

Isentropic Compressibility of Aqueous and Methanolic Electrolytic Solution

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(Received 4 March 2002 • accepted 28 June 2002)

Abstract—We studied the effect of ion-solvent and ion-ion interactions on the isentropic compressibility of aqueous and methanolic electrolytic solutions. In aqueous electrolytic solutions a critical concentration is attained and correlated with the completion of the primary hydration shell. Such a situation is lacking in methanolic solutions. An expression has been derived for estimating the hydration numbers of the electrolyte in its solutions by using the isentropic compressibility data.

Key words: Electrolytic Solutions, Ion Solvation, Speed of Sound, Isentropic Compressibility, Hydration Number

INTRODUCTION

Studies of the structure and dynamics of electrolytes either in aqueous or nonaqueous media have proliferated in recent years for their commercial exploitation in the fields of electrochemical, spectroscopic, high energy density batteries, hydrometallurgy etc. and for development of theoretical models. Wide ranges of interacting forces from van der Waals forces to electrostatic interaction and different equilibria prevail in different concentration regions. These impose considerable constraints on the free movement of the solvent molecules which leads to the formation of different species such as solvated ion, ion pairs (solvent-separated, solvent-shared or contact) etc. They also leave their mark on the transport properties of the electrolytic solutions. At the outset it should be emphasized that, because of the inherent complexity of solvent molecules around the ions, the study of electrolytic solutions is still in its infancy as far as the microscopic properties of the measurable quantities are concerned.

The measurement of speeds of sound in electrolytic solutions is soon amongst the many techniques hitherto used to provide reliable information concerning the structure of electrolytic solutions. This technique takes into account the important consequences of ion solvation, such as reduced volume and the compressibility of the solvent molecules. Since the electric fields of the ions exert a considerable electrostatic effect on the surrounding solvent molecules, the volume and the compressibility of the solvent molecules are reduced substantially. The isentropic compressibility (κ_s) which is a second pressure derivative of the Gibbs free energy can be precisely obtained from the measurement of density (ρ) and speed of sound (u) in solutions by the well known Newton Laplace equation [Strutt and Baron, 1896]:

$$\kappa_s = -V^{-1}(dV/dP)_s = (u^2\rho)^{-1} \quad (1)$$

This parameter is sensitive to the ionic and molecular interactions. So, the compressibility measurements carried out in solutions probe the solvent-solvent, ion-solvent and ion-ion interactions that can be characterized by the variation of thermodynamic parameters such as temperature, pressure and concentration. In this article, results have been summarized regarding the solvation of ions of aqueous and methanolic electrolytic solutions obtained from the measurements of speeds of sound.

RESULTS AND DISCUSSION

The temperature and concentration dependence of isentropic compressibility are frequently explained by using polynomial type equations with a large number of adjustable parameters without any theoretical origin [Horvath, 1985; Millero et al., 1982; Rohman and Mahiuddin, 1997]. It seems that these equations are not universal in explaining the concentration dependence of the isentropic compressibility in electrolytic solutions even though the equations fit the data fairly accurately. We observed that a polynomial equation of the following form,

$$\kappa_s = a + b(T - 273.15) + c(T - 273.15)^d \quad (2)$$

explains the temperature dependence of isentropic compressibility data within reasonable accuracy [Rohman, 2000; Rohman et al., 1999]. In Eq. (2), a , b and c are concentration-dependent parameters and d is an adjustable parameter. It has been observed that a , b and c vary nonlinearly with concentration and an equation of the form,

$$\kappa_s = A + Bm + Cm^p \quad (3)$$

can be obtained for describing the concentration dependence of isentropic compressibility at a particular temperature. In Eq. (3), A , B , C and D are temperature dependent adjustable parameters. This equation fits the concentration dependence of isentropic compressibility values of electrolytic solutions within reasonable accuracy. The values of the parameters of Eq. (3) for some of the electrolytic solutions investigated in this study are presented in Table 1.

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[‡]This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

Table 1. Least squares fitted values of the parameters of Eq. (3) for aqueous and methanolic electrolytic solutions at different temperatures

T/K	$10^{10} A/\text{Pa}^{-1}$	$10^{10} B/\text{Pa}^{-1} \text{ kg mol}^{-1}$	$10^{10} C/\text{Pa}^{-1} \text{ kg}^D \text{ mol}^{-D}$	D	std dev in $10^{12} \kappa_s/\text{Pa}^{-1}$
aqueous lithium bromide					
273.15	5.051±0.015	-4.062±0.101	3.487±0.091	1.04±0.81	3.1
298.15	4.491±0.009	-1.134±0.023	0.7375±0.0172	1.11±0.09	2.4
323.15	4.280±0.005	-1.378±0.017	1.036±0.014	1.09±0.07	0.9
aqueous sodium bromide					
273.15	5.025±0.012	-0.9851±0.0195	0.3335±0.0100	1.32±0.14	0.2
298.15	4.481±0.005	-0.6963±0.0086	0.2233±0.0044	1.32±0.06	0.9
323.15	4.266±0.002	-0.5573±0.0034	0.1633±0.0017	1.34±0.03	0.4
aqueous potassium bromide					
273.15	4.989±0.012	-0.6927±0.0229	0.1185±0.0095	1.63±0.32	2.2
298.15	4.463±0.003	-0.5617±0.0054	0.1356±0.0025	1.44±0.06	0.6
323.15	4.264±0.003	-0.4582±0.0048	0.0944±0.0021	1.49±0.08	0.6
aqueous sodium thiocyanate					
293.15	4.619±0.015	-2.359±0.42	1.805±0.034	1.07±0.04	2.2
298.15	4.541±0.014	-1.772±0.298	1.255±0.023	1.09±0.06	2.0
308.15	4.407±0.017	-0.9685±0.0147	0.5255±0.0093	1.16±0.06	1.7
323.15	4.293±0.010	-0.6170±0.0085	0.2468±0.0043	1.24±0.06	1.5
aqueous potassium thiocyanate					
273.15	4.979±0.033	-1.940±0.067	1.367±0.051	1.09±0.09	6.1
298.15	4.486±0.012	-2.934±0.056	2.493±0.049	1.04±0.02	2.3
323.15	4.290±0.010	-3.090±0.057	2.724±0.052	1.03±0.01	1.8
aqueous lithium nitrate					
298.15	4.452±0.012	-1.119±0.020	0.7149±0.0144	1.11±0.06	2.5
313.15	4.307±0.008	-0.8408±0.0111	0.4916±0.0075	1.13±0.06	1.6
323.15	4.250±0.006	-0.6941±0.0086	0.3725±0.0054	1.15±0.04	1.4
aqueous sodium nitrate					
278.15	4.824±0.005	-1.005±0.009	0.4175±0.0049	1.25±0.04	1.0
298.15	4.459±0.003	-0.6451±0.0043	0.1937±0.0020	1.34±0.03	0.6
323.15	4.249±0.003	-0.4603±0.0031	0.1001±0.0011	1.43±0.04	0.6
aqueous calcium nitrate					
273.15	4.964±0.034	-4.799±0.139	3.806±0.117	1.07±0.06	5.9
298.15	4.485±0.016	-7.974±0.150	7.188±0.139	1.03±0.09	2.8
323.15	4.286±0.010	-9.896±0.135	9.219±0.129	1.02±0.01	1.7
aqueous cadmium nitrate					
273.15	5.123±0.025	-9.043±0.190	7.833±0.172	1.05±0.02	2.6
298.15	4.542±0.014	-2.320±0.035	1.450±0.025	1.15±0.07	1.5
323.15	4.304±0.009	-1.394±0.016	0.6871±0.0100	1.23±0.06	1.0
aqueous sodium thiosulfate					
278.15	4.774±0.010	-2.626±0.031	1.331±0.021	1.25±0.06	1.7
298.15	4.399±0.073	-1.979±0.021	0.9115±0.0138	1.28±0.05	1.3
323.15	4.180±0.011	-1.471±0.027	0.5685±0.0160	1.34±0.10	2.0

Figs. 1 and 2 illustrate a typical example of concentration dependence of isentropic compressibility isotherms for aqueous and methanolic electrolytic solutions, respectively. It is interesting to observe the variation of isentropic compressibility isotherms with concentration, where both aqueous and methanolic solutions show dissimilar behaviors [Rohman and Mahiuddin 1997; Rohman et al., 1999]. The isentropic compressibility isotherms of aqueous electrolytic solutions decrease with increase in concentration, converge at a particular concentration and diverge in a reverse way. The con-

centration at which the isotherms converge is designated as the critical concentration. The critical concentration and the corresponding isentropic compressibility values for investigated electrolytic solutions are listed in Table 2. This concentration depends on the nature of the electrolyte used. At this concentration somewhat of a structural transition occurs in the solution which may be presumed due to the competition of the ion-solvent interaction and the hydration with the ion-ion interactions. Similar kind of structural transition has been reported from the study of viscosity, electrical conductivity,

Table 1. Continued

T/K	$10^{10} A/\text{Pa}^{-1}$	$10^{10} B/\text{Pa}^{-1} \text{ kg mol}^{-1}$	$10^{10} C/\text{Pa}^{-1} \text{ kg}^D \text{ mol}^{-D}$	D	std dev in $10^{12} \kappa_s/\text{Pa}^{-1}$
methanolic sodium thiocyanate					
293.15	9.816 ± 0.028	-1.987 ± 0.034	0.5862 ± 0.0146	1.41 ± 0.09	4.8
298.15	10.15 ± 0.03	-2.137 ± 0.039	0.6744 ± 0.0177	1.38 ± 0.09	5.1
308.15	10.89 ± 0.04	-2.765 ± 0.062	1.134 ± 0.035	1.28 ± 0.10	6.2
323.15	12.15 ± 0.05	-5.398 ± 0.173	3.447 ± 0.132	1.13 ± 0.10	8.4
methanolic potassium thiocyanate					
273.15	8.765 ± 0.020	-2.035 ± 0.036	0.723 ± 0.017	1.39 ± 0.17	1.5
298.15	10.53 ± 0.02	-9.879 ± 0.147	8.087 ± 0.131	1.06 ± 0.05	1.5
323.15	12.54 ± 0.03	57.63 ± 1.37	-59.90 ± 1.40	0.99 ± 0.01	2.6
methanolic lithium nitrate					
273.15	8.880 ± 0.020	-2.305 ± 0.028	1.108 ± 0.016	1.22 ± 0.04	3.9
298.15	10.31 ± 0.02	-6.943 ± 0.088	5.418 ± 0.074	1.07 ± 0.03	4.0
323.15	12.33 ± 0.04	-9.740 ± 0.202	7.833 ± 0.174	1.06 ± 0.06	7.9
methanolic calcium nitrate					
273.15	8.567 ± 0.090	-26.90 ± 1.22	25.10 ± 1.16	1.02 ± 0.01	10.3
298.15	10.10 ± 0.13	-64.61 ± 3.52	62.20 ± 3.43	1.01 ± 0.01	15.4
323.15	12.05 ± 0.18	-80.24 ± 4.81	77.48 ± 4.69	1.01 ± 0.01	21.3
methanolic cadmium nitrate					
273.15	8.607 ± 0.022	-4.758 ± 0.072	2.953 ± 0.053	1.15 ± 0.07	2.7
298.15	10.29 ± 0.03	-9.394 ± 0.152	7.110 ± 0.128	1.08 ± 0.06	3.2
323.15	12.34 ± 0.04	-29.12 ± 0.61	26.25 ± 0.57	1.03 ± 0.02	4.6

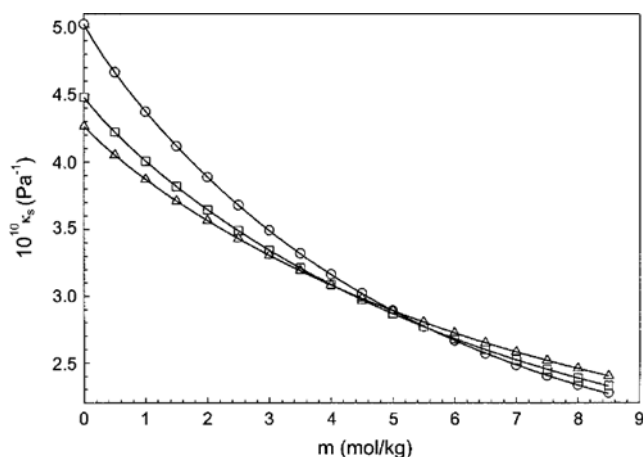


Fig. 1. A typical example of variation of isentropic compressibility isotherms with concentration for aqueous sodium bromide solutions at 273.15 K (open circles), 298.15 K (open squares) and 323.15 K (open triangles). Symbols and solid curves represent the experimental and calculated [from Eq. (3)] values respectively.

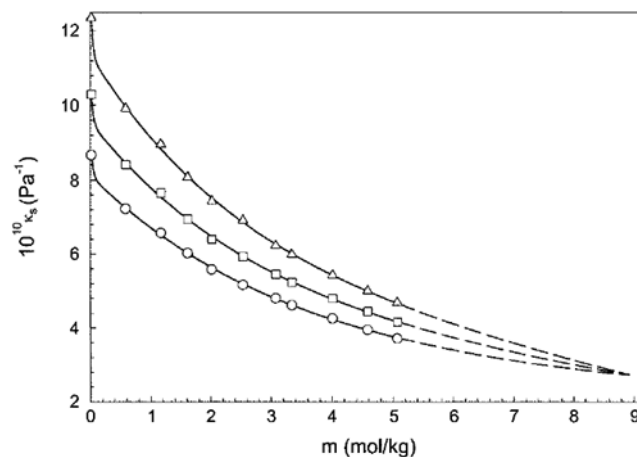


Fig. 2. A typical example of variation of isentropic compressibility isotherms with concentration for methanolic calcium nitrate solutions at 273.15 K (open circles), 298.15 K (open squares) and 323.15 K (open triangles). Symbols, solid curves and dotted curves represent the experimental, calculated [from Eq. (3)] and extrapolated values respectively.

molar enthalpy, refractive index [Angell and Bressel, 1972; Mahiuddin and Ismail, 1983, 1984; Mellor, 1952; Horne, 1972; Vaslow, 1969] etc. It must be envisaged that when the concentration of electrolytes in water medium is increased, there is a transition from the solvated ion due to the ion solvent interactions to the solvent-separated, the solvent-shared and the contact ion-pairs arising from the ion-ion interactions and is not restricted at a particular concentration but varies over a narrow range of concentration.

On increasing the salt concentration in the solution, the number

of free water molecules around the ion decreases gradually until a situation is reached where all the water molecules are involved in the primary hydration shell of the solute. The isentropic compressibility at that concentration becomes independent of temperature and assigned as critical isentropic compressibility, $\kappa_{s,h}$ (Table 2). Such a condition may be correlated with the saturation of the primary hydration shell since the water molecules are not compressed further and become independent of temperature. The lower value of $\kappa_{s,h}$ compared to water suggests strong ion-solvent interactions

Table 2. Critical concentration, critical isentropic compressibility ($K_{s,h}$) value and primary hydration number for aqueous and methanolic electrolytic solutions

Electrolytic solutions	Critical concentration (mol kg ⁻¹)	10 ¹⁰ $K_{s,h}$ (Pa ⁻¹)	Primary hydration number
LiBr+H ₂ O	10.8	2.61	5.1
NaBr+H ₂ O	5.1	2.88	10.9
KBr+H ₂ O	5.8	2.93	9.6
NaSCN+H ₂ O	3.0	3.12	18.5
KSCN+H ₂ O	4.8	3.18	11.6
LiNO ₃ +H ₂ O	3.8	3.34	14.6
NaNO ₃ +H ₂ O	4.5	3.04	12.3
Ca(NO ₃) ₂ +H ₂ O	2.7	2.92	20.6
Cd(NO ₃) ₂ +H ₂ O	2.5	2.93	22.2
Na ₂ S ₂ O ₃ +H ₂ O	2.0	2.64	27.8
NaSCN+CH ₃ OH	8.6	4.92	3.6
KSCN+CH ₃ OH	6.0	5.29	5.2
LiNO ₃ +CH ₃ OH	13.8	4.37	2.3
Ca(NO ₃) ₂ +CH ₃ OH	8.9	2.72	3.5
Cd(NO ₃) ₂ +CH ₃ OH	7.1	3.23	4.4

in aqueous solutions. On the other hand, in methanolic solutions the isentropic compressibility isotherms decrease smoothly with increase in concentration without any convergent within the limit of solubility. Methanolic solutions are more compressible than that of aqueous solutions at a particular concentration and interactions are found to be less compared to the aqueous solutions. This is attributed to the weak, slower and nonlinear solvation dynamics of ions in methanolic media [Roy and Bagchi, 1993, 1994].

The isentropic compressibility of aqueous electrolytic solutions is due to about 64% configurational and 36% vibrational compressibility [Davis (Jr) and Litovitz, 1965; Eisenberg and Kauzman, 1969]. In dilute solution the isentropic compressibility is predominantly governed by the configurational compressibility, whereas in the concentrated solutions it is due to the vibrational compressibility. At the concentration where the isotherm converges, water structure has totally collapsed since all the water molecules take part in the solvation. As a result, the isentropic compressibility isotherms converge at this concentration. Beyond this concentration, vibrational compressibility dominates over configurational which increase with the increase in temperature at a particular concentration due to the thermal motion. Owing to this fact, reversibility of the isentropic compressibility isotherms occurs. In methanolic solutions the isentropic compressibility increases with the increase in temperature at a particular concentration. Therefore, it may be presumed that the vibrational compressibility predominantly contributes to the isentropic compressibility within the concentration and temperature range of the study. Many authors have tried to compute the hydration numbers (n_h) from the compressibility data based on the Passynskii model [Bockris and Saluja, 1972]:

$$n_h = x_1/x_2(1 - \kappa_s/K_{s,1}) \quad (4)$$

In Eq. (4), x_1 and x_2 are mole fractions of solvent and solute in the solution. This model is based on the assumption that the solvent

molecules solvating ions were fully compressed by the electrical forces of ions. As a result the compressibility of the solvent molecules in the hydration shell is assumed to be zero. This is an approximation only.

The variation of isothermal compressibility (κ_T) of water molecules with pressure (P) and the electric field (E) due to electrostriction can be represented by using the relation [Marcus, 1985]:

$$\kappa_T = (\epsilon_0/4\pi)E(dE/dP)(d\epsilon/dP) \quad (5)$$

In Eq. (5), ϵ is the pressure-dependent dielectric constant and ϵ_0 is the free permittivity. Bockris and Saluja [1972] calculated the pressure experienced by the water molecules due to ion-dipole interaction is 10^9 - 10^{10} Pa and justified the zero compressibility of the hydrated water. Their error lies in consideration of total electrostatic pressure as effective pressure. Since according to this model [Marcus, 1985], the total electrostatic pressure consists of two parts, tractive and contractive. The tractive part prevents the flow of liquid in the hydration shell, whereas the contractive part contributes to the compressibility of the solvent molecules. As a result, practically 10^9 - 10^{10} Pa pressure is not experienced by the solvent molecules due to electrostatic interaction. Therefore, the term P in Eq. (5) cannot be considered as the effective pressure due to electrostatic interaction. As a result, the assumption of zero compressibility of the solvent molecules of the hydration shell cannot be confirmed by the experimental facts.

In order to improve the Passynskii equation, the Onori [1988] model based on effective medium theory [Sheng, 1983] is considered. In this theory, the isentropic compressibility of a complex medium is considered as a function of the relative volumes of constituent phases. The solution is described by parameters pertaining to the pure phases, free solvent and hydrated solvent with a compressibility of $K_{s,1}$ and $K_{s,h}$ respectively. In the present case the acoustic wave length is several orders of magnitude larger than the size of hydrated and free water. Therefore, according to this theory, the compressibility of the solutions can be expressed as:

$$\kappa_s = \phi_1 K_{s,1} + \phi_h K_{s,h} \quad (6)$$

where ϕ_1 and ϕ_h are the volume fractions of free water and hydrated water, respectively, and can be represented by

$$\phi_1 = (x_1 - x_2 n_h) V_1 / V \quad (7)$$

$$\phi_h = x_2 V_h / V \quad (8)$$

In Eqs. (7) and (8), V is the molar volume of solution, V_1 is molar volume of bulk water and V_h is the molar volume of hydrated shell. From Eqs. (6), (7) and (8)

$$\kappa_s V = (x_1 - x_2 n_h) K_{s,1} V_1 + x_2 K_{s,h} V_h \quad (9)$$

The apparent molal volume (V_ϕ) and conventional apparent molal isentropic compressibility ($K_{s,\phi}$) [Blandamer, 1998] can be represented as:

$$V_\phi = (V - x_1 V_1) / x_2 \quad (10)$$

$$K_{s,\phi} = (\kappa_s V - x_1 \kappa_{s,1} V_1) / x_2 \quad (11)$$

and rearranging, the following empirical equation:

$$n_h = [K_{s,\phi} - K_{s,h} V_\phi] / [V_1 (K_{s,h} - K_{s,1})] \quad (12)$$

is obtained. With the assumption that the hydrated water molecules in the primary hydration shell are incompressible (i.e., $K_{s,h}=0$), Eq. (12) can be reduced to the Passynskii equation [Bockris and Saluja, 1972]. Eq. (12) has a concentration limitation in its application for estimating the hydration number of the solute [Onori, 1988]. The estimated primary hydration numbers are found to be in good agreement with the available number of water molecules per mole of solute at the corresponding concentration. These values are in good agreement with the literature values [Hinton and Amis, 1971; Ohtaki and Radnai, 1993].

On the other hand, the isentropic compressibility isotherms of methanolic solution do not converge within the concentration and temperature range of solubility. However, on extrapolation the isentropic compressibility isotherms converge beyond the experimental concentration range (Fig. 2). By using the extrapolated $K_{s,h}$ values and Eq. (12), hydration numbers in methanolic solutions can be evaluated. These values are much smaller than that of aqueous solution.

CONCLUSIONS

The present investigations show that the study of isentropic compressibility of electrolytic solutions can provide reliable information regarding the ion-solvent and on-ion interactions in electrolytic solutions. In aqueous electrolytic solutions the ion-solvent interactions dominate up to a certain concentration beyond which a transition from ion-solvent to ion-ion interactions occurs leading to the formation of ion-pairs (solvent-separated, solvent-shared and contact). At this transition concentration, the primary hydration shell of the solute is completed, the structure of the bulk water collapses and the water molecules are rigidly bound in the primary hydration shell of the solute due to the strong ion-solvent interactions. At this concentration, the primary hydration numbers become equal to the number of available water molecules per mole of solute. This situation is reflected in the convergent point of the isentropic compressibility versus concentration plots at different temperatures. The primary hydration shell attains some critical isentropic compressibility value and is found to be independent of temperature. On the other hand, the ion-solvent interaction of electrolyte in methanol is weak. Therefore, the primary hydration shell of the electrolyte in methanol medium is not rigid. As a result the isentropic compressibility isotherms do not converge within its solubility range.

The configurational compressibility contributes to the isentropic compressibility up to a certain concentration at which the isentropic compressibility isotherms converge. Beyond the transition concentration, the vibrational compressibility dominates and contributes to the total isentropic compressibility in aqueous electrolytic solutions. The vibrational compressibility increases with the increase in temperature due to the thermal motion at a particular concentration resulting in reversibility of the isentropic compressibility isotherms. Whereas in methanolic solution it is the vibrational compressibility that controls the isentropic compressibility.

The general assumption of zero compressibility of the primary hydration shell is found to be incorrect. A simple expression has been derived for estimating the hydration numbers of the electrolyte in its solutions. The hydration numbers agree well with the reported values.

NOMENCLATURE

a	: parameter in Eq. (2) [Pa^{-1}]
A	: parameter in Eq. (3) [Pa^{-1}]
b	: parameter in Eq. (2) [$\text{Pa}^{-1} \text{K}^{-1}$]
B	: parameter in Eq. (3) [$\text{Pa}^{-1} \text{kg mol}^{-1}$]
c	: parameter in Eq. (2) [$\text{Pa}^{-1} \text{K}^{-d}$]
C	: parameter in Eq. (3) [$\text{Pa}^{-1} \text{kg}^D \text{mol}^{-D}$]
d	: constant in Eq. (2)
D	: constant in Eq. (3)
E	: electrostatic field [N C^{-1}]
m	: molality [mol kg^{-1}]
n_h	: hydration number
P	: pressure [Pa]
u	: speed of sound [m s^{-1}]
V	: molar volume of solution [$\text{m}^3 \text{mol}^{-1}$]
x_1	: mole fraction of solvent
x_2	: mole fraction of solute

Greek Letters

ϵ	: dielectric constant of solvent
ϵ_0	: free permittivity [$\text{C}^2 \text{N}^{-1} \text{m}^{-2}$]
ϕ_1	: volume fraction of free solvent
ϕ_h	: volume fraction of hydrated solvent
K_s	: isentropic compressibility of solution [Pa^{-1}]
K_T	: isothermal compressibility of solvent [Pa^{-1}]
$K_{s,1}$: isentropic compressibility of solvent [Pa^{-1}]
$K_{s,h}$: isentropic compressibility of primary hydration shell [Pa^{-1}]
ρ	: density [kg m^{-3}]

ACKNOWLEDGEMENTS

Financial support from the Department of Science & Technology and Council of Scientific & Industrial Research, New Delhi, India is gratefully acknowledged.

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