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The Solubility Study of Ion-pairs in Organic Solvents

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The solubilities of alkali picrates were measured in alcohols (13 species) and esters (19 species) at 25±0.2°C. It was found that the solubility data are well correlated with the solubility parameters of the solvents. It is also pointed out that the distribution ratios of the cesium picrate between the aqueous phase and the organic phase are apparently correlated with the solubility parameters of the extraction solvents.

In a previous paper,[1] it was reported that the solubilities of such ion-pairs as chloride, perchlorate, and tetraphenylborate salts of alkali metals and Ru(II)-$(phen)_3$ could be well correlated with the solubility parameters of solvents (δ_2). In the potassium halide systems,[2] the best linearity was found between the logarithmic solubilities ($\log S$) and $(\delta_1-\delta_2)^2$, where δ_1, corresponding to the hypothetical solubility parameters of the ion-pairs, was calculated to be $(U/V)^{1/2}$, (U: lattice energy of the ionic crystal; V: molar volume).

In the present paper, the solubilities of alkali picrates in 13 alcohols and 19 esters and the distribution ratios of cesium picrate in liquid-liquid partition systems were measured at 25±0.2°. Both sets of data are discussed in relation to the solubility parameters of solvents from the empirical point of view.

Experimental

Reagents. All the reagents used here were of a reagent-grade purity. The organic solvents were purified mainly by distillation, as has been described before.[1] The alkali picrates (K–Pic, Rb–Pic, Cs–Pic) were synthesized as follows. Picric acid was neutralized by the corresponding alkali carbonates in an acetone–water (1 : 1) mixture. The resulting precipitates were filtered and washed with water several times. After being recrystallized in water, the precipitates were dried *in vacuo* for 5 day.

Solubilities. The solubility measurements of alkali picrates were performed as follows: 10 ml portions of the organic solvents were placed in test tubes equipped with ground stoppers which contained appropriate amounts of the precipitates of alkali picrates. After the test tubes had been tightly sealed with parafilm, the solubility equilibria were established by shaking them in a thermostat at 25±0.2 °C for 10 day. The solubilities were then measured spectrophotometrically ($\lambda_{max}=355$ nm, $\varepsilon_{max}=16110$).

Extraction. The distribution of the cesium picrate was investigated as follows: 1 ml of a 2.0×10^{-5} M aqueous Cs_2SO_4 solution (containing ^{137}Cs as a tracer) and 4 ml of the 3.62×10^{-4} M aqueous sodium picrate (in alcohols) or 4 ml of the 2.42×10^{-2} M aqueous sodium picrate (in esters) were placed in polypropylene test tubes equipped with silicone rubber stoppers. After 5 ml of the organic solvent had then been added, the test tube was shaken vigorously for 10 min at 25±0.2°C. After the two phases had been separated by centrifugation, the distribution ratio was calculated as the ratio of the γ-radioactivities of the two phases. The γ-radioactivities were counted by using a well-type single-channel pulse-height analyzer (Osaka Dempa, Model LA-3T). Measurements in both the solubility study and the extraction study were repeated three times; the averages of the results are given in the table and figures.

Results and Discussion

Relation between log S and δ_2. The observed solubilities of alkali picrates in organic solvents are listed in Table 1, together with the solubility parameters of the solvents (δ_2). The logarithmic solubilities ($\log S$) are shown in Figs. 1 and 2 as a function of δ_2

TABLE 1. SOLUBILITIES OF ALKALI-PICRATE AT 25 °C

Solvent	δ_2*)	(M)×10^5 K-Pic	Rb-Pic	Cs-Pic
Alcohols				
(1) methanol	14.50[a)]	751	452	329
(2) ethanol	12.74	85.7	61.4	47.4
(3) 1-propanol	11.94	16.3	15.3	13.7
(4) 2-propanol	11.56	9.0	8.2	7.1
(5) 1-butanol	11.40	11.6	7.7	6.4
(6) isobutyl alcohol	11.19	4.8	5.1	4.6
(7) 2-butanol	11.05	3.3	3.0	2.5
(8) *n*-amyl alcohol	10.95	5.6	4.7	3.7
(9) isoamyl alcohol	10.79	4.1	3.0	2.5
(10) *tert*-amyl alcohol	10.21	1.5	1.1	0.7
(11) 1-hexanol	10.65	4.1	3.1	2.7
(12) 1-octanol	10.24	2.8	1.8	1.5
(13) 1-decanol	—	2.0	1.4	1.0
Esters				
(1) methyl formate	9.48[b)]	1640	646	331
(2) ethyl formate	8.90	395	196	104
(3) propyl formate	8.69	165	90.2	50.2
(4) butyl formate	8.53	91.8	49.7	25.7
(5) methyl acetate	9.01	724	331	159
(6) ethyl acetate	8.58	186	76.0	32.7
(7) propyl acetate	8.41	123	48.8	20.7
(8) isopropyl acetate	8.07	73.2	27.1	11.9
(9) *n*-butyl acetate	8.31	69.1	27.9	12.7
(10) isobutyl acetate	8.13	56.5	21.2	9.8
(11) 2-butyl acetate	8.01	50.7	18.7	9.9
(12) isoamyl acetate	8.07	39.9	15.8	6.2
(13) ethyl butyrate	8.22	28.2	12.7	6.4
(14) *n*-amyl acetate	8.21	47.7	18.9	8.0
(15) *n*-octyl acetate	8.00	24.3	9.5	4.7
(16) 2-ethyl hexylacetate	7.81	18.3	7.8	3.8
(17) ethyl propionate	8.37	60.2	24.5	11.8
(18) benzyl acetate	9.49	43.2	22.5	13.1
(19) ethyl benzoate	9.40	62.6	28.7	17.0

a) Calculated by using ΔH_{25} values cited from the literature.[4] b) Calculated by using ΔH_{25} values estimated according to the Hildebrand rule.

*) $\delta_2=\left(\dfrac{\Delta H_{25}-RT}{V}\right)^{1/2}$

of the solvents. Although smooth correlations are obtained between log S and δ_2, a slight bending is observed for all the systems. Exceptional deviations from the curves are noticed in the two phenyl-substituted esters, *i.e.*, benzyl acetate and ethyl benzoate. The difference in slope was noticeable between the alcohol system and the ester system. Although no clear explanation can be given here, the difference may be due to the high δ_2 values of alcohols, which seem to be derived from the structural characteristics of alcohols, such as H-bonding.

Table 2. The calculated δ_1 values of ion-pairs

	r_c+r_a (Å)	U (kcal/mol)	V(ml)	δ_1
K-Pic	4.33	122.09	97.8	35.33
Rb-Pic	4.48	118.33	108.3	33.06
Cs-Pic	4.69	113.45	124.3	30.21

Relation between log S *and* $(\delta_1-\delta_2)^2$. In order to find out a clearer correlation, the logarithmic solubilities (log S) were plotted against the difference in the solubility parameters of the solute and solvents as is shown in Figs. 3 and 4. The solubility parameters of the ion-pairs (δ_1) were approximated from the square root of the lattice-energy densities, $(U/V)^{1/2}$, as has been described in a previous paper.[2] In this calculation, 3.0 Å was used as the r_a value of the picrate anion.[3] The calculated values are shown in Table 2. As is shown in these figures, the plots, other than the two deviated plots in phenyl-substituted esters, give excellent straight lines.

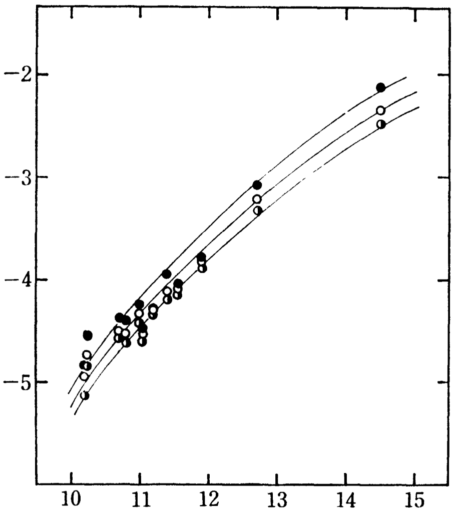


Fig. 1. The relation between log S and δ_2 in alcohol system.
(●): K-Pic, (○): Rb-Pic, (◑): Cs-Pic

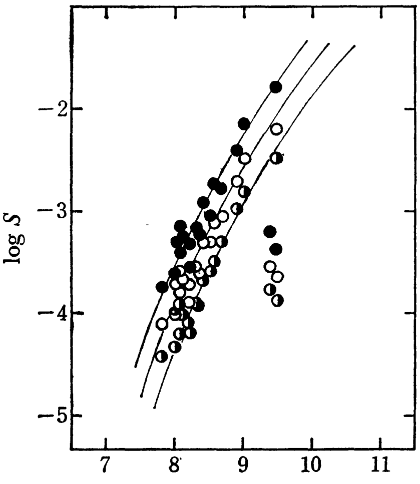
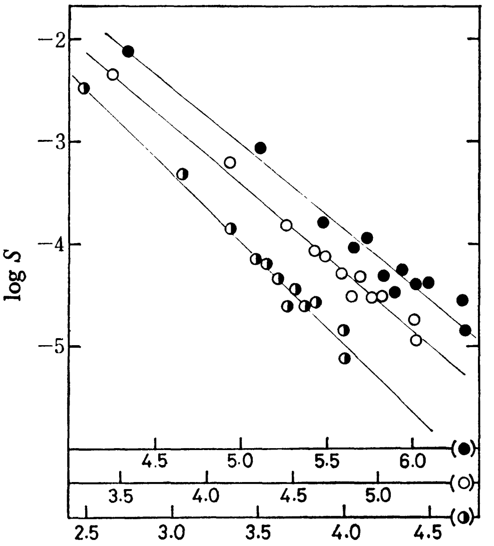
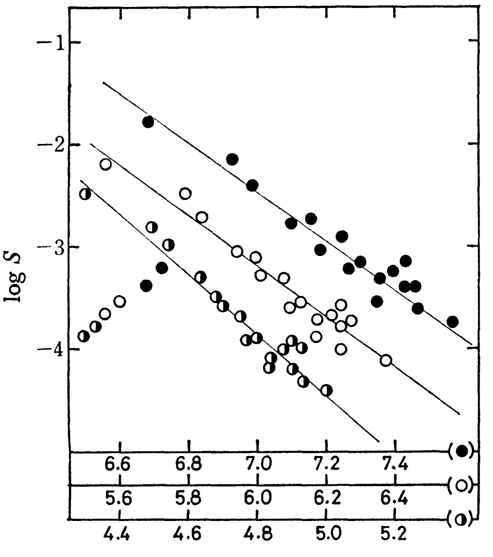


Fig. 2. The relation between log S and δ_2 in ester system.
(●): K-Pic, (○): Rb-Pic, (◑): Cs-Pic



$(\delta_1-\delta_2)^2\times 10^{-2}$

Fig. 3. The relation between log S and $(\delta_1-\delta_2)^2$ in alcohol system.
(●): K-Pic, (○): Rb-Pic, (◑): Cs-Pic



$(\delta_1-\delta_2)^2\times 10^{-2}$

Fig. 4. The relation between log S and $(\delta_1-\delta_2)^2$ in ester sytem.
(●): K-Pic, (○): Rb-Pic, (◑): Cs-Pic

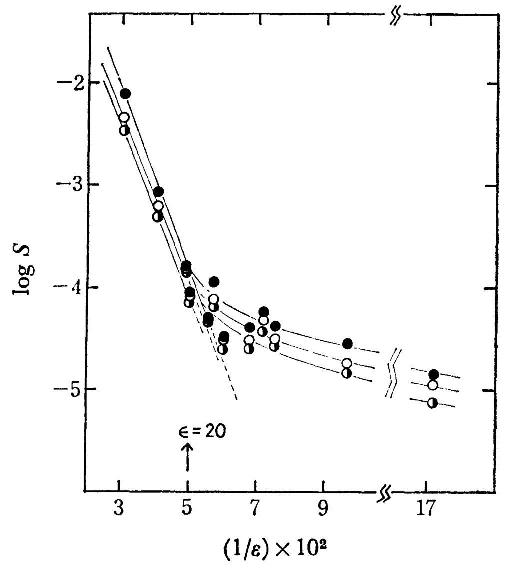


Fig. 5. The relation between log S and $1/\varepsilon$ in alcohol system.
(●): K-Pic, (○): Rb-Pic, (◑): Cs-Pic

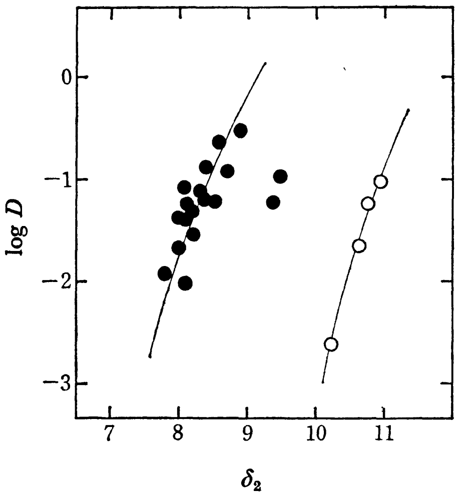


Fig. 6. The relation between log D and δ_2.
(○): alcohols, (●): esters

Relation between log S and 1/ε. In Fig. 5, for the sake of comparison one example of the plots between log S and the reciprocal of the dielectric constants ($1/\varepsilon$) of the solvents is shown in the alcohol system. Although a fairly good correlation is observed in the range of high dielectric constants ($\varepsilon \geqq 20$), no lenear relationship holds in the range of low dielectric constants. The same pattern was also obtained in the ester system.

Relation between log D and δ₂. In Fig. 6, the logarithmic distribution ratios (log D) are plotted against the δ_2 values of the extraction solvents. The deviations of the solubility parameters, which are caused by the mutual solubilities of the two phases, are not taken into account here. However, it can be concluded that fairly good correlations hold between log D and δ_2.

Conclusion

In the ion-pair system whose cation and anion are bulky and possess quite a low charge density, the solubilities and the distribution ratios may both be predicted from the δ_2 values of the solvents, so long as one sort of solvent is used. However, no clear discussion with respect to the slopes of the plots is developed here because of the lack of data.

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