Viscosities of Ammonium Sulfate, Potassium Sulfate, and Aluminum Sulfate in Water and Water + *N,N*-Dimethylformamide Mixtures at Different Temperatures

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Viscosities of ammonium sulfate, potassium sulfate, and aluminum sulfate in water and water + (5 %, 10 %, 15 %, and 20 %) *N,N*-dimethylformamide mixed solvent have been measured at T = (298.15 and 308.15) K and at atmospheric pressure. A molality range has been studied between (0.0081 and 0.1000) $\text{mol}\cdot\text{kg}^{-1}$. The viscosity data have been analyzed with the Jones−Dole equation, and B coefficients have been calculated. The results have been interpreted in terms of structure making/breaking behavior of these salts in water and water + DMF mixed solvents.

Introduction

Transport and thermodynamic properties of solutions of electrolytes in aqueous, nonaqueous, and mixed solvent are of interest in various technologies like high-energy density barriers, photoelectrochemical cells, electrodepositing, and wet electrolytic capacitors and in organic synthesis.

N,N-Dimethylfomamide is used as a solvent in the production of resins and polar polymers. Its major applications include protective coatings, adhesives, films, printing inks, capacitors and electroplating, separation of gas streams, and pharmaceuticals and in the production of polyurethane resin for synthetic leather.[1−4] Ammonium sulfate is used for the manufacture of ammonium alum, in the manufacture of H_2SO_4, freezing mixtures, flame proofing fabrics and paper, manufacture of viscose silk, tanning, in fractionation of proteins, and as a fertilizer.[5] The uses of potassium sulfate include manufacture of potassium alum, potassium carbonate, and glass, in the Kjeldhal determination of nitrogen.[5] Aluminum sulfate is used for manufacture of wood pulp, paper, aluminum salts, printing ink, lubricant, boiler cleaning agent, and clarifying fats and oils and for purification of water as deodorization, decolorizer in petroleum refining, and as mordant dying.[5]

The objectives of this work are to generate accurate data on viscosities of potassium sulfate, ammonium sulfate, and aluminum sulfate in water and water + DMF mixed solvent and also to study the structure making/breaking behavior of these salts. It reports such data at (298.15 and 308.15) K and at atmospheric pressure.

Experimental

Potassium sulfate (A.R. Grade purity > 99.5 %), ammonium sulfate (A.R. Grade purity > 99.5 %), and aluminum sulfate (A.R. Grade purity > 99.5 %) were obtained from s. d. fine- chem. The salts were dried over P_2O_5 to constant mass before use. Water−DMF mixtures of composition (0, 5, 10, 15, and 20) wt % DMF were prepared by mixing appropriate weights of water and DMF in an airtight, stoppered glass bottle. Masses were recorded on a Dhona balance with a precision of $\pm\ 1\cdot10^{-7}$ kg. The densities (ρ) of aqueous solutions were measured with the help of a $15\cdot10^{-6}\ \text{m}^3$ double arm pycnometer.[6,7] The uncertainty in the density measurements was $\pm\ 1\cdot10^{-7}\ \text{kg}\cdot\text{m}^{-3}$.

An Ubbelohde suspended-level viscometer[8,9] was used for the measurements of dynamic viscosities (η) of solutions. The viscometer was calibrated with triply distilled water.

Table 1. Viscosity η of Ammonium Sulfate in Water and Water + DMF Mixtures at T = (298.15 and 308.15) K

	$10^3\cdot\eta^b$			
m^a	T = 298.15 K	T = 308.15 K	T = 298.15 K	T = 308.15 K
	0 % DMF		5 % DMF	
0.0000	0.890	0.719	1.002	0.797
0.0081	0.897	0.725	1.011	0.803
0.0099	0.898	0.726	1.012	0.804
0.0201	0.902	0.729	1.017	0.808
0.0402	0.908	0.735	1.025	0.814
0.0599	0.913	0.740	1.032	0.820
0.0802	0.918	0.744	1.038	0.825
0.1000	0.922	0.748	1.044	0.830
	10 % DMF		15 % DMF	
0.0000	1.126	0.891	1.258	0.984
0.0081	1.134	0.893	1.265	0.990
0.0099	1.135	0.894	1.266	0.991
0.0201	1.140	0.896	1.271	0.996
0.0402	1.148	0.901	1.279	1.004
0.0599	1.155	0.905	1.286	1.011
0.0802	1.162	0.911	1.293	1.019
0.1000	1.168	0.914	1.299	1.026
	20 % DMF			
0.0000	1.391	1.080		
0.0081	1.399	1.083		
0.0099	1.400	1.084		
0.0201	1.406	1.087		
0.0402	1.415	1.094		
0.0599	1.424	1.101		
0.0802	1.432	1.108		
0.1000	1.440	1.115		

[a] $\text{mol}\cdot\text{kg}^{-1}$. [b] $\text{m}^{-1}\cdot\text{kg}\cdot\text{s}^{-1}$.

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Table 2. Least-Squares Fitted Values of Jones−Dole Coefficient B and Constant A of Equation 2 for Ammonium Sulfate in Water and Water + DMF Mixtures at T = (298.15 and 308.15) K

T/K	A^a	B^b
	0 % DMF	
298.15	0.0783	0.1131
308.15	0.0798	0.1529
	5 % DMF	
298.15	0.0857	0.1468
308.15	0.0672	0.2023
	10 % DMF	
298.15	0.0630	0.1738
308.15	0.0065	0.2397
	15 % DMF	
298.15	0.0460	0.1828
308.15	0.0426	0.2912
	20 % DMF	
298.15	0.0449	0.2099
308.15	0.0035	0.3101

[a] $(\mathrm{mol \cdot kg})^{-1/2}$. [b] $\mathrm{kg \cdot mol^{-1}}$.

Table 3. Viscosity η of Potassium Sulfate in Water and Water + DMF Mixtures at T = (298.15 and 308.15) K

	$10^3 \cdot \eta^b$			
m^a	T = 298.15 K	T = 308.15 K	T = 298.15 K	T = 308.15 K
	0 % DMF		5 % DMF	
0.0000	0.890	0.719	1.002	0.797
0.0081	0.895	0.723	1.007	0.801
0.0099	0.896	0.724	1.008	0.802
0.0201	0.899	0.727	1.012	0.805
0.0402	0.905	0.732	1.017	0.811
0.0599	0.909	0.737	1.023	0.816
0.0802	0.914	0.742	1.028	0.821
0.1000	0.918	0.746	1.033	0.826
	10 % DMF		15 % DMF	
0.0000	1.126	0.891	1.258	0.984
0.0081	1.123	0.892	1.263	0.988
0.0099	1.133	0.893	1.264	0.989
0.0201	1.137	0.895	1.268	0.993
0.0402	1.144	0.899	1.276	1.000
0.0599	1.151	0.904	1.283	1.007
0.0802	1.157	0.908	1.290	1.014
0.1000	1.163	0.913	1.296	1.020
	20 % DMF			
0.0000	1.391	1.080		
0.0081	1.397	1.081		
0.0099	1.398	1.082		
0.0201	1.403	1.085		
0.0402	1.411	1.092		
0.0599	1.419	1.099		
0.0802	1.427	1.106		
0.1000	1.435	1.113		

[a] $\mathrm{mol \cdot kg^{-1}}$. [b] $\mathrm{m^{-1} \cdot kg \cdot s^{-1}}$.

Table 4. Least-Squares Fitted Values of Jones−Dole Coefficient B and Constant A of Equation 2 for Potassium Sulfate in Water and Water + DMF Mixtures at T = (298.15 and 308.15) K

T/K	A^a	B^b
	0 % DMF	
298.15	0.0501	0.1575
308.15	0.0430	0.2421
	5 % DMF	
298.15	0.0418	0.1764
308.15	0.0356	0.2519
	10 % DMF	
298.15	0.0418	0.1959
308.15	−0.0079	0.2706
	15 % DMF	
298.15	0.0244	0.2289
308.15	0.0194	0.3084
	20 % DMF	
298.15	0.0278	0.2248
308.15	−0.0205	0.3737

[a] $(\mathrm{mol \cdot kg})^{-1/2}$. [b] $\mathrm{kg \cdot mol^{-1}}$.

Table 5. Viscosity η of Aluminum Sulfate in Water and Water + DMF Mixtures at T = (298.15 and 308.15) K

	$10^3 \cdot \eta^b$			
m^a	T = 298.15 K	T = 308.15 K	T = 298.15 K	T = 308.15 K
	0 % DMF		5 % DMF	
0.0000	0.890	0.719	1.002	0.797
0.0081	0.904	0.729	1.021	0.811
0.0099	0.908	0.732	1.025	0.815
0.0201	0.927	0.747	1.050	0.833
0.0402	0.967	0.777	1.098	0.869
0.0599	1.008	0.807	1.147	0.906
0.0802	1.050	0.839	1.195	0.942
0.1000	1.093	0.870	1.244	0.979
	10 % DMF		15 % DMF	
0.0000	1.126	0.891	1.258	0.984
0.0081	1.146	0.920	1.277	1.002
0.0099	1.150	0.925	1.283	1.006
0.0201	1.178	0.952	1.313	1.032
0.0402	1.234	1.002	1.377	1.082
0.0599	1.287	1.052	1.442	1.130
0.0802	1.347	1.100	1.508	1.182
0.1000	1.408	1.148	1.575	1.229
	20 % DMF			
0.0000	1.391	1.080		
0.0081	1.434	1.091		
0.0099	1.443	1.095		
0.0201	1.487	1.120		
0.0402	1.574	1.171		
0.0599	1.658	1.224		
0.0802	1.742	1.277		
0.1000	1.825	1.331		

[a] $\mathrm{mol \cdot kg^{-1}}$. [b] $\mathrm{m^{-1} \cdot kg \cdot s^{-1}}$.

Flow-time measurements were made with an electronic digital stopwatch with a precision of ± 0.01 s. The viscosities were averaged from three readings for each solution. The dynamic viscosity of solutions was calculated using the equation

$$\eta/\eta_o = (\rho t)/(\rho_o t_o) \tag{1}$$

where ρ, ρ_o, t, t_o, and η, η_o are density, flow time, and viscosity of aqueous solutions and water, respectively. Viscosity measurements were made in a transparent glass-walled water bath[6−10] having a thermal stability of 0.01 K. Viscosity measurements were made as a function of concentration (0.0080 and 1.0000) $\mathrm{mol \cdot kg^{-1}}$ of salts and temperature (298.15 and 308.15) K at atmospheric pressure. The uncertainty in the viscosity measurements was $3 \cdot 10^{-6}\ \mathrm{m^{-1} \cdot kg \cdot s^{-1}}$.

Results and Discussion

Table 1, Table 3, and Table 5 compile the viscosities η of ammonium sulfate, potassium sulfate, and aluminum sulfate in water and binary mixtures of water and 5 %, 10 %, 15 %, and 20 % *N*,*N*- dimethylformamide at various temperatures and at atmospheric pressure. Figures 1 to 6 illustrate the plots of variations of η as a function of concentration m of salts at (298.15 and 308.15) K. From these figures and tables, it is observed that there is a regular increment in the viscosities of solutions with increase in concentration at a fixed temperature. In water-rich solutions, η has a smaller value, while the *N*,*N*-DMF-rich solution shows a higher value for η. The η values decrease with the rise of temperature at a fixed concentration

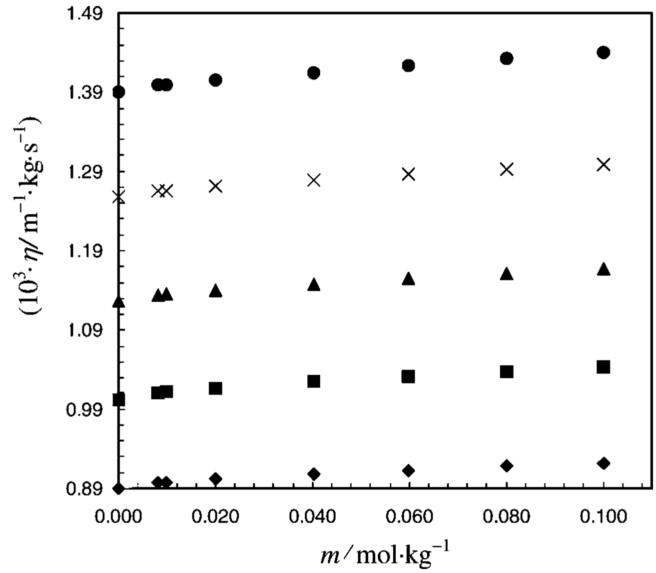

Figure 1. Viscosity η of ammonium sulfate in: ◆, water; ■, water + 5 % DMF; ▲, water + 10 % DMF; ×, water + 15 % DMF; ●, water + 20 % DMF as a function of molality m at 298.15 K.

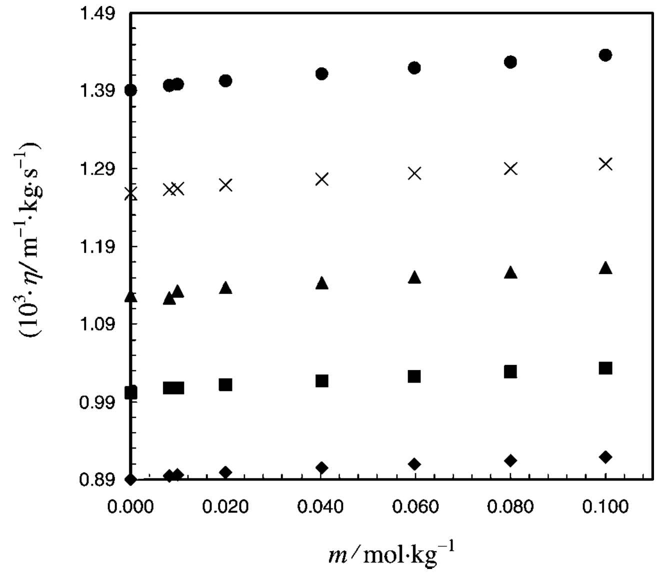

Figure 3. Viscosity η of potassium sulfate in: ◆, water; ■, water + 5 % DMF; ▲, water + 10 % DMF; ×, water + 15 % DMF; ●, water + 20 % DMF as a function of molality m at 298.15 K.

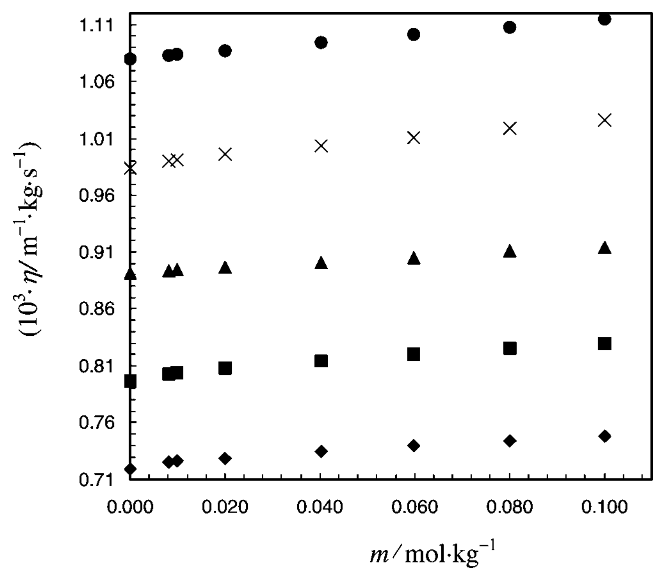

Figure 2. Viscosity η of ammonium sulfate in: ◆, water; ■, water + 5 % DMF; ▲, water + 10 % DMF; ×, water + 15 % DMF; ●, water + 20 % DMF as a function of molality m at 308.15 K.

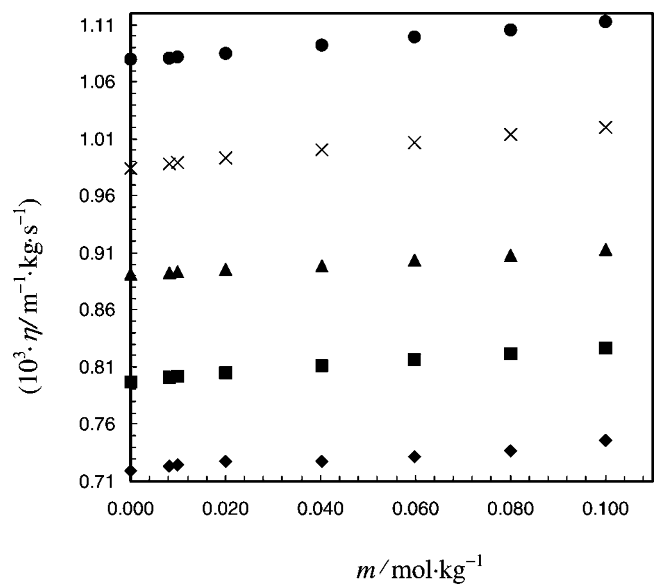

Figure 4. Viscosity η of potassium sulfate in: ◆, water; ■, water + 5 % DMF; ▲, water + 10 % DMF; ×, water + 15 % DMF; ●, water + 20 % DMF as a function of molality m at 308.15 K.

of solution. The viscosity data have been analyzed by using the Jones–Dole equation[11]

$$\eta/\eta_o = 1 + Am^{0.5} + Bm \qquad (2)$$

where η and η_o are the viscosities of solution and solvent, respectively. A is constant and independent of concentration. The Jones–Dole coefficient B is related to the effect of the ions on the structure of water. B is interpreted as a measure of the structure-forming and structure-breaking capacity of an electrolyte in solutions.[12] A positive value of the B coefficient indicates a structure-forming effect, and a negative value shows a structure-breaking effect. A least-squares method was used to calculate the constant A and Jones–Dole coefficient B. The values of A and B of all salts calculated from eq 2 are summarized in Table 2, Table 4, and Table 6, respectively. From these tables, it is understood that the B coefficient values are positive for all the salts. For ammonium sulfate and potassium sulfate, the B values increase with an increase in temperature and concentration of N,N-DMF. For aluminum sulfate, the B value decreases with an increase in temperature but increases with an increase in concentration of N,N-DMF. All the salts show structure-making behavior in water and water + N,N-DMF mixed solvents. The B value of aluminum sulfate > B value of potassium sulfate > B value of ammonium sulfate in water as well as in water + N,N-DMF mixed solvents. Therefore, the structure-making capacity of aluminum sulfate > potassium sulfate > ammonium sulfate in water as well as in water + N,N-DMF mixed solvents.

Conclusions

From a viscosity study of mixtures of aluminum sulfate, ammonium sulfate, and potassium sulfate in water as well as in water + N,N-DMF mixed solvents, it is inferred that

1. Viscosity values increase with an increase in the concentration of salts.

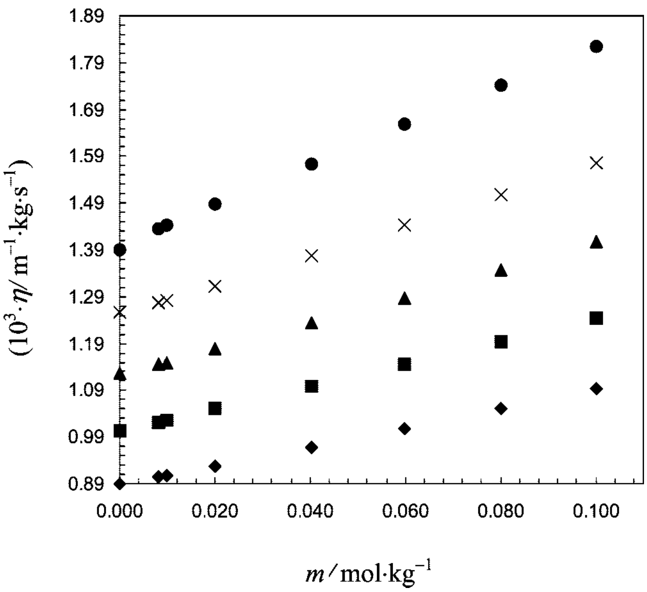

Figure 5. Viscosity η of aluminum sulfate in: ◆, water; ■, water + 5 % DMF; ▲, water + 10 % DMF; ×, water + 15 % DMF; ●, water + 20 % DMF as a function of molality m at 298.15 K.

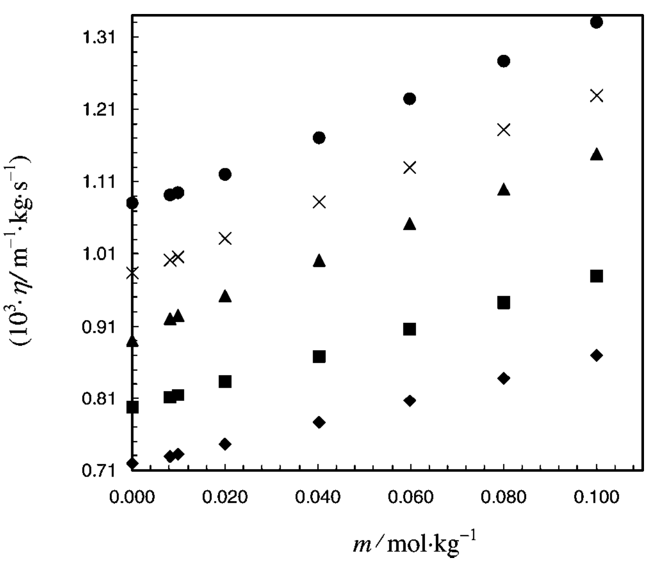

Figure 6. Viscosity η of aluminum sulfate in: ◆, water; ■, water + 5 % DMF; ▲, water + 10 % DMF; ×, water + 15 % DMF; ●, water + 20 % DMF as a function of molality m at 308.15 K.

2. The water-rich solutions have low viscosity values.
3. *N*,*N*-DMF-rich solutions have high viscosity values.
4. The *B* coefficient of aluminum sulfate in water as well as in water + *N*,*N*-DMF mixed solvent is greater than the *B* coefficient of potassium sulfate.
5. The *B* coefficient of potassium sulfate in water and in water + *N*,*N*-DMF mixed solvent is greater than the *B* coefficient of ammonium sulfate.
6. The *B* coefficients of all the salts increase with an increase of concentration of *N*,*N*-DMF.
7. With a rise of temperature, the *B* coefficient of aluminum sulfate decreases.
8. In water and water + *N*,*N*-DMF mixed solvent, aluminum sulfate has a greater tendency of structure making than potassium sulfate.

Table 6. Least-Squares Fitted Values of Jones−Dole Coefficient *B* and Constant *A* of Equation 2 for Aluminum Sulfate in Water and Water + DMF Mixtures at *T* = (298.15 and 308.15) K

T/K	A^a	B^b
	0 % DMF	
298.15	−0.0415	2.3922
308.15	−0.0436	2.2329
	5 % DMF	
298.15	−0.0107	2.4473
308.15	−0.0080	2.3044
	10 % DMF	
298.15	−0.0439	2.6110
308.15	0.1398	2.4343
	15 % DMF	
298.15	0.0804	2.7660
308.15	−0.0291	2.5990
	20 % DMF	
298.15	0.0891	2.8345
308.15	−0.0131	2.7477

[a] $(\mathrm{mol \cdot kg})^{-1/2}$. [b] $\mathrm{kg \cdot mol^{-1}}$.

9. In water and water + *N*,*N*-DMF mixed solvent, potassium sulfate has a greater tendency of structure making than ammonium sulfate.

Literature Cited

(1) Fiorito, A.; Larese, F.; Molinai, S.; Zanin, I. Liver Function Alterations in Synthetic Leather Workers Exposed to Dimethylformamide. *Am. J. Ind. Med.* **1997**, *32*, 255–260.
(2) Howard, P. H. *Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Solvents 2*; Lewis Publishers Inc.: Chelsea, MI, 1993; *Vol. IV*.
(3) Gescher, A. Metabolism of N,N-Dimethylformamide: Key to Understanding of its Toxicity. *Chem. Res. Toxicol.* **1993**, *6* (3), 245–251.
(4) Redlich, C.; Beckett, W. S.; Sparer, J.; Barwick, K. W.; Riely, C. A.; Miller, H.; Sigal, S. L.; Shalat, S. L.; Cullen, M. R. Liver Disease Associated with Occupational Exposure to the Solvent Dimethylformamide. *Ann. Intern. Med.* **1988**, *108*, 680–686.
(5) Maryadele,J. O. *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, 14th ed.;Merck and Co., Inc.: Whitehouse Station, NJ, 2006.
(6) Kharat, S. J. Density, Viscosity and Ultrasonic Velocity Studies of Aqueous Solutions of Sodium Acetate at Different Temperatures. *J. Mol. Liq.* **2008**, *140*, 10–14.
(7) Kharat, S. J. Density and Viscosity Studies of Aqueous Solutions of Cesium Trifluroacetate at Different Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 1292–1294.
(8) Kharat, S. J.; Nikam, P. S. Density and Viscosity Studies of Binary Mixtures of (aniline + benzene) and ternary Moxtures of (aniline + benzene + N,N-Dimethylformamide) at (298.15, 303.15, 308.15, and 313.15) K. *J. Mol. Liq.* **2007**, *131−132*, 81–86.
(9) Nikam, P. S.; Kharat, S. J. Density and Viscosity Studies of Binary Mixtures of N,N-Dimethylformamide with Toluene and Methyl Benzoate at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2005**, *50*, 455–459.
(10) Nikam, P. S.; Kharat, S. J. Densities and Viscosities of Binary Mixtures of N,N-Dimethylformamide with Benzyl Alcohol and Acetophenone at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 1291–1295. -459.
(11) Jones, G.; Dole, M. The Viscosity of Aqueous Solutions of Strong Electrolytes with Special Reference to Barium Chloride. *J. Am. Chem. Soc.* **1929**, *51*, 2950–2964.
(12) Hribar, B. N.; Southall, T.; Vlachy, V.; Dill, K. A. How Ions Affect the Structure of Water. *J. Am. Chem. Soc.* **2002**, *124* (41), 12302–12311.

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