

molar extinction coefficient of copper ion in all forms in the 1:1:1 solution at 608 $\mu\mu$ is indicated by $\bar{\epsilon}'_{1:1:1}$. An approximate value of β was first obtained by neglecting α in equation 17, and an approximate value of α was then calculated from the first ionization constant¹ of $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{6-}$ which has the value 1.7×10^{-4} . Successive solutions of these equations yielded the values for α and β given in Table II. The corresponding value for $\log K_s$ is 1.90 ± 0.20 . The mean value of K_m obtained by substituting this value, Bjerrum's value,² 20.04, and Watters and Aaron's corrected value,¹ 13.01, for the logarithms of the stability constants of $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{6-}$ and $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{6-}$ in equation 16 is 17.48, which is in fair agreement with the values 17.77 and 17.74 obtained in the pH experiments. The mean value of $\log K_m$ is accordingly 17.66 ± 0.18 .

The theoretical extinction curve 14, Fig. 1, for $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{6-}$ was readily calculated from similar data for a series of wave lengths using the following equation based on the conservation of copper ions and Beer's law.

$$\epsilon_m = (\bar{\epsilon}'_{1:1:1} - \beta\epsilon_{ea} - (1 - \alpha)\beta\epsilon_{p2} - \alpha\beta\epsilon_{p1}) / (1 - 2\beta) \quad (19)$$

The data for a few points are included in Table III.

The failure of curves 7 to 13, Fig. 1, to form a well-defined isosbestic point is due to two causes, dismutation of the mixed complex and dissociation of the dipyrrophosphatocuprate(II) complex. Both effects become increasingly important in the curves

TABLE III
CALCULATION OF MOLAR EXTINCTION COEFFICIENT OF
0.005 M $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{6-}$, ($\beta = 0.11$, $\alpha = 0.425$)

$\mu\mu$	ϵ	ϵ_{p1}	ϵ_{p2}	ϵ_{ea}	ϵ_m calcd.
520	14.4	1.0	0.8	55.2	10.5
560	27.8	2.2	4.4	60.2	26.6
600	37.2	5.0	10.4	43.2	40.4
620	38.2	7.4	13.6	34.0	41.6
640	38.0	10.0	17.0	25.6	43.0
660	36.8	13.4	20.2	19.0	41.9
680	33.6	17.2	23.2	13.6	38.2
700	30.8	20.6	25.0	9.4	34.8
740	23.4	25.4	25.8	5.0	25.7
780	16.0	26.2	23.6	2.4	16.6

corresponding to solutions approaching the composition of the mixed complex and are, within experimental error, of the magnitude predicted on the basis of equation 16.

The slight shift toward longer wave lengths of curves high in pyrophosphate which is barely observed in curve 1, Fig. 1, may be due to the formation of binuclear complexes. An investigation of this effect is under way.

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COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Solubility of Ethyl Acetate in Aqueous Electrolyte Solutions¹

BY A. P. ALTSHULLER² AND H. E. EVERSON

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The solubility of ethyl acetate in a number of aqueous alkali halide and quaternary ammonium iodide solutions has been investigated by means of the turbidimetric method at electrolyte concentrations from 0.025 to 0.400 M and in the temperature range from 20 to 40°. The experimental activity coefficients have been compared with those calculated from various equations based on the assumption of coulombic interactions. While fairly good semiquantitative agreement is found for ethyl acetate in solutions of alkali chlorides and bromides, the experimental activity coefficients for ethyl acetate in alkali fluoride solutions are somewhat higher than those found theoretically. The theoretical activity coefficients are uniformly higher than and even differ in sign from the coefficients found experimentally for ethyl acetate in alkali and quaternary ammonium iodide solutions. The additional influence of dispersion forces is discussed qualitatively. Solubility parameters, k_s , calculated from the McDevit-Long theory are compared with the k_s found experimentally. The importance in salt effect theory of the discrete structure of the solvent is discussed.

Although a number of studies have been made of the solubility of ethyl acetate in aqueous electrolyte solutions by Euler,³ Lunden,⁴ Linde,⁵ Glasstone, *et al.*,^{6a-c} and Schlesinger and Kubasowa⁷ these investigations, excepting those of Glasstone and his co-workers, have been rather limited in their

scope. The work of Glasstone, *et al.*,^{6a-c} was rather detailed, but many of the electrolyte concentrations employed were much too high to permit comparison with theory. A more serious weakness in this work lies in the poor agreement between Glasstone's solubility results for ethyl acetate in water^{6a} and those of other investigators.⁸ These facts made further investigation by another experimental method seem desirable, especially since the work of Glasstone, *et al.*,^{6a-c} has been employed in the past to test various theories of the salt effect.⁹⁻¹¹

(1) Based on a part of a dissertation submitted by A. P. Altshuller to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree doctor of philosophy, July, 1951.

(2) Laws Fellow 1950-51.

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The specific purpose of this investigation was to study the effects of most of the alkali halides and a few quaternary ammonium salts upon the solubility of ethyl acetate in water over a range of temperatures and at electrolyte concentrations between 0.025 and 0.400 *M*, and to compare the experimental results obtained with the results predicted by various theoretical equations which have been proposed.

Experimental

Materials.—The sodium, potassium and lithium salts employed were C.P. salts. The impurities listed were much too small to affect the results. No analyses were available for the rubidium and cesium salts. With the exceptions of the rubidium and cesium chlorides, it was found that these salts contained insoluble impurities which were probably aluminum and iron oxides. As a result it was necessary to recrystallize these salts. The rubidium and cesium salts were analyzed for sodium and potassium impurities by means of a Weichselbaum-Varney Universal Spectrophotometer. The salts all had less than 0.04% sodium as an impurity. The following potassium impurities were found: RbF, 0.6%; RbCl, 4.6%; RbBr, 0.2%; RbI, 0.2%; CsCl, 0.02%; CsBr, 0.02%; CsI, 0.00%. The quaternary ammonium salts were obtained from the Eastman Kodak Company. All of the salts were dried in a vacuum desiccator over phosphorus pentoxide before use.

The purity of the ethyl acetate has been discussed previously.⁸

Solubility Measurements.—The method used was that of Alexejew.¹² The details of the procedure have been discussed previously.⁸ The accuracy of the measurements is estimated to be about $\pm 0.5\%$.

The molarities of the salts are those in water before addition of ethyl acetate. The densities of water-ethyl acetate solutions in the temperature range from 20–40° differ from the densities of water itself by only about 0.001 g./ml. This fact indicates an appreciable volume contraction which ranges from 0.6 to 0.8%. In terms of the molarities after addition of ethyl acetate this would give values of 0.101, 0.201, 0.302 and 0.403 *M*. These changes in molarity would correspond to errors in solubility differences of no more than 0.005 g. of ethyl acetate/100 g. of water or less than 0.1%. This is less than what is probably the highest accuracy attainable by this method ($\pm 0.1^\circ$ error in temperature or 0.1% error in solubility) and is far less than the conservative estimate of error made above. The molalities of the salt solutions employed would differ by 1 to 2% from the molarities given above.

The dielectric constant results employed in the equations obtained from electrostatic theory have been previously reported.¹³

Experimental Results

Table I lists the values in g. of ethyl acetate/100 g. of water obtained by treating the experimental results by the method of least squares so as to make comparison possible at the same temperatures. When it was felt that extrapolation was not justified, values were omitted from Table I.

The experimental results indicate that the solubility of ethyl acetate in both water and electrolyte solutions is a linear function of the temperature in the range between 20 and 40°. The solubility of ethyl acetate in electrolyte solutions appears to be almost a linear function of the concentration. The salting out order for anions is clearly $F^- > Cl^- > Br^- > I^-$. The salting out ability of cations decreases with increasing radius except that lithium ion is out of order. The alkali metal iodides appear to salt out ethyl acetate to a small or negligible extent or salt it in to a negligible extent.

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TABLE I
SOLUBILITY OF ETHYL ACETATE IN ELECTROLYTE SOLUTIONS

Salt	Cs	(G. of ethyl acetate/100 g. of water)				
		20°	25°	30°	35°	40°
...	0.000	8.32	8.01	7.70	7.39	7.08
LiF	0.025	8.28	7.91	7.55	7.18	6.82
LiCl	.100	...	7.64	7.36	7.08	6.81
	.200	...	7.48	7.17	6.85	6.54
	.300	...	7.23	6.91	6.58	6.25
	.400	...	6.99	6.67	6.34	6.02
LiBr	.100	...	7.87	7.54	7.21	...
	.200	...	7.75	7.41	7.07	...
	.300	...	7.63	7.29	6.96	...
	.400	...	7.50	7.16	6.82	...
NaF	.100	7.81	7.50	7.18	6.86	...
	.200	7.34	7.02	6.70	6.39	...
	.300	6.87	6.53	6.20	5.86	...
	.400	6.38	6.07	5.76	5.46	...
NaCl	.100	7.98	7.67	7.36	7.05	6.74
	.200	7.73	7.39	7.04	6.70	6.36
	.300	7.34	7.02	6.69	6.37	6.04
	.400	7.10	6.73	6.36	5.99	5.63
NaBr	.100	8.12	7.79	7.45	7.12	...
	.200	7.94	7.59	7.24	6.89	...
	.300	7.73	7.37	7.01	6.65	...
	.400	7.56	7.18	6.81	6.43	...
NaI	.100	8.34	7.99	7.63	7.28	...
	.200	8.31	7.96	7.62	7.28	...
	.300	8.28	7.91	7.55	7.19	...
	.400	8.16	7.82	7.49	7.16	...
KCl	.100	7.96	7.64	7.32	7.00	...
	.200	7.71	7.39	7.08	6.76	...
	.300	7.43	7.09	6.75	6.41	...
	.400	7.21	6.82	6.42	6.03	...
KBr	.100	7.44	7.16	6.89
	.200	7.25	6.99	6.72
	.300	7.08	6.80	6.51
	.400	6.91	6.61	6.31
KI	.100	...	7.98	7.64	7.30	...
	.200	...	7.92	7.60	7.29	...
	.300	...	7.89	7.56	7.23	...
	.400	...	7.82	7.51	7.21	...
RbF	.100	7.84	7.51	7.19	6.87	6.55
	.200	7.39	7.08	6.77	6.46	6.15
	.300	6.99	6.68	6.38	6.07	5.77
	.400	6.59	6.31	6.02	5.74	5.46
RbCl	.100	8.03	7.70	7.36	7.03	...
	.200	7.76	7.41	7.06	6.71	...
	.300	7.51	7.14	6.78	6.42	...
	.400	7.28	6.84	6.39
RbBr	.397	7.41	7.13	...
	.194	7.20	6.86	...
RbI	.099	8.42	8.00	7.58
	.189	8.41	8.01	7.60
CsCl	.100	8.06	7.74	7.43	7.12	...
	.200	7.87	7.51	7.15	6.79	...
	.300	7.63	7.26	6.88	6.50	...
CsBr	.100	8.14	7.81	7.48	7.15	6.82
	.200	7.93	7.60	7.27	6.94	6.61
CsI	.100	...	8.07	7.68	7.29	...
	.200	...	8.08	7.71	7.34	...
(CH ₃) ₄ NI	.100	8.58	8.17	7.76
PhMe ₂ NI	.100	8.72	8.45	8.17	7.90	7.63

The quaternary ammonium iodides, especially asymmetrical trimethylphenylammonium iodide, salt in the ethyl acetate to an appreciable extent. The salt effect appears to increase with increasing temperature in the temperature range studied.

Discussion

In Table II the experimental activity coefficients, $f = S_0/S$, are compared at 30° with the results calculated by various electrostatic equations in columns A through F.

Columns A through D contain activity coefficients calculated employing various modifications of a Debye-McAulay type equation.¹⁴ Column A lists values obtained using D_0 , the dielectric constant of water, and b , the crystallographic radius of the ion, while the equation used to calculate the values in column B differs in that it employs b' , the effective radius.¹¹ To calculate the values in column C, an equation was used employing instead of D_0 , D , the dielectric constant of water saturated with ethyl acetate. Column D was obtained by use of an equation employing b' and D . The equation used to obtain the values in column E contains b' and D in its first term and has a second term correcting for the effects of the ionic atmosphere.¹¹ Column F was calculated by means of the Debye equation.¹⁵ The values of \bar{D} and $w = ((D - D_0)/D_0m)$ employed to calculate the values of $S = (N\epsilon^2w/2000kTD_0)$ or $S' = N\epsilon^2wD_0/2000kTD^2$ which were used in the equations from which columns A through E were calculated and the \bar{R}^4 used in the Debye equation from which column F was calculated, have been previously reported.¹⁸ For convenience in the following discussion only the letter designations will be employed.

The theoretical activity coefficients in C give the best agreement with the experimental coefficients for ethyl acetate in solutions of the alkali metal fluorides. Even the values in C, however, are 20 to 25% lower than those found experimentally. On the other hand, C gives good agreement with the experimental activity coefficients for ethyl acetate in solutions of alkali metal chlorides. The experimental coefficients for ethyl acetate in aqueous alkali metal bromide solutions are best represented by the values in D or E. The theoretical activity coefficients in D and E also compare well with the experimental values for ethyl acetate in lithium chloride solutions. The theoretical values calculated from the electrostatic theories fail to give agreement with the experimental results for ethyl acetate in alkali metal iodides and fail even more drastically in giving agreement with the experimental values in quaternary ammonium iodide solutions.

The values in D, E and F which should be the most "correct" in view of the additional refinements in the model used to derive them, only give good agreement with the experimental activity coefficients for ethyl acetate in solutions of the bromides. For the fluorides and chlorides the values in D, E and F are much lower than the

experimental activity coefficients. This situation may be improved somewhat if the dielectric constant lowering due to the electrolyte^{11,16} is also taken into consideration, since this would increase the values in D, E and F somewhat.

The temperature coefficient of the salt effect is found theoretically to be positive. This is in agreement with most of the experimental findings.

The need for the consideration of dispersion forces in any complete theory of the salt effect is rather well recognized.^{17,18} In view of the poor agreement with experiment shown by the only quantitative theory of dispersion forces in the salt effect,¹⁷ only a short qualitative discussion will be given here.¹⁹

Since the potential energy contributed by dispersion effects is proportional to the polarizability of the interacting particles, all other components being held constant, the dispersion effect will make increasing contributions with increasing polarizability or increasing volume of the ions involved. Thus of the halides, the iodide ion would have the largest dispersion effect and even larger cations, such as the quaternary ammonium ions, or anions such as the benzoates would have even more pronounced contributions to make to terms involving dispersion effects. Since the dispersion forces act in an opposite direction to the coulombic forces, the former will tend to decrease the activity coefficient of the neutral molecule. If the coulombic and the dispersion forces are assumed to be usually the only forces of importance, then in the present investigation the contribution of the dispersion effect seems almost equal to the coulombic interactions for ethyl acetate in the alkali metal iodides and considerably exceeds the coulombic effects for the quaternary ammonium iodides. The asymmetry of the phenyltrimethylammonium ion may also result in marked dipole field effects. A more adequate quantitative theory of dispersion forces in the salt effect is greatly to be desired.

Another approach to the problem has been made recently in the new "internal pressure" theory of McDevit and Long.²⁰ The experimental solubility parameters, k_s , found in this investigation are compared in Table III with the values of k_s found by employing the McDevit-Long theory. For ethyl acetate in aqueous electrolyte solutions at 30°, the equations employed reduce to $k_s' = 0.0375 (V_s - \bar{V}_s^0)$ and $k_s'' = 1.71 \times 10^{-3} dP_e/dC_s$. The values of V_s are taken from Lundén's paper,²¹ while the values of \bar{V}_s^0 are those given by Harned and Owen¹⁰ or Lundén.²¹ The values of dP_e/dC_s are those given by McDevit and Long.²⁰

As was found by McDevit and Long, the calculated results although they are in the right order are much larger than the experimental values.

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TABLE II
COMPARISON OF EXPERIMENTAL ACTIVITY COEFFICIENTS WITH ACTIVITY COEFFICIENTS CALCULATED FROM VARIOUS
"ELECTROSTATIC" EQUATIONS

Salt	Cs	Exp.	A	B	C	D	E	F
LiF	0.025	1.020	1.015	1.010	1.018	1.011	1.011	1.007
LiCl	.100	1.046	1.058	1.034	1.066	1.039	1.037	1.027
	.200	1.074	1.119	1.069	1.136	1.078	1.074	1.056
	.300	1.115	1.183	1.105	1.211	1.120	1.111	1.086
	.400	1.154	1.252	1.142	1.291	1.163	1.149	1.119
LiBr	.100	1.021	1.056	1.033	1.064	1.037	1.035	1.027
	.200	1.039	1.117	1.066	1.133	1.075	1.071	1.055
	.300	1.056	1.179	1.101	1.207	1.115	1.107	1.085
	.400	1.075	1.246	1.137	1.285	1.157	1.142	1.116
NaF	.100	1.073	1.051	1.036	1.058	1.041	1.039	1.028
	.200	1.149	1.104	1.073	1.120	1.083	1.079	1.057
	.300	1.242	1.160	1.112	1.184	1.128	1.119	1.092
	.400	1.337	1.219	1.153	1.253	1.174	1.159	1.122
NaCl	.100	1.046	1.045	1.031	1.051	1.035	1.034	1.027
	.200	1.094	1.092	1.063	1.106	1.072	1.067	1.054
	.300	1.151	1.142	1.095	1.162	1.119	1.100	1.086
	.400	1.211	1.194	1.129	1.222	1.148	1.134	1.118
NaBr	.100	1.034	1.044	1.030	1.050	1.034	1.032	1.027
	.200	1.064	1.089	1.060	1.102	1.068	1.064	1.054
	.300	1.098	1.137	1.092	1.157	1.105	1.096	1.084
	.400	1.131	1.187	1.124	1.215	1.142	1.128	1.115
NaI	.100	1.009	1.042	1.028	1.048	1.032	1.030	1.026
	.200	1.011	1.082	1.056	1.098	1.064	1.060	1.053
	.300	1.020	1.126	1.085	1.151	1.098	1.090	1.081
	.400	1.028	1.171	1.116	1.207	1.113	1.120	1.112
KCl	.100	1.052	1.038	1.029	1.043	1.033	1.031	1.027
	.200	1.088	1.078	1.058	1.088	1.066	1.062	1.055
	.300	1.141	1.118	1.088	1.135	1.101	1.092	1.084
	.400	1.199	1.160	1.119	1.184	1.137	1.123	1.116
KBr	.100	1.035	1.037	1.027	1.041	1.031	1.029	1.026
	.200	1.062	1.074	1.055	1.084	1.062	1.058	1.054
	.300	1.088	1.113	1.083	1.129	1.095	1.087	1.083
	.400	1.115	1.153	1.113	1.176	1.129	1.116	1.114
KI	.100	1.008	1.035	1.025	1.040	1.029	1.028	1.025
	.200	1.013	1.071	1.051	1.081	1.059	1.055	1.052
	.300	1.019	1.109	1.078	1.124	1.090	1.082	1.080
	.400	1.026	1.147	1.106	1.168	1.122	1.109	1.110
RbF	.100	1.071	1.041	1.033	1.047	1.037	1.036	1.028
	.200	1.138	1.083	1.066	1.095	1.075	1.071	1.056
	.300	1.207	1.127	1.101	1.146	1.113	1.104	1.086
	.400	1.279	1.173	1.137	1.199	1.157	1.142	1.119
RbCl	.100	1.049	1.035	1.028	1.040	1.031	1.030	1.026
	.200	1.091	1.071	1.055	1.081	1.063	1.058	1.054
	.300	1.136	1.109	1.084	1.124	1.096	1.087	1.083
	.400	1.205	1.147	1.114	1.168	1.130	1.117	1.114
RbBr	.097	1.039	1.033	1.026	1.038	1.029	1.028	1.025
	.194	1.070	1.066	1.051	1.076	1.059	1.054	1.051
RbI	.099	1.016	1.032	1.024	1.036	1.028	1.026	1.025
	.189	1.013	1.061	1.047	1.070	1.054	1.050	1.049
CsCl	.100	1.037	1.033	1.027	1.038	1.030	1.029	1.026
	.200	1.077	1.067	1.053	1.076	1.061	1.057	1.053
	.300	1.119	1.102	1.081	1.117	1.093	1.084	1.082
CsBr	.100	1.030	1.032	1.025	1.036	1.029	1.027	1.026
	.200	1.059	1.064	1.051	1.073	1.058	1.054	1.052
CsI	.100	1.003	1.030	1.024	1.034	1.027	1.025	1.025
	.200	0.999	1.061	1.048	1.069	1.055	1.050	1.050
(CH ₃) ₄ NI	.100	.992	1.025	1.021	1.029	1.024	1.023	1.022

TABLE III

COMPARISON OF SALT EFFECT CALCULATED FROM McDEVITT-LONG THEORY WITH EXPERIMENTAL SALT EFFECT AT 30°

Salt	$(V_s - \bar{V}_s^0)$, ml./mole	k_s' , calcd.	$\frac{dP_s}{dC_s}$, bar,		k_s , obs.	k_s'/k_s
			l./ mole	k_s'' , calcd.		
LiCl	5.5, 10.5	0.21, 0.39	200	0.34	0.17	1.2-2.3
LiBr	3.5	.1308	1.6
NaF	20	.7531	2.4
NaCl	11	.41	270	.46	.20	2.0
NaBr	9	.34	225	.38	.14	2.4
NaI	7	.26	175	.30	.03	9
KCl	10.5	.39	220	.38	.20	2.0
KBr	8	.3013	2.3
KI	6.5	.2403	8
RbCl	9.5	.36195	1.9
RbBr	7.5	.2815	1.9
RbI	5.5	.21025	8
CsCl	8	.30	165	.28	.16	1.9
CsBr	6.5	.24125	1.9
CsI	4.5	.1701	17
$(\text{CH}_3)_4\text{NI}$	-52	-2.0	-.035	57

The ratios of calculated to observed k_s as given in the last column of Table III are of some interest. Excepting the iodides, the ratio is 2.0 ± 0.4 , if the calculated values of k_s given in column 3 are used. If the k_s values from column 5 are employed, the ratios for the sodium halides are 2.3, 2.7, 1.9 and 10 going from fluoride to iodide. Thus the ratios for the fluorides, chlorides and bromides fall around two, but the ratio for the iodides is anomalously high. This result is not in accord with the proposal²⁰ that a multiplier of the form $a/a + b$, where a is the ion size and b the neutral molecule size, should be employed to take the dimensions of the particles into consideration. While it is possible that chemical interaction between the iodides and ethyl acetate^{6a-c} may explain the anomaly, the evidence in favor of this view is not very substantial at the present time.¹⁹

Thus far the solvent has been considered pretty much as a continuum. The discrete structure of the solvent may well be of great importance in a complete theory of the salt effect. In practically all of the studies of salting out or in, the solvent employed has been water. Only a few investigations have been made in solvent pairs such as water-alcohol mixtures or in non-aqueous solvents.

The structure of water, the effect of ions upon the structure of water and also a detailed consideration of the energy of hydration of ionic species has been given by Bernal and Fowler.²² Bernal and Fowler in evaluating the energy of hydration of ions include as the first term the Born expression for the energy of hydration considering the medium as a continuum. The second term includes various interactions occurring within the hydration sphere such as ion-dipole, ion-induced dipole, dipole-dipole interactions and it also includes the repulsive

energy. The third term is the energy of the water dipoles disoriented. Unfortunately, even in this simple case all of the contributions to the second term cannot be evaluated. The second term, $nP_{\text{eff}}(r)$, can be approximated by $p_z P$, where p_z is a constant for a given charge type and where P is equal to $\mu\epsilon z/(r + r_w)^2$ for most positive ions. Assuming a reasonable division of the energy of hydration between the positive and negative ions of a salt, very satisfactory agreement with experimental energies may be arrived at.

May this extended treatment also be applied to the salt effect phenomenon? When the solute molecules are non-polar the attractive forces which might bring them into the solvation sphere are much less than for the water dipoles. Furthermore, the water dipoles are much more numerous (10^2 or greater usually). When the solute molecules are polar, especially if they are as polar or more polar than the water dipoles, and if the polar solute is fairly soluble in water, an appreciable number of solvation spheres may be modified by the presence of solute molecules. However, the ability of the solute molecules to displace water molecules in the solvation sphere would probably also be considerably influenced by the size and shape of the solute dipoles. Both polar and non-polar solutes will cause structure breaking in the body of the solution. The structure breaking of the non-polar solute is mostly a volume effect while the polar solute would have both a volume and dipole effect on the water structure. The salt effect does seem amenable to similar treatment to that used by Bernal and Fowler, although the problem would be more difficult.

Frank and Evans²³ also have introduced an interesting concept termed "iceberg formation." While such a concept is closely related to the more familiar phenomena of dielectric saturation, Frank and Evans propose that "icebergs" may also form around non-polar molecules, the non-polar portions of polar molecules and around ions. In a system of solvent, electrolyte and solute molecules the electrolyte and solute molecules thus may be competitive iceberg formers. The exact orientation of the water dipoles around the ions and the solute molecules is assumed to be also of importance. These ideas are somewhat analogous to the earlier suggestions of Kruyt and Robinson.²⁴ If these concepts are valid then the body of the solution outside the solvation spheres especially in the region of solute molecules must also be considered in detail.

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