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STUDIES ON THE ACTIVITY COEFFICIENT OF BENZENE AND ITS DERIVATIVES IN AQUEOUS SALT SOLUTIONS *

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ABSTRACT

The solubilities of benzene, toluene, *o*-, *m*-, and *p*-xylenes, and naphthalene in water as well as in aqueous salt solutions were determined at 25 ° C by spectrophotometry. The salts used were NaF, KF, LiCl, NaCl, KCl, LiBr, NaBr, KBr, $NaNO_3$, $NaClO_3$, NH_4Cl, NH_4Br, NMe_4Br, NEt_4Br, $(NH_4)_2 SO_4$, Na_2SO_4, K_2SO_4, $MgCl_2$, $SrCl_2$, $BaCl_2$, $MgSO_4$, HCOONa, CH_3COONa, C_2H_5COONa, C_3H_7COONa, etc. The activity coefficients of these non-electrolytes, f, have also been calculated. The relationship between $\log f$ and c_s (salt concentration, 0–0.8 M) were all found to be straight lines through the origin, in agreement with Setschenow's experimental formula.

The salting-out constants of benzene and its derivatives in solutions of the above-mentioned 25 salts have been calculated by the formulas of (a) Debye and MacAulay, (b) Conway et al. (c) McDevit and Long, (d) the scaled particle theory and the scaled particle theory modified by Xie and Yang, and (e) the internal pressure theory modified by Xie et al. The theoretical values obtained from the internal pressure theory modified by Xie seems to coincide with the experimental value better than those from the other theories, but it will be further improved if the van der Waals force, except for the electrostatic force, is also taken into account.

INTRODUCTION

It is well-known that many non-electrolytes are less soluble in a salt solution than in the corresponding pure solvent. The effect is called the salt effect. This phenomenon is commonly utilized to separate a hydrophilic organic component from aqueous solution or to precipitate a protein. Studies of the salt effect are also of theoretical importance. It relates to the molecular interaction between ion, non-electrolyte, and water. In 1889, Setschenow gave an empirical formula for the salt effect

$$\log f = \log(S_0/S) = kc_s$$

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where S_0 and S are the solubilities of the non-electrolyte in water and in aqueous salt solution, respectively, f is the activity coefficient of the non-electrolyte, k is the empirical Setschenow parameter, and c_s is the molar concentration of electrolyte. Several main theories of the salt effect were presented in detail in the classical works of Huang [1] and Conway [2].

In this paper, the solubilities of benzene, toluene, *o*-, *m*-, and *p*-xylenes, and naphthalene in water as well as in the aqueous salt solutions were determined at 25 °C by spectrophotometry. The salts used were NaF, KF, LiCl, NaCl, KCl, LiBr, NaBr, KBr, $NaNO_3$, $NaClO_3$, NH_4Cl, NH_4Br, NMe_4Br, NEt_4Br, $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $MgCl_2$, $SrCl_2$, $BaCl_2$, $MgSO_4$, HCOONa, CH_3COONa, C_2H_5COONa, C_3H_7COONa, etc.

The salting-out constants of benzene and its derivatives in the solutions of the above-mentioned 25 salts have been calculated by the formulas of (a) Debye and MacAulay [3], (b) Conway et al. [4], (c) McDevit and Long [5], (d) the scaled particle theory [6] and the scaled particle theory modified by Xie and Yang [7], and (e) the internal pressure theory modified by Xie et al. [8]. The theoretical values obtained from the internal pressure theory modified by Xie et al. seems to coincide with the experimental values rather than those from the other theories.

EXPERIMENTAL

Benzene, toluene, and naphthalene were analytical reagents and were purified by standard methods [9]; *o*-, *m*-, and *p*-xylenes were gas chromatographical standard samples. Their physical constants were in agreement with the values reported in the literature. All 25 salts used were analytical reagents and were purified by recrystallization, and the water used in the experiments was redistilled.

The absorption spectra of aqueous solutions of the non-electrolytes were determined. The λ_{max} values were determined and found to be 252.4, 258.6, 262.0, 264.0, 267.0, and 276.0 nm for benzene, toluene, *o*-, *m*-, and *p*-xylenes, and naphthalene, respectively. These data were in agreement with those reported in the literature [9–12]. Within the range of salt concentration 0–0.8 M and at low concentrations of non-electrolyte, Beer's law can be applied [10,12]

$$\log f = \log(S_0/S) = \log(A_0/A) = kc_s$$

where A_0 and A are the absorbances of non-electrolyte in water and in aqueous salt solution, respectively.

10 ml water or salt solution and a certain amount of the non-electrolyte were sealed in ampoules. The ampoules were heated at 30–40 °C for about 30 min then put in a thermostat at 25.00 ± 0.005 °C [13]. The conditions of the experiments were as follows: the ampoules were fixed vertically on a

TABLE 1

The experimental salting-out constants (25.00 ± 0.005 ° C)

	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Naphthalene
NaF	0.254 [a]	0.329	0.349	0.379	0.347	0.343
KF	0.250 [b]	0.282	0.342	0.354	0.339	0.326
LiCl	0.141 [a]	0.168	0.180	0.185	0.187	0.180 [e]
NaCl	0.195 [a]	0.228	0.227	0.248	0.251	0.220 [e]
KCl	0.166 [a]	0.206	0.205	0.222	0.217	0.186 [e]
LiBr	0.126 [b]	0.113	0.120	0.125	0.133	0.097
NaBr	0.155 [a]	0.191	0.178	0.144	0.198	0.162
KBr	0.119 [a]	0.138	0.156	0.170	0.168	0.130
$NaNO_3$	0.119 [a]	0.144 [d]	0.141	0.165	0.146	0.131
$NaClO_3$	0.136	0.175	0.176	0.188	0.183	0.142
NH_4Cl	0.103 [a]	0.136	0.102	0.153	0.099	0.071
NH_4Br	0.12 [c]	0.09	0.01	0.09	−0.02	0.05
NMe_4Br	−0.24 [a]	−0.163	−0.198	−0.178	−0.200	−0.50
NEt_4Br	−0.56 [c]	−0.323	−0.414	−0.402	−0.413	−1.1
$(NH_4)_2SO_4$	0.405 [d]	0.428	0.496	0.551	0.499	0.476
Na_2SO_4	0.548 [a]	0.651 [d]	0.641	0.691	0.656	0.695
K_2SO_4	0.455	0.675 [d]	0.618	0.652	0.625	0.624
$MgCl_2$	0.290 [d]	0.320	0.311	0.369	0.318	0.301 [e]
$SrCl_2$	0.272	0.364	0.379	0.384	0.386	0.385
$BaCl_2$	0.334 [a]	0.376	0.393	0.412	0.407	0.401
$MgSO_4$	0.448 [d]	0.457	0.491	0.531	0.490	0.516
HCOONa	0.146	0.188	0.195	0.217	0.197	0.22
CH_3COONa	0.165	0.209 [d]	0.206	0.237	0.208	0.21
C_2H_5COONa	0.158	0.172	0.206	0.224	0.201	0.18
C_3H_7COONa	0.128	0.163	0.159	0.187	0.163	0.13

[a] Ref. 5.
[b] Ref. 22.
[c] Ref. 23.
[d] Ref. 24.
[e] Ref. 25.

rotatory shaft and rotated for 2 h. They were then fixed parallel on the rotatory shaft and rotated for 1 h, and finally laid up for 2 h in the thermostat. The absorbance of the aqueous solution in the ampoule was measured by Beckman DU-7HS spectrophotometer at each λ_{max} of these non-electrolytes using a 1 cm cell. Every experimental datum was taken as the average value of over four measured values.

The k values of benzene, toluene, *o*-, *m*-, and *p*-xylenes, and naphthalene in 25 aqueous salt solutions at 25 ° C are given in Table 1.

Among these 150 results, 124 values were reported by Huang and co-workers [12,14] and Xie and co-workers [15–21], and 26 were reported by other authors [5,22–25]. The logarithm of the activity coefficient of each non-electrolyte in each aqueous salt solution, log f, plotted against different salt concentrations, c_s, shows a good linear relationship which passes through the origin, fitting the Setschenow experimental formula. The salting-out order is NaF > KF; $BaCl_2 > SrCl_2 > MgCl_2 >$ NaCl > KCl > LiCl > NH_4Cl; NaBr > KBr > LiBr > $NH_4Br > NMe_4Br > NEt_4Br$; $Na_2SO_4 > K_2SO_4 > (NH_4)_2SO_4$; $CH_3COONa > C_2H_5COONa >$ HCOONa > C_3H_7COONa; $NaClO_3 > NaNO_3$.

RESULTS AND DISCUSSION

Calculation according to the Debye–MacAulay Theory (DMT)

In 1925, Debye and McAulay [3] proposed an electrostatic theory with a salting-out constant

$$k_\mathrm{s} = \frac{\beta e^2 N_0}{4.606 \times 10^3 kTD_\mathrm{c}} \sum_j \frac{\nu_j z_j^2}{r_j}$$

where k_s is the theoretical salting-out constant, e the electronic charge, N_0 Avogadro's number, D_0 the dielectric constant of water, k the Boltzman constant, T the absolute temperature, z_j the number and valence of ion j in the molecule, and r_j the radius of ion j. According to Sayler's method [26]

$$\beta = \frac{(D_0 - D)V_\mathrm{n}}{D_0}$$

where D is the dielectric constant of the non-electrolyte and V_n the molar volume of the non-electrolyte. The salting-out constants of these non-electrolytes by the 25 salts were calculated according to the DMT and are shown in Table 2.

Calculation according to the Conway–Desnoyers–Smith Theory (CDST)

In 1964, Conway et al. [4] considering the dielectric saturation effect near the ion and the primary hydration of the ion, obtained an expression for k as

$$k_\mathrm{s} = \frac{1}{2.303} \frac{4\pi N_0}{3000} \left(r_\mathrm{h}^3 - a^3\right) + \frac{z^2 e^2}{2000 kTD_0^2} \left(V_\mathrm{n} D_0 - \tfrac{9}{2} P_\mathrm{n}\right)\left(\frac{1}{r_\mathrm{h}} - \frac{1}{R}\right)$$

where r_h and a are the hydration radius and the Pauling radius of the ion, respectively, P_n is the total molar polarization of the non-electrolyte of molar volume V_n, R corresponds to the cosphere of influence of the salt ions (when $c \to 0$, $1/R \to 0$). The salting-out constant of these non-electrolytes were calculated according to CDST and are shown in Table 3.

TABLE 2

DMT theoretical values

	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Naphthalene
NaF	0.241	0.288	0.326	0.333	0.334	0.301
KF	0.201	0.239	0.271	0.277	0.278	0.250
LiCl	0.300	0.358	0.404	0.413	0.415	0.374
NaCl	0.217	0.259	0.293	0.299	0.300	0.270
KCl	0.176	0.210	0.238	0.243	0.244	0.220
LiBr	0.294	0.351	0.397	0.406	0.408	0.367
NaBr	0.211	0.252	0.285	0.291	0.292	0.264
KBr	0.170	0.203	0.230	0.235	0.237	0.213
$NaNO_3$	0.193	0.230	0.261	0.266	0.268	0.241
$NaClO_3$	0.189	0.225	0.255	0.260	0.262	0.236
NH_4Cl	0.166	0.198	0.224	0.229	0.230	0.207
NH_4Br	0.160	0.191	0.217	0.221	0.222	0.200
NMe_4Br	0.108	0.129	0.146	0.149	0.150	0.135
NEt_4Br	0.103	0.123	0.139	0.142	0.143	0.128
$(NH_4)_2SO_4$	0.368	0.439	0.497	0.508	0.511	0.460
Na_2SO_4	0.469	0.560	0.634	0.648	0.651	0.587
K_2SO_4	0.389	0.464	0.525	0.536	0.539	0.485
$MgCl_2$	0.979	1.168	1.321	1.349	1.357	1.222
$SrCl_2$	0.626	0.747	0.845	0.863	0.869	0.782
$BaCl_2$	0.548	0.654	0.740	0.756	0.761	0.685
$MgSO_4$	1.016	1.212	1.371	1.400	1.408	1.268
HCOONa	0.190	0.227	0.275	0.262	0.264	0.238
CH_3COONa	0.182	0.217	0.246	0.251	0.252	0.227
C_2H_5COONa	0.178	0.212	0.240	0.245	0.247	0.222
C_3H_7COONa	0.174	0.208	0.236	0.241	0.242	0.218

Calculation according to the internal pressure theory (IPT)

The internal pressure theory was developed by McDevit and Long [5] in 1952. Compression of the solvent due to the presence of ions (electrostriction or tension effect) was employed to derive an expression for the salting-out constant

$$k_s = \frac{\bar{V}_n^0\left(V_s - \bar{V}_s^0\right)}{2.303RT\beta_0} = \lim_{\substack{c_s \to 0 \\ V_n \to 0}} \frac{\bar{V}_n^0}{2.303RT}\frac{\partial P_e}{\partial c_s}$$

where $\bar{V}_n^0$ and $\bar{V}_s^0$ are the partial molar volumes of the non-electrolyte and the salt in infinitely diluted solution, respectively, V_s is the molar volume of the salt as in the molten state and the compressibility of pure water. When salt dissolves in water, it produces an effective pressure, termed P_e. The results were shown in Table 4.

TABLE 3

CDST theoretical values

	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Naphthalene
NaF	0.171	0.185	0.198	0.200	0.200	0.190
KF	0.162	0.176	0.190	0.192	0.193	0.182
LiCl	0.171	0.185	0.197	0.201	0.202	0.223
NaCl	0.154	0.176	0.194	0.198	0.198	0.182
KCl	0.149	0.172	0.191	0.194	0.195	0.174
LiBr	0.169	0.183	0.194	0.198	0.199	0.224
NaBr	0.151	0.173	0.191	0.194	0.195	0.180
KBr	0.146	0.166	0.188	0.191	0.192	0.172
$NaNO_3$	0.132	0.150	0.165	0.167	0.168	0.155
$NaClO_3$	0.135	0.145	0.159	0.161	0.162	0.149
NH_4Cl	0.152	0.167	0.181	0.183	0.183	0.173
NH_4Br	0.150	0.165	0.179	0.181	0.181	0.171
NMe_4Br	0.118	0.132	0.145	0.148	0.148	0.138
NEt_4Br	0.106	0.120	0.133	0.135	0.135	0.126
$(NH_4)_2SO_4$	0.344	0.372	0.423	0.430	0.431	0.388
Na_2SO_4	0.365	0.406	0.441	0.447	0.449	0.407
K_2SO_4	0.333	0.389	0.425	0.432	0.433	0.390
$MgCl_2$	0.361	0.402	0.435	0.441	0.442	0.415
$SrCl_2$	0.356	0.397	0.431	0.437	0.438	0.411
$BaCl_2$	0.353	0.395	0.429	0.435	0.437	0.408
$MgSO_4$	0.402	0.439	0.497	0.505	0.506	0.458
HCOONa	0.141	0.156	0.165	0.167	0.168	0.159
CH_3COONa	0.135	0.149	0.157	0.159	0.159	0.150
C_2H_5COONa	0.125	0.139	0.146	0.148	0.149	0.140
C_3H_7COONa	0.113	0.127	0.141	0.143	0.144	0.136

Calculation according to the scaled particle theory (SPT)

In 1970, Masterton and Lee [6] applied the scaled particle theory to a system of three components, giving the formula

$$k_s = k_\alpha + k_\beta + k_\gamma$$

In aqueous solution at 25 ° C

$$\begin{aligned} k_\alpha = {} & 2.15 \times 10^{20}(\sigma_3^3 + \sigma_4^3) - 2.47 \times 10^{-4}\phi_0 + \sigma_1\left[6.45 \times 10^{20}(\sigma_3^2 + \sigma_4^2)\right. \\ & \left. + 1.34 \times 10^{28}(\sigma_3^3 + \sigma_4^3) - 4.23 \times 10^{4}\phi_0\right] + \sigma_1^2\left[6.45 \times 10^{20}(\sigma_3 + \sigma_4)\right. \\ & \left. + 4.01 \times 10^{28}(\sigma_3^2 + \sigma_4^2) + 1.32 \times 10^{36}(\sigma_3^3 + \sigma_4^3) - 4.17 \times 10^{12}\phi_0\right] \end{aligned}$$

$$\begin{aligned} k_\beta = {} & -1.85 \times 10^{14}\left(\frac{\epsilon_1}{k}\right)^{1/2}\left[\alpha_3^{3/4} \times \frac{z_3^{1/4}(\sigma_1 + \sigma_3)^3}{\sigma_3^3} + \alpha_4^{3/4} \times \frac{z_4^{1/4}(\sigma_1 + \sigma_4)^3}{\sigma_4^3}\right] \\ & + 6.26 \times 10^{17}\phi_0\left(\frac{\epsilon_1}{k}\right)^{1/2}(\sigma_1 + \sigma_2)^3 + 4.00 \times 10^{-2}\phi_0\alpha_1/(\sigma_1 + \sigma_2)^3 \end{aligned}$$

$$k_\gamma = 0.016 - 4.34 \times 10^{-4}\phi_0$$

TABLE 4

IPT theoretical values

	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Naphthalene
NaF	0.670	0.800	0.908	0.926	0.928	0.838
KF	0.535	0.639	0.725	0.739	0.741	0.669
LiCl	0.313	0.374	0.425	0.432	0.434	0.392
NaCl	0.423	0.505	0.573	0.584	0.586	0.529
KCl	0.344	0.412	0.467	0.476	0.478	0.431
LiBr	0.266	0.318	0.361	0.367	0.369	0.333
NaBr	0.352	0.421	0.478	0.487	0.488	0.441
KBr	0.298	0.355	0.403	0.411	0.412	0.372
$NaNO_3$	0.282	0.337	0.382	0.389	0.391	0.392
$NaClO_3$	0.251	0.300	0.340	0.346	0.348	0.314
NH_4Cl	0.149	0.178	0.202	0.206	0.207	0.186
NH_4Br	−0.077	−0.092	−0.105	−0.107	−0.107	−0.097
NMe_4Br	−0.536	−0.640	−0.727	−0.741	−0.743	−0.671
NEt_4Br	−0.804	−0.960	−1.089	−1.110	−1.114	−1.006
$(NH_4)_2SO_4$	0.858	1.026	1.164	1.186	1.189	1.075
Na_2SO_4	1.331	1.590	1.804	1.838	1.844	1.666
K_2SO_4	1.150	1.374	1.558	1.558	1.593	1.439
$MgCl_2$	0.914	1.092	1.239	1.262	1.266	1.144
$SrCl_2$	1.181	1.412	1.601	1.632	1.637	1.479
$BaCl_2$	1.010	1.207	1.369	1.394	1.399	1.264
$MgSO_4$	1.540	1.852	2.101	2.140	2.148	1.940
HCOONa	0.356	0.425	0.482	0.491	0.493	0.445
CH_3COONa	0.496	0.592	0.672	0.684	0.687	0.620
C_2H_5COONa	0.400	0.478	0.542	0.552	0.554	0.500
C_3H_7COONa	0.384	0.458	0.520	0.530	0.531	0.480

The subscripts 1, 2, 3, and 4 in the equations represent the non-electrolyte, water, cation, and anion, respectively, σ is the diameter, $\sigma_1 = (V_n/N_0)^{1/3}$, α the polarizability, and ϕ_0 the apparent molal volume of the salt. ϵ_1/k is the energy parameter of the non-electrolyte, calculated by Mavroyannis–Stephen formula [27]. The calculated results are shown in Table 5. This formula, however, is valid only for non-polar non-electrolytes. The scaled particle theory has been modified by Xie and Yang for polar non-electrolyte (XSPT) [7]. XSPT gave results for small non-electrolytes and small spherical ions which were in better agreement with the experimental results than SPT.

The internal pressure theory modified by Xie et al. (XIPT)

McDevit and Long using Kirkwood's method calculated the electrostatic energy between ion and neutral molecule and gave the modified equation

$$k_s = \frac{\bar{V}_n^0\left(V_s - \bar{V}_s^0\right)}{2.303RT\beta_0}\,\frac{a}{a+b}$$

$$= \frac{\bar{V}_n^0}{2.303RT}\,\frac{\partial P_e}{\partial c_s}\,\frac{a}{a+b}$$

TABLE 5

SPT theoretical values

	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Naphthalene
NaF	0.198	0.217	0.226	0.232	0.233	0.178
KF	0.172	0.189	0.196	0.202	0.203	0.150
LiCl	0.122	0.132	0.135	0.140	0.140	0.100
NaCl	0.186	0.205	0.215	0.220	0.221	0.173
KCl	0.160	0.177	0.185	0.191	0.192	0.145
LiBr	0.086	0.094	0.094	0.099	0.099	0.055
NaBr	0.151	0.167	0.174	0.180	0.181	0.130
KBr	0.125	0.139	0.145	0.150	0.151	0.102
$NaNO_3$	0.830	0.922	1.00	1.00	1.01	0.931
$NaClO_3$	0.982	1.09	1.18	1.20	1.20	1.106
NH_4Cl	0.112	0.124	0.130	0.134	0.135	0.095
NH_4Br	0.077	0.087	0.090	0.094	0.095	0.018
NMe_4Br	1.469	1.645	1.785	1.803	1.807	1.726
NEt_4Br	1.909	2.140	2.329	2.349	2.354	2.282
$(NH_4)_2SO_4$	1.132	1.261	1.361	1.377	1.377	1.303
Na_2SO_4	1.375	1.535	1.645	1.682	1.682	1.555
K_2SO_4	1.258	1.401	1.509	1.528	1.528	1.449
$MgCl_2$	0.112	0.121	0.121	0.126	0.127	0.077
$SrCl_2$	0.076	0.081	0.077	0.083	0.084	0.017
$BaCl_2$	0.047	0.050	0.044	0.050	0.051	0.020
$MgSO_4$	1.451	1.612	1.729	1.753	1.754	1.611
HCOONa	1.05	1.17	1.25	1.26	1.26	1.186
CH_3COONa	1.76	2.01	2.06	2.19	2.19	2.020
C_2H_5COONa	2.37	2.64	2.85	2.89	2.89	2.733
C_3H_7COONa	3.06	3.41	3.68	3.73	3.73	3.536

where a is the average radius of the cation and anion, and b the radius of the non-electrolyte. At that time McDevit and Long gave no quantitative calculation. A calculation method was introduced by Xie et al. [8] for the modified internal pressure theory. The assumptions were that (a) except for the larger ions Latimer's radii of ions were used instead of the crystal radii, i.e., $r_L^+ = r_P^+ + 0.85$ (Å), and $r_L^- = r_P^- + 0.10$ (Å), where r_P is the Pauling radius, (b) a in the modified equation is the average of the radii of the cation and anion, i.e. $a = (r_L^+ + r_L^-)/2$, and (c) b is the radius of the non-electrolyte molecule

$$b = \left(\frac{3 \times 0.7402 V_n}{4 \pi N_0} \right)^{1/3}$$

The results according to XIPT are shown in Table 6.

In order to compare comprehensively the various theoretical k_s values with the experimental k values, some plots of the various theoretical k_s values against experimental k values were made. The calculated k_s from two SPT for salts containing a larger ion were not only of the opposite sign

TABLE 6

XIPT theoretical values

	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Naphthalene
NaF	0.237	0.278	0.301	0.306	0.306	0.283
KF	0.203	0.234	0.258	0.262	0.263	0.242
LiCl	0.113	0.130	0.144	0.145	0.146	0.135
NaCl	0.163	0.187	0.207	0.210	0.210	0.194
KCl	0.140	0.162	0.179	0.182	0.182	0.168
LiBr	0.099	0.114	0.125	0.127	0.128	0.118
NaBr	0.138	0.160	0.177	0.179	0.179	0.166
KBr	0.124	0.143	0.158	0.160	0.161	0.148
$NaNO_3$	0.122	0.141	0.156	0.158	0.159	0.163
$NaClO_3$	0.111	0.129	0.143	0.145	0.146	0.134
NH_4Cl	0.062	0.072	0.079	0.080	0.081	0.074
NH_4Br	−0.032	−0.037	−0.041	−0.042	−0.042	−0.039
NMe_4Br	−0.258	−0.299	−0.332	−0.337	−0.338	−0.311
NEt_4Br	−0.406	−0.470	−0.522	−0.530	−0.532	−0.489
$(NH_4)_2SO_4$	0.380	0.470	0.487	0.494	0.495	0.488
Na_2SO_4	0.551	0.636	0.703	0.714	0.715	0.714
K_2SO_4	0.536	0.620	0.640	0.649	0.651	0.643
$MgCl_2$	0.333	0.383	0.423	0.429	0.430	0.397
$SrCl_2$	0.467	0.539	0.595	0.604	0.606	0.559
$BaCl_2$	0.413	0.476	0.527	0.534	0.536	0.494
$MgSO_4$	0.610	0.771	0.782	0.793	0.796	0.801
HCOONa	0.155	0.179	0.200	0.203	0.204	0.186
CH_3COONa	0.231	0.270	0.299	0.303	0.304	0.277
C_2H_5COONa	0.194	0.225	0.251	0.255	0.256	0.233
C_3H_7COONa	0.192	0.222	0.249	0.253	0.253	0.231

to the experimental values, but were also higher in one magnitude (see Table 5) and most of the calculated k values from the McDevitt-Long internal pressure equation appear to be 2–4 times the experimental values (see Table 4). It is not possible to use diagrams to compare the IPT and two SPT values with the experimental values because of the large differences between them. Figures 1–3 give the experimental salting-out constants of benzene, toluene, *o*-xylene and naphthalene in NaCl, $NaNO_3$, NMe_4Br, Na_2SO_4, $MgCl_2$, and CH_3COONa aqueous solutions and the theoretical k_s values according to the DMT, CDST, and XIPT, respectively.

Comparison of Fig. 1 with Fig. 2 shows that, in Fig. 2, the points fall around a line which makes an angle of 45° to the abscissa. It seems that the results calculated according to Conway et al. electrostatic theory are better than those obtained from Debeye–MacAulay electrostatic theory.

However, the signs of the calculated values of the salt effect constant, k_s, for the salts containing large ions are just opposite to those of the experimental k values (e.g. for NR_4Br).

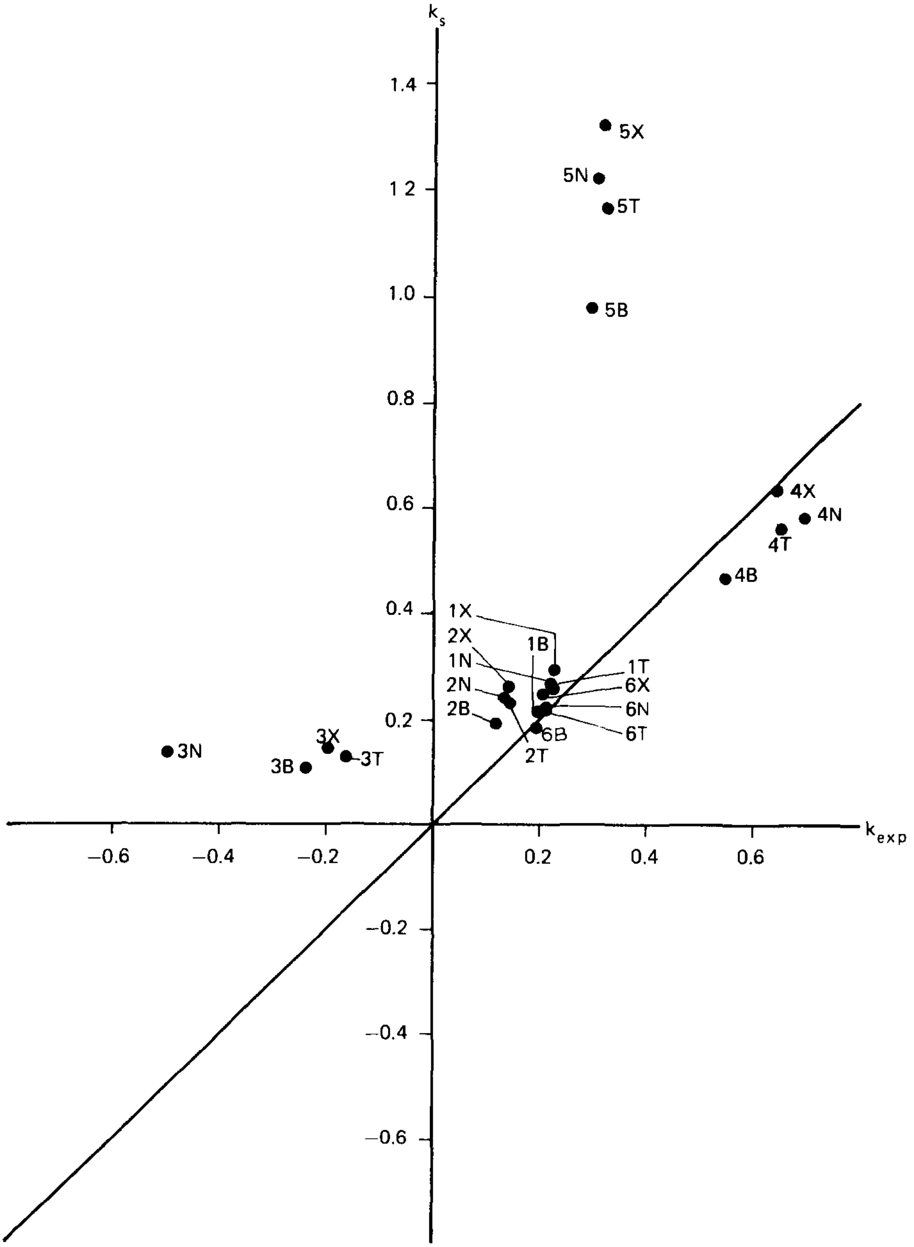

Fig. 1. Comparison of DMT-calculated k_s values and observed k values. Non-electrolytes: B, benzene; T, toluene; X, *o*-xylene; N, naphthalene. Salts: 1, NaCl; 2, $NaNO_3$; 3, NMe_4Br; 4, Na_2SO_4; 5, $MgCl_2$; 6, CH_3COONa.

In Fig. 3, the theoretical values obtained from the internal pressure theory modified by Xie seem to coincide with the experimental values rather than those from the other theories. This is because the XIPT was derived from

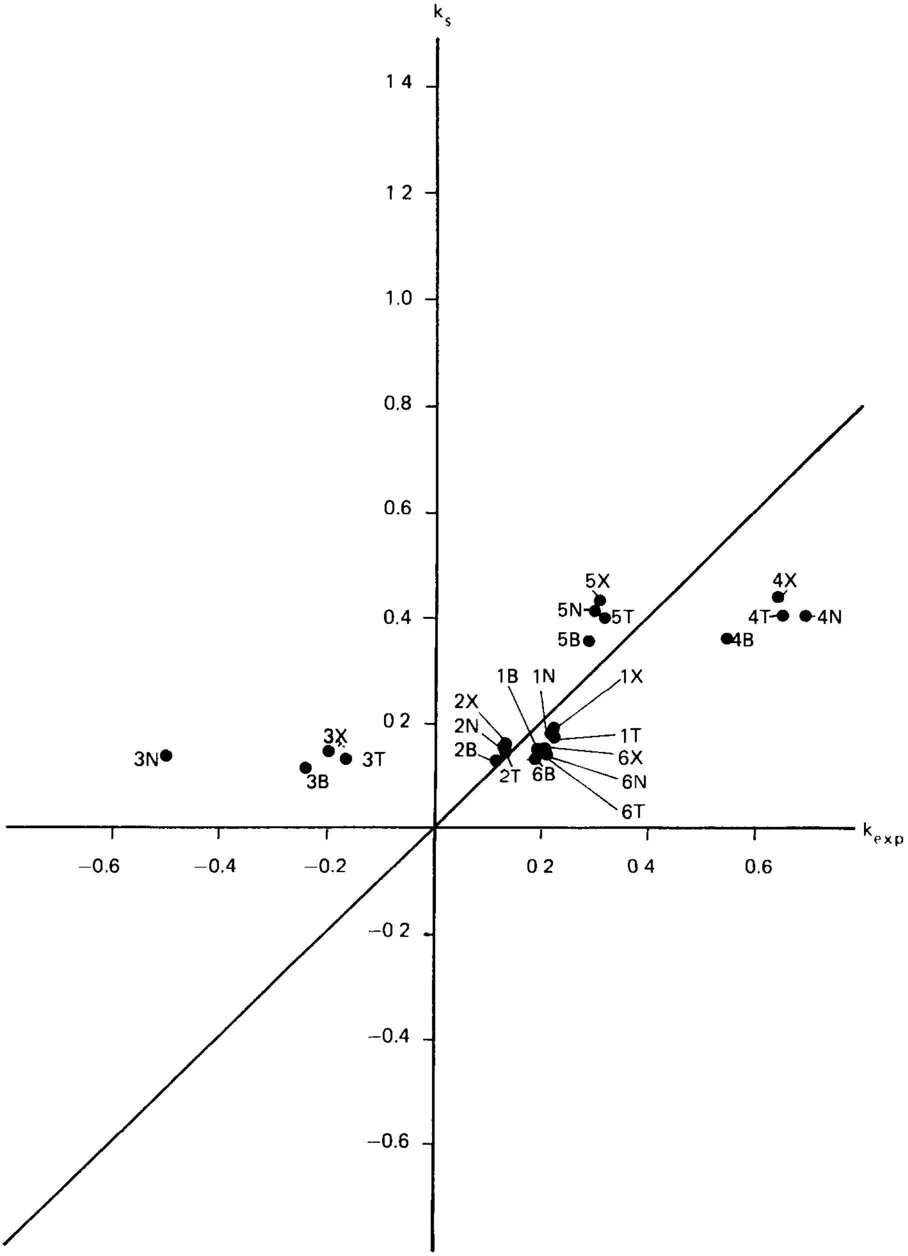

Fig. 2. Comparison of CDST-calculated k_s values and observed k values. For key, see Fig. 1.

thermodynamics and also many parameters including the Latimer radii were taken from experiments.

Figures 4–6 give the experimental values of k for *m*-xylene in the above-mentioned 25 aqueous solutions vs. the theoretical k_s values accord-

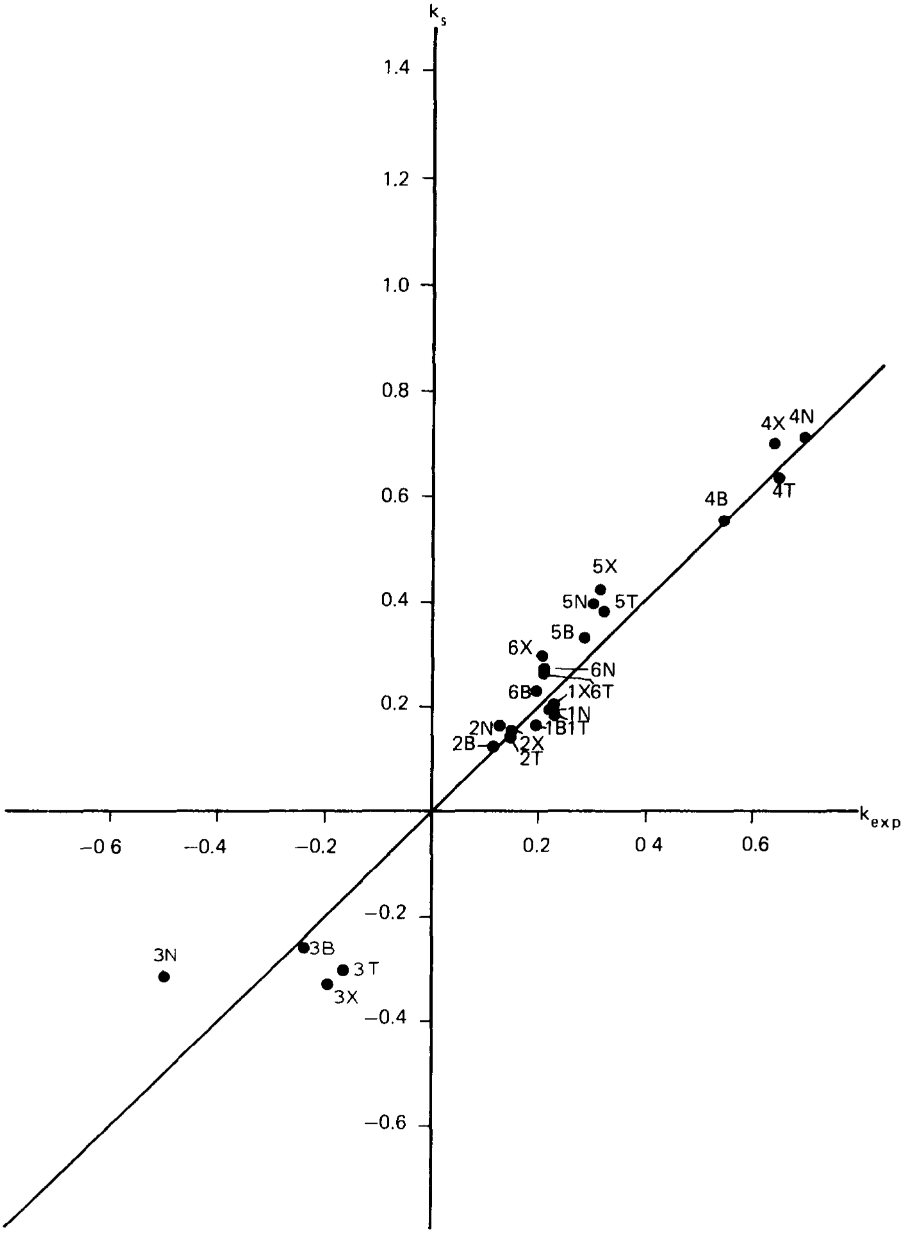

Fig. 3. Comparison of XIPT-calculated k_s values and observed k values. For key, see Fig. 1.

ing to the DMT, CDST, and XIPT, respectively. Comparison of Figs. 4–6 shows that the XIPT gives results in better agreement with the experimental results than do DMT and CDST.

On the other hand, for the salt containing a large ion, the van der Waals force obviously increases. For example, in the case of CH_3COONa,

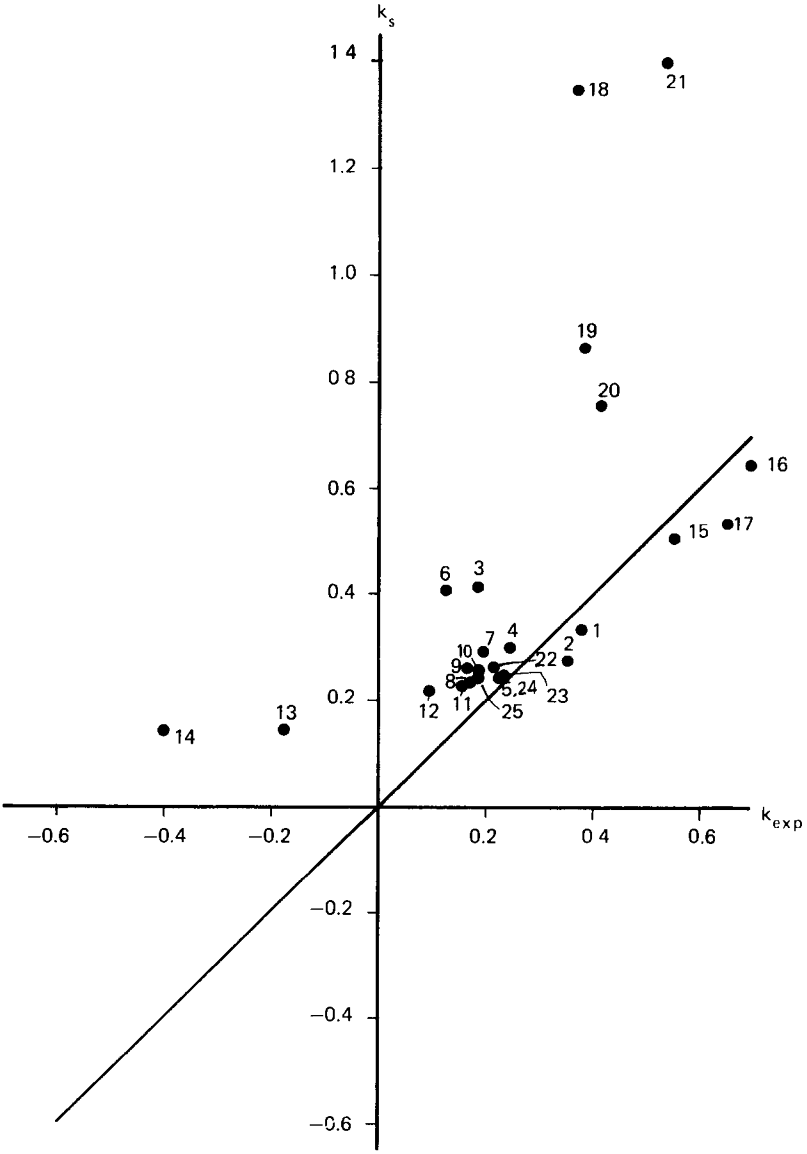

Fig. 4. DMT-calculated k_s vs. observed k for *m*-xylene. Salts: 1, NaF; 2, KF; 3, LiCl; 4, NaCl; 5, KCl; 6, LiBr; 7, NaBr; 8, KBr; 9, $NaNO_3$; 10, $NaClO_3$; 11, NH_4Cl; 12, NH_4Br; 13, NMe_4Br; 14, NEt_4Br; 15, $(NH_4)_2SO_4$; 16, Na_2SO_4; 17, K_2SO_4; 18, $MgCl_2$; 19, $SrCl_2$; 20, $BaCl_2$; 21, $MgSO_4$; 22, HCOONa; 23, CH_3COONa; 24, C_2H_5COONa; 25, C_3H_7COONa.

C_2H_5COONa, and C_3H_7COONa, the salt effect constants of these aromatic compounds decrease with increasing number of carbon atoms and the van der Waals force between them also increases with increasing ionic volume. For another example, the k value of each non-electrolyte in aqueous $NaNO_3$ solution is less than that in aqueous $NaClO_3$ solution because the NO_3^- and

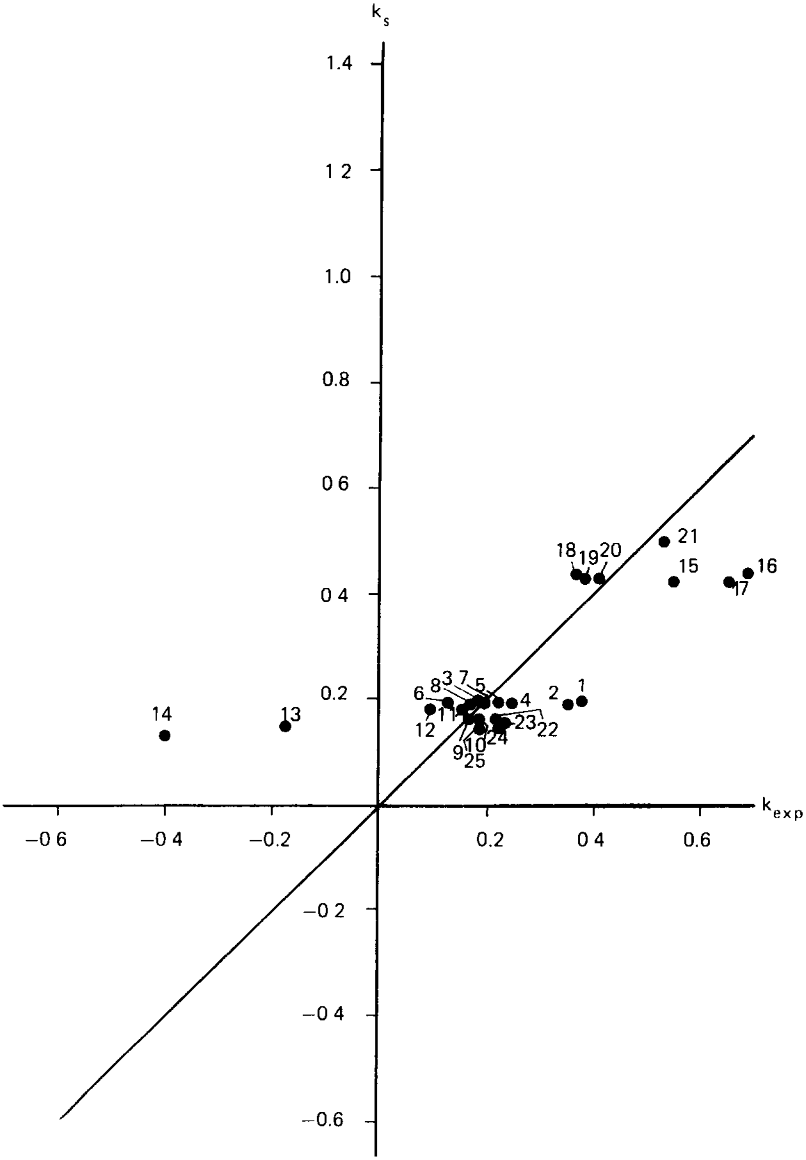

Fig. 5. CDST-calculated k_s vs. observed k for *m*-xylene. For key, see Fig. 4.

ClO_3^- ions have two different structures; NO_3^- is of trigonal structure with delocalized π bonding while ClO_3^- is of tetrahedral structure without delocalized π bonding but with a lone pair of electrons. Of course the van der Waals force interaction between the NO_3^- ion and the aromatic molecule is larger than that between the ClO_3^- ion and the aromatic molecule. Now the electrostatic force according to Kirkwood's method [28] is the only force considered in the $a/(a+b)$ term of XIPT. Thus it will be further

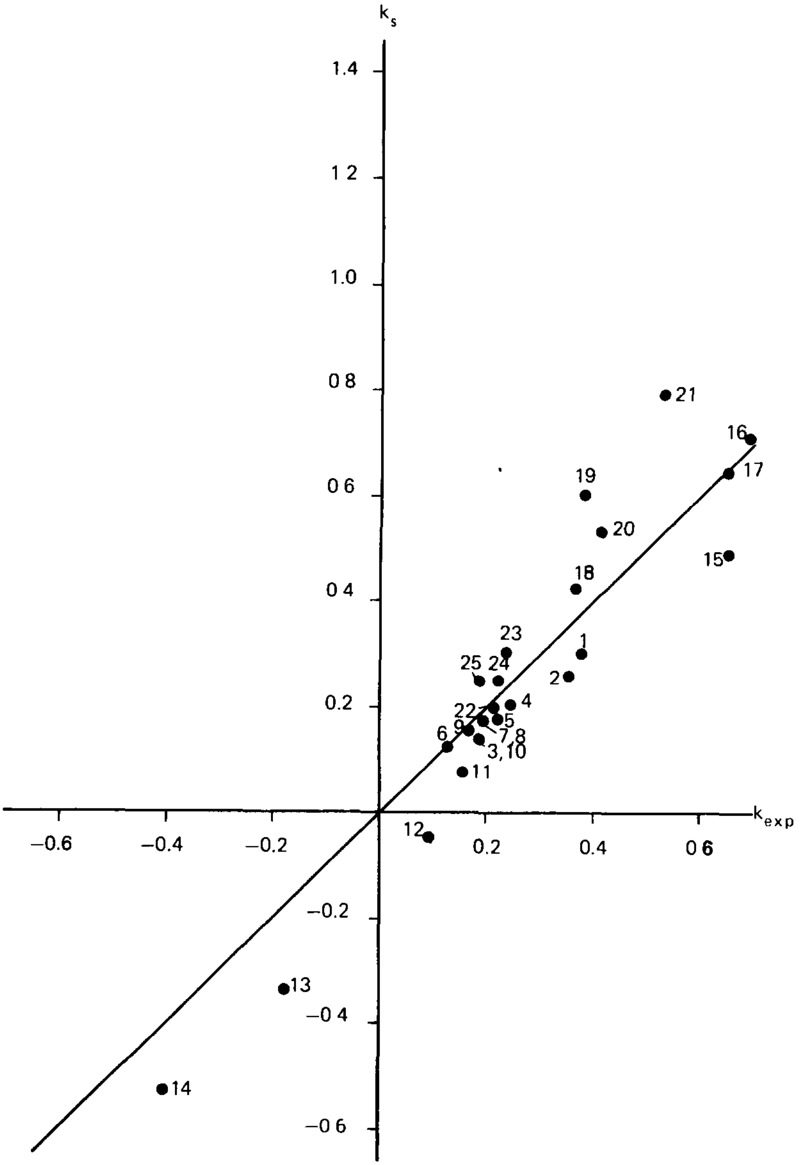

Fig. 6. XIPT-calculated k_s vs. observed k for *m*-xylene. For key, see Fig. 4.

improved if the van der Waals force, except for the electrostatic force, is also taken into account.

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