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Thermodynamic and transport properties of aqueous trisodium citrate system at 298.15 K

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Abstract

In this work, we report density, viscosity, refractive index and water activity data for the aqueous trisodium citrate ($C_6H_5Na_3O_7$) system at 298.15 K. The parameters of the Pitzer ion-interaction model are evaluated from isopiestic water activity data. The apparent molar volume at infinite dilution was calculated from density data and a new value for the conventional partial molar volume of citrate ion (Cit^{3-}) was derived. The experimental viscosity data have been fitted to the Kumar equation. Using this equation, the hydration number (h) and ion–solvent interaction parameter (B) for trisodium citrate were obtained.

Keywords: Trisodium citrate; Density; Viscosity; Refractive index; Water activity

1. Introduction

Sodium citrate is an important organic salt in biotechnology, pharmaceutics, and agriculture. The aqueous solutions of this salt with poly(ethylene glycol) and poly(propylene glycol) form two-phase systems, which can be used in biomolecular extraction [1,2,3]. Because of the potential use of this organic salt, accurate experimental values of thermodynamic and transport properties are needed. The published thermodynamic and transport properties for this system are limited, and new measurements are needed to supplement these studies. There are some experimental density data for the aqueous trisodium citrate system at 298.15 K [4].

In this study, we report density, viscosity, refractive index and water activity data for the aqueous trisodium citrate system at 298.15 K. The parameters of the Pitzer ion-interaction model [5] are evaluated for $C_6H_5Na_3O_7$ (aq) from isopiestic data. From density data, the apparent molar volume of trisodium citrate aqueous solution at infinite dilution was calculated and the conventional partial molar volume of Cit^{3-} ion was derived. The experimental viscosity data have been fitted to the Kumar equation [6].

2. Experimental

Trisodium citrate and sodium chloride were obtained from Merck (GR, min 99%) and used without further purification. The isopiestic method is used to obtain the activity of water. The isopiestic apparatus with five flasks was similar to the one used by Ochs et al. [7]. Two flasks contained the standard NaCl solution, two flasks contained the $C_6H_5Na_3O_7$ solution, and the central flask was used as a water reservoir. The apparatus was held in a constant temperature bath for at least 5 days for equilibration. The experimental method was described previously [8]. This technique is capable of giving the water activity with an absolute error of 0.02% or better. Density measurements were made with a Mettler TOLEDO densimeter (DE51). Precision of the instrument is $\pm 1\times10^{-5}$ g cm^{-3}. The temperature of the vibrating tube in the densimeter was controlled to within ± 0.05 °C.

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Table 1
Density, viscosity and refractive index for trisodium citrate solutions at 298.15 K

m (mol kg^{-1})	d (g cm^{-3})	η (mPa s)	n_D
0.0000	0.99704	0.8904	1.33252
0.0025	0.99754	0.8910	1.33338
0.0142	0.99985	0.9458	1.33336
0.0427	1.00545	0.9636	1.33474
0.0714	1.01060	1.0044	1.33597
0.1018	1.01644	1.0201	1.33734
0.1447	1.02411	1.0518	1.33935
0.2058	1.03528	1.0815	1.34205
0.2625	1.04336	1.1023	1.34409
0.3011	1.05189	1.1342	1.34624
0.3991	1.06833	1.1743	1.35023
0.5090	1.08582	1.236	1.35428
0.6573	1.10893	1.5148	1.35976
0.7737	1.12707	1.6171	1.36395
0.8857	1.14280	1.8882	1.36792
1.0695	1.16731	2.2181	1.37377
1.1976	1.18543	2.5634	1.37805
1.3583	1.20679	3.4103	1.38287
1.5724	1.22988	4.3152	1.38797
1.7373	1.25104	5.8477	1.39308
1.9146	1.26968	6.9626	1.39721

Viscosities were measured with an Ostwal d-type viscometer. The viscometer was calibrated with water (0.8904 mPa s) and toluene (0.5559 mPa s) at 298.15 K. Volume of the solutions used in the viscometer was 6 cm^3 as measured with a pipet. It was assumed that the viscosity η was related to the time of flow (t) and density of solution (d) according to

$$\eta = Adt - \frac{Bd}{t} \tag{1}$$

where A and B for the viscometer were found to be 0.0220 and −4.3960, respectively. The viscosity measurement was reproducible to within ±5%.

Refractive indices of the solution were measured using a Mettler TOLEDO refractometer with temperature control (RE50). The precision of the refractive index determination was 0.00001 refractive index units.

3. Results and discussion

Density, viscosity and refractive index values for the aqueous trisodium citrate system at 298.15 K are presented in Table 1. The experimental densities, viscosities and refractive indices have been fitted to the following equation:

$$F - F_w = \sum_i a_i m^i \tag{2}$$

The symbols F and F_w are density, viscosity or refractive index for solutions and pure water, respectively, m is the molality. In Eq. (2), the coefficients a_i, reported in Table 2, are fitting coefficients. In Fig. 1, our experimental data for density were compared by density data of Apelblat and Manzurola [4] (Figs. 2 and 3).

Table 2
Fitting coefficients of Eq. (2) and average relative errors

F	a_1	a_2	a_3	δ%
d	0.1900	−0.0319	0.0037	0.003
η	0.9337	−0.7717	1.0296	0.80
n_D	0.0476	−0.0098	0.0014	0.01

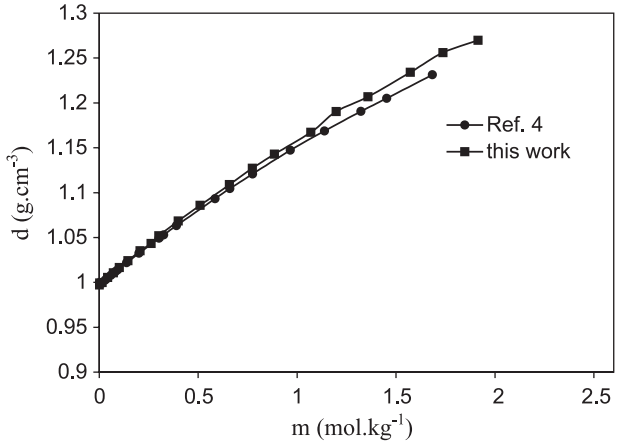

Fig. 1. Comparison of experimental density data of aqueous trisodium citrate system at 298.15 K.

The apparent molar volume is related to the solution density through

$$\phi_s = \frac{M_s}{d} + \frac{1000(d_w - d)}{m_s d d_w} \tag{3}$$

where M_s is the molar mass of solute. Apparent molar volume data are usually fitted by the following semi-empirical equation [9]

$$\phi_s = \phi_s^{\infty} + S_v m_s^{0.5} + b_v m_s \tag{4}$$

where ϕ_s^{∞} is the apparent molar volume at infinite dilution

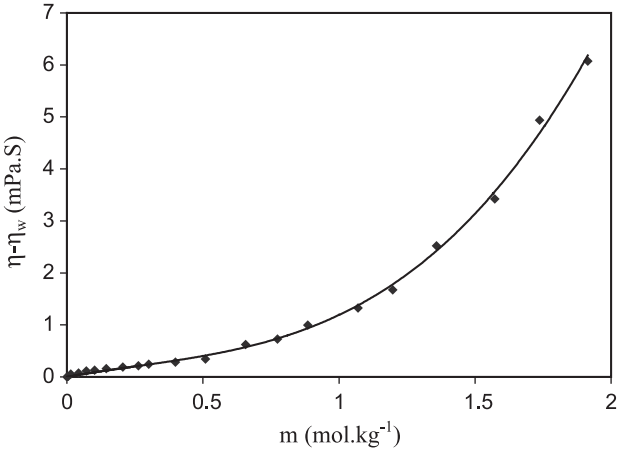

Fig. 2. Experimental viscosity data for aqueous trisodium citrate at 298.15 K.