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DENSITY AND APPARENT MOLAR VOLUME PREDICTION IN SOME TERNARY ELECTROLYTE SOLUTIONS

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The density predictive methods of Young and Patwardhan – Kumar have been tested for some aqueous electrolyte solutions: $MgCl_2$-NaCl-H_2O, $MgCl_2$-Na_2SO_4-H_2O, KCl-Na_2SO_4-H_2O, NaCl-Na_2SO_4-H_2O, and KCl-NaBr-H_2O. The properties of mixed-electrolyte solutions were estimated from corresponding properties of single-electrolyte solutions containing the components of mixture at the same ionic strength as that of mixed electrolyte solution. The Patwardhan – Kumar method gives slightly better prediction for all studied systems than Young's rule. From density the mean apparent volumes was calculated. The predictive accuracy of methods recommends them for most practical applications.

INTRODUCTION

Continuing our work on the thermodynamic of the electrolyte systems[1,2] this paper presents the study of prediction methods of volumetric properties of aqueous electrolyte systems. Density is one of the physical properties important for the understanding of interactions in solutions and in the design and analysis of industrial processes. Many industrial processes utilize aqueous solutions containing several solute components. The possible combinations of individual solutes in aqueous mixed solutions are extremely large. Direct measurements of the densities of these aqueous multicomponent solutions are sometime, impractical. Extensive data have been reported in the literature for densities of aqueous solutions of single solutes; the existing data for binary aqueous solutions of 306 inorganic substances has been critically evaluated.[3] Therefore, it is interesting and practically important to develop an approach that can make use of this information to provide reasonable predictions for multicomponent solutions.

Theoretical approaches for volumetric properties are usually limited to dilute and moderate solutions and require complicated numerical calculation. Semiempirical approaches are simpler, but need several adjustable parameters on specific experimental data. Generally, the density of aqueous electrolytes was correlated by various methods. One method presents the density by a power series in (molality)$^{1/2}$, the coefficients (6 to 16) in the equations being polynomial functions of temperature. Connaughton *et al*.[4] and Kumar *et al.*[5] represent the densities by a means of a polynomial equation in ionic strength. Roger and Pitzer,[6] Kumar and Atkinson[7] report the apparent molar volumes by different models. For aqueous electrolyte solutions, the mixing rule of Young[8] and the Patwardhan and Kumar (P-K) equations[9,10] are recommended.

The aim of this work is to test the particular methods for density prediction and calculate the apparent molar volume of mixed aqueous electrolyte solutions from single electrolyte solutions by simple equations without system-specific empirical constants. The available experimental data[9-11] was utilised. Five ternary systems were analysed, some with four different ions and another with a common anion, at different ionic strength at 298.15 K.

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RESULTS AND DISCUSSION

Young,[8,11] postulated that the density (d) and other properties of mixed electrolyte solutions at given ionic strength is linked to the densities (d_J) of its constituent binary subsystems at the same ionic strength by the equation:

$$d = \sum_J \frac{m_J}{\sum_J m_J} d_J \qquad (1)$$

m_J is the molality of the solute J.

Simple but sufficiently accurate predictive equations for density, and others properties (compressibility and thermal expansion) of aqueous mixed electrolyte solutions, without any empirical constants were proposed by Patwardhan and Kumar:[9,10]

$$d = \frac{\sum_J \psi_J}{\sum_J \left(\frac{\psi_J}{d_J^0} \right)} \qquad (2)$$

$$\psi_J = \left(1000 y_J + m_J M_J\right)$$

d is the density of mixed–electrolyte solution; d_J^0 - the density of single-electrolyte solutions at the same ionic strength as that of mixed–electrolyte solution; y_J - the ionic strength fraction of electrolyte in mixed system; I - the ionic strength of mixed system, m_i - the molalities of i species; z_i - the charge of ion i species; M_J- the molar mass of the solute J.

The methods and the test procedure have been described in a previous paper.[2]

The mean apparent molar volume is related to density of of mixture (d) and pure water (d^0) by equation:[5]

$$V_\phi^* = \frac{1000 \cdot (d_0 - d\ )}{\sum_J m_J \cdot d \cdot\ d_0} + \frac{\sum_J m_J \cdot M_J}{\sum_J m_J \cdot d} \qquad (3)$$

d_0 is equal to 0.997047 $g\ cm^{-3}$ at 298.15 K.

The accuracy of calculus was estimated by the mean relative deviation, σ:

$$\sigma = \frac{\sum_N \left| \frac{d_{i,\exp} - d_{i,calc}}{d_{i,\exp}} \right|}{N} 100 \qquad (4)$$

where $d_{i,\exp}$ is experimental value, $d_{i,calc}$ - predicted value, N- number of data.

The density of mixed electrolyte solutions was predicted from density of single-electrolyte solutions at the same ionic strength as that of mixed–electrolyte solution by Young and Patwardhan-Kumar methods. Published experimental densities for the single-electrolyte water with NaCl, KCl, $MgCl_2$, Na_2SO_4, NaBr solutions at 298.15 K[12] given in Table 1, have been used to test the applicability of proposed methods.

Table 1

Density for single electrolyte systems at 298.15 K

NaCl-H_2O		**KCl-H_2O**		**$MgCl_2$-H_2O**		**Na_2SO_4-H_2O**		**NaBr-H_2O**	
m, mol kg^{-1}	d, g cm^{-3}	m, mol kg^{-1}	d, g cm^{-3}	m, mol kg^{-1}	d, g cm^{-3}	m, mol kg^{-1}	d, g cm^{-3}	m, mol kg^{-1}	d, g cm^{-3}
0.1728	1.00409	0.2737	1.0097	0.2143	1.0134	0.14368	1.0151	0.19835	1.0126
0.3492	1.01112	0.5588	1.0225	0.4375	1.0298	0.29334	1.0332	0.40496	1.0284
0.7129	1.02530	0.8561	1.0354	0.6703	1.0463	0.44938	1.0515	0.62037	1.0447
1.0921	1.03963	1.1663	1.0484	0.9132	1.0631	0.61220	1.0701	0.84514	1.0613
1.4877	1.05412	1.4903	1.0616	1.1669	1.0801	0.78225	1.0890	1.07990	1.0785
1.9010	1.06879	1.8290	1.0750	1.4321	1.0974	0.96004	1.1083	1.32533	1.0961
2.3330	1.08365	2.1834	1.0886	1.7096	1.1149	1.14609	1.1279	1.58218	1.1142
2.7852	1.09872	2.5548	1.1024	2.0004	1.1326	1.34100	1.1479	1.85126	1.1329
3.2589	1.11401	2.9442	1.1164	2.3053	1.1506	1.54543	1.1683	2.13346	1.1522
3.7556	1.12954	3.3532	1.1307	2.6255	1.1689	1.76007	1.1890	2.42978	1.1721
4.2773	1.14533	0.2737	1.0097	0.2143	1.0134	0.14368	1.0151	0.19835	1.0126

Table 2

Predictive density and apparent molar volume for ternary electrolyte systems at different ionic strength and 298.15 K

y_2, mol kg^{-1}	d_{exp}, g cm^{-3}	d^{Y}_{pred} g cm^{-3}	d^{PK}_{pred}, g cm^{-3}	V^{*}_{Φ}, cm^3 mol^{-1}	y_2, mol kg^{-1}	d_{exp}, g cm^{-3}	d^{Y}_{pred} g cm^{-3}	d^{PK}_{pred}, g cm^{-3}	V^{*}_{Φ}, cm^3 mol^{-1}
$MgCl_2$-NaCl-H_2O					**$MgCl_2$-Na_2SO_4- H_2O**				
I=1					**I=1**				
0.1060	1.02410	1.03262	1.02847	17.94	0.0964	1.02379	1.02999	1.02910	18.82
0.2001	1.02541	1.03262	1.02888	18.00	0.2114	1.02543	1.02999	1.02967	19.22
0.2994	1.02677	1.03262	1.02905	18.08	0.3089	1.02694	1.02999	1.02984	19.22
0.3985	1.02813	1.03262	1.02913	18.14	0.4023	1.02835	1.02999	1.02993	19.32
0.5002	1.02951	1.03262	1.02919	18.21	0.5116	1.03003	1.02999	1.02999	19.35
0.5942	1.03079	1.03262	1.02922	18.25	0.5933	1.03131	1.02999	1.03003	19.30
0.6985	1.03219	1.03262	1.02925	18.32	0.6958	1.03293	1.02999	1.03006	19.19
0.7892	1.03342	1.03262	1.02927	18.36	0.7897	1.03444	1.02999	1.03008	19.02
0.8890	1.03475	1.03262	1.02928	18.42	0.8927	1.03612	1.02999	1.03010	18.77
		σ^{Y}=0.115%	σ^{PK}=0.106%				σ^{Y} =0.133%	σ^{PK} =0.122%	
I=3					**I=3**				
0.1035	1.07426	1.09680	1.08317	20.03	0.1093	1.07489	1.09070	1.08555	20.73
0.2029	1.07795	1.09680	1.08573	19.88	0.1986	1.07851	1.09070	1.08818	21.17
0.2996	1.08145	1.09680	1.08682	19.83	0.2997	1.08265	1.09070	1.08952	21.62
0.3651	1.08382	1.09680	1.08726	19.80	0.4088	1.08714	1.09070	1.09031	22.08
0.4896	1.08827	1.09680	1.08780	19.79	0.4949	1.09073	1.09070	1.09070	22.40
0.5938	1.09191	1.09680	1.08810	19.81	0.6017	1.09523	1.09070	1.09105	22.75
0.6887	1.09521	1.09680	1.08829	19.83	0.7045	1.09961	1.09070	1.09128	23.04
0.7909	1.09871	1.09680	1.08845	19.88	0.7927	1.10342	1.09070	1.09144	23.24
0.8977	1.10234	1.09680	1.08858	19.92	0.8957	1.10796	1.09070	1.09159	23.39
		σ^{Y} =0.289%	σ^{PK} =0.231%				σ^{Y} =0.337%	σ^{PK} = 0.274%	
KCl-Na_2SO_4-H_2O					**NaCl-Na_2SO_4- H_2O**				
I=1.5					**I=1**				
0.1039	1.06139	1.06079	1.06029	29.08	0.1049	1.03635	1.03652	1.03692	18.53
0.2059	1.06087	1.06079	1.05993	28.73	0.2089	1.03651	1.03652	1.03693	18.55
0.3080	1.06036	1.06075	1.05973	28.27	0.3126	1.03666	1.03652	1.03693	18.58
0.4080	1.05987	1.06075	1.05964	27.77	0.4118	1.03683	1.03652	1.03693	18.58
0.5100	1.05937	1.06075	1.05958	27.15	0.5030	1.03697	1.03652	1.03694	18.61
0.6064	1.05891	1.06071	1.05951	26.39	0.5984	1.03714	1.03652	1.03695	18.60
0.7060	1.05845	1.06075	1.05952	25.47	0.7060	1.03734	1.03652	1.03696	18.58
0.8060	1.05803	1.06075	1.05949	24.18	0.8037	1.03752	1.03652	1.03699	18.55
0.9040	1.05761	1.06075	1.05948	22.51					
		σ^{Y} =0.029%	σ^{PK} =0.003%				σ^{Y} =0.014%	σ^{PK} =0.013%	
					I=3				
					0.1079	1.10622	1.10770	1.10906	20.20
					0.2046	1.10672	1.10770	1.10909	20.41
					0.3145	1.10733	1.10770	1.10913	20.67
					0.4136	1.10793	1.10770	1.10919	20.92
					0.5125	1.10858	1.10770	1.10925	21.21
					0.7035	1.11000	1.10770	1.10950	21.86
					0.7985	1.11079	1.10770	1.10974	22.27
					0.8960	1.11162	1.10770	1.11028	22.79
							σ^{Y} =0.029%	σ^{PK} =0.008%	
KCl-NaBr-H_2O									
I=0.5					**I=2**				
0.1660	1.02239	1.02775	1.027463	27.80	0.1950	1.09357	1.11235	1.108425	28.97
0.3460	1.02523	1.02775	1.027528	27.14	0.4020	1.10633	1.11235	1.109654	28.15
0.5000	1.02767	1.02775	1.027619	26.56	0.5000	1.11240	1.11235	1.110535	27.76
0.6300	1.02974	1.02775	1.027751	26.05	0.6040	1.11880	1.11235	1.111852	27.37
0.8120	1.03261	1.02775	1.028205	25.40	0.7915	1.13038	1.11235	1.116505	26.65
		σ^{Y} =0.199%	σ^{PK} =0.185%				σ^{Y} 0.663%	σ^{PK}=0.517%	
I=1					**I=3**				
0.1420	1.04580	1.05700	1.055867	28.38	0.1240	1.12959	1.16350	1.154775	29.89
0.2850	1.05030	1.05700	1.056048	27.82	0.2560	1.14162	1.16350	1.156050	29.33
0.4050	1.05406	1.05700	1.056262	27.37	0.3813	1.15302	1.16350	1.157673	28.82
0.5000	1.05705	1.05700	1.056498	27.01	0.4990	1.16374	1.16350	1.159776	28.34
0.6140	1.06062	1.05700	1.056916	26.58					
0.7510	1.06494	1.05700	1.057841	26.05					
0.8720	1.06874	1.05700	1.059845	25.60					
		σ^{Y} =0.310%	σ^{PK} =0.256%				σ^{Y} 0.756%	σ^{PK} =0.643%	

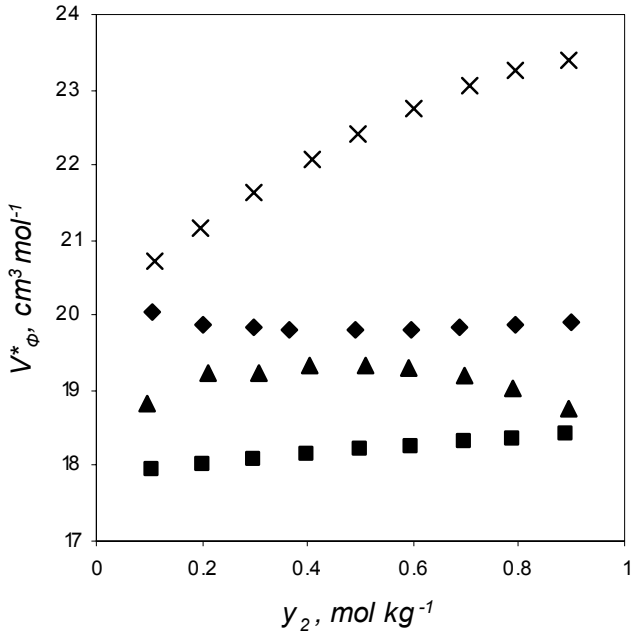

Fig. 1 – Mean apparent molar volumes versus ionic strength fraction for the systems: $MgCl_2$-NaCl at: ■ I=1, ◆ I=3 and $MgCl_2$-Na_2SO_4 at: ▲ I=1; × I=3.

Density prediction is compared in Table 2, where the experimental[13] and predicted values with both equations are given.

The following systems are studied: one having a common cation: NaCl-Na_2SO_4-H_2O, one having a common anion: $MgCl_2$-NaCl-H_2O, and three without a common ion: $MgCl_2$-Na_2SO_4-H_2O, KCl-Na_2SO_4-H_2O, KCl-NaBr- H_2O. The mean relative deviations are given for each system at different ionic strength.

From Table 2 it results that the P-K method gives better prediction for all studied systems than Young's rule. The Young is not sensible at ionic strength fraction variation. P-K equation can predict the density with an accuracy of 0.01 to 0.64% and the Young's rule with 0.03 to 0.75%, on the investigated domain of ionic strength. The mean relative deviations increase with the increase of ionic strength for all systems. Equations are generally recommended to be used for I=1 mol kg^{-1}.

The best results present both methods for the KCl-Na_2SO_4-H_2O and NaCl-Na_2SO_4-H_2O systems (σ = 0.001-0.01%). The $MgCl_2$ presence in the ternary systems decreases the accuracy of methods.

Also, Table 2 gives the mean apparent molar volumes calculated from experimental density with Eq. 3. for all systems and all ionic strengths. Few results are presented in Fig.1 for $MgCl_2$-NaCl-H_2O and $MgCl_2$-Na_2SO_4-H_2O systems. The calculated data show that the mean apparent molar volume increases with ionic strength, more evidently for $MgCl_2$-Na_2SO_4-H_2O system.

CONCLUSIONS

Predictive models for density have been presented and tested with available experimental data. The obtained predictive accuracy for $MgCl_2$-NaCl-H_2O, $MgCl_2$-Na_2SO_4-H_2O, KCl-Na_2SO_4-H_2O, NaCl-Na_2SO_4-H_2O, and KCl-NaBr-H_2O studied systems lies between of 0.01 to 0.64% for P-K method and of 0.03 to 0.75% for and the Young's rule on the investigated domain of ionic strength. The mean relative deviations increase with the increase of ionic strength for all systems.

The mean apparent molar volume was calculated from experimental density.

The Patwardhan – Kumar method, without any empirical constants can be used to predict satisfactorily the densities for aqueous mixed–electrolyte solutions using the densities of single electrolyte solutions. The Young method is recommended only for estimative calculations.

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