A SIMPLE PERTURBATION METHOD FOR ELECTROLYTE SOLUTIONS

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Dedicated to late Academician Eduard Hála.

The first order perturbation expansion of the Helmholtz free energy was used to calculate the thermodynamic properties of aqueous electrolytes. The restricted primitive model was used as the reference system. Its properties were determined using semiempirical formulae consistent with simulated Monte Carlo data. A simple expression with two adjustable parameters was chosen for the perturbation potential. Integral heats of dilution and osmotic coefficients of alkaline halides and tetraalkylammonium bromides were calculated. An excellent agreement with the tabulated data was found up to the concentrations of $2-3 \ mol/dm^3$.

The application of statistical thermodynamics to the study of electrolyte solutions provides a more prospective conception than the phenomenological description using empirical relations. The statistical thermodynamic treatment[1] requires interparticle potentials only as the input quantities. However, the potentials are not accurately known because neither the quantum mechanic calculations nor the macroscopic experiments provide a sufficient amount of information on interionic forces at present. Hence, the model potentials[2-11] instead of real ones are used, and their quality is tested a posteriori from results.

Among statistical thermodynamic theories of liquids the perturbation approach is rather popular. Its accuracy depends considerably on the choice of the reference system. Most often hard spheres are used for this purpose. However, hard spheres describing well the structure of simple fluids are not a reasonable starting point for electrolyte solutions. Strong electrostatic interactions should be included in the reference system. It is done in the restricted primitive model (RPM) of electrolytes[12]. Attempts to use this reference system have not been successful at elevated concentrations because of an inaccurate description of its thermodynamic and structural properties.

The aim of this work is to propose a fast and accurate perturbation method for electrolyte solutions based on the well-described reference restricted primitive model.

The method is tested on the calculation of the thermodynamic properties of real aqueous solutions of the 1–1 electrolytes.

THEORETICAL

The first order perturbation expansion in the Helmholtz free energy was chosen for the calculation of the thermodynamic quantities

$$F = F^{RPM} + F_1 , \qquad (1)$$

where

$$F_1/N_A kT = 3\beta\eta \sum_{i,j} \int_1^\infty g_{ij}^{RPM}(\bar{r}) \, u_{ij}^p(\bar{r}) \, \bar{r}^2 \, d\bar{r} ,$$

$\beta = 1/kT$, $\eta = (\pi/6) N_A vc \cdot 10^3 \sigma^3$, $\bar{r} = r/\sigma$, v is a number of ions produced by one molecule of solute on complete dissociation, N_A is Avogadro number, g_{ij}^{RPM} and F^{RPM} are the radial distribution function and the free energy of the reference system respectively. u^p is the perturbation potential, c is concentration in mol/dm^3, and σ is the ionic diameter in Å.

The restricted primitive model was chosen as the reference one

$$u_{ij}^{RPM}(\bar{r}) = \infty , \qquad \bar{r} < \sigma$$
$$= e_i e_j/(4\pi\varepsilon r) , \quad \bar{r} > \sigma \qquad (2)$$

where e_i, e_j are the charges of ions and ε the permitivity of a pure solvent.

Semiempirical formulae[13] for the radial distribution function of like and unlike ions were employed

$$g_{++}(q, \eta, \bar{r}) = g^{HS}(\eta, \bar{r}) \exp(AQ) + P , \qquad (3)$$

$$g_{+-}(q, \eta, \bar{r}) = g^{HS}(\eta, \bar{r}) \exp(BQ) - P , \qquad (4)$$

where g^{HS} denotes the radial distribution function of hard spheres and

$$Q = q \exp\left[y(1 - \bar{r})\right]/\left[\bar{r}(1 + y)\right] ,$$
$$P = 24\eta \sqrt{q} \exp(-\bar{r}) \sin(2 \cdot 5\bar{r} - 5)/(2 + 100\eta) ,$$
$$y = \varkappa\sigma = (24q\eta)^{1/2} ,$$
$$q = |e_i e_j|/(4\pi\varepsilon kT\sigma) .$$

The parameters A and B are

$$A = 1 \cdot 68084 q\eta - 0 \cdot 366750 q^2 \eta^{1/2} + 0 \cdot 054959 q^3 \eta^{1/3} - 1 ,$$
$$B = -2 \cdot 78229\eta + 1 \cdot 41312\eta^{1/2} - 0 \cdot 474233\eta^{1/3} + 1 .$$

Equations (3) and (4) were obtained by fitting Monte Carlo data[13] and are valid within the precision of the simulation in the range

$$q \in \langle 1\cdot5, 3\cdot6 \rangle , \quad \eta \in \langle 0, 0\cdot7q^{-3} \rangle .$$

We also note that Eqs (3), (4) reduce to the Debye–Hückel limiting law at low concentrations and approach the radial distribution function of hard spheres when $q \to 0$ (i.e. when T or ε approaches infinity).

For the perturbation potential a non-coulombic part of the Ebeling–Krienke potential[5] was used

$$u_{ij}^{p}(r) = D_{ij}[(\sigma + \sigma_w)/r] \exp [-r/(\sigma + \sigma_w)] ,$$

where σ_w is a diameter of the solvent molecule.

RESULTS AND DISCUSSION

The internal energy, E, and the osmotic coefficient, φ, were calculated from Eq. (1) using thermodynamic relations

$$E = E^{\mathrm{RPM}} + q \frac{\partial F_1}{\partial q} \left(1 + \frac{\mathrm{d} \ln \varepsilon}{\mathrm{d} \ln T} \right), \qquad (6)$$

TABLE I
Parameters of the perturbation potential and the Pauling ionic diameters

Substance	σ, Å	βD_{+-}	$-\dfrac{\partial D_{+-}}{\partial(1/\beta)}$	$-\beta S$	$\dfrac{\partial S}{\partial(1/\beta)}$
KF	2·69	0·2365	0·2869	0·3132	0·4858
LiCl	2·41	0·5402	0·3036	0·4124	0·9828
NaCl	2·76	0·3634	0·3676	0·5992	−0·1076
KCl	3·14	0·1241	0·4429	0·3040	0·3331
CsCl	3·50	−0·2578	0·7352	−0·3713	0·8185
LiBr	2·55	0·3707	0·4284	−0·0423	1·224
NaBr	2·90	0·3314	0·4885	0·4701	0·1382
KBr	3·28	0·1814	0·5082	0·4286	0·3276
NaI	3·11	0·3533	0·4516	0·4605	−0·0006
$(CH_3)_4NBr$	5·42	−0·5886	1·503	−0·6593	2·521
$(C_2H_5)_4NBr$	5·95	−0·4769	1·663	−0·3064	2·912
$(C_3H_7)_4NBr$	6·47	−0·4126	2·029	−0·1015	4·424
$(C_4H_9)_4NBr$	6·89	−0·5413	2·730	−0·3251	7·403

$$\varphi = \varphi^{RPM} + \eta \frac{\partial(F_1/\eta)}{\partial \eta}, \qquad (7)$$

where E^{RPM} and φ^{RPM} were calculated from the parametrized g_{++}, g_{+-} using the energy and the virial equation, respectively.
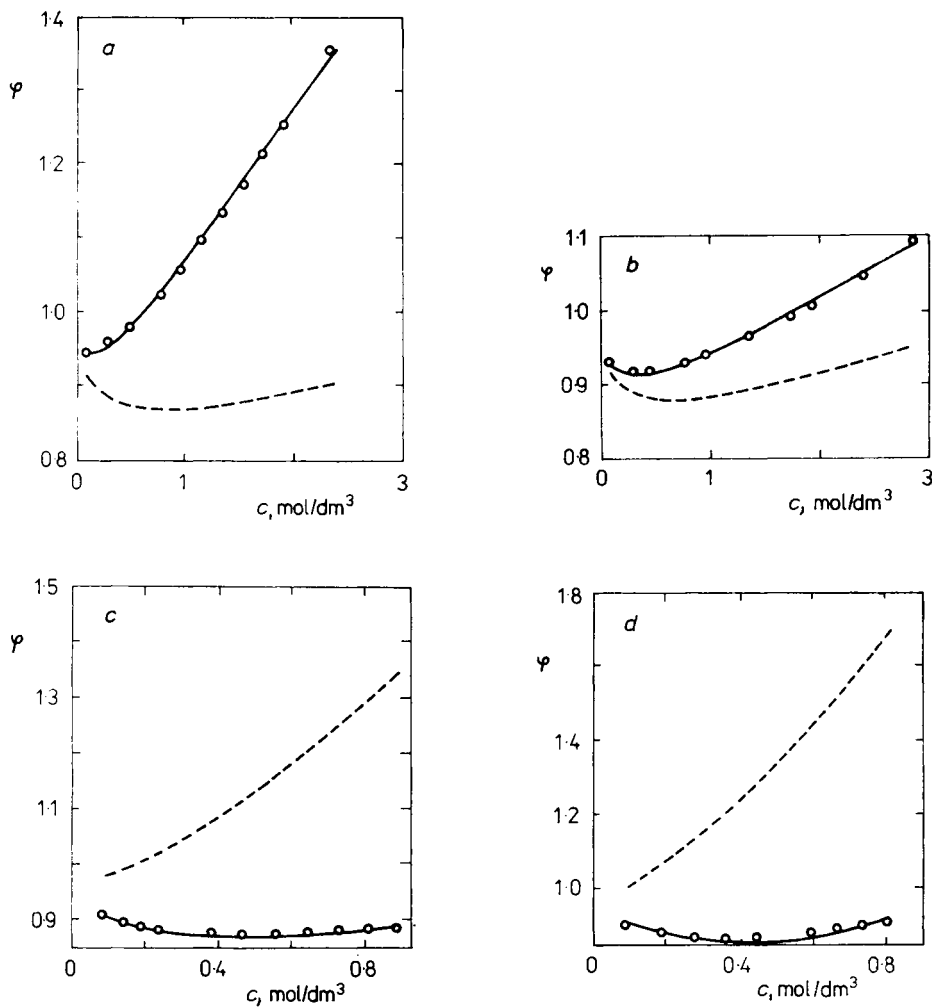

FIG. 1

Calculated and experimental osmotic coefficients for aqueous solution of LiBr (*a*), KF (*b*), $(CH_3)_4NBr$ (*c*), $(C_3H_7)_4NBr$ (*d*) at 298 K. Values are in McMillan–Mayer system of units. ——— the proposed method, — — — RPM, ○ experimental data

Experimental data for E and φ were taken from refs[14,15] for alkali halides, and from refs[16-18] for tetraalkylamonium bromides. The measured quantities are given in the Lewis–Randal system of units (independent variables T, P, m_i) while the calculated ones in the McMillan–Mayer system (variables T, V, c_i). The recalculations of the quantities were performed according to Faigl[8]. The calculated thermodynamic functions depend on parameters D_{ij} for the perturbation potential (5). The values
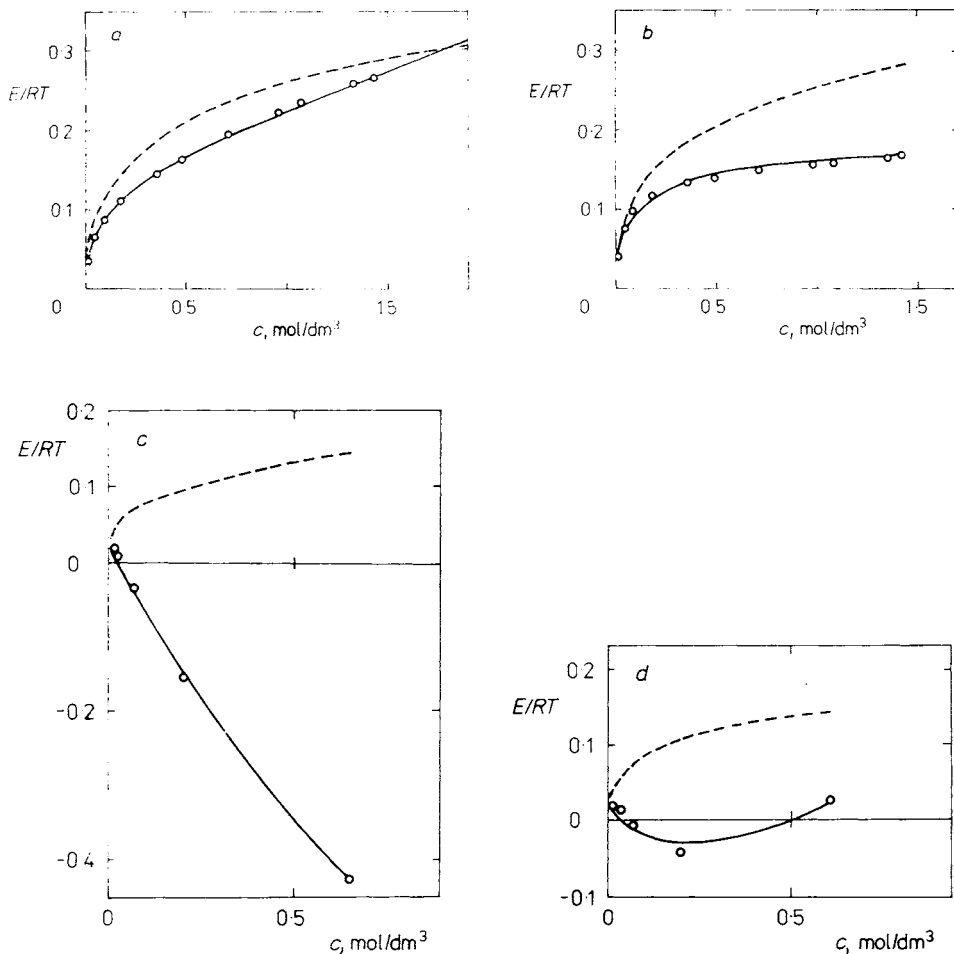

FIG. 2

Calculated and experimental excess internal energies for aqueous solution of LiBr (a), KF (b), $CH_3)_4NBr$ (c), $(C_3H_7)_4NBr$ (d) at 298 K. Values are in McMillan–Mayer system of units. —— the proposed method, — — — RPM, ○ experimental data

of D_{+-} and $S = D_{++} + D_{--}$ and the values of their temperature derivatives were fitted to the experimental data and they are given together with ionic diameters taken from refs[3,15] in Table I.

The results are shown in Figs 1 and 2. An excellent agreement between the calculated and the experimental values can be observed in a large concentration range for all the systems investigated. Results predicted by the restricted primitive model are plotted for comparison. It can be seen that the restricted primitive model itself describes the real solutions only very roughly.

The reliability of a simple perturbation method (Eq. (1)) used in this paper depends on the choice and the description of the reference potential, and on the choice of the perturbation potential. We believe that the restricted primitive model is a suitable reference system for electrolytes as it includes both the short range repulsion and strong long range electrostatic interactions. Description of the model used in this paper is based on the results of extensive machine simulations. Formulae (3) and (4) for the radial distribution function are as accurate as the original data. The suitability of the Ebeling–Krienke perturbation potential can be judged from results. The results show that it is flexible sufficiently.

It should be noted that the agreement of the calculated internal energies and osmotic coefficients with the data is caused to a large extent by fitting the parameters D and S, and their temperature derivatives to the data. No attempt was made to assure the consistency of D_{ii} for all binary systems studied. However, the fitting of the constants is on the level of the pair interionic potential, i.e. on a much deeper level than fitting constants of an empirical expression such as $\varphi = \varphi(c)$. It permits to describe two thermodynamic quantities in a large range of concentrations with four constants only, which is hardly possible for purely empirical relations. In addition, the proposed method is rather fast. It requires only the numerical calculation of the simple integral in Eq. (1).

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