Extension of the Dense System Equation of State to Electrolyte Solutions

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ABSTRACT: *In this work we have applied the Dense System Equation of State (DSEOS) to electrolyte solutions. We have found that this equation of state can predict the density of electrolyte solutions very accurately. It has been tested for different electrolytes solutions at different temperatures and compositions. A hypothetical binary model has been applied to find the dependencies of parameters of this equation of state on solution temperature and composition. Using such a simple model the heat capacity of NaCl solution was calculated for which the absolute percent deviation is less than 2 %. The DSEOS is tested for the following electrolytes: Na_2SO_4, $MgCl_2$, $MgSO_4$, KCl, NaCl, and NaBr. We found that the DSEOS predicts the density of aqueous electrolyte solutions mentioned above accurately so that its percent error in density is less than 0.04.*

KEY WORDS: *Dense system equation of state, Electrolyte solution, Hypothetical binary model, Heat capacity, Density.*

INTRODUCTION

Electrolytes solutions are extensively encountered in chemical process industries such as extraction, distillation, wastewater treatment and geology studies. Therefore proposing an appropriate model which simulates their behavior accurately and contains the minimum parameters possible has always drawn scientists' attention. An excellent review of theoretical approaches from Deby-Hückle to new models used in chemical engineering can be found in [1]. Electrolyte solutions with mixed solvents have also been under several investigations and extensive advances have been made in modeling their thermodynamic properties which are presented in a comprehensive review [2].

As electrolyte solutions are recently more investigated in biological systems, plenty of effort has been made to simulate the behavior of aqueous, nonaqueous, mixed solvent and mixed electrolytes solutions. This new models are generally the extension of previous models which were originally proposed for nonelectrolyte solutions [3-5]. New investigation about ionic clustering in electrolytes is done by *Given, J.A.* and *Stell G.* [6].

Due to the fact that an electrolyte solution is a dense system with long range coulombic interactions, which may be considered as a base potential, one may expect that those EOSs which are appropriate for the dense fluids are applicable for electrolyte solutions as well.

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1021-9986/07/1/17 16/$/3.60

Tait, Murnaghan, linear isotherm regulation (LIR) [7,8], and the dense system equation of state (DSEOS) [9] have been proposed for dense fluids.

In the nineteenth century during the study of glass and mercury compressibility, *Tait* suggested an empirical equation which relates volume (V) to pressure (P) as follows:

$$\frac{V_\circ - V}{PV_\circ} = \frac{A}{B' + P} \tag{1}$$

where A and B' are temperature dependent parameters and $V_\circ$ is the volume when pressure is zero.

Differential forms of equation (1) are:

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{A}{B' + P} \tag{2}$$

or

$$B = \left(\frac{1}{A}\right)B' + \left(\frac{1}{A}\right)P \tag{3}$$

where B is the inverse of the isothermal compressibility coefficient and is defined as:

$$B = -V(\frac{\partial P}{\partial V})_T \tag{4}$$

Equation (3) is called Murnaghan EOS.

The linear isotherm regularity (LIR) [7,8] is another EOS applicable for dense fluids. According to this EOS, linear relation for each isotherm exists as,

$$(Z-1)V^2 = A + B\rho^2 \tag{5}$$

where Z is compressibility factor, ρ is density and A and B are temperature dependent parameters. To derive LIR, the *Lennard-Jones* potential was used as the average effective pair potential in which the medium effect and long range attraction are both added to the nearest neighbor interactions [10].

LIR equation of state is accurate for temperatures lower than two times of the *Boyle* temperature ($T < 2T_B$) and densities greater than the *Boyle* density ($\rho > \rho_B \approx 1.8\ \rho_c$) where ρ_C is the critical density [7].

Later, another EOS with no temperature limitation was proposed for dense fluids. This EOS had originally been proposed for compressed solids [11]. Later, it was shown that such an EOS can be used for dense fluids as well [9]. However, the temperature dependencies of its parameters are different. This EOS is called the dense system equation of state (DSEOS). It relates reduced pressure P_r, reduced volume V_r and reduced density ρ_r by the following equation [11]:

$$P_r V_r^2 = A_\circ + A_1\rho_r + A_2\rho_r^2 \tag{6}$$

in which A_0, A_1, and A_2 are temperature dependent which, according to the *van der Waals* one fluid approximation, are expected to be composition dependent as well.

The temperature dependencies of the parameters are as follows [11]:

$$A_i(T) = T\left[C_i - \int \frac{e_i(T)}{T^2}dT\right] \tag{7}$$

where C_is are constant and $e_i(T)$s are the coefficients of the following equation which gives the internal energy (E) in terms of density(ρ)[11],

$$E = e_0(T) + e_1(T)\rho + e_2(T)\rho^2 + e_3(T)\rho^3 \tag{8}$$

In this work we have used experimental PVTx data of different electrolyte solutions to investigate the applicability of the DSEOS for such systems. In order to find the temperature and composition dependencies of the parameters of the DSEOS, a hypothetical binary model was proposed.

Among different EOSs applicable for dense fluids, dense system equation of state (DSEOS) was chosen to predict the density of electrolyte solution, since the temperature dependencies of its parameters are known and unlike LIR, it has no temperature limitation.

We found that the composition and temperature dependencies of its parameters for electrolyte solutions can be well represented by polynomials of third and forth order, respectively. The accuracy of the calculated densities was compared with the *Pitzer* [12], *Rowe* [13], self consistence local composition (SCLC) [14], and *Chen* [15] EOSs.

EQUATION OF STATE

We have used experimental data to check the applicability of DSEOS for electrolyte solutions. To check the validity of the EOS we started with NaCl solution due to the abundance of PVTx measurements [16-18]. Experimental PVTx data of NaCl solution for some isotherms are depicted in Fig. 1, for m=5.685 mol/kg. The result of similar fitting for the solution with other molalities is summarized in table 1. Also the results for other electrolyte solutions such as Na_2SO_4, $MgCl_2$, $MgSO_4$, and NaBr are shown in table 2 for which PVTx data are taken from references [16-21].

For the case of solids, the temperature dependencies of A_is in equation (7) were obtained by simply assuming that the heat capacity at constant volume (C_V) is constant when $T>\theta_D$, where θ_D is the *Deby* temperature. Such an assumption is incorrect for fluids [9]. For this reason it was assumed that C_V of a liquid linearly changes with T, which leads to [9]:

$$A_i(T) = a_i + b_i T + c_i T^2 - d_i T \ln T \tag{9}$$

However heat capacity of electrolyte solutions changes with molality of the solution as well. So we shall present a new model which can present both temperature and molality dependencies.

MODEL

To investigate the dependencies of DSEOS parameters on temperature and molality of the solution, a hypothetical binary model is employed. This model is used to predict the composition dependency of heat capacity at constant pressure (C_P) of electrolyte solutions. In order to present an appropriate model, we may look at the experimental values of the heat capacity of NaCl solution with respect to molality at 298 K and 1 bar [22-26]. With increasing NaCl molality , C_P decreases up to m≈ 4 mol/kg after which C_P increases. To explain such a behavior we may assume that the solution is composed of solvated ions and free solvent molecules without any interaction between them. As the molality increases the number of free solvent molecules decreases so at a specific molality (m≈ 4 mol/kg) there won't be any more free solvent molecules left in the solution, i.e. all solvent molecules are used in the solvation of ions. We may also monitor experimental molar conductivity of NaCl solution at 298 K and 1bar [27]. It can be seen that at a molality close to m≈ 4 mol/kg, the slope of molar conductivity versus molality changes. This variation in the trend may also be related to the change of the system components. So we may assume that at the minimum point of C_P versus molality the solution is composed of just one component i.e. the solvated ions. So we can use this point to calculate the average number of water molecules used to solvate the ions at a given temperature as follows:

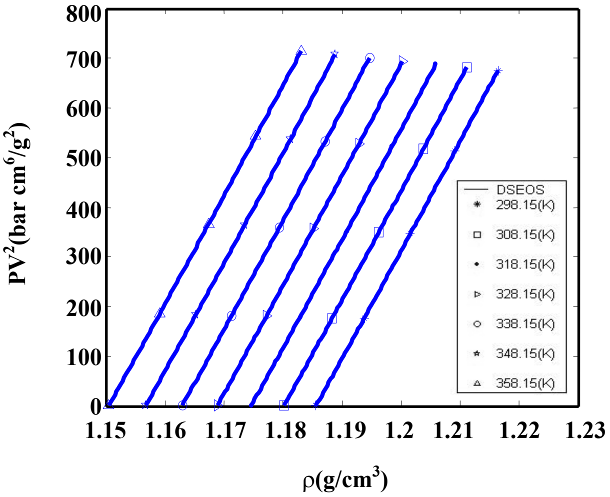

Fig. 1: Experimental data fitted in DSEOS for NaCl solution at different temperatures and m = 5.685 mol/kg.

$$n_r Y = \frac{m_w}{M_w} \tag{10}$$

where Y is the average number of moles of electrolyte, m_w is the mass of water in the solution, and M_w is the molecular weight of water. The value of Y may be related to absolute temperature T via a *Boltzmann* factor,

$$Y = a \exp(b/T) \tag{11}$$

If b/T<<1 then equation (11) may be reduced to:

$$Y = \frac{ab}{T} + a \tag{12}$$

We may use experimental values of C_P for NaCl aqueous solution [22-26] at 1 bar and any temperature to find the value of Y from the minimum value of C_P. The numerical values are summarized in table 3.

Ignoring the interaction between two components of the hypothetical mixture, the composition dependency of heat capacity is as follows:

$$C_p = \sum_i x_i C_{p,i} \tag{13}$$

where $C_{P,i}$ and x_i are the heat capacity at constant pressure and mol fraction, respectively.

One may consider the heat capacity at constant volume for each solvated ion, C_{VS}, as:

Table 1: The DSEOS parameters A_i, correlation coefficient (R^2), root of mean square error (rmse) and average percent error of density ($((\rho_{exp}-\rho_{cal})/\rho)*100$) for NaCl solution at various temperatures and molalities.

m=0.899 mol/kg						
T(K)	A_2	A_1	A_0	R^2	rmse	$((\rho_{exp}-\rho_{cal})/\rho)*100$
298	44672.9 ± 0.312e4	-109983 ± 0.662e4	64625.5 ± 0.314e4	0.99922	0.0937	0.027
308	45552.2 ± 0.614e4	-112370 ± 0.117e5	66194.9 ± 0.559e4	0.99929	0.1631	-0.036
318	45538.4 ± 0.748e4	-112886 ± 0.162e5	66806.9 ± 0.779e4	0.99937	0.2259	-0.028
328	45427.8 ± 0.611e4	-113124 ± 0.125e5	67255.6 ± 0.604e4	0.99944	0.1761	0.015
338	45034.6 ± 0.413e4	-112733 ± 0.801e4	67373.8 ± 0.387e4	0.99949	0.1146	0.009
348	44279.7 ± 0.489e4	-111486 ± 0.971e4	67013.6 ± 0.473e4	0.99954	0.1441	-0.023
358	43614.8 ± 0.576e4	-110328 ± 0.113e5	66662.9 ± 0.555e4	0.99957	0.1759	0.004
m= 2.99 mol/kg						
298	56729.5 ± 0.544e4	-129184 ± 0.123e5	70436.7 ± 0.554e4	0.98517	0.10080	-0.001
308	57188.7 ± 0.651e4	-130599 ± 0.012e5	71442.2 ± 0.189e4	0.98576	0.14150	-0.021
318	57444.0 ± 0.325e4	-131503 ± 0.142e5	72163.9 ± 0.117e4	0.98527	0.17735	-0.055
328	57360.1 ± 0.556e4	-131767 ± 0.169e5	72593.5 ± 0.317e4	0.98804	0.10858	0.059
338	55327.0 ± 0.227e4	-128429 ± 0.143e5	71368.6 ± 0.159e4	0.99406	0.07479	-0.063
348	55243.6 ± 0.378e4	-128485 ± 0.137e5	71624.6 ± 0.197e4	0.99530	0.13818	0.088
358	54374.9 ± 0.678e4	-127043 ± 0.115e5	71172.9 ± 0.246e4	0.99646	0.17830	0.026
m= 4.26 mol/kg						
298	65487.62 ± 0.131e4	-142655 ± 0.243e5	74636.4 ± 0.714e4	0.99655	0.11797	0.0025
308	65874.69 ± 0.451e4	-143872 ± 0.171e5	75514.3 ± 0.621e4	0.99568	0.11051	-0.027
318	65066.7 ± 0.232e4	-142827 ± 0.254e5	75334.8 ± 0.358e4	0.99373	0.04383	0.045
328	64991.0 ± 0.514e4	-142129 ± 0.741e5	7535.26 ± 0.679e4	0.98844	1.12141	0.078
338	63953.3 ± 0.224e4	-141608 ± 0.245e5	75375.9 ± 0.454e4	0.98318	0.093091	0.052
348	62004.8 ± 0.145e4	-138386 ± 0.122e5	74184.3 ± 0.789e4	0.98630	0.12794	-0.029
358	60514.5 ± 0.211e4	-135891 ± 0.134e5	73282.7 ± 0.331e4	0.98514	0.098991	-0.033

Table 2: Correlation coefficient (R^2) and root of mean square error (rmse) of DSEOS applied at different temperatures and concentrations for given electrolyte solutions.

NaBr								
	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
T(K)	m=0.1 mol/kg		m=1.0 mol/kg		m=4.0 mol/kg		m=8.0 mol/kg	
273	0.9999	0.3202	1.0000	0.1933	1.0000	0.1258	1.0000	0.0001
283	0.9999	0.2145	1.0000	0.1449	1.0000	0.1429	1.0000	0.2218
293	0.9999	0.1673	1.0000	0.1070	0.9999	0.1804	1.0000	0.2920
303	0.9999	0.1279	1.0000	0.1442	0.9999	0.1952	1.0000	0.2615
313	0.9999	0.0359	0.9999	0.0856	0.9998	0.2169	0.9994	0.2911
323	0.9999	0.0795	0.9999	0.1912	0.9996	0.1736	0.9987	0.3365
333	0.9999	0.0850	0.9999	0.1414	0.9993	0.2599	0.9998	0.3966
343	0.9999	0.1123	0.9999	0.0509	0.9989	0.3114	0.9999	0.3675
353	0.9999	0.0953	0.9999	0.0733	0.9980	0.3259	1.0000	0.7186
363	0.9999	0.0398	0.9999	0.1163	0.9977	0.3619	0.9999	0.4761
373	0.9999	0.0486	0.9999	0.1233	0.9975	0.2962	0.9999	0.5054
MgCl$_2$								
	m=0.008 mol/kg		m=0.088 mol/kg		m=0.248 mol/kg		m=0.328 mol/kg	
273	0.9999	0.7634	0.9999	0.7774	0.9999	0.7977	0.9999	0.8078
278	0.9999	0.6485	0.9999	0.6444	0.9999	0.6327	0.9999	0.6289
283	0.9999	0.6814	0.9999	0.6833	0.9999	0.6890	0.9999	0.6953
288	0.9999	0.7005	0.9999	0.7098	0.9999	0.7362	0.9999	0.7542
293	0.9999	0.6426	0.9999	0.6735	0.9999	0.7462	0.9999	0.7868
298	0.9999	0.6617	0.9999	0.6687	0.9999	0.6940	0.9999	0.7129
303	0.9999	0.7183	0.9999	0.6990	0.9999	0.6700	0.9999	0.6618
308	0.9999	0.7287	0.9999	0.7339	0.9999	0.7448	0.9999	0.7534
313	0.9999	0.8646	0.9999	0.8851	0.9999	0.9388	0.9999	0.9709
318	0.9999	0.7335	0.9999	0.7579	0.9999	0.8160	0.9999	0.8496
323	0.9999	0.7376	0.9999	0.7340	0.9999	0.7542	0.9999	0.7749

Table 2

	Na_2SO_4							
	m=0.049 mol/kg		m=0.129 mol/kg		m=0.209 mol/kg		m=0.329 mol/kg	
273	0.9999	0.7862	0.9999	0.8252	0.9999	0.8639	0.9999	0.9224
278	0.9999	0.6703	0.9999	0.7065	0.9999	0.7442	0.9999	0.8033
283	0.9999	0.7004	0.9999	0.7354	0.9999	0.7738	0.9999	0.8367
288	0.9999	0.7119	0.9999	0.7387	0.9999	0.7718	0.9999	0.8307
293	0.9999	0.6429	0.9999	0.6594	0.9999	0.6865	0.9999	0.7416
298	0.9999	0.6712	0.9999	0.6976	0.9999	0.7334	0.9999	0.7991
303	0.9999	0.7256	0.9999	0.7445	0.9999	0.7732	0.9999	0.8296
308	0.9999	0.7626	0.9999	0.8234	0.9999	0.8877	0.9999	0.9876
313	0.9999	0.8612	0.9999	0.8711	0.9999	0.8940	0.9999	0.9460
318	0.9999	0.7414	0.9999	0.7719	0.9999	0.8152	0.9999	0.8953
323	0.9999	0.7023	0.9999	0.6629	0.9999	0.6459	0.9999	0.6567
	$MgSO_4$							
	m=0.02 mol/kg		m=0.08 mol/kg		m=0.14 mol/kg		m=0.23 mol/kg	
273	0.9999	0.8031	0.9999	0.9356	0.9999	1.0642	0.9999	1.2307
278	0.9999	0.6918	0.9999	0.8326	0.9999	0.9697	0.9999	1.1470
283	0.9999	0.7151	0.9999	0.8377	0.9999	0.9651	0.9999	1.1351
288	0.9999	0.7165	0.9999	0.8046	0.9999	0.9133	0.9999	1.0694
293	0.9999	0.6306	0.9999	0.6670	0.9999	0.7507	0.9999	0.8925
298	0.9999	0.6741	0.9999	0.7572	0.9999	0.8666	0.9999	1.0282
303	0.9999	0.7358	0.9999	0.8198	0.9999	0.9276	0.9999	1.0884
308	0.9999	0.7705	0.9999	0.9123	0.9999	1.0547	0.9999	1.2455
313	0.9999	0.8527	0.9999	0.8704	0.9999	0.9307	0.9999	1.0469
318	0.9999	0.7320	0.9999	0.7843	0.9999	0.8749	0.9999	1.0257
323	0.9999	0.6995	0.9999	0.643	0.9999	0.6576	0.9999	0.7440

Table 3: Fitting experimental data for NaCl solution [22-26] into equations (11) and (12).

$Y = a \exp(b/T)$			$Y = \frac{ab}{T} + a$		
sse[a]	rmse[b]	R^2[c]	sse	rmse	R^2
0.0885	0.1717	0.9956	0.0644	0.1412	0.9954

a) Sum of square error, b) Correlation coefficient, c) Root of mean square error.

$$C_{VS} = C_{V,trans} + C_{V,rot} + C_{V,vib} + C_{V,nuc} + C_{V,elec} \qquad (14)$$

where $C_{V,trans}$, $C_{V,rot}$, $C_{V,vib}$, $C_{V,nuc}$, and $C_{V,elec}$ are the contribution of transitional, rotational, vibrational, nuclear, and electronic degrees of freedom, respectively. The contribution of nuclear and electronic degrees of freedom may be ignored. For the contribution of the translation and rotation the classical values of 3/2 R may be attributed, where R is gas constant. Assuming the harmonic oscillator approximation for the vibrations, their contribution may be given as [28]:

$$C_{V,vib} = Nk\sum_{j=1}^{\alpha}\left[\left(\frac{\theta_{Vj}}{T}\right)^2 \frac{\exp(-\theta_{Vj}/T)}{[1-\exp(-\theta_{Vj}/T)]^2}\right] \qquad (15)$$

where α is number of vibrational modes, T is absolute temperature, N is number of solvated electrolytes, k is the *Boltzmann* constant, and the characteristic vibrational temperature (θ_{vj}) is related to the frequency (ν_j) of the mode j as:

$$\theta_{vj} = h\nu_j/k \qquad (16)$$

The frequency (ν_j) is related to the force constant K_j and effective reduced mass μ_j as:

$$\nu_j = \frac{1}{2\pi}\sqrt{\frac{K_j}{\mu_j}} \qquad (17)$$

The number of vibrational modes is related to the number of solvated electrolytes as:

$$\alpha = 3(Y+2) - 6 \qquad (18)$$

Note that a solvated electrolyte includes Y molecules of water and 2 ions. The values of characteristic vibrational temperatures of water are 5360, 5160 and 2290 K for three vibrational modes [28].

The contributions of vibrational modes of water in equation (15) are discarded for simplicity. Since heat capacities at constant volume and constant pressure are close to each other, we shall deal with C_P instead of C_V from now on.

If all θ_{vj} in equation (15) are assumed to be equal, θ_{vj} may be substitute by c. As $c/T \ll 1$, *Taylor* expansion of exp(-c/T)may be used. By substituting Y from equation (12) in equation (18), and using *Taylor* expansion of exp(-c/T) the following result will be obtained:

$$C_{PS} = 3\left(\frac{ab}{T} + a\right)\exp(-c/T) \qquad (19)$$

C_{PS} is the heat capacity of the solvated ions. To simplify the above equation one may use *Taylor* expansion of exp(-c/T) again. By considering the first two terms of the expansion only, C_{PS} in equation (19) reduces to:

$$C_{PS} = 3a + \frac{3a(b-c)}{T} \qquad (20)$$

where the term abc/T^2 is discarded. The experimental data for NaCl solution [22-26] were used to test the validity of equation (20). The result is depicted in Fig. 2 for the temperature range of 273-373 K, for which the experimental data are reported.

Substituting mol fraction of both components in equation (13) we find:

$$C_P(m,T) = \frac{mC_{PC} + (m_w - m \times Y)C_{Pw}}{m_w + (1-Y)m} \qquad (21)$$

where m_w is the number of moles of water and *m* is that for the electrolyte. Substituting C_{PS} from equation (20) and *Y* from equation (12) gives:

$$C_P(m,T) = \frac{m\left(3a + \frac{3a(b-c)}{T}\right) + m_w C_{Pw}}{m_w + \left(1 - a - \frac{ab}{T}\right)m} - \qquad (22)$$

$$\frac{m\left(a + \frac{ab}{T}\right)C_{Pw}}{m_w + \left(1 - a - \frac{ab}{T}\right)m}$$

C_{Pw} is the heat capacity of pure water. C_P given by equation (22) is for the hypothetical mixture of solvated ions and free water molecules. A similar approach may be used to calculate the heat capacity of the hypothetical solution composed of ion pair and solvated ions. According to experimental data reported for C_{Pw}, [29] we may present the data simply by a 4 degree polynomial in terms of temperature (T).

$$C_{PW}\left(J/\text{mol K}\right) = 5.568\times10^{-8}T^4 - 7.458\times10^{-5}T^3 + 0.0375T^2 - 8.839T + 708 \qquad (23)$$

The correlation coefficient of this fitting is 0.9989 and the root mean square error is about 0.01189. Equation (22) is compared with experimental data [22-26] for NaCl solution versus molality at different temperatures, for which the deviation curve is shown in Fig. 3.

DEPENDANCIES OF EOS PARAMETERS ON TEMPERATURE AND MOLALITY

In order to find the temperature dependencies of the DSEOS parameters from equation (7), the temperature dependencies of e_is must be known in advance. Such temperature dependency may be given by [9]:

$$e_i = c_i' \int C_v dT + c_i'' \qquad (24)$$

where c_i' and c_i'' are constants. We may use C_P instead of C_V in equation (24) whose value is obtained from equation (22). The obtained expression for e_i may be substituted in equation (7) to find A_i as:

$$\begin{aligned} A_i = {} & \left[1/T(C_i+m)^2\right]\left[m^2 \ln(c_iT+m+mT)X_i(T)\right] - \qquad (25)\\ & 2m^2\ln(c_iT+m+mT) - m^2\ln(c_iT+m+mT)X_i(T)T + \\ & m^2T\ln((C_i+m)T) + m\ln(c_iT+m+mT)X_i(T) - \\ & m\ln(c_iT+m+mT)c_i + c_imTX_i(T)\ln(c_iT+m+mT) - \\ & 2c_im\ln(c_iT+m+mT) + mTX_i(T)\ln(c_iT+m+mT) + \\ & 2c_imT\ln((c_i+m)T) + c_i^2T\ln(c_iT+m+mT) + \\ & c_iTX_i(T)\ln(c_iT+m+mT) \end{aligned}$$

where:

$$X_i = a_{i4}T^4 + a_{i3}T^3 + a_{i2}T^2 + a_{i1}T + a_{i0}$$

and c_is and a_is are constants.

Equation (25) is too complicated to be tested with experiment. Hence we may use its *Taylor* expansion. This of course will lead to an indefinite polynomial.

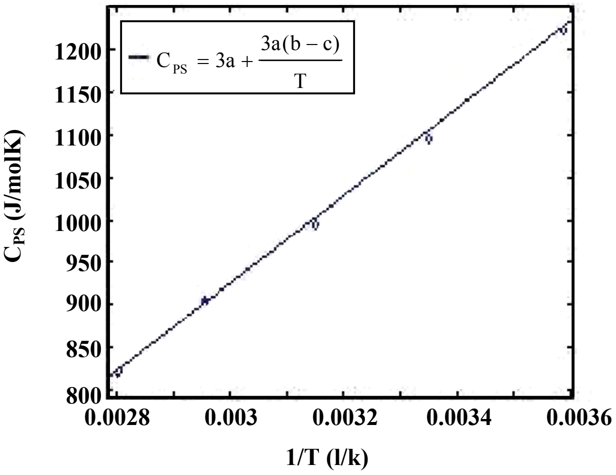

Fig. 2: fitting the heat capacity of each solvated ion (C_{PS}) versus 1/T.

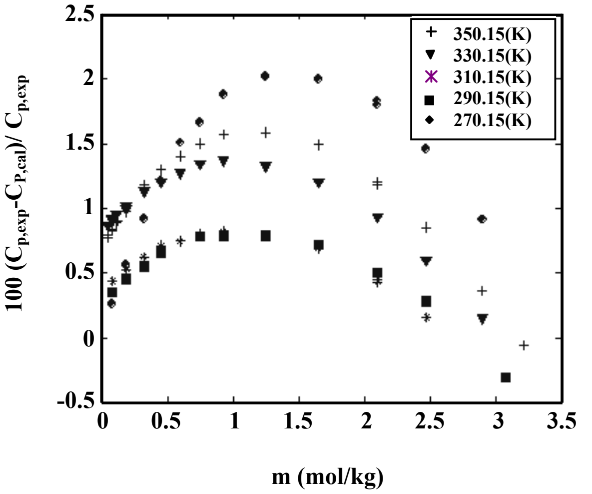

Fig. 3: Percent error of heat capacity for NaCl solution at different temperatures and 1 atm , calculated from equation (22).

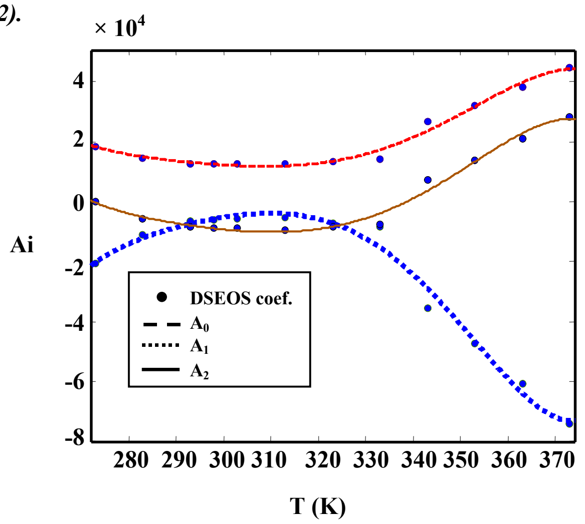

Fig. 4: The parameters of DSEOS which are fitted into equation (23) for NaCl solution with m=3.0 mol/kg.

However, experimental data can well be fitted into polynomials of third and forth order in terms of molality (m) and temperature (T), respectively. The temperature dependencies of the DSEOS parameters are shown in Fig. 4 where m=3.0 mol/kg for NaCl solution. The results for other molalities are summarized in table 4. The results for other electrolytes are briefly shown in table 5. In summery, the results show that we may present the temperature and molality dependency of the DSEOS parameters as:

$$A_i(T,m) = a_{i4}(m)T^4 + a_{i3}(m)T^3 + a_{i2}(m)T^2 + a_{i1}(m)T + a_{i0}(m) \qquad (26)$$

$$A_i(T,m) = a'_{i3}(T)m^3 + a'_{i2}(T)m^2 + a'_{i1}(T)m + a'_{i0}(T) \qquad (27)$$

The dependencies of the parameters on molality are also investigated for NaCl solution and other electrolytes. The results for NaCl solutions have been illustrated in Fig. 5 at different temperatures in terms of molality and summarized in table 6. The results for other electrolytes are summarized in table 7.

COMPARISON WITH OTHER EQUATIONS OF STATE

The density calculated by the DSEOD may be compared with those obtained from other EOSs [12,13].

In Fig. 6 the comparison has been made between the percent error of calculated densities of NaCl solutions for different equations of state at 368 K and m=5.96 mol/kg. The deviation for the other temperatures and molalities are given in table 8.

From this table, it can be concluded that the DSEOS and *Pitzer* equations of state predict the density of NaCl solution more accurately than the *Rowe* equation. This equation of state has a systematic error at high pressures.

Since the parameters of self consistence local composition model (SCLS) and Chen EOSs are not available at high temperatures and pressures, the DSEOS is compared with these two EOSs only at 298 K and 1 atm. The results are presented in table 9. According to table 9 the DSEOS and *Pitzer* EOSs can predict the density better than SCLC and *Chen* EOSs.

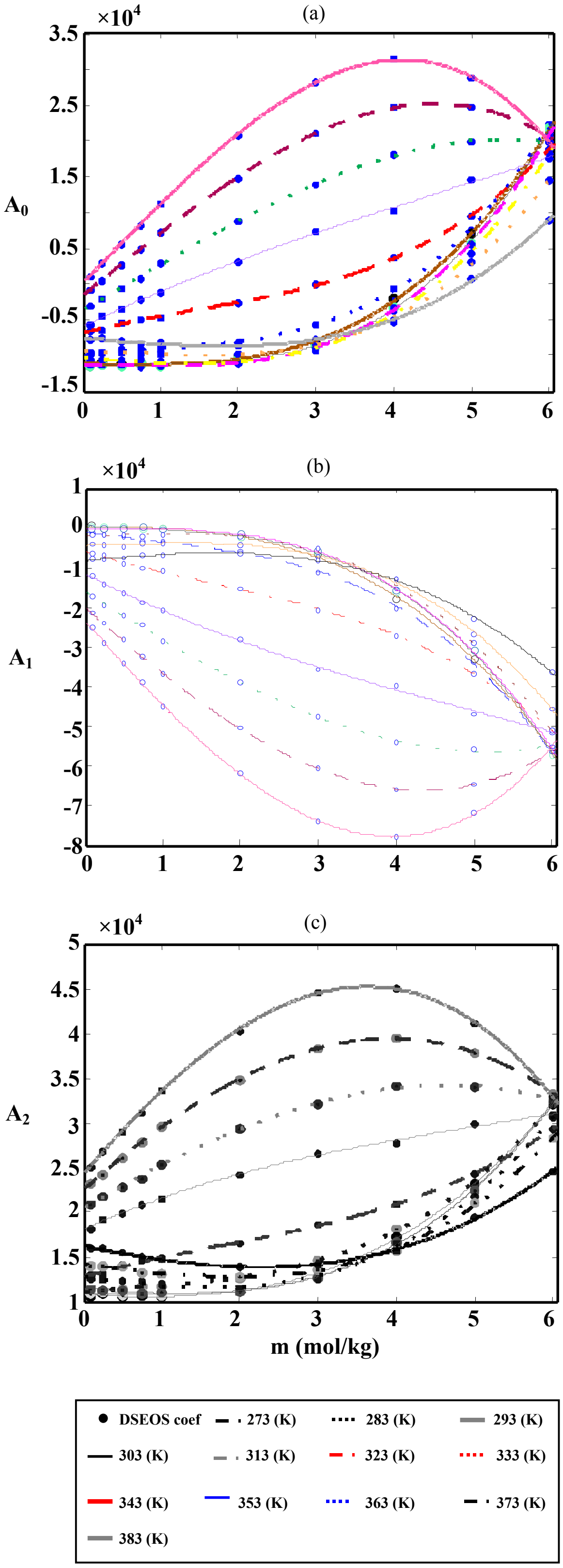

Fig. 5: Dependencies of DSEOS parameters (a) A_0, (b) A_1 and (c) A_2 of NaCl on molality at given temperatures.

Table 4: Values of coefficients of equation (26) for NaCl with different molalities. The correlation coefficient (R^2) and root of mean square error (rmse) are given.

	a_4/K^{-4}	a_3/K^{-3}	a_2/K^{-2}	a_1/K^{-1}	a_0	R^2	rmse
Coefficient	m=0.1 mol/kg						
A_2	4.99e-5	-0.0916	59.44	-16254.7	1.61e+07	0.9986	206.2
A_1	-1.40e-4	0.244	-152.2	40591.5	-3.9e+07	0.9987	418.5
A_0	9.47e-5	-0.156	94.56	-24790.3	2.4e+07	0.9987	212.4
m=1.0 mol/kg							
A_2	-5.8e-4	0.725	-331.7	66240.1	-4.9e+07	0.9985	854.9
A_1	1.20	-1.48	675.8	-133813	0.97e+07	0.9985	1790.0
A_0	-6.20e-4	0.759	-342.5	67149.5	-4.8e+07	0.9985	937.2
m=3.0 mol/kg							
A_2	-1.78	2.27	-1078	225168	-1.7e+07	0.9984	1916
A_1	3.95	-5.05	2395	-499459	3.8e+07	0.9984	4253
A_0	-2.20	2.80	-1328	276711	-2.1e+07	0.9984	2359
m=4.0 mol/kg							
A_2	-2.33	3.01	-1443	305425	-2.4e+07	0.9979	2128
A_1	5.32	-6.87	3295	-696710	5.5e+07	0.9979	4836
A_0	-3.04	3.92	-1879	397112	-3.1e+07	0.9979	2747
m=5.0 mol/kg							
A_2	-2.27	2.94	-1419	302132	-2.4e+07	0.9978	1968
A_1	5.30	-6.86	3310.3	-704412	5.6e+07	0.9978	4570
A_0	-3.09	4.00	-1930.0	410401	-3.3e+07	0.9978	2652
m=6.0 mol.kg							
A_2	-2.42	3.16	-1544	333668	-2.7e+07	0.9969	1717
A_1	5.75	-7.52	3675	-793848	6.4e+07	0.9969	4051
A_0	-3.42	4.47	-2186	472012	-3.8e+07	0.9969	2388

Table 5: Correlation coefficient (R^2) and root of mean square error (rmse) of equation (26) for some electrolytes solutions.

KCl								
	m=0.17 mol/kg		m=0.37 mol/kg		m=0.57 mol/kg		m=0.77mol/kg	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9999	926.0	0.9999	941.4	0.9999	954.6	0.9999	966.0
A_1	0.9999	1897	0.9999	1945	0.9999	1988	0.9999	2028
A_0	0.9999	971.5	0.9999	1004	0.9999	1035	0.9999	1065
NaBr								
	m=0.5 mo/kg		m=1.0 mol/kg		m=2.0 mol/kg		m= 4.0 mol/kg	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9999	141.8	0.9999	151.6	0.9999	131.6	0.9999	117.4
A_1	0.9999	294.5	0.9999	325.2	0.9999	300.7	0.9999	300.9
A_0	0.9999	152.9	0.9999	174.4	0.9999	171.8	0.9999	192.7
$MgCl_2$								
	m=0.08 mol/kg		m=0.17 mol/kg		m=0.25 mol/kg		m=0.33 mol/kg	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9821	227.45	0.98193	229.24	0.9872	231.87	0.9887	239.15
A_1	0.9835	461.28	0.9814	468.51	0.9881	477.31	0.9862	498.94
A_0	0.9815	233.92	0.9849	239.45	0.9876	245.73	0.9915	260.36
Na_2SO_4								
	m=0.009 mol/kg		m=0.089 mol/kg		m=0.208 mol/kg		m=0.329 mol/kg	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9789	228.09	0.9856	235.01	0.9944	246.85	0.9975	261.24
A_1	0.9814	462.8	0.9817	482.22	0.9918	514.74	0.9959	553.24
A_0	0.9814	234.81	0.981	247.77	0.9872	268.52	0.9948	293.13

Table 6: Coefficients of equation (27) for NaCl at different temperatures. The correlation coefficient (R^2) and root of mean square error (rmse) are given.

	a_3 /kg^{3}mol^{-3}	a_2 /kg^{2}mol^{-2}	a_1 /kg^{1}mol$^{-=1}$	a_0	R^2	rmse
Coefficient	T =273 K					
A_2	80.44	-442.809	2536.0	12689	0.9999	140.49
A_1	-223.4	1126.90	-6256.9	-5784.9	0.9999	296.22
A_0	152.9	-691.467	2936.2	-6921.3	0.9999	163.07
	T = 283 K					
A_2	119.2	-292.938	993.73	10959	0.9999	161.5
A_1	-333.0	992.310	-3323.5	-917.84	0.9999	394.22
A_0	226.2	-720.707	1547.0	-10063	0.9999	251.51
	T =293 K					
A_2	81.46	192.111	-513.26	10789	0.9999	241.62
A_1	-248.2	-57.990	-211.50	399.16	0.9999	515.22
A_0	177.5	-140.67	-93.477	-11171	0.9999	272.84
	T =298 K					
A_2	130.5	-186.046	19.03832	10893	0.9999	186.53
A_1	-362.4	841.299	-1607.1	678.09	0.9999	447.51
A_0	243.5	-669.633	783.09	-11533	0.9999	279.51
	T =303 K					
A_2	106.3	48.4500	-661.38	11417	0.9999	150.83
A_1	-306.8	326.294	-215.95	-34.670	0.9999	352.95
A_0	211.0	-381.228	56.315	-11309	0.9999	215.86
	T =313 K					
A_2	90.82	166.872	-1286.2	12791	0.9999	276.20
A_1	-265.7	57.0093	961.680	-2207.9	0.9999	593.37
A_0	183.4	-217.737	-520.66	-10423	0.9999	317.76

Table 6

	T =323 K					
A_2	94.42	15.8037	-1127.4	14178	0.9999	250.92
A_1	-265.7	57.0093	961.68	-2207.9	0.9999	539.81
A_0	183.4	-217.737	-520.66	-10423	0.9999	289.24
	T =333 K					
A_2	52.59	222.945	-1835.4	16241	0.9999	177.10
A_1	-162.1	-112.854	1800.16	-8273.7	0.9999	380.07
A_0	113.1	-75.9332	-857.41	-7581.1	0.9999	200.60
	T =343 K					
A_2	32.45	-499.257	3999.3	18016	0.9999	284.90
A_1	-58.67	931.559	-10128	-11505	0.9999	619.42
A_0	23.48	-345.335	5171.5	-5978.2	0.9999	338.56
	T =353 K					
A_2	-34.88	-326.465	5270.58	20323.4	0.9999	207.00
A_1	112.5	351.605	-12672	-15876	0.9999	432.63
A_0	-83.66	88.1505	6400.0	-3761.3	0.9999	226.18
	T =363 K					
A_2	-54.75	-675.164	7856.8	22362	0.9999	54.618
A_1	188.5	825.146	-17838	-19730	0.9999	115.43
A_0	-142.8	-11.6190	8933.9	-1781.9	0.9999	61.751
	T =373 K					
A_2	-100.5	-883.093	10378	24110	0.9999	183.98
A_1	323.9	955.075	-22714	-23038	0.9999	375.73
A_0	-235.7	91.9497	11237	-44.773	0.9999	190.08

Table 7: Correlation coefficient (R^2) and root of mean square error (rmse) of equation (27) for some electrolyte solutions.

KCl								
	T=273K		T=293K		T=303K		T=323K	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9999	0.043564	0.9999	2.30231	0.9999	3.158995	0.9999	3.01331
A_1	0.9999	0.245183	0.9999	4.238667	0.9999	5.69502	0.9999	5.407791
A_0	0.9999	0.285302	0.9999	2.156044	0.9999	2.837047	0.9999	2.686431
NaBr								
	T=278K		T=303K		T=348K		T=373K	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9987	139.5	0.9998	103.5	0.9988	135.0	0.9987	177.7
A_1	0.9988	316.1	0.9989	189.5	0.9988	259.6	0.9998	354.4
A_0	0.9987	191.0	0.9999	103.9	0.9999	135.4	0.9988	180.7
$MgCl_2$								
	T=273K		T=288K		T=313K		T=323K	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9995	17.21	0.9998	17.42	0.9998	17.95	0.9998	18.59
A_1	0.9995	34.21	0.9998	34.97	0.9998	36.30	0.9998	37.40
A_0	0.9995	16.91	0.9998	17.51	0.9998	18.30	0.9998	18.74
Na_2SO_4								
	T=273K		T=278K		T=303K		T=323K	
Coefficient	R^2	rmse	R^2	rmse	R^2	rmse	R^2	rmse
A_2	0.9997	16.450	0.9997	17.630	0.9998	19.260	0.9998	20.200
A_1	0.9997	32.650	0.9997	35.240	0.9998	38.400	0.9998	39.860
A_0	0.9997	16.209	0.9997	17.570	0.9998	19.088	0.9998	19.610

Table 8: Percent error in the calculated density of NaCl solution using Pitzer, DSEOS, and Rowe equations of state at different pressures, moalities and temperatures.

m=0.89 mol/kg									
T(K)	298(K)			328(K)			358(K)		
P (bar)	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}
1	-1.47	-2.28	-9800	0.391	-0.75	37.3	0.145	1.36	203
250	1.52	6.20	2120	-0.444	3.71	90.3	-0.220	-2.62	244
500	-1.67	-4.87	4110	2.060	-6.63	664	0.426	-0.347	946
750	1.91	0.244	1110	0.9230	5.15	1900	-0.785	3.13	2420
1000	-2.28	0.704	2470	-1.3800	-1.48	3830	0.132	-1.52	4750
m=2.99 mol/kg									
T(K)	298(K)			328(K)			358(K)		
P (bar)	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}
1	-2.634	0.627	-711	-0.774	0.258	-158	-0.373	1.97	174
250	2.71	-2.45	-632	0.852	-2.00	-155	0.484	-6.02	1.88
500	-2.94	3.59	-75.7	1.88	4.49	529	-7.93	6.25	9.38
750	3.35	-2.35	1000	-1.59	-4.00	1940	1.32	-2.30	2460
1000	3.94	0.574	2670	2.27	1.25	4170	2.08	0.010	4860
m=5.69 mol/kg									
T(K)	298(K)			328(K)			358(K)		
P (bar)	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}	Pitzer×10^{-4}	DSEOS×10^{-4}	Rowe×10^{-4}
1	0.290	-0.272	-457	0.0396	3.23	243	0.0327	1.01	392
250	0.313	-0.842	-601	0.0614	-9.16	81.1	-0.0195	-2.66	299
500	0.280	4.19	-175	0.0539	8.12	704	0.0605	1.94	913
750	0.190	-4.77	849	-0.0935	-1.64	2110	-0.156	0.0870	228
1000	0.043	1.69	2540	-0.272	-0.548	4370	0.307	-0.373	4450

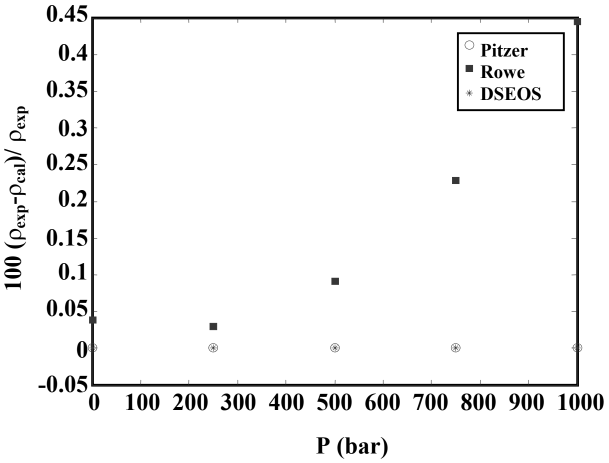

Fig. 6: Percent deviations of calculated density for NaCl solution obtained from Pitzer(○), Rowe(■), and DSEOS(*) at 368 K and m= of 5.96 mol/kg.

RESULTS AND DISCUSSION

It has been shown that in polar and associating liquids, the structural properties are governed by the same molecular mechanics as normal fluids, whereas the long range electrostatic forces play only a marginal role and may be treated as a perturbation only [30]. Therefore, one may expect that in electrolyte solutions, long range Columbic interactions may be considered as a base potential. Then the equations of state which have been used for dense fluids are expected to be appropriate for the electrolyte solutions as well.

Among all EOSs applicable for dense fluids we chose the DSEOS for which the temperature dependencies of its parameters are known and unlike LIR it does not have any temperature limitation. As it was shown in tables 1 and 2 and in Fig. 1, the experimental data can be well fitted in this EOS.

In order to find the dependencies of the DSEOS parameters on temperature and molality of the solution, a hypothetical binary model was proposed. In this simple model, the solution is assumed to be composed of solvated ions and free water molecules at low concentrations. As the concentration increases the number of free water molecules decreases so at a specific molality, there is no free water molecule left. If the concentration of the solution increases the ion pairs would appear and may be considered as the second component of the solution. In this binary model, the interactions between both components are discarded.

Table 9: Standard deviation for the calculated density obtained from different EOSs for different electrolyte solutions at 298 K and 1 atm. The reported results all are multiplied by a factor of 10^5.

Systems	Molality Range (mol/ kg)	SCLC	Pitzer	Chen	DSEOS
NaCl	0.3780-5.9934	1.9	1.3	1.9	1.34
KCl	0.0214-4.8181	6	5.8	5.8	3.0
Na_2SO_4	0.11946-1.46960	1	0.8	2	0.96
$MgCl_2$	0.00961-5.27571	2.8	3.9	2.9	1.39
$MgSO_4$	0.09079-2.39917	11.6	4	5.5	6.32

The calculated heat capacities of different solutions were compared with the experimental data (Fig. 3). As shown in Fig. 3, the deviation in C_P has a special trend, in such a way that its maximum value is about 2.1 %. We may expect that the deviation is mainly due to the interactions between the components, which are discarded in the model for simplicity of calculation.

Finally the comparison of the DSEOS with other EOSs is presented in tables 8 and 9 and Fig. 6. It is found that the DSEOS is capable of predicting the density of electrolyte solutions with the accuracy comparable with that of *Pitzer* [12] EOS and better than *Rowe* [13], SCLC [14] and *Chen* [15] EOSs.

Acknowledgement

We appreciate Sharif University of Technology for the financial support.

Received : 12th February 2006 ; Accepted : 31st July 2006

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