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## The Solubilities of Hydrocarbons in Concentrated Salt Solutions and Their Correlation with the Clathrate Water Theory, Ion–Ion Associations, and Structures of Polymers\*

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### SUMMARY

The solubility of benzene, benzoic acid, and hexanol in aqueous solutions containing various salts or dipolar molecules was examined. Both the anion and cation of guanidinium or other salts determine the salting-in properties. The solubility of benzene was found to be a linear function of the molar concentration of salt,  $C_S$ , to the saturation point of the salt; i.e., the solubility constant  $k_S$  remains the same. In other words, the interaction of benzene with hydrated ions is the same at extremely low ionic strengths as at high ionic strengths. This result agrees with the proposal that the B region (or negatively hydrated region) of ions consists of a single monomolecular layer of water molecules. Moreover, since in such concentrated salt solutions all water molecules are hydrated, the disappearance of any proposed clathrate structure in concentrated salt solutions should alter the value of  $k_S$ . Consequently, the constant  $k_S$  values

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\*Part of this work was done at the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Ill.

show that water clathrate structures do not surround hydrocarbons. The solubility studies in concentrated salt solutions at 25 and 60°C also show that clathrate water structures cannot exist around hydrocarbons, since in all cases the solubility of the hydrocarbon increases with an increase in temperature. The association of  $\text{NH}_4^+$  and  $\text{OH}^-$  ions to form the dipolar  $\text{NH}_4^{\delta+}\text{OH}^{\delta-}$  molecule reduces the amount of electrostatic charge per surface area, and hence the solubility of benzene in  $\text{NH}_4\text{OH}$  solutions is increased. In concentrated solutions of  $\text{NH}_4\text{Cl}$  (or  $\text{HCl}$ ) there appears to be a similar electrostatic interaction between the  $\text{NH}_4^+$  and  $\text{Cl}^-$  (or  $\text{H}^+$  and  $\text{Cl}^-$ ) ions which reduce the charge per unit surface area on these ions. From these results it is concluded that solubility studies of benzene can be used to detect ion association reactions. Thiourea salts-in more than urea because of less charge per unit surface area, indicating that urea as well as thiourea exists as a zwitterion. Positive hydration is shown to exist for fluoride ions. These results are applied to the properties of proteins and other polymers.

## INTRODUCTION

The properties of polymers are determined primarily by the interaction of their hydrophobic, polar, or ionic subunits with the solvent system. Therefore, in order to understand the solution properties of polymers more thoroughly, the solubility of benzene, benzoic acid, and hexanol in various salt solutions was determined. As will be seen, such studies yield information not only with regard to hydrophobic groups on polymers but also with regard to electrostatically charged groups such as amino, guanidinium, and carboxylate groups.

As shown previously [1], the addition of a salt to water may increase or decrease the solubility of benzene. The solubility increases when the effective dielectric constant of the ion is greater than that of water and decreases when it is less. The effective dielectric constant of an ion depends on its charge per unit surface area and the influence this charge has on associated water. The domain of this loosely associated water has a thickness of one water molecule [1]. Frank and Wen [2] have termed such domains B regions, whereas Samoilov [3] has designated them as regions of negatively hydrated water. Benzene can penetrate these domains, because as will be seen in this paper benzene is soluble in concentrated salt solutions. Moreover, these results will add further evidence presented previously [4] that a clathrate water structure does not surround benzene or other hydrocarbons in aqueous mediums.

## EXPERIMENTAL

The solubility of benzene in various salt solutions was obtained by placing approximately 40 ml of salt solution and 5 ml of benzene in a 50-ml glass-stoppered volumetric flask. The two-phase system was shaken for about 30 min on a mechanical shaker and then immersed in a constant-temperature bath ( $25.00 \pm 0.03^\circ\text{C}$ ) for about 20 hr. Twenty-five milliliters of the salt solution saturated with benzene was removed with a pipet to which a metal syringe needle had been fitted to the tip with Teflon tubing. To prevent benzene from entering the needle, air pressure was applied on the pipette during immersion. Immediately after removal, the solution was pipetted into 60 ml of isooctane which had been placed in a 125-ml separatory funnel. After moderate shaking, the salt solution was separated from the isooctane and two similar extractions with isooctane were done.

All the isooctane was then combined and the volume made up to 200 ml. The concentration of benzene was obtained using a Cary\* Model 14 spectrophotometer. An extinction coefficient of  $E_1 \text{ cm}^{1\%} = 27.0$  at  $\lambda = 255 \text{ m}\mu$  was used to determine the concentration of benzene in the isooctane. Further extractions with isooctane showed no increase in the amount of benzene. The solubility of benzene in solvents at  $60^\circ\text{C}$  was done in a similar manner, the flask being shaken after attaining a temperature of  $60^\circ\text{C}$ .

An alternative method was also tried but was not used to obtain the reported results. This method gave the same results or, in some cases, slightly less benzene per unit volume of salt. The method consisted of centrifuging the two-phase system (salt solution and benzene) in a separatory funnel using an International Centrifuge. A fraction of the salt solution was isolated by removing the separatory funnel from the centrifuge and opening the stopcock. Isooctane was used as before to extract the benzene.

The determination of the solubility of hexanol and benzoic acid in various solutions was carried out in the same manner as that for benzene except  $\text{CCl}_4$  was substituted for isooctane for extraction of hexanol. The extinction coefficients were  $E_1 \text{ cm}^{1\%} = 1.585$  at  $\lambda = 1407 \text{ m}\mu$  for hexanol in  $\text{CCl}_4$  and  $E_1 \text{ cm}^{1\%} = 1025$  at  $\lambda = 230 \text{ m}\mu$  for benzoic acid in isooctane. The solubility of hexanol in pure water at  $25^\circ\text{C}$  was found to be 0.638 g/100 ml of water and that of benzoic acid 1.632 g/100 ml of water.

The purest grade of chemical was used at all times.

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\*Mention of trade names or products does not constitute endorsement over those not named.

## RESULTS AND DISCUSSION

## Comparison of Our Solubility Results with Others

In all the studies, the solubility of benzene in the solvent ( $S_3$ ) was divided by its solubility in pure water ( $S_3^0$ ) to give the relationship  $f_3 = (S_3^0/S_3)f_3^0 = S_3^0/S_3$ , since  $f_3^0 = 1 =$  the activity coefficient of benzene in pure water [5, 6]. The activity coefficient of benzene in the salt solution is  $f_3$ . From the Setschenow equation, the characteristic constant  $k_s$  was obtained from the relationship

$$k_s = \log f_3/C_s = (1/C_s) \log(S_3^0/S_3) \quad (1)$$

where  $C_s$  is the molarity of the salt [1, 5, 6].

To determine whether our results are comparable to others, the absolute solubility of benzene in distilled water at 25°C was obtained as described in the experimental. We obtained a value of 1.76 g/liter, which is in agreement with the values obtained by McDevit and Long [5] (1.77 g/liter at 25°C), assuming that their reported units of moles per liter is a typographical error. Venable and Nauman [7] obtained a similar value of 1.79 g/liter at 30°C. The same value (1.79) was obtained by Bohon and Claussen [8] at 25°C. Converting mole-fraction values to grams per liter, Arnold et al. [9] and Franks et al. [10] obtained values between 1.71 and 1.74 g/liter, which are slightly less than our value of 1.76. It is concluded that our results are comparable to those obtained by others.

Further comparison of our results with others is made in Table 1, where values of  $S_3/S_3^0$  and  $k_3$  for various solvents having salt concentrations of 4 moles/liter are listed. Good agreement is obtained for aqueous salt solutions of NaCl, KCl, and LiCl, even though the values of  $k_s$  were obtained at high salt concentrations. Our value of  $k_s = 0.186$  for NaCl solutions is intermediate between the values of McDevit and Long [5] and Saylor et al. [6]. The value of 0.186 is in good agreement with the theoretical value of  $k_s = 0.183$  reported for NaCl solutions in the previous paper [1]. Our observed values of  $k_s$  for HCl and  $NH_4Cl$  are lower than those reported by McDevit and Long [5] and Saylor et al. [6]. These discrepancies will be discussed below.

## Solubility of Benzene in Concentrated Salt Solutions

As pointed out by Long and McDevit [11], the activity coefficient of a nonelectrolyte may be expressed as a power series of molar con-

**Table 1.** Ratio of  $(S_3/S_3^0)$  as Obtained from Solubility ( $S_3$ ) of Benzene in Various 4 M Salt Solutions to That  $(S_3^0)$  in Water

Aqueous solvent	$S_3/S_3^0$ ( $C_S = 4$ M)	$k_S$	$k_S^a$	Aqueous solvent	$S_3/S_3^0$ ( $C_S = 4$ M)	$k_S$
GHC1	1.54	-0.047	—	GSCN	4.4	-0.150
HCl	0.81	0.023	0.048 (0.041)	DMSO	3.0	-0.120
NH <sub>4</sub> Cl	0.45	0.087	0.103	Thiourea	2.0 <sup>b</sup>	-0.077
LiCl	0.28	0.138	0.141 (0.136)	NH <sub>4</sub> OH	1.7	-0.059
KCl	0.22	0.164	0.166 (0.163)	GHC1	1.5	-0.047
NH <sub>4</sub> F	0.22	0.164	—	Urea	1.3	-0.032
NaCl	0.18	0.186	0.195 (0.178)	1/2 G <sub>2</sub> CO <sub>3</sub>	0.59	0.056
				1/2 G <sub>2</sub> SO <sub>4</sub>	0.57	0.061

<sup>a</sup>These values of  $k_S$  were obtained from the data of McDevit and Long [5]. Values in parentheses were obtained from Saylor et al. [6] corrected from molality to molarity.

<sup>b</sup>Obtained by extrapolating  $\log(S_3^0/S_3)$  to a 4 M thiourea solution.

centration of salt ( $C_S$ ) and nonelectrolyte ( $C_3$ ) for aqueous salt solutions by the empirical equation

$$\log f_3 = \sum_{n=1}^{\infty} k_S C_S^n + \sum_{m=1}^{\infty} k_3 C_3^m + \sum_{\substack{n=1 \\ m=1}}^{\infty} k_{nm} C_S^n C_3^m \quad (2)$$

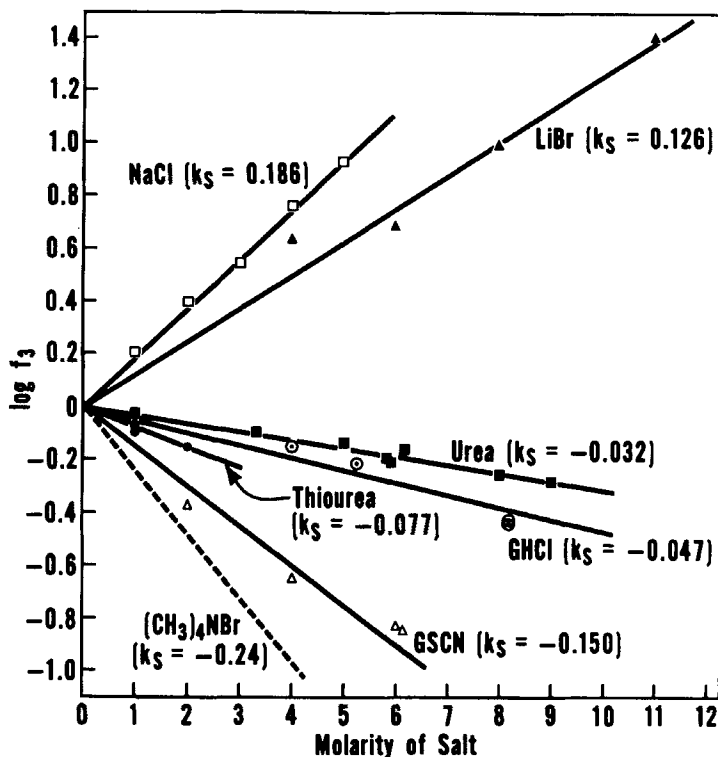
for all species of salts present. If the nonlinear terms are insignificant, then Eq. (2) becomes equal to

$$\log f_3 = \log (S_3^0/S_3) = k_S C_S + k_3 C_3 \quad (3)$$

But  $k_3 C_3$  is usually negligible, since the solubility of the nonelectrolyte is usually low [6]. Consequently, Eq. (3) can be approximated by Eq. (1).

It is generally assumed that at high salt concentrations the linear Eqs. (1) and (3) are incorrect and that the empirical Eq. (2) must be used [11]. To investigate whether  $C_3^2$  or higher terms must be employed, values of  $S_3^0/S_3 = f_3$  were obtained for concentrated salt solutions. A plot of  $\log f_3$  versus its molar concentration is given in Fig. 1. Within experimental error, linear plots are obtained for the solubility of benzene in aqueous solutions containing NaCl, LiBr, urea, and possibly guanidinium chloride (GHC1), and thiourea up to the saturation point of the salts. The thiourea is only soluble up to concentrations of about 2 M and hence it is difficult to tell whether concentration effects occur in this solvent. The six points obtained for the GHC1 indicate that a linear function (or at least an approximate linear function) is obtained. The guanidinium thiocyanate (GSCN) solutions show a concave upward curvature. In 6 M GSCN, the concentration of benzene is increased by about six times that in water, and consequently the concave upward curvature of the points may be due to the  $k_3 C_3$  term of Eq. (3). As shown in Table 1, the values of  $k_S$  obtained in concentrated solutions of NaCl, KCl, and LiCl also agree with those obtained for dilute solutions. Consequently, the nonlinear terms of Eq. (2) are absent and, in addition, strong interactions (sharing of electrons) between ions does not occur. Rather, the results at high ionic strength are linear with respect to  $C_S$ , just as those at low salt concentration.

The results therefore are in agreement with the theory that the B regions determine the solubility of benzene and not the stability of a "clathrate" structure. That is, as the concentration of salt increases, the amount of water that is not hydrated to the ions decreases, and, as shown by previous calculations [12], it finally disappears at about 4 M salt. Hence any clathrate structure would also disappear, and one would expect a change in the value of  $k_S$ . In other words, using the hydrated radii of Nightengale [13], the calculations show that 4.8 moles of hydrated NaCl and 4.3 moles of hydrated LiBr occupy a volume



**Fig. 1.** Logarithm of the activity coefficient of benzene in various salt solutions [ $\log f_3 = \log (s_3^0/S_3)$ ] is plotted versus the molar concentration of salt. The salt solutions and the corresponding values of  $k_s$  are indicated in the figure.

of 1 liter. For NaCl the greatest concentration used to obtain the solubility of benzene was 5.0 M. For LiBr it was 11.0 M. Hence the linearity in the  $\log f_3$  versus  $C_s$  plots goes up to or past the volume occupied by the hydrated ions. Clathrate structures surrounding the benzene molecule could not possibly exist under such conditions.

In considering the structure of an aqueous solution containing high concentrations of salt, one must bear in mind that the positions of the water molecules surrounding an ion are not static. According to Samoilov [3], those water molecules hydrated to an ion are not permanently fixed but are exchangeable with the medium. Moreover, Brownian movement of the ions enables the formation of sporadic areas where the concentration of salt is lower or greater than that



of the total medium. Ion pairs or groups of pairs (small crystallites) may also form, but the formation of such pairs or aggregates of pairs cannot appreciably involve the sharing of electrons, since this would reduce the electrostatic charge per unit surface area. A reduction in the electrostatic charge of the ion will also change the value of the effective dielectric constant ( $D_{\pm}$ ) of the ion's atmosphere (its B region) [1]. This change is extremely important, since the value of  $D_{\pm}$  governs the solubility of benzene. Such a reduction would thus increase the solubility of benzene, and hence the  $\log f_3$  versus  $C_S$  relationship would no longer be linear. The concentrated aqueous salt solutions, therefore, contain ions at different degrees of hydration with the possibility of ion pairs (anion plus cation). However, just as in salt crystals, these ion pairs or their aggregates do not involve appreciable sharing of electrons.

#### Association of Ions ( $\text{NH}_4\text{OH}$ , $\text{NH}_4\text{Cl}$ , $\text{HCl}$ ) as Predicted from Solubility of Benzene in Solvents

In Table 1 it is seen that 4 M ammonium hydroxide salts-in benzene even more effectively than 4 M guanidinium chloride. But the hydroxide ion has a greater ability to salt-out benzene than the chloride ion [1, 5]. Moreover, the ammonium ion has only a slight or no tendency to salt-in benzene, and its effectiveness is less than that of the cesium ion [1, 5]. Hence the  $\text{NH}_4\text{OH}$ , if it were completely ionized, should salt-out benzene instead of salting it in. Furthermore, if normal concentration effects are present, as in the above case of GSCN, the solubility of benzene should decrease, not increase, with an increase in the concentration of  $\text{NH}_4\text{OH}$ . Moreover, such effects were absent for ions which salted-out benzene. Hence the increase in the solubility of benzene (from salting out to salting in) cannot be due to normal concentration effects. The results on  $\text{NH}_4\text{OH}$  must be due to its low dissociation constant in water ( $K = 1.79 \times 10^{-5}$  at  $25^\circ\text{C}$ ) [14] and a consequent decrease in the charge per unit surface area of the dipolar molecule. The  $\text{NH}_4\text{OH}$  molecule must thus exist in water as a dipolar molecule with only a partial separation of the electrostatic charges. In other words, previous calculations [1] show that an increase in the solubility of benzene must be the result of an increase in the value of  $D_{\pm}$ . Furthermore, the value of  $D_{\pm}$  is a function of the charge per unit surface area on an ion. Hence the association of  $\text{NH}_4^+$  and  $\text{OH}^-$  ions results in a reduction of the electrostatic charge on the ions.

The positive values of  $k_S$  for  $\text{NH}_4\text{F}$  and  $\text{NH}_4\text{Cl}$  given in Table 1 show that these salts are more dissociated than  $\text{NH}_4\text{OH}$  in water. However, as seen in Table 1, the value of  $k_S$  obtained for 4 M  $\text{NH}_4\text{Cl}$  at neutral pH is 0.087, while that obtained by McDevit and Long [3] at much lower concentrations is 0.103. This increase in the solubility of benzene with an increase in the concentration of  $\text{NH}_4\text{Cl}$

must be due to the association of  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions at high concentrations just as in the case of  $\text{NH}_4\text{OH}$ . Such an association may even have occurred at the low concentrations used by McDevit and Long [5]. The results of Scatchard et al. [15, 16] also indicate that  $\text{NH}_4\text{Cl}$  associates in aqueous solutions.

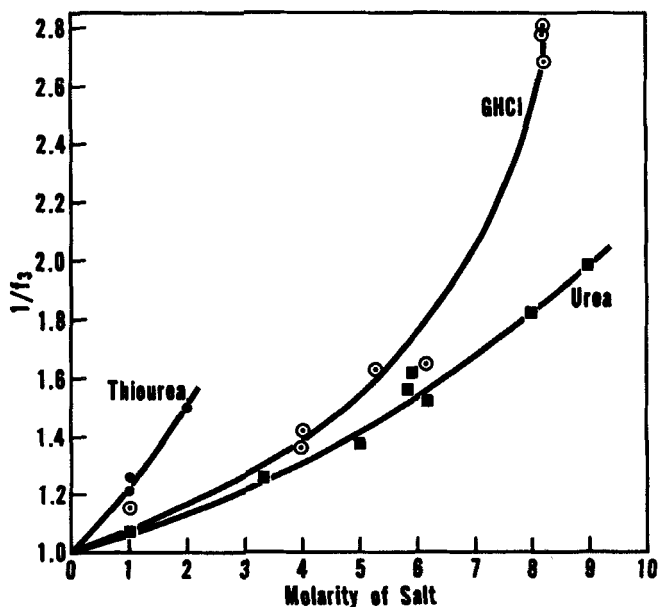
The general trend in such an association of  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions can be obtained by examining the change in the calculated dielectric decrement  $\delta_+$  of the ammonium ion. According to Fig. 3 in the previous paper [1], the theoretical value of  $\delta_+$  for the  $\text{NH}_4^+$  ion should be approximately equal to that of the  $\text{Rb}^+$  ion ( $\delta_+ = 1.2$ ), since both have the same crystal radius ( $r_x = 1.48 \text{ \AA}$ ). However, at the concentration used by McDevit and Long [5], the lower value of  $\delta_+ = -1.3$  is obtained. Using our value of  $k_s$  obtained at a concentration of 4 M, the value of the dielectric decrement is further decreased to  $\delta_+ = -3.7$ . This continual decrease of  $\delta_+$  with an increase in salt concentration signifies that the ammonium and chloride ions are associating together in water with a consequent reduction in charge per unit surface area. Some association most likely occurs for the other salts listed in Table 1. But except for  $\text{HCl}$ , the agreement of  $k_s$  obtained in these concentrated solutions with that obtained at much lower salt concentrations shows that such associations do not result in the reduction of the electrostatic charge of the ions.

Examination of Table 1 shows that the ions  $\text{H}^+$  and  $\text{Cl}^-$  must also be associating together in some manner to reduce the electrostatic charge per unit surface area, since the solubility of benzene in 4 M  $\text{HCl}$  ( $k_s = 0.023$ ) is greater than that at lower concentrations of  $\text{HCl}$  ( $k_s = 0.048$ ). Values of  $k_s$  may therefore be valuable for obtaining information concerning the association of ions in solution.

### Salting-In and Salting-Out Properties of Various Ions and Dipolar Molecules

The salting-out sequence  $\text{Na}^+ > \text{K}^+ > \text{Li}^+ > \text{NH}_4^+ > \text{H}^+$  > guanidinium can be obtained from Table 1 if the  $\text{Cl}^-$  ion is used as the common anion. The reasons for this sequence have been explained previously [1]. In summary, the  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{H}^+$  ions contain a tightly bound, monomolecular hydration shell (A region or positive hydration) plus an outside, loosely bound, monomolecular hydration shell (B region or negative hydration). The salting-out sequence  $\text{Na}^+ > \text{Li}^+ > \text{H}^+$  is obtained for benzene because this sequence is determined entirely by the effective dielectric constant of the B region, the B region of the hydrated  $\text{H}^+$  ion having the largest value of  $D_+$ . The B region of  $\text{Na}^+$  is extremely small or does not exist. Consequently,  $D_+$  is very near zero for the hydrated  $\text{Na}^+$  ion.

A similar comparison can be obtained for the salting-in ability of urea and thiourea (Fig. 2 and Table 1). Thiourea salts-in benzene more than urea. Because the oxygen atom is more electronegative



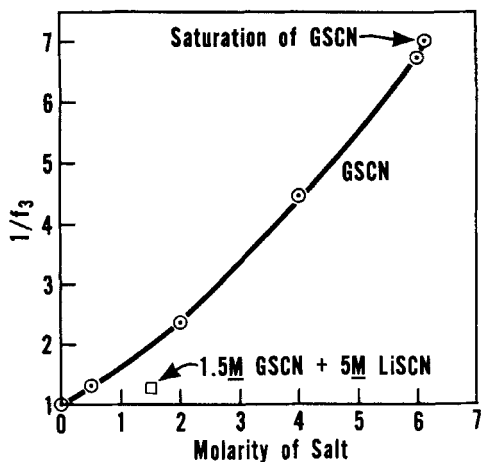
**Fig. 2.** Plot of  $1/f_3 = S_3/S_3^0$  versus the molar concentration of thiourea (●), guanidinium chloride (○), or urea (■). Here  $S_3$  = solubility of benzene in salt solution and  $S_3^0$  = its solubility in water.

than the sulfur atom, the separation of charges on the urea molecule will most likely be greater than that on the thiourea molecule. Hence the thiourea molecule has less charge per unit surface area. Since this reduction in charge per unit area results in an apparent increase in the dielectric constant, the urea molecule must exist as a zwitterion as proposed by Colacicco [17] and as deduced from our study [18] of the effect of salts on the dispersing power and solubility of urea. In other words, the charge per unit area on the urea molecule must be greater than that for the guanidinium ion. Otherwise, a reduction in charge density in going from urea to thiourea would result in a decrease rather than an increase in the salting in of benzene. The dipolar urea molecule must thus have a charge per surface area greater than that at the "maximum" of  $1.5 \times 10^{-2}$  esu/Å discussed previously [1].

In dimethyl sulfoxide (DMSO) two factors may contribute to its ability to solubilize hydrocarbons. First, there is a separation of charge in the  $\text{>S=O}$  bond. Second, the methyl groups may aid by the formation of hydrophobic bonds just as in the case of the  $(\text{CH}_3)_4\text{N}^+$

ion discussed previously [1]. If such is the case, then diethyl sulfoxide should be a better solvent for hydrocarbons than DMSO.

The best agent examined for dispersing hydrophobic groups was aqueous guanidinium thiocyanate (GSCN). Results on this solvent are given in Figs. 1 and 3 and Table 1. The increase in solubility of benzene in aqueous GSCN as compared to that in aqueous  $\text{GHCl}$  is due to the reduction in charge per unit surface area on the anion. In this respect, guanidinium cyanate (GOCN) may be a better dispersing agent than GSCN, since the negative charge may be distributed more evenly on the  $\text{OCN}^-$  ion than on the  $\text{SCN}^-$  ion.



**Fig. 3.** Relative solubility of benzene in aqueous GSCN solutions ( $S_3/S_3^0 = 1/f_3$ ) versus the molarity of salt. The points (⊙) represent GSCN and (□) represents the mixture of GSCN and LiSCN. The reduction in the solubility of benzene in the mixed salt solution is due to the lower value of  $D_+$  for the  $\text{Li}^+$  ion as compared to that of the  $\text{G}^+$  ion.

Results on the dispersion of high-amylose corn starch granules [12] show that the solubility of these granules goes through a maximum at 6 M LiBr and 6 M LiSCN. This maximum is absent when salt solutions such as aqueous  $\text{GHCl}$  or GSCN are employed. In other words, the maximum occurs only with salts which have positive hydration (A regions). This maximum is due to the disappearance of the B regions on the  $\text{Br}^-$  and  $\text{SCN}^-$  ions [12]. No such maximum is obtained for the solubility of benzene in aqueous LiBr solutions (Figs. 1 and 4). The absence of such a maximum or minimum may be due to the fact that the solubility of benzene in these solvents is already decreasing, and any further decrease is not noticeable above experimental error.

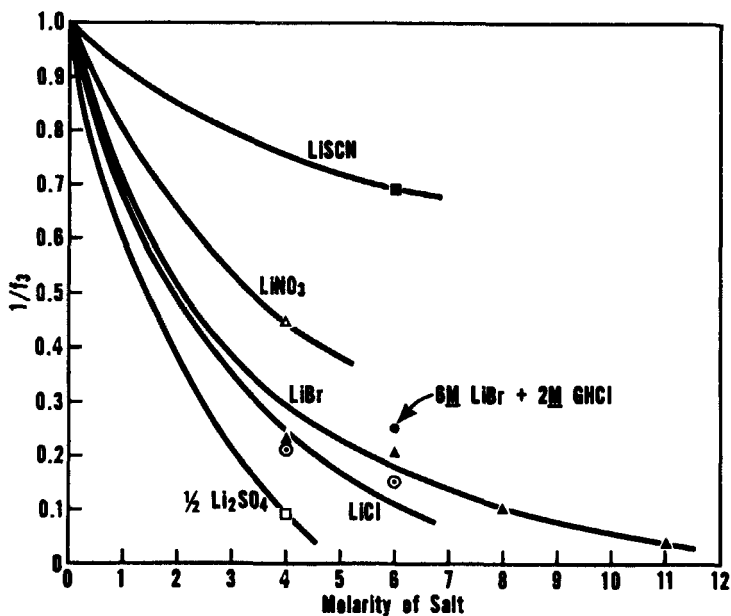


Fig. 4. Relative solubility of benzene in solutions containing lithium salts ( $S_3/S_3^0 = 1/f_3$ ) versus the molarity of salt.

For mixed salts (GHCl + LiBr) addition of a salt (GHCl) which has a more effective B region than that of LiBr increases the solubility of benzene (Fig. 4). For the GSCN + LiSCN mixture, addition of a salt (LiSCN) which has a less effective B region decreases the solubility of benzene (Fig. 3). These results on mixed solvents for solubilizing benzene are in agreement with those [12] for solubilizing starch. Consequently, the results show that each ion acts independently and that the net value of  $D_{\pm}$  is the sum of the values of  $D_{\pm}$  for all the ions present.

In all the above examples, it is seen that the solvent properties of a salt or dipolar molecule can readily be explained on the basis of charge density on the surface of the ion or molecule. This result substantiates the previously proposed theory [1].

#### Positive Hydration of Anions

Previous results such as those reported by McDevit and Long [5] are not conclusive with respect to confirming or disputing the presence of positive hydration (A regions) on anions. Therefore, the solubility of benzene and benzoic acid in various salts was studied

to determine if such hydration exists around anions. By using a common cation ( $K^+$ ), the effect of the anion can be deduced. That is, the  $K^+$  ions should behave the same toward either the benzene or benzoic acid no matter what its counterion ( $F^-$ ,  $Cl^-$ , or  $Br^-$ ), since A regions are not present in the  $K^+$  ion [1]. The results of this study are reported in Table 2.

If the fluoride ion is surrounded by positively hydrated water molecules (A regions), the polarized water molecules in these regions should attract the un-ionized as well as the ionized hydrogen atom of benzoic acid and, consequently, increase the solubility of the acid. In other words, by applying the "localized hydrolysis" theory of Harned and Owen [19] to the previous concepts [1, 20], it is seen that positively hydrated water (A regions) surrounding cations repel acids, whereas that surrounding anions should attract acids because of a reversion of the position of the water dipole. The results of Table 2 are made more explicit in Table 3. Here the ratio of the solubility of benzene (or benzoic acid) in one salt solution divided by that in another is given. The solubility of benzene in 4 M KBr divided by that in 4 M KCl is the same as that for benzoic acid. In both of these salts there are no A regions. Consequently, there should be no difference in their ratios. Moreover, this constant ratio shows that the interaction of these ions with the benzoate and  $H^+$  ions of any dissociated benzoic acid molecules is absent or minor. That is, any interaction of the B region with the

Table 2. Solubility Ratio ( $S_3/S_3^0$ ) for Benzene and Benzoic Acid in Various Solvents<sup>a</sup>

Aqueous solvent	Benzene		Benzoic acid	
	$S_3/S_3^0$ ( $C_2 = 4$ M)	$k_s$	$S_3/S_3^0$ ( $C_2 = 4$ M)	$k_s$
KI	0.43	0.092	—	—
KBr	0.29	0.134	0.37	0.108
K acetate	0.25	0.151	—	—
KCl	0.22	0.164	0.29	0.135
KOH	0.13	0.222	—	—
KF	0.10	0.250	0.19	0.180

<sup>a</sup>Solubility of benzene in pure water at 25°C was found to be 1.76 g/liter and that of benzoic acid was 16.3 g/liter.

dissociated or undissociated carboxylic acid group has no effect on the solubility of the benzoic acid, since the same ratio is obtained for both benzene and benzoic acid. This ratio (KBr/KCl) can thus be considered as a control.

Consider now the solubility of benzoic acid in 4 M KCl and in 4 M KF. If A regions are absent, then the ratio KCl/KF would be the same, since these B regions appear to have no effect on the carboxylic acid group or its dissociation products. Thus KCl/KF should be 2.27 instead of 1.525 for benzoic acid. The lower value of 1.525 means that the fluoride ion has enhanced the solubility of benzoic acid. This effect is not as great as the repulsion observed for the  $\text{Li}^+$  and  $\text{Na}^+$  ions because of the larger radius of the fluoride ion. Nevertheless, the results in Table 3 show definitely that the fluoride ion produces positively hydrated water molecules. As seen in Table 2, the values of  $S_3/S_3^0$  for KOH is very close to that for KF. Hence positively hydrated water may also be associated with the hydroxide ion.

Table 3. Comparison of Solubility Properties of Anions

Solvents	Values of $S_1/S_2^a$	
	Benzene	Benzoic acid
4 M KBr/4 M KCl	1.280	1.275
4 M KCl/4 M KF	2.27	1.525

<sup>a</sup>Values of  $S_1/S_2$  were obtained from the ratios ( $S/S^0$ ) reported in Table 2:  $(S_1/S_1^0)/(S_2/S_2^0) = S_1/S_2$ .

### Solubility of Benzene in Salt Solutions at High Temperatures

To further examine whether clathrate water structures exist around hydrocarbons, the solubility of benzene in 6 M GSCN, 6 M LiCl, and water at 25 and 60°C was determined, and the results are given in Table 4. The ratio  $S_3/S_3^0$  shows that benzene is about 6.2 times more soluble in 6 M GSCN than in water at both 25 and 60°C. Moreover, the ratio  $S_3/S_3^0$  shows that the solubility of benzene in 6 M LiCl as compared to that in water is approximately one sixth that of water. Again this is true at both temperatures. But from many studies it is known that both the  $\text{G}^+$  and  $\text{SCN}^-$  ions destroy hydrogen bonds. Yet if the clathrate theory is applied to the above results, one must conclude the opposite: 6 M GSCN stabilizes, whereas 6 M

Table 4. Solubility ( $S_3$ ) of Benzene and Hexanol in Various Solvents

Solute	Aqueous solvent	$S_3$ of solute (g/liter of solution)		$S_3/S_3^0$		$S_3$ at 60°C
		25°C	60°C	25°C	60°C	$S_3$ at 25°C
Benzene	6 M GSCN	10.61	14.22	6.2	6.3	1.34
Benzene	6 M LiCl	0.27	0.38	0.16	0.17	1.40
Benzene	Water	1.71 <sup>a</sup>	2.26 <sup>a</sup>	1.00	1.00	1.32
Hexanol	6 M GSCN	34.1	—	5.4	—	—
Hexanol	6 M LiCl	1.0	—	0.16	—	—
Hexanol	Water	6.4	—	1.00	—	—

<sup>a</sup>These values were obtained from Table 1 of Franks et al. [10].

LiCl destroys clathrates. That is, the presence of a clathrate water structure is supposed to increase the solubility of a hydrocarbon [4]. Consequently, the solubility results at 25°C alone show that clathrates do not surround hydrocarbons.

The increase in temperature should increase the ability of the solvent to destroy clathrate structures. Nevertheless, the solubility of benzene increases with an increase in temperature in all three solvents. If clathrate structures are being destroyed, the solubilities should decrease, not increase, with temperature. Again this contradicts the clathrate theory.

The stable  $S_3/S_3^0$  ratio indicates that the effective dielectric constants of the ions do not change with temperature. Consequently, the increases in the solubility of benzene with an increase in temperature for pure water and for the GSCN and LiCl salt solutions must be due to a destruction of water clusters and not to a change in the values of  $D_{\pm}$ . That is, water clusters are destroyed because of an increase in the thermal motion of the water molecules [4]. The resulting increase in the amount of unbonded water molecules produces an increase in the solubility of benzene.

The solubility of hexanol in good and poor solvents was also examined to determine whether the solubility changes are the same for straight-chain hydrocarbons. The results for the six-carbon alcohol are essentially the same as those for the six-carbon benzene ring. Hence the results on benzene are not due to some peculiarity of the benzene ring. Consequently, it is concluded that clathrate water structures do not exist around hydrocarbons.



## APPLICATION OF RESULTS TO POLYMERS

The results given above on (1) the solubility of benzene and hexanol in the salt solutions and (2) the constant  $k_s$  values obtained at high and low values of salt concentration show that clathrate water structures cannot exist around hydrocarbons. Hence the hydrophobic groups of polymers do not have such clathrate structures either.

The solubility results on the carbonate ion show that this ion would salt-out any nearby hydrophobic groups. The same should be true for the carboxylate ion of proteins. Thus, in addition to electrostatic repulsion forces, the expansion of many proteins during the neutralization of their carboxylate groups ( $R-CO_2^- + H^+ \rightarrow RCO_2H$ ) may be due to the salting in of hydrophobic groups. Moreover, the presence of guanidinium groups on the protein would aid this solubilization of hydrophobic groups, because, as seen above, the guanidinium ion is extremely effective in solubilizing hydrocarbons. The solubility studies also show which ions will salt-in or salt-out hydrophobic groups on proteins.

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