Table III. Coefficients of Eq 1 and Standard Deviations $\sigma(\Delta\epsilon)$ for the Systems Water (1) + $H(CH_2)_nOCH_2$–CH_2OH (2) at 298.15 K

n	A'_0	A'_1	A'_2	A'_3	A'_4	$\sigma(\Delta\epsilon)$	N
0	13.9172	−2.6887	0.2252			0.0486	30
1	19.2285	−1.9785	−0.0906			0.0596	20
2	15.5167	6.6099	0.7008	−6.1475	0.1949	0.0591	25
4	−11.2605	10.5111	15.0639	7.1495	12.2569	0.1111	34

ethanol vary in a linear way with x_2^{-1} in the range $x_2 \simeq$ 0.45–0.85 as can be seen in Figure 2. It is evident that these mixtures are highly structured, containing interesting metastable aggregates. No such linear regions were to be found in the plots of $Z_{\phi,2}$ vs x_2^{-1} for any system studied.

Numerous models have been proposed for the patterns of molecular aggregation that exists in mixtures of water with H-bond-forming organic species (*15–18*). We propose to examine the respective merits of these models in a detailed analysis of both the thermodynamic and dielectric properties of the alkoxyethanol–water systems.

Registry No. 1,2-Ethanediol, 107-21-1; 2-methoxyethanol, 109-86-4; 2-ethoxyethanol, 110-80-5; 2-butoxyethanol, 111-76-2.

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Molar Refractivities of Tetra-*n*-alkylammonium Salts and Ions

Neomi Soffer, Michael Bloemendal, and Yizhak Marcus*

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

The refractive index and density of dilute solutions of tetra-*n*-alkylammonium bromides in water and in *N*,*N*-dimethylformamide (DMF) were measured at 298.15 K. The following values of the infinite dilution molar refractivities (in $cm^3\ mol^{-1}$) were found: NH_4Br 15 ± 2, $(CH_3)_4NBr$ 36 ± 2, $(C_2H_5)_4NBr$ 47 ± 1, $(C_2H_5)_4NI$ 61 ± 2, $(C_3H_7)_4NBr$ 73 ± 2 (in water) and 68 ± 2 (in DMF), $(C_4H_9)_4NBr$ 91 ± 2 (in both solvents), $(C_5H_{11})_4NBr$ 108 ± 2 (in water) and 110 ± 2 (in DMF), $(C_6H_{13})_4NBr$ 128 ± 3, and $(C_7H_{15})_4NBr$ 150 ± 3. They yield a slope of 19.0 $cm^3\ mol^{-1}$ per four methylene groups added in the alkyl chains, when plotted against the length of the latter. The calculated polarizabilities of the cations are proportional to their van der Waals volumes.

Introduction

The molar refractivities, R, or polarizabilities, $\alpha = 3R/4\pi N_{Av}$ (N_{Av} is Avogadro's number) of the tetra-*n*-alkylammonium cations are useful quantities, relating to their interactions with the surroundings in solutions. Although they may be calculated approximately from group contributions (*1*), very few experimental values of them have been reported.

The present study was undertaken to provide such data from the measurement of refractive index values, n_D, and densities, d, of dilute solutions of those tetra-*n*-alkylammonium bromides that are soluble in water and in *N*,*N*-dimethylformamide (DMF) at 298.15 K. These ranged from $n_C = 1$ to $n_C = 5$ in water (n_C is the number of carbon atoms in the alkyl chain) and from $n_C = 3$ to $n_C = 7$ in DMF. The n_D and d values of dilute aqueous solutions of ammonium bromide and tetraethylammonium iodide were also measured for the purpose of comparison and checking. The molar concentrations, c, of the solutions ranged from 0.005 to 0.1 M (M = mol L^{-1}).

The apparent molar refractivity of the solute is given by

$$R_D = (1000/c)[(n_D^2 - 1)/(n_D^2 + 2) - (d - cM/1000) \times (1/d_0)(n_{D0}^2 - 1)/(n_{D0}^2 + 2)] \quad (1)$$

where n_{D0} and d_0 are the refractive index and density of the solvent and M is the molar mass (in g mol^{-1}). The subscript D is used on R and n to designate values measured at the mean yellow sodium line.

The values of R_D can, in principle, depend on the solvent and on the concentration c of the solution. Infinite dilution values, R_D^{∞}, obtained by extrapolation, are best employed for the purpose of further considerations of the solute–solvent interactions.

Experimental Section

The density and refractive index measurements were made essentially as in our previous work (*2*), with a Sodev 020 densitometer and a Bausch & Lomb dipping refractometer. The temperature was held constant at 298.15 K, controlled to ±0.001 K for the density and to ±0.05 K for the refractive index measurements.

Triply distilled water and spectral grade methanol, ethanol, and DMF were employed. Solutions were prepared by weight from the solid salts and the solvent and were then diluted volumetrically. The tetra-*n*-alkylammonium bromides were pure commercial products (Eastman Kodak), except for the ethyl-substituted salt. This was prepared in aqueous solution from tetraethylammonium iodide by means of an anion exchange resin column in the bromide form.

The densitometer was calibrated with water and methanol, using their reported densities at 298.15 K: d_0 = 0.997 045 g cm^{-3} for water (*3*) and d_0 = 0.785 818 g cm^{-3} for methanol (*4*). The density of ethanol was then measured, the resulting d_0 = 0.784 31 g cm^{-3} agreeing completely with its reported

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Table I. Molar Concentrations, c/M, Densities, d/g cm^{-3}, Refractive Index Values, n_D, and Molar Refractivities, R_D/cm^3 mol^{-1}, of Dilute Solutions of Tetra-n-alkylammonium Salts at 298.15 K

c	d	n_D	R_D
NH_4Br in Water			
0.005	0.997 48	1.332 79	(32.5)
0.010	0.997 84	1.332 61	8.8
0.015	0.998 16	1.332 76	13.8
0.020	0.998 45	1.332 78	13.8
0.025	0.998 76	1.332 97	16.1
0.030	0.999 05	1.333 00	15.4
0.100	1.002 90	1.337 81	(37.8)
$(CH_3)_4NBr$ in Water			
0.004	0.997 20	1.332 65	41.5
0.008	0.997 25	1.332 68	37.5
0.012	0.997 38	1.332 78	38.0
0.020	0.997 72	1.333 07	40.2
0.100	1.000 88	1.334 58	35.4
$(C_2H_5)_4NBr$ in Water			
0.018	0.998 07	1.333 04	47.8
0.036	0.998 16	1.333 58	47.7
0.054	0.999 68	1.333 78	46.1
0.072	1.000 74	1.334 27	46.2
0.108	1.003 11	1.335 55	47.5
$(C_3H_7)_4NBr$ in Water			
0.005	0.997 31	1.332 77	72.0
0.010	0.997 44	1.333 01	74.1
0.015	0.997 64	1.333 22	72.9
0.020	0.997 76	1.333 50	75.0
0.100	1.000 01	1.336 61	71.7
$(C_4H_9)_4NBr$ in Water			
0.005	0.997 43	1.332 97	106.7
0.010	0.997 37	1.333 03	89.3
0.015	0.997 46	1.333 32	90.6
0.020	0.997 61	1.333 66	92.6
0.100	0.999 48	1.337 61	90.0
$(C_5H_{11})_4NBr$ in Water			
0.005	0.997 48	1.332 95	108.1
0.010	0.997 53	1.333 11	101.0
0.015	0.997 67	1.333 55	108.0
0.020	0.997 73	1.333 87	108.8
0.100	0.999 06	1.338 68	108.8
$(C_2H_5)_4NI$ in Water			
0.010	0.998 01	1.333 09	64.8
0.015	0.998 36	1.333 18	59.3
0.020	0.998 40	1.333 33	61.4
0.025	0.998 73	1.333 57	62.3
0.030	1.003 30	1.333 62	(30.2)
0.100	1.003 95	1.336 20	59.1
$(C_3H_7)_4NBr$ in DMF			
0.005	0.943 74	1.428 16	62.9
0.010	0.944 00	1.428 25	65.3
0.015	0.944 38	1.428 43	67.1
0.020	0.944 61	1.428 47	66.5
0.100	0.949 34	1.430 60	69.6
$(C_4H_9)_4NBr$ in DMF			
0.005	0.943 62	1.428 20	88.8
0.010	0.943 85	1.428 33	88.9
0.015	0.944 17	1.428 37	87.8
0.020	0.944 31	1.428 70	91.8
0.100	0.948 30	1.430 94	90.0
$(C_5H_{11})_4NBr$ in DMF			
0.005	0.943 56	1.428 35	112.8
0.010	0.943 60	1.428 25	112.0
0.015	0.943 78	1.428 50	111.2
0.020	0.943 97	1.428 67	111.0
0.100	0.947 12	1.430 98	108.3
$(C_6H_{13})_4NBr$ in DMF			
0.005	0.943 40	1.428 20	131.3
0.010	0.943 44	1.428 49	137.9
0.015	0.943 62	1.428 46	131.6
0.020	0.943 83	1.428 67	128.2
0.100	0.946 01	1.431 12	125.2
$(C_7H_{15})_4NBr$ in DMF			
0.005	0.943 22	1.428 38	(175.6)
0.010	0.943 24	1.429 00	(186.6)
0.015	0.943 36	1.428 53	150.5
0.020	0.943 49	1.428 88	153.9
0.100	0.945 18	1.431 64	147.7

value (*4*). The dipping refractometer was calibrated as in our previous work (*2*).

The uncertainty in the measured refractive index, $\delta(\Delta n_D)$, where $\Delta n_D = n_D - n_{D0}$, is estimated at $\pm 5 \times 10^{-5}$. The uncertainty in the measured density, $\delta(\Delta d)$, where $\Delta d = d - d_0$, is estimated at $\pm 3 \times 10^{-5}$ g cm^{-3} (fewer averagings having been taken than in our previous work (*2*)). The uncertainty in the concentration is estimated at ±0.1% and does not affect the overall precision of the results appreciably. The resulting uncertainty in the molar refractivity R_D is

$$\delta R_D = (1/c^2)\delta c + (600/c)\ \delta(\Delta n_D) + (200/c)\ \delta(\Delta d)/d_0 \tag{2}$$

It ranges from 4 cm^3 mol^{-1} at $c = 0.005$ M to 0.2 cm^3 mol^{-1} at $c = 0.1$ M. Thus measurements at $c < 0.005$ M are too uncertain to be useful.

Results

The refractive index measured at 298.15 K in pure water was n_{D0}(W) = 1.332 52, that measured in pure *N*,*N*-dimethylformamide was n_{D0}(DMF) = 1.427 16. The corresponding values from the literature are (*5*) 1.332 503 and 1.428 17, respectively.

The values of the refractive index, n_D, and the density, d, measured for dilute solutions at concentrations c M of the tetra-n-alkylammonium bromides from $n_C = 0$ (i.e., ammonium bromide) to $n_C = 5$ in water, of these salts from $n_C = 3$ to $n_C = 7$ in DMF, and of tetraethylammonium iodide in water, are presented in Table I.

Table I shows that in these dilute solutions the values of R_D have no systematic trend with the concentration c. Weighted averages of the results, except for outlying values enclosed in parentheses, were calculated, the weight factors being the reciprocals of the uncertainties, δR_D, eq 2. These averages are taken to represent the infinite dilution molar refractivities of the salts, R_D^∞, and are shown in Table II, together with their standard deviations.

Discussion

A small discrepancy is noted between the value of n_{D0}(DMF) found in this work at 298.15 K and that reported by Riddick et al. (*5*), which is traceable to a secondary source, Dreisbach (*6*), and finally to unpublished data from the Dow Co. Other references in ref *5* lead to results differing by up to 0.0013 units from the one quoted there. We see no reason to prefer other values over ours, measured under the same conditions as our other data.

The three salts, for which there are R_D^∞ values for both aqueous and DMF solutions (Table II) show good agreement, i.e., independence from the nature of the solvent, within experimental error. This is a generally expected property of infinite dilution molar refractivities.

Individual ionic values of R_D^∞ have been obtained by Heydweiller (*7*) for aqueous solutions. They are based on R_D^∞(Na$^+$,aq) = 0.65 cm^3 mol^{-1}. For the present purpose the values R_D^∞(NH$_4^+$,aq) = 4.65, R_D^∞(Br$^-$,aq) = 11.60, and R_D^∞(I$^-$,aq) = 17.53, all in cm^3 mol^{-1}, are relevant. Subtraction of the value

Table II. Infinite Dilution Molar Refractivities, R_D^∞/cm^3 mol^{-1}, at 298.15 K, of Tetra-*n*-alkylammonium Salts in Water and DMF, and the Derived Values for Their Cations, R_{D+}^∞/cm^3 mol^{-1}, and Their Polarizabilities, $\alpha_+/10^{-30}$ m^3, and Values of R_{D+}/cm^3 mol^{-1} Calculated from the Molar Refractivities of Tetraalkylgermanes

		in water		in DMF			
salt	n_C	R_D^∞	R_{D+}^∞	R_D^∞	R_{D+}^∞	α_+	$R_D(R_4Ge) - 8.4$
NH_4NBr	0	15 ± 2	3 ± 2			1.2	
$(CH_3)_4NBr$	1	36 ± 2	24 ± 2			9.5	24.4
$(C_2H_5)_4NBr$	2	47 ± 1	35 ± 1				
$(C_2H_5)_4NI$	2	61 ± 2	43 ± 2			17.7	41.9
$(C_3H_7)_4NBr$	3	73 ± 1	61 ± 1	68 ± 2	56 ± 2	24.0	60.7
$(C_4H_9)_4NBr$	4	91 ± 1	79 ± 1	90 ± 1	78 ± 1	31.5	74.7
$(C_5H_{11})_4NBr$	5	108 ± 2	96 ± 2	110 ± 2	98 ± 2	39.0	97.2
$(C_6H_{13})_4NBr$	6			128 ± 4	118 ± 4	46.5	
$(C_7H_{15})_4NBr$	7			150 ± 3	138 ± 3	54.5	

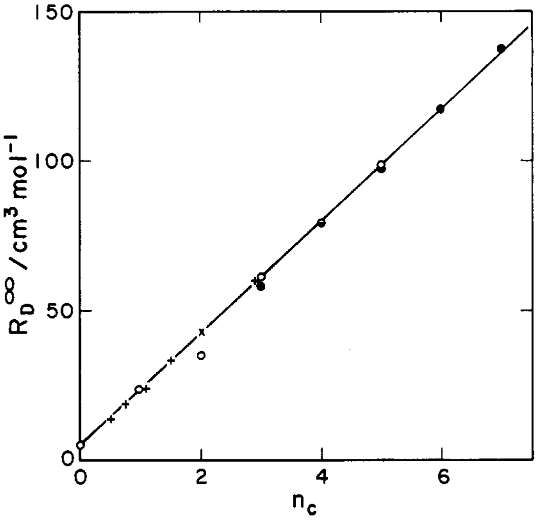

Figure 1. The molar refractivities at infinite dilution, R_{D+}^∞, of the tetra-*n*-alkylammonium cations plotted against the number n_C of carbon atoms per alkyl chain. Data: O, aqueous solutions; ●, DMF solutions; X, from iodide salt. The R_{D+} values of asymmetrical alkylammonium cations from ref *8* are plotted against $^1/_4$ the total number of carbon atoms in the chains, as + symbols.

for the bromide anion from those of the bromide salts (and that of the iodide anion from the R_D^∞ of tetraethylammonium iodide) yields the R_{D+}^∞ values for the cations, also shown in Table II.

It is seen that the value of R_{D+}^∞ for the ammonium ion agrees within its experimental error with that in the literature (*7*). The value of R_{D+}^∞ for tetramethylammonium in Table II agrees with that, 22.9 cm^3 mol^{-1}, found previously (*8*) from its bromide salt in formamide.

The values of R_{D+}^∞ are plotted in Figure 1 against n_C, the number of carbon atoms per alkyl chain. The data for the 12 entries are seen to lie on a straight line, $r_{cor} = 0.9980$, with a slope of 19.0 cm^3 mol^{-1} per four methylene groups added in the four alkyl chains. The values for the tetraethylammonium cation obtained from the data for the bromide salt are slightly below the line. A possible reason is a systematic error in the concentration, the solutions not having been prepared by weighing out the solid salt. The group-additive values of R_D of organic compounds yield, according to Bondi (*1*), a slope of 18.5 cm^3 mol^{-1} for four methylene groups, in agreement with the value found here.

Poole et al. (*9*) measured molar refractivities of some asymmetrical alkylammonium nitrates and thiocyanates that are liquid at room temperature. From the R_{D-} values of Batsanov (*10*), obtained for ions in crystals and the gas phase, 16.5 cm^3 mol^{-1} for SCN$^-$ and 10.8 cm^3 mol^{-1} for NO_3^-, R_{D+} values have been calculated for the alkylammonium cations, which are presented in Table III, and are also entered in Figure 1. The diagram shows that the data for the asymmetrical cations of the neat liquid salts lie on the same line as do our data for the symmetrical ions in water and DMF.

Table III. Molar Refractivities (in cm^3 mol^{-1}) of Asymmetrical Alkylammonium Salts and Cations

compd	R_D	R_{D+}
Liquid Salt (*8*)		
$C_2H_5NH_3NO_3$	23.9	13
$C_3H_7NH_3NO_3$	28.6	18
$(C_4H_9)_3NHNO_3$	68.4	57
$(C_3H_7)_2NH_2SCN$	48.9	33
$C_4H_9NH_3SCN$	39.5	23
2-$C_4H_9NH_3SCN$	40.0	24
In Benzene (*11*)		
$(C_4H_9)_3NHNO_3$	80.4	70
$(C_8H_{17})_3NHNO_3$	132.5	122
$(C_{12}H_{25})_3HNO_3$	183.9	173
$(C_4H_9)_3NHClO_4$	91.9	79
$(C_8H_{17})_3NHClO_4$	144.3	131
$(C_{12}H_{25})_3NHClO_4$	195.6	183

Poole et al. (*9*) have measured also the molar refractivities of hexyltriethylammonium hexyltriethylborate and of tetrahexylammonium benzoate. Subtraction of our R_{D+}^∞ value for $(C_6H_{13})_4N^+$ from the latter and the mean of the values for the isomeric $(C_3H_7)_4N^+$ and $(C_4H_9)_3NH^+$ from the former yields single ion values, R_{D-}, of 67 and 26 cm^3 mol^{-1}, respectively, for the anions $(C_2H_5)_3C_6H_{13}B^-$ and benzoate, which have not been reported previously.

Our molar refractivity data for the tetra-*n*-alkylammonium cations in solution can also be compared with the molar refractivities of the tetra-*n*-alkylgermanes, obtained by Mogul et al. (*11*). The data of Batsanov (*10*) suggest that the contribution to *R* of the positively charged nitrogen atom is close to zero, whereas that of the covalently bound germanium atom is 8.4 cm^3 mol^{-1}. Hence, the substitution of Ge by N$^+$ in the tetraalkyl species should lower *R* by that amount. The results of this subtraction are shown in Table II and agree well with our values.

Paljk et al. (*12*) measured the molar refractivities of some trialkylammonium nitrates and perchlorates in benzene solution, as shown in Table III. Subtraction of Batsanov's values of R_{D-} for nitrate (10.8) and perchlorate (13.2) yields the cation values also shown in this table. These are seen to be significantly higher than expected on the basis of Figure 1. Those based on the nitrates are about 10 cm^3 mol^{-1} and those based on the perchlorates are about 20 cm^3 mol^{-1} too high. Trialkylammonium salts in solvents of low relative permittivity are known to behave far from ideally and form ion pairs even at high dilution (*12*). Thus, although R_{D+}^∞ is largely insensitive to the solvent when the salt is completely dissociated, it is strongly sensitive to ion pair formation.

The polarizabilities of the tetra-*n*-alkylammonium cations, $\alpha_+ = (3/4\pi N_{Av})R_{D+}^\infty$, are shown in Table II. The ratio of the α_+ values to the van der Waals volumes, V_{vdW}, of those cations where the data are known (*13*, *14*) is constant: $\alpha_+/V_{vdW} = 0.105 \pm 0.002$, and is independent of n_C. This ratio can be used for the calculation of van der Waals radii, r_{vdW}, for the $n_C = 6$ and $n_C = 7$ cations that were not reported previously:

0.473 and 0.498 nm, respectively.

On the other hand, the polarizabilities α_+ divided by the cubes of the "real dimension" of the cations (*14*) yield values that decrease strongly with n_C: from 0.94 for $n_C = 1$, to 0.42 for $n_C = 7$. These "real dimensions" pertain to curled-up conformations of the alkyl chains in the unsolvated state, whereas those derived from the refractivities in both water and DMF pertain to straightened-out chains. This suggests that the tetra-*n*-alkylammonium cations are similarly solvated in water and in DMF.

Registry No. DMF, 68-12-2; $(CH_3)_4NBr$, 64-20-0; $(C_2H_5)_4NBr$, 71-91-0; $(C_2H_5)_4NI$, 68-05-3; $(C_3H_7)_4NBr$, 1941-30-6; $(C_4H_9)_4NBr$, 1643-19-2; $(C_5H_{11})_4NBr$, 866-97-7; $(C_6H_{13})_4NBr$, 4328-13-6; $(C_7H_{15})_4NBr$, 4368-51-8; NH_4Br, 12124-97-9.

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Excess Volumes of (*n*-Nonane + *n*-Undecane) between 288.15 and 308.15 K

Manuel Garcia, Carlos Rey, Vicente P. Villar,* and Julio R. Rodriguez

Departamento de Fisica da Materia Condensada, Facultade de Fisica, Universidade de Santiago, Santiago de Compostela, Spain

Excess molar volumes of (*n*-nonane + *n*-undecane) have been determined from density measurements at 288.15, 293.15, 298.15, 303.15, and 308.15 K. Density was obtained with an Anton Paar densimeter. The molar volumes of (*n*-nonane + *n*-undecane), (*n*-octane + *n*-undecane), and (*n*-heptane + *n*-undecane) are given as functions of temperature and the mole fraction of *n*-undecane. For each of these three binary mixtures, the coefficient of thermal expansion is plotted against the mole fraction of *n*-undecane at three temperatures.

Introduction

In previous articles (*1*, *2*) the excess volumes of (*n*-heptane + *n*-undecane) and (*n*-octane + *n*-undecane) at 288.15, 293.15, 298.15, 303.15, and 308.15 K have been determined. This article reports similar measurements for $(x)n\text{-}C_9H_{20} + (1 - x)n\text{-}C_{11}H_{24}$ together with three-parameter empirical equations fitted to the results obtained at each temperature. Third-degree polynomials in the mole fraction of *n*-undecane $(1 - x)$ have been fitted, at each temperature T, to the molar volumes of all three binary mixtures; and a polynomial in T has been fitted to the coefficients of the molar volume equations to obtain an expression for the molar volume as a function of $(1 - x)$ and T, and hence an expression for the coefficient of thermal expansion as a function of the same variables for $0 \leqslant x \leqslant 1$ in the temperature range investigated.

Experimental Section

Densities were measured with an Anton Paar DMA 60/602 densimeter with a resolution of $\pm 1.5 \times 10^{-6}$ g cm^{-3}. The temperature of the water bath containing the oscillator tube was kept constant to within ±0.005 K with a Hetofrig thermostat. The operational technique has been described elsewhere (*3*). The *n*-nonane (Fluka purum >99 mol %) and *n*-undecane (Merk >99 mol %) were carefully dried with Union Carbide Type 4 A molecular sieve (from Fluka) and were used directly without further purification. The observed densities of *n*-nonane and *n*-undecane at the various temperatures employed are given in Table I along with published values (*4*–*6*) for comparison.

Table I. Experimental Densities (g cm^{-3}) at Various Temperatures and Comparison with Literature Values

	T/K				
	288.15	293.15	298.15	303.15	308.15
	Experimental				
n-nonane	0.72176	0.71785	0.71396	0.71007	0.70617
n-undecane	0.74429	0.74059	0.73690	0.73320	0.72951
	Literature				
n-nonane		0.71763[a]	0.71381[a]	0.70976[c]	
n-undecane		0.74017[b]	0.7365[c]	0.73284[c]	

[a] Reference *4*. [b] Reference *5*. [c] Reference *6*.

Results and Discussion

Table II list the excess molar volumes V_m^E calculated from the observed densities for each temperature T and each value of the mole fraction of *n*-nonane x. For each T, equations of the form

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1 - x)\sum_{k<3} A_k(2x - 1)^k \qquad (1)$$

were fitted to the experimental results. The parameters A_k and the standard deviations of fit are listed in Table III, and Figure 1 shows the fitted V_m^E curves together with the experimental points. In all cases V_m^E is negative and the curves are asymmetric with a minimum at $x = 0.473$.

Third-degree polynomials

$$V_m = \sum_{k<4} B_k(1 - x)^k \qquad (2)$$

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