Chemistry

DENSITIES AND VOLUMETRIC PROPERTIES OF L-ASCORBIC ACID SOLUTIONS IN WATER–ETHANOL MIXTURES AT TEMPERATURES FROM 298.15 TO 318.15 K

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This paper studies volumetric properties of L-ascorbic acid+ethanol–water ternary systems. The densities of solution of L-ascorbic acid (vitamin C) in ethanol–water mixtures with various compositions have been measured over the available concentration range at temperatures from 298.15–318.15 K. Apparent molar volumes, standard partial molar volumes and transfer partial molar volumes of L-ascorbic acid were determined in ethanol–water mixtures. The competitive intermolecular interactions between molecules of ascorbic acid and components of ethanol–water mixtures are responsible for the irregular volumetric behavior of these systems.

Keywords: density, L-ascorbic acid, ethanol, appear molar volumes, limiting partial molar volumes, transfer partial molar volumes.

Introduction. L-ascorbic acid (vitamin C, AA) is one of the most essential nutrients for the maintenance of human health. AA concentration in brain is highly regulated. The brain normally contains high concentrations of vitamin C, which is actively taken through the choroids plexus [1, 2]. However, its specific functions in the central nervous system (CNS) are only beginning to be elucidated. AA acts as a part of the intracellular antioxidant network and as such is an important neuro-protective constituent. Growing evidence indicates that AA also acts as a neuro-modulator. Recently, it has become clear that antioxidant nutrients, including vitamin C, are important for neurological function [1–5]. High intake of vitamin E and C has been found to be associated with lower risk of Alzheimer's disease [6]. Therefore, the objective of some studies was to assess the protective effect of physiological concentrations of AA against the ethanol mediated toxic effects and prostaglandin E2 (PGE2) production in Human brain astrocyte cells relevant to neurological damage [7–9]. Therefore, the studies of the physicochemical properties of solutions of AA are important for fundamental science and applications.

The AA+(ethanol–water) systems are of interest, because that of the ability of their components to form hydrogen bonds. In our recent publications novel and interesting physicochemical properties such as volumetric, surface tension and thermochemical as well as vibrational spectra of solutions of AA in water and dimethyl sulfoxide (DMSO)–water mixtures have been reported [10, 11].

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Particularly, the hydrogen bond formed between AA and both of water and DMSO has been studied by means of *ab initio* and Density Functional Theory (DFT) calculations [12]. Although AA is able to form hydrogen-bonded complex with water molecule the solution process is endothermic [10]. Obviously in that case the endothermic process of solution of crystalline AA in water is predominated. For comparison, it is worthy to notice that the process of mixing ethanol and water is exothermic [13] and very strong hydrogen bonding between ethanol and water takes place [14]. We believe that the competitive intermolecular interactions will take place between AA and the components of ethanol–water mixed solvent.

In this work on the basis of densitometric measurements volumetric properties, i.e. apparent molar volumes V_ϕ, standard partial molar volumes V_ϕ^0 and transfer partial molar volumes V_{tr}^0 of AA in ethanol–water mixtures in the temperature range 298.15–318.15 K have been calculated.

Materials and Methods. AA is white to slightly yellow, odorless crystalline powder with a freely solubility in water and sparingly soluble in ethanol. AA was supplied by "Aldrich Chemical Co" (99.7%). Ethanol (EtOH) was purchased from "Aldrich Chemical Co" (99.7%) and was used without further drying or purification.

The densities of solutions of AA in water and EtOH–water mixtures were measured with an Anton Paar DMA 4500 vibrating-tube densimeter at the temperature range 298.15–318.15 K. All solutions were prepared gravimetrically using double-distilled water. The accuracy of the density and temperature measurements was $\pm 1\cdot 10^{-5}$ $g\cdot cm^{-3}$ and ± 0.01 K respectively. The densimeter was calibrated with dry air and double-distilled water.

Results and Discussion.

Densities and Apparent Molar Volumes. The experimental values of densities of AA solutions in water and EtOH–water mixtures with various compositions ($X_{EtOH} \approx 0.01$; 0.1; 0.25 and 0.5, where X is mole fraction) at the temperature range 298.15–318.15 K are listed in Tab. 1.

As is evident from experimental data, the increase in temperature leads to the decrease in density.

Apparent molar volumes V_ϕ of AA in binary aqueous solutions have been calculated by the Eq. (1) and in ternary systems by the Eq. (2) according to the procedure developed in [15]:

$$V_{\phi,2} = \frac{1000(\rho_0 - \rho)}{m\,\rho\,\rho_0} + \frac{M}{\rho}, \tag{1}$$

where M is the molar weight of AA ($g\cdot mol^{-1}$); ρ_0, ρ are the densities of the pure water and binary solutions ($g\cdot cm^{-3}$); m_2 is the molal concentration of AA in water ($mol\cdot kg^{-1}$);

$$V_{\phi,3} = \frac{M_3}{\rho} + \frac{\rho_0 - \rho}{\rho\,\rho_0}\left(\frac{M_2\,m_2 + 1000}{a\,m_2}\right), \tag{2}$$

where M_3, M_2 are the molar weights of AA and ethanol respectively ($g\cdot mol^{-1}$); ρ_0, ρ are the of the mixed solvent (EtOH–water) and ternary solutions ($g\cdot cm^{-3}$); m_2 is the molal concentration of ethanol in EtOH–water mixture ($mol\cdot kg^{-1}$); $a = n_3/n_2$, where n_3 and n_2 are the numbers of moles of AA and ethanol respectively.

Densities of AA solutions in water and EtOH–water mixtures in the temperature range of 298.15–318.15 K

T, K	298.15	303.15	308.15	313.15	318.15
$m,\ mol\cdot kg^{-1}$			$\rho,\ \ g\cdot cm^{-3}$		
			AA+H_2O		
0.0000	0.99820	0.99704	0.99564	0.99402	0.99221
0.1072	1.00560	1.00439	1.00294	1.00127	0.99941
0.1916	1.01144	1.01017	1.00867	1.00696	1.00505
0.2965	1.01852	1.01720	1.01563	1.01387	1.01192
0.3933	1.02506	1.02368	1.02207	1.02026	1.01826
0.4889	1.03089	1.02944	1.02779	1.02594	1.02391
0.5996	1.03829	1.03679	1.03508	1.03317	1.03109
0.7044	1.04433	1.04278	1.04101	1.03906	1.03694
0.8030	1.05042	1.04879	1.04698	1.04499	1.04284
0.8968	1.05667	1.05501	1.05315	1.05112	1.04893
0.9884	1.06125	1.05956	1.05767	1.05561	1.05338
		AA+(EtOH–H_2O),	$X_{EtOH} = 0.0111$		
0.0000	0.99320	0.99176	0.99011	0.98825	0.98620
0.1259	1.00111	0.99961	0.99790	0.99598	0.99389
0.2099	1.00640	1.00488	1.00313	1.00121	0.99917
0.3097	1.01277	1.01117	1.00937	1.00737	1.00520
0.4163	1.01959	1.01795	1.01609	1.01405	1.01183
0.5245	1.02674	1.02505	1.02315	1.02106	1.01880
0.6309	1.03366	1.03190	1.02995	1.02782	1.02552
0.7355	1.04030	1.03848	1.03648	1.03418	1.03197
0.8309	1.04628	1.04447	1.04242	1.04021	1.03784
		AA+(EtOH–H_2O),	$X_{EtOH} = 0.1003$		
0.0000	0.96379	0.96114	0.95821	0.95484	0.95184
0.1036	0.97147	0.96889	0.96612	0.96318	0.96011
0.2080	0.97916	0.97644	0.97363	0.97067	0.96757
0.3362	0.98671	0.98406	0.98123	0.97826	0.97514
0.4338	0.99310	0.99041	0.98756	0.98458	0.98145
0.5330	0.99957	0.99689	0.99403	0.99103	0.98790
0.6326	1.00644	1.00379	1.00094	0.99794	0.99481
0.7299	1.01213	1.00948	1.00661	1.00358	1.00042
0.8400	1.01934	1.01664	1.01373	1.01068	1.00744
		AA+(EtOH–H_2O),	$X_{EtOH} = 0.2506$		
0.0000	0.91911	0.91514	0.91112	0.90702	0.90286
0.1121	0.92733	0.92338	0.91937	0.91528	0.91113
0.2308	0.93530	0.93135	0.92734	0.92326	0.91912
0.3391	0.94352	0.93960	0.93560	0.93153	0.92740
0.4537	0.95094	0.94702	0.94303	0.93897	0.93484
0.5841	0.96288	0.95909	0.95518	0.95116	0.94705
0.6793	0.96783	0.96400	0.96004	0.95600	0.95189
0.8945	0.98298	0.97920	0.97525	0.97123	0.96713
1.0213	0.98837	0.98448	0.98053	0.97651	0.97243
		AA+(EtOH–H_2O),	$X_{EtOH} = 0.5009$		
0.0000	0.85797	0.85365	0.84925	0.84479	0.84025
0.0776	0.86373	0.85940	0.85501	0.85055	0.84603
0.1074	0.86612	0.86184	0.85745	0.85299	0.84847
0.2033	0.87370	0.86944	0.86506	0.86062	0.85611
0.3218	0.88273	0.87847	0.87410	0.86966	0.86516
0.4030	0.88877	0.88450	0.88009	0.87568	0.87116
0.4979	0.89527	0.89108	0.88673	0.88232	0.87784

Apparent molar volumes of AA in the water and EtOH–water mixtures
in the temperature range of 298.15–318.15 K

T, K	298.15	303.15	308.15	313.15	318.15
$m, mol \cdot kg^{-1}$	$V_\phi, cm^3 \cdot mol^{-1}$				
AA+H$_2$O					
0.1072	106.884	107.409	107.945	108.493	108.956
0.1916	106.307	106.889	107.429	108.034	108.489
0.2965	106.100	106.737	107.282	107.837	108.335
0.3933	105.682	106.280	106.837	107.404	107.878
0.4889	106.516	107.096	107.645	108.185	108.672
0.5996	105.739	106.325	106.888	107.428	107.909
0.7044	106.439	107.039	107.592	108.126	108.613
0.8030	106.297	106.883	107.430	107.949	108.441
0.8968	105.484	106.073	106.616	107.134	107.617
0.9884	106.345	106.921	107.457	107.982	108.455
AA+(EtOH–H$_2$O), X_{EtOH} = 0.0111					
0.1259	112.718	113.276	113.848	114.433	114.868
0.2099	112.053	112.513	113.085	113.473	114.021
0.3097	111.052	111.651	112.231	112.791	113.296
0.4163	110.123	110.685	111.285	111.824	112.350
0.5245	108.812	109.369	109.938	110.481	110.995
0.6309	107.899	108.488	109.056	109.586	110.095
0.7355	107.300	107.862	108.432	109.143	109.463
0.8309	106.839	107.291	107.866	108.391	108.888
AA+(EtOH–H$_2$O), X_{EtOH}=0.1003					
0.1036	102.093	101.420	99.796	95.294	96.061
0.2080	101.568	101.993	101.429	99.330	99.910
0.3362	106.810	106.900	106.671	105.463	105.949
0.4338	106.752	106.944	106.840	105.954	106.382
0.5330	106.517	106.670	106.624	105.964	106.332
0.6326	105.491	105.577	105.531	104.986	105.307
0.7299	106.119	105.880	105.886	105.473	105.816
0.8400	105.469	104.972	105.039	104.715	105.132
AA+(EtOH–H$_2$O), X_{EtOH} = 0.2506					
0.1121	103.879	103.737	103.698	103.655	103.608
0.2308	106.708	106.703	106.748	106.739	106.726
0.3391	103.650	103.549	103.551	103.514	103.474
0.4537	104.943	104.90	104.908	104.887	104.889
0.5841	98.233	97.901	97.706	97.566	97.484
0.6793	101.349	101.167	101.122	101.074	101.04
0.8945	100.140	99.144	99.100	99.037	98.999
1.0213	103.538	102.026	102.018	101.995	101.97
AA+(EtOH–H$_2$O), X_{EtOH} = 0.5009					
0.0776	103.720	103.908	103.738	103.740	103.370
0.1074	101.213	100.690	100.537	100.506	100.205
0.2033	98.347	97.906	97.723	97.530	97.257
0.3218	97.939	97.649	97.476	97.337	97.101
0.4030	97.935	97.734	97.729	97.510	97.385
0.4979	99.193	98.820	98.657	98.485	98.275

The calculated values of V_ϕ for binary and ternary systems reported in Tab. 2. The influence of ethanol on the volumetric behavior has been revealed by the change of V_ϕ of ternary system compared with the V_ϕ of the binary aqueous solutions of AA.

Contrary to the V_ϕ in AA+H$_2$O binary solutions, the V_ϕ in ternary systems are irregularly changed with molality of solutions (Tab. 2). It is interesting that the effect of ethanol on the values of V_ϕ is not altered monotone with increasing in quantity of ethanol in EtOH–H$_2$O mixture and with increasing of temperature.

Standard Partial Molar Volumes. The standard partial molar volumes V_ϕ^0, which are taken to be apparent molar volumes at the infinite dilution, were estimated from the plots of V_ϕ versus molality of solutions by extrapolating using the equation

$$V_\phi = V_\phi^0 + S_v m, \tag{3}$$

where V_ϕ^0 is the infinite dilution apparent molar volume that equals the standard partial molar volume and S_v is an experimentally determined parameter (slope constant).

Partial molar volumes at infinite dilution are considered of particular interest because of their usefulness in examining solute-solvent interactions, as solute-solute interactions can be assumed to be eliminated at infinite dilution. At infinite dilution, the partial molar volume and apparent molar volume are equal.

The standard partial molar volumes V_ϕ^0 for AA binary and ternary solutions at 298.15–318.15 K temperature range are presented in Tab. 3.

T a b l e   3

Standard partial molar volumes V_ϕ^0 (cm^3·mol^{-1}) of AA in binary and ternary solutions in the temperature range of 298.15–318.15 K

T, K	AA+H$_2$O	AA+(EtOH–H$_2$O), X_{EtOH} = 0.0111	AA+(EtOH–H$_2$O), X_{EtOH} = 0.1003	AA+(EtOH–H$_2$O), X_{EtOH} = 0.2506	AA+(EtOH–H$_2$O), X_{EtOH} = 0.5009
298.15	106.447	113.747	107.404	105.113	102.349
303.15	107.024	114.304	107.441	105.491	102.173
308.15	107.570	114.883	107.630	105.482	101.991
313.15	108.151	115.367	107.156	105.446	101.978
318.15	108.621	115.890	106.623	105.413	101.612

For comparison, the corresponding data for standard partial molar volumes of AA in water and ethanol–water mixtures at 298.15 K are depicted in Figure.

As it follows from these data, the values of standard partial molar volumes increase with an increase in temperature for binary solution of AA and when the quantity of ethanol is negligible (see Figure). However, with increasing quantity of EtOH in EtOH–H$_2$O mixtures the values of standard partial molar volumes decrease.
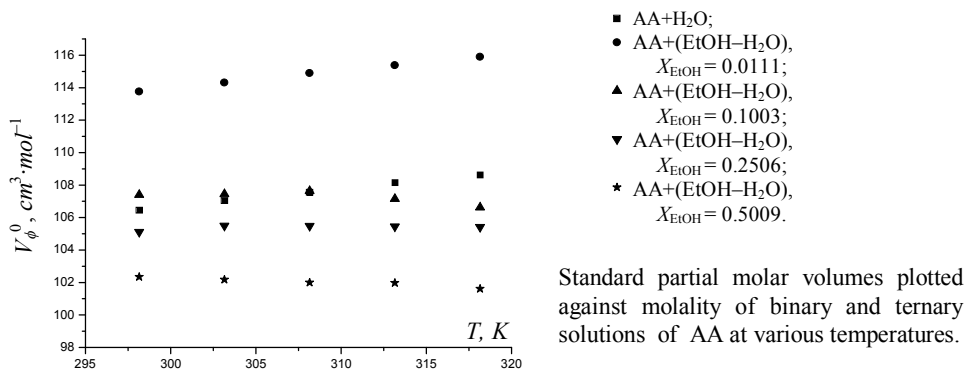
It is known that standard partial molar volume V_ϕ^0 comprises four contributions [16] as

$$V_\phi^0 = (V_{VW} + V_V) + (V_S + V_h), \tag{4}$$

where V_{VW} is the intrinsic van der Waals volume; V_V is the void volume; V_S is the contribution from solute-solvent interactions and V_h is the hydrophobic hydration. We believe that the latter has main contribution in the increase of V_ϕ^0 for ternary solution when the quantity of ethanol is negligible. The results obtained show that the values of standard partial molar volumes of AA do not change monotonously

with increasing quantity of ethanol in EtOH–H$_2$O mixture. We believe that competitive intermolecular interactions are responsible for the observed phenomena. In ternary systems the strongest interaction between AA and components of EtOH–H$_2$O mixtures, i.e. ethanol and water molecules lead to the non-monotonic changes of partial molar volumes for AA.

- ■ AA+H$_2$O;
- ● AA+(EtOH–H$_2$O), X_{EtOH} = 0.0111;
- ▲ AA+(EtOH–H$_2$O), X_{EtOH} = 0.1003;
- ▼ AA+(EtOH–H$_2$O), X_{EtOH} = 0.2506;
- ★ AA+(EtOH–H$_2$O), X_{EtOH} = 0.5009.

Standard partial molar volumes plotted against molality of binary and ternary solutions of AA at various temperatures.

Transfer Partial Molar Volumes. The transfer partial molar volumes ΔV_{tr}^0, of AA from the water to the aqueous ethanol solution have been calculated by equation

$$\Delta V_{tr}^0 = V_\varphi^0 \left(AA + (EtOH - H_2O) \right) - V_\varphi^0 \left(AA + H_2O \right). \qquad (5)$$

Table 4

Transfer partial molar volumes ΔV_{tr}^0 (cm$^3 \cdot$ mol^{-1}) of AA from water to the aqueous ethanol solutions in the temperature range of 298.15–318.15 K

T, K	AA+(EtOH–H$_2$O), X_{EtOH} = 0.0111	AA+(EtOH–H$_2$O), X_{EtOH} = 0.1003	AA+(EtOH–H$_2$O), X_{EtOH} = 0.2506	AA+(EtOH–H$_2$O), X_{EtOH} = 0.5009
298.15	7.303	0.957	−1.334	−4.098
303.15	7.280	0.467	−1.533	−4.851
308.15	7.313	0.060	−2.088	−5.579
313.15	7.216	−0.995	−2.705	−6.173
318.15	7.269	−1.998	−3.208	−7.009

The transfer partial molar volumes for ternary solutions at the temperature range 298.15–318.15 *K* are presented in Tab. 4. These values can be interpreted on the basis of the Gurney model [17] on the overlapping solvate spheres of solutes during their dissolution in water, as shown in [18, 19]. Positive values obtained for AA+(EtOH–H$_2$O) system containing 0.01 *mol* fraction of EtOH indicate that in partial molar volume of AA predominates the contribution caused by hydrophobic hydration.

However, for the ternary systems containing large quantity of ethanol the transfer partial molar volumes are negative and become more negative with increasing mole fraction of ethanol and temperatures from 298.15 to 318.15 *K*. We suggest that in this case the strong interaction between AA and ethanol molecules by the hydrogen bonding leads to the decrease of partial molar volumes of AA.

Conclusion. The volumetric results obtained show that the changes of standard partial molar volumes of AA are irregular due to competitive intermolecular

interactions. In the AA+(EtOH–H$_2$O) systems the strongest interaction between AA and ethanol molecules by the hydrogen bonding leads to the decrease of partial molar volumes of AA.

REFERENCES

1. **Siushansian R., Wilson J.X.** Ascorbate Transport and Intracellular Concentration in Cerebral Astrocytes. // J. Neurochem., 1995, v. 65, p. 41–49.
2. **Rice M.E.** Ascorbate Regulation and Its Neuroprotective Role in the Brain. // Trends Neurosci., 2000, v. 23, p. 209–216.
3. **Daskalopoulos R., Korcok J,, Tao L., Wilson J.X.** Accumulation of Intracellular Ascorbate from Dehydroascorbic Acid by Astrocytes is Decreased after Oxidative Stress and Restored by Propofol. // Glia, 2002, v. 39, p. 124–132.
4. **Wilson J.X., Peters C.E., Sitar S.M., Daoust P., Gelb A.W.** Glutamate Stimulates Ascorbate Transport by Astrocytes. // Brain Res., 2000, v. 858, p. 61–66.
5. **Grundman M., Delaney P.** Antioxidant Strategies for Alzheimer's Disease. // Proc. Nutr. Soc., 2002, v. 61, p. 191–202.
6. **Engelhart M.J., Geerlings M.I., Ruitenberg A., van Swieten J.C., Hofman A., Witteman J.C., Breteler M.M.** Dietary Intake of Antioxidants and Risk of Alzheimer Disease. // JAMA, 2002, v. 287, p. 3223–3229.
7. **Sánchez-Moreno C., Paniagua M., Madrid A., Martín A.** Protective Effect of Vitamin C Against the Ethanol Mediated Toxic Effects on Human Brain Glial Cells. // J. Nutr. Biochem., 2003, v. 14, № 10, p. 606–613.
8. **Yanardag R., Ozsoy-Sacan O., Ozdil S., Bolkent S.** Combined Effects of Vitamin C, Vitamin E, and Sodium Selenate Supplementation on Absolute Ethanol-Induced Injury in Various Organs of Rats. // Int. J. Toxicology, 2007, v. 26, p. 513–523.
9. **Ginter E., Zloch Z., Ondrejcka R.** Influence of Vitamin C Status on Ethanol Metabolism in Guinea-Pigs. // Physiol. Res., 1998, v. 47, p. 137–141.
10. **Kazoyan E.A., Terzyan A.M., Markarian Sh.A.** Thermodynamic Properties of L-Ascorbic Acid's Solutions in Dimethyl Sulfoxide and Dimethyl Sulfoxide+Water Mixtures. // Russ. J. Phys. Chem. A, 2011, № 4, p. 612–616.
11. **Zatikyan A.L., Kazoyan E.A., Bonora S., Markarian Sh.A.** Ascorbic Acid Vibrational Spectra in Sulfoxide Solvents. // Russ. J. Appl. Spectroscopy, 2008, v. 75, № 5, p. 664–669.
12. **Niazazari N., Zatikyan A.L, Markarian Sh.A.** *Ab Initio* and DFT Study of Hydrogen Bond Interactions between Ascorbic Acid and Dimethyl Sulfoxide Based on FT-IR and FT-Raman Spectra. // Spectrochim. Acta A, 2013, v. 110, p. 217–225.
13. **Costigan M.J., Hodges L.J., Marsh K.N., Stokes R.H., Tuxford C.W.** The Isothermal Displacement Calorimeter: Design Modifications for Measuring Exothermic Enthalpies of Mixing. // Australian J. Chem., 1980, v. 33, № 10, p. 2103–2119.
14. **Nose A., Hojo M.** Hydrogen Bonding of Water–Ethanol in Alcoholic Beverages. // J. Biosci. Bioeng., 2006, v. 102, p. 269–280.
15. **D'Aprano A., Donato I.D., Goffedi M., Liveri V.T.** Volumetric and Transport Properties of Aerosol-OT Reversed Micelles Containing Light and Heavy Water. // J. Sol. Chem., 1992, v. 21, p. 323–331.
16. **Kumar A., Singh M., Gupta K.C.** An Estimation of Hydrophilic and Hydrophobic Interaction of Aqueous Urea, Methylurea, Dimethylurea and Tetramethylurea from Density and Apparent Molal Volume at 30.0^{o}C. // Phys. Chem. Liq., 2010, v. 48, № 1, p. 1–6.
17. **Gurney R.W.** Ionic Processes in Solution. NY: McGraw Hill, 1953.
18. **Lepori L., Gianni P.** Partial Molar Volumes of Ionic and Nonionic Organic Solutes in Water: A Simple Additivity Scheme Based on the Intrinsic Volume Approach. // J. Sol. Chem., 2000, v. 29, p. 405–447.
19. **Tyunina E.Yu., Badelin V.G.** Interaction of L-Phenylalanine with Nicotinic Acid in Buffer Solution by Volumetric Measurements at Various Temperatures. // J. Sol. Chem., 2016, v. 45, p. 475–482.