A SIMPLE CORRELATION BETWEEN POINTS WITH ACTIVITY COEFFICIENT UNITY FOR 1:1 ELECTROLYTES AT 298 K

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ABSTRACT

When experimental data for activity coefficients are analyzed,one typical feature of the variation of logarithm of mean ionic activity coefficient with ionic strength is the presence of a minimum in the curve. The presence of this minimum gives rise to a new point at which $\ln\gamma_{\pm}$ takes a value of zero in spite of the ionic strength being different from zero. In this paper the position of both points has been determined for 151 electrolytes using Pitzer equations to describe the dependence of $\ln\gamma_{\pm}$ on ionic strength.

KEY WORDS

Pitzer equations, activity coefficients, ionic strength

Introduction

Experimental determination of activity coefficients and their interpretation in the light of the current theories represent an outstanding topic in Solution Chemistry. The great ability to deal with data at high ionic strength, for both single and mixed electrolytes, explains the currently widespread use of the model proposed by Pitzer. As a matter of fact, the Pitzer equations are being successfully used in a large number of different fields, like Oceanography or Geochemistry, where complex saline solutions often appear [1]

When experimental activity coefficient data are analyzed, one typical feature of the variation of logarithm of mean ionic activity coefficient ($\ln\gamma_{\pm}$) with ionic strength (I) is the presence of a minimum in the curve (fig. 1). This shape appears as a result of the balance among two opposite contributions, *viz.* a negative one, Debye-Huckel type, and one or more positive ones, arising from other kind of interactions, which, as a rule, are the so-called

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specific interactions.

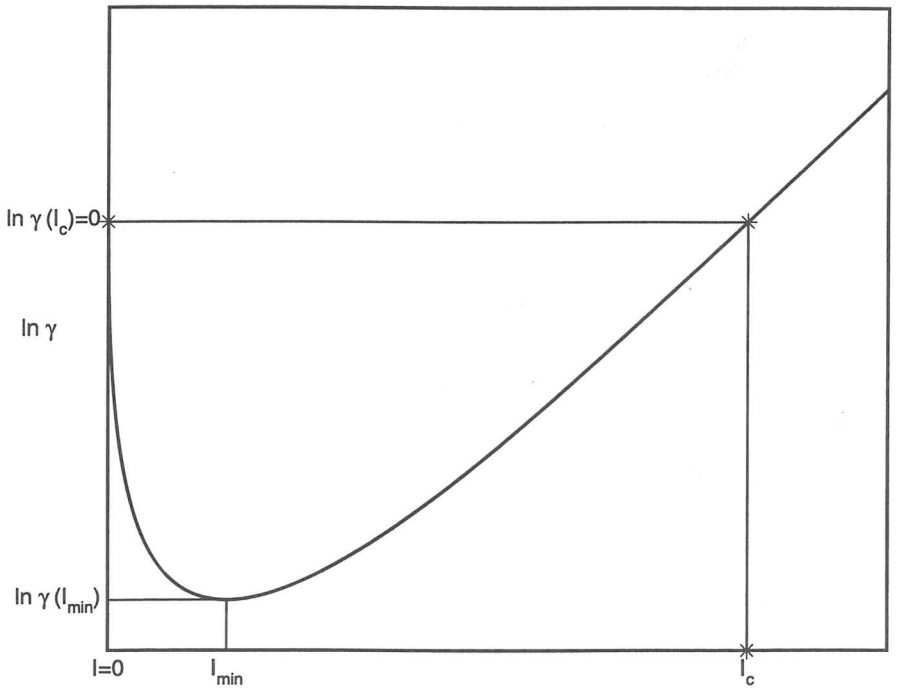

Figure 1. General trend of $\ln\gamma_{\pm}$ vs Ionic Strength, showing the minimum and the interception point with I axis

As it can be seen in figure 1, the presence of that minimum in the curves gives rise to a new particular point, the intersection of the curve with the ionic strength axis, I_c, at which $\ln\gamma_{\pm}$ takes a value of zero in spite of the ionic strength being different from zero.

In this paper, Pitzer equations have been used to evaluate the logarithm of the mean ionic activity coefficient $\ln\gamma_{\pm}$ of a series of 1:1 electrolytes, taken from [2], in order to determine the position of the two points with $\ln\gamma_{\pm}=1$ and $\ln\gamma_{\pm}=0$, on $\ln\gamma_{\pm}$ vs I plots.

Methodology

The position of the minimum, I_{min}, and the position of the intersection point, I_c, is determined by solving the equations

$$\frac{d\ln\gamma_{\pm}}{dI}=0 \qquad (1)$$

and

$$\ln\gamma_{\pm}=0 \qquad (2)$$

The dependence of $\ln\gamma_{\pm}$ vs ionic strength has been derived by means of Pitzer equations:

$$\ln\gamma_{MX}=f^{\gamma}+2I\,B_{MX}+I^2\,B'_{MX}+1.5\,I^2C^{\phi}_{MX} \qquad (3)$$

where the different coefficients are defined in table 1 and the interaction parameters for each electrolyte were taken from tables 2, 3, 4 and 5 of [2].

Table 1. Coefficients appearing in Pitzer equation for activity coefficients.

Coefficients of eq. 3	First derivative
$f^{\gamma}=-A_{\phi}\left[\frac{\sqrt{I}}{1+1.2\sqrt{I}}+\frac{2}{1.2}\ln(1+1.2\sqrt{I})\right]$	$f^{\gamma\prime}=-A_{\phi}\left(\frac{1.5+1.2\sqrt{I}}{\sqrt{I}\,(1+1.2\sqrt{I})^2}\right)$
$B_{MX}=\beta^{(0)}_{MX}+\frac{\beta^{(1)}_{MX}}{2I}\left[1-(1+1.2\sqrt{I})\exp(-2\sqrt{I})\right]$	$B_{MX}{}'=\frac{\beta^{(1)}_{MX}}{2I^2}\left[-1+(1+1.2\sqrt{I}+2I)\exp(-2\sqrt{I})\right]$
$B_{MX}{}'=\frac{\beta^{(1)}_{MX}}{2I^2}\left[-1+(1+1.2\sqrt{I}+2I)\exp(-2\sqrt{I})\right]$	$B_{MX}{}''=\left(\frac{-\beta^{(1)}_{MX}}{I^3}\left[-1+(1+1.2\sqrt{I}+2I)e^{-2\sqrt{I}}\right]-\frac{\beta^{(1)}_{MX}}{I^{3/2}}e^{-2\sqrt{I}}\right)$

Eqs (1) and (2) applied to eq. (3), in order to obtain the desired points, involves a numerical solution since solving them analytically is not possible. A program in Fortran was written to accomplish this task, where the subroutines rtsafe and dbrent from ref. [3] were used to find the intersection point and the position of the minimum, respectively.

Finally, the results were compared with those obtained by application of Bronsted equation, which is the single model which lets one solve analytically the singular points of ln $\gamma_{\pm}$ *vs.* I curves.

Results and Discussion

The values of I_{min} and I_c obtained from the calculation for the studied electrolytes appear in tables 2 and appendix, together with the values of $\ln\gamma_{\pm}$ at I_{min} and the maximum value of ionic strength for the experimental data, I_n. In table 2 are listed electrolytes that show both minimum and intersection point , these values are given, ordered from the smallest to the greatest value of I_{min}. In appendix 1 appear the values of I_{min} and I_c obtained for all the studied electrolytes. In some cases there is no minimum or intersection point or its value is out of the range of ionic strength used in the experiment, these cases are indicated in the table with the *No* label.

Table 2. Electrolytes that shows minimum and interception point in the interval 0-I_n. Ionic Strength in the minimum, I_{min} and in the interception point with Ionic Strength axis, I_c, for the curves $\ln\gamma_{\pm}$ vs I, obtained from the solutions of eq. (1) and (2). I_n is the maximum available ionic strength. The value of $\ln\gamma_{\pm}$ (I_{min}) is listed too.

Electrolyte	I_n	I_{min}	ln γ	I_c
Bu_4NF	1.7000	0.0643	-0.1368	0.2954
Pr_4NF	2.0000	0.0928	-0.1605	0.4278
Et_4NF	2.0000	0.1066	-0.1631	0.5477
HI	6.0000	0.1987	-0.2096	1.0969
Me_4NF	3.0000	0.2377	-0.2439	1.1556
$LiClO_4$	3.5000	0.2717	-0.2405	1.4867
HBr	6.2000	0.2750	-0.2465	1.4495
Methane SA	60000	3327	-2474	20967
$HClO_4$	5.5000	0.3695	-0.2812	1.8426
Li ethane S	4.0000	0.3711	-2742	22333
HCl	6.0000	0.3727	-0.2803	1.9517

Electrolyte	I_n	I_{min}	ln γ	I_c
Na propionate	3.0000	0.3746	-0.2801	22002
Cs acetate	3.5000	0.3882	-0.2740	2.2779
LiBr	2.5000	0.3958	-0.2928	1.9699
Rb acetate	3.5000	0.4077	-0.2818	23601
K acetate	3.5000	0.4309	-2881	25385
Ethane SA	4.0000	0.4375	-0.2874	25849
$LiClO_3$	4.2000	0.4477	-0.3068	24243
LiCl	6.0000	0.4535	-0.2988	23546
Et_4N ethane S	40000	5028	-3463	25120
Na acetate	3.5000	0.5069	-0.3035	30850
Me_4N ethane S	4.0000	0.5252	-0.3476	29311
KOH	5.5000	0.5359	-0.3139	27662
Na ethane S	4.0000	0.5366	-0.2989	37429
Li NO_3	6.0000	0.5453	-0.3192	31939
Li NO_2	6.0000	0.5549	-0.3122	33805
NaI	3.5000	0.5917	-0.3183	31783
Li methane S	4.0000	0.6005	-0.3318	33794
Me_4N methane S	4.0000	0.6056	-0.3527	32816
Et_4N methane	4.0000	0.6068	-0.3693	31161
HNO_3	6.0000	0.6577	-0.3219	43460
NaOH	6.0000	0.9854	-0.4028	45817

The following main features have been observed:

a) 71 electrolytes exhibit the minimum in the ionic strength range of $0<I<I_n$

b) 52 electrolytes exhibit the minimum in the range of ionic strength between I=0 and I=2 mol Kg^{-1}.

c) 43 electrolytes fulfill the condition $I_{min}\in(0.1\text{-}1.0)$.

d) The smallest value of I_{min} corresponds to MgOHCl – I_{min}=0.08 mol Kg^{-1} – and the greatest one to CsBr,– I_{min} =4.5 mol Kg^{-1}.

e) 83 electrolytes show non or out of range minimum.

f) 32 electrolytes show both minimum and intersection point , these values are given in table 2, ordered from the smallest to the greatest value of I_{min}. Plots of $\ln\gamma_{\pm}$ vs. I for several electrolytes of this group are shown in fig. 2 to illustrate the behaviour.

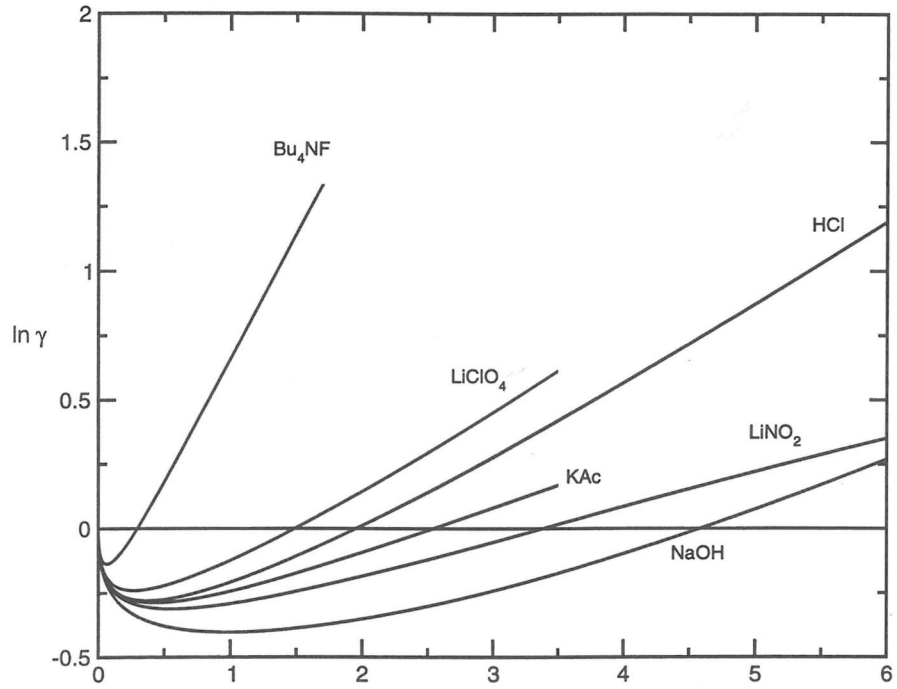

Figure 2. Some representative curves of 1:1 electrolytes, it can be seen the minimum (Bu_4NF) and the maximum (NaOH) values for I_c .

According to fig. 3, a high correlation has been found between the position of the minimum of the curves, I_{min}, and the intersection point, I_c, obtained by means of the Pitzer equations (table 2). The following correlation equation was obtained

$$\ln I_c = 1.07\,(0.03) + 1.77\,(0.03)\ln I_{min} \qquad r=0.99 \tag{4}$$

where the error of the parameters are given into brackets.

This correlation may be justified in a simple way and in qualitative terms by use of the Bronsted equation [4,5]

$$\ln \gamma_{\pm} = P\sqrt{I} + QI \tag{5}$$

where P and Q are constants at fixed pressure, temperature and solvent. This model is the only one that provides analytical solutions for both the position of the minimum and the intersection point, according to:

$$I_{min} = \left[\frac{P}{2Q}\right]^2 \tag{6}$$

and

$$I_c = \left[\frac{P}{Q}\right]^2 \tag{7}$$

Combination of both equations yields the theoretical relation:

$$I_c = 4I_{min} \tag{8}$$

which, in logarithmic form, becomes

$$\ln I_c = 1.38 + \ln I_{min} \tag{9}$$

which agrees quite closely with the experimental fit (eq. 4). However, it can be seen that eq.(4) and (9) refer to straight lines, but with different slopes and intercepts. In fact, it is not expected both expressions to be statistically comparable taking into account the simplicity of Bronsted model.

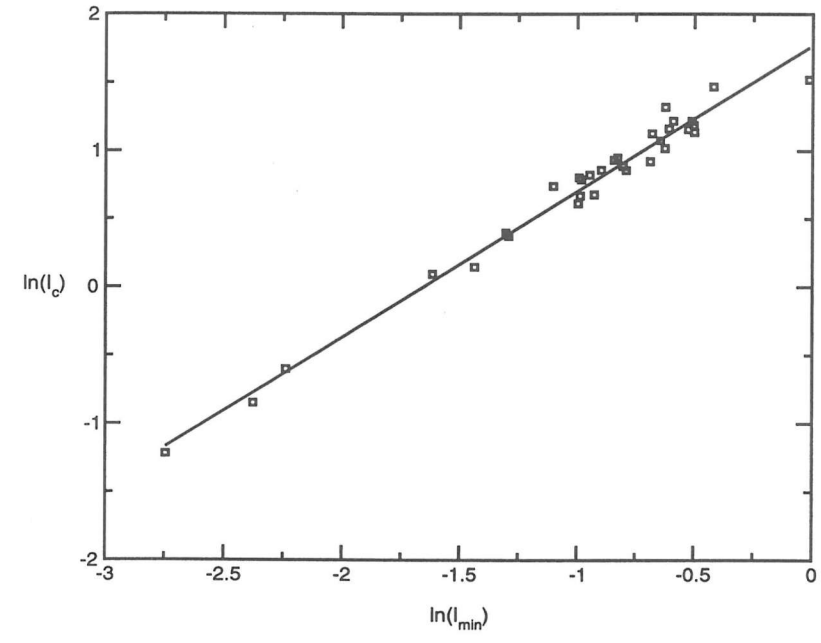

Figure 3. Plot of $\ln(I_c)$ vs $\ln(I_{min})$ according to Pitzer Model, see eq. (4).

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REFERENCES

1. Pytkowicz, R. M. (1979). *Activity coefficients in electrolyte solutions*. West Palm Beach, Fla., CRC Press.
2. Pitzer, K. S. (1991). *Activity coefficients in electrolyte solutions.* Boca Raton, CRC Press.
3. Press, W. H., B. P. Flannery, et al. (1992). *Numerical recipes in FORTRAN : the art of scientific computing. Cambridge [England]* ; New York, NY, USA, Cambridge University Press.
4. J.N. Bronsted, *J. Am Chem. Soc.*, 44 (1922) 877
5. J.N. Bronsted, *J. Am Chem. Soc.*, 44 (1922) 938

Appendix 1 Ionic Strength in the minimum, I_{min} and in the interception point with Ionic Strength axis, I_c, for the curves $\ln\gamma_{\pm}$ vs I, obtained from the solutions of eq. (1) and (2). I_n is the maximum available ionic strength. The value of $\ln\gamma_{\pm}$ (I_{min}) is listed too.

Electrolyte	I_n	I_{min}	ln γ	I_c
HCl	6.0000	0.3727	-0.2803	1.9517
HBr	6.2000	0.2750	-0.2465	1.4495
HI	6.0000	0.1987	-0.2096	1.0969
$HClO_4$	5.5000	0.3695	-0.2812	1.8426
HNO_3	6.0000	0.6577	-0.3219	4.3460
$H(HSO_4)$	1.0000	0.2206	-0.2183	No
$H(HSO_4)$	1.0000	0.1933	-0.2031	No
LiCl	6.0000	0.4535	-0.2988	2.3546
LiBr	2.5000	0.3958	-0.2928	1.9699
LiI	1.4000	0.2618	-0.2398	No
LiOH	4.0000	No	No	No
$LiClO_3$	4.2000	0.4477	-0.3068	2.4243
$LiClO_4$	3.5000	0.2717	-0.2405	1.4867
$LiBrO_3$	5.0000	1.0818	-0.4201	No
Li NO_2	6.0000	0.5549	-0.3122	3.3805
Li NO_3	6.0000	0.5453	-0.3192	3.1939
NaF	1.0000	No	No	No
NaCl	6.0000	1.2318	-0.4242	No
NaBr	4.0000	0.8740	-0.3757	No
NaI	3.5000	0.5917	-0.3183	3.1783
NaOH	6.0000	0.9854	-0.4028	4.5817
$NaClO_3$	3.5000	2.9219	-0.6208	No
$NaClO_4$	6.0000	2.2511	-0.4989	No
$NaBrO_3$	2.5000	No	No	No
NaCNS	4.0000	0.8114	-0.3424	No
Na NO_2	5.0000	3.0329	-0.5811	No
Na NO_3	6.0000	No	No	No
NaHSe	2.0000	No	No	No
$NaHCO_3$	1.0000	No	No	No

Electrolyte	I_n	I_{min}	ln γ	I_c
$NaHSO_4$	1.0000	No	No	No
NaH_2PO_4	6.0000	No	No	No
NaH_2AsO_4	1.2000	No	No	No
$NaB(OH)_4$	4.5000	3.7772	-1.0220	No
$NaBF_4$	6.0000	No	No	No
KF	2.0000	1.2188	-0.4437	No
KCl	4.8000	2.7351	-0.5636	No
KBr	5.5000	2.3400	-0.5248	No
KI	4.5000	1.6697	-0.4529	No
KOH	5.5000	0.5359	-0.3139	2.7662
$KClO_3$	0.7000	No	No	No
$KBrO_3$	0.5000	No	No	No
KCNS	5.0000	No	No	No
$K NO_2$	5.0000	No	No	No
$K NO_3$	3.8000	No	No	No
$KHCO_3$	1.0000	No	No	No
$KHSO_4$	1.0000	No	No	No
KH_2PO_4	1.8000	No	No	No
KH_2AsO_4	1.2000	No	No	No
KSCN	5.0000	No	No	No
KPF_6	0.5000	No	No	No
RbF	3.5000	0.8443	-0.3576	No
RbCl	7.8000	3.4301	-0.6293	No
RbBr	5.0000	4.4732	-0.6655	No
RbI	5.0000	3.9573	-0.6657	No
$Rb NO_2$	5.0000	No	No	No
$Rb NO_3$	4.5000	No	No	No
CsF	3.2000	0.6323	-0.3394	No
CsCl	7.4000	4.1882	-0.7404	No
CsBr	5.0000	4.7649	-0.7995	No
CsI	3.0000	No	No	No
CsOH	1.0000	0.4671	-0.3018	No
$Cs NO_2$	6.0000	No	No	No
$Cs NO_3$	1.4000	No	No	No

Electrolyte	I_n	I_{min}	ln γ	I_c
$Ag NO_3$	6.0000	No	No	No
$TiClO_4$	0.5000	No	No	No
$Ti NO_3$	0.4000	No	No	No
NH_4Cl	6.0000	3.6185	-0.5814	No
NH_4Br	2.5000	No	No	No
NH_4I	7.5000	2.7199	-0.4874	No
NH_4HCO_3	0.7000	No	No	No
NH_4HIPO_4	3.5000	No	No	No
NH_4ClO_4	2.0000	No	No	No
$NH_4 NO_3$	6.0000	No	No	No
(MgOH)Cl	1.0000	0.0801	-0.1219	No
Li acetate	4.0000	0.8213	-0.3696	No
Na forrnate	3.5000	1.4138	-0.4169	No
Na acetate	3.5000	0.5069	-0.3035	3.0850
Na propionate	3.0000	0.3746	-0.2801	2.2002
NaH malonate	5.0000	No	No	No
NaH succinate	5.0000	3.4397	-0.6528	No
NaH adipate	0.7000	No	No	No
K acetate	3.5000	0.4309	-0.2881	2.5385
KH malonate	5.0000	No	No	No
KH succinate	4.5000	No	No	No
KH adipate	1.0000	No	No	No
Rb acetate	3.5000	0.4077	-0.2818	2.3601
Cs acetate	3.5000	0.3882	-0.2740	2.2779
Tl acetate	6.0000	No	No	No
Methane SA	6.0000	0.3327	-0.2474	2.0967
Li methane S	4.0000	0.6005	-0.3318	3.3794
Na methane S	4.0000	1.3473	-0.4241	No
K methane S	4.0000	No	No	No
NH_4 rmethane S	4.0000	2.2674	-0.5162	No
Me_4N methane S	4.0000	0.6056	-0.3527	3.2816
Et_4N methane	4.0000	0.6068	-0.3693	3.1161
Bu_4N methane S	4.0000	0.3648	-0.2779	No
Ethane SA	4.0000	0.4375	-0.2874	2.5849

Electrolyte	I_n	I_{min}	ln γ	I_c
Li ethane S	4.0000	0.3711	-0.2742	2.2333
Na ethane S	4.0000	0.5366	-0.2989	3.7429
K ethane S	4.0000	1.1458	-0.4025	No
NH_4 ethane S	4.0000	0.9972	-0.4029	No
Me_4N ethane S	4.0000	0.5252	-0.3476	2.9311
Et_4N ethane S	4.0000	0.5028	-0.3463	2.5120
Bu_4N ethane S	4.0000	0.3184	-0.2427	No
Benzene SA	5.0000	1.5748	-0.3994	No
Li benzene S	4.5000	0.5742	-0.2871	No
Na benzene S	2.5000	No	No	No
p-Toluene SA	5.0000	3.5508	-0.8490	No
Li p-toluene S	4.5000	3.0819	-0.5683	No
Na p-toluene S	4.0000	No	No	No
K p-toluene S	3.5000	No	No	No
2,5 Me_2 benzene A	4.5000	4.0892	-1.2214	No
Li 2,5 Me_2 benzee S	3.5000	No	No	No
Na 2,5 Me_2 benzee S	1.0000	No	No	No
p-Et benzene SA	2.0000	No	No	No
Li p-Et benzene	5.0000	3.7469	-0.9964	No
Na p-Et benzene	2.5000	No	No	No
Mesitylene SA	2.0000	No	No	No
Li mesitylene S	2.0000	No	No	No
Na mesitylene S	1.0000	No	No	No
Me_4NF	3.0000	0.2377	-0.2439	1.1556
Et_4NF	2.0000	0.1066	-0.1631	0.5477
Pr_4NF	2.0000	0.0928	-0.1605	0.4278
Bu_4NF	1.7000	0.0643	-0.1368	0.2954
Me_4NCl	3.4000	1.8728	-0.6481	No
Et_4NCl	3.0000	1.4357	-0.6104	No
Pr_4NCl	2.5000	0.8519	-0.5377	No
Bu_4NCl	2.5000	0.8281	-0.4884	No
Me_4NBr	3.5000	3.1462	-0.9378	No
Et_4NBr	4.0000	2.7916	-1.0560	No
Pr_4NBr	3.5000	2.0951	-1.0266	No
Bu_4NBr	4.5000	No	No	No
Me_4NI	0.3000	No	No	No
Et_4NI	2.0000	No	No	No
Pr_4NI	0.5000	No	No	No
Choline Cl	6.0000	2.6541	-0.7726	No
Choline Br	6.0000	5.6333	-1.1413	No
$MeNH_3ClO_4$	4.0000	No	No	No
$Me_2NH_2ClO_4$	7.5000	No	No	No
Me_3NHClO_4	1.8000	No	No	No
Me_3BzNCl	3.5000	No	No	No
Me_3BzNBr	3.0000	No	No	No
$Me_2OEtBzNCl$	4.0000	No	No	No
$MC_2OEtBzNBr$	3.0000	No	No	No
$(HOC_2H_4)_4NF$	4.0000	1.1787	-0.4550	No
$(HOC_2H_4)_4NBr$	3.0000	No	No	No
Me_3SCl	6.0000	3.0976	-0.8299	No
Me_3SBr	6.0000	No	No	No
Me_3SI	6.0000	No	No	No
Bu_3SCl	6.0000	No	No	No
Bu_3SBr	6.0000	No	No	No

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