

Thermodynamic transfer functions at infinite dilution and clathrate formation of ethanolamines in water

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Abstract

The ultrasonic velocities and densities of solutions of water in various binary aqueous solutions of ethanolamines were measured over the full range of compositions at 298, 308 and 318 K. The experimental data in the dilute region with mole fraction of water <0.1 was analyzed to determine the partial molar volume and adiabatic compressibilities at infinite dilution. Compressibility isotherms intersect approximately at a common point for triethanolamine (TEA), methyldiethanolamine (MDEA), dimethylethanolamine (DMEA) and diethylethanolamine (DEEA) and this is attributed to the formation of quasi-clathrate-like structures in the liquid solutions. The standard thermodynamic transfer functions were calculated to evaluate the environment of water at infinite dilution in these systems. The transfer functions of water between the various ethanolamines are considerably larger for ethanolamines that differ in their degree of hydrophobicity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ethanolamines are an important class of compounds that are used in a wide variety of household and industrial applications. Ethanolamines are instrumental for the removal of acidic gases such as CO_2 and H_2S from gas streams in the natural gas and petroleum industry and for treating gas streams in chemical production industries. In the petroleum and natural gas industry, the removal of acid constituents from process streams is commonly achieved by reacting these impurities with aqueous ethanolamines [1–5].

The enhancement of the water structure in dilute aqueous non-polar solutes containing hydrophobic functional groups is well known in literature [6–11]. The thermodynamic properties of aqueous polar organic compounds are determined predominately by the hydrophobic interactions. Sound velocity measurements have been useful in the study of water mixtures with various solutes to understand the type of intermolecular interactions as well as the formation of clathrate types of compounds in water [12–19]. The solute molecules are expected to be accommodated in short living water cages of a bulky water lattice. The amine guest molecules are located in the voids of the water lattice. In case of larger molecules like ethanolamines, the clathrate-like structure seems to be more probable than that of an ice-like structure since they are sterically more convenient. The ethanolamines can enhance the structure of water in dilute aqueous

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solutions since they have a hydrophobic functional group (i.e. water in their environment become more bulky and ordered).

A comparison of the solute behavior in various solvents is provided by the standard thermodynamic functions of transfer $Y_s^{m \rightarrow n}$ defined as follows:

$$Y_s^{m \rightarrow n} = Y_s^{\infty(n)} - Y_s^{\infty(m)}, \quad (1)$$

where $Y_s^{\infty(m)}$ and $Y_s^{\infty(n)}$ are the partial molar quantities of a solute (s) in solvents m and n, respectively. The standard functions of transfer can be regarded as a measure of the difference in the interactions of a given solute with the solvents under consideration. A study of standard function of transfer of water between two different polar organic solvents can provide useful information in terms of coupling of water with the pure solvents. Similar environments should therefore result in a smaller value of the function of transfer while increasing differences should lead to a larger value of the standard function of transfer.

2. Experimental

Monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), dimethylethanolamine (DMEA), ethylethanolamine (EDEA) and diethylethanolamine (DEEA) were obtained from Aldrich Chemicals at 99% purity and were used as received. All aqueous solutions of these ethanolamines were prepared with triply deionized water by mass on an analytical balance.

The density measurements were obtained using an Anton Paar DMA 45 Digital Density Meter operating in a static mode. The measurements obtained are accurate to $5 \times 10^{-5} \text{ g cm}^{-3}$. The ultrasonic velocities were measured using a Nusonics Velocimeter (Model 6080) employing the sing-around technique. Rapid and accurate measurements of sound velocity as a function of ethanolamine concentrations were made by successive additions of known mass of ethanolamines to the thermostated beaker containing a known

Table 1
Experimental densities and sound velocities of ethanolamines

Ethanolamine	T (K)	Density, $\rho(\text{g cm}^{-3})$		Sound velocity, $u (\text{m s}^{-1})$
		This work	Literature	
MEA	298	1.01180	1.0118 [19], 0.9360 [22]	1717.7
	308	1.00467		1686.7
	318	0.99817		1653.5
DEA	298	1.09370	1.0937 [19]	1721.4
	308	1.08741		1697.2
	318	1.08204		1673.2
TEA	298	1.1215	1.1213 [19]	
	308	1.1156		
	318	1.1108		
DMEA	298	0.88334	0.88221 [22] 0.8744 [20]	1338.4
	308	0.87546		1301.5
	318	0.86728		1265.6
DEEA	298	0.87952		1346.1
	308	0.87140		1306.8
	318	0.86182		1265.6
MDEA	298	1.03688	1.0359 [21]	1568.3
	308	1.02901		1537.8
	318	1.02264		1507.0
EDEA	298	1.00949	1.0100 [21]	1501.5
	308	1.00233		1471.4
	318	0.99558		1441.8

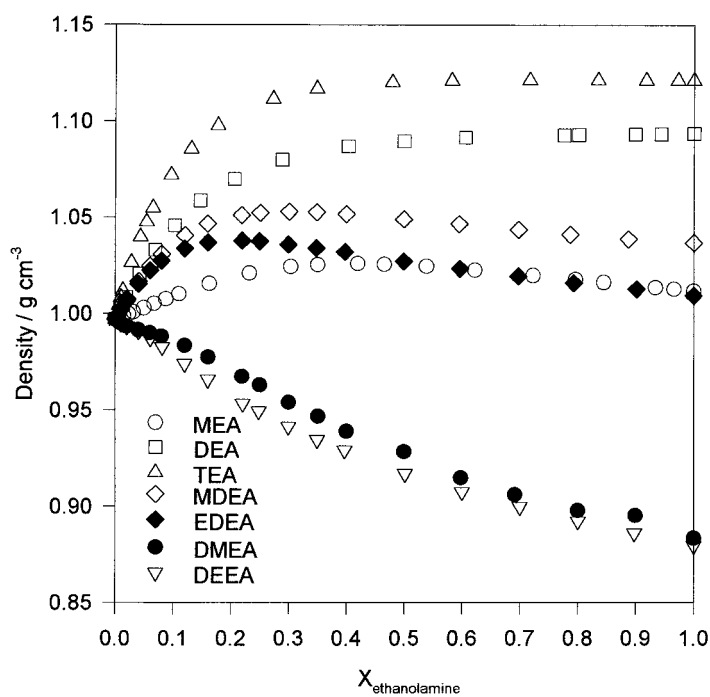


Fig. 1. Plots of density of aqueous ethanolamines as a function of mole fraction of ethanolamines at 298 K.

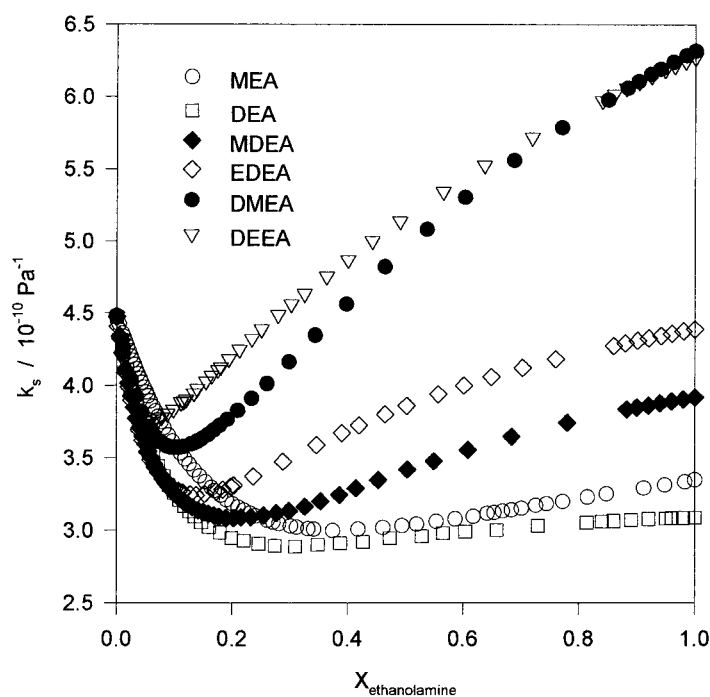


Fig. 2. Plots of adiabatic compressibility versus mole fraction of ethanolamines at 298 K.

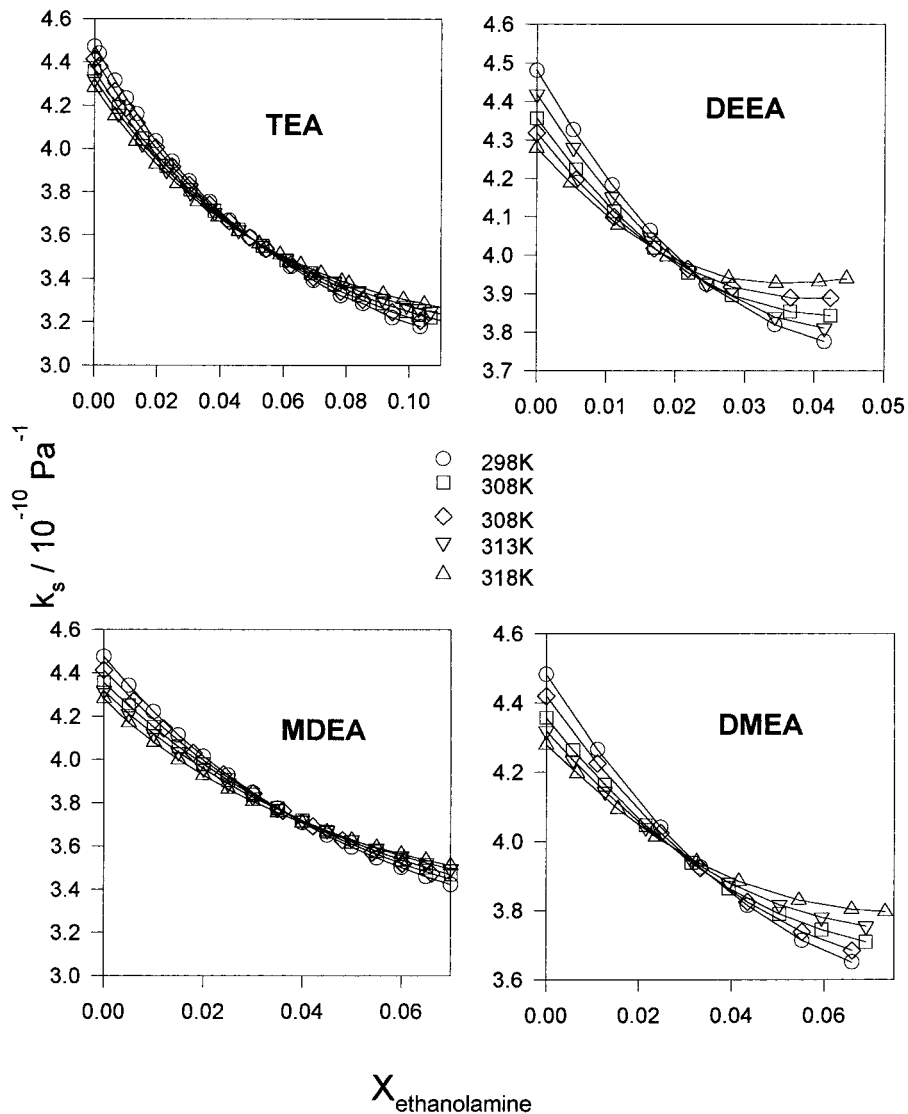


Fig. 3. Adiabatic compressibility isotherms in the dilute region.

amount of water. The velocity measurements are accurate to $\pm 0.1 \text{ m s}^{-1}$.

3. Results and discussion

The densities and the speed of sound values of the pure ethanolamines together with the literature values [19–21] are presented in Table 1. The ultrasonic velocities and densities of aqueous solutions of the

ethanolamines were measured in the whole concentration range at temperatures of 298, 308, 318 K and the excess functions, such as V_E and β_s^E are reported in one of our previous publications [23]. Molar volumes (V) of the solution were calculated by

$$V = \frac{X_1 M_1 + (1 - X_1) M_2}{\rho}, \quad (2)$$

where X_1 , M_1 and M_2 are mole fraction of water, molar masses of water and ethanolamine, respectively, and ρ

Table 2
Partial molar quantities at infinite dilution as a function of temperature

Ethanolamine	T (K)	$V_{\text{H}_2\text{O}}$ ($\text{cm}^3 \text{mol}^{-1}$)		$K_{\text{H}_2\text{O}} (\times 10^{-15})$ ($\text{m}^3 \text{Pa}^{-1}$)
		This work	Literature	
MEA	298	16.0	16.1 [14]	2.73
	308	16.9		3.43
	318	17.3		3.65
DEA	298	16.9	16.9 [14]	4.33
	308	16.5		3.96
	318	17.3		3.47
DMEA	298	11.3		−12.62
	308	13.3		−18.81
	318	14.6		−22.14
DEEA	298	8.7		−14.30
	308	9.5		−25.20
	318	11.7		−32.20
MDEA	298	15.3	14.2 [16]	−1.42
	308	16.3		−0.54
	318	16.5		−1.62
EDEA	298	13.6	14.4 [16]	−3.98
	308	14.9		−3.17
	318	15.4		−4.08
TEA	298	16.0	16.0 [14]	
	308	16.4		
	318	16.9		

is density of the solution. Adiabatic compressibility (k_s) and molar adiabatic compressibility (K_s) were calculated using the following equations:

$$k_s = \frac{1}{u^2 \rho} \quad \text{and} \quad K_s = V \times k_s. \quad (3)$$

Densities and adiabatic compressibilities at 298 K of binary aqueous mixtures of ethanolamines as a function of composition are presented in Figs. 1 and 2, respectively. The molar volumes and molar adiabatic compressibilities in the dilute region is fitted to the following equation (Fig. 3):

$$y = b_0 + b_1(1 - X). \quad (4)$$

The values of the coefficients b_0 and b_1 were determined by least-squares method. The partial molar quantities Y_m of the m th component of a binary solution is given by

$$Y_m = Y - (1 - X_m) \left[\frac{\partial Y}{\partial (1 - X_m)} \right]_{T,P}, \quad (5)$$

where $m = 1, 2$ and Y is the corresponding molar property and X_m is the mole fraction of the m th component. From Eqs. (4) and (5), one can deduce that the partial molar quantity of water at infinite dilution in the solution of ethanolamine is equal to the value of b_0 . The partial molar quantities at 298, 308 and 318 K were determined in the dilute region with mole fraction of water < 0.1 and the values are presented in Table 2. Hepler and co-workers [19–21] have calculated partial molar volumes at infinite dilution of MEA, DEA, TEA, MDEA and EDEA, employing the Redlich-Kister's coefficients for excess volumes and the following equations:

$$V_2^0 = V_2^* + \sum_{n=1} A_n, \quad (6)$$

$$V_1^0 = V_1^* + \sum_{n=1} A_n (-1)^{n-1}, \quad (7)$$

where V_1^* , V_2^* are molar volumes of pure components 1 and 2, respectively, and A_n are Redlich-Kister parameters. The values obtained in the present study

Table 3
Partial molar volume of transfer of water between ethanolamines

m → n	$V_s^{m \rightarrow n}$ (cm ³ mol ⁻¹)		
	298 K	308 K	318 K
MEA → DEA	0.9	-0.4	0
MEA → TEA	0	-0.5	-0.4
MEA → MDEA	-0.7	-0.2	-0.8
MEA → EDEA	-2.4	-2.0	-1.9
MEA → DMEA	-4.7	-3.6	-2.7
MEA → DEEA	-7.3	-7.4	-5.6
DEA → TEA	-0.9	-0.1	-0.4
DEA → MDEA	-1.6	-0.2	-0.8
DEA → EDEA	-3.3	-1.6	-1.9
DEA → DMEA	-5.6	-3.2	-2.7
DEA → DEEA	-8.2	-7.0	-5.6
TEA → MDEA	-0.7	-0.1	-0.4
TEA → EDEA	-2.4	-1.5	-1.5
TEA → DMEA	-4.7	-3.1	-2.3
TEA → DEEA	-7.3	-6.9	-5.2
MDEA → DMEA	-4.0	-3.0	-1.9
MDEA → EDEA	-1.7	-1.4	-1.1
MDEA → DEEA	-6.6	-6.8	-4.8
EDEA → DMEA	-2.3	-1.6	-0.8
EDEA → DEEA	-4.9	-5.4	-3.7
DMEA → DEEA	-2.6	-3.8	-2.9

are in excellent agreement with the literature values. The values of transfer functions of water between ethanolamines were calculated from Eq. (1) and are presented in Tables 3 and 4. Within the narrow tem-

Table 4
Standard adiabatic compressibilities of transfer of water between ethanolamines

m → n	$K_{S,W}^{m \rightarrow n} \times 10^{-14}$ (m ³ Pa ⁻¹ mol ⁻¹)		
	298 K	308 K	318 K
DEA → MEA	0.95	0.96	0.96
MDEA → MEA	2.48	2.63	2.78
EDEA → MEA	3.77	4.00	4.25
DMEA → MEA	4.36	4.74	5.15
DEEA → MEA	6.34	6.91	7.59
MDEA → DEA	1.54	1.67	1.82
EDEA → DEA	2.83	3.04	3.15
DMEA → DEA	3.41	3.75	4.19
DEEA → DEA	5.39	5.95	6.63
EDEA → MDEA	1.29	1.37	1.48
DMEA → MDEA	1.87	2.11	2.37
DEEA → MDEA	3.86	4.28	4.82
DMEA → EDEA	0.58	0.74	0.89
DEEA → EDEA	2.57	2.91	3.05
DEEA → DMEA	1.99	2.17	2.43

Table 5
Concentrations of intersection of compressibility isotherms and clathrate composition

Ethanolamine	$X_{\text{ethanolamine}}$	Amine:H ₂ O
TEA	0.054	1:18
MDEA	0.040	1:24
DMEA	0.033	1:29
DEEA	0.022	1:44

perature range 298–318 K, the compressibility isotherms for TEA, DMEA, MDEA and DEEA exhibit evidence for a point of intersection at lower concentrations, indicating clathrate-like structure formation in the systems. The approximate clathrate composition can be calculated from the intersection point and are presented in Table 5.

3.1. Transfer functions

The partial molar volumes of water at infinite dilution are smaller than the corresponding molar volumes of pure water at the same temperature. This observation is consistent with the idea that the molar volume of pure water is a sum of the actual molecular volume plus the empty volume arising from the hydrogen-bonded “open” structure of liquid water. Monoethanolamine, diethanolamine and triethanolamine will mix substitutionally with water leading to a smaller decrease in volume. It is reasonable to suggest that the small values of the molar volume on transfer of water from MEA → DEA, DEA → TEA and MEA → TEA constitute the strong evidence for an essential similarity of the surroundings of a water molecule in these solvents at infinite dilution. Larger values are observed on transfer of water to an ethanolamine with a greater degree of hydrophobic character.

The values of partial molar adiabatic compressibilities of water at infinite dilution are all negative except for monoethanolamine and diethanolamine. Water molecules are less likely to occupy the free intermolecular spaces in these liquid ethanolamines due to their relatively high hydrophilic nature. Water molecules have a greater incentive to fill in the intermolecular spaces with the remaining ethanolamines. This results in a decrease in the structural compressibility leading to negative values of K_s . The transfer function of molar compressibilities is also influenced by the hydrophobic character of the two solvents in question.

3.2. Clathrate formation

Many dilute aqueous solutions of non-electrolyte exhibit a common intersection point in adiabatic compressibility isotherms and this phenomenon may be attributed to the formation of clathrate-like structures in the solution. The added solute enhances water–water interactions such that the orientation of the liquid resembles a clathrate structure. Endo [16] attributed the intersection points to formation of clathrate-like structures and concluded that the concentration of the zero temperature coefficient of adiabatic compressibility ($\partial k/\partial T = 0$) due to the fact that the instantaneous compressibility, k_∞ (compression of molecules and intermolecular distances) and structural compressibility, k_{st} (breakdown of intermolecular bonds) become simultaneously temperature independent. The stoichiometry of the clathrate-like structure formed in the solution may not correspond to the concentration of the intersection point in view of the incomplete occupancy of the available empty spaces may shift the concentration at which $\partial k_{st}/\partial T \cong 0$ to a higher composition than that of the true clathrate composition.

In conclusion, the model of aqueous solutions of ethanolamines can be represented as the formation of clathrate structures arising due to hydrophobic hydration. At higher concentrations, these structures gradually decay with an increase in ethanolamine content [22]. The hydrophobic hydration is also accompanied by hydrophilic interactions through hydrogen bonding. From the study of the transfer function, one can conclude that the nature of water at infinite dilution is very similar in monoethanolamine, diethanolamine and triethanolamine and is different in the remaining ethanolamines. This can be attributed to the difference in the hydrophilic and hydrophobic nature of these ethanolamines.

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