

CHAPTER X

Apparent Molar Volumes and Viscosity *B*-coefficients of Nicotinamide in Aqueous Tetrabutylammonium Bromide Solutions at 298.15, 308.15 and 318.15 K*

10.1. Introduction

Enzymes are the functional unit of cell metabolism as they catalyze different reactions to degrade nutrient molecules into simple ones. Many enzymes require a non-protein cofactor for their catalytic activities. Vitamins are essential precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways.¹ Nicotinamide, commonly known as vitamin B₃,² is a water-soluble vitamin, an essential micronutrient and a reactive moiety of the coenzyme nicotinamide adenine dinucleotide (NAD).

It is an essential part of the coenzyme- nicotinamide adenine dinucleotide phosphate (NADP), its reduced form NADPH, and NAD along with its reduced form NADH. It also serves to maintain normal function of the digestive systems and cholesterol levels in human body.¹ The combination of nicotinic acid and nicotinamide is clinically referred to as niacin,³⁻⁵ since nicotinic acid is readily converted in the body into the amide and for nutritional purposes the two have equal biological activities. Nicotinamide is also an interesting molecule for its two nitrogen atoms- one in the heterocyclic ring and the other as the amide group.

Tetraalkylammonium salts are bulky in nature and are known to orient water molecules around them depending on their alkyl chain.^{6,7} Salts like tetrabutylammonium bromide (TBAB) can give a better insight into the effect of electrostatic and hydrophobic interactions on the stability of vitamins as these salts are known to influence macromolecular conformations by weakening attraction or repulsion inter- and intra-

charge-charge interactions and by affecting hydrophobic interactions through the side chain of the alkyl groups. Although there have extensive studies on various properties of nicotinamide,^{2,8-12} studies on partial molar volumes and viscosity of nicotinamide in aqueous salt solutions are still rare. As partial molar volumes and viscosity *B*-coefficients of a solute reflects the cumulative effects^{13,14} of the solute-solute and solute-solvent interactions in solutions, in this chapter we attempted to study these properties for nicotinamide in aqueous binary mixtures of tetrabutylammonium bromide (TBAB) at $T = (298.15, 308.15 \text{ and } 318.15)$ K to unravel the various interactions prevailing in the ternary systems under investigation.

10.2. Experimental Section

10.2.1. Chemicals

Nicotinamide was purchased from Sigma Chemical Company, USA and used as such. Its mass purity as supplied by the vendor is 99%. TBAB was purified by dissolving it in mixed alcohol medium and recrystallising from the solvent ether medium.⁶ After filtration, the salt was dried *in vacuo* for few hours. Triply distilled, degassed water with a specific conductance $<10^{-6} \text{ S.cm}^{-1}$ was used for the preparation of different aqueous TBAB solutions. The physical properties of different aqueous TBAB solutions are listed in Table 1.

Stock solutions of nicotinamide in different aqueous TBAB solutions were prepared by mass and the working solutions were prepared by mass dilution. The conversion of molality into molarity was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molarity of the nicotinamide solutions is evaluated to $\pm 0.0001 \text{ mol.dm}^{-3}$.

10.2.2. Measurements

The densities were measured with an Ostwald-Sprengel-type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at $T = (298.15, 308.15 \text{ and } 318.15)$ K with doubly distilled water and benzene.

The pycnometer with the test solution was equilibrated in a water bath maintained at ± 0.01 K of the desired temperatures. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. Adequate precautions were taken to avoid evaporation losses during the time of actual measurements. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty in density was estimated to be ± 0.0001 g.cm⁻³ and that of the temperature is ± 0.01 K.

The viscosity was measured by means of a suspended Ubbelohde-type viscometer thoroughly cleaned, dried and calibrated at $T = (298.15, 308.15$ and $318.15)$ K with triply distilled water and purified methanol. It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a stopwatch correct to ± 0.1 s. In all determinations, an average of triplicate measurements was taken into account. Viscosity of solution (η) is given by the following equation:

$$\eta = (Kt - L/t) \rho \quad (1)$$

where K and L are the viscometer constants; and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ± 0.003 mPa.s. Details of the methods and techniques of density and viscosity measurements have been described elsewhere.^{15,16}

The experimental values of concentrations (c), densities (ρ), viscosities (η) and derived parameters at various temperatures are reported in Table 2.

10.3. Results and Discussion

For the analysis of solvation state of nicotinamide in aqueous TBAB solutions and the interaction between nicotinamide and TBAB, data of partial molar volumes are important. For this purpose, the apparent molar volumes (ϕ_v) were determined from the solution densities using the following equation:^{15,17}

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (2)$$

where M is the molar mass of the solute, c is the molar concentration of the solution; ρ_0 and ρ are the densities of the solvent and solution, respectively. As the plots of ϕ_v against square root of molar concentration \sqrt{c} , were non-linear, ϕ_v values were fitted to the following equation:¹⁰

$$\phi_v = \phi_v^0 + A_v\sqrt{c} + B_v c \quad (3)$$

where ϕ_v^0 is the partial molar volume at infinite dilution; A_v and B_v are two adjustable parameters. The ϕ_v^0 values have been determined by fitting the dilute data ($c < 0.1$) to equation (3) using a weighted least squares fit. The values of ϕ_v^0 , A_v and B_v at each temperature are reported in Table 3. The estimated uncertainties in ϕ_v^0 are equal to standard deviation (σ), the root mean square of the deviations between the experimental and calculated ϕ_v for each data point. Our ϕ_v^0 values for the aqueous nicotinamide solutions at $T = (298.15 \text{ and } 308.15) \text{ K}$ were in good agreement with the ϕ_v^0 values reported earlier¹⁰ within the experimental uncertainty. Table 3 shows that ϕ_v^0 values are generally positive and increase with a rise in both the temperature and molarity of TBAB in the mixtures. This indicates the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperatures and higher molarity of TBAB in the solutions. The crystal structure of nicotinamide is well reported by Wright and King.¹¹ In the crystal, nicotinamide is linked by two weak hydrogen bonds from the hydrogen atoms of amide N-atom to the O-atom of one neighbouring molecule and to the ring N-atom of another molecules in such a fashion that a two-dimensional network parallel to (010) plane is formed with a inter-planer distance of 3.579 nm at $T = 295.15 \text{ K}$. Charman *et al.*¹² also reported the structure of nicotinamide in aqueous solution. They studied the concentration-dependent self-association of nicotinamide in solution by ¹H and ¹³C NMR spectroscopy and osmometric measurements. Their results justified that nicotinamide associates in aqueous solution with the amide

groups of each nicotinamide molecule creating large associated species at higher concentrations. This fact justifies the observed decrease in apparent molar volume with increasing concentration. This also manifests that the effect of parameter A_v predominates over that of parameter B_v in characterizing ϕ_v values in equation (3).

The partial molar volumes ϕ_v^0 were fitted to a polynomial of the following type in terms of absolute temperature T :

$$\phi_v^0 = a_0 + a_1 T + a_2 T^2 \quad (4)$$

Values of the coefficients of the above equation for different nicotinamide solutions are listed in Table 4.

The partial molar expansibilities ϕ_E^0 can be obtained by the following equation:¹⁸

$$\phi_E^0 = \left(\delta \phi_v^0 / \delta T \right)_p = a_1 + 2 a_2 T \quad (5)$$

The ϕ_E^0 values for different ternary solutions at $T = (298.15, 308.15$ and $318.15)$ K are given in Table 5. Table 5 reveals that ϕ_E^0 value increases as the temperature increases up to 0.05 mol.dm^{-3} of TBAB in mixtures, but there after ϕ_E^0 value decreases slightly with increasing temperature within the error range. This fact may be attributed to gradual disappearance of caging or packing effect^{19,20} in the ternary solutions.

According to Hepler,²¹ the sign of $\left(\delta \phi_E^0 / \delta T \right)_p$ is a better criterion in characterizing the long-range structure-making and breaking ability of the solutes in solution. The general thermodynamic expression used is as follows:

$$\left(\delta \phi_E^0 / \delta T \right)_p = \left(\delta^2 \phi_v^0 / \delta T^2 \right)_p = 2 a_2 \quad (6)$$

If the sign of $\left(\delta \phi_E^0 / \delta T \right)_p$ is positive or small negative, the solute is a structure maker, otherwise it is a structure breaker. As evident from Table 5, nicotinamide predominantly acts as a structure maker and its structure making ability increases with a rise in temperature but decreases to some extent as the molarity of TBAB increases in the mixtures. This observation is in line with the observation made by Kundu and Kishore.¹⁰ They

suggested that nicotinamide acts as water-structure promoter due to hydrophobic hydration. The small negative values of $(\delta\phi_E^0/\delta T)_p$ at 0.10 and 0.15 mol.dm⁻³ aqueous TBAB solutions are probably due to higher structure promoting ability of TBAB than nicotinamide with comparatively higher ϕ_V^0 value in aqueous solution⁷ originating from hydrophobic hydration with greater degree of hydrogen bonding than the bulk water.²²

Partial molar volumes of transfer ($\Delta\phi_V^0$) from water to different aqueous TBAB solutions have been determined using the relations:^{23,24}

$$\Delta\phi_V^0 = \phi_V^0 \text{ (Aqueous TBAB solution)} - \phi_V^0 \text{ (Water)} \quad (7)$$

The $\Delta\phi_V^0$ value, by definition, is free from solute-solute interactions and therefore provides information regarding solute-cosolute interactions.²³ As can be seen from Table 7, the value of $\Delta\phi_V^0$ is positive at all the experimental temperatures and increases monotonically with the molarity of TBAB in the ternary mixtures. The concentration dependence of the thermodynamic properties of the solutes in aqueous solutions can be explained in terms of overlap of hydration co-spheres. According to the co-sphere model, as developed by Friedman and Krishnan,²⁵ the effect of overlap of the hydration co-spheres is destructive. The overlap of hydration co-spheres of two ionic species results in an increase in volume but that of hydration co-spheres of hydrophobic-hydrophobic groups and ion-hydrophobic groups results in a net volume decrease. The positive values of $\Delta\phi_V^0$ indicate that hydrophobic-hydrophobic and ion-hydrophobic group interactions are predominant and the overall effect of the overlap of the hydration co-spheres of nicotinamide and TBAB reduce the effect of electrostriction of water by nicotinamide molecules and this effect increases with the molarity of TBAB in the ternary mixtures as shown in figure 1 ($\Delta\phi_V^0$ versus molarity of TBAB in solution). In addition, standard partial molar volumes of the solute have also been explained by a simple model:^{26, 27}

$$\phi_V^0 = \phi_{VW} + \phi_{Void} - \phi_S \quad (8)$$

where ϕ_{vw} is the Vander Waals volume, ϕ_{void} is the volume associated with voids or empty space and ϕ_s the shrinkage volume due to electrostriction. Assuming the ϕ_{vw} and ϕ_{void} have the same magnitudes in water and in aqueous TBAB solutions for the same solute,²⁸ the increase in ϕ_V^0 values and the concomitant positive $\Delta\phi_V^0$ values can be attributed to the decrease in the shrinkage volume of water by nicotinamide in presence of TBAB. This fact suggests that TBAB has a dehydration effect on the hydrated nicotinamide.

In the literature,¹⁰ pyridine has been stated as a structure-breaker in aqueous solution and the structure-promoting propensity of nicotinamide has been assigned to the $-\text{CONH}_2$ group. Thus, the interactions between nicotinamide and TBAB in water can roughly be summarized as follows: (i) interaction of Bu_4N^+ ion with the N-atom in the heterocyclic ring of nicotinamide, (ii) interaction of Bu_4N^+ ion with the N-atom in the amide group of nicotinamide, (iii) interaction of Bu_4N^+ ion with the O-atom in the amide group of nicotinamide, (iv) interaction of Br^- ion with the N-atom in the amide group of nicotinamide and (v) ionic-hydrophobic interactions between ions of TBAB and non-polar part of nicotinamide molecules. While interactions (i)-(iv) contribute positively, interaction (v) contribute negatively to ϕ_V^0 values. Therefore, the overall positive ϕ_V^0 values indicate that ionic-group interactions predominate over ionic-hydrophobic interactions and thus reduce the electrostriction of water molecules by nicotinamide imparting positive values of $\Delta\phi_V^0$.

The viscosity data of the aqueous and aqueous electrolytic solutions of nicotinamide have been analyzed using the Jones-Dole²⁹ equation:

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (9)$$

where $\eta_r = \eta/\eta_0$, η_0 and η are the viscosities of solvent and solution, respectively. The *A* and *B* are the constants estimated by a least-squares method and reported in Table 6.

A perusal of Table 6 shows that the values of the *A* coefficient are generally negative for all the solutions under investigation at all

experimental temperatures. These results indicate the presence of weak solute-solute interactions and these interactions further decrease with an increase in both the temperature and molarity of TBAB in the mixtures. The viscosity *B*-coefficient³⁰ reflects the effects of solute-solvent interactions on the solution viscosity. Table 6 illustrates that the values of the viscosity *B*-coefficient for nicotinamide in the studied solvent systems are positive, thereby suggesting the presence of strong solute-solvent interaction and these types of interactions are strengthened with a rise in both the temperature and molarity of TBAB in the mixtures.

Viscosity *B*-coefficients of transfer (ΔB) from water to different aqueous TBAB solutions have been determined using the relations:^{23,24}

$$\Delta B = B(\text{aqueous TBAB solution}) - B(\text{water}). \quad (10)$$

The ΔB values shown in Table 7 and depicted graphically in Figure 1 (ΔB versus molarity of TBAB in solution) as a function of molarity of TBAB in solutions at the experimental temperatures support the results obtained from $\Delta\phi_v^0$ values discussed above.

The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity as suggested by Feakings *et al.*³¹ using the following equation:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + RT(1000B + \bar{V}_2^0 - \bar{V}_1^0)/\bar{V}_1^0 \quad (11)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and solute, respectively. The contribution per mole of the solute to the free energy of activation of viscous flow, $\Delta\mu_2^{0*}$, of the solutions was determined from the above relation. The free energy of activation of viscous flow for the pure solvent/solvent mixture, $\Delta\mu_1^{0*}$, is given by the relation:^{31,32}

$$\Delta\mu_1^{0*} = \Delta G_1^{0*} = RT \ln(\eta_0 \bar{V}_1^0 / hN_A) \quad (12)$$

where N_A is the Avogadro's number and the other symbols have their usual significance. The values of the parameters $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are reported in Table 8. Table 8 shows that $\Delta\mu_1^{0*}$ is almost constant at all the solvent compositions and temperatures, implying that $\Delta\mu_2^{0*}$ is dependent mainly on the viscosity *B*-coefficients and $(\bar{V}_2^0 - \bar{V}_1^0)$ terms. But $\Delta\mu_2^{0*}$ values were

found to be positive at all the experimental temperatures and this suggests that the process of viscous flow becomes difficult as the temperature and molarity of TBAB in solutions increases. Hence the formation of the transition state becomes less favourable.³¹ According to Feakings *et al.*³¹ $\Delta\mu_2^{0\ddagger} > \Delta\mu_1^{0\ddagger}$ for solutes having positive viscosity *B*-coefficients and indicates a stronger solute-solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure.³¹ The greater the value of $\Delta\mu_2^{0\ddagger}$, the greater is the structure-making tendency of the solute and the positive values of $\Delta\mu_2^{0\ddagger}$ for nicotinamide in the different aqueous TBAB solutions suggests nicotinamide to be a net structure promoter in these ternary mixtures. The entropy of activation for electrolytic solutions has been calculated using the relation:³¹

$$\Delta S_2^{0\ddagger} = -d(\Delta\mu_2^{0\ddagger})/dT \quad (13)$$

where $\Delta S_2^{0\ddagger}$ has been obtained from the negative slope of the plots of $\Delta\mu_2^{0\ddagger}$ against *T* by using a least squares treatment.

The activation enthalpy ($\Delta H_2^{0\ddagger}$) has been calculated using the relation:³¹

$$\Delta H_2^{0\ddagger} = \Delta\mu_2^{0\ddagger} + T \Delta S_2^{0\ddagger} \quad (14)$$

The value of $\Delta S_2^{0\ddagger}$ and $\Delta H_2^{0\ddagger}$ are listed in Table 8 and they were found to be negative for all the experimental solutions at all the temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state.^{31,32}

10.4. Conclusion

In summary, ϕ_v^0 and viscosity *B*-coefficient values for nicotinamide indicate the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperatures and higher molarity of TBAB in the ternary solutions. Nicotinamide also acts as a

water-structure promoter due to hydrophobic hydration in the presence of TBAB. Interestingly enough, this study revealed that TBAB has dehydration effects on the hydrated nicotinamide and thus, deserves more experimental investigations in this regard.

References

- [1] F. A. Robinson, *The Vitamin B-Complexes*, Chapman & Hall, London, (1951), Ch. 4.
- [2] S. Cakir, I. Bulut, E. Bicer, O. Cakir, *J. Coord. Chem.*, **56** (2003) 511.
- [3] A. N. Nesmeyanov, N. A. Nesmeyanov, *Fundamentals of Organic Chemistry*, vol. 3, Mir Publishers, Moscow, (1981), p. 393.
- [4] A. S. Fauci, E. Braunwald, K. J. Isselbacher, J. D. Wilson, J. B. Martin, D. L. Kasper, S. L. Hauser, D. L. Long, *Harrison's Principles of Internal Medicine*, vol. 1, 14th ed., McGraw-Hill, New York, (1998).
- [5] C. R. W. Edwards, I. A. D. Bouchier, C. Haslett, E. R. Chilvers, *Davidson's Principles and Practice of Medicine*, 17th ed., BPC Paulton Books Limited, Great Britain, (1996).
- [6] M. N. Roy, B. Sinha, V. K. Dakua, *Pak. J. Sci. Ind. Res.*, **49** (2006) 153.
- [7] L. H. Blanco, E. F. Vargas, *J. Solution Chem.*, **35** (2006) 21.
- [8] H. G. Windmuller, C. J. Ackerman, H. Bakerman, O. Mickelsen, *J. Biological. Chem.*, **234** (1959) 889.
- [9] M. Iwaki, N. P. J. Cotton, P. G. Quirk, P. R. Rich, J. B. Jackson, *J. Am. Chem. Soc.*, **128** (2006) 2621.
- [10] A. Kundu, N. Kishore, *J. Solution. Chem.*, **32** (2003) 703.
- [11] W. B. Wright, G. S. D. King, *Acta Crystallogr.*, **7** (1954) 283.
- [12] W. N. Charman, C. S. C. Lai, D. J. Craik, *Aust. J. Chem.*, **46** (1993) 377.
- [13] J. M. McDowall, C. A. Vincent, *J. Chem. Soc. Faraday Trans*, **1** (1974) 1862.
- [14] M. R. J. Deck, K. J. Bird, A. J. Parker, *Aust. J. Chem.*, **28** (1975) 955.

- [15] M. N. Roy, B. Sinha, V. K. Dakua, *J. Chem. Eng. Data*, **51** (2006) 590.
- [16] M. N. Roy, B. Sinha, *J. Mol. Liq.*, **133** (2007) 89.
- [17] B. Sinha, V. K. Dakua, M. N. Roy, *J. Chem. Eng. Data*, **52** (2007) 1768.
- [18] M. N. Roy, B. Sinha, R. Dey, *Int. J. Thermophys.*, **26** (2005) 1549.
- [19] F. J. Millero, *Structure and Transport Process in Water and Aqueous Solutions*, Ed. R. A. Horne, New York, (1972).
- [20] M. L. Parmar, D. S. Banyal, *Indian. J. Chem.*, **44A** (2005) 1582.
- [21] L. G. Hepler, *Can. J. Chem.*, **47** (1969) 4617.
- [22] W. Y. Wen, *Water and Aqueous Solution*, Ed. R. A. Horne, Willey-Interscience, New York, (1972), p. 613.
- [23] K. Belibagli, E. Agranci, *J. Solution. Chem.*, **19** (1990) 867.
- [24] C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.*, **37** (2005) 37.
- [25] H. L. Friedman, C. V. Krishnan, in: F. Franks (Ed.) *Water: A comprehensive Treatise*, vol. 3, Plenum Press, New York, (1973), Ch. 1.
- [26] R. K. Wadi, P. Ramasami, *J. Chem. Soc. Faraday Trans*, **93** (1997) 243.
- [27] R. Bhat, J. C. Ahluwalia, *J. Phys. Chem.*, **89** (1985) 1099.
- [28] A. K. Mishra, J. C. Ahluwalia, *J. Chem. Soc. Faraday Trans I*, **77** (1981) 1469.
- [29] G. Jones, M. Dole, *J. Am. Chem. Soc.*, **51** (1929) 2950.
- [30] F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.*, **82** (1978) 784.
- [31] D. Feakins, D. J. Freemantle, K. G. Lawrence, *J. Chem. Soc. Faraday Trans I*, **70** (1974) 795.
- [32] S. Glasston, K. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, (1941).

Table 1: Density (ρ) and viscosity (η) of different aqueous TBAB solutions at different temperatures.

Aqueous TBAB solution / mol · dm ⁻³	<i>T</i> / K	$\rho \times 10^{-3}$ / kg · m ⁻³	η / mPa · s
0.05	298.15	0.9982	0.8712
	308.150	0.9952	0.7107
	318.15	0.9914	0.5908
0.15	298.15	0.9991	0.9352
	308.15	0.9962	0.7378
	318.15	0.9923	0.6163
0.10	298.15	1.0006	0.9974
	308.15	0.9970	0.7774
	318.15	0.9934	0.6526

Table 2: Molar concentration (c), density (ρ), viscosity (η), apparent molar volume (ϕ_v) and $(\eta_r - 1)/\sqrt{c}$ for nicotinamide in different aqueous TBAB solutions at different temperatures.

c / mol · dm ⁻³	$\rho \times 10^{-3}$ / kg · m ⁻³	η / mPa · s	$\phi_v \times 10^6$ / m ³ · mol ⁻¹	$\frac{\eta_r - 1}{\sqrt{c}}$
0.00^a				
$T = 298.15$ K				
0.0199	0.9976	0.837	95.83	0.0730
0.0319	0.9980	0.840	95.65	0.0806
0.0518	0.9985	0.846	95.47	0.0923
0.0718	0.9990	0.851	95.37	0.1019
0.0877	0.9995	0.855	95.34	0.1067
0.0997	0.9998	0.857	95.32	0.1108
$T = 308.15$ K				
0.0198	0.9946	0.673	96.56	0.0903
0.0318	0.9949	0.677	96.34	0.1065
0.0516	0.9955	0.684	96.05	0.1277
0.0716	0.9960	0.690	95.85	0.1420
0.0874	0.9965	0.695	95.74	0.1546
0.0993	0.9968	0.700	95.68	0.1657
$T = 318.15$ K				
0.0197	0.9908	0.566	98.59	0.0604
0.0317	0.9911	0.569	98.15	0.0831
0.0515	0.9916	0.575	97.71	0.1084
0.0713	0.9921	0.581	97.42	0.1303
0.0871	0.9925	0.585	97.29	0.1454
0.0990	0.9929	0.588	97.20	0.1541

(Continued)

Table 2 (Continued)

c / mol · dm ⁻³	$\rho \times 10^{-3}$ / kg · m ⁻³	η / mPa · s	$\phi_v \times 10^6$ / m ³ · mol ⁻¹	$\frac{\eta_r - 1}{\sqrt{c}}$
0.05^a				
<i>T</i> = 298.15 K				
0.0200	0.9987	0.878	96.76	0.0523
0.0320	0.9990	0.881	96.37	0.0621
0.0521	0.9996	0.886	95.98	0.0762
0.0680	1.0000	0.890	95.83	0.0832
0.0840	1.0004	0.894	95.73	0.0907
0.0980	1.0008	0.898	95.68	0.0968
<i>T</i> = 308.15 K				
0.0200	0.9957	0.712	99.78	0.0113
0.0319	0.9960	0.714	99.09	0.0274
0.0519	0.9965	0.719	98.07	0.0492
0.0678	0.9969	0.723	97.51	0.0657
0.0837	0.9973	0.727	96.97	0.0781
0.0977	0.9977	0.731	96.53	0.0896
<i>T</i> = 318.15 K				
0.0199	0.9918	0.591	104.44	0.0035
0.0318	0.9920	0.593	103.81	0.0230
0.0517	0.9925	0.598	102.18	0.0554
0.0676	0.9929	0.602	101.26	0.0742
0.0834	0.9933	0.606	100.38	0.0911
0.0973	0.9936	0.610	99.90	0.1039

(Continued)

Table 2 (Continued)

c / mol · dm ⁻³	$\rho \times 10^{-3}$ / kg · m ⁻³	η / mPa · s	$\phi_v \times 10^6$ / m ³ · mol ⁻¹	$\frac{\eta_r - 1}{\sqrt{c}}$
0.10^a				
$T = 298.15$ K				
0.0199	0.9996	0.936	98.53	0.0078
0.0320	0.9999	0.939	98.22	0.0212
0.0519	1.0004	0.943	97.59	0.0382
0.0719	1.0009	0.949	97.24	0.0537
0.0878	1.0013	0.953	96.97	0.0634
0.0998	1.0016	0.956	96.86	0.0709
$T = 308.15$ K				
0.0199	0.9966	0.743	103.75	0.0468
0.0319	0.9968	0.749	103.14	0.0879
0.0517	0.9973	0.759	102.03	0.1293
0.0716	0.9977	0.770	101.17	0.1652
0.0875	0.9981	0.779	100.66	0.1886
0.0994	0.9984	0.786	100.44	0.2055
$T = 318.15$ K				
0.0198	0.9926	0.617	107.08	0.0078
0.0318	0.9928	0.622	105.77	0.0499
0.0515	0.9933	0.629	103.87	0.0890
0.0713	0.9937	0.637	103.09	0.1288
0.0872	0.9941	0.645	102.62	0.1585
0.0991	0.9943	0.651	102.32	0.1795

(Continued)

Table 2 (Continued)

c / mol · dm ⁻³	$\rho \times 10^{-3}$ / kg · m ⁻³	η / mPa · s	$\phi_v \times 10^6$ / m ³ · mol ⁻¹	$\frac{\eta_r - 1}{\sqrt{c}}$
0.15^a				
$T = 298.15$ K				
0.0200	1.0011	0.995	98.86	-0.0148
0.0320	1.0014	0.998	98.45	0.0056
0.0520	1.0019	1.004	97.80	0.0285
0.0720	1.0024	1.010	97.28	0.0481
0.0880	1.0028	1.017	97.02	0.0674
0.1000	1.0031	1.021	96.87	0.0762
$T = 308.15$ K				
0.0199	0.9973	0.776	105.71	-0.0092
0.0319	0.9976	0.781	104.54	0.0235
0.0518	0.9980	0.789	103.31	0.0641
0.0717	0.9984	0.798	102.33	0.1016
0.0877	0.9988	0.806	101.68	0.1260
0.0997	0.9991	0.813	101.37	0.1434
$T = 318.15$ K				
0.0198	0.9936	0.650	110.50	-0.0270
0.0318	0.9938	0.654	109.53	0.0107
0.0516	0.9941	0.661	108.37	0.0599
0.0714	0.9945	0.670	107.40	0.1018
0.0874	0.9948	0.677	107.11	0.1268
0.0993	0.9950	0.683	106.92	0.1504

^a = molarity of TBAB in water in mol · dm⁻³.

Table 3: Limiting Partial Molar Volume (ϕ_V^0) adjustable parameters A_V and B_V for nicotinamide in different aqueous TBAB solutions with standard deviations σ at different temperatures.

T / K	$\phi_V^0 \times 10^6$ / $\text{m}^3 \cdot \text{mol}^{-1}$	$A_V \times 10^6$ / $\text{m}^3 \cdot \text{mol}^{-1.5}$	$B_V \times 10^6$ / $\text{m}^3 \cdot \text{mol}^{-2}$	σ
0.00^a				
298.15	96.87	-9.38	14.21	0.01
308.15	97.71	-9.48	9.60	0.01
318.15	100.86	-19.85	26.17	0.01
0.05^a				
298.15	99.01	-20.25	30.81	0.01
308.15	102.72	-21.47	5.37	0.03
318.15	107.99	-22.82	-11.04	0.16
0.10^a				
298.15	100.41	-14.47	9.93	0.06
308.15	107.95	-25.70	12.92	0.10
318.15	115.37	-72.28	98.05	0.13
0.15^a				
298.15	101.05	-16.80	11.06	0.05
308.15	110.97	-41.08	35.41	0.04
318.15	115.97	-46.37	55.38	0.11

^a = molarity of TBAB in water in $\text{mol} \cdot \text{dm}^{-3}$.

Table 4: Values of Various Coefficients of equation (4) for nicotinamide in different aqueous TBAB solutions.

Aqueous TBAB solution / mol·dm ⁻³	$a_0 \times 10^6$ / m ³ ·mol ⁻¹	$a_1 \times 10^6$ / m ³ ·mol ⁻¹ ·K ⁻¹	$a_2 \times 10^6$ / m ³ ·mol ⁻¹ ·K ⁻²
0.00	1132.986	-6.919	0.011
0.05	705.021	-4.358	0.008
0.10	-179.515	1.118	-0.001
0.15	-2454.844	15.907	-0.025

Table 5: Limiting partial molar expansibility (ϕ_E^0) for nicotinamide in different aqueous TBAB solutions at different temperatures.

Aqueous TBAB solution / mol·dm ⁻³	$\phi_E^0 \times 10^6$ / m ³ ·mol ⁻¹ ·K ⁻¹			$\left(\frac{\delta \phi_E^0}{\delta T}\right)_p \times 10^6$ / m ³ ·mol ⁻¹ ·K ⁻²
	298.15 K	308.15 K	318.15 K	
0.00	-0.360	-0.140	0.080	0.022
0.05	0.412	0.572	0.732	0.016
0.10	0.522	0.502	0.482	-0.002
0.15	0.999	0.499	-0.001	-0.050

Table 6: Values of *A* and *B*-coefficients with standard errors for nicotinamide in different aqueous TBAB solutions at different temperatures.

Aqueous TBAB solution / mol · dm ⁻³	<i>A</i> × 10 ³ / m ^{3/2} · mol ^{-1/2}			<i>B</i> × 10 ⁶ / m ³ · mol ⁻¹		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0.00	0.042 (±0.002)	0.030 (±0.001)	-0.014 (±0.001)	0.221 (±0.003)	0.424 (±0.002)	0.538 (±0.005)
0.05	0.016 (±0.001)	-0.054 (±0.002)	-0.076 (±0.004)	0.258 (±0.001)	0.458 (±0.001)	0.580 (±0.003)
0.10	-0.043 (±0.001)	-0.076 (±0.001)	-0.127 (±0.002)	0.362 (±0.001)	0.898 (±0.001)	0.966 (±0.001)
0.15	-0.088 (±0.000)	-0.133 (±0.005)	-0.169 (±0.001)	0.519 (±0.001)	0.874 (±0.050)	1.010 (±0.001)

Standard errors are given the parentheses.

Table 7: Partial molar volumes and viscosity *B*-coefficients of transfer ($\Delta\phi_v^0$ and ΔB) from water to different aqueous TBAB solutions for nicotinamide at different temperatures.

Aqueous TBAB solution / mol·dm ⁻³	$\phi_v^0 \times 10^6$ / m ³ ·mol ⁻¹	$\Delta\phi_v^0 \times 10^6$ / m ³ ·mol ⁻¹	$B \times 10^6$ / m ³ ·mol ⁻¹	$\Delta B \times 10^6$ / m ³ ·mol ⁻¹
T = 298.15 K				
0.00	96.87	0.00	0.221	0.00
0.05	99.01	2.14	0.258	0.037
0.10	100.41	3.55	0.362	0.141
0.15	101.05	4.18	0.519	0.298
T = 308.15 K				
0.00	97.71	0.00	0.424	0.00
0.05	102.72	5.01	0.458	0.034
0.10	107.95	10.24	0.898	0.474
0.15	110.97	13.26	0.874	0.450
T = 318.15 K				
0.00	100.86	0.00	0.538	0.00
0.05	107.99	7.13	0.580	0.042
0.10	115.37	14.51	0.966	0.428
0.15	115.97	15.11	1.010	0.472

Table 8: Values of $\bar{V}_2^0 - \bar{V}_1^0$, $\Delta\mu_1^{0\#}$, $\Delta\mu_2^{0\#}$, $T\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ for nicotinamide in different aqueous TBAB solutions at different temperatures.

Parameters	298.15 K	308.15 K	318.15 K
0.00 mol · dm⁻³			
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	80.85	80.51	89.61
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	8.99	8.74	8.60
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	50.21	80.29	98.93
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-726.17	-750.53	-774.89
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-675.96	-670.24	-675.96
0.05 mol · dm⁻³			
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	80.87	84.44	89.53
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	9.12	8.92	8.75
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	54.96	84.91	104.69
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-741.41	-766.28	-791.14
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-686.45	-681.36	-686.45
0.10 mol · dm⁻³			
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	82.19	89.58	96.93
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	9.30	9.03	8.86
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	69.61	146.76	161.31
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1367.02	-1412.87	-1458.72
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1297.40	-1266.10	-1297.40
0.15 mol · dm⁻³			
$(\bar{V}_2^0 - \bar{V}_1^0) \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	82.76	92.51	97.45
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	9.47	9.18	9.04
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	91.03	143.35	167.19
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1135.24	-1173.31	-1211.39
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1044.20	-1029.96	-1044.20

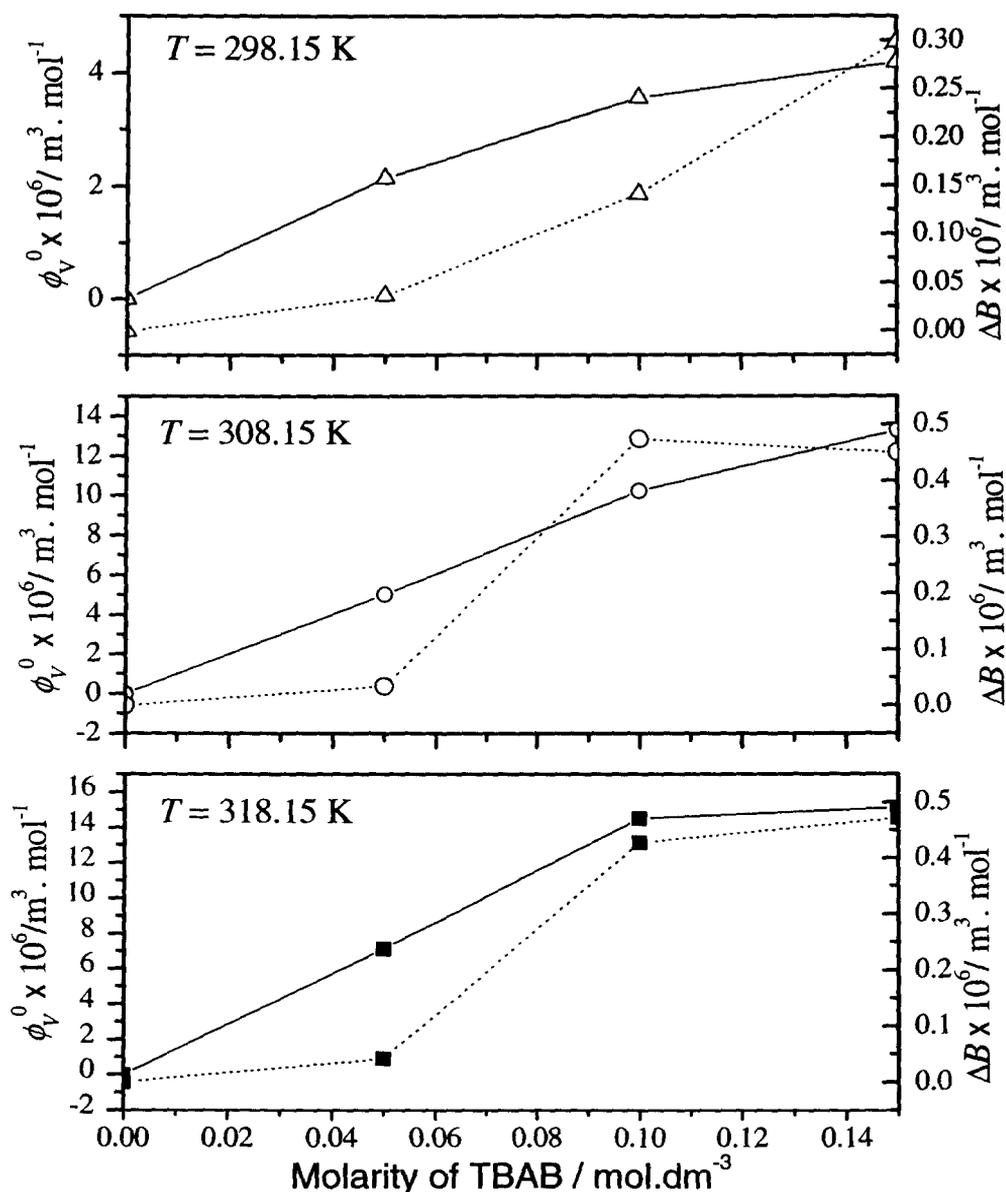


Figure 1: Plots of partial molar volume of transfer ($\Delta\phi_v^0$) and viscosity B -coefficient of transfer (ΔB) from water to different aqueous TBAB solutions against molarity of TBAB for nicotinamide at different temperatures. Solid lines for $\Delta\phi_v^0$ and dotted lines for ΔB , $T = 298.15 \text{ K}$ (Δ); $T = 308.15 \text{ K}$ (o); $T = 318.15 \text{ K}$ (\blacksquare).