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Volumetric Properties of Single Aqueous Electrolytes from Zero to Saturation Concentration at 298.15 °K Represented by Pitzer's Ion-Interaction Equations

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The ion interaction approach developed by Pitzer allows the prediction of various thermodynamic characteristics of multiple-solute electrolyte solutions, if the respective parameters for each type of single-solute electrolyte solution are known. The present paper discusses the Pitzer approach to the calculations of the volumetric properties of single-solute electrolyte solutions. The databases for the densities and the apparent molal volumes versus concentrations were created at 298.15 °K using essentially all published relevant data for each single-solute electrolyte solution. Poor experimental data were discarded by a statistical treatment applied to these databases. Proper treatment of all good quality density and apparent molal volume data, in a wide range of concentrations from infinite dilution through saturation, allowed us to evaluate the volumetric ion interaction parameters ($\tilde{V}^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX}) at 298.15 °K for 102 electrolytes. Strong linear relationships between the $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, or C^V_{MX}, and $\beta^{(0)V}_{MX}$ volumetric ion interaction parameters were observed for all analyzed solutes with slopes depending on the solute valency types. © *1996 American Institute of Physics and American Chemical Society.*

Key words: Pitzer's approach; thermodynamics; aqueous electrolyte solutions; density; apparent molal volumes; unrestricted and restricted volumetric ion interaction parameters.

Contents

1. Introduction

Volumetric characteristics (such as solution density, apparent molal volumes, ionic apparent volumes, etc.) of multiple-solute electrolyte solutions in a wide range of solute concentrations and solution temperatures are of fundamental importance for the understanding of numerous physicochemical processes occurring in various branches of the chemical industry as well as in the natural environment. The most important application of the volumetric solution properties is in calculating the pressure effects on the ionic activity coefficients, the osmotic coefficients, the mineral solubility, etc., in complex electrolyte solutions.

Pitzer[1–3] suggested a theoretical model which allows the prediction of various thermodynamic properties of multiple-solute electrolyte solutions by using so-called ion interaction parameters, calculated from the appropriate experimental data for single-solute electrolyte solutions and for ternary solutions. Among such properties are solution density and apparent molal volumes of solutes. One of the main objectives of this paper is to suggest the best sets of the volumetric ion interaction parameters for use in the calculation of the densities and the apparent molal volumes of solutes in highly concentrated natural brines and in complex electrolyte solutions.

In our recent publication[4] we discussed in detail the Pitzer approach for volumetric calculations of single-solute electrolyte solutions at 298.15 °K. That publication dealt with solutions formed by various electrically neutral combinations of

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the following ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-}. The choice of those ions was dictated by the necessity of treating various natural waters and hypersaline brines in their natural environment. As a rule, the above ions are the major ions of natural waters. In this paper we will extend such an approach to a wider class of electrolytes, for which reliable values of either density or apparent molal volumes exist.

2. The Pitzer Ion Interaction Model for Volumetric Properties of Single-Solute Electrolyte Solutions

2.1. System of Basic Equations

The Pitzer ion interaction approach to the calculations of volumetric quantities of multiple-solute electrolyte solutions is based on the use of the combination of the proper volumetric quantities of single-solute electrolyte solutions computed by using volumetric ion interaction parameters. Any attempt to describe thermodynamic properties of multiple-solute electrolyte solutions (in particular, those of natural brines) in terms of some relevant single-solute electrolyte parameters can be justified only if all of these parameters have been obtained by using the same theoretical model which includes hypotheses, definitions, and experimental data processing. As we have pointed out previously,[4] there were often considerable differences not only among the volumetric ion interaction parameters computed by various authors, but also among the parameters computed for a particular single-solute electrolyte by the same author(s) at different times. One of the main reasons for the large scatter of these parameters was the use of various sets of experimental data, sometimes seriously inaccurate, for calculating these parameters. Other reasons were some errors in the ion interaction approach equations used for the calculation of apparent molal volumes[5–12] which differ from the commonly accepted equations developed by Rogers and Pitzer.[13] Therefore we decided to dismiss, for the further discussion, all the volumetric ion interaction parameters calculated in the above-mentioned papers, and recalculate them by correct equations by using all the reliable experimental data for these particular solutes.

The molal volume, V, of a solution can be expressed in terms of its Gibbs energy, G, by

$$V=\left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2}, \tag{1}$$

where the subscripts "T," "n_1," and "n_2" indicate that in differentiating G with respect to pressure, P, the corresponding characteristics (absolute temperature, T, and the numbers of moles of the solvent, n_1, and of the solute, n_2, in the solution, respectively) are held constant. In the further discussion, the symbol $(\partial G/\partial P)_{T,n_1,n_2}$, and also all similar symbols with other functions in place of G, will be abbreviated by omission of n_1 and n_2 for the sake of brevity.

The Gibbs energy of a single-solute electrolyte solution is given as

$$G=n_1G_1^0+n_2\bar{G}_2^0+G^{ex}+n_2\nu RT(\ln m-1), \tag{2}$$

where G_1^0 is the Gibbs energy of pure solvent, $\bar{G}_2^0$ is the partial molal Gibbs energy of the solute, G^{ex} is the excess Gibbs energy, which will be discussed later, ν is the total number of ions forming a solute molecule, m is the molal concentration of the solution, and R is the gas constant. Substitution of Eq. (2) into Eq. (1) yields

$$\begin{aligned} V&=n_1\left(\frac{\partial G_1^0}{\partial P}\right)_T+n_2\left(\frac{\partial \bar{G}_2^0}{\partial P}\right)_T+\left(\frac{\partial G^{ex}}{\partial P}\right)_T \\ &=n_1V_1^0+n_2\bar{V}_2^0+\left(\frac{\partial G^{ex}}{\partial P}\right)_T \\ &=n_1V_1^0+n_2(\bar{V}_2^0+\Delta V^{ex}) \end{aligned} \tag{3}$$

with

$$\Delta V^{ex}=\frac{1}{n_2}\left(\frac{\partial G^{ex}}{\partial P}\right)_T, \tag{4}$$

where V_1^0 is the molal volume of the pure solvent, $\bar{V}_2^0$ (or $\bar{V}_{MX}^0$ in another way of definition) is the partial molal volume of the solute in a single-solute electrolyte solution at infinite dilution, and ΔV^{ex} is the excess volume. The transformation of Eq. (3) allows one to obtain the apparent molal volume, V_ϕ, for a single solute, as

$$V_\phi=\frac{V-n_1V_1^0}{n_2}=\frac{1000(\rho_0-\rho)}{m\rho\rho_0}+\frac{M}{\rho}=\bar{V}_2^0+\Delta V^{ex}, \tag{5}$$

where ρ and ρ_0 are the mass densities of the solution and pure solvent, respectively, and M is the molecular weight of the solute. The excess Gibbs energy, G^{ex}, of a real, single-solute or multiple-solute electrolyte solution is, by definition, the difference between the Gibbs energy of the real solution and that of the respective hypothetical ideal electrolyte solution system under the same thermodynamic conditions. The following phenomenological expression for the excess Gibbs energy of a single-solute electrolyte solution containing 1 kg of solvent was suggested by Pitzer:[1–3]

$$\begin{aligned} G^{ex}=RT\Big\{&-A_\Phi\left(\frac{4I}{b}\right)\ln(1+bI^{1/2}) \\ &+2m^2\nu_M\nu_X[\beta_{MX}^{(0)}+\beta_{MX}^{(1)}g(\alpha_1I^{1/2})+\beta_{MX}^{(2)}g(\alpha_2I^{1/2}) \\ &+m(\nu_Mz_M)C_{MX}]\Big\} \end{aligned} \tag{6}$$

with

$$g(\alpha_iI^{1/2})=\frac{2}{(\alpha_iI^{1/2})^2}[1-(1+\alpha_iI^{1/2})\exp(-\alpha_iI^{1/2})], \tag{7}$$

where ν_M, ν_X, z_M, and z_X are the numbers of cations and anions in an electrolyte molecule, and their charges, respectively; and I is the ionic strength of an electrolyte solution, defined by

$$I=\frac{1}{2}\sum_i m_iz_i^2. \tag{8}$$

Here m_i is the ion molal concentration; b, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, α_1, α_2, and C_{MX} are Pitzer's ion interaction parameters;[1,3] A_ϕ is the Debye–Hückel parameter in the osmotic function, which is expressed through physical constants and physicochemical properties of a solvent as follows:

$$A_\pi=\frac{1}{3}\left(\frac{2J_1N_0\rho_0}{1000}\right)^{1/2}\left(\frac{e^2}{\epsilon kT}\right)^{3/2}, \tag{9}$$

wherein N_0 is the Avogadro number; ϵ is the relative permittivity of a solvent at the temperature T; k is the Boltzmann constant; and e is the positive electronic charge.

Sometimes, the quantity C^{ϕ}_{MX} is used instead of C_{MX}. These quantities are related by

$$C^{\phi}_{MX}=2|z_Mz_X|^{1/2}C_{MX}. \tag{10}$$

Substituting Eq. (6) into Eq. (4), and suggesting that "b," "α_1," and "α_2" are independent of P, we obtain

$$\begin{aligned}\Delta V^{ex}=RT\Bigg\{&-\left(\frac{\partial A_\phi}{\partial P}\right)_T\left(\frac{4I}{bm}\right)\ln(1+bI^{1/2})\\&+2m\nu_M\nu_X\Bigg[\left(\frac{\partial\beta^{(0)}_{MX}}{\partial P}\right)_T+\left(\frac{\partial\beta^{(1)}_{MX}}{\partial P}\right)_T g(\alpha_1I^{1/2})\\&+\left(\frac{\partial\beta^{(2)}_{MX}}{\partial P}\right)_T g(\alpha_2I^{1/2})+m(\nu_Mz_M)\left(\frac{\partial C_{MX}}{\partial P}\right)_T\Bigg]\Bigg\}\\&=\frac{A_VI}{bm}\ln(1+bI^{1/2})+2RT\nu_M\nu_Xm(B^V_{MX}\\&+m\nu_Mz_MC^V_{MX}),\end{aligned} \tag{11}$$

where A_V, B^V_{MX}, and C^V_{MX} are defined by

$$A_V=-4RT\left(\frac{\partial A_\phi}{\partial P}\right)_T, \tag{12}$$

$$\begin{aligned}B^V_{MX}&=\left(\frac{\partial\beta^{(0)}_{MX}}{\partial P}\right)_T+\left(\frac{\partial\beta^{(1)}_{MX}}{\partial P}\right)_T g(\alpha_1I^{1/2})\\&\quad+\left(\frac{\partial\beta^{(2)}_{MX}}{\partial P}\right)_T g(\alpha_2I^{1/2})\\&=\beta^{(0)V}_{MX}+\beta^{(1)V}_{MX}g(\alpha_1I^{1/2})+\beta^{(2)V}_{MX}g(\alpha_2I^{1/2}),\end{aligned} \tag{13}$$

$$C^V_{MX}=\left(\frac{\partial C_{MX}}{\partial P}\right)_T. \tag{14}$$

None of the parameters A_ϕ, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C_{MX} depends on n_1 and n_2. Therefore the meaning of the symbol of partial differentiation in Eqs. (12)–(14) is different from the meaning of the partial differentiation symbols in Eqs. (1), (3), and (4).

Substituting Eq. (11) into Eq. (5) yields

$$\begin{aligned}V_{\phi,MX}=\bar V^0_{MX}+\nu|z_Mz_X|\left(\frac{A_V}{2b}\right)\ln(1+bI^{1/2})\\+2RT\nu_M\nu_X[mB^V_{MX}+m^2\nu_Mz_MC^V_{MX}].\end{aligned} \tag{15}$$

The following numerical values of the Pitzer parameters have been used for the further calculations throughout this study: $A_V=1.875$ cm^3 kg$^{1/2}$ mol$^{-3/2}$ at 298.15 °K;[13] $b=1.2$ kg$^{1/2}$ mol$^{-1/2}$ for all charge types; $\alpha_1=2.0$ kg$^{1/2}$ mol$^{-1/2}$, and $\beta^{(2)V}_{MX}=0$ for 1:1, 1:2, and 2:1 electrolytes, and $\alpha_1=1.4$ kg$^{1/2}$ mol$^{-1/2}$ and $\alpha_2=12$ kg$^{1/2}$ mol$^{-1/2}$ for 2:2 electrolytes.[3] Then the density of a single-solute solution can be calculated as

$$\rho=\frac{1000+mM}{(1000/\rho_0)+mV_{\phi,MX}}. \tag{16}$$

2.2. Calculations of Volumetric Ion Interaction Parameters for Single-Solute Electrolyte Solutions

Pitzer's ion interaction approach allows the prediction of various thermodynamic characteristics of multiple-solute electrolyte solutions, if ion interaction parameters for each type of single-solute electrolyte solution are known. In particular, for calculations of volumetric characteristics of complex solutions at a first approximation, one needs the set of respective volumetric ion interaction parameters, $\bar V^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX}, for all relevant single-solute electrolyte solutions. It is understood that any attempt to describe thermodynamic properties of multiple-solute electrolyte solutions (in particular, those of natural brines) in terms of the Pitzer ion interaction parameters of some relevant single-solute electrolyte solutions can be justified only if all of these parameters have been obtained by using the same methods. Therefore, the volumetric ion interaction parameters which were computed under dissimilar definitions and by using dissimilar experimental data processing methods are conceptually incorrect. Hence, none of them can be recommended as a basis for further computations of the apparent molal volumes and of the solution densities in multiple-solute electrolyte solutions in general, and in natural brines in particular. Thus, in order to make the computation reliable, all the parameters should be determined by *one and the same method*. In light of the above, it seems to be expedient to solve the following three interrelated problems:

(1) To create and statistically analyze the database of densities and apparent molal volumes for single-solute electrolyte solutions under study at 298.15 °K available in the literature.

(2) To compute the volumetric ion interaction parameters $\bar V^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX} at 298.15 °K by using the most reliable density and apparent molal volume data for single-solute electrolyte solutions from the created database.

(3) To make a comparative survey of all calculated values of volumetric ion interaction parameters at 298.15 °K by exposing them to a certain statistical criterion of reliability. The best (most reliable) values so obtained are then recommended for further usage in the density and apparent molal volume calculations at 298.15 °K.

The above three problems are attacked in this paper. The following procedure was used for the calculations of volumetric Pitzer's ion interaction parameters. Using essentially all published relevant data, a complete database for the den-

TABLE 1. Literature sources of experimental densities and apparent molal volumes used for $\bar{V}^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX} calculations at 298.15 °K.

Electrolyte	References		
	All experimental data from these studies were used	Only part of the experimental data from these studies was used	All experimental data from these studies were discarded
NaF	18–20		21
KF	18–20, 22	23, 24	
RbF	18, 19		24, 25
CsF	18, 19	24, 25	
HCl	17, 20, 26, 27	19, 28–31	22, 32
LiCl	18, 20, 21, 33	19, 22, 25, 34–37	32, 38
NaCl	5, 15, 16, 19–21, 25, 28, 33, 35, 39–51	12, 22, 27, 32, 52–61	62
KCl	19–21, 35, 39, 41, 57, 63–67	11, 22, 25, 32, 33, 46, 48, 56, 68–71	36, 49, 58, 59, 61, 72–74
RbCl	19, 20, 35	22, 25, 59	21
CsCl	19, 21, 22, 25, 54, 75	20, 35, 59, 61	76
NH_4Cl	17, 20, 23, 77	78	68, 79
$MgCl_2$	20, 26, 33, 41, 43, 45, 46, 80–83	42, 47, 73, 84, 85	86–89
$CaCl_2$	20, 26, 33, 43, 50, 75, 81, 88, 90, 91	5, 11, 80, 84, 89	46, 86, 92
$SrCl_2$	20, 80, 81, 90		62, 78
$BaCl_2$	20, 26, 34, 81	84, 93	22, 80
$CuCl_2$		17	
$ZnCl_2$	9, 94, 95		17
$CdCl_2$	9, 94, 96		17
$MnCl_2$	82, 94		9, 17
$FeCl_2$		53	
$CoCl_2$	9, 92		17, 82
$NiCl_2$	9, 43, 82, 92	97	17
LiBr	18, 98	19, 99	22, 100
NaBr	12, 18, 20, 64, 98, 101	19, 22, 33, 84	8, 34, 61
KBr	18, 20–23, 36, 51, 60	19, 25, 63, 67, 84, 102	61, 65
RbBr	18, 19, 22, 101		
CsBr	18, 19, 22, 103		
NH_4Br	20	17, 104	
$MgBr_2$	17		
$CaBr_2$	17		8
$SrBr_2$	17		
$BaBr_2$	17		
$CuBr_2$	103		
$ZnBr_2$	17		8
$CdBr_2$	17		
LiI	17, 98	22	
NaI	19, 20, 22, 25, 71, 98, 99	18	91, 105
KI	18–21, 23, 36, 39, 67, 71	25	22, 70, 72
RbI	18, 19	22	
CsI	18, 19, 22	93, 106	
MgI_2		17	
CaI_2	17		
SrI_2		17	
BaI_2	17		
CdI_2	17		72
NiI_2	107		
$LiNO_3$		39, 108, 109	
$NaNO_3$	20	72, 110, 111	84
KNO_3	21, 26, 99	20, 58, 84, 111	23, 68, 70
$RbNO_3$	112	17	
$CsNO_3$		17, 68, 69	

TABLE 1. *(Continued.)*

Electrolyte	References		
	All experimental data from these studies were used	Only part of the experimental data from these studies was used	All experimental data from these studies were discarded
$AgNO_3$	113	109, 114, 115	116–118
$TlNO_3$	112		17
NH_4NO_3	17	117	64, 79, 116, 119, 120
$Mg(NO_3)_2$	17	111, 121	122
$Ca(NO_3)_2$	17		
$Sr(NO_3)_2$		111	
$Ba(NO_3)_2$		111	
$Zn(NO_3)_2$		111	
$Cd(NO_3)_2$	84, 92	123	111
$Fe(NO_3)_2$	111		
$Co(NO_3)_2$	17, 124		
$Ni(NO_3)_2$	17	111	
$Pb(NO_3)_2$	17		111, 125
$LiClO_3$		126	
$KClO_3$	17, 68		
$LiClO_4$		127, 128	
$NaClO_4$	51		34
$AgClO_4$		115, 118	
$TlClO_4$		129	
NH_4ClO_4	17	23	
$Mg(ClO_4)_2$	92	130	124
$Ca(ClO_4)_2$		130	
$Sr(ClO_4)_2$		130	
$Ba(ClO_4)_2$		34, 130	
$Cu(ClO_4)_2$		92	
$Cd(ClO_4)_2$	96		
KSCN	131	93, 132	17
$NaCH_3COO$		133	17, 74
KCH_3COO		72	17, 74
$TlCH_3COO$		129	
NH_4CH_3COO	17		124
$Mg(CH_3COO)_2$		89	
$Ca(CH_3COO)_2$		89	
NaH_2PO_4		134	17
KH_2PO_4		134	17
$KBrO_3$		17, 68	
K_2CrO_4		114	
$NaHCO_3$	20, 135		136
$KHCO_3$	20		
Na_2CO_3	135, 137		17, 20, 64, 90, 136
K_2CO_3	20, 137		17
Li_2SO_4	34	17, 53, 138	
Na_2SO_4	20, 23, 26, 34, 41, 45, 47	39, 42, 49, 55, 56, 84, 138	17, 64, 139
K_2SO_4	20, 26, 65, 140	49, 73, 114, 138	23, 69
Rb_2SO_4	17		
Cs_2SO_4		17	
$(NH_4)_2SO_4$	17, 34, 59		
$BeSO_4$	73, 141		17
$MgSO_4$	20, 41, 45, 47, 56, 59	42, 55, 73, 89, 121	
$CuSO_4$	142	77	17, 121
$ZnSO_4$	142		17, 59, 143, 144
$CdSO_4$	142		145
$MnSO_4$	142		17, 121
$CoSO_4$	142		17
$NiSO_4$	142	78	17

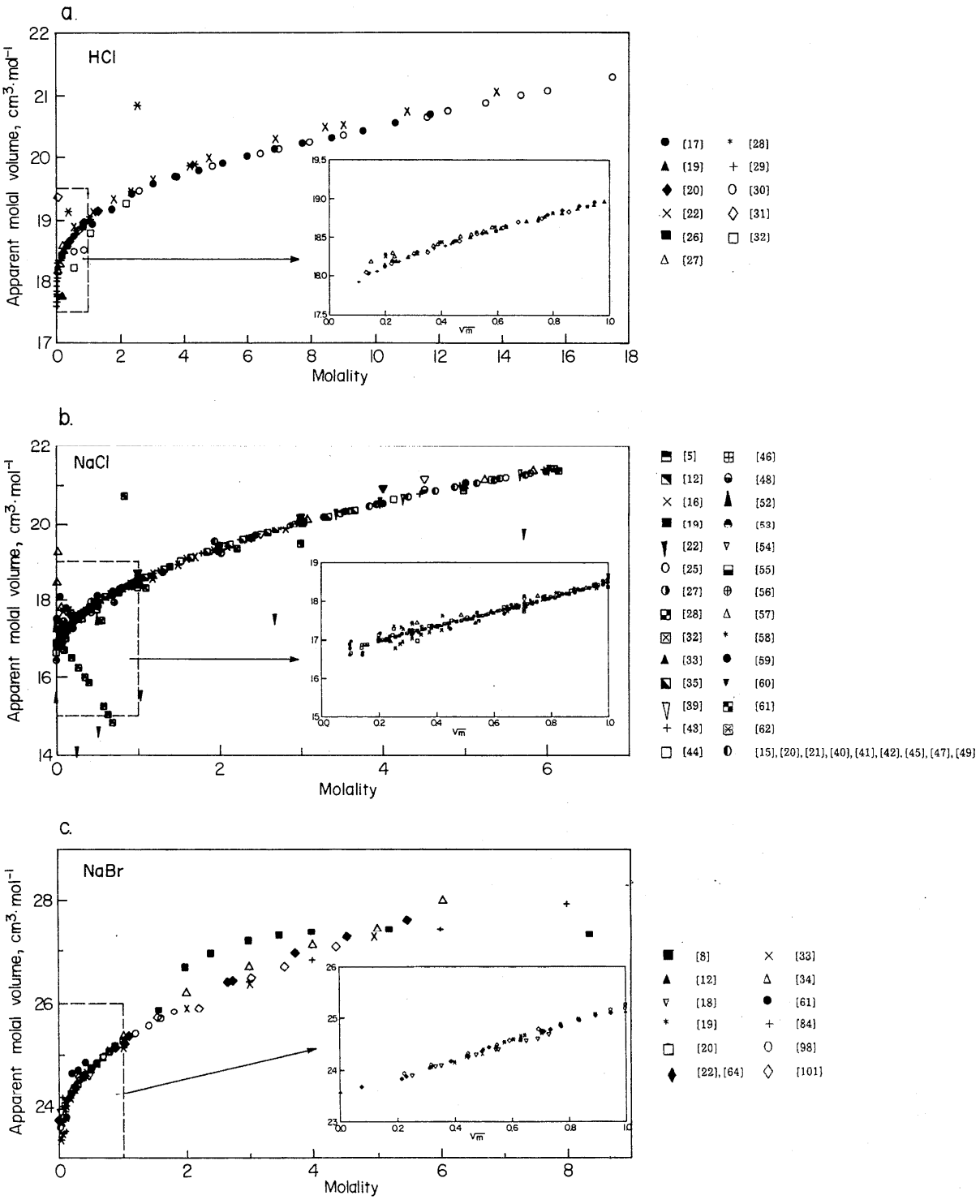

FIG. 1. (a) Apparent molal volumes of HCl at 298.15 °K. (b) Apparent molal volumes of NaCl at 298.15 °K. (c) Apparent molal volumes of NaBr at 298.15 °K. (d) Apparent molal volumes of KBr at 298.15 °K. (e) Apparent molal volumes of $MgBr_2$ at 298.15 °K. (f) Apparent molal volumes of $CaBr_2$ at 298.15 °K.

sities and apparent molal volumes at 298.15 °K versus concentrations was created for each single-solute electrolyte solution under study. After the new types of densimeters[14–16] were developed, the precision of density measurements was greatly improved, reaching $\pm 2\times10^{-6}$ g cm^{-3}. Therefore, only those densities which were measured with an error not exceeding 1×10^{-4} g cm^{-3}, and only those apparent molal volumes which were calculated by using the above high pre-

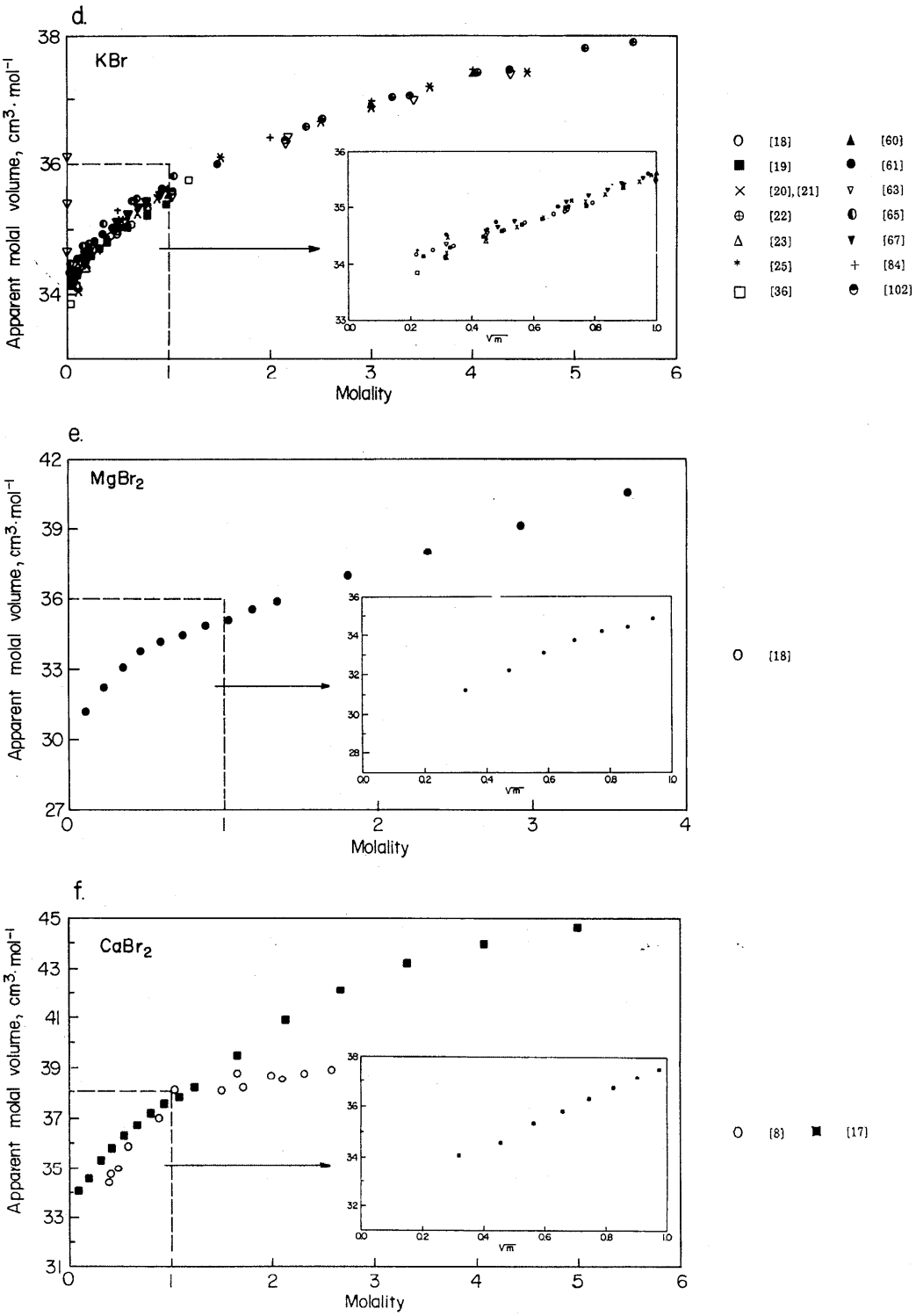

FIG. 1. (*Continued.*)

cision densities, have been included in our database. An exception has been made only for a few solutions for which updated experimental density data were either very limited or unreliable (incorrect) or absent. In these cases we have used less precise data obtained before 1928 and collected in I.C.T..[17] In the cases when the literature densities were expressed in $g\,ml^{-1}$, they were recalculated in $g\,cm^{-3}$. The literature sources[5,8,9,11,12,15–145] which we considered for the

TABLE 2. The unrestricted sets of volumetric ion interaction parameters at 298.15 °K.

Solute	$\tilde{V}^0_{MX}$ ($cm^3\ mol^{-1}$)	$\beta^{(0)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(1)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(2)V}_{MX}\times 10^2$ ($kg\ mol^{-1}\ bar^{-1}$)	$C^V_{MX}\times 10^6$ [a] ($kg^2\ mol^{-2}\ bar^{-1}$)	Density$\times 10^6$ ($g\ cm^{-3}$)		Apparent molal volume[b] ($cm^3\ mol^{-1}$)	Upper level of concentration (mol/kg H_2O)
						$(\Delta\rho)_{av}$[c]	std $(\Delta\rho)$[d]	std (ΔV_ϕ)[d]	
NaF[e]	−2.426	2.4693	0.3169		−0.4068	2	8	0.03	0.8
KF	7.758	1.6500	2.0715		−0.5128	3	237	0.04	13.2
RbF	12.706	2.6401	−0.3477		3.4040	−1	20	0.01	0.9
CsF	19.948	1.3351	2.8529		−0.4064	10	779	0.07	16.1
HCl[e]	17.824	0.0550	−0.7401		0.02398	6	84	0.04	17.5
LiCl[e]	16.866	0.3853	1.5553		−0.1541	5	514	0.07	19.6
NaCl[e,f]	16.620	1.2335	0.43543		−0.6578	4	97	0.07	6.1
KCl[e]	26.848	1.2793	0.8948		−0.7131	3	64	0.06	4.7
RbCl[e]	31.943	1.1682	1.4930		−0.5901	3	97	0.03	7.9
CsCl[e]	39.155	1.0732	1.9031		−0.5218	8	572	0.08	11.4
NH_4Cl[e]	36.069	0.7905	−1.7655		−0.4833	4	84	0.09	7.4
$MgCl_2$[e]	14.083	1.6933	−5.2068		−0.5698	1	186	0.12	5.8
$CaCl_2$[e,f]	17.612	1.3107	−2.4575		−0.1265	13	595	0.18	7.7
$SrCl_2$[e]	18.400	3.2044	−9.8894		−2.1913	3	185	0.16	3.0
$BaCl_2$[e]	22.975	0.1921	6.7563		4.982	2	277	0.24	1.5
$CuCl_2$[e]	8.571	5.4268	−13.066		−4.932	0	64	0.07	1.9
$ZnCl_2$[g,h]	6.098	5.1645	53.668		−2.1931	10	3113	0.83	7.9
$ZnCl_2$[e,i]	10.864	19.449	−47.112		−24.422	5	121	0.15	1.5
$CdCl_2$[g]	24.438	1.8523	−17.248		−0.7808	2	679	0.25	6.4
$MnCl_2$[g]	17.834	0.9712	0.1700		−0.3289	0	504	0.16	6.0
$FeCl_2$[g]	13.688	4.3044	0.3599		···	1	3	0.22	0.3
$CoCl_2$[g]	10.361	1.5532	−2.3882		−0.4014	−1	65	0.21	2.9
$NiCl_2$[e]	6.244	2.0006	−2.7753		−0.7344	0	316	0.31	5.4
LiBr	23.758	0.2399	0.2406		−0.1744	13	517	0.05	17.7
NaBr[e]	23.479	0.7607	0.9525		−0.3491	2	99	0.05	8.0
KBr	33.688	1.0101	1.1526		−0.6328	4	150	0.08	5.6
RbBr	38.829	1.0990	0.3518		−0.6246	2	103	0.06	6.7
CsBr	46.068	1.1396	1.0237		−0.9269	8	65	0.04	5.3
NH_4Br	42.569	0.5204	−0.4220		−0.4520	5	57	0.04	6.8
$MgBr_2$	28.788	0.60798	3.1073		0.5359	35	171	0.10	4.4
$CaBr_2$	32.300	2.6894	−16.029		−1.2951	2	76	0.15	5.0
$SrBr_2$	31.335	0.9033	23.853		−0.3093	−1	172	0.20	3.3
$BaBr_2$[g]	43.464	2.7492	−22.474		−0.8994	2	75	0.06	2.2
$CuBr_2$	22.812	2.1271	−5.8262		−0.5743	1	79	0.08	4.0
$ZnBr_2$[g,h]	11.898	3.8197	118.03		−1.5438	58	4740	1.14	8.2
$CdBr_2$	34.278	5.6775	7.7591		−6.5743	30	245	0.22	2.4
LiI	35.340	−0.1421	−0.6226		−0.0611	3	259	0.04	13.9
NaI[e]	34.998	0.5381	−0.4369		−0.2805	12	170	0.06	11.3
KI	45.151	0.5398	1.4438		−0.2479	7	185	0.07	8.6
RbI	50.187	0.9301	0.7037		−0.8622	4	22	0.04	3.3
CsI	57.382	0.3183	3.8737		0.5552	1	43	0.06	3.5
MgI_2	50.174	1.5892	−25.782		−1.7906	−1	47	0.07	2.4
CaI_2	52.279	1.5269	−25.241		−0.6873	−4	116	0.09	2.3
SrI_2	53.268	1.4733	−14.478		0.3219	−1	150	0.19	2.4
BaI_2	59.107	1.9489	10.368		−2.0110	−2	882	0.42	3.8
CdI_2	53.902	−11.523	117.91		17.286	26	164	0.15	1.8
NiI_2	41.736	0.9438	−21.790		−0.1101	2	311	0.09	3.7
$LiNO_3$	28.042	0.0325	2.6946		0.000018	18	915	0.15	24.0
$NaNO_3$[e]	28.007	2.0388	−0.0426		−1.6140	7	299	0.11	5.8
KNO_3	38.324	1.2625	1.4979		−0.5642	11	153	0.08	3.4
$RbNO_3$	43.148	0.8182	4.4152		1.0277	1	53	0.04	3.2
$CsNO_3$	50.672	−12.349	28.508		62.53	−2	7	0.13	0.8
$AgNO_3$[e]	27.558	0.5458	11.051		−0.0728	0	515	0.61	12.7
$TlNO_3$[e]	39.701	−37.617	88.845		···	6	13	0.15	0.3
NH_4NO_3	47.399	0.2002	−1.0171		−0.0344	25	547	0.09	27.1
$Mg(NO_3)_2$	38.238	2.5089	−25.127		−1.1029	31	321	0.16	3.7
$Ca(NO_3)_2$	40.921	2.7008	−11.996		−0.6760	29	77	0.04	13.0
$Sr(NO_3)_2$[g]	43.870	3.3060	−15.862		−1.7387	31	146	0.06	3.0
$Ba(NO_3)_2$	45.460	−4.9325	66.440		···	27	88	0.34	0.4
$Zn(NO_3)_2$	33.335	1.3078	−3.1086		−0.0202	72	245	0.08	5.0
$Cd(NO_3)_2$[e]	43.883	1.4553	−15.925		−0.2454	−15	776	0.39	5.0
$Fe(NO_3)_2$[g]	−2.119	10.404	−24.859		−3.999	66	230	0.08	3.0
$Co(NO_3)_2$[e]	29.569	0.1356	29.118		0.7389	9	891	0.58	5.5

TABLE 2. (*Continued.*)

Solute	$\tilde{V}^0_{MX}$ ($cm^3\ mol^{-1}$)	$\beta^{(0)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(1)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(2)V}_{MX}\times 10^2$ ($kg\ mol^{-1}\ bar^{-1}$)	$C^V_{MX}\times 10^6$ [a] ($kg^2\ mol^{-2}\ bar^{-1}$)	Density$\times 10^6$ ($g\ cm^{-3}$)		Apparent molal volume[b] ($cm^3\ mol^{-1}$)	Upper level of concentration ($mol/kg\ H_2O$)
						$(\Delta\rho)_{av}$[c]	std $(\Delta\rho)$[d]	std (ΔV_ϕ)[d]	
$Ni(NO_3)_2$[g]	25.903	3.0239	15.269		−1.8318	14	875	0.70	4.0
$Pb(NO_3)_2$[e,j]	39.769	−32.399	156.20		91.54	11	282	0.33	1.3
$LiClO_3$[h]	35.733	0.0187	4.0216		−0.0028	−60	2562	0.17	89.8
$KClO_3$[e]	45.681	−0.7162	−27.555		···	0	16	0.06	0.3
$LiClO_4$[g]	42.153	−3.1395	15.574		5.6665	0	185	0.16	3.2
$NaClO_4$[e]	43.140	0.6475	2.0790		−0.2230	2	3	0.00	11.1
$AgClO_4$	42.348	0.6984	0.9783		−0.1808	0	762	0.19	8.4
$TlClO_4$	53.192	−16.159	67.066		···	26	59	0.28	0.5
NH_4ClO_4	61.515	−3.5133	12.040		9.362	18	29	0.12	1.4
$Mg(ClO_4)_2$	66.893	−0.7061	1.3878		5.040	0	493	0.67	2.4
$Ca(ClO_4)_2$	68.990	3.1220	0.6368		−1.0443	1	581	0.66	2.4
$Sr(ClO_4)_2$[g]	68.811	−10.065	68.771		18.145	4	1114	1.41	2.4
$Ba(ClO_4)_2$	77.370	2.5771	−23.982		−0.7867	−1	850	0.5	4.6
$Cu(ClO_4)_2$	62.949	−10.807	11.911		···	−1	23	0.18	0.2
$Cd(ClO_4)_2$[g]	68.612	2.5487	−22.122		3.1846	2	60	0.06	1.1
$KBrO_3$[e,j]	43.034	−11.952	50.638		···	13	30	0.14	0.1
KSCN[e,j]	49.434	0.4036	2.4620		−0.0890	−34	301	0.11	24.1
NaH_2PO_4[e]	24.124	−11.102	95.839		17.078	−1	518	0.56	4.6
KH_2PO_4	35.545	−51.676	170.64		203.62	1	241	0.70	1.1
$NaCH_3COO$[e]	39.152	−6.1882	15.257		39.098	1	10	0.02	0.9
KCH_3COO[g]	52.888	0.5408	1.3193		···	1	3	0.02	0.5
$TlCH_3COO$	51.618	4.2548	2.3139		−4.0051	2	145	0.11	3.0
NH_4CH_3COO	60.343	0.7806	−3.4985		−0.2450	28	31	0.02	10.6
$Mg(CH_3COO)_2$[g]	49.528	−1.7422	97.770		−0.2367	26	673	0.76	1.1
$Ca(CH_3COO)_2$	64.435	−0.07169	11.668		···	26	288	1.07	0.5
Li_2SO_4	12.580	3.1291	4.2957		−1.1938	2	161	0.14	3.1
Na_2SO_4[e]	11.776	5.3250	12.932		−2.914	2	90	0.15	1.5
K_2SO_4	32.050	−2.3199	36.414		29.11	4	68	0.16	0.7
Rb_2SO_4	44.019	10.380	−5.3378		−12.246	10	156	0.14	1.8
Cs_2SO_4[g]	67.249	15.756	−108.14		···	26	236	0.32	0.9
$(NH_4)_2SO_4$	50.721	3.1513	5.8466		−0.9924	−61	571	0.25	6.2
$BeSO_4$[e]	3.680	−2.5511	48.206	0.0109	5.097	−5	368	0.58	3.7
$NaHCO_3$[e,k]	23.181	−1.162	17.8		···	−3	9	0.05	1.0
$NaHCO_3$	23.07	−5.3518	26.848		17.982	−2	12	0.03	1.0
$KHCO_3$[k]	33.371	−0.2705	16.95		···	−12	31	0.19	1.0
$KHCO_3$	34.34	7.0283	−8.4507		−16.738	1	1	0.00	1.0
Na_2CO_3[e,k]	−6.48	5.98	8.16		−3.25	−6	19	0.23	1.7
Na_2CO_3	−6.987	4.0836	19.801		0.2064	0	45	0.14	1.7
K_2CO_3[l]	14.130	3.4950	16.473		−0.8478	−2	378	0.25	7.6
K_2CrO_4[e,j]	37.114	3.1671	18.574		−0.4902	8	128	0.52	2.9

[a]The unrestricted volumetric ion interaction parameters for the solutions with a concentration limit less than 0.7 mol/kg H_2O (and 0.9 for Cs_2SO_4) have been fitted by a reduced equation without the C^V_{MX} parameter.

[b]The arithmetical means of the differences of experimental apparent molal volumes from calculated ones for all solutes have been obtained to be equal to 0.

[c]$(\Delta\rho)_{av}$ is the arithmetical mean of the differences between experimental and calculated densities for a proper electrolyte solution.

[d]std $(\Delta\rho)$ and std (ΔV_ϕ) are the standard deviations of the differences between experimental and calculated densities and apparent molal volumes, respectively, for all existing good quality literature data for a proper electrolyte.

[e]The unrestricted volumetric ion interaction parameters which are recommended for all further volumetric calculations (see text for explanation).

[f]The paper of Oakes *et al.* (Ref. 50) was inadvertently overlooked, and their precise density data for NaCl and $CaCl_2$ were missing in our earlier publication (Ref. 4). Our attention was drawn to this paper only after all the calculations were finished; therefore we decided not to change the volumetric ion interaction parameters calculated without the experimental data of Oakes *et al.* Ref. 50, since the inclusion of their data changed the volumetric ion interaction parameters very insignificantly for NaCl and $CaCl_2$ solutions: $\tilde{V}^0_{NaCl}=16.619$, $\beta^{(0)}_{NaCl}=1.2279\times10^{-5}$, $\beta^{(1)}_{NaCl}=0.44991\times10^{-5}$, $C^V_{NaCl}=-0.6523\times10^{-6}$, and $\tilde{V}^0_{CaCl_2}=17.601$, $\beta^{(0)}_{CaCl_2}=1.3416\times10^{-5}$, $\beta^{(1)}_{CaCl_2}=2.7077\times10^{-5}$, $C^V_{CaCl_2}=-0.1461\times10^{-6}$.

[g]The calculated $\tilde{V}^0_{MX}$ values do not obey the additivity rule (see further discussion related to Table 3), and therefore these unrestricted sets of the volumetric ion interaction parameters are unreliable ones and are not recommended for any of the volumetric calculations.

[h]The obtained set of volumetric ion interaction parameters is unreliable since the fitting of the density data by Pitzer's equation [Eq. (16)] using this set is poor, and therefore this set is not recommended for volumetric calculations.

[i]The recommended values of the unrestricted volumetric ion interaction parameters for $ZnCl_2$ were calculated for a reduced concentration interval with $m<1.5$ (see explanation to Table 6).

[j]The correctness of the $\tilde{V}^0_{MX}$ values for these cases cannot be determined at the present stage by the additivity rule, since only one limiting apparent molal volume exists with either the cation or anion under study.

[k]Taken from Monnin (Ref. 146).

[l]The unrestricted set of volumetric ion interaction parameters for K_2CO_3 solutions presented in our earlier work (Ref. 4) was calculated with an error. This led us at that time to the wrong conclusion that the $\tilde{V}^0_{K_2CO_3}$ values disobeyed the additivity rule, while the new recalculated $\tilde{V}^0_{K_2CO_3}$ values (this work) were found to obey the additivity rule (see Table 3).

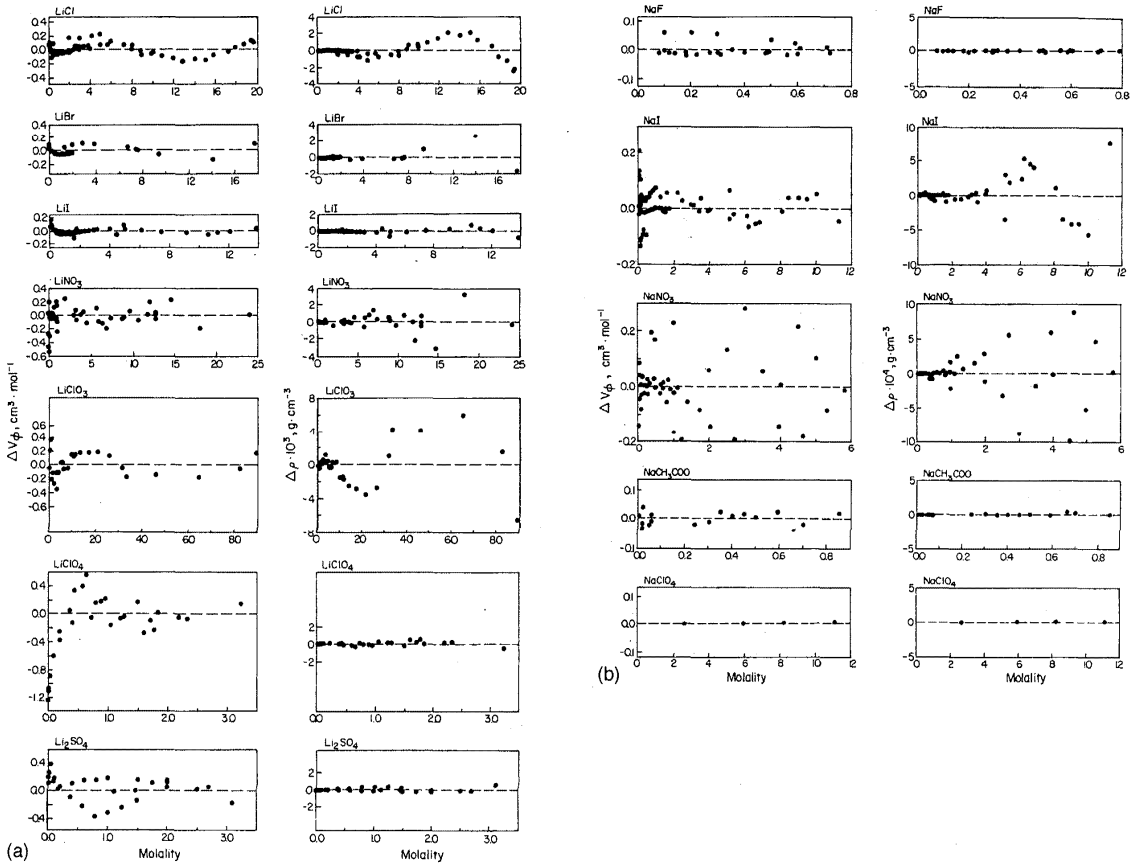

FIG. 2. (a) The comparison between experimental and calculated apparent molal volumes and densities of lithium salt solutions at 298.15 °K. (b) The comparison between experimental and calculated apparent molal volumes and densities of hydrochloric acid and of sodium salt solutions at 298.15 °K. (c) The comparison between experimental and calculated apparent molal volumes and densities of potassium salt solutions at 298.15 °K. (d) The comparison between experimental and calculated apparent molal volumes and densities of rubidium salt solutions at 298.15 °K. (e) The comparison between experimental and calculated apparent molal volumes and densities of cesium salt solutions at 298.15 °K. (f) The comparison between experimental and calculated apparent molal volumes and densities of argentum salt solutions at 298.15 °K. (g) The comparison between experimental and calculated apparent molal volumes and densities of tallium salt solutions at 298.15 °K. (h) The comparison between experimental and calculated apparent molal volumes and densities of ammonium salt solutions at 298.15 °K. (i) The comparison between experimental and calculated apparent molal volumes and densities of magnesium salt solutions at 298.15 °K. (j) The comparison between experimental and calculated apparent molal volumes and densities of calcium salt solutions at 298.15 °K. (k) The comparison between experimental and calculated apparent molal volumes and densities of strontium salt solutions at 298.15 °K. (l) The comparison between experimental and calculated apparent molal volumes and densities of barium salt solutions at 298.15 °K. (m) The comparison between experimental and calculated apparent molal volumes and densities of cobalt salt solutions at 298.15 °K. (n) The comparison between experimental and calculated apparent molal volumes and densities of nickel salt solutions at 298.15 °K. (o) The comparison between experimental and calculated apparent molal volumes and densities of copper salt solutions at 298.15 °K. (p) The comparison between experimental and calculated apparent molal volumes and densities of zinc salt solutions at 298.15 °K. (q) The comparison between experimental and calculated apparent molal volumes and densities of cadmium salt solutions at 298.15 °K. (r) The comparison between experimental and calculated apparent molal volumes and densities of beryllium and lead salt solutions at 298.15 °K.

creation of our database are cited in Table 1. An attempt was made to cover all the information available in the literature up to the end of 1993. However, in very rare cases we expect that some papers could have been inadvertently overlooked. We would appreciate any reader's comments on missing papers.

The density and apparent molal volume values as a function of the electrolyte concentration, taken from the literature, have been approximated by the least mean squares polynomial of the orders from 2 through 4 of the variable $m^{1/2}$. The values of the densities and apparent molal volumes, which deviated from the best fit curve by two or more standard deviations, were discarded from the databases. Figures 1(a)–1(f) present, as an example, a comparison of all the existing experimental apparent molal volumes of several electrolytes (HCl, NaCl, NaBr, KBr, $MgBr_2$, $CaBr_2$) in aqueous solutions at 298.15 °K. As can be seen from Figs. 1(a)–1(f), some experimental data obviously lie outside the general trend. Some points, for instance for NaBr solutions[19,33,84] and for KBr solutions,[63,67,102] deviate from the fit curve so much that they were not even presented in Figs. 1(c) and 1(d). The reasons for such deviations could be experimental errors in measuring both the solution concentrations and densities. Table 1 also contains our comments regarding the use of experimental data from various publications. The remaining data were consistent with one another,

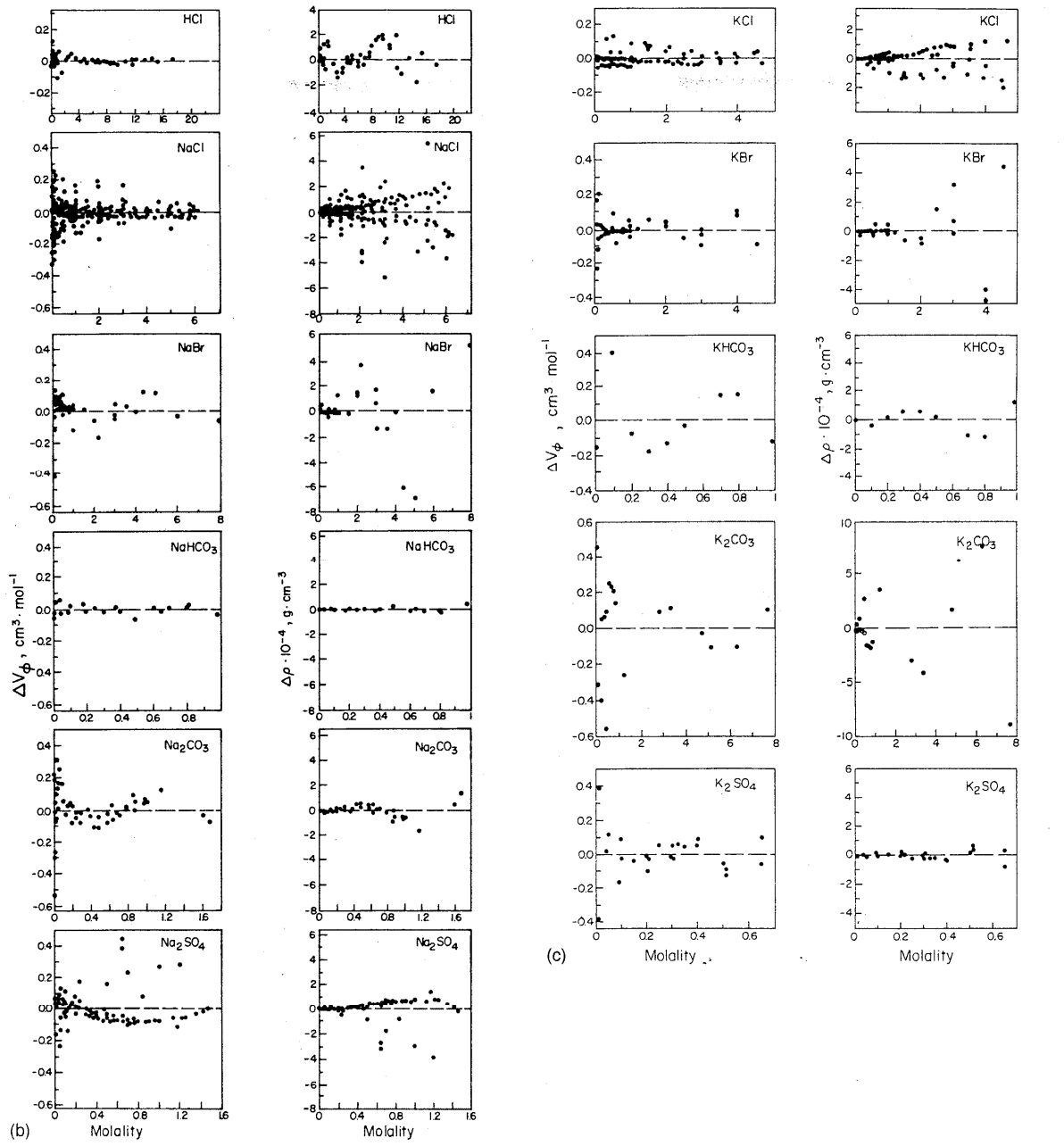

FIG. 2. (*Continued*)

and they were included in our database for further consideration.

For each type of electrolyte solution under consideration, the values of parameters $\bar{V}^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX} were calculated by the least-squares method from the experimental data by the following procedure. After substituting Eqs. (12)–(14) in Eq. (15), and its rearrangement, the following equation for apparent molal volumes was obtained:

$$V_{\phi,MX} = \bar{V}^0_{MX} + A_0 + A_1\beta^{(0)V}_{MX} + A_2\beta^{(1)V}_{MX} + A_3\beta^{(2)V}_{MX} + A_4 C^V_{MX}, \tag{17}$$

where A_0, A_1, A_2, A_3, and A_4 are concentration-dependent parameters. Some of these parameters (A_0, A_1, and A_4) are identical for all different valency-type electrolytes, while the parameter A_2 is different for 1:1, 1:2, 2:1, and 2:2 electrolytes. The term $A_3\beta^{(2)V}_{MX}$ was used only for 2:2 electrolytes.

$$A_0 = 0.416\,67 A_V \nu |z_M z_X| \ln(1 + 1.2I^{1/2}), \tag{18}$$

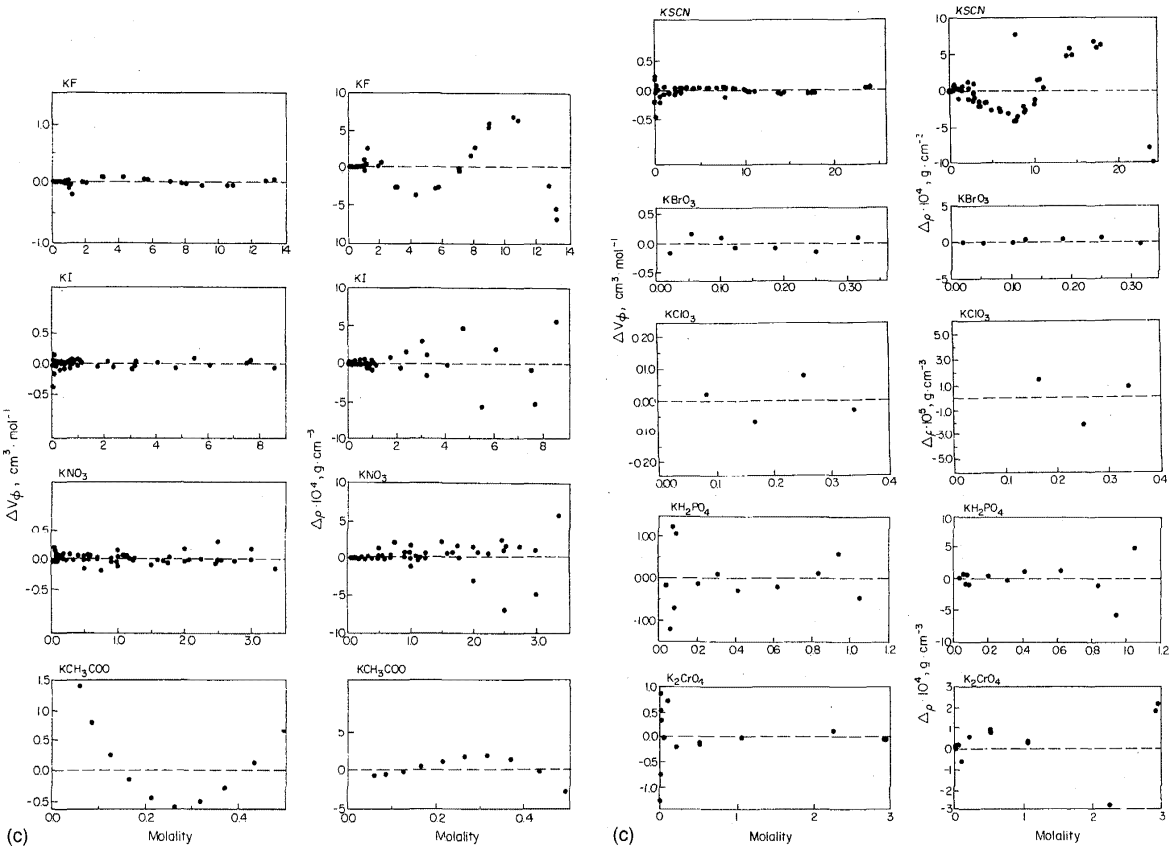

FIG. 2. (*Continued.*)

$$A_1 = 2RT\nu_M\nu_X m, \tag{19}$$

$$A_4 = 2RT\nu_M^2\nu_X z_M m^2. \tag{20}$$

For 1:1, 1:2, and 2:1 electrolytes,

$$A_2 = 2RT\nu_M\nu_X m\left(\frac{1}{2I}\right)[1-(1+2I^{1/2})\exp(-2I^{1/2})] \tag{21}$$

For 2:2 electrolytes,

$$A_2 = 2RT\nu_M\nu_X m\left(\frac{1}{0.98I}\right)[1-(1+1.4I^{1/2})\exp(-1.4I^{1/2})], \tag{21a}$$

$$A_3 = 2RT\nu_M\nu_X m\left(\frac{1}{72I}\right)[1-(1+12I^{1/2})\exp(-12I^{1/2})]. \tag{22}$$

In the framework of this method, we have minimized the squared differences of the experimental values of the apparent molal volumes at the different solute concentrations and those given by the respective test function [Eq. (15)]. The computations were carried out in the double precision mode using a FORTRAN program (created by Professor Ya. Iosilevskii) for inverting matrices by the Gauss–Jordan method.[4] The values of the volumetric ion interaction parameters so obtained are presented in Table 2. For the convenience of further discussion, we will call these sets of volumetric ion interaction parameters, which include the apparent molal solute volumes computed along with other parameters by Eq (17), "unrestricted volumetric ion interaction parameters."

For the selection of the best set of volumetric ion interaction parameters for each electrolyte type, each of the set should be checked for their reliability. We conducted such a check by two procedures: (a) by the comparison of the experimental densities and apparent molal volumes of solute of single-solute electrolyte solutions with those calculated by using the obtained sets of volumetric ion interaction parameters, and (b) by the ion-additivity rule applied to the calculated apparent molal volumes of solutes at infinite dilution. After both of these procedures were carried out, we were able to discard some sets of unrestricted volumetric ion interaction parameters which were not in conformity with the selected standards.

The first checking procedure consisted of the following steps:

(a) Apparent molal volumes of solutes and densities of solutions were calculated by Eqs. (15) and (16), respectively, by using the obtained sets of unrestricted volumetric ion interaction parameters for the whole range of concentrations in which experimental data were available.

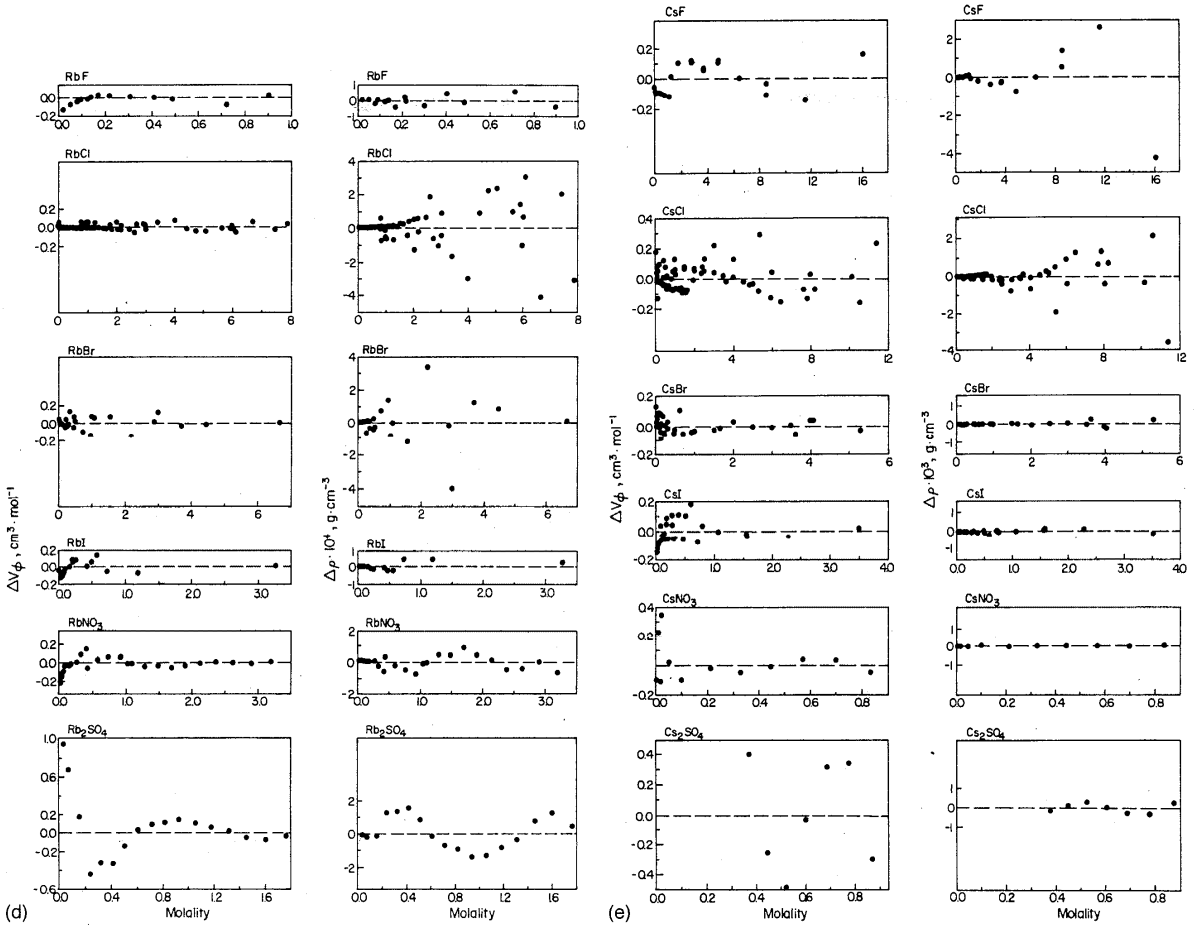

FIG. 2. (*Continued.*)

(b) The obtained values were then compared with the proper experimental values of the same concentrations.

The arithmetical means of the differences between experimental and calculated values of solution densities, $(\Delta\rho)_{av}=(\rho_{exp}-\rho_{calc})_{av}$, and between those of apparent molal volumes, $(\Delta V_\phi)_{av}=(V_{\phi,exp}-V_{\phi,calc})_{av}$, along with their standard deviations std($\Delta\rho$) and std(ΔV_ϕ), respectively, are presented in Table 2. Given a single-solute electrolyte type, a good set of unrestricted volumetric ion interaction parameters is, by definition, that for which $\Delta\rho_{av}$ and std($\Delta\rho$) are small. In this case, it turns out that if std($\Delta\rho$) is small, then std(ΔV_Φ) is small as well. Using this criterion, some poor sets of unrestricted volumetric ion interaction parameters have been discarded for the single-solute electrolyte solutions under study and are marked by the sign "*h*."

Figures 2(a)–2(r) give the comparison between experimental and calculated apparent molal volumes and densities of 102 single-solute electrolyte solutions at 298.15 °K at a wide concentration range. These figures allow one to see at a glance how good each Pitzer equation fit really is, how scattered the data were, what data had to be excluded, etc. The obtained results demonstrate the relatively high precision of volumetric calculations for single electrolyte solutions with the recommended sets of volumetric ion interaction parameters. However, it was observed that for some salts, the obtained fits often have systematic deviations from the data, i.e., the residuals cycle around the fit. The cycling of deviations is not specific to any particular equation; it arises for any equation that is not flexible enough to fit exactly. The cycling of deviations can be reduced in two ways, either by reducing the concentration range, or by including additional terms in the fitting equation. For various papers from 1973 onward for Pitzer's equations,[1] a maximum concentration limit for an equation application less than the range of the measurements was sometimes shown. In our opinion, it is desirable for most purposes to use only the usual terms through C and to reduce the concentration range of data so that the amplitude of deviations is acceptably near the experimental uncertainty. Later, we will demonstrate on LiCl solutions how a decrease in concentration range influences the amplitude of the deviations.

The second procedure of the analysis of the unrestricted volumetric ion interaction parameters was based on the physico-chemical definition that an apparent molal volume of an electrolyte at infinite dilution was an ionic additive property. Thus, the correctness of the obtained $\bar{V}^0_{MX}$ values in

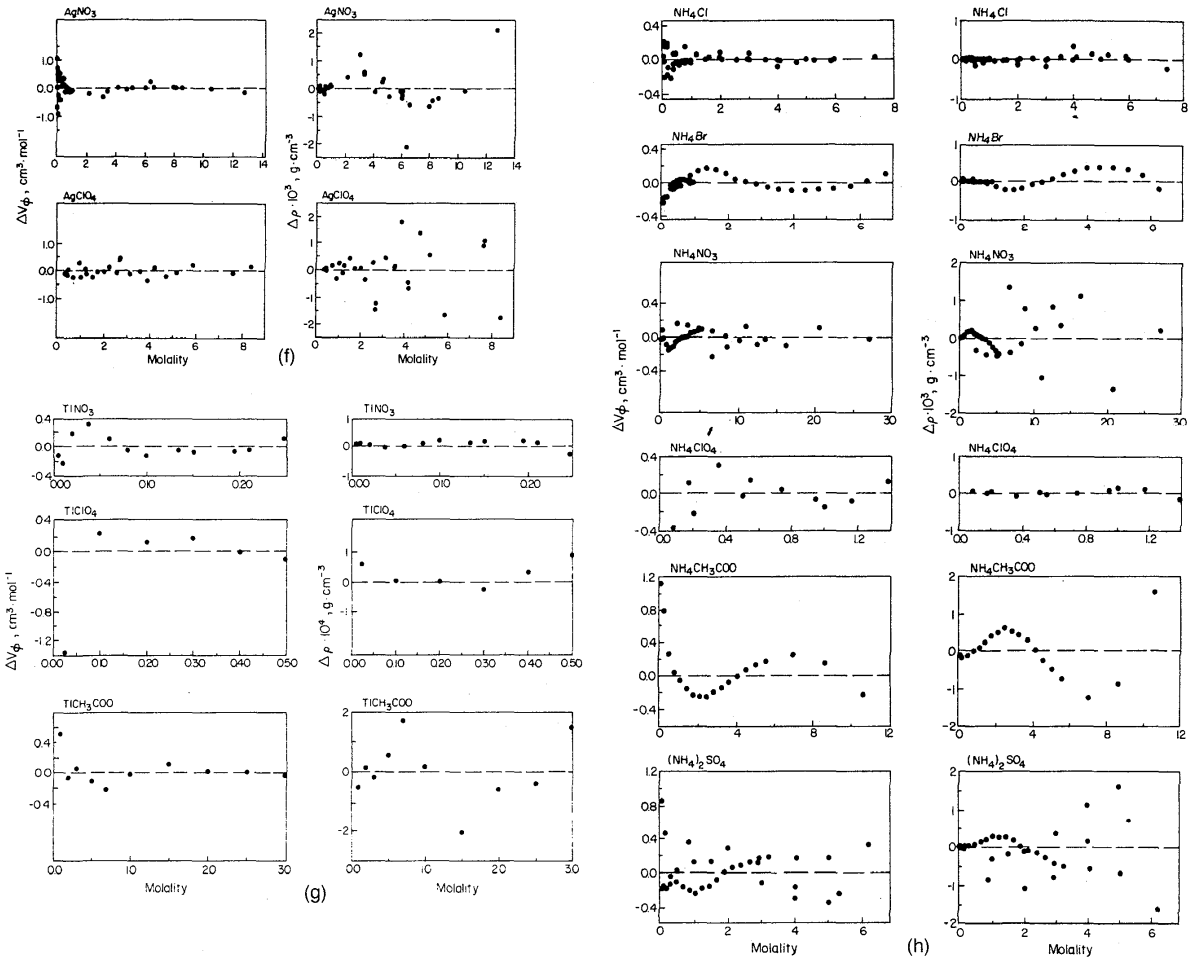

FIG. 2. (*Continued.*)

the sets of unrestricted volumetric ion interaction parameters can be verified by their obedience to the ionic additivity rule. Mathematically, the partial molal volume of the solute is the partial derivative of the molal solution volume with respect to moles of the solute at constant temperature, pressure, and moles of solvent:

$$\bar{V}_2 = \left(\frac{\partial V_{MX}}{\partial n_2}\right)_{T,P,n_1}. \tag{23}$$

According to the conventional physico-chemical definition, all limiting molal characteristics of the solute at infinite dilution must be independent of the ionic association phenomenon occurring in solutions of any finite solute concentration. Still, since the limiting characteristics are in practice found by extrapolating the respective characteristics at finite solute concentrations, the result obtained depends on the association phenomenon through the extrapolation procedure. A classical example of the solution of such a problem is the calculation of the limiting equivalent conductances by various conductance equations even for electrolyte solutions with strong ionic association, such as electrolyte solutions in organic solvents with moderate and low dielectric constants.[147] However, in most other cases, it is possible to neglect the role of ionic pairs formation at 298.15 °K when extrapolating the $\bar{V}_{MX}$ values to $\bar{V}^0_{MX}$ for dilute aqueous solutions.

The apparent solute molal volume for an electrolyte solution at infinite dilution must be additive with regard to the apparent volumes of the ions forming a solute molecule. The results of checking the obedience to the additivity rule of the values of $\bar{V}^0_{MX}$ from the sets of the unrestricted volumetric ion interaction parameters (Table 2) obtained by the least-squares method, as described above, are presented in Table 3 and in Fig. 3.

As can be seen from Table 3, some of the values of $\bar{V}^0_{MX}$ from the unrestricted volumetric ion interaction parameters do not obey the additivity rule. The values of $\bar{V}^0_{MX'} - \bar{V}^0_{MX'}$ or $\bar{V}^0_{M'X} - \bar{V}^0_{M''X}$ which do not obey the additivity rule are put in brackets. It should be emphasized that large deviations from the additivity rule are especially profound in the cases when only a few precise experimental values of V_ϕ are available for dilute solutions (below 0.1 mol/kg H_2O)

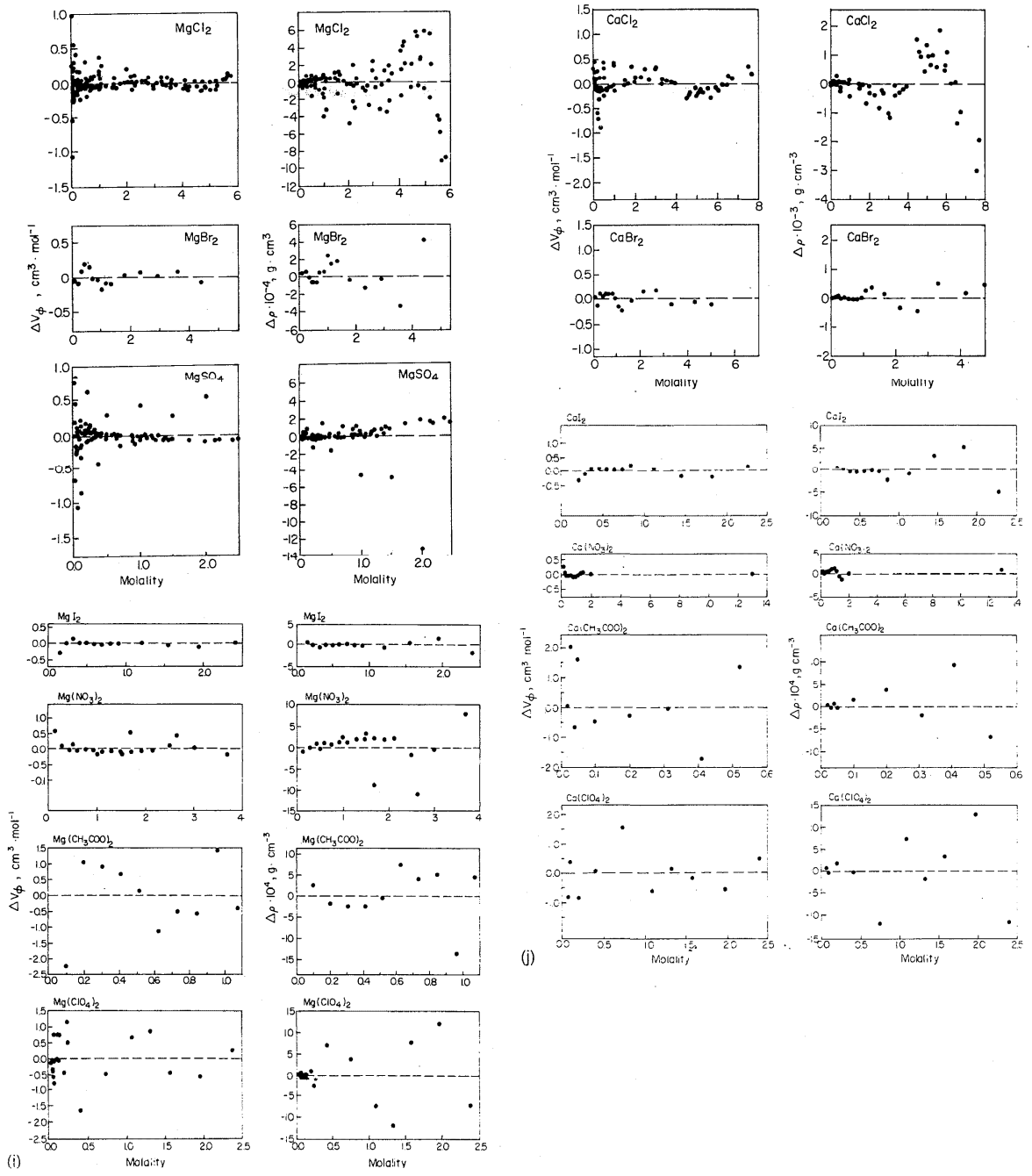

FIG. 2. (*Continued.*)

The disobedience to the additivity rule was probably a reason why Monnin [146] calculated his values of $\bar{V}^0_{MX}$ for $KHCO_3$, K_2CO_3, K_2SO_4, and $MgSO_4$ solutions by the additivity rule rather than to calculate them, along with the values of the other volumetric ion interaction parameters, by the least-squares method with varying $\bar{V}^0_{MX}$.

The disobedience of some of the obtained $\bar{V}^0_{MX}$ values to the additivity rule helped us to trace additional poor sets of unrestricted volumetric ion interaction parameters. These additional poor sets of unrestricted parameters were marked by the sign "g" in Table 2. The limiting apparent molal volumes marked by "i" in Table 2 cannot be analyzed by the application of the additivity rule, at the present state of our knowledge, since only one apparent molal volume exists with either the cation or anion for the solutes under question. Thus, the sets of unrestricted volumetric ion interaction parameters marked by g and h cannot be used for any volumetric calculations, since either their $\bar{V}^0_{MX}$ values disobey the additivity

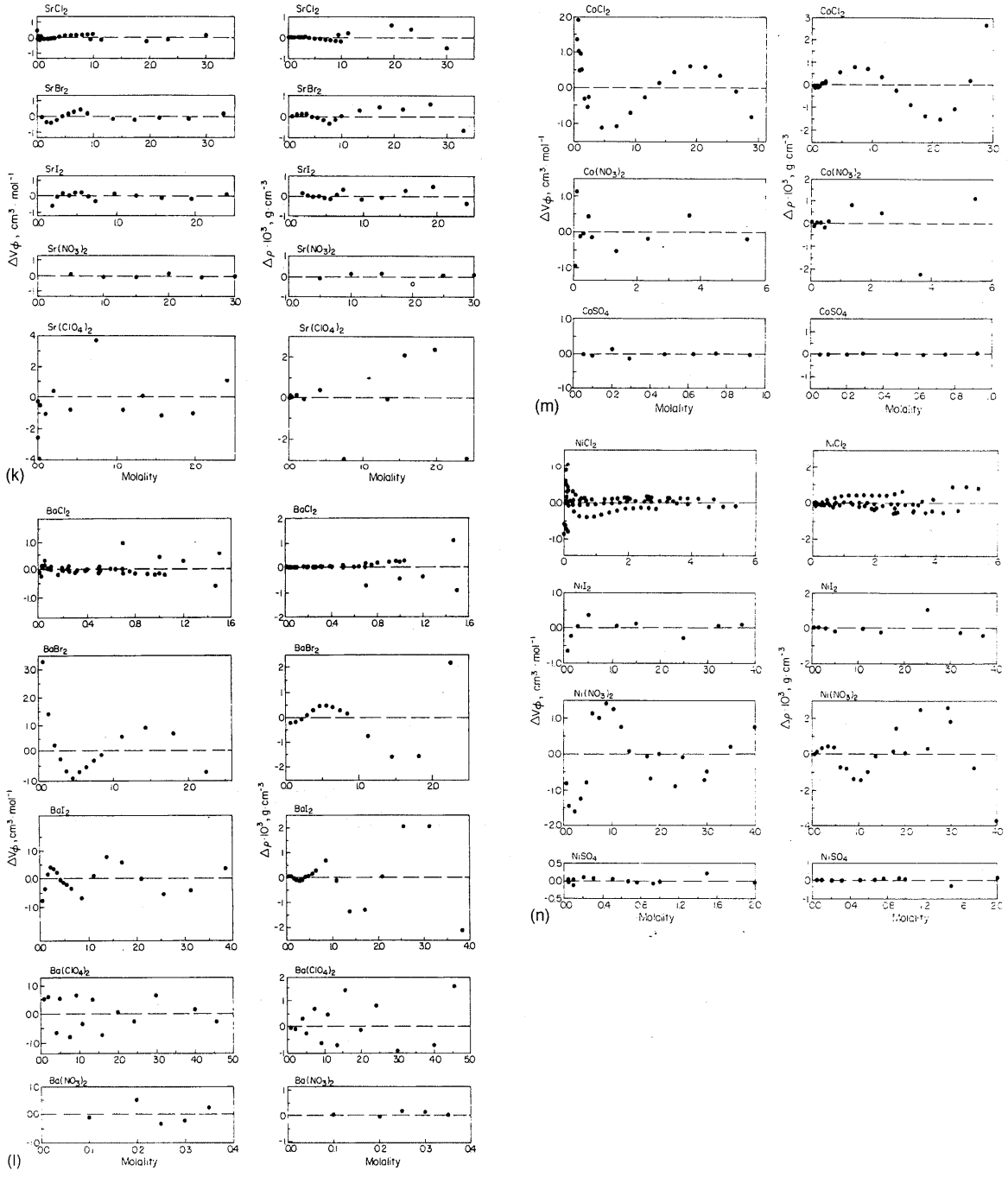

FIG. 2. (*Continued.*)

rule, or their fitting of volumetric experimental data is very poor. The sets of unrestricted volumetric ion interaction parameters recommended by us for further volumetric calculations are marked by "e." The $\bar{V}^0_{MX}$ values from these recommended sets were used for their splitting into ionic apparent volumes at infinite dilution, as described below.

We would like here to attract the reader's attention to the problem of the $\beta^{(2)V}$ parameter calculation. The $\beta^{(2)}$ parameter was designed more than 20 years ago by Pitzer and Mayorga[148] in order to represent partial ionic association of M^{2+} and X^{2-} ions to the ionic pair $MX^{(0)}$ in 2:2 electrolyte solutions. They concluded that there were many advantages in representing some thermodynamic properties (activity and osmotic coefficients) of these electrolytes by including the appropriate virial coefficient (with $\beta^{(2)}$) into the Pitzer equation and without chemical association equilibria. Such a

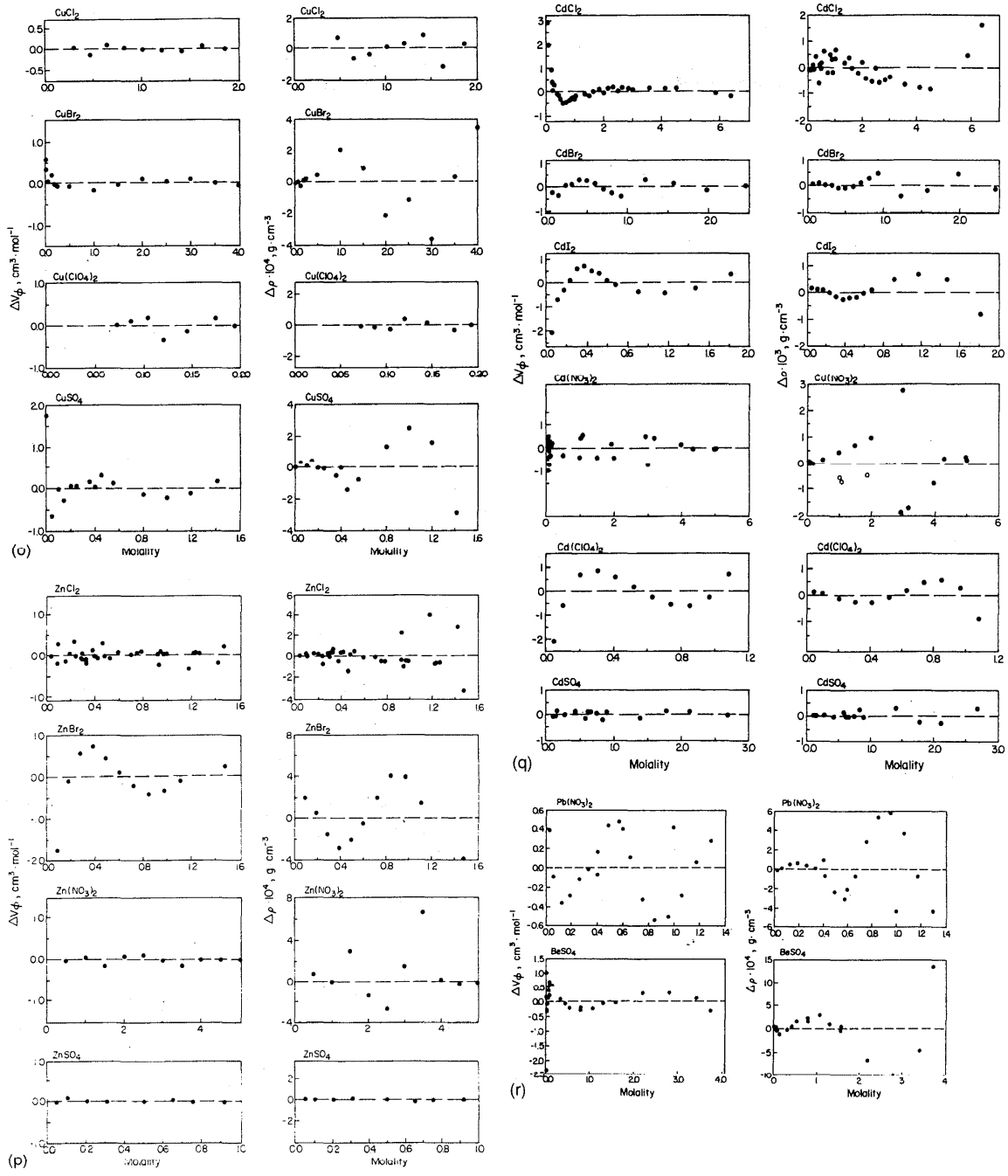

FIG. 2. (*Continued.*)

modified equation has been successfully applied for thermodynamic calculations both to 2:2 electrolyte solutions (sulfates) and to mixed electrolytes involving one component of the 2:2 type.

As can be seen from Eq. (22), the concentration-dependent term "A_3" contains the exponential "$e^{-12I^{1/2}} = e^{-24m^{1/2}}$," item. Owing to the large negative factor "-24" in the exponent, this term becomes concentration independent at all concentrations larger than ~0.15 mol/kg solvent. The analysis of Eqs. (17) and (22) demonstrates that there is an effective redundancy between $\bar{V}^0_{MX}$ and $\beta^{(2)V}_{MX}$. Reliable values of $\beta^{(2)V}$ can be obtained only for solutions for which precise density data are available for very dilute solutions. Since for almost all 2:2 electrolytes (sulfates) reliable density data for

TABLE 3. Checking the additivity of the apparent molal volumes at infinite dilution obtained by Pitzer's approach at 298.15 °K.

$\bar{V}^0_{MX}-\bar{V}^0_{M'X}$	Anions												
	F	Cl	Br	I	NO_3	ClO_4	HCO_3	CH_3COO	H_2PO_4	CO_3	SO_4	Avg.	Std.
Li–Na		0.25	0.28	0.34	(0.04)[a]	(−0.99)[a]					0.40	0.32	0.06
K–Na	10.18	10.23	10.21	10.15	10.32		11.27	(13.74)[a]	11.42	10.56	10.14	10.50	0.47
Rb–Na	15.13	15.32	15.35	15.19	15.14						16.12	15.38	0.34
Cs–Na	22.37	22.53	22.59	22.38	22.67						(27.74)[a]	22.51	0.11
Ag–Na					−0.45	−0.79						−0.62	0.17
Tl–Na					11.69	10.05		12.47				11.40	1.01
NH_4–Na		19.45	19.09		19.39	18.37		21.19			19.47	19.50	0.85
Ca–Mg		3.53	3.51	2.11	2.68	2.10		(14.92)[a]				2.79	0.64
Sr–Mg		4.32	2.55	3.09	(5.6)[a]	(1.92)[a]						3.32	0.74
Ba–Mg		8.89	(14.68)[a]	8.93	7.22	10.48						8.88	1.15
Mn–Mg		(3.75)[a,b]											
Fe–Mg		(−0.396)[a]			(−40.36)[a]								
Co–Mg		(−3.72)[a]			−8.67								
Ni–Mg		−7.84		−8.44	(−12.3)[a]							−8.14	0.30
Cu–Mg		−5.51	−5.98			−3.94						−5.14	0.87
Zn–Mg		−3.22[c]	(−16.89)[a]		−4.90							−4.06	0.84
Cd–Mg		(10.35)[a]	5.49	3.73	5.64	(1.72)[a]						4.95	0.87
Pb–Mg					1.53[b]								

	$\bar{V}^0_{MX}-V^0_{MCl}$												
Cations (M)	F–Cl	Br–Cl	I–Cl	NO_3–Cl	ClO_3–Cl	ClO_4–Cl	SCN–Cl	CH_3COO–Cl	HCO_3–Cl	BrO_3–Cl	H_2PO_4–Cl	CO_3–2Cl	SO_4–2Cl	CrO_4–2Cl
Li		6.89	18.47	11.18	18.87	(25.29)[a]							−21.15	
Na	−19.05	6.86	18.38	11.39		26.52		22.53	6.45		7.50	−40.23	−21.46	
K	−19.09	6.84	18.30	11.48	18.83		22.59[b]	(26.04)[a]	7.49	16.19[b]	8.70	−39.57	−21.65	−16.58[b]
Rb	−19.24	6.89	18.24	11.21									−19.87	
Cs	−19.21	6.91	18.23	11.52									(−11.06)[a]	
NH_4		6.50		11.33		25.45		24.27					−21.42	
Mg		7.35	18.05	12.08		26.40		(17.72)[a]						
Ca		7.34	17.33	11.65		25.69		23.41						
Sr		6.47	17.43	(12.73)[a]		(25.21)[a]								
Ba		(10.24)[a]	18.07	11.24		27.20								
Fe				(−15.81)[a]										
Co				(9.60)[a]										
Ni			17.75	(9.83)[a]										
Cu		7.12				27.19								
Zn		(0.52)[a,c]		11.24[c]										
Cd		(4.92)[a]	(14.73)[a]	(9.72)[a]		(22.09)[a]								
Avg.	−19.14	6.92	18.03	11.43	18.85	26.41		23.41	6.97		8.10	−39.90	−21.11	
Std.	0.08	0.28	0.37	0.26	0.02	0.67		0.71	0.52		0.60	0.33	0.64	

[a]The values in parentheses are poor, discarded results which were not taken into consideration for the calculations of average values.
[b]Only one $\Delta\bar{V}^0_{MX}$ value exists.
[c]The value $\bar{V}^0_{ZnCl_2}$ was taken from Table 6 and was calculated for upper concentration level less than 1.5 M.

very dilute solutions (Table 1) at 298.15 °K are missing, we decided to delete the sets of unrestricted volumetric ion interaction parameters for these electrolytes, except $BeSO_4$, from Table 2. The case of $BeSO_4$ can be considered as an exception. Since the data of Kaminsky,[73] that extend down to $m=0.0006$, appear to be reliable, we were inclined to retain the unrestricted set of volumetric ion parameters for $BeSO_4$for further volumetric calculations.

2.3. Ionic Apparent Volumes at Infinite Dilution at 298.15 °K

The limiting apparent molal volumes make the dominant contribution to the calculation of the mass density of complex electrolyte solutions by Pitzer's approach. Thus, usage of values of $\bar{V}^0_{MX}$ which disobey the additivity rule can lead to large errors in calculating volumetric characteristics of multiple-solute electrolyte solutions. In these cases it is therefore preferable first to calculate $\bar{V}^0_{MX}$ in terms of the apparent ionic volumes by the additivity rule, and then to calculate the remaining four volumetric ion interaction parameters $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX} by the least-squares method with $\bar{V}^0_{MX}$ fixed. The volumetric ion interaction parameters obtained by the above-described procedure (with the fixed $\bar{V}^0_{MX}=\bar{V}^0_{M^+}+\bar{V}^0_{X^-}$ value) will be called in further discussion "the restricted volumetric ion interaction parameters."

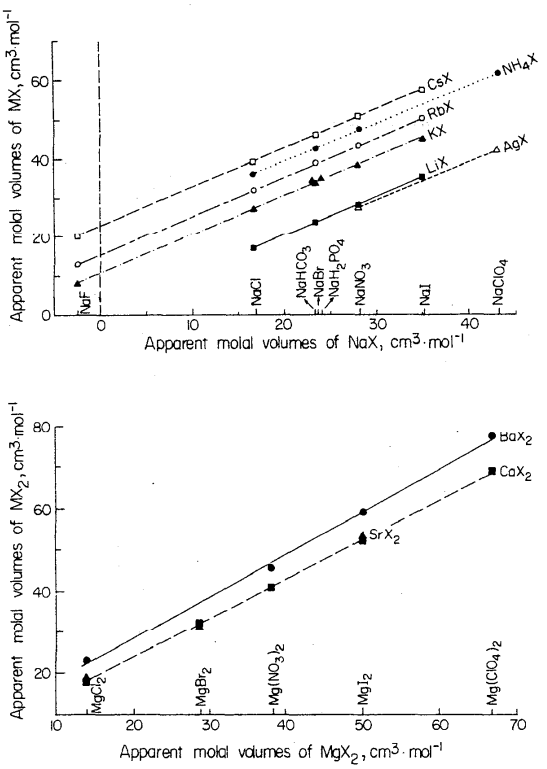

FIG. 3. The additivity correlations between limiting apparent molal volumes of various solutes at 298.15 °K.

Several detailed surveys discussing the methods of calculation of apparent molal volumes and splitting those volumes into ionic contributions have recently been published by Millero[149,150] and Krumgalz.[151,152] In the framework of those methods, the apparent solute molal volumes at infinite dilution were found either by the Masson,[153] or by the Redlich–Meyer,[154,155] or by the Owen–Brinkley[156] equations. The experimental coefficients of proportionality (S_V^*) between apparent molal volumes and the square root of the respective concentrations were used for the extrapolation to infinite dilution by the above methods, whereas the Pitzer approach produces the values $\tilde{V}^0_{MX}$ obtained with the theoretically correct Debye–Hückel coefficient (A_V). Therefore, we will use values of $\tilde{V}^0_{MX}$ obeying the additivity rule (from the sets of unrestricted volumetric ion interaction parameters) for the calculation of apparent ionic volumes at infinite dilution in our further calculations.

There are several different methods used for the separation of limiting molal apparent volumes of solutes into ionic contributions.[149–151] Millero[149] suggested two sets of ionic limiting apparent volumes for aqueous solutions at 298.15 °K based on two different assumptions: $\tilde{V}^0_{H^+} = 0$ and $\tilde{V}^0_{H^+} = -5.4$ cm³ mol⁻¹. Recently, Krumgalz[151] has suggested another set of limiting ionic apparent volume calculations which was based on the extrapolation method of Conway *et al.*[157,158]

TABLE 4. Apparent volumes of ions at infinite dilution at 298.15 °K and apparent molal volumes of the solutes used for their calculations.

Electrolyte	$\tilde{V}^0_{MX}$ (cm³ mol⁻¹)	Ion	$\tilde{V}^0_{ion}$ (cm³ mol⁻¹) This study	$\tilde{V}^0_{ion}$ (cm³ mol⁻¹) Millero (Ref. 149)	$\tilde{V}^0_{ion,ours} - \tilde{V}^0_{ion,Millero}$ (cm³ mol⁻¹)
HCl	17.824[a]	H^+	0	0	0
		Cl^-	17.82_4	17.83	−0.01
LiCl	16.866[a]	Li^+	-0.95_6	−0.88	−0.08
NaCl	16.620[a]	Na^+	-1.20_4	−1.21	0.01
KCl	26.848[a]	K^+	9.02_4	9.02	*0.00*
RbCl	31.943[a]	Rb^+	14.13_3	14.07	0.06
CsCl	39.155[a]	Cs^+	21.33_1	21.34	−0.01
NH_4Cl	36.069[a]	NH_4^+	18.24_5	17.86	0.39
$MgCl_2$	14.083[a]	Mg^{2+}	-21.56_5	−21.17	−0.40
$CaCl_2$	17.612[a]	Ca^{2+}	-18.03_6	−17.85	−0.19
$SrCl_2$	18.400[a]	Sr^{2+}	-17.24_8	−18.16	0.91
$BaCl_2$	22.975[a]	Ba^{2+}	-12.67_3	−12.47	−0.20
$CuCl_2$	8.571[a]	Cu^{2+}	-27.07_7	−27.76	0.68
$ZnCl_2$	10.864[b]	Zn^{2+}	-24.78_4	−21.6	−3.2
$NiCl_2$	6.244[a]	Ni^{2+}	-29.40_4	−24.0	−5.40
NaF	−2.426[a]	F^-	-1.22_2	−1.16	−0.06
NaBr	23.479[a]	Br^-	24.68_3	24.71	−0.03
NaI	34.998[a]	I^-	36.20_2	36.22	−0.02
$NaNO_3$	28.007[a]	NO_3^-	29.21_1	29.00	0.21
$NaHCO_3$	23.181[c]	HCO_3^-	24.38_5	23.4	0.99
$NaClO_4$	43.140[a]	ClO_4^-	44.34_4	44.12	0.22
$NaCH_3COO$	39.152[a]	CH_3COO^-	40.35_6	40.46	−0.10
Na_2CO_3	−6.48[c]	CO_3^{2-}	-4.07_2	−4.3	0.23
Na_2SO_4	11.776[a]	SO_4^{2-}	14.18_4	13.98	0.20
NaH_2PO_4	24.124[a]	$H_2PO_4^-$	25.32_8	29.1	−3.77
$AgNO_3$	27.558[a]	Ag^+	-1.65_3	−0.7	-0.9_5
$TlNO_3$	39.701[a]	Tl^+	10.49_0	10.6	-0.1_1
$Cd(NO_3)_2$	43.883[a]	Cd^{2+}	-14.53_9	−20.0	5.4_6
$Co(NO_3)_2$	29.569[a]	Co^{2+}	-28.85_3	−24.0	-4.8_5
$Pb(NO_3)_2$	39.769[a]	Pb^{2+}	-18.65_3[d]	−15.5	-3.1_5
$BeSO_4$	3.680[e]	Be^{2+}	-10.50_4[d]	−12.0	1.50
$KClO_3$	45.681[a]	ClO_3^-	36.65_7	*36.66*	*−0.00*
KSCN	49.434[a]	SCN^-	40.4_1[d]	35.7	4.71
$KBrO_3$	43.034[a]	BrO_3^-	34.0_1[d]	35.3	−1.29
K_2CrO_4	37.114[a]	CrO_4^{2-}	19.0_7[d]	19.7	-0.6_3

[a]The $\tilde{V}^0_{MX}$ values were taken from Table 2.
[b]The value $\tilde{V}^0_{ZnCl_2}$ was taken from Table 6 for $m<1.5$.
[c]The values were taken from Monnin (Ref. 146).
[d]These values were calculated from data existing only for a single electrolyte. Therefore, they must be used with greater caution, until new data related to an electrolyte with the same ion are obtained, and these values will be validated.
[e]The $\tilde{V}^0_{BeSO_4}$ values was taken from the set of unrestricted volumetric ion interaction parameters presented in Table 2 (see the text).

For the splitting of a value $\tilde{V}^0_{MX}$ into the ionic contributions, we have adopted, for all further calculations, the convention that $\tilde{V}^0_{H^+} = 0$ cm³ mol⁻¹. We preferred this assumption in order to be able to use it for future splitting of $\tilde{V}^0_{MX}$ values into ionic contributions at temperatures other than 298.15 °K. Then, using $\tilde{V}^0_{Cl^-} = \tilde{V}^0_{HCl}$, the $\tilde{V}^0_{M^+}$ values (the cation apparent volumes at infinite dilution) were calculated from $\tilde{V}^0_{MCl}$ values as $\tilde{V}^0_{M^+} = \tilde{V}^0_{MCl} - \tilde{V}^0_{Cl^-}$. Most of the $\tilde{V}^0_{X^-}$ values (the anion apparent volumes at infinite dilution) were calculated from the values of $\tilde{V}^0_{MX}$ for the sodium salts in each case. The values of $\tilde{V}^0_{MX}$ for the sodium salts have been used because they are usually known with a greater accuracy

TABLE 5. The restricted volumetric ion interaction parameters recommended for volumetric properties calculation at 298.15 °K.

Solute	$\bar{V}^0_{MX}$ ($cm^3\ mol^{-1}$)	$\beta^{(0)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(1)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(2)V}_{MX}\times 10^2$ ($kg\ mol^{-1}\ bar^{-1}$)	$C^V_{MX}\times 10^{6\ a}$ ($kg^2\ mol^{-2}\ bar^{-1}$)	m_{max}	Density$\times 10^6$ ($g\ cm^{-3}$)		Apparent molal volume ($cm^3\ mol^{-1}$)	
							$(\Delta\rho)_{av}$[b]	Std $(\Delta\rho)$[c]	$(\Delta V_\phi)_{av}$[b]	Std (ΔV_ϕ)[c]
KF	7.80	1.6843	1.6223		−0.5316	13.2	1	161	0.00	0.03
RbF	12.91	12.378	−20.248		−47.833	0.9	−1	26	−0.01	0.05
CsF	20.10	1.4344	1.3434		−0.4547	16.1	3	465	0.00	0.04
$CdCl_2$	21.12	0.4381	17.988		0.0746	6.4	0	127	0.00	0.19
$CoCl_2$	6.80	−6.0069	66.361		8.5426	2.9	−3	882	0.17	0.81
LiBr	23.73	0.22105	0.53870		−0.1660	17.7	4	269	0.00	0.03
KBr	33.71	1.0660	0.8337		−0.7017	5.6	2	190	0.00	0.05
RbBr	38.82	1.0619	0.57925		−0.5868	6.7	2	103	0.00	0.06
CsBr	46.01	0.91219	2.1934		−0.6393	5.3	8	73	0.01	0.05
NH_4Br	42.92	1.2286	−5.4386		−1.1622	6.8	5	189	−0.03	0.11
$MgBr_2$	27.80	−0.0468	14.569		1.0696	4.4	34	388	0.02	0.18
$CaBr_2$	31.33	2.1496	−5.2328		−0.8976	5.0	0	490	0.02	0.22
$SrBr_2$	32.12	1.7931	13.073		−1.2458	3.3	−1	308	−0.02	0.24
$BaBr_2$	36.70	−12.160	97.186		20.766	2.2	−2	928	0.18	1.13
$CuBr_2$	22.29	1.4782	2.5087		−0.00471	4.0	0	167	0.06	0.19
$ZnBr_2$	24.58	44.067	−150.25		−69.89	1.5	25	266	−0.07	0.67
$CdBr_2$	34.83	6.7086	−1.3153		−7.9666	2.5	31	237	−0.01	0.24
LiI	35.24	−0.20494	0.23708		−0.0254	13.9	3	186	0.01	0.04
KI	45.22	0.66609	0.44090		−0.3546	8.6	7	163	−0.01	0.08
RbI	50.33	3.1909	−6.1170		−5.2690	3.3	4	17	−0.03	0.07
CsI	57.53	1.5698	−0.75677		−2.7409	3.5	1	55	−0.03	0.08
MgI_2	50.84	2.6493	−35.889		−3.2096	2.4	−1	79	−0.01	0.10
CaI_2	54.37	4.5269	−55.226		−4.766	2.3	−4	251	−0.01	0.16
SrI_2	55.15	4.1735	−41.830		−3.229	2.4	−1	222	−0.01	0.25
BaI_2	59.73	2.5822	1.8569		−2.601	3.8	−1	1001	−0.03	0.44
CdI_2	57.86	1.0942	35.550		−4.5043	1.8	27	371	−0.12	0.71
NiI_2	43.00	2.4657	−40.801		−1.5350	3.7	4	424	−0.06	0.29
$LiNO_3$	28.24	0.090709	1.1405		−0.0196	24.0	19	859	−0.03	0.16
KNO_3	38.24	0.70025	3.7168		0.4637	3.4	3	188	0.00	0.05
$RbNO_3$	43.34	2.3289	−1.2892		−1.7615	3.2	1	35	−0.02	0.07
$CsNO_3$	50.54	−21.808	46.883		108.48	0.8	−2	18	0.02	0.14
NH_4NO_3	47.46	0.20914	−1.3660		−0.0371	27.1	25	550	−0.00	0.10
$Mg(NO_3)_2$	36.86	1.4967	−8.9155		−0.1506	3.7	31	403	0.02	0.22
$Ca(NO_3)_2$	40.39	2.4026	−5.9216		−0.5749	13.0	28	67	0.01	0.09
$Sr(NO_3)_2$	41.17	1.7733	12.490		−0.2257	3.0	31	185	0.00	0.10
$Ba(NO_3)_2$	45.75	−3.2269	57.867		···	0.4	27	77	−0.00	0.31
$Zn(NO_3)_2$	33.64	1.3876	−5.8099		−0.0733	5.0	72	255	0.00	0.08
$Ni(NO_3)_2$	29.01	5.5749	−23.947		−4.1150	4.0	16	1440	−0.12	0.92
$LiClO_3$	35.70	0.01784	4.1879		−0.0027	89.8	−58	2529	0.00	0.17
$LiClO_4$	43.38	3.7510	−12.827		−6.583	3.2	0	200	−0.17	0.46
$AgClO_4$	42.69	1.0017	−2.3035		−0.4234	8.4	1	791	−0.00	0.19
$TlClO_4$	54.83	15.425	−22.622		···	0.5	26	38	−0.16	0.55
NH_4ClO_4	62.59	16.502	−40.404		−54.52	1.4	18	86	−0.02	0.19
$Mg(ClO_4)_2$	67.12	0.057163	−4.1006		3.975	2.4	0	505	−0.02	0.67
$Ca(ClO_4)_2$	70.65	6.9527	−31.371		−6.148	2.4	1	756	−0.06	0.74
$Sr(ClO_4)_2$	71.43	−2.3722	10.058		7.7156	2.4	6	1536	−0.55	1.79
$Ba(ClO_4)_2$	76.02	1.6762	−8.0522		−0.0745	4.6	−4	1018	0.04	0.55
$Cu(ClO_4)_2$	61.61	−29.098	76.177		···	0.2	−1	23	0.00	0.18
$Cd(ClO_4)_2$	74.15	42.045	−197.45		−96.637	1.1	2	404	−0.13	0.87
KH_2PO_4	34.36	−103.79	282.40		417.95	1.1	0	98	0.00	0.23
$KHCO_3$	33.41	−1.9568	21.604		···	1.0	1	58	0.03	0.16
KCH_3COO	49.44	−64.446	185.49		···	0.5	1	139	0.12	0.63
$TlCH_3COO$	50.85	−0.54481	21.502		4.7593	3.0	1	107	0.03	0.19
NH_4CH_3COO	58.66	−0.47609	12.130		0.595	10.6	31	623	0.08	0.36
$Mg(CH_3COO)_2$	59.26	51.682	−161.16		−130.99	1.1	26	600	−0.07	1.13
$Ca(CH_3COO)_2$	62.79	−11.364	70.821		···	0.5	26	334	0.21	1.15
Li_2SO_4	12.27	2.6559	9.1982		−0.6533	3.1	2	199	0.04	0.18
K_2SO_4	32.23	1.1054	26.016		16.192	0.7	4	69	−0.01	0.16
Rb_2SO_4	42.45	5.1830	28.369		−3.1266	1.8	10	96	0.06	0.34
Cs_2SO_4	56.846	−9.6535	67.823		53.72	0.9	26	245	0.00	0.36
$(NH_4)_2SO_4$	50.674	3.1273	6.3778		−0.9771	6.2	−61	566	0.00	0.25
$MgSO_4$	−7.38	4.9809	14.491	1.4346	0.3969	2.5	5	218	0.00	0.28
$CuSO_4$	−12.89	22.037	−48.993	4.2329	−31.22	1.4	3	131	0.08	0.53
$CdSO_4$	−0.355	2.2668	34.156	−0.55351	2.9173	2.7	2	155	0.00	0.12

TABLE 5. (*Continued.*)

Solute	$\bar{V}^0_{MX}$ ($cm^3\ mol^{-1}$)	$\beta^{(0)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(1)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(2)V}_{MX}\times 10^2$ ($kg\ mol^{-1}\ bar^{-1}$)	$C^V_{MX}\times 10^6$ [a] ($kg^2\ mol^{-2}\ bar^{-1}$)	m_{max}	Density$\times 10^6$ ($g\ cm^{-3}$)		Apparent molal volume ($cm^3\ mol^{-1}$)	
							$(\Delta\rho)_{av}$ [b]	Std $(\Delta\rho)$ [c]	$(\Delta V_\phi)_{av}$ [b]	Std (ΔV_ϕ) [c]
$ZnSO_4$	−10.600	−1.5341	45.535	0.7585	15.5098	0.9	0	7	0.00	0.03
$CoSO_4$	−14.67	−2.1614	43.869	3.455	18.263	0.9	0	21	0.00	0.07
$NiSO_4$	−15.22	5.9619	23.967	1.8039	−0.1446	2.0	−2	110	0.00	0.09
K_2CO_3	13.98	3.4471	18.043		−0.8240	7.6	0	104	0.00	0.08

[a]The volumetric ion interaction parameters for the solutions with a concentration limit less than 0.7 mol/kg H_2O have been fitted by a reduced equation without the C^V_{MX} parameter.
[b]$(\Delta\rho)_{av}$ and $(\Delta V_\phi)_{av}$ are the arithmetical means of the differences between experimental and calculated densities and apparent molal volumes for a proper electrolyte, respectively.
[c]Std $(\Delta\rho)$ and std (ΔV_ϕ) are the standard deviations of the differences between experimental and calculated densities and apparent molal volumes, respectively, for all existing good quality literature data for a proper electrolyte.

than those for any other salt. The limiting apparent ionic volumes at 298.15 °K calculated in this paper in the above way, and also those reviewed by Millero,[149,150] are listed in Table 4.

However, some limiting ionic apparent volumes could neither be calculated from chlorides nor from sodium salts, since the apparent molal volumes at infinite dilution for these salts were not determined until now. In such cases they could be calculated from the combination of apparent molal volumes for other salts. For instance, $\bar{V}^0_{Ag^+}$ could be calculated as an averaged value based on $\bar{V}^0_{NO_3^-}$ and $\bar{V}^0_{ClO_4^-}$ values. Then, the obtained value will be $\bar{V}^0_{Ag^+} = 1.8_2 \pm 0.1_7$ $cm^3\ mol^{-1}$. Similar calculations could be carried out to obtain $\bar{V}^0_{Tl^+}$, $\bar{V}^0_{Cd^{2+}}$, and $\bar{V}^0_{Co^{2+}}$ values. However, we see no real advantage in averaged $\bar{V}^0_{ion}$ values based on several ionic

TABLE 6. Comparison of the unrestricted volumetric ion interaction parameters calculated in various concentration ranges for several electrolytes at 298.15 °K.

Solute	Upper level of concentration (mol/kg H_2O)	$\bar{V}^0_{MX}$ ($cm^3\ mol^{-1}$)	$\beta^{(0)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(1)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$C^V_{MX}\times 10^6$ ($kg^2\ mol^{-2}\ bar^{-1}$)	Density$\times 10^6$ ($g\ cm^{-3}$)		Apparent molal volume ($cm^3\ mol^{-1}$)
						$(\Delta\rho)_{av}$ [a]	Std [b] $(\Delta\rho)$	Std (ΔV_ϕ) [b]
KF	13.2	7.759	1.6514	2.0469	−0.5134	5	240	0.04
	1.8	7.752	1.1912	3.0857	0.8437	2	18	0.02
CsF	16.1	19.952	1.3419	2.7371	−0.4088	2	778	0.07
	4.9	20.032	1.9251	0.0800	−1.0805	15	117	0.04
LiCl	19.6	16.866	0.3853	1.5553	−0.1541	5	514	0.07
	2.1	16.945	0.3964	0.4782	0.4641	2	39	0.03
CsCl	11.4	39.155	1.0732	1.9031	−0.5218	8	572	0.08
	7.8	39.191	1.3086	0.8549	−0.8010	7	310	0.07
$ZnCl_2$	8.0	6.098	5.1645	53.668	−2.1931	10	3113	0.83
	1.5	10.864	19.449	−47.112	−24.422	5	121	0.15
$MnCl_2$	6.0	17.834	0.9712	0.1700	−0.3289	0	304	0.16
	3.9	18.045	1.5333	−4.5588	−0.9221	−1	312	0.14
$ZnBr_2$	8.2	11.898	3.8197	118.03	−1.5438	58	4740	1.14
	1.5	19.194	24.893	−33.531	−32.822	24	192	0.18
LiI	13.9	35.340	−0.1421	−0.6226	−0.0611	3	259	0.04
	2.1	35.427	0.3999	−2.8468	−1.0072	2	36	0.03
NaI	11.3	34.998	0.5381	−0.4369	−0.2805	12	170	0.06
	3.5	35.053	1.1816	−2.5833	−1.4546	8	41	0.06
BaI_2	3.8	59.107	1.9489	10.3680	−2.0110	−2	882	0.42
	0.85	57.506	−13.685	73.158	35.879	−3	30	0.09
KSCN	24.1	49.434	0.4036	2.4620	−0.0890	−34	301	0.11
	5.0	49.463	0.5685	1.4208	−0.199995	−24	60	0.13
$LiNO_3$	24.0	28.042	0.0325	2.6946	0.000018	18	915	0.15
	5.9	27.958	0.3523	4.8745	0.3846	13	220	0.16
$AgNO_3$	12.7	27.558	0.5458	11.051	−0.0728	0	515	0.61
	5.1	27.472	−1.0889	16.565	2.3387	0	258	0.68
$LiClO_3$	89.8	35.733	0.0187	4.0216	−0.0028	−60	2562	0.17
	6.5	35.715	−0.8108	6.8771	1.0048	−10	459	0.16
$AgClO_4$	8.4	42.348	0.6984	0.9783	−0.1808	0	762	0.19
	4.7	42.728	1.8558	−5.2081	−1.8173	0	607	0.20

[a]$(\Delta\rho)_{av}$ is the arithmetical means of the differences between experimental and calculated densities for a proper electrolyte solution.
[b]Std $(\Delta\rho)$ and std (ΔV_ϕ) are the standard deviations of the differences between experimental and calculated densities and apparent molal volumes, respectively, for all existing good quality literature data for a proper electrolyte.

TABLE 7. The volumetric ion interaction parameters of LiCl solutions calculated in various concentration intervals at 298.15 °K.

Concentration interval (mol/kg H_2O)	$\bar{V}^0_{MX}$ ($cm^3\ mol^{-1}$)	$\beta^{(0)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$\beta^{(1)V}_{MX}\times 10^5$ ($kg\ mol^{-1}\ bar^{-1}$)	$C^V_{MX}\times 10^6$ ($kg^2\ mol^{-2}\ bar^{-1}$)	Density$\times 10^6$ ($g\ cm^{-3}$)		Apparent molal volume ($cm^3\ mol^{-1}$)
					$(\Delta\rho)_{av}$[a]	Std $(\Delta\rho)$[b]	Std (ΔV_ϕ)[b]
0–19.58[c]	16.866	0.3853	1.5553	−0.1541	5	514	0.07
0–2.22[d]	16.87	−0.3194	2.8428	2.0996	−1	42	0.04
2.5–5.0[d]	16.87	0.6112	0.4837	−0.2991	−1	227	0.06
5.7–10.0[d]	16.87	0.3313	2.8154	−0.1771	11	277	0.03
10.9–19.58[d]	16.87	−0.02164	6.4924	0.003123	20	283	0.02

[a]$(\Delta\rho)_{av}$ is the arithmetical means of the differences between experimental and calculated densities for a proper electrolyte.
[b]Std $(\Delta\rho)$ and std (ΔV_ϕ) are the standard deviations of the differences between experimental and calculated densities and apparent molal volumes, respectively, for all existing good quality literature data for a proper electrolyte.
[c]Unrestricted volumetric ion interaction parameters calculated for the whole concentration range.
[d]Restricted volumetric ion interaction parameters, calculated with fixed value of $\bar{V}^0_{LiCl}$ equal to 16.87 $cm^3\ mol^{-1}$, for limited concentration intervals.

partners in the calculation of ionic apparent volumes at infinite dilution. Therefore we suggest basing the calculation of $\bar{V}^0_{Ag^+}$, $\bar{V}^0_{Tl^+}$, $\bar{V}^0_{Cd^{2+}}$, $\bar{V}^0_{Co^{2+}}$, and $\bar{V}^0_{Pb^{2+}}$ on $\bar{V}^0_{NO_3^-} = 29.21_1$ $cm^3\ mol^{-1}$. This procedure avoids unnecessary complexity compared to the procedure of averaged values' calculations. In addition, the nitrate reference for the determination of $\bar{V}^0_{Cd^{2+}}$ allowed us to avoid the problem related to a tendency toward ion association which arises to some extent for chlorides such as $CdCl_2$. The corresponding cadmium nitrate is essentially free from this effect.

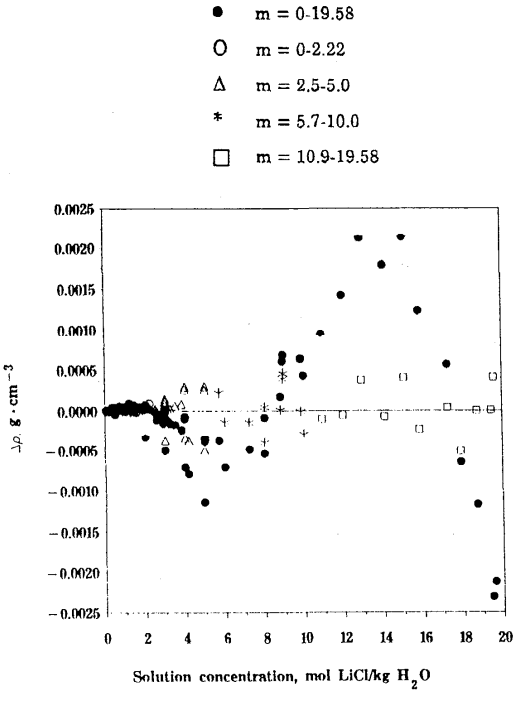

FIG. 4. The deviations of fitted densities of LiCl solutions at 298.15 °K calculated for various concentration ranges from experimental densities.

It is worth mentioning here that the $\bar{V}^0_{Cu^{2+}}$ and $\bar{V}^0_{Ni^{2+}}$ values (Table 4), based on chloride reference, are reasonable, since the ion association is not strong in these cases. Since we used the fit of $ZnCl_2$ to only $m=1.5$, the chloride reference is good for $\bar{V}^0_{Zn^{2+}}$ too. The $\bar{V}^0_{Be^{2+}}$, $\bar{V}^0_{SCN^-}$, $\bar{V}^0_{ClO_3^-}$, $\bar{V}^0_{BrO_3^-}$, and $\bar{V}^0_{CrO_4^{2-}}$ values were calculated on the basis of the only electrolyte by using apparent molal volumes of proper counterions: $\bar{V}^0_{SO_4^{2-}}$ for Be^{2+} and $\bar{V}^0_{K^+}$ for SCN^-, ClO_3^-, BrO_3^-, and CrO_4^{2-}. As can be seen from Table 4, the limiting apparent ionic volumes at 298.15 °K calculated by us are, in most cases (except those for Zn^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, SCN^-, and $H_2PO_4^-$), in fairly good agreement with those proposed by Millero.[149]

2.4. Recommended Volumetric Ion Interaction Parameters

After obtaining limiting apparent ionic volumes for a number of ions, we can try to solve the problem of the determination of the volumetric ion interaction parameters for electrolytes for which the $\bar{V}^0_{MX}$ values in the unrestricted sets were found either to disobey the additivity rule (these electrolytes are marked by the sign g in Table 2), or to give poor fitting of experimental densities (the electrolytes marked by

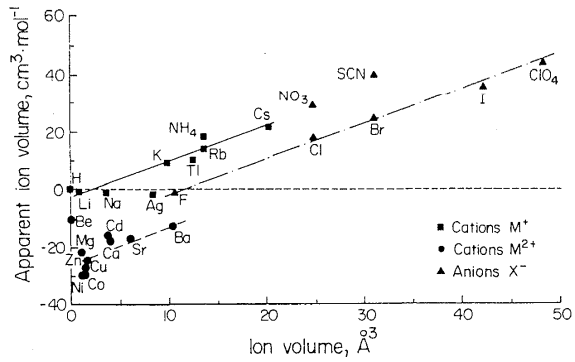

FIG. 5. Dependence of apparent ion volumes at infinite dilution at 298.15 °K on ion volume.

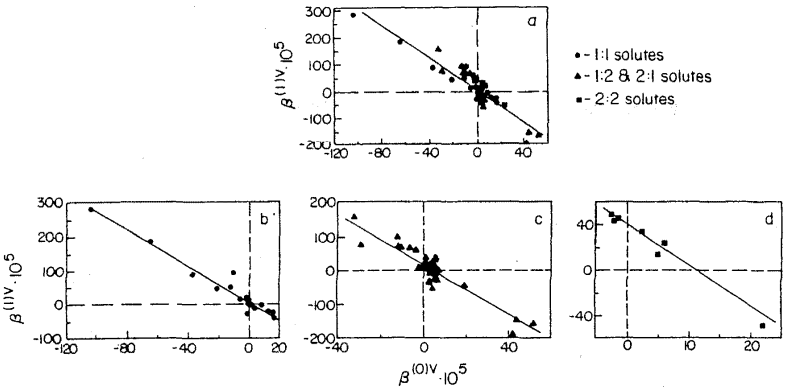

FIG. 6. The relationship between $\beta^{(1)V}$ and $\beta^{(0)V}$ for 1:1, 1:2, 2:1, and 2:2 electrolytes at 298.15 °K. (a) Total pool of data; (b) 1:1 electrolytes; (c) 1:2 and 2:1 electrolytes; (d) 2:2 electrolytes.

h in Table 2). Our major purpose is to provide the user interested in a complex mixed system with an unambiguous set of parameters including $\bar{V}^0_{MX}$ values. Therefore we decided that restricted volumetric ion interaction parameters should be used for all cases where the sum of ionic apparent volumes at infinite dilution differs even slightly from the $\bar{V}^0_{MX}$ values from unrestricted sets of volumetric ion interaction parameters for the salts in Table 2. Using our ionic apparent volumes at infinite dilution (Table 4), we calculated the $\bar{V}^0_{MX}$ values for these electrolytes by the additivity rule. Then using these $\bar{V}^0_{MX}$ values as fixed ones, we again fitted the parameters $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX} by Eq. (17). The obtained sets of the restricted volumetric ion interaction parameters are presented in Table 5.

Now we reached a point when it is possible to select and recommend the best sets of volumetric ion interaction parameters for their use in the calculation of volumetric properties of complex electrolyte solutions. The recommended sets are the following: (a) the sets of unrestricted volumetric ion interaction parameters for electrolytes with $\bar{V}^0_{MX}$ obeying the additivity rule (the electrolytes marked with the sign e in Table 2). Among these electrolytes are sodium salts, chlorides, and several nitrates and potassium salts which were used for the splitting of the $\bar{V}^0_{MX}$ values into ionic contributions; (b) the sets of restricted volumetric ion interaction parameters (Table 5) for electrolytes for which the $\bar{V}^0_{MX}$ values from the unrestricted sets (Table 2) either disobeyed the additivity rule or differ even slightly from the values obtained as a sum of ionic contributions. This approach differs from our earlier approach,[4] according to which all the recommended sets of volumetric ion interaction parameters for single electrolytes, formed from major ions of natural waters, were unrestricted sets; (c) for systems of $NaHCO_3$ and Na_2CO_3, Monnin's[146] parameters are recommended to be used. For some electrolytes, marked in Table 2 by the sign "g" [$MnCl_2$, $MnSO_4$, $FeCl_2$, and $Fe(NO_3)_2$], for which $\bar{V}^0_{MX}$ disobeys the additivity rule, we could not calculate restricted sets of volumetric ion interaction parameters, since one of the limiting ionic apparent volumes is unknown for these electrolytes at the present state of our knowledge. Therefore, none of the sets of volumetric ion interaction parameters can be recommended for these electrolytes at present.

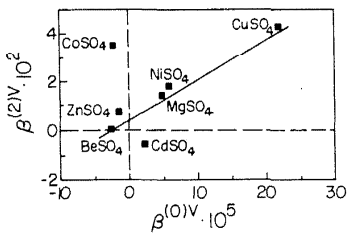

FIG. 7. The relationship between $\beta^{(2)V}$ and $\beta^{(0)V}$ at 298.15 °K.

It is understood that once some new and precise experimental densities of single-solute electrolyte solutions become available, the recommended sets of ion interaction parameters should be updated. However, we deeply believe that the presented "best values" of these parameters can be used for various purposes for several years without need for revisions.

As we mentioned above, the ion interaction equations are not expected to be accurate to very high molalities with just the B and C virial coefficients. The deviations for the calculations of ionic activity coefficients usually become serious about 6 molal. Therefore, Pitzer and Mayorga[159] and Pitzer[3] presented the highest concentrations at which the calculated osmotic and activity coefficients are valid. These concentrations are usually less than salt solubilities. For instance, Anstiss and Pitzer[160] showed that for $ZnCl_2$ solutions, the simple equation fitted to about $m=1.2$, while the solubility of $ZnCl_2$ is equal to 20.94 mol/kg H_2O.[161] We must be aware that the volumetric equations may start to deviate in the same range. Indeed, poor fitting of the density data was observed in some cases for solutions, marked with the sign "h" in Table 2, covering very expanded concentration intervals. Therefore, we decided to recalculate the volumetric ion interaction parameters over the reduced concentration range for this group of highly soluble electrolytes: KF, CsF, LiCl,

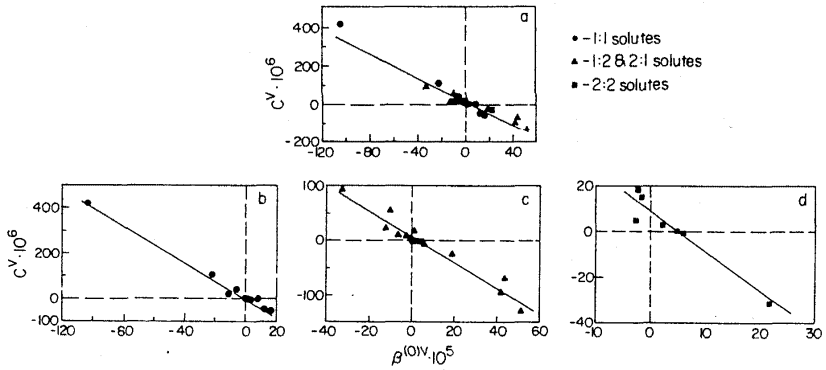

FIG. 8. The relationship between C^V and $\beta^{(0)V}$ for 1:1, 1:2, 2:1, and 2:2 electrolytes at 298.15 °K. (a) Total pool of data; (b) 1:1 electrolytes; (c) 1:2 and 2:1 electrolytes; (d) 2:2 electrolytes.

$CsCl$, $ZnCl_2$, $MnCl_2$, $ZnBr_2$, LiI, NaI, BaI_2, $LiNO_3$, $LiClO_3$, $AgNO_3$, and $AgClO_4$. The obtained parameters, along with those calculated in extended concentration ranges and taken from Table 2, are presented in Table 6.

A comparison of these two groups of volumetric ion interaction parameters demonstrates that only for $ZnCl_2$ and $ZnBr_2$ solutions do the $\tilde{V}^0_{MX}$ values calculated over different concentration ranges vary considerably from each other. However, for all the discussed solutions, the precision of the calculations was significantly improved when they were done in a reduced concentration range. Table 3 demonstrates that the $\tilde{V}^0_{ZnCl_2}$ calculated for $m<1.5$ obeys the additivity rule. Therefore, we accepted for all future calculations the $\tilde{V}^0_{ZnCl_2} = 10.864\ cm^3\ mol^{-1}$ calculated over this reduced concentration range ($m<1.5$) as the most reliable value.

It is possible that for highly soluble electrolytes, it is worth calculating several sets of volumetric ion interaction parameters in various concentration ranges. As an example of such calculations, we considered LiCl solutions. The use of the experimental data in the whole concentration range (0–19.58 mol/kg H_2O) yields the set of the volumetric ion interaction parameters which fit densities with standard deviation equal to 0.000 514 g cm^{-3}. In Table 7 we presented the restricted volumetric ion interaction parameters with the fixed $\tilde{V}^0_{LiCl}=16.87\ cm^3\ mol^{-1}$ calculated for various concentration

TABLE 8. The coefficients "a" and "b" for Eqs. (25a) and (25b) at 298.15 °K.

Relationship	Type of solute	Coefficients a	b	n[a]	R[b]
$\beta^{(1)V}_{MX}\times 10^5 = a + b\beta^{(0)V}_{MX}\times 10^5$	All together	8.71	−3.05 ±0.13	102	0.920
		0	−3.05 ±0.14	102	0.906
	1:1	5.64	−2.67 ±0.10	47	0.972
		0	−2.72 ±0.10	47	0.967
	1:2 and 2:1	11.85	−3.91 ±0.24	48	0.922
		0	−3.73 ±0.26	48	0.900
	2:2	39.28	−3.92 ±0.24	7	0.991
$\beta^{(2)V}_{MX}\times 10^5 = a + b\beta^{(0)V}_{MX}\times 10^5$	2:2	0.38	0.173±0.039	6[c]	0.913
$C^V_{MX}\times 10^6 = a + b\beta^{(0)V}_{MX}\times 10^5$	All together	8.40	−3.25 ±0.10	92	0.957
		0	−3.19 ±0.12	92	0.943
	1:1	4.20	−3.97 ±0.07	40	0.993
		0	−3.99 ±0.08	40	0.992
	1:2 and 2:1	5.93	−2.31 ±0.09	45	0.968
		0	−2.18 ±0.11	45	0.951
	2:2	9.01	−1.80 ±0.23	7	0.960

[a]Number of points used for calculations.
[b]Correlation coefficient.
[c]Calculations were done without $CoSO_4$.

intervals: 0–2.2; 2.5–5.0; 5.7–10.0; 10.9–19.58 mol/kg H_2O. By using the restricted volumetric ion interaction parameters from Table 7 for various concentration ranges, we demonstrated (Fig. 4) a considerable decrease in the deviations of the fitted densities, by equations for limited concentration ranges, from experimental densities. Therefore, for the highly soluble electrolytes (Table 6), the volumetric ion interaction parameters calculated for a limited range should be chosen in preference to those over the full range.

2.5. Analysis of Volumetric Ion Interaction Parameters

Using the multilayer hydration models of Gurney,[162] Eigen and Wicke,[163] and Frank and Wen[164] for ion–water interactions, Millero[165] has shown that the ionic limiting partial volume, $\bar{V}^0_{ion}$ can be attributed to the following components:

$$\bar{V}^0_{ion} = \bar{V}^0_{intr} + \bar{V}^0_{electr} + \bar{V}^0_{str} + \bar{V}^0_{cage}, \quad (24)$$

where $\bar{V}^0_{intr}$ is the positive increment in the $\bar{V}^0_{ion}$ value due to intrinsic ion volume (as a rule an intrinsic ionic volume in a solution is considered to be proportional to its crystallographic volume); $\bar{V}^0_{electr}$ is the negative increment in the $\bar{V}^0_{ion}$ value due to the decrease in molal solute volume related to ion–solvent interaction; $\bar{V}^0_{su}$ is the increment due to solvent structure destruction in the region of the ionic cosphere; and $\bar{V}^0_{cage}$ is the negative increment due to the filling of the intermolecular cavities of the water structure either by ions or by their parts. The latter increment was found by one of us[151] to be significant for large tetraalkylonium ions in aqueous solutions and negligible for mineral ions. Therefore Eq. (24) for aqueous solutions with simple ions will contain only the first three components. All components of Eq. (24) are not absolute volumes in a physical sense, actually they are limiting changes in the solute molal volume upon the addition of one mole of solute to such a large solution volume that this addition will not alter the solution concentration. Therefore, the negative partial volume of an ion means that with the addition of the ion, the decrease in the solution volume due to ion–solvent interaction is more than the increase in the solution volume due to the intrinsic ionic volume. The presentation of the apparent volumes at infinite dilution as a function of ionic dimensions [the ionic dimensions were calculated using crystal radii, except SCN^-, NO_3^-, and ClO_4^- anions for which ionic volumes were calculated by a geometrical model (Krumgalz, unpublished results)] (Fig. 5) demonstrates linear dependence (with a few exceptions) with separate lines for uni- and bivalent cations and for univalent anions with practically similar slope. Among the exceptions are the ions Ag^+, Be^{2+}, NO_3^-, and SCN^-.

Pitzer and Mayorga[159] observed some relationship between the parameters $\beta^{(0)}$ and $\beta^{(1)}$, used for the calculation of ion activity and osmotic coefficients, for various electrolytes. They observed that the closest relationship existed for 1:1 inorganic electrolytes. Based on the recommended sets of parameters presented in Tables 2 and 5, we analyzed the pairwise relationship between various volumetric ion interaction parameters at 298.15 °K. Figures 6–8 present the relationship between the parameters $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, C^V_{MX}, and $\beta^{(0)V}_{MX}$ for various electrolytes (1:1, 1:2, 2:1, and 2:2 solutes). As can be seen from Figs. 6–8, there are fairly good linear dependences with high correlation coefficients between $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, C^V_{MX}, and $\beta^{(0)V}_{MX}$ both for the whole pool of data and data for each electrolyte type. The points for all solutes in Figs. 6–8 fall on straight lines which pass either through the origin [Eq. 25(a)] or very close to it [Eq. 25(b)]

$$(\beta^{(1)V}_{MX}, \beta^{(2)V}_{MX}, \text{ or } C^V_{MX}) = \beta^{(0)V}_{MX}, \quad (25a)$$

$$(\beta^{(1)V}_{MX}, \beta^{(2)V}_{MX}, \text{ or } C^V_{MX}) = a + b\beta^{(0)V}_{MX}. \quad (25b)$$

The coefficients a and b for these linear correlations are summarized in Table 8. By analogy with the Pitzer and Mayorga[159] conclusion concerning the $\beta^{(1)}$ and $\beta^{(0)}$ relationship, we can assume that such a type of relationship between $\beta^{(1)V}_{MX}$ and $\beta^{(0)V}_{MX}$ indicates that short-range forces follow opposite patterns for ++ and −− interactions as compared to +− interionic ones. Figures 6(b)–6(d) demonstrate the fine structure of the relationship between the $\beta^{(1)V}_{MX}$ and $\beta^{(0)V}_{MX}$ parameters for various valency types of solutes. As can be seen from these figures, each type of electrolyte has various slopes for linear relationships (Table 8). The C^V_{MX} vs $\beta^{(0)V}_{MX}$ relationship is presented by a straight line too, with a fine structure for each type of solute. The relationships presented in Figs. 6–8 can be used for checking the self-consistency of the obtained parameters $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, C^V_{MX}, and $\beta^{(0)V}_{MX}$ and for the estimation of such parameters when there are no accurate density measurements at very low concentrations.

3. Acknowledgments

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