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STUDY OF VOLUMETRIC AND VISCOMETRIC PROPERTIES OF CATIONIC SURFACTANT CETYLPYRIDINIUM BROMIDE IN AQUEOUS SOLUTIONS OF ASCORBIC ACID

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Volumetric and viscometric properties of cationic surfactant cetylpyridinium bromide in aqueous ascorbic acid solutions were studied. The apparent molar volumes, standard partial molar volumes in dilute solutions, transfer apparent molar volumes at infinite dilution and viscosity *B*-coefficients were determined. It was concluded that the behavior of volumetric and viscometric properties in studied ternary system is mainly determined by hydrophobic interactions.

Keywords: ascorbic acid, cationic surfactant, volumetric properties, viscometric properties.

Introduction. Pyridinium cationic surfactants have bactericidal activity against a wide range of Gram-positive and some Gram-negative organisms [1]. Ascorbic acid (AsA) has immune-stimulating effect, e.g. important for defense against infections such as common cold. It also acts as inhibitor of histamine, a compound that is released during allergic reaction. As a powerful antioxidant it can neutralize pollutants and toxins. Ascorbic acid plays an important role for the synthesis of several important peptide hormones neurotransmitters and creatinine.

The studies on partial molar volume and viscosity of cationic surfactants in aqueous vitamins solutions are rare [2, 3]. Volumetric and viscometric properties are important because they reflect the effects of solute–solute and solute–solvent interactions. In this paper the study of volumetric and viscometric properties of cetylpyridinium bromide (CPBr) in aqueous ascorbic acid solutions at different temperatures at atmospheric pressure is presented to understand interactions existing in ternary system.

Materials and Methods. Cationic surfactant cetylpyridinium bromide (CPBr) (“Aldrich”, 98%) and ascorbic acid (“BioXtra crystalline”, “Sigma”, ≥ 99.0%) were used without further purification. All the samples were prepared by directly mixing the appropriate amounts of both components, using twice-distilled water. Densities of solutions were measured using a vibrating–tube digital densimeter DMA-4500 (Anton Paar, Austria) with precision of $\pm(5\cdot10^{-5})\ g\cdot cm^{-3}$. The solutions were thermostated with precision of $\pm0.01\ K$. The densimeter was calibrated with dry air and pure water under atmospheric pressure.

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The flow times of the solutions and the solvents were measured using an Ubbelhode type viscometer placed in a thermostated water bath. The flow time for pure water at 303.15 *K* was 215.4 *s*, the constancy of temperature of thermostat was ±0.05 *K*. The relative viscosity η_r has been calculated as the ratio of flow times $\eta_r = \eta_{solution} / \eta_{solvent}$.

Results and Discussion.

Volumetric Properties. The apparent molar volumes, ϕ_v were determined from solution densities data using the following equation [4]:

$$\phi_v = \frac{1000(\rho_0 - \rho)}{m\rho_0\rho} + \frac{M}{\rho}, \tag{1}$$

where M and m are the molar mass and molality of solute respectively, ρ and ρ_0 are the densities of solution and solvent respectively. The values of density and apparent molar volumes are given in Tab. 1.

Table 1

Densities and apparent molar volumes of CPBr in aqueous ascorbic acid solutions at different temperatures

m, $mol \cdot kg^{-1}$	ρ, $g \cdot cm^{-1}$	ϕ_v, $cm^3 \cdot mol^{-1}$	ρ, $g \cdot cm^{-1}$	ϕ_v, $cm^3 \cdot mol^{-1}$	ρ, $g \cdot cm^{-1}$	ϕ_v, $cm^3 \cdot mol^{-1}$	ρ, $g \cdot cm^{-1}$	ϕ_v, $cm^3 \cdot mol^{-1}$
	298.15 *K*		303.15 *K*		308.15 *K*		313.15 *K*	
[AsA] = 0 $mol \cdot kg^{-1}$								
0.000	0.99807	–	0.99571	–	0.99385	–	0.99233	–
0.020	0.99814	337.12028	0.99580	336.89557	0.99398	335.47936	0.99248	334.96094
0.050	0.99831	335.75815	0.99598	335.92716	0.99420	334.89910	0.99273	334.36903
0.070	0.99844	335.22702	0.99611	335.61348	0.99438	334.26026	0.99291	334.01843
0.090	0.99861	334.45329	0.99626	335.11589	0.99456	333.87859	0.99312	333.44850
0.100	0.99872	333.91484	0.99637	334.58611	0.99467	333.52696	0.99322	333.29092
0.130	0.99903	332.94550	0.99664	333.93736	0.99495	333.16860	0.99355	332.68869
[AsA] = 0.1 $mol \cdot kg^{-1}$								
0.000	0.99872	–	0.99637	–	0.99467	–	0.99322	–
0.020	0.99885	333.87563	0.99653	333.12680	0.99485	332.66500	0.99341	332.62716
0.050	0.99908	333.09722	0.99679	332.63716	0.99514	332.16395	0.99372	332.01680
0.070	0.99925	332.68376	0.99697	332.40453	0.99537	331.48117	0.99396	331.35781
0.090	0.99943	332.51969	0.99717	332.01834	0.99559	331.18352	0.99420	330.95633
0.100	0.99953	332.29041	0.99728	331.76923	0.99573	330.75553	0.99437	330.28098
0.130	0.99987	331.18556	0.99758	331.46053	0.99609	330.30990	0.99477	329.72000
[AsA] = 0.5 $mol \cdot kg^{-1}$								
0.000	0.99959	–	0.99932	–	0.99917	–	0.99891	–
0.020	0.99974	332.58347	0.99948	332.16728	0.99934	331.71187	0.99910	330.78734
0.050	0.99998	332.20344	0.99973	331.88403	0.99961	331.32191	0.99940	330.38754
0.070	1.00015	331.94693	0.99990	331.74182	0.99980	331.05874	0.99961	330.11783
0.090	1.00033	331.66496	1.00007	331.52329	1.00000	330.77012	0.99984	329.70814
0.100	1.00042	331.24741	1.00017	331.43787	1.00011	330.55583	0.99996	329.50172
0.130	1.00071	331.14597	1.00045	331.15276	1.00045	329.99727	1.00029	329.27754

Standard partial molar volumes ϕ_v^0 are obtained by least-squares fitting to the following equation [4]:

$$\phi_v = \phi_v^0 + S_v m. \tag{2}$$

ϕ_V^0 reflects the volume change of the solute arising from the solute–solvent interactions. It means that the change in ϕ_V^0 at different [AsA] and temperature should reflect the changes occurring in its environment in the solution. The parameter S_V provides information regarding solute–solute interactions. The derived values of the parameter ϕ_V^0 as a function of [AsA] and temperature are reported in Tab. 2. Extrapolation, according to Eq. (2), assumes AsA to be a non-electrolyte, and the effect of small extent of hydrolysis of AsA on ϕ_V values was assumed to be negligible. Actually the rough calculation of values of AsA based on pK_a to estimate the correction to be applied to ϕ_V due to hydrolysis has shown that the magnitude of the correction lies within the range of uncertainties at the lowest concentrations studied. It was much smaller at higher concentrations due to the decrease of the degree of hydrolysis [5, 6].

The changes of ϕ_V^0 with temperature may be due to the result of the following effects [7]: 1) at higher temperature the thermal energy of water molecules is increased, causing fast movement of the bulk electrostricted water molecules from the interaction pyridinium ion and non-polar group of ascorbic acid, resulting in a positive volume change; 2) an increase in temperature renders the CPBr–CPBr interaction giving rise to small negative volume change; 3) a decrease in CPBr–water interactions causing positive volume change; 4) the water–water interactions decreasing with the increasing temperature giving rise to small negative change in volume. From Tab. 2 it follows, that values of ϕ_V^0 decrease with the increase of temperature, thus, with increase of temperature the CPBr–CPBr interactions become more significant and water–water interactions decrease in studied ternary system.

Table 2

Partial molar volumes in dilute solutions ϕ_V^0 ($cm^3 \cdot mol^{-1}$) and S_V ($cm^3 \cdot mol^{-1}$) for CPBr–AsA aqueous solutions at different temperatures

[AsA], $mol \cdot kg^{-1}$	ϕ_V^0	S_V	ϕ_V^0	S_V	ϕ_V^0	S_V	ϕ_V^0	S_V
	298.15 *K*		303.15 *K*		308.15 *K*		313.15 *K*	
0	337.79409	–37.70750	337.39167	–26.68356	335.89701	–22.10697	335.40661	–21.00690
0.1	334.34734	–23.70824	333.43140	–15.59092	333.14295	–22.38838	333.26986	–27.52193
0.5	332.85257	–13.07240	332.35669	–9.20231	332.08543	–15.42783	331.08063	–14.57324

One of the best parameters to investigate interactions in multicomponent systems is the transfer volume of CPBr from water to AsA solutions. The transfer of apparent molar volume at infinite dilution of CPBr from water to AsA solutions is calculated by the following equation:

$$\Delta\phi_{tr}^0 = \phi_V^0 \text{ (in aqueous AsA solution)} - \phi_V^0 \text{ (in water)}. \qquad (3)$$

The calculated values of $\Delta\phi_{tr}^0$ are given in Tab. 3, and they are negative. In [8] pyridine has been noted as a structure-breaker in aqueous solutions. The interactions between CPBr and AsA in water can be summarized as follows:

1) interaction of pyridinium ion of CPBr with –O–H group of AsA;
2) interaction of pyridinium ion of CPBr with –O atom of the cyclic ring of AsA;
3) of pyridinium ion of CPBr with –O atom of carboxylic acid group of AsA;

4) interaction of Br^- ion with –H atom of the –O–H group of AsA;

5) ion-hydrophobic interactions between CPBr ions and non-polar part of AsA molecules;

6) hydrophobic–hydrophobic interactions between alkyl chain of CPBr and non-polar part of AsA [2].

Interactions 1)–4) lead to positive values of $\Delta\phi_{tr}^0$ and interactions 5) and 6) lead to negative values of volumes of transfer, because of the reduction of water structure that is formed around those groups as a result of the cosphere overlap as it was developed by Frank and Evans [9, 10]. CPBr acts as water structure-breaker due to hydrophobic hydration in the presence of AsA, and AsA has hydration effect on the hydrated CPBr.

Table 3

Transfer of apparent molar volume at infinite dilution $\Delta\phi_{tr}^0$ of CPBr from water to AsA solutions at different temperatures

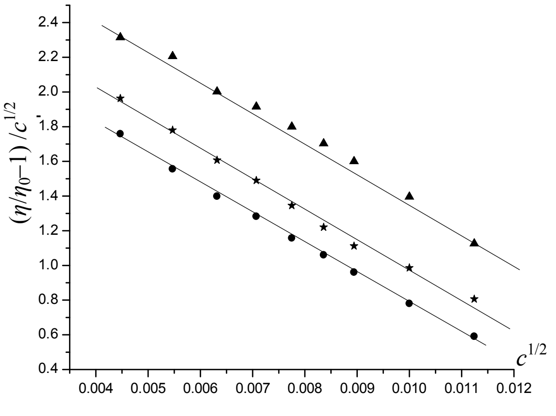
[AsA], $mol{\cdot}kg^{-1}$	$\Delta\phi_{tr}^0$, $cm^3{\cdot}mol^{-1}$			
	298.15 *K*	303.15 *K*	308.15 *K*	313.15 *K*
0.1	–3.44675	–3.96027	–2.75406	–2.13675
0.5	–4.94152	–5.03498	–3.81158	–4.32598

Viscometric Properties. The viscosity data were analyzed by using Jones–Dole equation [11]:

$$\eta_r = 1 + Ac^{1/2} + Bc, \tag{4}$$

$$\frac{\eta_r - 1}{c^{1/2}} = A + Bc^{1/2}, \tag{5}$$

where *A* and *B* are the Falkenhagen [12] and Jones–Dole [11, 12] coefficients respectively. Coefficient *A* accounts for AsA–AsA interactions, and *B* reflects structural modifications included by AsA–CPBr–water interactions [13]. A good fit and a linear dependence of $\frac{\eta/\eta_o - 1}{c^{1/2}}$ versus $c^{1/2}$ were obtained for CPBr–AsA–water solutions at studied temperatures (see Figure). The viscosity data used to characterize the effect of CPBr on the viscosity *B*-coefficients of aqueous AsA solutions are given in Tab. 4.



$\frac{\eta/\eta_0 - 1}{c^{1/2}}$ vs. $c^{1/2}$ dependence for system CPBr–AsA–water at 303.15 *K*.

● 0.0 $mol{\cdot}kg^{-1}$ AsA;
★ 0.1 $mol{\cdot}kg^{-1}$ AsA;
▲ 0.5 $mol{\cdot}kg^{-1}$ AsA.

The viscosity *B*-coefficients are positive both in the absence and presence of ascorbic acid for the aqueous solutions of CPBr. It is well known that the *B*-coefficient represents solute–solvent interactions and depends on various factors [13, 14]. If the decrease of viscosity due to the structure-breaking effect is dominant, rather than the increase of viscosity arising from orientation effect of solvent molecules, then *B*-coefficient will be negative. It follows from Tab. 4, in the studied systems structure-breaking component of viscosity dominates.

Table 4

Viscosity B-coefficients of CPBr in aqueous AsA solutions at different temperatures

[AsA], $mol \cdot kg^{-1}$	*B*-coefficients, $dm^3 \cdot mol^{-1}$			
	298.15 *K*	303.15 *K*	308.15 *K*	313.15 *K*
0.0	–189.28	–198.93	–210.24	–217.94
0.1	–80.96	–86.54	–92.63	–94.64
0.5	–36.80	–42.81	–49.31	–56.39

Viscosity *B*-coefficients of transfer Δ*B* from water to aqueous AsA solutions were calculated using the equation:

$$\Delta B = B \text{ (in aqueous AcsA solution)} - B \text{ (in water)}. \quad (6)$$

The calculated Δ*B* values are negative for studied systems at different temperatures (Tab. 5), which confirms detected behaviors from volumetric property studies and as it has been obtained in studied ternary system the hydrophobic–hydrophobic interactions are dominant.

Table 5

Values of ΔB at different temperatures

[AsA], $mol \cdot kg^{-1}$	Δ*B*, $dm^3 \cdot mol^{-1}$			
	298.15 *K*	303.15 *K*	308.15 *K*	313.15 *K*
0.1	–108.32	–112.39	–117.61	–123.30
0.5	–152.48	–156.12	–160.93	–161.55

Thus, from this study it can be concluded:

1. CPBr–CPBr interactions increase and water–water interactions decrease with increase of temperature;
2. hydrophobic–hydrophobic interactions play significant role over interactions in studied systems.

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