

VOLUMETRIC PROPERTIES OF AQUEOUS SOLUTIONS OF ALKALI HALIDES

by

TORBEN GRAVES PEDERSEN¹⁾, CHRISTIAN DETHLEFSEN²⁾ and AASE HVIDT²⁾

¹⁾ Department of Chemistry, Carlsberg Laboratory,
Gamle Carlsberg Vej 10, DK-2500 Copenhagen Valby

²⁾ Department of Chemistry, H.C. Ørsted Institute,
5, Universitetsparken, DK-2100 Copenhagen Ø

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The density of aqueous solutions of LiF, NaF, or KF, at room temperature, is measured as a function of the concentration. The measurements, together with corresponding data available on other alkali halides, are used to illustrate the concentration dependence of the apparent molar volume of the electrolytes in aqueous solution.

The data is in accordance with the conception that an essential, negative contribution to the volume is due to a progressive hydration of the ions upon dilution (i.e. with increasing water concentration).

The peculiar behaviour of the Li⁺-salts, compared with the other alkali halides, is associated with the small size of the Li⁺-ion compared with a water molecule.

1. INTRODUCTION

The partial volume of a component in solution can be obtained from measurements of the density of the solution as a function of the concentration. In this way density measurements are used as a tool in attempts to elucidate pressure effects on chemical equilibria or reaction rates (1, 13, 14, 17), or to explain the sedimentation of macromolecular systems by ultracentrifugation (16, 19). More generally, the density of liquid systems may contribute information about the weak molecular interactions in the liquid state. Although the detailed interpretation is far from accomplished, some insight into liquid systems at the molecular level - in particular the behaviour of water as a solvent - is gained from density measurements (7, 9, 10, 14, 17). Whereas the volume change on mixing two nonpolar liquids is usually less than 1 to 2 cm³mole⁻¹ (13), volume effects exhibited in

aqueous systems can be considerably larger. The ionization volume of water (-22.3 cm³mole⁻¹ (14, 15)), as well as the negative partial volume of f.ex. MgSO₄ in dilute aqueous solution (8), indicate that at least part of the volume effects observed in aqueous solutions of electrolytes must be due to interactions of the ions with solvent water, i.e. to solvation effects known as electrostriction of water (5).

In the literature most volumetric investigations of aqueous solutions focus interest on estimates of the volume of the solute at infinite dilution. It is the aim of the present paper, in addition, to illustrate the concentration dependence of the volume of aqueous solutions of alkali halides over the entire solubility range. Comprehensive data on the density of solutions, at room temperature, of most of the alkali halides is available in the literature, although information about the fluorides is limited. By means of an

automatic densimeter equipment we have measured the density of aqueous solutions of LiF, NaF, or KF as a function of the concentration. These measurements, together with available data on alkali halide solutions, are presented as plots of the apparent molar volume of the salts versus the mole fraction. The mole fraction concentration scale is chosen in order to draw immediate attention to the concentration of both components in the solutions, an alkali halide and water. In the discussion of the experimental data the non-ideal volumetric behaviour of the solutions is associated with solute-solvent interactions, considered as hydration of the ions.

2. MATERIALS

LiF, NaF, and KF are analytical grade from E. Merck, Darmstadt. The salts are dried at 200 °C for 48 hours, and used without any further purification.

Water used is glass distilled.

3. EXPERIMENTAL

Densities are measured by means of a vibrating-tube densimeter cell (Anton Paar, Model DMA 02) (20), calibrated with air and with pure water. The density of water at 25 °C is 0.997048 gcm⁻³ (12). The cell is built into a computer controlled set-up for automatic measurements of the density of solutions as a function of the concentration. Details of the equipment are described elsewhere (4).

Starting solutions of the salts are prepared by weighing, and automatically diluted by stepwise additions of pure water. The equipment makes it possible, with a moderate effort, to obtain a number of density measurements - appropriately distributed over a given concentration range - sufficient for a numerical fitting of a model with 4 - 5 adjustable parameters (4).

4. THEORETICAL

The apparent molar volume of a solute, at the mole fraction x_1 , is defined as

$$V_1^{\text{app}} = (V_m - x_0 V_0^*)/x_1. \quad (1)$$

V_m is the molar volume of the solution. The subscripts 1 and 0 refer to the solute (an alkali

halide) and to water, respectively, ($x_1 + x_0 = 1$). The superscript * indicates the pure, liquid state at the temperature of the experiments. V_1^{app} represents the volume increment per mole of solute added to a known amount of solvent.

Eq. (1) is in accordance with the following formulation of V_1^{app} in terms of the directly measured densities, d , and weight fractions, w ,

$$V_1^{\text{app}} = M_1 [1/d_0^* + (1/d - 1/d_0^*)/w_1]. \quad (2)$$

In attempts to interpret volumetric data it may be useful to consider the following formulation of V_1^{app}

$$V_1^{\text{app}} = V_1^* + V_m^E/x_1, \quad (3)$$

where V_m^E is the molar excess volume of the solution

$$V_m^E = V_m - (x_1 V_1^* + x_0 V_0^*).$$

In eq. (3) the apparent molar volume of the solute is considered as a sum of the molar volume (V_1^*) of the pure solute in a (hypothetical) liquid state, i.e. for $x_1 = 1$, and V_m^E/x_1 which is the excess volume of the solution per mole of the solute.

We have tentatively estimated V_1^* of alkali halides at room temperature by extrapolating volumetric data on the molten salts (11), assuming a constant expansivity coefficient, α , over the entire temperature range, viz.

$$V_1^*(298 \text{ K}) = V_1^*(T)[1 + \alpha(298 - T)]. \quad (4)$$

Table I summarizes the calculated values of V_1^* , together with the molar volume of the salts in the crystalline state (V_1^{cr}), and the "intrinsic" volume, defined as

$$V_1^{\text{intr}} = 4\pi/3 (R^3 + R_0^3)L, \quad (5)$$

In eq. (5) R denotes the ionic radii ((2)p.61), and L is Avogadro's number. Estimated values of the intrinsic volume of water vary from 6.5 to 12.4 cm³mol⁻¹ ((2) p. 534, (6), (21)).

The volume of a liquid is a sum of the intrinsic volume of the molecular and/or ionic species present, and the empty space between them. On the assumption that the intrinsic volume remains constant, the excess volume of a liquid mixture is the difference between the empty space in the mixture and in the pure components. Thus the excess volume is a measure of a difference in the packing of the species present in the two states.

Serious problems are burdening attempts to interpret volumetric data on aqueous solutions of electrolytes. Difficulties involved in achieving

Table I.

Calculated molar volumes, in $\text{cm}^3 \text{mol}^{-1}$, of alkali halides at 25°C .
The ionic radii, in Å, (ref. (2), p. 61) are given in parenthesis.

v_1^{intr}	intrinsic volume (eq. (5))
v_1^{cr}	crystal volume (ref. (24))
V_1^*	liquid volume (eq. (4))

	F^- (1.33)	Cl^- (1.81)	Br^- (1.96)	I^- (2.19)
Li^+ (0.68)	6.73 9.96 11.61	15.77 20.43 24.10	19.82 25.12 30.26	27.28 32.95 38.07
Na^+ (0.98)	8.32 15.05 16.38	17.36 26.96 29.58	21.38 32.16 35.10	28.89 40.84 44.82
K^+ (1.33)	11.88 23.43 23.69	20.94 37.68 38.02	24.93 43.27 43.87	32.46 53.04 53.99
Rb^+ (1.48)	14.12 29.35 -	23.14 43.80 42.30	26.88 49.37 48.37	34.69 59.83 58.85
Cs^+ (1.67)	17.70 36.91 33.63	26.76 42.42 48.79	30.75 47.93 54.84	38.25 57.61 66.82

a reasonable estimate of V_1^* (in eq. (3)) of a salt makes the calculated value of the excess volume of a solution somewhat uncertain. Another problem is related to the fact that the intrinsic volume of a water molecule, and of some of the ions considered, is comparable to the free space in the liquids. The particles of one component can enter in part into interstices of the other component, and in this way give rise to negative contributions to the excess volume, which are independent of the electric charge, and difficult to evaluate (2, 10).

It is well known that structural changes of water may give rise to rather unique volume

effects, and volumetric investigations are therefore, in spite of the above mentioned reservations, considered to be useful as a tool to elucidate interactions of water with solute species (1, 2, 10, 13, 17). Structural changes of water do not explicitly enter treatments of electrolyte solutions along the lines of the DEBYE-HÜCKEL theory ((2) p. 409); the charged species considered are defined as "hydrated ions", and only interactions between such species are involved. In the present paper we focus on the hydration of the ions, which is considered as solute-solvent equilibria (23). Such equilibria are displaced with changes in the concentration, and the

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Table II.

Density, d , of aqueous solutions of LiF, NaF and KF at 25 °C. a stands for $10^4 w_1$ (for LiF) and $10^3 w_1$ (for NaF and KF), where w_1 is the weight fraction of the alkali halide. b stands for $(d - d_O^*)10^3/gcm^{-3}$. $d_O^*=0.997048 gcm^{-3}$ (12).

a	b	a	b	a	b	a	b
LiF							
3.77	0.407	5.29	0.565	6.80	0.729	8.32	0.886
3.82	0.411	5.32	0.571	6.83	0.730	8.33	0.887
4.07	0.438	5.59	0.596	7.10	0.759	8.62	0.917
4.12	0.444	5.62	0.601	7.13	0.761	8.63	0.918
4.38	0.471	5.89	0.628	7.41	0.791	8.92	0.950
4.42	0.477	5.92	0.633	7.43	0.793	8.93	0.951
4.68	0.503	6.20	0.661	7.71	0.823	9.22	0.982
4.72	0.508	6.22	0.666	7.73	0.824	9.23	0.982
4.98	0.535	6.50	0.694	8.01	0.854	9.52	1.013
5.02	0.539	6.53	0.698	8.03	0.855	9.53	1.014
NaF							
0.594	0.627	2.255	2.370	6.609	6.910	16.769	17.485
0.632	0.670	2.329	2.448	6.865	7.178	16.951	17.678
0.670	0.705	2.389	2.510	7.068	7.401	17.643	18.393
0.707	0.746	2.406	2.530	7.120	7.444	18.104	18.879
0.745	0.790	2.480	2.602	7.374	7.699	18.521	19.306
0.783	0.826	2.540	2.667	7.580	7.931	19.252	20.069
0.820	0.867	2.691	2.827	7.629	7.966	19.396	20.211
0.858	0.906	2.841	2.982	7.886	8.237	20.264	21.108
0.895	0.944	2.992	3.139	8.090	8.458	20.402	21.263
0.933	0.984	3.143	3.299	8.140	8.499	21.141	22.021
0.971	1.022	3.293	3.452	8.394	8.757	21.546	22.449
1.008	1.066	3.443	3.612	8.599	8.988	22.010	22.918
1.046	1.105	3.539	3.714	9.108	9.518	22.696	23.641
1.083	1.143	3.594	3.768	9.617	10.045	22.879	23.825
1.121	1.183	3.744	3.923	10.128	10.572	23.749	24.724
1.122	1.184	3.796	3.984	10.636	11.101	23.838	24.823
1.158	1.221	3.895	4.080	11.146	11.629	24.624	25.626
1.196	1.258	4.046	4.240	11.651	12.152	24.977	26.010
1.197	1.266	4.052	4.254	12.159	12.682	25.483	26.521
1.234	1.301	4.196	4.394	12.374	12.923	26.116	27.189
1.273	1.346	4.308	4.513	12.666	13.206	26.356	27.424
1.349	1.425	4.345	4.551	13.175	13.732	27.224	28.326
1.424	1.502	4.497	4.710	13.256	13.842	27.258	28.372
1.500	1.581	4.563	4.787	13.684	14.261	28.081	29.213
1.575	1.663	4.646	4.861	14.136	14.753	28.401	29.557
1.651	1.741	4.798	5.018	14.190	14.782	28.949	30.095
1.726	1.818	4.821	5.049	14.695	15.308	29.535	30.731

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a	b	a	b	a	b	a	b
1.802	1.899	4.947	5.168	15.013	15.667	30.669	31.907
1.877	1.974	5.076	5.319	15.200	15.833	31.795	33.068
1.952	2.059	5.331	5.581	15.702	16.347	32.929	34.239
2.028	2.137	5.587	5.850	15.798	16.481	34.066	35.418
2.088	2.198	5.842	6.116	15.891	16.573	35.196	36.588
2.103	2.215	6.099	6.379	16.213	16.877	36.311	37.744
2.178	2.294	6.353	6.646	16.715	17.389	37.440	38.894
2.238	2.350						
KF							
3.012	2.611	28.622	24.508	71.669	62.270	134.070	119.095
3.385	2.929	30.057	25.736	71.921	62.596	135.925	120.616
3.756	3.248	31.499	26.974	72.194	62.796	139.412	124.066
4.127	3.568	32.929	28.200	74.016	64.340	140.271	124.660
4.498	3.887	33.176	28.617	75.079	65.398	144.532	128.640
4.870	4.204	34.349	29.422	76.326	66.382	144.679	128.975
5.241	4.524	35.784	30.653	76.943	67.014	148.822	132.623
5.611	4.839	37.204	31.876	78.238	68.200	149.943	133.913
5.983	5.162	38.109	32.895	78.660	68.453	155.157	138.806
6.351	5.476	38.625	33.101	81.391	71.014	160.269	143.625
6.573	5.661	40.034	34.313	81.667	71.220	165.392	148.489
6.721	5.792	40.554	35.005	84.504	73.781	170.494	153.320
6.790	5.803	41.454	35.544	86.366	75.437	175.540	158.124
7.092	6.108	42.856	36.756	87.633	76.576	177.745	160.105
7.312	6.292	42.997	37.134	90.720	79.347	180.490	162.873
7.814	6.693	44.269	37.978	91.015	79.591	185.445	167.614
8.051	6.934	45.661	39.179	93.808	82.114	187.499	169.356
8.834	7.553	47.071	40.390	95.635	83.767	190.381	172.351
9.528	8.200	47.869	41.368	96.872	84.865	195.273	176.968
10.263	8.829	49.326	42.706	99.930	87.613	197.091	178.716
10.883	9.287	50.290	43.480	100.246	87.932	206.563	188.023
11.000	9.420	52.605	45.575	101.179	88.939	215.829	197.181
11.733	10.094	52.688	45.578	102.960	90.336	225.020	206.250
11.939	10.179	55.101	47.600	104.814	92.075	234.061	215.353
12.470	10.637	55.854	48.422	105.988	93.055	242.941	224.347
13.094	11.157	57.478	49.767	106.778	94.026	251.731	233.324
13.204	11.259	59.094	51.271	108.996	95.694	260.407	242.239
13.934	11.986	59.877	51.879	109.346	96.193	268.878	251.014
14.125	11.989	62.250	53.964	112.328	99.086	277.282	259.775
14.667	12.503	62.333	54.122	113.871	100.309	285.551	268.445
16.192	13.791	62.570	54.244	117.826	104.115	293.793	277.176
19.942	17.091	64.623	55.969	118.336	104.400	301.769	285.646
21.399	18.332	65.542	56.952	122.788	108.475	309.793	294.245
22.850	19.569	66.973	58.114	123.294	109.139	317.628	302.722
24.294	20.807	67.392	58.530	127.182	112.519	325.322	311.080
25.740	22.038	68.735	59.776	128.711	114.139	332.939	319.395
27.187	23.278	69.338	60.207	131.593	116.593	340.440	327.486

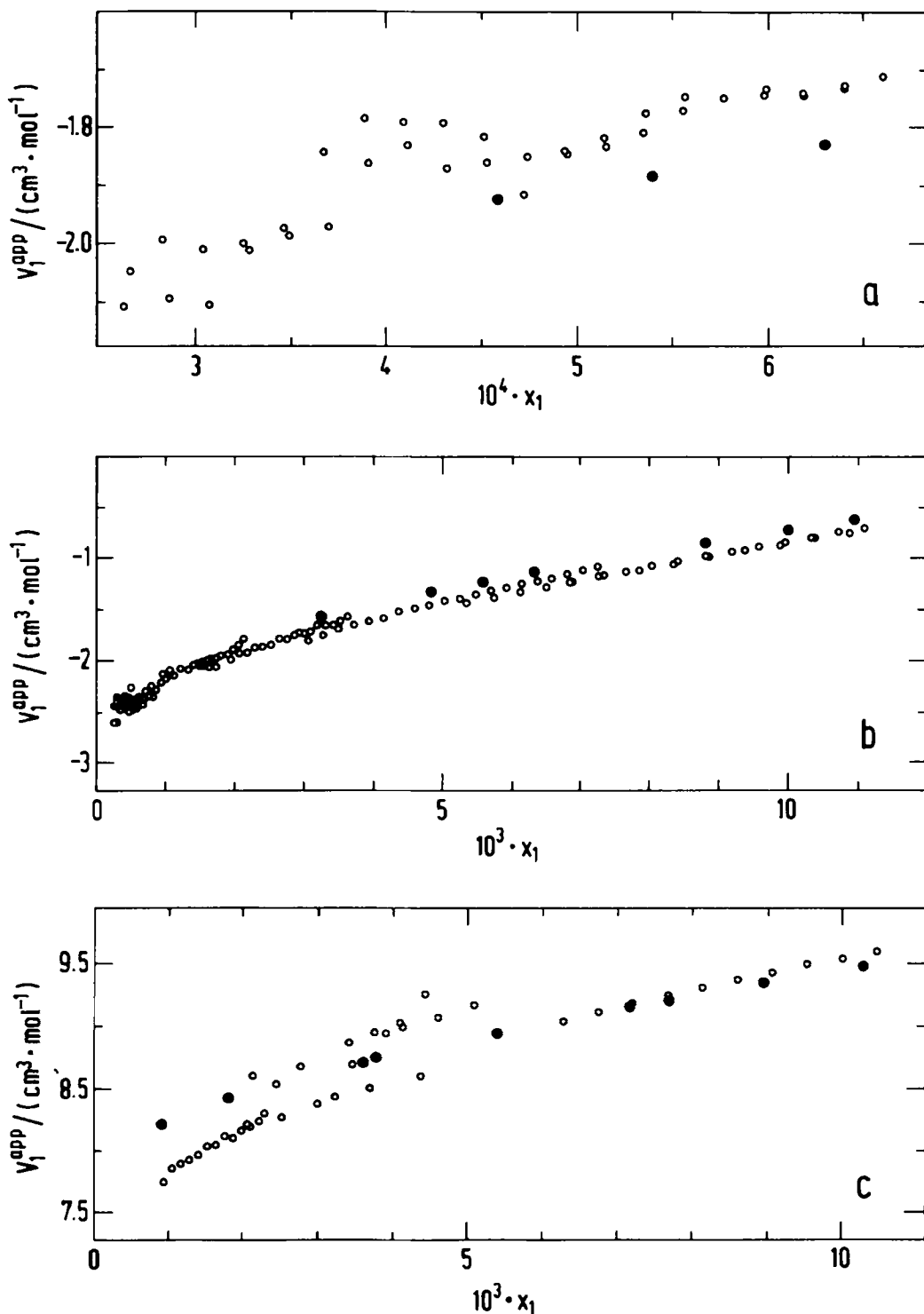


Figure 1. The apparent molar volume, V_1^{app} , of a: LiF, b: NaF, and c: KF in aqueous solution at 25 °C. V_1^{app} is calculated according to eq. (2) for values of the density reported in Table II (○), and in Ref. (3) (●). x_1 is the mole fraction of the salts.

accompanying volume changes are suggested to be the main source of the non-ideal concentration dependence observed of the volume of aqueous electrolyte solutions.

5. RESULTS

The density of aqueous solutions, at room temperature, of LiF, NaF, or KF is measured over the entire solubility range. The experimental results are reported in Table II. Measurements on the most dilute solutions are illustrated in Figure 1 by plots of V_1^{app} (calculated according to eq. (2)) vs. the mole fraction. This figure includes data available in the literature (3). It may be noted that the apparent molar volume of LiF and NaF in aqueous solution is negative.

Measurements, made by our equipment, of the density of NaCl solutions are in agreement with corresponding data in International Critical Tables (8). They support the conclusion reached previously (22) that the data in reference (8) are comparable with data obtained by vibration tube densimeters.

6. DISCUSSION

The apparent molar volume, V_1^{app} , of alkali chlorides, bromides, and iodides in aqueous

solution at room temperature, calculated from available experimental data (8), is presented in Figure 2 as a function of the mole fraction. It is seen from this figure, and from the fluoride volumes in Figure 1, that apart from the Li^+ -salts, V_1^{app} of the salts is larger the larger the ions involved (see Table I), and increases with increasing concentration.

The peculiar behaviour of the Li^+ -salts is more obvious from the plots in Figure 3, which represents the function $V_1^{\text{app}} - V_1^*$ i.e. (according to eq. (3)) the excess volume of the solutions per mole of the salt (V_m^E/x_1). It appears from this figure that the excess volume of the solutions is in all cases negative, and - with the exception of the Li^+ -salts - numerically larger the smaller the ions.

It was discussed, already in 1894 by DRUDE and NERNST (5), that the dissociation of electrolytes in aqueous solution gives rise to negative volume changes. Considering two oppositely charged, monovalent ions as spheres, immersed in a uniform dielectric medium with the dielectric constant ϵ , the electrostatic contribution to the Gibbs free energy may be expressed as

$$G_{el} = -e^2/\epsilon r, \quad (6)$$

where e is the elementary charge, and r is the interionic distance. The corresponding contribution to V_1^{app} is

$$V_{el} = (\partial G_{el}/\partial P)_T = -G_{el}(\partial \ln \epsilon / \partial P). \quad (7)$$

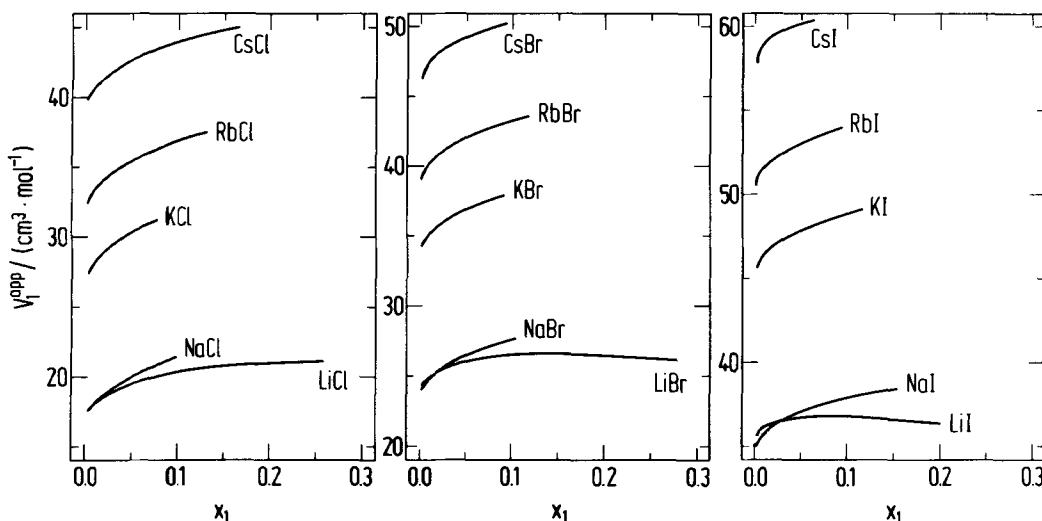


Figure 2. The apparent molar volume, V_1^{app} , calculated according to eq. (2) for values of the density reported in Ref. (8). x_1 is the mole fraction of the salts.

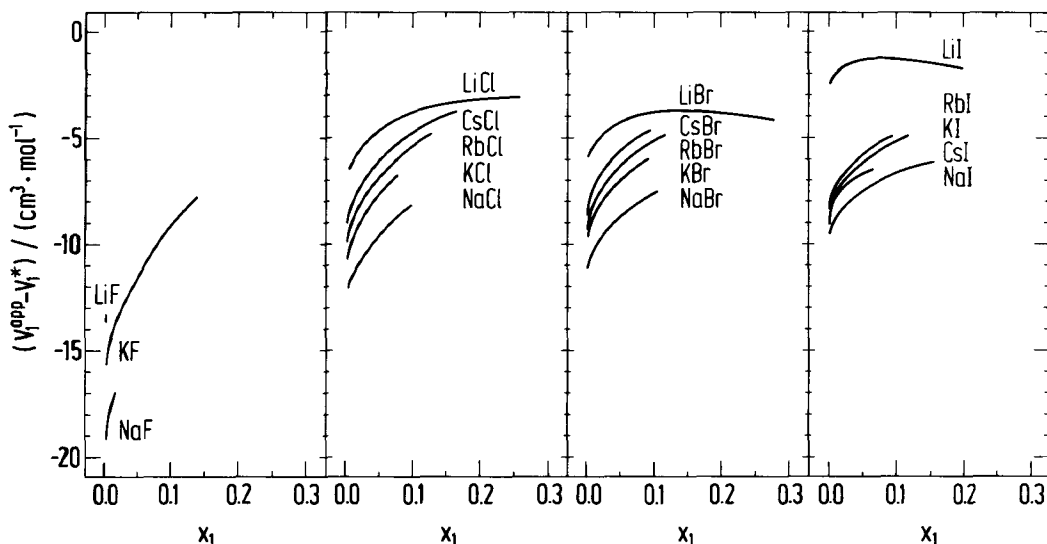


Figure 3. The excess volume of aqueous alkali halide solutions at 25°C, calculated per mole of the solute, $V_1^{\text{app}} - V_1^* = V_m^E/x_1$ (see eq. (3)). x_1 is the mole fraction of the salts. Experimental data as in Fig. 1 and 2.

Figure 4 shows plots of the electrostatic contribution to the free energy and the volume of dilute electrolyte solutions, calculated according to eq. (6) and (7), for $\epsilon = 78.3$, and $\partial \ln \epsilon / \partial P = 47.10 \times 10^{-6} \text{ bar}^{-1}$ (18). The smallest distance between two ions is the sum of the ionic radii, so according to this model the volume change of dissociation is $-V_{ei}(R_+ + R_-)$.

This simple model of electrostatic interaction, based on the assumption that the solvent is uniform, is unable to account for the concentration dependence of the apparent molar volume of alkali halides, seen in Figure 1 and 2. In particular, the model does not explain the negative values of V_1^{app} observed for LiF and NaF ($V_1^{\text{intr}} - V_{ei}(R_+ + R_-) > 0$, see Table I and Figure 4). A more likely explanation of the experimental data is the existence of local structural changes of water around the ions, i.e. of ion hydration (2, 9, 23).

In discussions of the hydration of ions it is sometimes assumed that an ion, dissolved in water, is and remains surrounded by a sphere of a certain number of water molecules, bound to the ion. Apart from the objection, that it is not possible to state unambiguously what is meant by a water molecule being "bound to an ion", hydration sphere models - with a constant num-

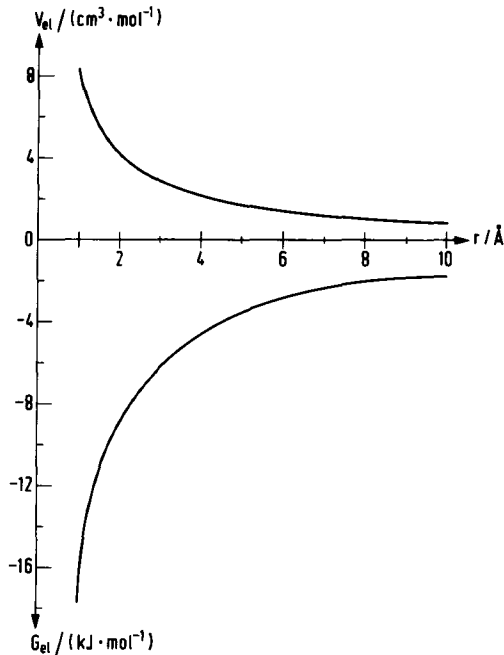


Figure 4. The electrostatic contribution to the molar volume, V_{ei} , and the molar Gibbs free energy, G_{ei} , of an electrolyte, calculated according to eq. (6) and (7). r is the distance between the two monovalent ions.

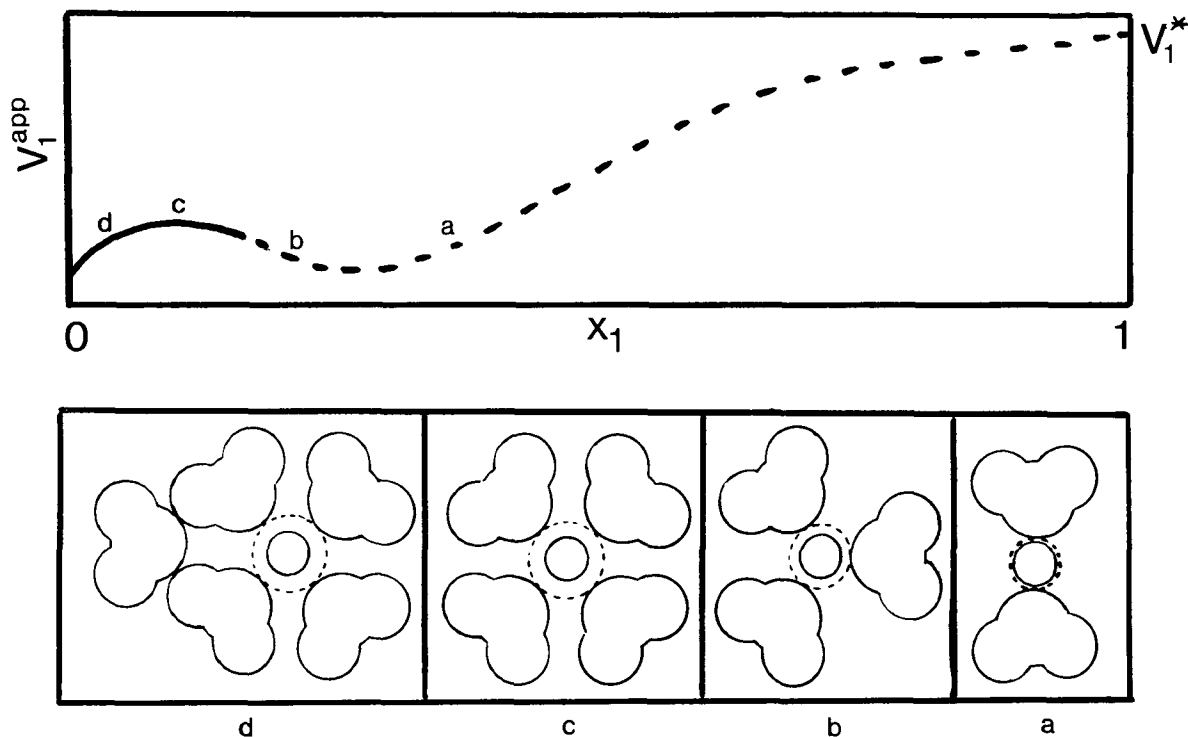


Figure 5. Outline of the course of the hydration of a Li^+ -ion. x_1 is the mole fraction of a Li-salt.

ber of water molecules bound per ion - can hardly explain the concentration dependence of the volume, illustrated in Figures 1 - 3. There is no tendency of a levelling off of the apparent molar volume of the alkali halides, when the concentration approaches zero. On the contrary, the steepness ($\partial V_1^{\text{app}}/\partial x_1$) of the curves increases for $x_1 \rightarrow 0$.

The volumetric data is, however, in accordance with the equilibrium model of ionic hydration, proposed by STOKES and ROBINSON (23). In this model the hydration of an electrolyte is formally treated as a series of consecutive equilibria between the cation, C^+ , and water: $\text{C}^+(\text{H}_2\text{O})_{i-1} + \text{H}_2\text{O} \rightleftharpoons \text{C}^+(\text{H}_2\text{O})_i$, of which $K_{i+1}/K_i < 1$, where K_i is the equilibrium constant of the i 'th reaction. The model is shown to give good quantitative account of the osmotic coefficient of electrolytes up to high concentrations (23). In the development of this model, volume changes due to the hydration are ignored, but a consideration of the concentration dependence of the volume of alkali halide solutions may actually support

the model. The decrease of the apparent molar volume of the electrolytes, when the concentration approaches zero, is in accordance with displacement towards the right-hand side of hydration equilibria $\text{C}^+(\text{H}_2\text{O})_{i-1} + \text{H}_2\text{O} \rightleftharpoons \text{C}^+(\text{H}_2\text{O})_i$ and $\text{A}^+(\text{H}_2\text{O})_{j-1} + \text{H}_2\text{O} \rightleftharpoons \text{A}^+(\text{H}_2\text{O})_j$ of which the volume change $\Delta V^0 < 0$.

The remarkable behaviour of the Li^+ -salts - the relatively small electrostriction of water and the maximum of the apparent molar volume of LiBr and LiI as a function of the concentration (see Figure (2)) - may be associated with the small size of the Li^+ -ion, compared with a water molecule. The volume change of the binding of the first and the second water molecule to a Li^+ -ion is supposedly negative, due to electrostatic interactions between the ion and the dipolar water molecules (Figure 5a). However, three or four water molecules, attached to a Li^+ -ion, may require some extra space, due to the mutual repulsion of the dipolar water molecules, oriented by the ion (Figure 5b - c). The further addition of water molecules to the hydration

sphere appears to be accompanied by the "normal" volume decrease (Figure 5d). This hypothetical course of the hydration of a Li^+ -ion, and of V_1^{app} of a Li-salt is outlined in Figure 5. Unfortunately, the dotted part of the curve, representing V_1^{app} , eludes experimental verification, due to the low solubility of the Li-salts. The value of V^* of Li-salts (Table I), i.e. of $V_1^{\text{app}}(x = 1)$ indicates that a minimum of V_1^{app} must occur at a concentration beyond the experimentally accessible range.

It is an essential feature of the hydration equilibrium model, that the standard Gibbs free energy for the attachment of a water molecule to an ion changes by an amount $-RT \ln K_i$ for each successive step of the hydration (23). For most of the electrolytes considered this free energy change is estimated to be negative for the attachment of the first water molecules, but positive for the attachment of the fifth (or higher) water molecules (23). This means that labile hydration equilibria exist in dilute aqueous electrolyte solutions, and they apparently give rise to measurable volume changes. Similar volume effects observed in aqueous solutions of non-electrolytes have been associated with the unique ability of water to undergo structural changes (introduced by solute species), characterized by relatively small changes in Gibbs free energy, but remarkably large changes in volume and enthalpy (4, 10). Such solute-solvent interactions are decisive for the thermodynamic properties of aqueous solutions, and they may explain the pronounced deviations from ideality which are typical of even very dilute aqueous solutions.

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REFERENCES

- ASANO, T. & W.J. LE NOBLE: Activation and reaction volumes in solution. *Chem. Rev.* 78, 407-489 (1978)
- CONWAY, B.E.: Ionic hydration in chemistry and biophysics. Elsevier, Amsterdam (1981)
- DESNOYERS, J.E., M. AREL, G. PERRON & C. JOLICOEUR: Apparent molal volumes of alkali halides in water at 25 °C. Influence of structural hydration interactions on the concentration dependence. *J. Phys. Chem.* 73, 3346-3351 (1969)
- DETHLEFSEN, C., P.G. SØRENSEN & AA. HVIDT: Excess volumes of propan-1-ol and water at 278.15, 288.15 and 298.15 K. *J. Solution Chem.* 191-210 (1984)
- DRUDE, P. & W. NERNST: Über Elektrostriktion durch freie Ionen. *Zeitschrift für physikalische Chemie* 15, 79-85 (1894)
- EDWARD, J.T.: Molecular volumes and the Stokes-Einstein equation. *J. Chem. Educ.* 47, 261-270 (1970)
- FRANK, H.S. & M.W. EVANS: Free volume and entropy in condensed systems. *J. Chem. Phys.* 13, 507-532 (1945)
- GILLESPIE, L.J.: Density (specific gravity) and thermal expansion (under atmospheric pressure) of aqueous solutions of inorganic substances and of strong electrolytes. In: E.W. Washburn, ed., *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, McGraw-Hill, New York, Vol. 3, pp. 77-95 (1928)
- GURNEY, R.W.: Ionic processes in solution, chapter 11. McGraw-Hill Book Company, Inc. (1953)
- HVIDT, AA.: Interactions of water with nonpolar solutes. *Ann. Rev. Biophys. Bioeng.* 12, 1-20 (1983)
- JANZ, G.J.: *Molten Salts Handbook*. Academic Press, New-York-London (1967)
- KELL, G.S.: Effects of isotopic composition, temperature, and dissolved gases on the density of liquid water. *J. Phys. Chem. ref. Data* 6, 1109-1131 (1977)
- KELM, H. & D.A. PALMER: Determination of volumes of activation. In: H. Kelm, ed., *High Pressure Chemistry*. D. Reidel Publishing Company, Holland, U.S.A., England. pp. 281-309 (1978)
- LE NOBLE, W.J.: Organic model reactions under pressure. In: H. Kelm, ed., *High Pressure Chemistry*, D. Reidel Publishing Company, Holland, U.S.A., England. pp. 325-363 (1978)
- LINDERSTRØM-LANG, K. & C.F. JACOBSEN: The contraction accompanying enzymatic breakdown of proteins. *Compt. Rend. Trav. Lab. Carlsberg, Ser. Chim.* 24, 1-48 (1941)
- MESELSON, M., F.W. STAHL & J. VINOGRAD: Equilibrium sedimentation of macromolecules in density gradients. *Proc. Natl. Acad. Sci. U.S.A.* 43, 581-588 (1957)
- MILLERO, F.J.: The molal volumes of electrolytes. *Chem. Rev.* 71, 147-176 (1971)

18. OWEN, B.B., R.C. MILLER, C.E. MILNER & H.L. COGAN: The dielectric constant of water as a function of temperature and pressure. *J. Phys. Chem.* 65, 2065-2074 (1961)
19. PEDERSEN, T.G. & J.B. IFFT: The buoyant titration of ovalbumin in four alkali halides. Hydration and ion binding. *Carlsberg Res. Commun.* 43, 65-76 (1978)
20. PICKER, P., E. TREMBLAY, & C. JOLICOEUR: A high-precision digital readout flow densimeter for liquids. *J. Solution Chem.* 3, 377-384 (1973)
21. PIEROTTI, R.A.: Aqueous solutions of nonpolar gases. *J. Phys. Chem.* 69, 281-288 (1965)
22. ROMANKIW, L.A. & I. CHOU: Densities of aqueous NaCl, KCl, MgCl₂ and CaCl₂ binary solutions in the concentration range 0.5-6.1 m at 25, 30, 35, 40 and 45 °C. *J. Chem. Eng. Data* 28, 300-305 (1983)
23. STOKES, R.H. & R.A. ROBINSON: Solvation equilibria in very concentrated electrolyte solutions. *J. Solution Chem.* 2, 173-184 (1973)
24. WEAST, R.C.: *Handbook of Chemistry and Physics*, 56th edition, B66-B160 (1976)