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RAPID COMMUNICATIONS

Chang approximation for the osmotic pressure of dilute to concentrated solutions

Ho Nam Chang[*,**,†,‡], **Kyeong Rok Choi**[*,‡], **Sang Yup Lee**[*], **Mi-Hyang Seon**[**], **and Yoon-Seok Chang**[**]

*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology,
291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea
**Lab to Market, 396 World Cup buk-ro, Mapo-gu, Seoul 03925, Korea

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Abstract−As many regions around the world are facing water scarcity, reverse osmosis (RO) has attracted attention to supply fresh water to such areas. To design and develop energy-efficient RO processes, accurate osmotic pressure values of salt water are critical, yet conventional models of osmotic pressure have significant deviations from the actual values. In addition, absence or high charge of authentic osmotic pressure databases prevents accessing authentic data. Here, we propose combining the Chang correction factor, a polynomial in solution concentration, with traditional osmotic pressure models to approximate the osmotic pressure of dilute to concentrated solutions with high accuracy. The Chang correction factor is determined by regressing a handful of authentic osmotic pressure data divided by theoretical values calculated using traditional models. Multiplication of resulting polynomials back to corresponding traditional models enables accurate approximation of the authentic osmotic pressure of dilute to concentrated solutions with R^2 approaching 1. In addition, generality of the strategy over aqueous and organic solutions is demonstrated by approximating osmotic pressure of NaCl and sucrose aqueous solutions and $C_2H_4Cl_2$-C_6H_6 and $C_3H_6Br_2$-$C_2H_4Br_2$ organic solutions. The approximation strategy proposed and assessed here will be useful to simulate and develop processes for seawater desalination and various industries with high importance.

Keywords: Osmotic Pressure, Approximation, Chang Correction Factor, Dilute Solution, Concentrated Solution

INTRODUCTION

Fresh water is essential to sustaining life. Although water covers 71% of the Earth's surface, most is saline filling up seas (96.5%) and salt lakes (0.9%) [1-3]. Only 2.5% of total water on the Earth is fresh water in forms of glaciers and ice (1.7%), groundwater (0.75%), and atmospheric moisture (0.001%). In particular, fresh water easily accessible by human accounts for only 0.014% of Earth's water while demands on fresh water are continuously increasing with the rapid growth of population (currently 7.7 billion worldwide) [4]. Today, four billion people suffer from severe water scarcity, and many parts of the world are also facing water scarcity in different severity [5,6]. Thus, supply of fresh water by desalinating seawater has been highly stressed to achieve sustainable development.

Among various modes of desalination, reverse osmosis (RO) is one of the most important strategies to obtain fresh water from salt water [6]. To design and simulate such processes, calculating osmotic pressure of saline with high accuracy is critical. To describe osmotic pressure of infinitely dilute solutions, van't Hoff [7] suggested a mathematical model

$$\pi=\frac{nRT}{V} \tag{1}$$

where molar concentration of solutes n counts dissociation or association of solutes into ions or multimers, respectively. For application to more practical solutions, Morse and Frazer [8] suggested to substitute the molarity term $\frac{n}{V}$ in Eq. (1) with a molality term $\frac{n}{V'}$, as described in Eq. (2)

$$\pi=\frac{nRT}{V'}=\frac{RT}{V_o}\left(\frac{x_i}{1-x_i}\right) \tag{2}$$

where V, V′, V_o, and x_i are volume of solution, volume of solvent, molar volume of solvent, and mole fraction of solute, respectively. On the other hand, Lewis [9] developed Eq. (3)

$$\pi-\frac{1}{2}\alpha\pi^2=-\frac{RT}{V_o}\ln(1-x_i) \tag{3}$$

where α is coefficient of compressibility of solvent. As $\alpha \ll 1$ for liquids in general, Eq. (3) can be simplified to Eq. (4) for solutions of moderate concentration.

$$\pi=-\frac{RT}{V_o}\ln(1-x_i) \tag{4}$$

Nevertheless, osmotic pressure of concentrated solutions calculated by Lewis equation is significantly different from actual values and is inappropriate in simulation of RO processes. Nowadays, OLI Software (OLI Systems, Inc., Morris Plains, NJ) using Eq. (5)

$$\pi=\frac{RT}{V_o}\ln(a_{H_2O}) \tag{5}$$

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[†] To whom correspondence should be addressed.
E-mail: hnchang@kaist.edu

[‡] These authors contributed equally to this work.

Table 1. Predicted osmotic pressures of NaCl aqueous solutions at 298.15 K

NaCl concentration		Density	Osmotic pressure (bar)							
(wt%)	(mol m^{-3})	(kg m^{-3})[a]	van't Hoff	Morse and Fraser	Lewis	van't Hoff-Chang	Morse-Fraser-Chang	Lewis-Chang	OLI	OLI regression
1.00	171.82	1004.09	8.518	8.544	8.517	7.584	7.610	9.262	7.610	9.262
2.00	346.04	1011.12	17.155	17.262	17.154	15.489	15.519	16.364	15.519	16.364
3.00	522.71	1018.23	25.914	26.160	25.913	23.726	23.743	23.955	23.743	23.955
4.00	701.78	1025.30	34.792	35.243	34.798	32.306	32.298	32.034	32.298	32.034
5.00	883.36	1032.47	43.794	44.517	43.810	41.241	41.201	40.603	41.201	40.603
6.00	1067.38	1039.63	52.917	53.989	52.954	50.541	50.467	49.660	50.467	49.660
7.00	1253.96	1046.88	62.167	63.664	62.231	60.219	60.114	59.206	60.114	59.206
8.00	1443.01	1054.12	71.539	73.550	71.646	70.287	70.156	69.242	70.156	69.242
9.00	1634.69	1061.46	81.042	83.653	81.202	80.758	80.611	79.766	80.611	79.766
10.00	1828.87	1068.79	90.669	93.981	90.902	91.645	91.493	90.779	91.493	90.779
11.00	2025.78	1076.24	100.431	104.540	100.749	102.962	102.820	102.281	102.820	102.281
12.00	2225.15	1083.65	110.315	115.340	110.747	114.722	114.606	114.272	114.606	114.272
13.00	2427.42	1091.22	120.343	126.388	120.901	126.941	126.866	126.752	126.866	126.752
14.00	2632.11	1098.72	130.491	137.693	131.213	139.633	139.614	139.720	139.614	139.721
15.00	2839.81	1106.39	140.788	149.264	141.688	152.814	152.864	153.178	152.864	153.178
16.00	3049.99	1114.01	151.208	161.110	152.331	166.500	166.628	167.125	166.628	167.125
17.00	3263.16	1121.76	161.776	173.242	163.145	180.707	180.918	181.560	180.918	181.560
18.00	3479.08	1129.54	172.480	185.669	174.135	195.452	195.745	196.485	195.745	196.485
19.00	3697.65	1137.32	183.316	198.404	185.306	210.754	211.117	211.898	211.117	211.898
20.00	3919.68	1145.33	194.323	211.457	196.663	226.631	227.043	227.800	227.043	227.800
21.00	4143.48	1153.07	205.419	224.840	208.210	243.101	243.528	244.191	243.528	244.192
22.00	4372.14	1161.40	216.755	238.567	219.953	260.185	260.578	261.071	260.578	261.072
23.00	4600.79	1169.00	228.090	252.650	231.898	277.903	278.195	278.440	278.195	278.441
24.00	4836.80	1177.76	239.791	267.103	244.050	296.277	296.379	296.298	296.379	296.299
25.00	5069.69	1185.09	251.337	281.942	256.415	315.328	315.128	314.645	315.128	314.645
26.00	5314.03	1194.43	263.450	297.182	268.999	335.080	334.439	333.481	334.439	333.481
26.47	5429.88	1198.80	269.194	304.489	274.991	344.612	343.707	342.503	343.707	342.503
Error sum of squares against OLI			2.707×10^4	7.068×10^3	2.309×10^4	2.125×10^0	3.250×10^0	2.275×10^0	0	1.372×10^1

[a] Values retrieved from Refs. [10-12].

provides a reliable approximation to the osmotic pressure of dilute to concentrated solutions. However, accurate data is inaccessible to many researchers due to the high price of the software. Thus, a method for simple yet accurate approximation to osmotic pressure of dilute to concentrated solutions is desired to facilitate research on RO processes.

In this study, we propose introducing the Chang correction factor $\varepsilon(C)$, a continuous polynomial in concentration C of solution, to a traditional osmotic pressure model $\Pi(C)$ to approximate actual osmotic pressure $\pi(C)$ of dilute to concentrated NaCl solutions with high accuracy, as described in Eq. (6).

$$\pi(C)=\Pi(C)\cdot\varepsilon(C) \tag{6}$$

The accuracy of the models is assessed by comparing the approximated osmotic pressure values to the authentic values. In addition, the accuracy of the approximation is compared to that of polynomials obtained by regressing the authentic data. Moreover, our strategy is applied to approximate osmotic pressure of various solutions other than NaCl solutions to examine generality of the strategy.

RESULTS AND DISCUSSION

Assuming complete dissociation of NaCl into Na^+ and Cl^- ions, van't Hoff, Morse and Frazer, and Lewis osmotic pressure of 1.00-26.47% (w/w) NaCl aqueous solutions at 298.15 K were calculated using Eq. (1), Eq. (2), and Eq. (4), respectively (Table 1; see Supplementary Table 1 for detailed procedure of calculation). As shown in Fig. 1, the osmotic pressure values calculated by the three traditional models significantly deviate from the authentic data retrieved from OLI software (OLI values) as NaCl concentration increases to the saturation point [i.e., 26.47% (w/w)]. To determine the mathematical equation of the Chang correction factor $\varepsilon(C)$ for each osmotic pressure model, OLI values were divided by the osmotic pressure values calculated by van't Hoff, Morse and Frazer, and Lewis equations, respectively, following Eq. (7) derived from the definition of Chang correction factor described in Eq. (6).

$$\varepsilon(C)=\frac{\pi(C)}{\Pi(C)} \tag{7}$$

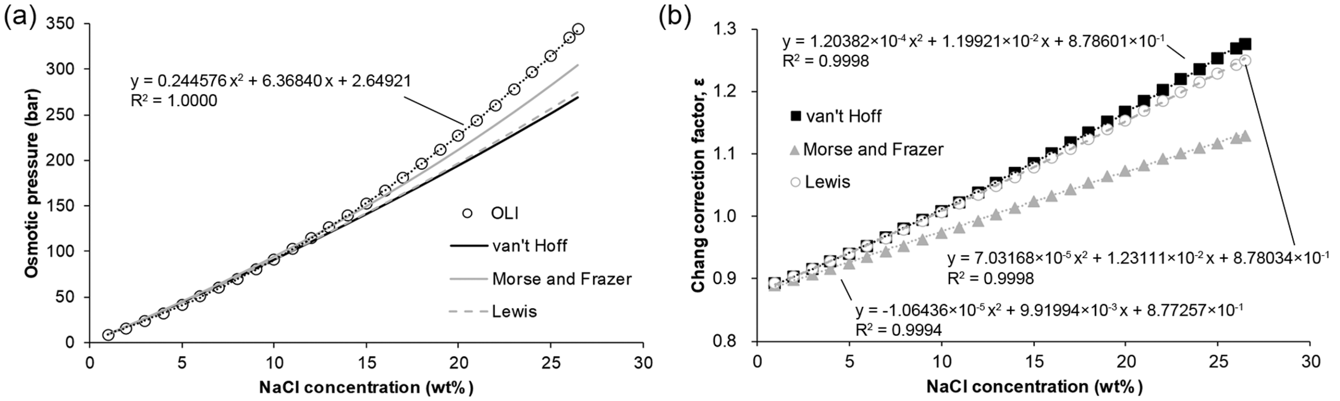

Fig. 1. Osmotic pressure (a) and Chang correction factor (b) of van't Hoff, Morse and Frazer, and Lewis osmotic pressure models.

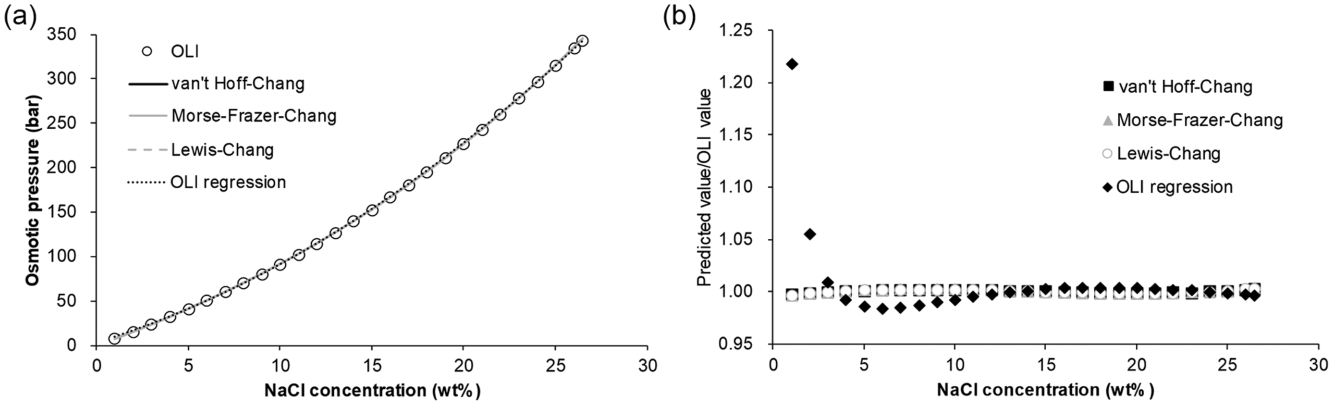

Fig. 2. Osmotic pressure of NaCl solutions calculated by Chang approximation (a) and the values divided by the authentic OLI values (b).

As shown in Fig. 1(b), the resulting plots were successfully regressed to 2nd-order polynomials with $R^2>0.999$, suggesting Eq. (8), Eq. (9), and Eq. (10) as Chang correction factors for van't Hoff, Morse and Frazer, and Lewis models, respectively,

$$\varepsilon_{vH,NaCl}(C_{wt})=1.20382\times10^{-4}C_{wt}^2+1.19921\times10^{-2}C_{wt}+8.78601\times10^{-1} \tag{8}$$

$$\varepsilon_{MF,NaCl}(C_{wt})=-1.06436\times10^{-5}C_{wt}^2+9.91994\times10^{-3}C_{wt}+8.77257\times10^{-1} \tag{9}$$

$$\varepsilon_{L,NaCl}(C_{wt})=7.03168\times10^{-5}C_{wt}^2+1.23111\times10^{-2}C_{wt}+8.78034\times10^{-1} \tag{10}$$

, where C_{wt} is NaCl concentration in weight percent (wt%).

Subsequently, the above Chang correction factors were combined with the traditional osmotic pressure models according to Eq. (6), resulting in van't Hoff-Chang, Morse-Frazer-Chang, and Lewis-Chang osmotic pressure models (Table 1 and Supplementary Table 1) that almost overlap the authentic OLI values in Fig. 2(a). To quantitatively assess the accuracy of the Chang approximations, sum of squared errors (SSE) and R^2 against the authentic OLI values were calculated taking sum of squares total (SST) of 286884 (Table 1 and Supplementary Table 1). While SSE and R^2 of traditional osmotic pressure models are greater than 7,000 and less than 0.98, those of Chang approximations are less than 3.3 and greater than 0.99998, respectively. Moreover, the accuracy of the values were compared with those calculated by Eq. (11) that is obtained by regressing the OLI values (OLI regression) with R^2 of 0.99995 [Fig. 1(a)].

$$\Pi_{regression}(C_{wt})=0.244567C_{wt}^2+6.36840C_{wt}+2.64921 \tag{11}$$

Once the predicted values of Chang approximation and OLI regression are divided by the authentic OLI values, those of Chang approximation show minimal deviation from 1.00, while those of OLI regression show larger deviation over the entire concentration range [Fig. 2(b)]. Similarly, SSE and R^2 of OLI regression against OLI values are 13.72 and 0.99995, respectively (Table 1 and Supplementary Table 1). These results suggest that the osmotic pressure of NaCl solutions calculated by Chang approximations are satisfactory in terms of accuracy and more reliable than simple regression of the OLI values.

Depending on the purpose of application, expressing equations of osmotic pressure with respect to other measures of concentration rather than weight percent (e.g., mole fraction, molarity, and molality) may be preferred. To examine the compatibility of our strategy with such other measures of concentration, mathematical equations of Chang correction factor were determined with respect to NaCl mole fraction, Na^+ and Cl^- ion mole fraction, and NaCl molarity and applied to approximate osmotic pressure of NaCl solutions (Supplementary Tables 2-4). Regardless of the measures of concentration used, SSE values of van't Hoff-Chang, Morse-Frazer-Chang, and Lewis-Chang models are less than 2.8, and R^2 values are equal or greater than 0.99999. On the other hand, SSE and R^2 values of 2nd-order polynomials obtained by regressing the authentic OLI values span 1.59-49.38 and 0.99983-0.99994, respectively (Supplementary Tables 2-4). When the predicted osmotic pressure values were divided by OLI values, resulting values of OLI regression showed larger deviation from 1 than those of Chang approximation (Supplementary Tables 2-4). All these data collectively support that the accuracy of Chang approximation is guaranteed regardless of the measures of solution concentration and is more reliable than that of OLI regression. Then, extension of our approximation strategy to other various aqueous and organic solutions was assessed. Osmotic pressure data calculated following van't Hoff, Morse and Frazer, and Lewis equations and authentic osmotic pressure data were retrieved from previous reports of Lewis [9] and Morse and Frazer [8]. For 0.1-1.0 molal (i.e., mol/kg water) sucrose aqueous solutions, both Morse and Frazer model and Lewis model are already plausible to describe osmotic pressure of the solutions with SSE of 0.216-0.549 and R^2~0.999 taking SST of 492.6 (Supplementary Table 5). As a result, regression of the Chang correction factor to 2nd-order polynomials leads to relatively small R^2 values for Morse and Frazer model and Lewis model (0.5172 and 0.7533, respectively), while that of van't Hoff model is 0.9927. Nevertheless, the accuracy of Morse-Frazer-Chang and Lewis-Chang approximations, as well as van't Hoff-Chang approximation, were much improved compared to that of original models (SSE of 0.039-0.057 and R^2~0.9999).

To examine the Chang approximation for the osmotic pressure of dilute to extremely concentrated (solute mole fraction >0.9) organic solvents, our strategy was applied to $C_2H_4Cl_2$-C_6H_6 and $C_3H_6Br_2$-$C_2H_4Br_2$ solute-solvent solutions (Supplementary Tables 6 and 7). Similar to the osmotic pressure of sucrose solutions, the Lewis equation is already plausible with R^2 around 0.999, while those of van't Hoff equation and Morse and Frazer equation have negative values (i.e., seriously incompatible models). Once Chang correction factors of 2nd-order polynomial are applied, R^2 values of Lewis-Chang equations were improved to ~0.9999 and those of van't Hoff-Chang and Morse-Frazer-Chang equations were improved to higher than 0.99, while those of 2nd-order regression of authentic data are 0.985-0.990 (Supplementary Tables 6 and 7). The accuracy of the approximation are further improved when Chang correction factors of 4th-order polynomial are used. For $C_2H_4Cl_2$-C_6H_6 solutions, R^2 values of van't Hoff-Chang, Morse-Frazer-Chang, and Lewis-Chang equations are 0.99999, 1.00000, and 1.00000, respectively, where R^2 value of 4th-order regression of authentic data is 0.99999 (Supplementary Tables 6 and 7). For $C_3H_6Br_2$-$C_2H_4Br_2$ solutions, van't Hoff-Chang, Morse-Frazer-Chang, and Lewis-Chang equations are 0.9994, 0.9999, and 0.9999, respectively, where R^2 value of 4th-order regression of authentic data is 0.9993. These results imply that our strategy is highly accurate to approximate the osmotic pressure of dilute to extremely concentrated organic solutions as well as aqueous solutions of ionic and non-ionic solutes.

CONCLUSIONS

We developed a simple strategy to approximate osmotic pressure of dilute to concentrated aqueous/organic solutions. The Chang correction factor in form of 2nd- or 4th-order polynomial equation was calculated by regressing authentic data divided by values derived from the traditional osmotic pressure models. Subsequently, the polynomials were multiplied back to the corresponding traditional models to generate new continuous equations approximating authentic osmotic pressure data. In terms of accuracy, the approximation equation is generally superior or at least comparable to that of polynomial equations directly fitted to the authentic data over entire range of concentration. In addition, the approximation is compatible with any measures of concentration, guaranteeing wide applications of the strategy for various purposes. Our method of approximating osmotic pressure will expedite developing energy-efficient RO processes for desalinating seawater to supply fresh water in areas of water scarcity, as well as many other industrial processes of high importance.

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NOMENCLATURE

a_{H_2O}	: chemical activity of H_2O
C	: molarity of solute [mol m^{-3}]
C_{wt}	: weight percent of solute [% (w/w)]
i	: van't Hoff coefficient
n	: moles of solute [mol]
p	: vapor pressure of solution [bar]
p_o	: vapor pressure of solvent [bar]
R	: ideal gas constant (0.00008314 $m^3\cdot bar\cdot K^{-1}\cdot mol^{-1}$)
T	: temperature [K]
V	: volume of solution [m^3]
V'	: volume of solvent [m^3]
V_o	: molar volume of solvent [$m^3\cdot mol^{-1}$]
x_i	: mole fraction of solute
α	: coefficient of compressibility of solvent [bar^{-1}]
ε	: Chang correction factor
π	: osmotic pressure [bar]

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

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Ho Nam Chang*,**,†,‡, **Kyeong Rok Choi***,‡, **Sang Yup Lee***, **Mi-Hyang Seon****, **and Yoon-Seok Chang****

*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology,
291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea
**Lab to Market, 396 World Cup buk-ro, Mapo-gu, Seoul 03925, Korea

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