EQUILIBRIUM INTERACTION OF THE SOLUTE SPECIES ENTERING INTO THE HOLES OF A SOLVENT BODY

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With the discovery of interstitial compounds and various other observations along with the advancement of theories on the nature of the solvents one is led to suspect the presence of ordered structure of liquids having some unoccupied spaces, referred to in this paper as "holes". It is possible that very minute quantities of solute species of tolerably small size temporarily occupy some of these "holes". The duration of such occupation may be attained with some distortions of both solvent holes and the solute species depending on the polarizability and structural differences of the components. A theoretical framework has been constructed where it is shown that a plot of V/V_S versus $S/V_1 - V_S$ will give a straight line at the lower end of concentrations, where V, S, V_S and V_1 are molar volume of solute, molar volume of solvent, apparent molar volume and molar volume of monomer respectively. The slope of this plot is $K\beta$ and the intersection is K/V_1, where K is the equilibrium constant and β is the number of moles of "holes". Hence K and β can be found out.

Key words: Equilibrium interaction, Solute species holes.

INTRODUCTION

One of the logical treatments that can be conceived on the basis of law of mass action (which is essentially statistical in nature(takes the following form:

$$\text{Species + holes} \rightleftharpoons \text{"species in hole"}$$

and $k = \dfrac{[\text{Species in hole}]}{[\text{species}] \, [\text{hole}]}$, where bracket indicates the concentration in terms of number of species as well as holes per unit volume.

Testing of this model of interaction can be based on the assumption that a species entering into the holes loses a part or whole of its volume, if calculated on the basis of the simple additivity rule (i.e. $v = w_1 v_1 + w_2 v_2$; where v is the specific volume of the mixture, v_1 and v_2 are those of solute and solvent and $1 = w_1 + w_2$). If V is expressed as the volume which contains one mole of A (i.e., acid), of which α fraction has entered into the holes and each cm^3 of solvent has only β moles of holes (i.e. 10^{23} x 6.06 x β holes per cm^3) then,

$$K = \frac{\alpha V}{(1 - \alpha)(\beta S - \alpha)}$$

where 'S' expresses the actual volume of the solvent initially added to make the mixture.

Now the volume, V, contains solvent S and free A, while the rest of A remains inside the hole without con-

tributing its volume to the bulk, thus, $V = S + (1 - \alpha) V_1$ where V_1 is the molar volume of A. Hence we can write, $V - S = V_S = (1 - \alpha) V_1$ or,

$$\alpha = \frac{V_1 - V_S}{V_1} \qquad \text{Now, putting } Z = V_1 - V_S$$

We get, $\alpha = Z/V_1$ and $\dfrac{\alpha}{1 - \alpha} = Z/V_S$

Hence $K = \dfrac{Z \, VV_1}{V_S \, (\beta V_1 \, S - Z)}$

or $K/V_1 = \dfrac{(\beta V_1 \, S - Z)}{Z} = \dfrac{V}{V_S}$

Therefore, $V/V_S = \dfrac{K \beta S}{Z} \qquad - K/V_1$

Putting back $Z = V_1 - V_S$, finally we have the relation,

$$V/V_S = K \beta \frac{S}{(V_1 - V_S)} - K/V_1 \quad \ldots \ldots (1)$$

Therefore, a plot of V/V_S against $S/V_1 - V_S$ will give a straight line at the lower end of concentrations. The slope of this plot gives $K\beta$ and the intersection gives K/V_1. Since the molar volume of acetic acid monomer known to be

about 55.21^1 cm^3 (average V_1 value in CCl_4 and in bengene), β and K can be found.

EXPERIMENTAL

Reagents and their purification. Acetic acid. E. Merck acetic acid is dried by shaking with P_2O_5 in the cold and allowing to stand for several hours, then the liquid is drained off and distilled. The distilled liquid is frozen in an ice-bath. When half protion of acids is transformed into fine fibrous crystal the remaining acid in transferred into another flask. This procedure of fractional crystallization is repeated several time and the product is finally kept in an air-tight flask placed in a desiccator containing P_2O_5.

Cyclohexane. It is first dried by shaking with P_2O_5 and allowed to stand for about 12 hours. The liquid is decanted and distilled. The distillate is treated with metallic sodium in the form of thread. It is then refluxed for about 2-3 hours, cooled and distilled and a centre cut of constant of boiling point 80-82° is collected.

High boiling hydrocarbon or kerosene oil (HBH). It is dried with CaO and allowed to stand for about 24 hours, shaking occasionally. It is than distilled and collected within the boiling range 158°-200°. Then it is treated with H_2SO_4 followed by alkaline potassium permanganate. Again it is treated with H_2SO_4 and decanted. Then it is treated with sodium thread as described above and finally distilled for collection.

Volume measurement. The specific volume, i.e. the reciprocal of density, is measured by a sophisticated instrument [2], a magnetic float densimeter. The readings are taken [3] within O to about 8 x 104 weight fraction. The results are tabulated in the Table 1, 2 and 3.

RESULTS

In the present work two systems, (i) acetic acid-kerosene (HBH) and (ii) acetic acid-cyclohexane, acetic acid as the solute species, have been investigated for the "solute-hole equilibrium effect".

It must be noted that extremely accurate and precise measurement of density (or specific volume) is needed to investigate the empirical basis of such a construct. The measurements of specific volume have been carried out by magnetic float densimeter as stated previously [2]. V, the molar volume of solute species, S, the molar volume of solvent and $V - S$ or V_S, the apparent molar volume of solute, have been calculated by the relations: $V = \dfrac{v}{w} \times M$ and $S = V_S (\dfrac{1-w}{w}) \times M$ where, v is the specific volume of the solute, W is the weight fraction of acid, M is the molecular weight of acetic acid and V_S is the specific volume of solvent.

Molar volume of acetic acid monomer (V_1) is about 55.21 cm^3. Now V/V_S and $S/V_1 - V_S$ for both the systems (HBH and cyclohexane) have been calculated and given in Table 2 and 3 respectively and the plots of V/V_S

Table 1. Specific volume of the system (i) acetic acid in HBH and in (ii) cyclohexane.

Weight fraction	Specific volume of system (i) in cm^{3}gm^{-1}	Specific volume of system (ii) in cm^{3}gm^{-1}
0.0	1.323345	1.299916
0.0001	1.323279	1.299800
0.0002	1.323216	1.299689
0.0003	1.323155	1.299578
0.0004	1.323099	1.299463
0.0005	1.323045	1.299360
0.0006	1.322998	1.299256
0.0007	1.322959	1.299155
0.0008	1.322923	1.299057
0.0009	1.322891	1.298972
0.0010	1.322862	1.298903

Table 2. System: Acetic acid in HBH.

Weight fraction x 10^4	V/V_S	$S/V_1 - V_S$
1	19950.52	51697.41
2	9751.98	27472.67
3	6391.20	19244.92
4	4670.38	15673.85
5	3657.87	13508.02
6	2959.54	12654.43
7	2444.35	12935.52
8	2077.01	13430.87

Table 3. System acetic acid in cyclohexane.

Weight fraction x 10^4	V/V_S	S/V_1 V_S
1	92809.74	16681.37
2	39377.56	8616.07
3	24988.68	5807.59
4	19391.84	4321.48
5	13834.50	3552.87
6	10827.13	3010.46
7	8646.15	2633.80
8	7180.45	2342.55
9	5747.37	2159.90
10	4526.94	2053.78

versus $S/V_1 - V_S$ are shown in Fig. 1 and 2 respectively. The results of K and β are given in Table 4. These results were obtained by using a much bigger graph which is in the Fig. 1 and 2 in a smaller scale. The intersections are in the negative which rightly conform to the equation 1. The slopes and intersection so obtained were used to calculate β and K.

The deviation of the straight line at the lower end of both the graphs were observed. This is the region of comparatively higher concentration. Here the free monomer of

Table 4. Results of the systems of acetic acid in HBH and cyclohexane.

Solvent	K/V_1	K (litre mole^{-1})	β_K	β (mole litre^{-1})
HBH	1.8×10^3	220.8	0.4151	0.004418
Cyclohexane	4.0×10^3	99.36	5.0322	0.0227
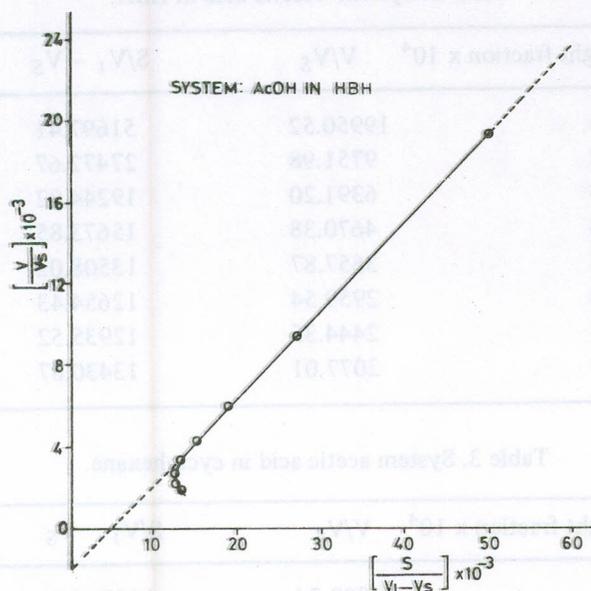
Fig. 1. Plot of V/V_S versus $S/(V_1 - V_S)$.

acid or even dimer may exist after entering into the holes. These may cause different sort of interactions with the solvent (solute-solvent, monomer — dimer etc.) and ultimately occurs deviation from ideal or normal behaviour.
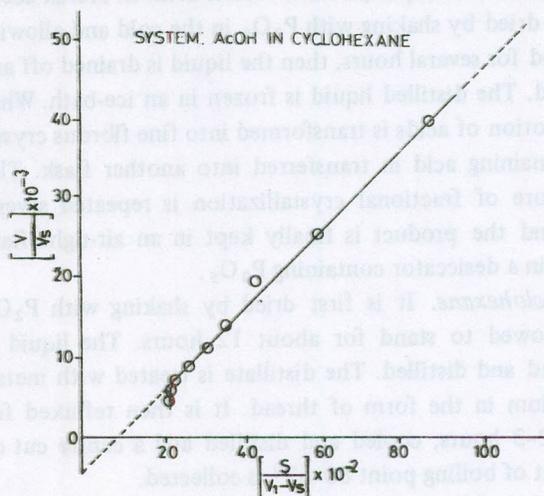
Fig. 2. Plot of V/V_S versus $S/(V_1 - V_S)$.

DISCUSSIONS

Figure 1 and 2 show that the equation 1 very closely represents the variation of the parameters from (near) zero concentration upto about 0.0006 weight fraction solution. The equilibrium constant are neither too high nor too low. Similarly the numbers of holes are within reasonable values. A sample calculation for the cyclohexane system indicates that only one hole of the size of one molecule of acetic acid monomer exists per 450 molecules of cyclohexane. In HBH such a calculation is not pressible as the molecular weight is not known but the molecular holes exist only one fifth times that of cyclohexane.

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