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The Adsorption Theory of Electrolytes and the Volumetric Properties of Some Nitrate-Water Systems. From Fused Salts to Dilute Solutions

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Summary. On the basis of the *Brunauer-Emmet-Teller* adsorption model extended by *Stokes* and *Robinson* to concentrated electrolyte solutions, from the *Stokes-Robinson* equation for water activity, and from the *Abraham* equation for electrolyte activity, *Ally* and *Braunstein* have derived equations for the partial excess molar volumes of salt and water in salt-water systems. In their equations, only one *BET* parameter is considered to be pressure dependent. In the present publication, complete equations are proposed, taking into account the dependence of both *BET* constants on pressure. These equations are tested successfully with nitrate-water systems containing mono and divalent cations over a concentration range from fused salts to water: [0.500 $LiNO_3$–0.500 KNO_3+H_2O], [0.467 $TlNO_3$–0.214 $CsNO_3$–0.319 $Cd(NO_3)_2+H_2O$], [$N(C_2H_5)_4NO_3+H_2O$], [0.515 $AgNO_3$–0.485 $TlNO_3+H_2O$], and [$AgNO_3$–$TlNO_3$–$M(NO_3)_n+H_2O$] (M=Na, K, Cs, Cd, Ca; $x(AgNO_3)/x(TlNO_3)$ as in the preceding system $x(M)$ being varied from 0.025 to 0.125 depending on the cation). Additivity rules which involve the partial derivatives of the *BET* constants with respect to pressure are also proposed.

Keywords. Molten salts; Nitrates; Hydrate melts; Aqueous solutions; BET model; Molar volumes; Partial excess molar volumes.

Adsorptionstheorie der Elektrolyte und volumetrische Eigenschaften einiger Nitrat-Wasser-Systeme. Von Salzschmelzen zu verdünnten Lösungen

Zusammenfassung. Auf der Basis des *Brunauer-Emmet-Teller*-Modells, von *Stokes* und *Robinson* für konzentrierte Elektrolytlösungen erweitert, sowie ausgehend von den Gleichungen nach *Stokes-Robinson* für die Aktivität von Wasser und nach *Abraham* für die *Aktivität* von Elektrolyten, leiteten *Ally* und *Braunstein* Beziehungen für die partiellen molaren Zusatzvolumina von Salz und Wasser in Salz-Wasser-Systemen her, in denen nur ein *BET*-Parameter als druckabhängig behandelt wird. In der vorliegenden Publikation werden vollständige Gleichungen vorgestellt, die die Druckabhängigkeit beider *BET*-Konstanten berücksichtigen und die erfolgreich an Nitrat-Wasser-Systemen getestet wurden, die mono- und divalente Kationen enthalten und deren Konzentrationsbereich von Salzschmelzen bis zu reinem Wasser reicht: [0.500 $LiNO_3$–0.500 KNO_3+H_2O], [0.467 $TlNO_3$–0.214 $CsNO_3$–0.319 $Cd(NO_3)_2+H_2O$], [$N(C_2H_5)_4NO_3+H_2O$], [0.515 $AgNO_3$–0.485 $TlNO_3+H_2O$] und [$AgNO_3$–$TlNO_3$–$M(NO_3)_n+H_2O$] (M=Na, K, Cs, Cd, Ca; $x(AgNO_3)/x(TlNO_3)$ wie im vorhergehenden System: $x(M)$ je nach Kation zwischen 0.025 und 0.125). Zusätzlich werden Additivitätsregeln, die sich auf partielle Ableitungen der *BET*-Parameter bezüglich des Drucks beziehen, vorgestellt.

Introduction

For practical applications and theoretical investigations, concentrated aqueous solutions and hydrate melts have been the objects of intense attention, and their study is seriously expanding. Due to concern about pollution and security problems, areas of technological interests include energy storage and generation, *e.g.* solar energy storage, exploitation of geothermal energy sources, and molten salts based fluids in nuclear reactors which could contain more or less water. With regard to theoretical investigations, it has been suggested now and then that melts containing water as a solute could be the right starting point for a deeper understanding of the behaviour of very ionic solutions. From two recent critical reviews of current theories concerning concentrated electrolytes by *Ally* and *Braunstein* [1, 2], it appears that the concept of ionic quasi-lattice is the most promising concept. Closely related to this concept is the adsorption theory of electrolyte solutions which was initiated by *Stokes* and *Robinson* [3] as an extension of the theory of gas adsorption on solid surfaces developed by *Brunauer*, *Emmet*, and *Teller* [4].

Within the framework of this theory, *Ally* and *Braunstein* [1] have proposed interesting equations for calculating the partial excess molar volumes of salt and water in salt-water systems. They have verified these equations with the salt-water systems [$LiBr+H_2O$] and [0.606 $LiNO_3$–0.218 KNO_3–0.176 $NaNO_3+H_2O$]. In this abbreviated notation, the numbers before the chemical formula represent the salt mole fractions x_i of component i in the anhydrous melt. Their study was done at different temperatures and for water mole fractions x_w over the interval from 0.76 to 0.99 for the LiBr solutions and from 0.6 to 0.99 for the ternary salt solutions.

The aim of the present work was first to test further these equations with other salt-water systems over larger water concentration ranges. In the course of our study, we derived equations for the partial excess molar volumes more complete than those previously proposed [1] and made new observations confirming the value of the adsorption theory as a powerful tool.

In order to provide a solid experimental basis, we selected salt-water systems for which quite abundant data on molar volume and water activity were accumulated. These systems are:

1) [0.500 $LiNO_3$–0.500 KNO_3+H_2O]
2) [0.467 $TlNO_3$–0.214 $CsNO_3$–0.319 $Cd(NO_3)_2+H_2O$]
3) [$N(C_2H_5)_4NO_3+H_2O$]
4) [0.515 $AgNO_3$–0.485 $TlNO_3+H_2O$]
5) [$AgNO_3$–$TlNO_3$–$M(NO_3)_n+H_2O$] (M=Na, K, Cs, Cd, Ca; $x(AgNO_3)/x(TlNO_3)$ as in the preceding system; $x(M)$ varying from 0.025 to 0.125 depending on the cation).

Throughout this paper, "salt" in the context of salt-water systems designates a single salt or a mixture of salts whose composition is kept constant so that it can be thermodynamically treated as a single salt.

Basic Equations for the Volumetric Properties

General equations independent from any model

The molar volume of the salt water-system, V, is related to its density ρ by

$$V = \frac{x_s \sum_i x_i M_i + x_w M_w}{\rho} \tag{1}$$

where M_i is the molar mass of the salt i, M_w the molar mass of water, x_i the mole fraction of the salt i in the anhydrous salt system, and x_s the mole fraction of salt in the salt-water system.

The excess molar volume of the solution V^{ex} is defined by

$$V^{ex} = V - V^{id} \tag{2}$$

where V^{id} is the ideal molar volume given by the expression

$$V^{id} = x_s V_s^o + x_w V_w^o \tag{3}$$

in which V_s^o is the molar volume of the anhydrous salt and V_w^o is the molar volume of pure water.

The molar volume V may be expressed as a function of the partial molar volume of salt ($\bar{V}_s$) and the partial molar volume of water ($\bar{V}_w$):

$$V = x_s \bar{V}_s + x_w \bar{V}_w \tag{4}$$

The partial excess molar volume of salt ($\bar{V}_s^{ex}$) and water ($\bar{V}_w^{ex}$) are given respectively by

$$\bar{V}_s^{ex} = \bar{V}_s - V_s^o \tag{5}$$

$$\bar{V}_w^{ex} = \bar{V}_w - V_w^o \tag{6}$$

The partial excess molar volumes are related to the excess molar volume of the solution by

$$V^{ex} = x_s \bar{V}_s^{ex} + x_w \bar{V}_w^{ex} \tag{7}$$

with

$$\bar{V}_w^{ex} = \mathrm{R}T\left(\frac{\partial \ln a_w}{\partial P}\right)_{T,x_w} \tag{8}$$

$$\bar{V}_s^{ex} = \mathrm{R}T\left(\frac{\partial \ln a_s}{\partial P}\right)_{T,x_s} \tag{9}$$

where R is the gas constant, T the temperature, P the pressure, a_w the water activity, and a_s the salt activity.

Equations for $\bar{V}_s^{ex}$ and $\bar{V}_w^{ex}$ from the BET model with one volumetric parameter ε'

On the basis of the *BET* model [4], *Ally* and *Braunstein* [1] have proposed the following equations for the partial excess molar volumes of water and salt:

$$\bar{V}_{\mathrm{w}}^{\mathrm{ex}} = \epsilon' \Omega_{\mathrm{w}\epsilon} \tag{10}$$

$$\bar{V}_{\mathrm{s}}^{\mathrm{ex}} = \epsilon' \Omega_{\mathrm{s}\epsilon} \tag{11}$$

where

$$\epsilon' = \left(\frac{\partial \epsilon}{\partial P}\right)_{\mathrm{T},x_{\mathrm{w}}} \tag{12}$$

$$\Omega_{\mathrm{w}\epsilon} = \frac{c(a_{\mathrm{w}} - 1 + rR_{\mathrm{s}})}{c(1 - rR_{\mathrm{s}}) - 2a_{\mathrm{w}}(c-1) - 2} \tag{13}$$

$$\Omega_{\mathrm{s}\epsilon} = \frac{rc(r(\lambda - 1) + R_{\mathrm{w}})}{r[c - 2 - 2\lambda(c-1)] - cR_{\mathrm{w}}} \tag{14}$$

$$R_{\mathrm{w}} = \frac{x_{\mathrm{w}}}{x_{\mathrm{s}}} \tag{15}$$

$$R_{\mathrm{s}} = \frac{x_{\mathrm{s}}}{x_{\mathrm{w}}} \tag{16}$$

The parameter ϵ is given by

$$\epsilon = E_{\mathrm{L}} - E \tag{17}$$

in which E_{L} is the molar energy level of water where the nearest neighbours are only water molecules as in pure water and E is the molar energy level of water on sites close to the ions.

The parameters c and r in Eqs. (13) and (14) are usually called the *BET* constants because they were introduced by *Stokes* and *Robinson* [3] in their adaptation of the *BET* model [4] to concentrated electrolyte solutions. The parameter r is the number of moles of available sites per mole of salt where water is at the molar energy level E. The parameter c is related to ϵ by

$$c = \exp\left(\frac{\epsilon}{\mathrm{R}T}\right) \tag{18}$$

In Eq. (13) the water activity a_{w} is given by the *Stokes-Robinson* equation [3]:

$$\frac{a_{\mathrm{w}}(1 - x_{\mathrm{w}})}{x_{\mathrm{w}}(1 - a_{\mathrm{w}})} = \frac{1}{cr} + \frac{(c-1)}{cr} a_{\mathrm{w}} \tag{19}$$

In Eq. (14), the parameter λ is given by the *Abraham* equation [5]:

$$\frac{\lambda(1 - x_{\mathrm{s}})}{x_{\mathrm{s}}(1 - \lambda)} = \frac{r}{c} + \frac{r(c-1)}{c}\lambda \tag{20}$$

The parameter λ is related to the salt activity a_{s} by

$$\lambda^{\mathrm{r}} = a_{\mathrm{s}} \tag{21}$$

Equations for $\bar{V}_s^{ex}$ and $\bar{V}_w^{ex}$ from the BET model with two volumetric parameters ϵ' and r'

In the derivation of Eqs. (10) and (11), *Ally* and *Braunstein* [1] assumed arbitrarily that the pressure dependence in the model is entirely contained in the energy parameter ϵ. Now, we will assume that not only the energy parameter ϵ, but also the structural parameter r is pressure dependent. In this case, $\bar{V}_w^{ex}$ can be derived by the following treatment.

From a combination of Eq. (19) and (16), we obtain:

$$-(c-1)a_w^2 + (c-2-crR_s)a_w + 1 = 0 \tag{22}$$

Differentiating with respect to P at constant T and x_w, Eq. (22) gives

$$\left(\frac{\partial \ln a_w}{\partial P}\right)_{T,x_w} = \frac{(a_w - 1 + rR_s)\left(\frac{\partial c}{\partial P}\right)_{T,x_w} + cR_s\left(\frac{\partial r}{\partial P}\right)_{T,x_w}}{c(1-rR_s) - 2a_w(c-1) - 2} \tag{23}$$

From Eqs. (12) and (18), we have

$$\left(\frac{\partial c}{\partial P}\right)_{T,x_w} = \frac{c}{\mathrm{R}T}\epsilon' \tag{24}$$

Setting

$$\left(\frac{\partial r}{\partial P}\right)_{T,x_w} = r' \tag{25}$$

and taking into consideration Eqs. (23) and (24), Eq. (8) becomes

$$\bar{V}_w^{ex} = \frac{(a_w - 1 + rR_s)c\epsilon' + cR_sRTr'}{c(1-rR_s) - 2a_w(c-1) - 2} \tag{26}$$

Then, $\bar{V}_w^{ex}$ can be expressed as a sum of two parts, one pertaining to ϵ' and another pertaining to r'

$$\bar{V}_w^{ex} = \epsilon'\Omega_{w\epsilon} + r'\Omega_{wr} \tag{27}$$

in which

$$\Omega_{w\epsilon} = \frac{c(a_w - 1 + rR_s)}{c(1-rR_s) - 2a_w(c-1) - 2} \tag{28}$$

$$\Omega_{wr} = \frac{cR_s\mathrm{R}T}{c(1-rR_s) - 2a_w(c-1) - 2} \tag{29}$$

Now, with regard to $\bar{V}_s^{ex}$, the treatment is as follows: from Eq. (21) we can write

$$\left(\frac{\partial \ln a_s}{\partial P}\right)_{T,x_s} = r\left(\frac{\partial \ln\lambda}{\partial P}\right)_{T,x_s} + \ln\lambda\left(\frac{\partial r}{\partial P}\right)_{T,x_s} \tag{30}$$

From Eq. (20) and Eq. (15), we obtain:

$$-r(c-1)\lambda^2 + [r(c-1) - cR_w - r]\lambda + r = 0 \tag{31}$$

Differentiating with respect to P at constant T and x_s, Eq. (31) gives

$$\left(\frac{\partial \ln\lambda}{\partial P}\right)_{T,x_s} = \frac{\lambda^2\left[r\left(\frac{\partial c}{\partial P}\right)_{T,x_s} + (c-1)\left(\frac{\partial r}{\partial P}\right)_{T,x_s}\right]}{r\lambda[c-2-2\lambda(c-1)] - c\lambda R_w} + \frac{-\lambda\left[(r-R_w)\left(\frac{\partial c}{\partial P}\right)_{T,x_s} + (c-2)\left(\frac{\partial r}{\partial P}\right)_{T,x_s}\right] - \left(\frac{\partial r}{\partial P}\right)_{T,x_s}}{r\lambda[c-2-2\lambda(c-1)] - c\lambda R_w} \quad (32)$$

From Eqs. (24), (25), (30), and (32), Eq. (9) becomes

$$\bar{V}_s^{ex} = \frac{\lambda^2 r^2 c\epsilon' + \lambda^2(c-1)rRTr' - \lambda(r-R_w)rc\epsilon'}{r\lambda[c-2-2\lambda(c-1)] - c\lambda R_w} + \frac{-\lambda(c-2)rRTr' - rRTr'}{r\lambda[c-2-2\lambda(c-1)] - c\lambda R_w} + r'RT\ln\lambda \quad (33)$$

Then, $\bar{V}_s^{ex}$ can be rearranged in a sum of two parts, one pertaining to ϵ' and another pertaining to r':

$$\bar{V}_s^{ex} = \epsilon'\Omega_{s\epsilon} + r'\Omega_{sr} \quad (34)$$

in which

$$\Omega_{s\epsilon} = \frac{rc[r(\lambda-1)+R_w]}{r[c-2-2\lambda(c-1)] - cR_w} \quad (35)$$

$$\Omega_{sr} = \frac{RTr[(c-1)\lambda^2 - (c-2)\lambda - 1]}{r\lambda[c-2-2\lambda(c-1)] - c\lambda R_w} + RT\ln\lambda \quad (36)$$

It should be noticed that utilization of Eqs. (27) and (34) is a convenient method to evaluate the partial excess molar volumes instead of performing differentiation of the function $V^{ex} = f(x_w)$ which generally involves some uncertainty. In particular, the partial excess molar volume of water at infinite dilution in the molten salt $\bar{V}_{w\infty}^{ex}$ can be readily calculated by the following simple limiting form of Eq. (27):

$$(\bar{V}_w^{ex})_{x_w \to 0} = \bar{V}_{w\infty}^{ex} = -\epsilon' - \frac{RTr'}{r} \quad (37)$$

Determination of the Volumetric Parameters; Discussion of Results

The parameters r and c were determined by fitting Eq. (19) to know values of a_w. The parameters ϵ' and r' were determined by fitting Eq. (7), in which $\bar{V}_s^{ex}$ and $\bar{V}_w^{ex}$ are expressed by Eqs. (27) and (34), to the experimental curve $V^{ex} = f(x_w)$. Knowing the values of r, c, ϵ', and r', the values of $\bar{V}_s^{ex}$ and $\bar{V}_w^{ex}$ could be calculated by means of Eqs. (27) and (34). We performed nonlinear least-squares fittings using the *Marquardt* method (TK Solver Plus Software).

The densities ρ of the [0.500 $LiNO_3$–0.500 KNO_3 + H_2O] system required for the calculation of the molar volumes by means of Eq. (1) were measured by a pycnometric method the technical details of which are given elsewhere [6]. The results are given in Table 1 as functions of the temperature and the water mole fraction. The molar volumes were linearly fitted to allow extrapolations and/or interpolations to chosen temperatures where the water activities are available.

Table 1. Density ρ and molar volume V of the [0.500 $LiNO_3$–0.500 KNO_3 + H_2O] system as functions of the water mode fraction x_w and the temperature T

$x_w = 0$			$x_w = 0.100$		
T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)	T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)
430.9	1.947	43.67	409.9	1.926	40.67
435.8	1.944	43.75	417.3	1.920	40.79
440.2	1.940	43.82	424.2	1.913	40.93
448.0	1.934	43.97	435.8	1.904	41.13
457.0	1.928	44.11	445.0	1.896	41.30
$x_w = 0.200$			$x_w = 0.300$		
T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)	T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)
393.6	1.892	37.85	385.0	1.847	35.15
405.3	1.882	38.05	395.6	1.837	35.33
414.2	1.877	38.15	405.0	1.832	35.44
423.4	1.870	38.31	414.2	1.823	35.61
434.7	1.860	38.50	426.0	1.814	35.79
$x_w = 0.400$			$x_w = 0.500$		
T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)	T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^{-6}$ ($m^3 \cdot mol^{-1}$)
383.6	1.785	32.61	378.7	1.712	30.09
395.6	1.777	32.77	383.6	1.709	30.14
405.0	1.767	32.95	387.4	1.706	30.19
413.9	1.761	33.06	395.8	1.698	30.34
418.8	1.758	33.11	405.0	1.691	30.46
			413.6	1.686	30.55
$x_w = 0.600$			$x_w = 0.700$		
T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)	T (K)	$\rho \times 10^{-3}$ ($kg \cdot m^{-3}$)	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)
368.2	1.631	27.48	355.3	1.526	24.97
371.9	1.628	27.53	356.6	1.524	25.00
378.8	1.621	27.64	365.8	1.515	25.15
382.7	1.619	27.68	371.9	1.511	25.22
387.3	1.616	27.73	378.4	1.506	25.30
392.2	1.611	27.82	385.3	1.502	25.37

Table 1. (*Continued*)

$x_w = 0.800$			$x_w = 0.900$		
T (K)	$\rho \times 10^{-3}$ $(\mathrm{kg \cdot m^{-3}})$	$V \times 10^6$ $(\mathrm{m^3 \cdot mol^{-1}})$	T (K)	$\rho \times 10^{-3}$ $(\mathrm{kg \cdot m^{-3}})$	$V \times 10^6$ $(\mathrm{m^3 \cdot mol^{-1}})$
350.7	1.386	22.66	344.4	1.210	20.42
360.9	1.378	22.79	350.7	1.204	20.52
371.7	1.369	22.94	357.4	1.200	20.59
376.7	1.364	23.02	360.8	1.198	20.62
380.4	1.362	23.06	365.8	1.193	20.71
			371.4	1.189	20.78

$x_w = 0.980$		
T (K)	$\rho \times 10^{-3}$ $(\mathrm{kg \cdot m^{-3}})$	$V \times 10^6$ $(\mathrm{m^3 \cdot mol^{-1}})$
343.4	1.029	18.80
351.9	1.022	18.92
360.5	1.017	19.02
365.6	1.014	19.07
371.4	1.010	19.15

The water activity values for this system were those provided by *Simonson* [7] at four temperatures (373, 393, 413, and 433 K) over the whole water concentration range. As an illustration of the validity of the *BET* model for this system at 393 K, Fig. 1 shows how well the curve calculated by means of Eq. (19) is in agreement with the water activity data over practically the whole concentration range.

The molar volumes and water activity values for the [0.467 $TlNO_3$–0.214 $CsNO_3$–0.319 $Cd(NO_3)_2$ + H_2O] system as functions of the water mole fraction at 368, 376, and 386 K are available from a previous work [8]. It was found that the *BET* model is valid for this system over practically the whole concentration range.

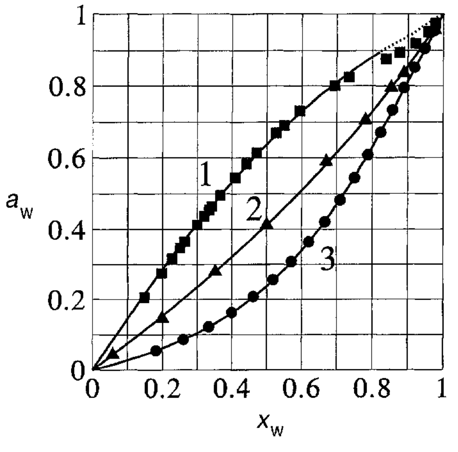

Fig. 1. Water activity a_w as a function of the water mole fraction x_w; 1: [0.515 $AgNO_3$–0.485 $TlNO_3$+H_2O] at 372 K (Ref. [10]); 2: [$N(C_2H_5)_4NO_3$+H_2O] at 298 K (Ref. [9]); 3: [0.500 $LiNO_3$–0.500 KNO_3+H_2O] at 393 K (Ref. [7])

For the [$N(C_2H_5)_4NO_3+H_2O$] system, the molar volumes and water activities have been determined as functions of the water mole fraction at 298 K by *Biquard*, *Letellier*, and *Fromon* [9]. It can be seen from Fig. 1 that this system also obeys the *BET* model over practically the whole concentration range.

Concerning the systems [0.515 $AgNO_3$–0.485 $TlNO_3$ + H_2O] and [$AgNO_3$–$TlNO_3$–$M(NO_3)_n$ + H_2O] where M = Na, K, Cs, Cd, or Ca, the molar volumes and water activities at 372 K were those provided by *Trudelle-Abraham* [10] as functions of the water mole fraction. For M = Na, K, or Cs, the water activities have been measured up to $x_w \approx 0.6$, and for the other systems up to $x_w \approx 0.97$. For these latter systems, the validity range of the *BET* model depends on the concentration of the added cation (Cd or Ca). For example, for the system [0.515 $AgNO_3$–0.485 $TlNO_3$+H_2O], the validity range extends up to $x_w \approx 0.8$, as shown in Fig. 1, whereas it covers practically the whole concentration range when x (Cd) = 0.125.

Values of c, r, ϵ, r', and ϵ' are given in Table 2 for the above-mentioned systems at given temperatures. The experimental and calculated values of the molar volumes and excess molar volumes of the systems are listed in Tables 3 to 11 as functions of the water mole fraction at given temperatures, along with the values of $\bar{V}_w^{ex}$ and $\bar{V}_s^{ex}$ calculated by means of Eqs. (27) and (34). The molar volumes of pure

Table 2. The parameters r, c, ϵ, r', and ϵ' for some nitrate-water systems

Salt System	T (K)	r	c	$\epsilon \times 10^{-3}$ ($J \cdot mol^{-1}$)	$r' \times 10^9$ (Pa^{-1})	$\epsilon' \times 10^6$ ($m^3 \cdot mol^{-1}$)
[0.500 $LiNO_3$–0.500 KNO_3]	373	1.77	2.62	+2.99	0.10	+1.76
	393	1.87	2.21	+2.59	0.16	+1.71
	413	1.93	1.93	+2.26	0.31	+1.50
	433	1.92	1.83	+2.17	0.56	+1.15
[0.467 $TlNO_3$–0.214 $CsNO_3$–0.319 $Cd(NO_3)_2$	368	1.36	2.32	+2.57	0.70	+1.55
	376	1.39	2.20	+2.46	0.52	+2.14
	383	1.42	2.09	+2.35	0.51	+2.20
[$N(C_2H_5)_4NO_3$]	298	1.54	0.88	−0.31	0.76	+0.10
[0.515 $AgNO_3$–0.485 $TlNO_3$]	372	0.51	1.37	+0.97	0.58	−1.99
[0.502 $AgNO_3$–0.473 $TlNO_3$–0.025 $NaNO_3$]	372	0.52	1.52	+1.29	0.53	−1.68
[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 $NaNO_3$]	372	0.55	1.51	+1.27	0.55	−1.63
[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 KNO_3]	372	0.52	1.44	+1.13	0.57	−2.24
[0.502 $AgNO_3$–0.473 $TlNO_3$–0.025 $CsNO_3$]	372	0.49	1.48	+1.21	0.55	−2.12
[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 $CsNO_3$]	372	0.50	1.43	+1.11	0.56	−2.20
[0.476 $AgNO_3$–0.449 $TlNO_3$–0.075 $CsNO_3$]	372	0.51	1.38	+1.00	0.57	−2.20
[0.464 $AgNO_3$–0.436 $TlNO_3$–0.100 $Cs(NO_3)$]	372	0.52	1.33	+0.88	0.53	−1.79
[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 $Cd(NO_3)_2$]	372	0.66	1.78	+1.78	0.58	−0.64
[0.476 $AgNO_3$–0.449 $TlNO_3$–0.075 $Cd(NO_3)_2$]	372	0.74	1.98	+2.11	0.62	−0.47
[0.464 $AgNO_3$–0.436 $TlNO_3$–0.100 $Cd(NO_3)_2$]	372	0.81	2.20	+2.44	0.60	+0.09
[0.451 $AgNO_3$–0.424 $TlNO_3$–0.125 $Cd(NO_3)_2$]	372	0.90	2.27	+2.54	0.61	+0.45
[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 $Ca(NO_3)_2$]	372	0.65	1.92	+2.02	0.61	−1.17
[0.476 $AgNO_3$–0.449 $TlNO_3$–0.075 $Ca(NO_3)_2$]	372	0.73	2.07	+2.25	0.63	−0.90
[0.464 $AgNO_3$–0.436 $TlNO_3$–0.100 $Ca(NO_3)_2$]	372	0.80	2.28	+2.54	0.60	−0.35

Table 3. Molar volume V, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$, and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water molar fraction x_w and the temperature T for the [0.500 $LiNO_3$–0.500 KNO_3+H_2O] system

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
			$T=373$ K			
0	42.68	42.68	0	0	−1.935	0
0.100	39.99	40.10	−0.30	−0.19	−1.846	−0.005
0.200	37.53	37.53	−0.37	−0.37	−1.736	−0.025
0.300	34.97	34.99	−0.55	−0.53	−1.590	−0.074
0.400	32.46	32.46	−0.67	−0.67	−1.393	−0.182
0.500	30.01	29.97	−0.73	−0.77	−1.133	−0.398
0.600	27.55	27.55	−0.80	−0.80	−0.814	−0.793
0.700	25.23	25.20	−0.73	−0.76	−0.481	−1.415
0.800	22.96	22.96	−0.62	−0.62	−0.216	−2.212
0.900	20.80	20.82	−0.38	−0.36	−0.062	−3.081
0.980	19.17	19.19	−0.11	−0.09	−0.007	−4.011
1	18.80	18.80	0	0	0	–
			$T=393$ K			
0	43.02	43.02	0	0	−1.989	0
0.100	40.36	40.43	−0.27	−0.20	−1.898	−0.011
0.200	37.84	37.86	−0.40	−0.38	−1.782	−0.030
0.300	35.28	35.30	−0.56	−0.54	−1.631	−0.082
0.400	32.75	32.77	−0.70	−0.68	−1.436	−0.182
0.500	30.28	30.27	−0.78	−0.79	−1.188	−0.392
0.600	27.83	27.83	−0.84	−0.84	−0.886	−0.771
0.700	25.49	25.47	−0.79	−0.81	−0.563	−1.369
0.800	23.24	23.22	−0.65	−0.67	−0.281	−2.226
0.900	21.06	21.08	−0.43	−0.41	−0.092	−3.302
0.980	19.42	19.47	−0.16	−0.11	−0.012	−4.687
1	19.10	19.10	0	0	0	–
			$T = 413$ K			
0	43.36	43.36	0	0	−2.051	0
0.100	40.72	40.77	−0.25	−0.20	−1.960	−0.005
0.200	38.16	38.19	−0.42	−0.39	−1.846	−0.026
0.300	35.59	35.62	−0.60	−0.57	−1.701	−0.075
0.400	33.04	33.08	−0.75	−0.71	−1.517	−0.176
0.500	30.56	30.58	−0.85	−0.83	−1.284	−0.369
0.600	28.10	28.13	−0.91	−0.89	−1.002	−0.718
0.700	25.76	25.75	−0.86	−0.87	−0.688	−1.308
0.800	23.51	23.48	−0.72	−0.75	−0.386	−2.224
0.900	21.32	21.35	−0.52	−0.49	−0.149	−3.599
0.980	19.66	19.79	−0.27	−0.14	−0.023	−5.860
1	19.45	19.45	0	0	0	–

Table 3 (*continued*)

$T=433$ K						
0	43.71	43.71	0	0	−2.200	0
0.100	41.09	41.10	−0.24	−0.22	−2.167	−0.005
0.200	38.47	38.51	−0.47	−0.43	−2.063	−0.024
0.300	35.90	35.93	−0.66	−0.63	−1.928	−0.069
0.400	33.36	33.37	−0.81	−0.80	−1.753	−0.165
0.500	30.83	30.85	−0.96	−0.94	−1.526	−0.353
0.600	28.38	28.37	−1.02	−1.03	−1.243	−0.705
0.700	26.03	25.98	−0.99	−1.04	−0.909	−1.334
0.800	23.78	23.70	−0.85	−0.93	−0.559	−2.402
0.900	21.58	21.60	−0.66	−0.64	−0.243	−4.252
0.980	19.90	20.14	−0.44	−0.20	−0.042	−7.956
1	19.86	19.86	0	0	0	–

Table 4. Molar volume V, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$, and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water mole fraction x_w and the temperature T for the [0.467 $TlNO_3$–0.214 $CsNO_3$–0.319 $Cd(NO_3)_2$+H_2O] system

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
$T=368$ K						
0	60.99	60.99	0	0	−3.125	0
0.198	51.97	52.03	−0.65	−0.59	−2.884	−0.030
0.490	39.04	39.00	−1.24	−1.28	−2.057	−0.531
0.630	32.99	32.97	−1.37	−1.39	−1.396	−1.391
0.784	26.64	26.66	−1.23	−1.21	−0.672	−3.175
0.814	25.44	25.46	−1.15	−1.13	−0.550	−3.660
0.936	20.89	20.87	−0.54	−0.56	−0.153	−6.623
1	18.73	18.73	0	0	0	–
$T=376$ K						
0	61.15	61.15	0	0	−3.309	0
0.200	52.08	52.06	−0.61	−0.63	−2.957	−0.045
0.400	43.09	43.09	−1.14	−1.14	−2.342	−0.326
0.630	33.09	33.13	−1.40	−1.36	−1.263	−1.537
0.707	29.96	29.94	−1.28	−1.30	−0.892	−2.288
0.845	24.48	24.45	−0.92	−0.95	−0.359	−4.165
0.900	22.33	22.36	−0.74	−0.71	−0.204	−5.229
1	18.84	18.84	0	0	0	–
$T=383$ K						
0	61.35	61.35	0	0	−3.344	0
0.151	54.43	54.46	−0.52	−0.49	−3.066	−0.024
0.300	47.74	47.72	−0.89	−0.91	−2.678	−0.142
0.430	41.91	41.93	−1.20	−1.18	−2.202	−0.422
0.576	35.57	35.57	−1.35	−1.35	−1.522	−1.125
0.725	29.36	29.34	−1.25	−1.27	−0.809	−2.475
0.829	25.16	25.19	−1.03	−1.00	−0.409	−3.881
1	18.94	18.94	0	0	0	–

Table 5. Molar volume V, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$, and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water mole fraction x_w for the [$N(C_2H_5)_4+H_2O$] system at 298 K

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
0	89.30	89.30	0	0	−1.323	0
0.181	76.20	76.19	−0.21	−0.22	−1.113	−0.022
0.375	62.20	62.19	−0.39	−0.40	−0.885	−0.111
0.559	48.98	48.98	−0.51	−0.51	−0.659	−0.315
0.664	41.46	41.48	−0.55	−0.53	−0.522	−0.533
0.814	30.88	30.85	−0.44	−0.47	−0.310	−1.161
0.900	24.83	24.84	−0.36	−0.35	−0.175	−2.003
0.958	20.85	20.86	−0.22	−0.21	−0.077	−3.380
1	18.07	18.07	0	0	0	–

Table 6. Molar volume V, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$, and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water mole fraction x_w for the [0.515 $AgNO_3$–0.485 $TlNO_3+H_2O$] system at 372 K

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
0	46.38	46.38	0	0	−1.527	0
0.127	42.67	42.66	−0.20	−0.21	−1.718	+0.010
0.186	40.94	40.94	−0.31	−0.31	−1.719	+0.010
0.262	38.72	38.71	−0.43	−0.44	−1.650	−0.011
0.319	37.05	37.05	−0.53	−0.53	−1.558	−0.049
0.337	36.53	36.52	−0.55	−0.56	−1.523	−0.066
0.382	35.22	35.22	−0.62	−0.62	−1.428	−0.120
0.445	33.40	33.41	−0.70	−0.69	−1.278	−0.226
0.525	31.13	31.13	−0.76	−0.76	−1.074	−0.419
0.613	28.66	28.65	−0.79	−0.80	−0.847	−0.720
0.676	26.95	26.94	−0.78	−0.79	−0.691	−1.004
0.765	24.51	24.52	−0.74	−0.73	−0.478	−1.558
0.850	22.34	22.33	−0.59	−0.60	−0.293	−2.348
0.901	21.06	21.05	−0.46	−0.47	−0.189	−3.090
0.928	20.36	20.37	−0.40	−0.39	−0.134	−3.680
0.986	19.04	19.05	−0.13	−0.12	−0.025	−6.619
1	18.78	18.78	0	0	0	–

water are those given by *Kell* [11]. Very good agreement is observed between experimental and calculated values practically over the whole water concentration range for all systems. Yet, the situation is different if ϵ' is used as the unique volumetric parameter, that is when the fitting procedure is repeated with $r' = 0$. As

Table 7. Molar volume V, excess molar V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$, and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water mole fraction x_w for the [$AgNO_3$–$TlNO_3$–$NaNO_3$+H_2O] system at 372 K

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
[0.502 $AgNO_3$–0.473 $TlNO_3$–0.025 $NaNO_3$]						
0	46.23	46.23	0	0	−1.472	0
0.088	43.67	43.67	−0.13	−0.14	−1.647	+0.007
0.146	41.98	41.97	−0.23	−0.24	−1.689	+0.012
0.244	39.15	39.15	−0.40	−0.40	−1.647	−0.001
0.322	36.89	36.87	−0.51	−0.53	−1.528	−0.048
0.459	32.97	32.95	−0.68	−0.70	−1.213	−0.254
0.562	30.05	30.04	−0.75	−0.76	−0.943	−0.538
0.657	27.43	27.41	−0.75	−0.77	−0.701	−0.919
0.728	25.49	25.50	−0.75	−0.74	−0.533	−1.300
0.786	23.96	23.98	−0.70	−0.68	−0.405	−1.700
0.898	21.07	21.11	−0.50	−0.46	−0.178	−2.959
0.932	20.27	20.30	−0.38	−0.35	−0.117	−3.629
0.989	18.98	19.00	−0.11	−0.09	−0.018	−6.617
1	18.78	18.78	0	0	0	–
[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 $NaNO_3$]						
0	46.07	46.07	0	0	−1.463	0
0.114	42.80	42.79	−0.19	−0.18	−1.614	+0.090
0.142	41.99	41.98	−0.23	−0.22	−1.630	+0.011
0.185	40.74	40.74	−0.29	−0.29	−1.636	+0.012
0.227	39.52	39.51	−0.37	−0.36	−1.617	+0.007
0.290	37.70	37.69	−0.47	−0.46	−1.551	−0.016
0.355	35.85	35.82	−0.55	−0.56	−1.443	−0.069
0.416	34.10	34.08	−0.61	−0.63	−1.314	−0.150
0.477	32.39	32.37	−0.68	−0.70	−1.169	−0.267
0.516	31.29	31.27	−0.71	−0.73	−1.071	−0.363
0.578	29.55	29.53	−0.74	−0.76	−0.913	−0.555
0.637	27.93	27.91	−0.75	−0.77	−0.765	−0.786
0.718	25.73	25.73	−0.75	−0.75	−0.569	−1.199
0.798	23.59	23.62	−0.70	−0.67	−0.389	−1.769
0.835	22.66	22.69	−0.64	−0.61	−0.312	−2.112
0.932	20.28	20.29	−0.37	−0.36	−0.122	−3.640
0.993	18.89	18.91	−0.08	−0.06	−0.012	−7.519
1	19.78	18.78	0	0	0	–

illustrated in Figs. 2 and 3, showing $V^{ex} = f(x_w)$ for different systems, allowance should generally be made for variation of r with P. To dispense with r' could bring about more or less pronounced deviations of the calculated curves from the experimental values depending on the nature of the system and the temperature. However, the assumption made by *Ally* and *Braunstein* [1] that one volumetric

Table 8. Molar volume *V*, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$, and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water mole fraction x_w for the [0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 KNO_3+H_2O] system at 372 K

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
0	46.52	46.52	0	0	−1.150	0
0.130	42.73	42.74	−0.19	−0.18	−1.500	+0.019
0.206	40.50	40.51	−0.31	−0.30	−1.554	+0.029
0.275	38.48	38.49	−0.41	−0.40	−1.524	+0.019
0.354	36.21	36.19	−0.50	−0.52	−1.421	−0.030
0.472	32.78	32.76	−0.64	−0.66	−1.175	−0.206
0.573	29.91	29.89	−0.72	−0.74	−0.931	−0.475
0.648	27.80	27.79	−0.74	−0.75	−0.746	−0.767
0.754	24.87	24.90	−0.74	−0.71	−0.497	−1.357
0.845	22.45	22.48	−0.62	−0.59	−0.297	−2.167
0.927	20.42	20.44	−0.40	−0.38	−0.135	−3.487
1	18.78	18.78	0	0	0	–

Table 9. Molar volume *V*, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$, and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water mole fraction x_w for the [$AgNO_3$–$TlNO_3$–$CsNO_3$+H_2O] system at 372 K

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
		[0.502 $AgNO_3$–0.473 $TlNO_3$–0.025 $CsNO_3$]				
0	46.75	46.75	0	0	−1.352	0
0.117	43.31	43.31	−0.18	−0.18	−1.615	+0.015
0.208	40.60	40.61	−0.34	−0.33	−1.661	+0.022
0.256	39.16	39.18	−0.42	−0.40	−1.628	+0.012
0.302	37.81	37.82	−0.49	−0.48	−1.569	−0.011
0.372	35.78	35.77	−0.57	−0.58	−1.437	−0.079
0.433	33.99	33.98	−0.65	−0.66	−1.294	−0.175
0.503	31.98	31.95	−0.70	−0.73	−1.115	−0.334
0.576	29.88	29.88	−0.77	−0.77	−0.926	−0.556
0.624	28.52	28.51	−0.77	−0.78	−0.801	−0.744
0.664	27.38	27.39	−0.78	−0.77	−0.701	−0.926
0.757	24.85	24.86	−0.73	−0.72	−0.481	−1.469
0.822	23.10	23.12	−0.65	−0.63	−0.338	−2.012
0.892	21.30	21.32	−0.51	−0.49	−0.197	−2.871
0.926	20.45	20.46	−0.39	−0.38	−0.131	−3.537
0.974	19.33	19.33	−0.18	−0.18	−0.045	−5.307
1	18.78	18.78	0	0	0	–

Table 9 (*continued*)

		[0.489AgNO$_3$–0.461 TlNO$_3$–0.050 CsNO$_3$]				
0	47.12	47.12	0	0	−1.264	0
0.146	42.77	42.78	−0.22	−0.21	−1.566	+0.020
0.195	41.29	41.32	−0.32	−0.29	−1.589	+0.025
0.301	38.13	38.13	−0.46	−0.46	−1.515	−0.002
0.402	35.14	35.14	−0.60	−0.60	−1.334	−0.102
0.498	32.31	32.30	−0.69	−0.70	−1.109	−0.288
0.573	30.12	30.07	−0.75	−0.74	−0.918	−0.511
0.629	28.52	28.52	−0.76	−0.76	−0.784	−0.714
0.678	27.16	27.16	−0.75	−0.75	−0.667	−0.935
0.775	24.45	24.48	−0.72	−0.69	−0.444	−1.534
0.885	21.52	21.54	−0.52	−0.50	−0.213	−2.701
0.934	20.31	20.30	−0.34	−0.35	−0.119	−3.664
1	18.78	18.78	0	0	0	–
		[0.476 AgNO$_3$–0.449 TlNO$_3$–0.075 CsNO$_3$]				
0	47.45	47.45	0	0	−1.257	0
0.093	44.66	44.67	−0.14	−0.13	−1.484	+0.010
0.138	43.28	43.28	−0.20	−0.20	−1.542	+0.017
0.215	40.95	40.97	−0.34	−0.32	−1.563	+0.021
0.275	39.15	39.16	−0.42	−0.41	−1.522	+0.007
0.365	36.46	36.45	−0.53	−0.54	−1.389	−0.057
0.431	34.46	34.47	−0.63	−0.62	−1.254	−0.146
0.503	32.32	32.33	−0.70	−0.69	−1.088	−0.293
0.579	30.12	30.12	−0.74	−0.74	−0.906	−0.508
0.657	27.87	27.86	−0.74	−0.75	−0.717	−0.816
0.726	25.91	25.90	−0.71	−0.73	−0.555	−1.181
0.828	23.11	23.11	−0.61	−0.61	−0.333	−1.970
0.884	21.58	21.60	−0.52	−0.50	−0.217	−2.667
0.971	19.41	19.41	−0.20	−0.20	−0.052	−5.121
1	18.78	18.78	0	0	0	–
		[0.464 AgNO$_3$–0.436 TlNO$_3$–0.100 CsNO$_3$]				
0	47.81	47.81	0	0	−1.362	0
0.115	44.29	44.29	−0.17	−0.17	−1.525	+0.007
0.184	42.20	42.20	−0.27	−0.27	−1.528	+0.007
0.267	39.65	39.65	−0.40	−0.40	−1.458	−0.014
0.321	38.04	38.03	−0.47	−0.48	−1.381	−0.046
0.357	36.92	36.92	−0.52	−0.52	−1.316	−0.079
0.416	35.15	35.14	−0.58	−0.59	−1.200	−0.153
0.500	32.64	32.62	−0.64	−0.66	−1.017	−0.309
0.540	31.44	31.44	−0.69	−0.69	−0.926	−0.407
0.598	29.76	29.76	−0.71	−0.71	−0.797	−0.579
0.664	27.81	27.82	−0.72	−0.71	−0.648	−0.834
0.719	26.25	26.25	−0.69	−0.69	−0.530	−1.100
0.777	24.61	24.61	−0.64	−0.64	−0.409	−1.460
0.822	23.38	23.36	−0.57	−0.59	−0.320	−1.817
0.869	22.08	22.08	−0.50	−0.50	−0.230	−2.313
0.906	21.09	21.10	−0.43	−0.41	−0.163	−2.848
0.956	19.80	19.81	−0.26	−0.25	−0.074	−4.094
1	18.78	18.78	0	0	0	–

Table 10. Molar volume V, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_{\mathrm{w}}^{\mathrm{ex}}$, and partial excess molar volume of the salt $\bar{V}_{\mathrm{s}}^{\mathrm{ex}}$ as functions of the water mole fraction x_{w} for the [$AgNO_3$–$TlNO_3$–$Cd(NO_3)_2$+H_2O] system at 372 K

x_{w}	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{\mathrm{ex}} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_{\mathrm{w}}^{\mathrm{ex}} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_{\mathrm{s}}^{\mathrm{ex}} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
		[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 $Cd(NO_3)_2$]				
0	47.77	47.77	0	0	−2.078	0
0.076	45.40	45.40	−0.16	−0.16	−2.104	+0.001
0.114	44.21	44.22	−0.25	−0.24	−2.101	+0.000
0.189	41.90	41.91	−0.40	−0.39	−2.055	−0.008
0.250	40.00	40.00	−0.52	−0.52	−1.974	−0.031
0.287	38.87	38.88	−0.59	−0.58	−1.907	−0.056
0.321	37.82	37.83	−0.66	−0.65	−1.833	−0.088
0.412	35.04	35.04	−0.79	−0.79	−1.588	−0.232
0.476	33.13	33.11	−0.85	−0.87	−1.391	−0.390
0.546	31.02	31.01	−0.91	−0.92	−1.163	−0.629
0.602	29.41	29.39	−0.92	−0.94	−0.987	−0.866
0.670	27.42	27.42	−0.93	−0.94	−0.779	−1.088
0.788	24.09	24.13	−0.85	−0.81	−0.456	−2.111
0.847	22.50	22.52	−0.70	−0.68	−0.311	−2.764
0.899	21.12	21.16	−0.58	−0.54	−0.197	−3.565
0.930	20.38	20.40	−0.44	−0.42	−0.134	−4.244
1	18.78	18.78	0	0	0	–
		[0.476 $AgNO_3$–0.449 $TlNO_3$–0.075 $Cd(NO_3)_2$]				
0	48.45	48.45	0	0	−2.121	0
0.101	45.21	45.23	−0.23	−0.21	−2.159	+0.002
0.155	43.52	43.52	−0.33	−0.33	−2.153	+0.001
0.190	42.37	42.39	−0.43	−0.41	−2.136	−0.003
0.275	39.69	39.69	−0.60	−0.59	−2.041	−0.033
0.325	38.11	38.12	−0.69	−0.68	−1.949	−0.073
0.387	36.17	36.18	−0.80	−0.79	−1.797	−0.157
0.446	34.33	34.33	−0.88	−0.88	−1.601	−0.284
0.483	33.20	33.20	−0.93	−0.93	−1.500	−0.389
0.551	31.15	31.13	−0.96	−0.98	−1.266	−0.640
0.606	29.52	29.46	−0.95	−1.01	−1.072	−0.907
0.696	26.84	26.83	−0.97	−0.98	−0.773	−1.467
0.761	24.95	24.97	−0.93	−0.91	−0.575	−2.001
0.771	24.65	24.67	−0.92	−0.90	−0.544	−2.100
0.857	22.28	22.30	−0.74	−0.72	−0.313	−3.128
0.898	21.21	21.24	−0.61	−0.59	−0.216	−3.828
0.939	20.16	20.18	−0.43	−0.41	−0.124	−4.886
0.953	19.81	19.84	−0.37	−0.35	−0.094	−5.405
1	18.78	18.78	0	0	0	–
		[0.464 $AgNO_3$–0.436 $TlNO_3$–0.100 $Cd(NO_3)_2$]				
0	49.15	49.15	0	0	−2.381	0
0.104	45.73	45.74	−0.26	−0.25	−2.372	−0.001
0.171	43.55	43.56	−0.42	−0.41	−2.336	−0.007

Table 10 (*continued*)

0.215	42.08	42.10	−0.53	−0.51	−2.292	−0.017
0.282	39.91	39.92	−0.66	−0.65	−2.189	−0.052
0.338	38.11	38.12	−0.78	−0.77	−2.065	−0.109
0.352	37.65	37.66	−0.80	−0.79	−2.028	−0.128
0.423	35.37	35.37	−0.92	−0.92	−1.810	−0.267
0.509	32.70	32.66	−0.99	−1.03	−1.496	−0.544
0.576	30.59	30.57	−1.05	−1.07	−1.235	−0.855
0.688	27.23	27.22	−1.04	−1.05	−0.822	−1.569
0.732	25.92	25.91	−0.99	−1.00	−0.672	−1.937
0.793	24.13	24.16	−0.94	−0.91	−0.485	−2.539
0.892	21.42	21.44	−0.65	−0.63	−0.227	−3.954
0.927	20.48	20.51	−0.51	−0.48	−0.146	−4.772
0.975	19.30	19.31	−0.23	−0.22	−0.047	−6.885
1	18.78	18.78	0	0	0	–
		[0.451 $AgNO_3$–0.424 $TlNO_3$–0.125 $Cd(NO_3)_2$]				
0	49.84	49.84	0	0	−2.546	0
0.136	45.29	45.29	−0.34	−0.34	−2.479	−0.005
0.187	43.58	43.58	−0.47	−0.47	−2.431	−0.015
0.240	41.78	41.79	−0.61	−0.60	−2.359	−0.035
0.269	40.82	40.84	−0.68	−0.66	−2.310	−0.051
0.315	39.28	39.30	−0.78	−0.76	−2.212	−0.092
0.399	36.51	36.51	−0.92	−0.92	−1.976	−0.225
0.454	37.73	37.72	−1.00	−1.01	−1.785	−0.368
0.537	32.09	32.07	−1.08	−1.10	−1.463	−0.686
0.607	29.87	29.85	−1.11	−1.13	−1.175	−1.072
0.675	27.78	27.75	−1.09	−1.12	−0.907	−1.551
0.712	26.68	26.64	−1.05	−1.09	−0.773	−1.857
0.761	25.16	25.18	−1.04	−1.02	−0.605	−2.327
0.823	23.36	23.39	−0.91	−0.88	−0.414	−3.056
0.901	21.21	21.23	−0.64	−0.62	−0.211	−4.357
0.954	19.81	19.84	−0.39	−0.36	−0.091	−5.954
1	18.78	18.78	0	0	0	–

parameter, *i.e.* ϵ', is sufficient, appears quite acceptable for some systems at given temperatures, for example for [0.500 $LiNO_3$–0.500 KNO_3+H_2O] at 393 K, and for practical purposes could be often useful as illustrated in a patent held by these authors [12].

Additivity rules concerning r and the product $r\epsilon$ have been observed in a study of nitrate-water systems [5]. From these additivity rules, we will demonstrate that additivity rules involving the volumetric parameter r' and ϵ' may be anticipated.

From the additivity rule concerning r, one can write

$$r = \sum_i x_i r_i \tag{38}$$

where the subscript i refers to the component i in the mixture of salts. By differentiation we obtain

$$\frac{\partial r}{\partial P} = \sum_i x_i \frac{\partial r_i}{\partial P} \tag{39}$$

Table 11. Molar volume *V*, excess molar volume V^{ex}, partial excess molar volume of water $\bar{V}_w^{ex}$ and partial excess molar volume of the salt $\bar{V}_s^{ex}$ as functions of the water mole fraction x_w for the [$AgNO_3$–$TlNO_3$–$Ca(NO_3)_2$+H_2O] system at 372 K

x_w	$V \times 10^6$ ($m^3 \cdot mol^{-1}$)		$V^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)		$\bar{V}_w^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)	$\bar{V}_s^{ex} \times 10^6$ ($m^3 \cdot mol^{-1}$)
	Experimental	*BET* model	Experimental	*BET* model	*BET* model	*BET* model
[0.489 $AgNO_3$–0.461 $TlNO_3$–0.050 $Ca(NO_3)_2$]						
0	47.68	47.68	0	0	−1.732	0
0.069	45.56	45.57	−0.13	−0.12	−1.847	+0.004
0.145	43.21	43.22	−0.27	−0.26	−1.923	+0.012
0.232	40.53	40.53	−0.44	−0.44	−1.931	+0.013
0.330	37.52	37.52	−0.62	−0.62	−1.817	−0.033
0.448	33.92	33.92	−0.81	−0.81	−1.527	−0.224
0.524	31.65	31.63	−0.87	−0.89	−1.288	−0.451
0.612	29.08	29.06	−0.91	−0.93	−1.002	−0.829
0.712	26.19	26.19	−0.91	−0.91	−0.691	−1.443
0.786	24.12	24.14	−0.84	−0.82	−0.484	−2.067
0.880	21.61	21.65	−0.65	−0.61	−0.252	−3.250
0.932	20.29	20.33	−0.47	−0.43	−0.137	−4.378
1	18.78	18.78	0	0	0	–
[0.476 $AgNO_3$–0.449 $TlNO_3$–0.075 $Ca(NO_3)_2$]						
0	48.30	48.30	0	0	−1.769	0
0.076	45.91	45.92	−0.15	−0.14	−1.860	+0.004
0.200	41.99	42.01	−0.40	−0.38	−1.938	+0.014
0.335	37.74	37.77	−0.66	−0.63	−1.839	−0.027
0.377	36.44	36.46	−0.71	−0.71	−1.761	−0.071
0.461	33.88	33.86	−0.82	−0.84	−1.546	−0.228
0.534	31.63	31.62	−0.90	−0.91	−1.316	−0.457
0.607	29.42	29.41	−0.95	−0.96	−1.069	−0.787
0.729	25.87	25.87	−0.92	−0.92	−0.675	−1.588
0.788	24.17	24.19	−0.87	−0.85	−0.501	−2.137
0.840	22.75	22.77	−0.77	−0.75	−0.362	−2.749
0.889	21.42	21.46	−0.64	−0.60	−0.240	−3.532
0.989	18.96	19.00	−0.16	−0.12	−0.023	−8.108
1	18.78	18.78	0	0	0	–
[0.464 $AgNO_3$–0.436 $TlNO_3$–0.100 $Ca(NO_3)_2$]						
0	49.02	49.02	0	0	−1.970	0
0.073	46.66	46.67	−0.16	−0.15	−2.008	+0.002
0.161	43.80	43.83	−0.35	−0.32	−2.037	+0.005
0.238	41.32	41.35	−0.51	−0.48	−2.017	−0.000
0.318	38.75	38.75	−0.64	−0.64	−1.932	−0.034
0.372	37.04	37.03	−0.73	−0.74	−1.831	−0.088
0.506	32.82	32.79	−0.90	−0.93	−1.443	−0.401
0.605	29.75	29.72	−0.96	−0.99	−1.090	−0.845
0.756	25.26	25.26	−0.92	−0.92	−0.917	−1.932
0.829	23.15	23.18	−0.81	−0.78	−0.784	−2.728
0.926	20.55	20.56	−0.48	−0.47	−0.470	−4.471
1	18.78	18.78	0	0	0	–

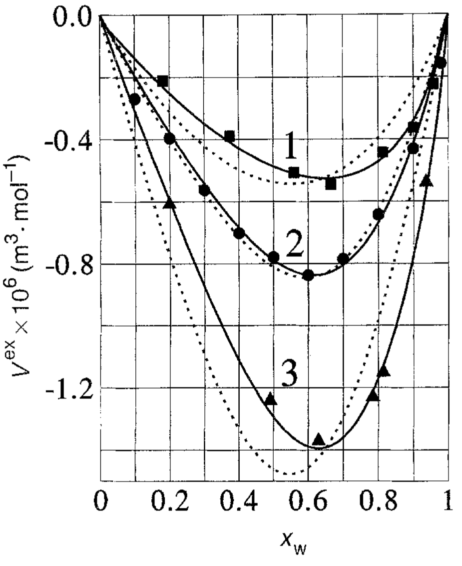

Fig. 2. Experimental and calculated excess molar volumes V^{ex} as functions of the water mole fraction x_w; 1: [$N(C_2H_5)_4NO_3+H_2O$] at 298 K (Ref. [9]); 2: [0.500 $LiNO_3$–0.500 KNO_3+H_2O] at 393 K (this work); 3: [0.467 $TlNO_3$–0.214 $CsNO_3$–0.319Cd $(NO_3)_2+H_2O$] at 368 K (Ref. [8]); symbols: experimental values, solid line: calculated curve with ϵ' and r' from Table 2, dotted line: calculated curve with r' set zero

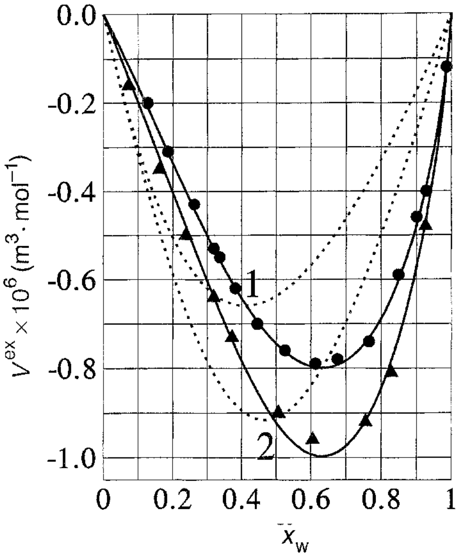

Fig. 3. Experimental and calculated excess molar volumes V^{ex} as functions of the water mole fraction x_w; 1:[0.515 $AgNO_3$–0.485 $TlNO_3+H_2O$] at 372 K (Ref. [10]); 2: [0.464 $AgNO_3$–0.436 $TlNO_3$–0.100 $Ca(NO_3)_2+H_2O$] at 372 K (Ref. [10]); symbols: experimental values, solid line: calculated curve with ϵ' and r' from Table 2, dotted line: calculated curve with r' set to zero

and

$$r' = \sum_i x_i r'_i \tag{40}$$

From the additivity rule concerning the product $r\epsilon$, one can write

$$r\epsilon = \sum_i x_i r_i \epsilon_i \tag{41}$$

whence

$$(r\epsilon)' = \frac{\partial}{\partial P}(r\epsilon) = \sum_i x_i \frac{\partial}{\partial P}(r_i \epsilon_i), \tag{42}$$

$$(r\epsilon)' = \epsilon \frac{\partial r}{\partial P} + r \frac{\partial \epsilon}{\partial P} = \sum_i x_i \left(\epsilon_i \frac{\partial r_i}{\partial P} + r_i \frac{\partial \epsilon_i}{\partial P} \right), \tag{43}$$

and

$$(r\epsilon)' = \epsilon r' + r\epsilon' = \sum_i x_i(\epsilon_i r_i' + r_i \epsilon_i'). \tag{44}$$

Eq. (44) may be tested with the system [0.515 $AgNO_3$–0.485 $TlNO_3$+ H_2O] doped with Cd, Ca, Cs, and Na. Since the ratio x(Ag)/x(Tl) is always fixed at 1.06, a linear relationship should be observed between the partial derivative $(r\epsilon)'$ of the product $(r\epsilon)$ with respect to the pressure P and the mole fraction of the doping component $x(M)$. Figure 4 shows the existence of such a linear relationship. The values of r' in Table 2 are quasi-constant as $x(M)$ is varied. More investigations about those additivity rules are in progress.

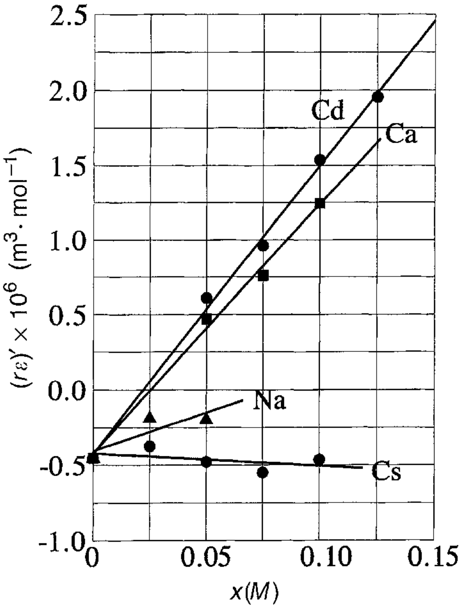

Fig. 4. Partial derivative $(r\epsilon)'$ of the product $(r\epsilon)$ with respect to the presure P for the systems [$AgNO_3$–$TlNO_3$–$M(NO_3)_n$ + H_2O] with M =Cd, Ca, Cs, and Na as function of the doping cation mole fraction $x(M)$ in the anhydrous salt mixture at 372 K

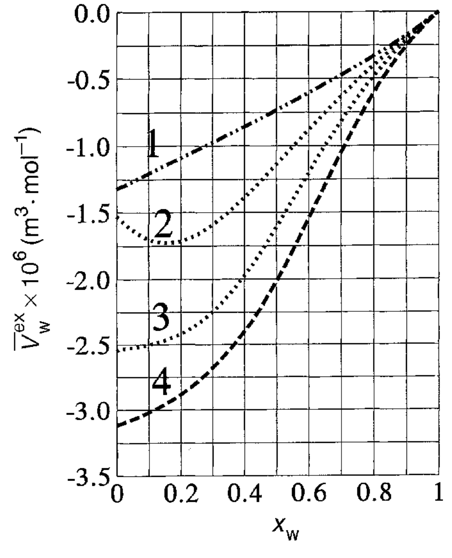

Fig. 5. Partial excess molar volume of water $\bar{V}_w^{ex}$ as function of the water mole fraction x_w; 1: [$N(C_2H_5)_4NO_3$+H_2O] at 298 K (Ref. [9]); 2: [0.515 $AgNO_3$–0.485 $TlNO_3$+H_2O] at 372 K (Ref. [10]); 3: [0.451 $AgNO_3$–0.424 $TlNO_3$–0.125 $Cd(NO_3)_2$+H_2O] at 372 K (Ref. [10]); 4: [0.467 $TlNO_3$–0.214 $CsNO_3$–0.319 $Cd(NO_3)_2$+H_2O] at 368 K (Ref. [8])

In Figs. 5 and 6, some typical curves of $\bar{V}_w^{ex}$ and $\bar{V}_s^{ex}$ *vs*. x_w are shown as examples. What is striking in Fig. 5 is the variety of shapes exhibited by the $\bar{V}_w^{ex}$ curves. Whatever the shape (quasi-straight line, curve with an inflection point, curve with a minimum), the *BET* model yields equations compatible with a great diversity in the behaviour of the systems. In Fig. 6, contrary to $\bar{V}_w^{ex}$, the curves of $\bar{V}_s^{ex}$ have a common shape, and what is especially remarkable is that the values of $\bar{V}_s^{ex}$ remain small and quasi-constant over a relatively large concentration range ($x_w \approx 0$–0.4), presumably due to the fact that the structure of dilute solutions of water in the salts is similar to the anhydrous salts themselves. Beyond this concentration range, the relative positions of the curves are in accordance with the hydrating power of the cations. The correlation between the volumetric parameters r' and ϵ' and the cationic hydrating power is clearly revealed in Fig. 7 where $\bar{V}_{w\infty}^{ex}$ calculated by

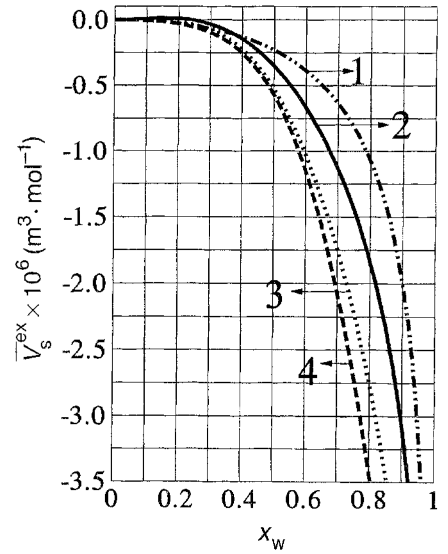

Fig. 6. Partial excess molar volume of salt $\bar{V}_s^{ex}$ as function of the water mole fraction x_w; 1: [N(C$_2$H$_5$)$_4$NO$_3$+H$_2$O] at 298 K (Ref. [9]); 2: [0.515 AgNO$_3$–0.485 TlNO$_3$+H$_2$O] at 372 K (Ref. [10]); 3: [0.451 AgNO$_3$–0.424 TlNO$_3$–0.125 Cd(NO$_3$)$_2$+H$_2$O] at 372 K (Ref. [10]); 4: [0.467 TlNO$_3$–0.214 CsNO$_3$–0.319 Cd(NO$_3$)$_2$+H$_2$O] at 368 K (Ref. [8])

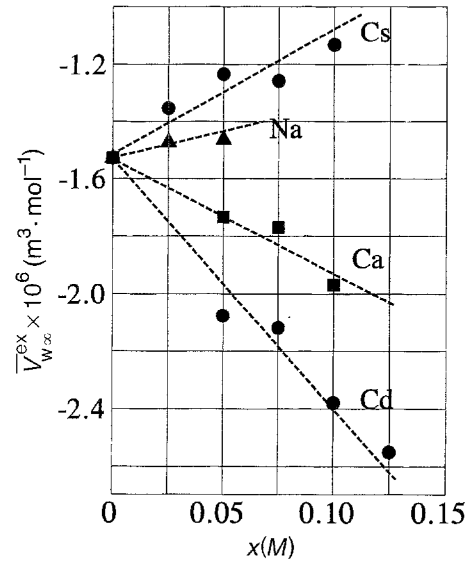

Fig. 7. Partial excess molar volume of water at infinite dilution in the molten salt $\bar{V}_{w\infty}^{ex}$ for the system [AgNO$_3$–TlNO$_3$–M(NO$_3$)$_n$+H$_2$O] with M = Cd, Ca, Cs, and Na as function of the doping cation mole fraction $x(M)$ in the anhydrous salt mixture at 372 K

Eq. (37) is given for the systems [$AgNO_3$–$TlNO_3$–$M(NO_3)_n$ + H_2O] with M = Cd, Ca, Cs, and Na as function of the doping cation mole fraction $x(M)$ in the anhydrous salt mixture. As $x(M)$ increases, $V^{ex}_{w\infty}$ increases for cations with low hydrating power and decreases for cations with high hydrating power.

At this point of the discussion, it seems appropriate to emphasize the consistency of the *BET* equations with the experimental data and the good correlation between the volumetric parameters and the cationic hydrating power, all the more as Eq. (20) has attracted criticisms from *Voigt* [13], although, in our opinion, those criticims were refuted by *Braunstein* and *Ally* [14].

Conclusions

Rigorous treatment of the volumetric properties of nitrate-water systems can be successfully performed using adsorption theory, practically from fused salts to water with monovalent and divalent cations. Generally, the two *BET* parameters and their partial derivatives with respect to pressure are required. These parameters take on values which appear to be chemically significant as evidenced, for example, in the partial excess molar volumes of water at infinite dilution in the salts. In some instances, meaningful calculations can be made with only three parameters. Observed additivity rules which are applicable to the *BET* parameters and their derivatives with respect to pressure should increase the predicting power of the adsorption theory. Further extension of this treatment to various concentrated electrolytes other than nitrates is expected to be feasible.

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