

Salting coefficient of triethanolamine in major seawater salts

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Abstract

Activity coefficient of triethanolamine (TEA) in major seawater salts (NaCl, KCl, CaCl₂ and MgCl₂) has been determined using the distribution method. It increases slowly in KCl, remains almost constant in NaCl and decreases in the other salts. Pitzer model has been used to fit the experimental data and the corresponding interaction parameters have been determined.

Keywords

Pitzer model; Setschenow coefficient; Salting coefficient; Triethanolamine

1. Introduction

A variety of experimental methods have been used to obtain activity coefficients of neutral molecules, or its logarithm ($\log \gamma_N$), as a function of salt concentration or ionic strength (I). The most important are solubility, distribution and vapour pressure measurements [1]. In this paper, distribution of triethanolamine (TEA) between aqueous solutions (with different amounts of salt in it) and an organic phase (isobutanol) has been used to determine $\log \gamma_N$ versus I [2]. As it has been stated by Long and McDevit [1] the influence of salts on the activity coefficients of nonelectrolytes in aqueous solutions is of both fundamental and applied interest. It may cause an increase (*salting in*) or decrease (*salting out*) of solubility of organic molecules when a salt is added to the solution [3]. Implications of these phenomena for chemical and biological sciences are discussed in ref. [4]. They are important to understand drugs behaviour in solutions and biological systems[5]. Salting out principle has been used in the purification of chemicals or to explain the formation of urinary stones [4]. In this paper, $\log \gamma_N$ versus I has been determined in major seawater salts (NaCl, KCl, CaCl₂ and MgCl₂) without sulphate and in artificial seawater.

1.1. Theory

When two phases are in equilibrium (aqueous and organic phases), the chemical potential of a component (TEA) is the same in each phase, therefore [6],

$$\begin{aligned}\mu_{\text{aq}} &= \mu_{\text{org}} \\ \mu_{\text{aq}}^0 + RT \ln a_{\text{aq}} &= \mu_{\text{org}}^0 + RT \ln a_{\text{org}}\end{aligned}\quad (1)$$

where μ is the chemical potential of TEA in the phase indicated by the subscript, μ^0 the standard chemical potential and a is the activity. When the composition of the solutions is described in terms of the molality scale, Eq. (1) becomes:

$$\mu_{\text{aq}}^0 + RT \ln(m_{\text{aq}} \gamma_{\text{aq}}) = \mu_{\text{org}}^0 + RT \ln(m_{\text{org}} \gamma_{\text{org}})\quad (2)$$

where m is the molality and γ is the activity coefficient in the molal scale. This expression rearranges to:

$$\exp\left(\frac{\mu_{\text{aq}}^0 - \mu_{\text{org}}^0}{RT}\right) = \frac{m_{\text{org}} \gamma_{\text{org}}}{m_{\text{aq}} \gamma_{\text{aq}}} = K_D^m \frac{\gamma_{\text{org}}}{\gamma_{\text{aq}}}\quad (3)$$

where K_D^m is the concentration ratio of TEA for the organic phase and the aqueous solution. If it is considered that the system behaves ideally when no salt is added to the aqueous phase, Eq. (3) becomes:

$$\exp\left(\frac{\mu_{\text{aq}}^0 - \mu_{\text{org}}^0}{RT}\right) = \frac{m'_{\text{org}}}{m'_{\text{aq}}} = K_D \quad (4)$$

where K_D is the distribution ratio of TEA for the organic phase and pure water. Substitution of the expression of exponential function by K_D of Eq. (4), in Eq. (3) results in:

$$\frac{\gamma_{\text{aq}}}{\gamma_{\text{org}}} = \frac{K_D^m}{K_D} \quad (5)$$

If concentration in organic phase is low enough, $\gamma_{\text{org}} \approx 1$, it then follows, after taking logarithms of both sides, that:

$$\ln \gamma_{\text{aq}} = \ln \frac{K_D^m}{K_D} \quad (6)$$

$\ln \gamma$ versus I for TEA in different salts has been obtained using values of K_D and K_D^m , at different ionic strengths determined as described in the experimental part.

The Pitzer equation for the logarithm of the activity coefficient of a neutral species, N, is [7]:

$$\ln \gamma_N = 2 \left(\sum_c m_c \lambda_{Nc} + \sum_a m_a \lambda_{Na} \right) + \sum_c \sum_a m_c m_a \zeta_{caN} \quad (7)$$

where the sums are over the cations, c , and over the anions, a , m_i the molality of species i , λ_{ij} the second virial coefficient and it represents the short-range interaction in the presence of the solvent between solute particles i and j and ζ_{ijk} accounts for triple interactions among the three species indicated by the subscript. In last equation, it has been assumed that neutral molecule concentration is low enough so that the terms with m_N can be neglected. On the other hand, triple interaction terms are not required for many systems but, as Pitzer states, they can be significant in others; in the former case, the equation remains the same as that of proposed by Setschenow [7].

2. Experimental

A 25 mL aqueous aliquot, containing TEA (<0.5 g) (MERCK, PA) and salt (NaCl, KCl, MgCl₂ or CaCl₂, MERCK, PA) to adjust the ionic strength to the desired value, was shaken with 50 mL of isobutanol (MERCK, PA) at 25 °C [2]. After complete separation of the two layers (4–5 h), TEA concentration in each phase was determined by titration with a standard solution of hydrochloric acid, using bromocresol green as indicator. The distribution coefficients, K_D^c , are obtained by dividing the concentration of TEA in the organic phase by its concentration in the aqueous phase and are shown in Table 1. Salt concentration in organic phase can be considered negligible [8]. The NaCl and KCl solutions were made by weight, while stock solutions of known molarity (standardised by density measurements) of CaCl₂ and MgCl₂ were used to dilute to the desired concentration [9].

Table 1.

Distribution coefficients of triethanolamine (TEA) between isobutanol and aqueous solution with different salts (molar scale is used)

Electrolyte	I (mol L ⁻¹)	[TEA] _{aq}	[TEA] _{org}	ρ	K_D^c
Water	0.000	0.0947	0.0254	0.99704	0.268 ± 0.002
NaCl	0.500	0.0922	0.0239	1.01758	0.259 ± 0.002
	1.500	0.0944	0.0254	1.05676	0.269 ± 0.002
	2.000	0.0883	0.0238	1.07573	0.270 ± 0.002
KCl	2.000	0.0892	0.0276	1.08698	0.309 ± 0.001
	2.500	0.0630	0.0218	1.10847	0.346 ± 0.002
MgCl ₂	0.517	0.0664	0.0173	1.01009	0.261 ± 0.001
	1.422	0.0981	0.0204	1.03235	0.208 ± 0.001
	2.124	0.1203	0.0233	1.04928	0.194 ± 0.001
	2.584	0.1052	0.0183	1.06023	0.174 ± 0.001
CaCl ₂	0.237	0.1114	0.0206	1.00475	0.185 ± 0.001
	0.474	0.1333	0.0195	1.01228	0.146 ± 0.001
	1.013	0.1558	0.0157	1.02901	0.101 ± 0.001
	1.422	0.1250	0.0096	1.04142	0.077 ± 0.001
	2.026	0.1476	0.0093	1.05939	0.063 ± 0.001
	2.370	0.1361	0.0083	1.06947	0.061 ± 0.001

[TEA]_{aq} is TEA concentration in aqueous solution (mol L⁻¹); [TEA]_{org} the same in organic solvent and ρ is the density of the aqueous phase (kg L⁻¹).

3. Results and discussion

Distribution constants have been determined using the molar concentration scale, Table 1, but in order to apply Pitzer equations, it is necessary to use the molality scale. The relationship between molality, m_i and molarity, c_i , for species i in a solution with a density ρ , is expressed by the following equation [10]:

$$m_i = \frac{c_i}{\rho - M_{\text{salt}} c_{\text{salt}}} \quad (8)$$

where M_{salt} is the molar mass of the salt. As it can be seen, to perform the conversion between concentration scales, density of solutions is needed. The concentration of the inert electrolyte is much higher than that of the reacting species, so density of solutions has been considered equal to that of solutions containing only the salt, that was taken from ref. [11].

On the other hand, hydrolysis of TEA has not been taken into account because its effect is of the same order than the experimental error. As an example, consider TEA in KCl 2 M, where $[\text{TEA}] = 0.0892$ (see Table 1) when hydrolysis is not taken into account, if $\text{p}K = 8.291$ [12] for TEAH, then the recalculated concentration of the neutral molecule would be $[\text{TEA}] = 0.0888$, the difference between these two values is in the same figure than the experimental error, and distribution constant should be $K_D = 0.310$ instead of $K_D = 0.309 \pm 0.001$. Besides, $\ln \gamma_N$ is obtained by dividing distribution constants in saline media by its value in pure water, if the same correction is applied in pure water where $\text{p}K = 7.762$ [13], then $K_D^c = 0.269$ instead of $K_D^c = 0.268$, and $\ln \gamma_N$ should be 0.082 instead of 0.081 ± 0.009 , the difference between both of them is again less than the experimental error.

Data of $\ln \gamma_N$ versus I , in the molal scale, obtained from the quotient $\ln(K_D^m/K_D)$, Eq. (6), are listed in Table 2 and represented in Fig. 1. It is observed that $\ln \gamma_N$ in NaCl does not vary significantly over the range of ionic strength used in this study; in KCl, it increases, but very slowly, with salt concentration, while it decreases for MgCl_2 and CaCl_2 . Exactly the same trend was found for TRIS, tris-(hydroxymethyl)-aminomethane or 2-amino-2-(hydroxymethyl)-1,3-propanediol, by Millero et al. as it can be seen in Fig. 3 of ref. [9], which is quite similar to Fig. 1 in this paper. These authors determined stoichiometric dissociation constants of TRIS and used Pitzer model to estimate $\ln \gamma_N$ versus I in NaCl, KCl, MgCl_2 and CaCl_2 in an indirect way; a similar procedure was followed in ref. [14]. The lower values of $\ln \gamma_N$ in magnesium and calcium salts indicates a strong interaction of the neutral molecule with these cations: possibly due to formation of complexes, as it is stated by Millero et al. [9] and [15]. In Pitzer model, short-range interactions are taken into account by introducing specific interaction parameters, in this case λ_{ij} and ζ_{ijk} . Alternatively, unusually strong attractive interaction can be represented by association equilibrium constants [7]. Any of these two methods

can be used indistinctly in many systems; however, a major advantage of the interaction approach is that calculations are much simpler and besides, the treatment is the same when repulsive interactions predominate. Therefore, Pitzer model has been used to fit the experimental data. In Fig. 1, it can be observed that the behaviour of $\ln \gamma_N$ versus I is linear when NaCl, KCl or MgCl₂ are used, while this is not the case in CaCl₂ medium, where a curvature is clearly appreciated. Because of this, Eq.(7) up to the linear term has been used for the former electrolytes, while third virial coefficient is taken into account for CaCl₂. $\ln \gamma_N$ in NaCl, using Pitzer model, Eq. (7) is given by:

$$\ln \gamma_N = 2m(\lambda_{NNa} + \lambda_{NCl}) = 2I(\lambda_{NNa} + \lambda_{NCl})$$

the corresponding expression for KCl is obtained by changing Na for K, while in CaCl₂ medium:

$$\ln \gamma_N = \frac{2}{3}I(\lambda_{NCa} + 2\lambda_{NCl}) + \frac{2}{9}I^2\zeta_{NCaCl}$$

this equation is valid for MgCl₂ when Ca is substituted by Mg and besides $\zeta_{NMgCl} = 0$. The values of the interaction parameters are given in Table 3, and Pitzer functions are displayed together with the experimental data in Fig. 1. Pitzer parameters should be used inside the range of concentrations used in the fits. As stated above, triple interaction terms are not required for many systems, but they can be significant in others. This is what happens here, ζ_{NCaCl} seems to be necessary to explain the experimental data, while the other triple interaction terms are negligible. Of course, examples of this behaviour can be found in the literature: third virial coefficient has been used for the activity coefficient of ammonia in ammonium nitrate [16] and ammonium sulfate solutions [17] and for O₂ in different salts [10]. On the other hand, interaction parameters in Table 3 can be used to estimate $\ln \gamma_N$ in a mixture of the studied salts, by means of Eq. (7). An approximation to the composition of natural seawater (without sulfate) is found in ref. [18]: $m(\text{NaCl}) = 0.4266$, $m(\text{KCl}) = 0.01058$, $m(\text{CaCl}_2) = 0.01077$ and $m(\text{MgCl}_2) = 0.05518 \text{ mol kg}^{-1}$. In this medium, the value for the activity coefficient of TEA found using Eq. (7) is $\ln \gamma_N = -0.069$ and the expected value for the distribution coefficient would be:

$$K_D^c(\text{Pitzer}) = 0.253$$

while the value obtained experimentally in this study is:

$$K_D^c(\text{experimental}) = 0.261$$

Table 2.

Activity coefficients of triethanolamine (TEA) in different salts (molal scale is used)

Electrolyte	I (mol kg ⁻¹)	$\ln \gamma_N$
Water	0.000	0.000
NaCl	0.506	-0.044 ± 0.010
	1.548	-0.026 ± 0.010
	2.086	-0.032 ± 0.011
KCl	2.132	0.081 ± 0.009
	2.711	0.178 ± 0.010
MgCl ₂	0.520	-0.031 ± 0.010
	1.440	-0.264 ± 0.011
	2.163	-0.342 ± 0.009
	2.641	-0.453 ± 0.011
CaCl ₂	0.238	-0.371 ± 0.009
	0.477	-0.610 ± 0.009
	1.022	-0.986 ± 0.009
	1.438	-1.261 ± 0.010
	2.058	-1.463 ± 0.010
	2.414	-1.498 ± 0.011

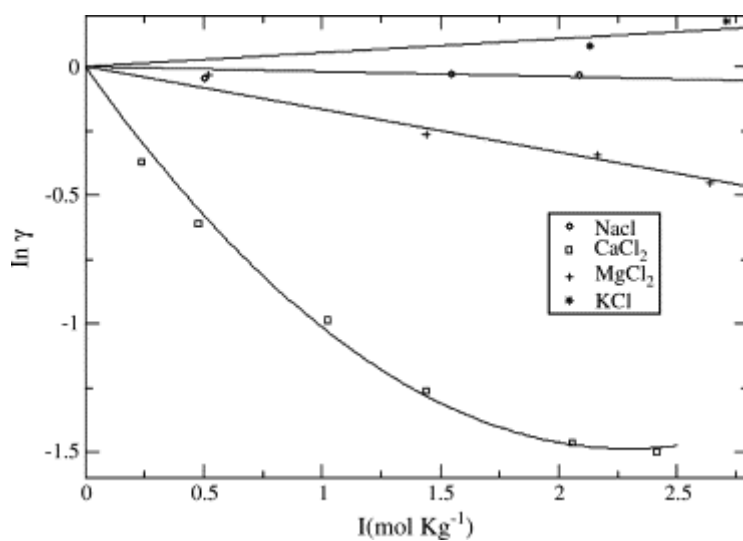


Fig. 1. Logarithm of the activity coefficient of triethanolamine (TEA) in different salts. Symbols represent experimental data and lines correspond to Pitzer model (molal scale is used).

Table 3.

Pitzer interaction parameters for triethanolamine (TEA) in different salts

$\lambda_{\text{NNa}} + \lambda_{\text{NaCl}} = -0.009 \pm 0.005$	
$\lambda_{\text{NK}} + \lambda_{\text{NaCl}} = 0.028 \pm 0.007$	
$\lambda_{\text{NMg}} + 2\lambda_{\text{NaCl}} = -0.250 \pm 0.015$	
$\lambda_{\text{NCa}} + 2\lambda_{\text{NaCl}} = -1.94 \pm 0.09$	$\zeta_{\text{NCaCl}} = 1.3 \pm 0.1$

Agreement is quite good—a great advantage of Pitzer model is that the properties in mixed electrolytes can be predicted with considerable accuracy from the properties in the pure components [7]. Calculation of activity coefficient of nonelectrolytes in mixed electrolyte solutions with Pitzer model can be found in ref.[19].

4. Conclusions

Activity coefficients of a neutral molecule (TEA) have been determined in different saline media (NaCl, KCl, MgCl₂ and CaCl₂). These kinds of measurements are interesting by their own and by their practical implications. Selected salts are the major constituents of seawater and the parameters obtained by fitting experimental data to Pitzer model can be used to estimate activity coefficients in complex mixtures such as seawater; illustrating how to calculate properties in mixed electrolytes from those in the pure components. On the other hand, acid–base equilibria of organic substances in saline solutions are influenced by the activity coefficient of the neutral species appearing in the equilibria, so this paper can be understood as a previous step to the determination of dissociation constants of TEA in the salts used here and different mixtures, that it is under study in this laboratory.

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