}$ ) in these mixed solvent media since viscometry is well-suited to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles [12–14].

## 2. Experimental

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction was collected. The purified solvent had a density ( $\rho_0$ ) of  $0.92497 \text{ g}\cdot\text{cm}^{-3}$  and a viscosity ( $\eta_0$ ) of  $1.8277 \text{ mPa}\cdot\text{s}$  at 298.15 K; these values are found to be in good agreement with the literature values [15,16]. Triply distilled water with a specific conductance of less than  $10^{-6} \text{ S}\cdot\text{cm}^{-1}$  at 308.15 K was used for the preparation of the mixed solvents by mass. The physical properties of 2-ethoxyethanol-water mixed solvents used in this study at 308.15, 313.15, 318.15, and 323.15 K are reported in Table 1. The relative permittivities of 2-ethoxyethanol-water mixtures at the experimental temperatures were obtained with the equations as described in the literature [17] using the literature density and relative permittivity data of the pure solvents [7,18] and the densities of the mixed solvents given in Table 1.

Tetrabutylammonium bromide was of purissimum grade (Fluka) and was purified as described in the literature [19]. It

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was purified by recrystallization. The recrystallized salt was dried *in vacuo* at elevated temperatures for 12 h immediately prior to use.

Sodium tetraphenylborate (Fluka, purissimum) was recrystallized from acetone and dried *in vacuo* at 353.15 K for 72 h. Sodium bromide (Fluka, purissimum) was dried *in vacuo* for 72 h and was used without further purification.

The kinematic viscosities ( $\nu$ ) were measured by means of a suspended level Ubbelohde viscometer. The viscometer was kept in a vertical position in a water thermostat controlled to  $\pm 0.01$  K. The kinematic viscosity ( $\nu$ ) and the absolute viscosity ( $\eta$ ) are given by the following equations:

$$\nu = Ct - K/t \quad (1)$$

$$\eta = \nu\rho \quad (2)$$

where  $t$  is the efflux time,  $\rho$  is the density, and  $C$  and  $K$  are the characteristic constants of the viscometer. The values of the constants  $C$  and  $K$ , determined by using the density and the viscosity values of water and 2-methoxyethanol [20], were found to be  $1.646 \times 10^{-5} \text{ cm}^2 \text{ s}^{-2}$  and  $-0.02331647 \text{ cm}^2$ , respectively. The calibration constants were also checked with methanol [21]. The uncertainty of the viscosity results was within  $\pm 0.003 \text{ mPa}\cdot\text{s}$ . The required densities ( $\rho$ ) were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of about 0.1 cm. The relative viscosity ( $\eta_r$ ) was obtained as the ratio of the absolute viscosity of the solution ( $\eta$ ) to that of the pure solvent ( $\eta_0$ ).

The solutions were prepared by mass for the viscosity runs, the molalities being converted to molarities by the use of densities. In order to avoid moisture pick-up, all solutions were prepared in a dehumidified room with utmost care. In all cases the experiments were performed at least in several replicates for each solution and the results were averaged. Several independent solutions were prepared and the runs were performed to ensure the reproducibility of the results.

Table 1  
Properties of 2-ethoxyethanol+water mixtures with 0.25, 0.50, and 0.75 mass fractions ( $w_1$ ) of 2-ethoxyethanol at 308.15, 313.15, 318.15, and 323.15 K

$T$ (K)	$\rho_0$ ( $\text{g cm}^{-3}$ )	$\eta_0$ (mPa s)	$\epsilon$
$w_1=0.25$			
308.15	1.00354	1.8430	60.13
313.15	1.00021	1.5293	58.70
318.15	0.99781	1.2738	57.37
323.15	0.99582	1.0923	56.11
$w_1=0.50$			
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.96
$w_1=0.75$			
308.15	0.95451	1.7002	27.93
313.15	0.95147	1.5293	27.29
318.15	0.94873	1.3498	26.68
323.15	0.94625	1.1901	26.10

Table 2

Theoretical  $A$ -coefficients, the viscosity  $B$ -coefficients and the free energies of activation for viscous flow of electrolytes in 2-ethoxyethanol+water mixtures with 0.25, 0.50, and 0.75 mass fractions ( $w_1$ ) of 2-ethoxyethanol at 308.15, 313.15, 318.15, and 323.15 K

Electrolyte	$A$ ( $\text{dm}^{3/2} \text{ mol}^{-1/2}$ )	$B$ ( $\text{dm}^3 \text{ mol}^{-1}$ )	$\Delta\mu_2^{\ddagger}$ ( $\text{kJ mol}^{-1}$ )
$w_1=0.25$			
$T=308.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0067	0.447	82.78
NaBr	0.0049	0.190	35.30
NaBPh <sub>4</sub>	0.0116	0.447	84.26
$T=313.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0075	0.450	83.93
NaBr	0.0056	0.193	35.85
NaBPh <sub>4</sub>	0.0124	0.455	86.02
$T=318.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0084	0.454	85.30
NaBr	0.0064	0.194	36.19
NaBPh <sub>4</sub>	0.0133	0.474	89.06
$T=323.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0092	0.455	86.28
NaBr	0.0071	0.196	36.76
NaBPh <sub>4</sub>	0.0140	0.480	90.77
$w_1=0.50$			
$T=308.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0085	0.616	77.70
NaBr	0.0074	0.224	31.29
NaBPh <sub>4</sub>	0.0108	0.608	77.61
$T=313.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0088	0.632	79.50
NaBr	0.0078	0.238	32.59
NaBPh <sub>4</sub>	0.0112	0.624	79.41
$T=318.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0097	0.646	81.22
NaBr	0.0085	0.244	33.21
NaBPh <sub>4</sub>	0.0120	0.634	80.84
$T=323.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0103	0.654	84.49
NaBr	0.0090	0.257	34.58
NaBPh <sub>4</sub>	0.0126	0.645	82.58
$w_1=0.75$			
$T=308.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0147	0.747	63.13
NaBr	0.0147	0.193	24.02
NaBPh <sub>4</sub>	0.0188	0.634	57.88
$T=313.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0148	0.778	65.18
NaBr	0.0146	0.206	24.72
NaBPh <sub>4</sub>	0.0184	0.663	59.74
$T=318.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0149	0.787	66.35
NaBr	0.0144	0.227	26.03
NaBPh <sub>4</sub>	0.0182	0.693	61.98
$T=323.15 \text{ K}$			
Bu <sub>4</sub> NBr	0.0158	0.796	67.45
NaBr	0.0149	0.242	23.49
NaBPh <sub>4</sub>	0.0189	0.706	63.24

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