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### The Interaction of Polyvinylpyrrolidone with Aromatic Compounds in Aqueous Solution. Part I. Thermodynamics of the Binding Equilibria and Interaction Forces<sup>1</sup>

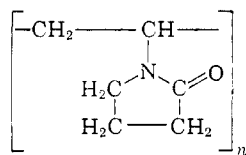
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Polyvinylpyrrolidone (PVP) in aqueous solution displays a strong binding affinity toward dissolved aromatic compounds; the binding equilibria for such compounds ("cosolutes") both non-ionic (nitrobenzene, phenol, benzoic acid, etc.) and anionic (sodium benzoate, sodium naphthoate, etc.), have been studied over the temperature range 3 to 60° by the equilibrium dialysis method. The binding constants at 30°, and hence the free energies of binding, increase as the size of the aromatic system is increased; an increase in the number of polar groups (as in the series: phenol, resorcinol, phloroglucinol) also leads to an increase in the binding constant. The thermodynamic functions obtained from the temperature dependence of the binding constants show there to be entropy *gains* during the binding process in almost all the systems; the greatest gains (*ca.* 18 e.u. for benzene) are observed for the least soluble and least polar compounds, the smallest (*ca.* 0 e.u. for sodium benzoate) for the highly soluble and highly polar anions. The entropy gains are taken as evidence for the breakdown of so-called "iceberg" water-structure in the vicinity of the solute molecules in the course of the binding process. From a consideration of the observed entropy and enthalpy changes and from available thermodynamic data on relevant systems, it appears that the binding process involves two main effects: (1) an entropy gain due to the disordering of the "icebergs" (*i.e.*, the formation of a so-called "hydrophobic bond") and (2) an exothermic interaction between the PVP and the aromatic  $\pi$ -electron system of the cosolute molecule. Infrared spectra of dry PVP films containing varying concentrations of aromatic compounds also were taken. There are strong indications from these of the presence of polymer-cosolute hydrogen-bonding and also significant shifts in the cosolute aromatic C-H out-of-plane deformation bands in the 700-800  $\text{cm}^{-1}$  region.

#### Introduction

The interaction of polyvinylpyrrolidone (PVP) in aqueous solution with various cosolutes, such



Polyvinylpyrrolidone

as the triiodide ion,<sup>3</sup> azo dyes<sup>4</sup> and sodium alkyl

(1) This work was supported by the National Institutes of Health under Contract A2253(C1); it was presented in part before the Division of Polymer Chemistry at the 138th National Meeting of the American Chemical Society, New York City, September, 1960.

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(3) S. Barkin, H. P. Frank and F. R. Eirich, *Ric. Scient.*, "Simposio Internazionale di Chimica" Macromolecolare, **25A**, 844 (1955).

(4) H. P. Frank, S. Barkin and F. R. Eirich, *J. Phys. Chem.*, **61**, 1375 (1957).

sulfates,<sup>5</sup> has been studied intensively in recent years, but the phenomenon of the binding of cosolutes of such very diverse chemical nature by the polymer has not yet been explained satisfactorily. It is well-known that such cosolute binding by macromolecules is not limited to the systems mentioned above; thus proteins display binding capacities which are very similar in strength and nature to those observed for PVP,<sup>6,7</sup> and both polyvinyl acetate and polyvinyl alcohol display analogous effects.<sup>8</sup> It is also apparent that this type of interaction is very often one which depends little on the specific chemical characteristics of the binding partners as long as certain general conditions are fulfilled. Thus quite frequently there appears to be an interaction between the hydrocarbon segments of the polymer molecule and similar por-

(5) S. Barkin, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1957.

(6) I. Klotz and J. M. Urquhart, *J. Am. Chem. Soc.*, **71**, 1597 (1949).

(7) F. Karush and M. Sonnenberg, *ibid.*, **71**, 1369 (1949).

(8) S. Saito, *Koll. Z.*, **143**, 66 (1955); **154**, 19 (1957).

tions of the low molecular weight cosolute; Kauzmann<sup>9</sup> recently has pointed out the significance of such interactions in aqueous solution and has applied this so-called "hydrophobic bond" concept to aqueous protein solutions and to the binding of cosolutes by proteins in aqueous solution. For the present studies on PVP it was felt that in order to understand more about this kind of interaction it would be necessary to use the most simple types of cosolutes, varying their chemical nature in a systematic fashion. To avoid the complicating feature of micelle formation which occurs with long chain *aliphatic* water-soluble species,<sup>5</sup> we have concentrated on *aromatic* compounds, using benzene, benzene derivatives and polynuclear aromatic derivatives as cosolutes. The program carried out has included studies both on the thermodynamics of the binding equilibrium itself and on the effects of the bound cosolutes on the solution properties of the polymer molecules. The first subject will be discussed in this paper, the second in Part II.<sup>10</sup>

In the work reported in the present paper the binding equilibria have been studied at different temperatures in order to gain some insight into the nature of the binding process; the infrared absorption spectra of PVP films with varying additive contents (but in the absence of a solvent) also were studied.

### Experimental

**Materials.**—Polyvinylpyrrolidone: PVP K-90 ( $M_w = 1.01 \times 10^6$ )<sup>10</sup> was obtained through the courtesy of General Aniline and Film Corporation. A viscometric and light-scattering characterization of the polymer is given in Part II.<sup>10</sup> To prepare the polymer for equilibrium dialysis measurements, aqueous solutions of it were deionized by passages through cationic and anionic ion-exchange columns and then dialyzed against distilled water in cellulose casings (Fisher Scientific Company) to remove any remaining diffusible material.

**Cosolutes.**—The compounds used were either reagent grade chemicals or, in the cases of the majority of the anionic cosolutes, were prepared by neutralization of the corresponding reagent grade acid with the equivalent amount of alkali; sodium 3-phenanthroate was prepared by alkaline hydrolysis of ethyl 3-phenanthroate,<sup>11</sup> the salt finally being recrystallized from aqueous acetone.

**Water.**—Singly distilled water was used.

**Methanol.**—Commercial methanol was dried over calcium oxide and distilled.

**Dialysis Technique.**—The cellulose casings (Fisher Scientific Company) were freed of soluble material by being leached in frequently changed water at 60° for at least three days. The dialysis bags prepared from these casings were filled with 10 ml. of solution (polymer plus cosolute) and sealed by knotting. The liquid in the outer compartment, in which the bags were immersed and with which equilibrium was to be established, was identical in volume and in cosolute concentration but contained no polymer. Approximately three days was allowed for equilibration, which was accelerated by occasional shaking. The experiments were carried out at 3, 30 and 60°. The solutions in the outside compartment were analyzed, both before and after equilibration, by means of a Beckman DU spectrophotometer. The cosolutes used had convenient ultraviolet absorption bands between 220 and 300 m $\mu$ ; checks showed that Beer's law was obeyed by all the cosolutes except aniline and aniline hydrochloride, and with these two a point-by-point calibration of optical density *versus* concentration was used. In all the systems corrections had to be applied to take

into account ultraviolet absorption due to small remaining amounts of diffusible material in the PVP and leachable material from the casings. With aniline and with aniline hydrochloride the determination of these corrections proved to be very troublesome since there appeared to be a reaction occurring between these cosolutes and the casings which kept producing soluble material; the corrections with either of these cosolutes could not be controlled even after extended leaching of the casings followed by treatment with aqueous cosolute solution; the data for these cosolutes are accordingly rather uncertain, those for aniline hydrochloride being so uncertain that they are omitted entirely. The cellulose casings did not show any measurable degree of binding or interaction with any of the other cosolutes.

Dialysis experiments with methanol as solvent also were carried out. The casings were subjected to additional treatment with methanol after the leaching with water. The experiments were carried out at 0 and 30°. The experimental procedure was essentially the same as that with water; the cellulose casings were, however, much less flexible in methanol and accordingly more difficult to handle.

**Isothermal Distillation.**—Since experimental difficulties prevent the use of the dialysis technique with benzene as cosolute, an isothermal distillation technique was used to determine the solubility of benzene in water and PVP solutions. The apparatus used is shown in Fig. 1. Water-saturated benzene was introduced into A, a capillary tube of known internal diameter, by distillation from bulb B. A suitable volume (generally about 7 ml.) of water or polymer solution then was introduced into bulb B, and the entire system was frozen in liquid nitrogen, evacuated, sealed off at the constriction C and placed in a thermostat at 30°. The distillation of the benzene from A into B was followed with a cathetometer; by plotting the logarithm of the height of the meniscus against reciprocal time it was possible to extrapolate to infinite time, *i.e.*, the saturation point for the water or PVP solution. After the completion of the experiment at 30° the distillation vessel was placed in a thermostat at 60.5° and the motion of the meniscus followed again; finally the vessel was opened, the amount of aqueous liquid determined by weighing and the total volume of the vessel was also measured to obtain the correction for the amount of benzene in the vapor phase.

**Infrared Spectra.**—Spectra of PVP films containing varying concentrations of aromatic compounds were obtained over the region 2.5–15  $\mu$  on a Perkin-Elmer "Infracord" spectrophotometer. The films were cast from chloroform-methanol solutions directly onto sodium chloride windows, and the latter mounted in a closed air-tight cell, with Teflon side-walls, and containing desiccant, and finally dried at 70° *in vacuo*; the PVP films which, being highly hygroscopic, ordinarily in the open air develop a water absorption band at about 2.8  $\mu$  within a few minutes, could be scanned after this treatment without any measurable pick-up of water. A pure PVP film and Nujol mulls of the aromatic compounds were used to obtain the necessary reference spectra; the spectra of nitrobenzene and phenol were obtained on the liquids as such, in addition that of nitrobenzene was determined in carbon disulfide solution and that of phenol on a solid film. All the spectra were calibrated by the band of polystyrene (0.07 mm. film) at 6.24  $\mu$  (1603 cm.<sup>-1</sup>). The resolution of the instrument,  $\pm 0.02 \mu$ , was considered sufficient to show the presence of any marked spectral shifts.

### Results

**Dialysis.**—The polymer and cosolute concentrations used in these experiments ranged from 1 to 2 g./100 ml. and from  $10^{-3}$  to  $10^{-2}$  mole/liter, respectively; the binding constants were independent of PVP concentration over the range indicated. In systems in which ionic species were used as cosolutes a Donnan correction deriving from the equation

$$[I]_o^2 = [I]_i \times [I]_{i,\text{tot}} \quad (1)$$

(where  $[I]_o$  and  $[I]_i$  are the free anion concentrations in the outside and inside compartment, respectively, and  $[I]_{i,\text{tot}}$  is the total anion concentration in the inside compartment) had to be applied to calculate the number of bound ions. With

(9) W. Kauzmann, *Advances in Protein Chem.*, **14**, 1 (1959).

(10) P. Molyneux and H. P. Frank, *J. Am. Chem. Soc.*, **83**, 3175 (1961).

(11) We are grateful to Professor R. H. Martin, of the Free University of Brussels, for a gift of this ester

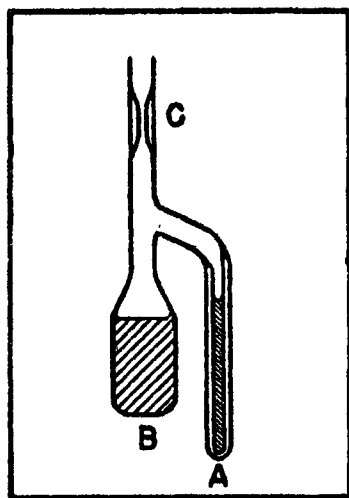


Fig. 1.—Isothermal distillation vessel.

two anionic cosolutes, sodium benzoate and sodium biphenyl-4-carboxylate, a number of dialysis experiments were carried out at 30° in the presence of 0.1 *M* sodium chloride, which should suppress any Donnan effect. The direct numerical results of these runs agreed fairly well with those of the comparable, corrected salt-free runs.

All the dialysis data were evaluated in the form of the rearrangement, equation 2, of the Langmuir isotherm, as suggested by Klotz<sup>12</sup>; in equation

$$1/r = 1/nKa + 1/n \quad (2)$$

$2r$  is the number of mole of cosolute bound per basemole (*i.e.*, monomer unit) of polymer,  $n$  is the number of binding sites per basemole,  $a$  is the molar concentration of free cosolute at equilibrium and  $K$  is the binding constant (in liter/mole) for the cosolute on the binding sites (a binding site involves a chain segment containing a certain number of monomer units). A characteristic set of results is shown in Fig. 2, where  $1/r$  is plotted against  $1/a$ ; the slope of this plot is  $1/nK$ , the intercept on the ordinate axis is  $1/n$ .

It is remarkable that in all the systems, and regardless of temperature, the intercept of the  $1/r$  versus  $1/a$  plot, representing  $1/n$  (the reciprocal of the number of binding sites per basemole PVP, and hence the minimum number of monomer units which can accommodate one cosolute molecule or ion) has an essentially constant value of  $10 \pm 3$ ; this figure is closely similar to that obtained for azo dyes with PVP<sup>4</sup>; it is surprising that ten monomer units should be needed to provide a binding site even for such comparatively small molecules as nitrobenzene or phenol and that there is no correlation between the size of the cosolute and the number of monomer units involved. Perhaps the steric configurations of adjacent monomer units play a certain role in the binding process so that, for instance, binding only occurs onto a sequence of adjacent monomeric units with identical configuration (isotactic sequence); this, however, is only a possibility and at present there seems to be no satisfactory explanation for the surprisingly large size of the

(12) I. M. Klotz, F. Walker and R. Pivan, *J. Am. Chem. Soc.*, **68**, 1486 (1946).

binding site. For the calculation of the slope, and hence of  $K$ ,  $1/n$  was taken as ten exactly; the accuracy of  $K$  under these circumstances is estimated as approximately  $\pm 7\%$  (see Fig. 2).

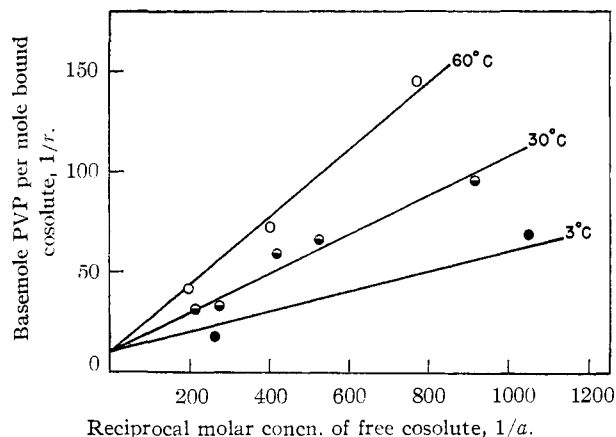


Fig. 2.—Basemole PVP per mole bound phloroglucinol versus reciprocal molar concentration of free phloroglucinol at 3, 30 and 60°; from equilibrium dialysis.

The binding constants,  $K$ , so-obtained, for PVP-cosolute systems in aqueous solution at different temperatures are listed in Table I.

TABLE I  
BINDING CONSTANTS,  $K$ , (L./MOLE) FOR PVP-COSOLUTE SYSTEMS IN AQUEOUS SOLUTION

Cosolute	Temp., °C.		
	3	30	60
Benzene	...	3.5 <sup>a</sup>	4.8 <sup>a</sup>
Benzoic acid	34	30	24
Phthalic acid	...	15	...
<i>p</i> -Hydroxybenzoic acid	...	62	...
Phenol	13.2	14.5	15.6
Resorcinol	48	26	15
Hydroquinone	...	38	...
Catechol	...	31	...
Pyrogallol	...	50	...
Phloroglucinol	190	97	59
2-Naphthol	159	120	81
Aniline	...	11	...
Nitrobenzene	80	80	80
Sodium benzoate	76	33	18
Disodium phthalate	...	10	...
Sodium <i>p</i> -hydroxybenzoate	...	69	...
Sodium 2-naphthoate	75	37	19
Sodium biphenyl-4-carboxylate	127	75	43
Sodium 3-phenanthroate	625	300	145

<sup>a</sup> From isothermal distillation, see below.

**Isothermal Distillation.**—The solubilities of benzene in water and PVP solutions were determined by the isothermal distillation technique at 30 and 60.5°; appropriate corrections were applied to take into account the benzene in the vapor phase; the water content of the benzene phase was neglected. The results obtained are listed in Table II together with the literature data<sup>13</sup> for the solubility of benzene in water; the agreement with the literature results is fairly good at 30° but not good at 60.5°. The results are plotted as  $1/r$  versus  $1/a$ , to get comparable with those from dialysis equilib-

(13) R. L. Bohon and W. F. Claussen, *ibid.*, **73**, 1571 (1951).

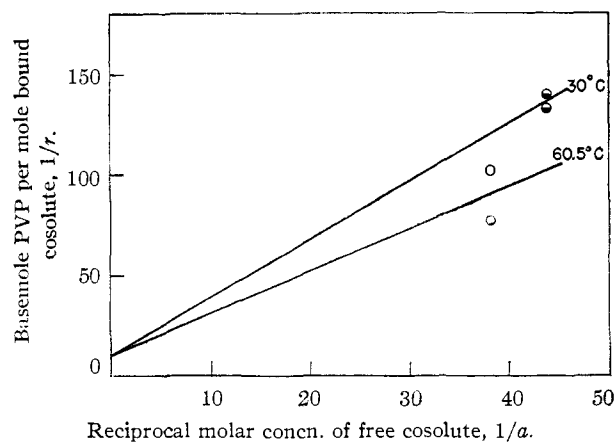


Fig. 3.—Basemole PVP per mole bound benzene *versus* reciprocal molar concentration of free benzene at 30 and 60.5°; from isothermal distillation.

ria, in Fig. 3. A linear relationship of  $1/r$  *versus*  $1/a$ , with intercept  $1/n = 10$ , was assumed for the binding of the benzene, on analogy with the behavior of the other cosolutes; under this assumption the values for the binding constant,  $K$ , (see Table I) were calculated to be 3.5 l./mole at 30° and 4.8 l./mole at 60.5°.

TABLE II  
SOLUBILITY OF BENZENE IN WATER AND IN AQUEOUS PVP SOLUTIONS

PVP concn., g./1000 g. water	Temp., °C.	Benzene concn., g./1000 g. water This work	Ref. 13
0	30	1.78	1.85
0	60.5	2.04	2.30 <sup>a</sup>
14.0	30	1.85	..
14.0	60.5	2.13	..
28.0	30	1.93	..
28.0	60.5	2.13	..

<sup>a</sup> Extrapolated.

**Dialysis in Methanol.**—Nitrobenzene and 2-naphthol also were studied as cosolutes with PVP in methanol as solvent. A characteristic set of experimental data is shown in Fig. 4; the results derived from the dialysis equilibria at 0 and 30° are listed in Table III.

TABLE III  
BINDING CONSTANTS  $K$  (L./MOLE) FOR PVP-COSOLUTE SYSTEMS IN METHANOL

Cosolute	Temp., °C.	
	0	30
Nitrobenzene	173	57
2-Naphthol	375	65

The value of the intercept,  $1/n$ , for these systems was  $100 \pm 20$ ; this result is even more difficult to explain than that for water since it indicates that in methanol only one cosolute molecule can be bound by a chain segment of one hundred monomeric units, a site-size ten times that in water.

**Thermodynamic Functions from the Equilibrium Data.**—From the data in Tables I, and III, thermodynamic functions for the binding of one mole of cosolute by one mole of vacant binding site on PVP can be obtained in the customary manner from the binding constant and its temperature dependence, and these functions are listed in Table IV.

TABLE IV  
THERMODYNAMIC FUNCTIONS FOR THE BINDING OF ONE MOLE OF COSOLUTE BY ONE MOLE OF VACANT BINDING SITE ON PVP; IN AQUEOUS SOLUTION, AND AT 303°K., EXCEPT WHERE OTHERWISE INDICATED

Cosolute	$\Delta F$ , kcal./mole	$\Delta H$ , kcal./mole	$\Delta S_u$ , e.u.
Benzene, 318°K.	-1.1	2.4	18
Nitrobenzene	-2.6	0	17
Phenol	-1.6	0.5	15
Benzoic acid	-2.05	-1.0	12
Resorcinol	-1.95	-3.8	2
Phloroglucinol	-2.75	-4.0	4
2-Naphthol	-2.85	-1.7	12
Sodium benzoate	-2.1	-4.5	0
Sodium 2-naphthoate	-2.15	-4.4	1
Sodium biphenyl-4-carboxylate	-2.6	-3.6	5
Sodium 3-phenanthroate	-2.4	-4.7	4
Nitrobenzene (in methanol, 288°K.)	-4.2	-9.6	-12
2-Naphthol (in methanol, 288°K.)	-3.9	-6.1	-1

The temperatures quoted in Table IV are the averages of the experimental temperatures. The

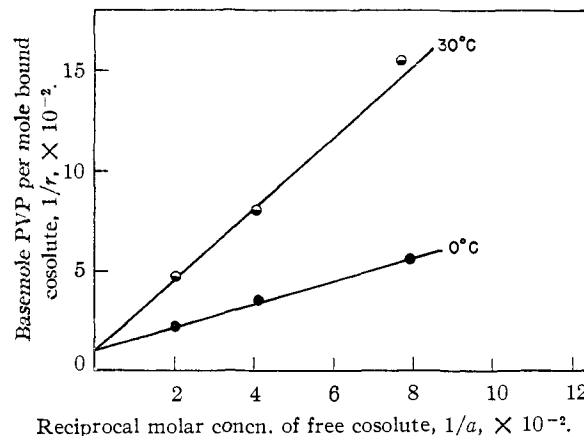


Fig. 4.—Basemole PVP per mole bound 2-naphthol,  $\times 10^{-2}$ , *versus* reciprocal molar concentration of free 2-naphthol,  $\times 10^{-2}$ , in methanol; from equilibrium dialysis.

values of the free energy change during the binding process,  $\Delta F$ , listed in the second column of this table, were calculated from the equation:  $\Delta F = -RT \ln K$ ; the values of the enthalpy change,  $\Delta H$ , listed in the third column, were calculated from the equation:  $\Delta H = RT^2 d \ln K/dT$ ; the fourth column contains the values of the so-called "unitary" entropy change,<sup>9,14</sup>  $\Delta S_u$ , which is related to the over-all entropy change,  $\Delta S$  (given by  $\Delta S = -d \Delta F/dT$ ), by the relationship:  $\Delta S_u = \Delta S + 7.98$ ; the "cratic" term 7.98 (e.u.) originates from the expression  $-R \ln 1/55.6$  (where 55.6 (mole/l.) is the concentration of water in a highly diluted aqueous solution) and has to be included to take into account the reduction in the number of independent solute species by one on the combination of one molecule of cosolute with one molecule of the PVP (for a more detailed discussion see ref. 9).

(14) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

The listed values of  $\Delta H$  and  $\Delta S_u$  represent the averages of values determined between 3 and 30°, and 30 and 60°; the limits of error involved, as derived from the above stated accuracy of  $K$ , are approximately  $\pm 0.4$  kcal./mole and  $\pm 2$  entropy units, respectively.

**Infrared Spectra.**—The spectra of dry PVP films containing varying concentrations of selected aromatic compounds were taken: the films were quite clear in all cases. The spectra were compared with reference spectra of the pure compounds (PVP, and aromatic compound) and the observed shifts in absorption maxima are listed in Table V.

TABLE V  
INFRARED SHIFTS FOR PVP FILMS CONTAINING VARYING CONCENTRATIONS OF AROMATIC COMPOUNDS

Aromatic additive	Basemole PVP/mole additive	Shifts in maxima, $\text{cm.}^{-1}$ (ref. additive $\rightarrow$ PVP + additive)
Nitrobenzene	1 and 10	795 $\rightarrow$ 800, 703 $\rightarrow$ 712
Phenol	1.4	3330 $\rightarrow$ 3170, 689 $\rightarrow$ 696
Phenol	10	3330 $\rightarrow$ 3130, 689 $\rightarrow$ 693
Phenol	20	3330 $\rightarrow$ 3080, 689 $\rightarrow$ 694
Phloroglucinol	1.4, 10 and 25	817 $\rightarrow$ 833, 678 $\rightarrow$ 687 ( $\pm 3$ )
Benzoic acid	1.5 to 30	2530 $\rightarrow$ 2470, 709 $\rightarrow$ 718 ( $\pm 1$ )
Sodium benzoate	2.8	708 $\rightarrow$ 714
Sodium benzoate	10	708 $\rightarrow$ 724
Sodium 3-phenanthroate	2.1	813 $\rightarrow$ 818, 704 $\rightarrow$ 709
	10	813 $\rightarrow$ 821, 704 $\rightarrow$ 709

No shifts were observed in the bands of the PVP. With additives which are capable of hydrogen bonding there were generally shifts in the O-H stretching bands to lower wave numbers, indicating changes in the hydrogen bond structures; no detailed conclusions can be drawn, however, on the basis of these rather low resolution spectra. With all the additives the aromatic C-H out-of-plane deformation bands at about  $700 \text{ cm.}^{-1}$  ( $800 \text{ cm.}^{-1}$  for sodium 3-phenanthroate) showed characteristic shifts toward higher wave numbers; the aromatic band at about  $750 \text{ cm.}^{-1}$ , the effect of ring substituents upon which has been studied systematically by Fassel and co-workers,<sup>15</sup> is unfortunately obscured in the present case by a strong PVP band at  $755 \text{ cm.}^{-1}$ .

### Discussion

From the thermodynamic data listed in Table IV, it is evident that the binding process in aqueous solutions is in nearly all cases accompanied by an entropy gain and that the enthalpies of binding vary from a positive, *i.e.*, unfavorable, value in the case of benzene, to a highly negative (favorable) one for sodium 3-phenanthroate. It should be clear that the binding process is a composite one, involving as it does two species, the polymer and the aromatic cosolute, both of which exist in aqueous solution in some hydrated form. In this discussion the so called "iceberg" concept of H. S. Frank and M. W. Evans<sup>16</sup> will be used to develop the conclusions (see also ref. 9): it is an assumption

(15) R. D. Kross, V. A. Fassel and M. Margoshes, *J. Am. Chem. Soc.*, **78**, 1332 (1956).

(16) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

of this concept that hydrocarbon groups, such as are present both in the polymer and in the aromatic cosolutes, are surrounded in aqueous solution with one or more layers of water molecules which are more highly ordered than the molecules in ordinary liquid water; owing to the higher degree of ordering these layers approximate to an ice-like structure and have been termed<sup>15</sup> "icebergs." In the cases of the polar aromatic compounds such as the phenols, carboxylic acids, and anions, there will also be true hydration about the substituent group. In accordance with a recent publication<sup>9</sup> it will be assumed that the entropy changes (*i.e.*, the  $\Delta S_u$  values) in the course of the binding process are solely due to the disordering, partial or total, of the "icebergs" which accompany the polymer and cosolute molecules; the complex containing the polymer molecule and the bound cosolute molecule or ion will thus be accompanied by either a less ordered "iceberg" or by an "iceberg" containing a lesser number of water molecules, as compared with the "icebergs" of the two separate entities; the release of water molecules from the ordered structure should produce a proportional gain in entropy.

Analyzing the binding process into a series of steps involving the "dehydration" of both the binding partners, the formation of the complex between these two "dehydrated" entities and then the "rehydration" of the bound system (polymer molecule plus cosolute molecule), the binding enthalpy can be divided into five contributions:

(1) Enthalpy will have to be provided to break (or bend<sup>17</sup>) hydrogen bonds in order to disorder all the water molecules in the "icebergs" associated with the polymer and the cosolute.

(2) Enthalpy will also have to be provided to overcome any specific interactions (*e.g.*, true hydration) between the water and the cosolute and between the water and the polymer.

(3) Enthalpy will be gained in the actual binding process between the "dehydrated" entities.

(4) Enthalpy then will be gained by interactions between the water and the bound system (*i.e.*, reformation of true hydration).

(5) Enthalpy will, finally, also be gained by the re-forming (or unbending<sup>16</sup>) of hydrogen bonds in the "icebergs" associated with the bound system.

Assuming additivity of these enthalpies the overall enthalpy of binding  $\Delta H$  will then be given by

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 \quad (3)$$

In order to simplify this an enthalpy  $\Delta H_b$  defined by

$$\Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5 \quad (4)$$

is introduced, and one then obtains, through the identification of  $\Delta S_u$  with the over all "iceberg" disordering

$$\Delta H = \Delta H_1 + \Delta H_b = \Delta S_u(h/s) + \Delta H_b \quad (5)$$

where  $s$  is the entropy gain for releasing one water molecule from the iceberg structure and  $h$  is the corresponding enthalpy requirement. Figure 5 shows the plot of  $\Delta H$  versus  $\Delta S_u$  for the aqueous

(17) J. A. Pople, *Proc. Roy. Soc. (London)*, **A205**, 163 (1951); we are grateful to a referee for bringing this paper to our attention.

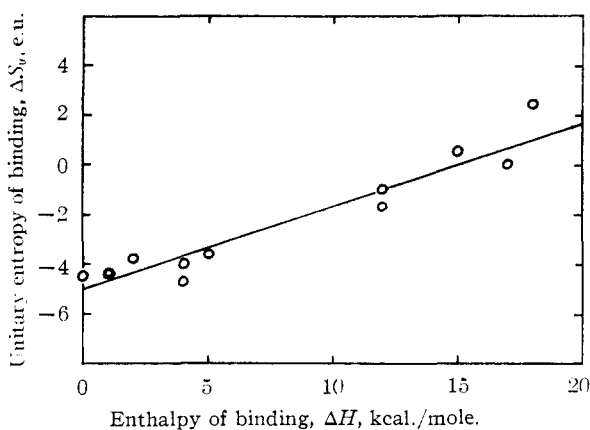


Fig. 5.—Over-all enthalpy of binding,  $\Delta H$ , versus unitary entropy of binding,  $\Delta S_u$ , for aqueous PVP-cosolute systems.

solute systems listed in Table IV. The fact that the data for all systems studied fit fairly closely the indicated linear relation (with an r.m.s. deviation of  $\Delta H$  of about 0.5 kcal./mole) would seem to indicate that  $\Delta H_b$  is essentially constant (at the value of  $-5$  kcal./mole, the intercept on the ordinate axis) and mainly determined by the contribution of the binding process  $\Delta H_3$ , representing the interaction of the polar groups of the polymer with the  $\pi$ -electron system of the aromatic cosolutes.<sup>18</sup> Any additional special interaction due to ionic groups or to groups capable of hydrogen bonding might of course also contribute and could possibly be responsible for the more significant deviations from the line in Fig. 5; the slope of the line,  $h/s$ , is  $0.34 \times 10^3$  ( $^{\circ}\text{K.}$ ) indicating the "icebergs" to have an apparent "melting point" of about  $340^{\circ}\text{K.}$ , or about  $70^{\circ}\text{C.}$

In the light of the above considerations the lack of binding of anilinium and naphthylammonium ions is rather curious; no reliable results were obtained for this type of cosolute in the equilibrium dialysis studies, but there is strong evidence for the absence of the binding of such cations from

(18) For  $\Delta H_b$  to be strictly equal to  $\Delta H_3$  then  $\Delta H_2 = -\Delta H_1$ , i.e., the dehydration and hydration contributions (2) and (4) must cancel; this, however, cannot be so if, for instance, otherwise hydratable groupings on the polymer or the cosolute molecule are covered up as a consequence of the interaction between them.

the solution behavior<sup>10</sup> and also from other studies in the literature.<sup>19</sup> One would expect that the strength of the interaction of these ions with PVP would be quite comparable to that, for instance, of the benzoate or naphthoate ions. Perhaps such aromatic cations, being more strongly hydrated than anions, would not produce any disordering of the "icebergs" about the polymer molecules and hence would not produce appreciably entropy gains; the difference in behavior may also be related to the proximity of the ionic charge to the aromatic ring in the cations, and it is notable in connection with this that the solution studies<sup>10</sup> indicate that the phenolate ion, where the charge is also close to the ring, also does not seem to be bound.

For the two cosolutes where methanol was (also) used as solvent the  $\Delta S_u$  values are negative, in contrast to the positive  $\Delta S_u$  values obtained in water; it is notable that the two pairs of  $\Delta H$  and  $\Delta S_u$  values for the measurements in methanol give points on the  $\Delta H$  versus  $\Delta S_u$  plot which lie close to the (back-extension of the) line in Fig. 5 for the measurements in water.

A brief discussion may finally be made of the results of the infrared measurements; it is felt that the observed effects do not allow more than tentative conclusions to be made, and more detailed investigations would have to be conducted along these lines, preferably, if possible, on the aqueous PVP-cosolute solutions themselves. Other workers<sup>15</sup> have observed variations in aromatic C-H out-of-plane deformation bands with change in the nature of the substituent groups and have correlated these shifts with the electron attracting nature of the substituents, the bands at approximately  $750$  and  $700$   $\text{cm.}^{-1}$  being shifted in the same direction and in a very similar manner; it seems possible that the shifts observed in the presence of PVP are brought about by the interaction of the polar groups on the polymer with the aromatic  $\pi$ -electrons on the cosolute and that this interaction may have a similar basis, as far as infrared shifts are concerned, as that of the substitution of an electron attracting group on the ring itself.

(19) W. Scholtan, *Makromol. Chem.*, 11, 131 (1953).