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Densities and Viscosities of Citric Acid in Aqueous Cetrimonium Bromide Solutions with Reference to the Manifestation of Solvation

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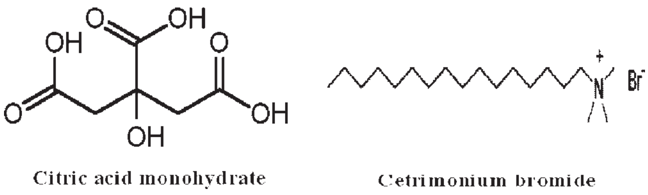
ABSTRACT: Apparent molar volumes (V_ϕ) and viscosity *B*-coefficients for citric acid in (0.001, 0.003, and 0.005) mol·dm^{-3} aqueous cetrimonium bromide (*N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide, $C_{19}H_{42}NBr$) solutions have been determined from solution density and viscosity measurements at T = (298.15, 308.15, and 318.15) K and p = 0.1 MPa as a function of the concentration of citric acid. The apparent molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution (V_ϕ^0), using the Redlich–Meyer equation, and the obtained parameters have been interpreted in terms of solute–solvent interactions. The viscosity data were analyzed using the Jones–Dole equation, and the derived parameters *A* and *B* have also been interpreted in terms of solute–solute and solute–solvent interactions, respectively, in the mixed solutions. The structure-making or -breaking ability of the electrolyte has been discussed in terms of sign of d*B*/d*T*. The activation parameters of viscous flow for the ternary solutions studied have also been calculated and explained by the application of transition state theory.

INTRODUCTION

It is well-known that the reaction medium plays an important role in determining reactivity reflected in thermodynamic, transport, and spectral properties.[1,2] Gaining insight into the mechanism of such interactions, thermodynamic and transport studies involving one or more electrolytes in pure or mixed solvent systems are highly useful. Studies on the apparent molar volumes and viscosity *B*-coefficients of electrolytes at infinite dilution provide valuable information regarding ion–ion, ion–solvent, and solvent–solvent interactions.[3] The addition of electrolyte could break or make the structure of a liquid,[4−6] as viscosity being a property of the liquid depending upon the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

Citric acid, ($C_6H_8O_7 \cdot H_2O$), that is, 2-hydroxypropane-1,2,3-tricarboxylic acid, is a tribasic, environmentally acceptable, and versatile chemical. As it occurs in metabolism of almost all living beings, its interactions in an aqueous solution is of great value to the biological scientists. In the pharmaceutical industry, citric acid is used as a stabilizer in various formulations, as a drug component and as an anticoagulant in blood for transfusions and also used as an acidifier in many pharmaceuticals. Citric acid can be used in food coloring to balance the pH level of the normally basic dye. Citric acid's ability to chelate metals makes it useful in soaps and laundry detergents, as well as water softening.

Cetrimonium bromide is one of the components of the topical antiseptic cetrimide. It is also widely used as an active ingredient for hair conditioners, detergent sanitizers, disinfection agents, and softener for textiles and paper products. Understanding the behavior of citric acid in cetrimonium bromide solution will be of the utmost importance in the biological and pharmaceutical science (e.g., advanced lice treatment, etc.). Cetrimonium bromide forms micelles in water. Depending on the temperature and concentration of the cetrimonium bromide, water is forced to attain a specific structural form. The addition of acid to this solution will perturb the structure of the solution which is expected to affect the volumetric and viscometric properties to a high degree.



Citric acid monohydrate

Cetrimonium bromide

Figure 1. The 2-dimensional picture of the molecules relating to this work.

To the best of our knowledge, the properties of this ternary solution have not been reported earlier. As apparent molar volumes and viscosity *B*-coefficients of a solute gives cumulative effects of solute–solute, solute–solvent, and solvent–solvent interactions in solutions, in this paper, we attempted to study those properties for the citric acid in (0.001, 0.003, and 0.005) mol·dm^{-3} aqueous cetrimonium bromide solutions at different temperatures to explain the various interactions prevailing in the ternary systems under investigation.

EXPERIMENTAL SECTION

Materials. Citric acid monohydrate (CA) was purchased from Himedia. Its mass purity as supplied is 0.99. The reagent was always placed in the desiccator over P_2O_5 to keep them in dry atmosphere.

Cetrimonium bromide (CB) (Thomas Baker, India, mass fraction purity 0.99) was used as such without further purification. Deionized, doubly distilled, degassed water with a specific conductance of $1 \cdot 10^{-6}$ S·cm^{-1} was used for the preparation of different aqueous cetrimonium bromide solutions. The 2-D representations of the investigated solvent molecules are shown in Figure 1 for a

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Table 1. Molarity (c), Densities (ρ), Viscosities (η), Apparent Molar Volume (V_ϕ), and $(\eta_r - 1)/(c)^{1/2}$ for Citric Acid in Different Aqueous Cetrimonium Bromide Solutions at Different Temperatures

C $\mathrm{mol \cdot dm^{-3}}$	$\rho \cdot 10^{-3}$ $\mathrm{kg \cdot m^{-3}}$	η $\mathrm{mPa \cdot s}$	$V_\phi \cdot 10^6$ $\mathrm{m^3 \cdot mol^{-1}}$	$(\eta_r - 1)/(c^{1/2})$
		0.001[a]		
		$T = 298.15$ K		
0.0000	0.9971	0.8978	0.00	0.0000
0.0250	0.9978	0.9228	185.83	0.1762
0.0450	0.9988	0.9374	173.03	0.2081
0.0550	0.9995	0.9450	167.52	0.2243
0.0650	1.0002	0.9518	163.10	0.2360
0.0750	1.0010	0.9596	158.89	0.2512
0.0850	1.0018	0.9665	155.71	0.2623
		$T = 308.15$ K		
0.0000	0.9942	0.7436	0.00	0.0000
0.0249	0.9946	0.7613	191.62	0.1504
0.0449	0.9956	0.7726	179.12	0.1841
0.0553	0.9962	0.7782	174.04	0.1980
0.0648	0.9968	0.7841	169.92	0.2142
0.0748	0.9975	0.7896	166.40	0.2261
0.0847	0.9982	0.7951	163.11	0.2382
		$T = 318.15$ K		
0.0000	0.9906	0.6173	0.00	0.0000
0.0248	0.9910	0.6301	197.32	0.1311
0.0447	0.9918	0.6390	185.04	0.1662
0.0551	0.9923	0.6434	180.61	0.1802
0.0645	0.9929	0.6481	176.04	0.1963
0.0745	0.9935	0.6528	173.03	0.2110
0.0843	0.9941	0.6568	170.01	0.2204
		0.003[a]		
		$T = 298.15$ K		
0.0000	0.9973	0.9087	0.00	0.0000
0.0250	0.9979	0.9349	185.52	0.1823
0.0450	0.9990	0.9515	172.85	0.2221
0.0550	0.9996	0.9597	167.23	0.2391
0.0650	1.0004	0.9676	162.70	0.2542
0.0750	1.0012	0.9752	158.62	0.2672
0.0850	1.0019	0.9834	156.04	0.2820
		$T = 308.15$ K		
0.0000	0.9943	0.7516	0.00	0.0000
0.0249	0.9947	0.7701	194.95	0.1562
0.0449	0.9956	0.7830	180.08	0.1971
0.0548	0.9962	0.7895	177.15	0.2152
0.0648	0.9968	0.7960	172.35	0.2321
0.0747	0.9976	0.8021	167.44	0.2460
0.0847	0.9983	0.8085	164.35	0.2602
		$T = 318.15$ K		
0.0000	0.9907	0.6217	0.00	0.0000
0.0248	0.9909	0.6352	203.62	0.1383
0.0447	0.9917	0.6451	190.75	0.1782
0.0546	0.9922	0.6506	185.06	0.1991
0.0645	0.9927	0.6561	180.91	0.2180
0.0744	0.9933	0.6608	177.32	0.2303
0.0843	0.9939	0.6656	174.11	0.2432
		0.005[a]		
		$T = 298.15$ K		
0.0000	0.9974	0.9213	0.00	0.0000
0.0250	0.9979	0.9510	188.62	0.2042
0.0450	0.9990	0.9712	174.13	0.2552
0.0550	0.9997	0.9807	169.30	0.2751
0.0650	1.0005	0.9900	162.71	0.2923
0.0750	1.0012	1.0003	159.20	0.3130
0.0850	1.0021	1.0089	155.51	0.3261
		$T = 308.15$ K		
0.0000	0.9944	0.7596	0.00	0.0000
0.0249	0.9947	0.7807	197.34	0.1762
0.0449	0.9957	0.7958	182.69	0.2251
0.0548	0.9962	0.8032	177.46	0.2450
0.0648	0.9969	0.8111	172.04	0.2663
0.0747	0.9977	0.8182	167.36	0.2822
0.0847	0.9984	0.8266	164.04	0.3030
		$T = 318.15$ K		
0.0000	0.9908	0.6349	0.00	0.0000
0.0248	0.9910	0.6506	205.04	0.1573
0.0447	0.9917	0.6626	191.18	0.2062
0.0546	0.9922	0.6686	185.73	0.2271
0.0645	0.9928	0.6749	179.83	0.2482
0.0744	0.9934	0.6815	176.97	0.2690
0.0843	0.9941	0.6875	173.18	0.2853

[a] Molarity of cetrimonium bromide in water in $\mathrm{mol \cdot dm^{-3}}$.

better understanding. The physical properties of different aqueous cetrimonium bromide solutions are listed in Table 1.

Apparatus and Procedure. Stock solutions of citric acid in different aqueous cetrimonium bromide solutions were prepared by mass, and the conversion of molality into molarity was done[7] using density values. Adequate precautions were made to reduce evaporation losses during mixing.

The density was measured with an Anton Paar density meter (DMA 4500M). The uncertainty in the density measurements was ± 0.0002 $\mathrm{g \cdot cm^{-3}}$. It was calibrated by double-distilled water and dry air.[8] The viscosity was measured by means of suspended Ubbelohde[9] type viscometer, calibrated at the experimental temperatures with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow time. The viscosity of solution is given by the following equation:

$$\eta = (Kt - L/t)\rho \tag{1}$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ± 0.002 mPa·s.

RESULTS AND DISCUSSION

The experimental values of concentrations c, densities ρ, viscosities η, and derived parameters at various temperatures are reported in Table 1.

For the analysis of solvation state of citric acid in aqueous cetrimonium bromide solutions and the interaction between citric acid and cetrimonium bromide, data of partial molar volumes are important. For this purpose, the apparent molar volumes (V_ϕ) were determined from the solution densities using the following standard expression:[10]

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \tag{2}$$

where M is the molar mass of the solute, c is the molar concentration of the solution, and ρ_0 and ρ are the densities of the solvent and the solution, respectively. As the plots of V_ϕ values against the square root of molar concentration ($c^{1/2}$) were nonlinear, V_ϕ values were fitted to the following equation:[11]

$$V_\phi = V_\phi^0 + A_V c^{1/2} + B_V c \tag{3}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and A_V and B_V are two adjustable parameters. The V_ϕ^0 values have been determined by fitting the dilute data ($c < 0.1$ mol·dm^{-3}) to eq 3 using a weighted least-squares fit.

Values of V_ϕ^0, A_V, and B^V along with the corresponding standard deviation (σ) are listed in Table 2. The estimated uncertainties in V_ϕ^0 are equal to standard deviation (σ), the root-mean-square of the deviation between the experimental and the calculated V_ϕ^0 for each data point. A perusal of Table 2 reveals that the V_ϕ^0 values are positive and increase with rise in both temperature as well as the molarity of cetrimonium bromide in the solutions as depicted in Figures 2 and 3. This indicates the presence of strong solute−solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of cetrimonium bromide in the solutions.

The observed result can also be explained in view of the molar volume of solute and that of solvent mixtures studied here. The greater the difference in the molar volume the greater is the fitness of the solute molecules in the solvent mixture rendering higher solute−solvent interaction. The same type of work has been done by the workers reported earlier.[12] The limiting partial molar volume of citric acid is far greater than that of the cetrimonium bromide solution reported in Table 2, and the said volume of the citric acid further increases with the temperature

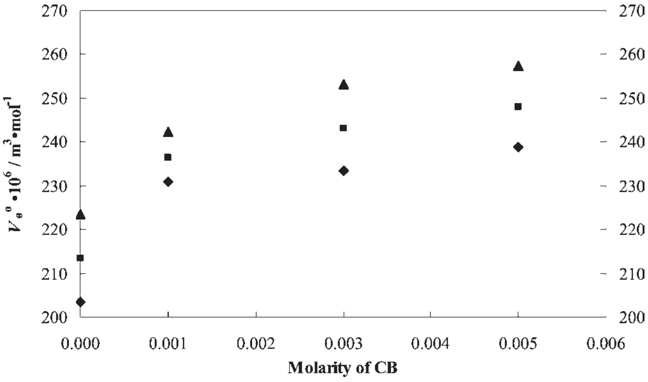

Figure 2. Plot of V_ϕ^0 of citric acid as a function of concentration of different aqueous cetrimonium bromide solutions, ◆, T = 298.15 K; ■, T = 308.15 K; and ▲, T = 318.15 K.

Table 2. Limiting Partial Molar Volume (V_ϕ^0), Adjustable Parameters A_V and B_V, and Values of Viscosity A and B Coefficients for Citric Acid in Different Aqueous Cetrimonium Bromide Solutions with Standard Deviations σ and Limiting Partial Molar Volume of (Water + Cetrimonium Bromide) at Different Temperatures

T	$V_\phi^0 \cdot 10^6$	A_V	B_V		$V_\phi^0 \cdot 10^6$	$A \cdot 10^{-3}$	$B \cdot 10^6$
K	m^3 mol^{-1}CA	cm^3·mol$^{-1.5}$	cm^3·mol^{-2}	σ	m^3·mol^{-1} CB + H_2O	m$^{3/2}$·mol$^{-1/2}$	m^3·mol^{-1}
				0.000[a]			
298.15	203.55	−232.83	237.06	0.039	18.07	0.076 (±0.002)	0.529 (±0.009)
308.15	213.29	−262.76	303.30	0.014	18.12	0.049 (±0.002)	0.563 (±0.009)
318.15	223.41	−288.54	338.08	0.050	18.19	0.026 (±0.003)	0.592 (±0.012)
				0.001[a]			
298.15	230.91	−315.63	195.49	0.022	18.07	0.072 (±0.004)	0.649 (±0.015)
308.15	236.46	−321.86	239.64	0.001	18.13	0.045 (±0.004)	0.663 (±0.015)
318.15	242.32	−328.63	273.41	0.004	18.19	0.022 (±0.004)	0.683 (±0.017)
				0.003[a]			
298.15	233.36	−343.47	263.61	0.091	18.08	0.065 (±0.001)	0.743 (±0.006)
308.15	243.04	−348.36	268.63	0.002	18.14	0.032 (±0.001)	0.784 (±0.006)
318.15	253.20	−363.64	313.30	0.006	18.20	0.011 (±0.005)	0.804 (±0.019)
				0.005[a]			
298.15	238.95	−354.60	231.76	0.031	18.09	0.059 (±0.003)	0.919 (±0.013)
308.15	247.97	−357.44	234.17	0.038	18.15	0.026 (±0.004)	0.943 (±0.017)
318.15	257.39	−380.22	309.23	0.009	18.22	0.003 (±0.004)	0.970 (±0.018)

[a] Molarity of cetrimonium bromide in water in mol·dm^{-3}.

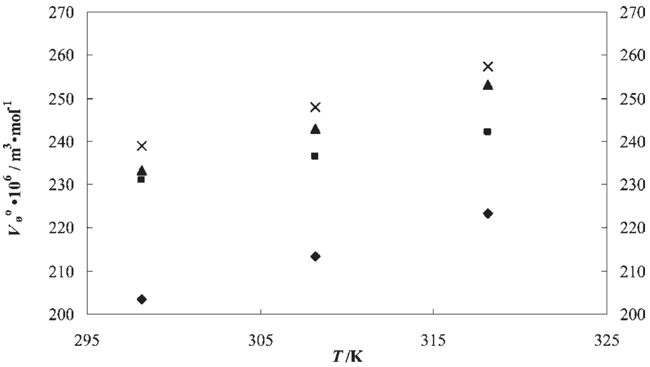

Figure 3. Plot of V_ϕ^0 of citric acid as a function of temperature (T/K) of different aqueous cetrimonium bromide solutions, ◆, 0.000 M; ■, 0.001 M; ▲, 0.003 M; and ×, 0.005 M.

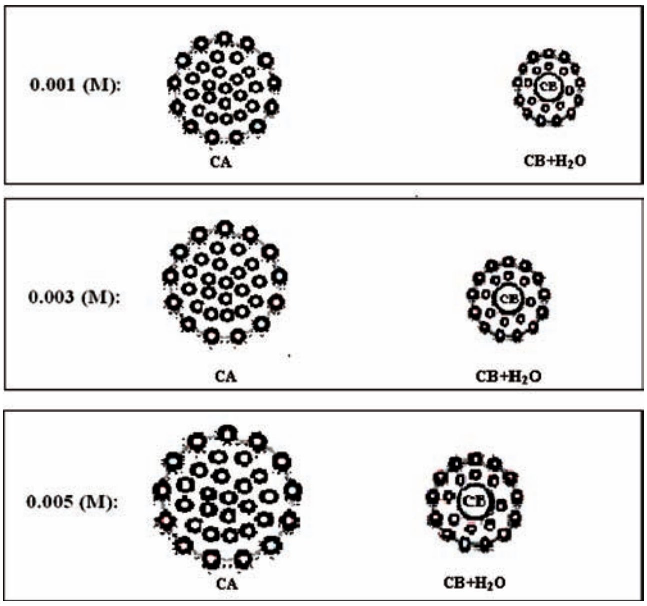

Figure 4. Schematic representations of the relevant molecules, in connection with solute–solvent interactions.

and the concentration of the cetrimonium bromide. Hence the citric acid easily fits in the cetrimonium bromide solution resulting in more solute–solvent interaction between them which is an excellent agreement with the conclusion drawn from the values of V_ϕ^0. Schematic representations of the relevant molecules, in connection with solute–solvent interactions, are shown in Figure 4.

The variations of V_ϕ^0 with temperature were fitted to a polynomial of the following:

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \qquad (4)$$

where T is the temperature in K. Values of coefficients of the above equation for the citric acid for aqueous cetrimonium bromide mixtures are reported in Table 3.

The interactions between citric acid and cetrimonium bromide in water can roughly be summarized as follows: (i) interaction of the R_4N^+ ion of cetrimonium bromide with the negative pole of the O-atom of an alcoholic –OH group of citric acid, (ii) interaction of the R_4N^+ ion of cetrimonium bromide with the negative pole of the O-atom of three acidic –OH groups of citric acid, (iii) interaction of the R_4N^+ ion of cetrimonium bromide with the negative pole of the O-atom of three –C=O groups of citric acid, (iv) interaction of the Br$^-$ ion of cetrimonium bromide with the positive pole of the H-atom of –OH and –COOH groups of citric acid, and (v) ionic–hydrophobic interactions between ions of cetrimonium bromide and nonpolar part of citric acid molecules. The interactions i–iv contribute positively, whereas interaction v contributes negatively to V_ϕ^0 values. The overall positive V_ϕ^0 values indicate that ionic-group interactions predominate over ionic–hydrophobic interactions and thus reduce the electrostriction of water molecules by citric acid.

Table 3. Values of Various Coefficients of eq 4 for Citric Acid in Different Aqueous Cetrimonium Bromide Solutions

aqueous CB solution	$a_0 \cdot 10^6$	$a_1 \cdot 10^6$	$a_2 \cdot 10^6$
mol·dm^{-3}	m^3·mol^{-1}	m^3·mol^{-1}·K^{-1}	m^3·mol^{-1}·K^{-2}
0.000	86.416	−0.170	0.0019
0.001	207.843	−0.385	0.0016
0.003	165.251	−0.487	0.0024
0.005	154.984	−0.319	0.0020

The viscosity data of the experimental solutions of acid have been analyzed using the Jones–Dole equation,[13]

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (5)$$

where $\eta_r = \eta/\eta_0$, and η are the viscosities of the solvent and solution, respectively, and c is the molar concentration of a solution. A and B are the Jones–Dole[13] constants estimated by a least-squares method and reported in Table 2. The values of the A coefficient are found to decrease with both increase in temperature and the molarity of cetrimonium bromide. These results indicate the presence of very weak solute–solute interactions, and these interactions further decrease with the rise of both experimental temperatures and concentration of cetrimonium bromide.

The viscosity B-coefficient[14,15] is a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules. From Table 2 it is evident that the values of the B-coefficient of citric acid in the studied solvent systems suggests the presence of strong solute–solvent interactions, and these type of interactions are strengthened with a rise in both temperature and molarity of cetrimonium bromide. These conclusions are in excellent agreement with those drawn from V_ϕ^0 values discussed earlier.

It has been reported in a number of studies[16,17] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table 2 that the values of the B-coefficient increase with a rise in temperature (positive dB/dT), suggesting the structure-breaking tendency of citric acid in the solvent systems.

The viscosity data have also been analyzed on the basis of transition state theory for the relative viscosity of the solutions as suggested by Feakins et al.[18] using the relation,

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + RT(1000B + \bar{V}_2^{\,0} - \bar{V}_1^{\,0})/\bar{V}_1^{\,0} \qquad (6)$$

where $\bar{V}_1^{\,0}$ and $\bar{V}_2^{\,0}$ are the partial molar volumes of the solvent and solute, respectively. $\Delta\mu_2^{0\neq}$ is the contribution per mole of the

Table 4. Values of $(\bar{V}_2^{\,0} - \bar{V}_1^{\,0})$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$, and $\Delta H_2^{0\neq}$ for Citric Acid in Different Aqueous Cetrimonium Bromide Solutions at Different Temperatures

parameters	298.15	308.15	318.15
	0.000[a]		
$(\bar{V}_2^{\,0} - \bar{V}_1^{\,0})\cdot 10^6/\mathrm{m^3\cdot mol^{-1}}$	185.48	195.17	205.22
$\Delta\mu_1^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	9.17	8.94	8.75
$\Delta\mu_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	98.00	107.16	115.90
$T\Delta S_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−266.87	−275.82	−284.77
$\Delta H_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−168.87	−168.66	−168.87
	0.001[a]		
$(\bar{V}_2^{\,0} - \bar{V}_1^{\,0})\cdot 10^6/\mathrm{m^3\cdot mol^{-1}}$	212.84	218.33	224.13
$\Delta\mu_1^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	9.18	9.02	8.83
$\Delta\mu_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	118.21	124.53	131.94
$T\Delta S_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−204.71	−211.58	−218.44
$\Delta H_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−86.50	−87.04	−86.50
	0.003[a]		
$(\bar{V}_2^{\,0} - \bar{V}_1^{\,0})\cdot 10^6/\mathrm{m^3\cdot mol^{-1}}$	215.28	224.90	235.00
$\Delta\mu_1^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	9.22	9.05	8.85
$\Delta\mu_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	131.33	142.43	151.01
$T\Delta S_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−293.34	−303.18	−313.02
$\Delta H_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−162.01	−160.75	−162.01
	0.005[a]		
$(\bar{V}_2^{\,0} - \bar{V}_1^{\,0})\cdot 10^6/\mathrm{m^3\cdot mol^{-1}}$	220.85	229.82	239.18
$\Delta\mu_1^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	9.25	9.08	8.90
$\Delta\mu_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	156.12	165.62	175.65
$T\Delta S_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−291.20	−300.96	−310.73
$\Delta H_2^{0\neq}/\mathrm{KJ\cdot mol^{-1}}$	−135.08	−135.34	−135.08

[a] Molarity of cetrimonium bromide in water in $\mathrm{mol\cdot dm^{-3}}$.

solute to the free energy of activation of viscous flow, and $\Delta\mu_1^{0\neq}$ is the free energy of activation per mole of solvent mixture. The $\Delta\mu_1^{0\neq}$ value has been calculated by the relation:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_0\bar{V}_1^{\,0}/hN_{\mathrm{A}}) \qquad (7)$$

where h is Planck's constant and N_{A} is Avogadro's number. The values of the parameters $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are reported in Table 4.

The entropy of activation for electrolytic solutions has been calculated using the relation:[18]

$$\Delta S_2^{0\neq} = -\mathrm{d}(\Delta\mu_2^{0\neq})/\mathrm{d}T \qquad (8)$$

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

The activation enthalpy $(\Delta H_2^{0\neq})$ has been calculated using the relation:[18]

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \qquad (9)$$

The value of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are also listed in Table 4.

From Table 4 it is evident that $\Delta\mu_1^{0\neq}$ is practically constant at all the solvent compositions and at all temperatures, implying that $\Delta\mu_2^{0\neq}$ is mainly dependent on the viscosity *B*-coefficients and $(\bar{V}_2^{\,0} - \bar{V}_1^{\,0})$ terms. Positive $\Delta\mu_2^{0\neq}$ values at all experimental temperatures and solvent composition suggests that the process of viscous flow becomes difficult as the temperature and molarity of cetrimonium bromide in solution increases. So the formation of the transition state becomes less favorable. According to Feakins et al.,[18] $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for electrolytes having positive *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.[18,19] The values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are found to be negative for all of the experimental solutions and all experimental 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.[18,20]

■ CONCLUSION

In summary, V_ϕ^0 and viscosity *B*-coefficient values for citric acid indicate the presence of strong solute−solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of cetrimonium bromide in the ternary solutions. Also, citric acid was found to act as a structure breaker in the ternary mixtures studied, and cetrimonium bromide has a dehydration effect on the hydrated citric acid.

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