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The Application of the Regular Solution Theory to the Ion-pair Systems

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Synopsis. The solubilities of these ion-pairs, KCl, KBr, and KI, were measured in alcohols. The logarithmic solubilities could be well correlated with the solubility parameters of the solvents.

In the previous paper,[1] the solubilities of such ion-pairs as chloride, perchlorate, and tetraphenylborate salts of alkali metals and Ru(II)(phen)$_3$ could be well correlated to the solubility parameters of solvents.

In this study, the solubilities of the typical ion-pairs, KCl, KBr, and KI, were measured in alcohols. By using the solubility parameters of the ion-pairs (δ_1) calculated from the lattice energies of the ionic crystals, a better application of the regular solution theory to the ion-pair systems will be suggested.

Experimental

All the reagents used here were purchased as reagent-grade pure. The alcohols were purified by distillation as has been described before.[1] The solubility measurements were performed gravimetrically at 25 °C in a fashion similar to that previously described.[1]

Results and Discussion

The solubilities of KCl, KBr, and KI in alcohols are shown in Fig. 1 as a function of the solubility parameters of the solvents (δ_2), which were calculated according to Eq. (1) by using the heat of vaporization at 25 °C (ΔH_{25}) cited from the literature.[2)]

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

Although smooth correlations are obtained between the solubilities of the ion-pairs and δ_2, a slight bending is observed for all the systems, as is shown in Fig. 1.

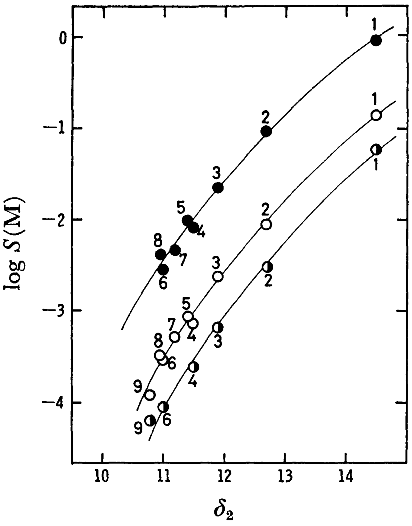

Fig. 1. The relation between log S and δ_2.
In all the figures, (◑): KCl, (○): KBr, (●): KI
(1): methanol, (2): ethanol, (3): 1-propanol, (4): 2-propanol, (5): 1-butanol, (6): 2-butanol, (7): isobutyl acohol, (8): 1-amyl alcohol, (9): isoamyl alcohol

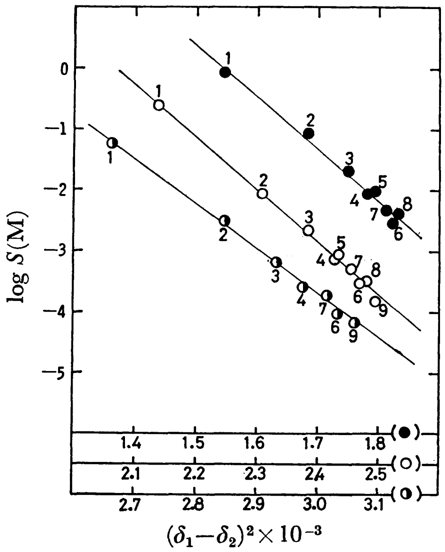

Fig. 2. The relation between log S and $(\delta_1-\delta_2)^2$

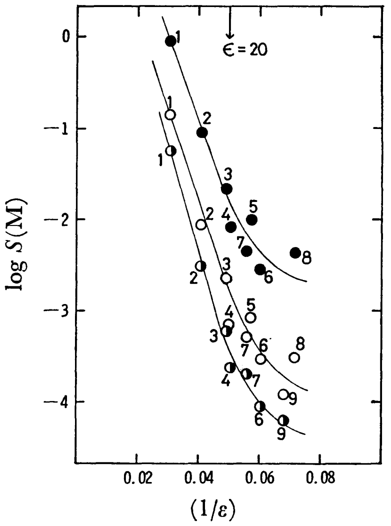

Fig. 3. The relation between log S and $1/\varepsilon$

TABLE 1. THE CALCULATED δ_1 VALUES OF ION-PAIRS

	r_c+r_a (Å)	U (kcal/mol)	V (ml^3)	δ_1
KCl	3.14	162.78	37.29	66.11
KBr	3.28	156.64	42.50	60.75
KI	3.49	148.25	51.20	53.76

Therefore, the solubility parameters of the ion-pairs (δ_l) were estimated from the square root of the lattice energy density, $(U/V)^{1/2}$, where the lattice energy, U, was approximated from Eq. (2), which was derived by Kapustinskii,[3] and the molar volume, V, from Eq. (3):

$$U = 574.4\left(\frac{z_1 z_2}{r_c + r_a}\right)\left(1 - \frac{0.345}{r_c + r_a}\right) \tag{2}$$

$$V = 2N(r_c + r_a)^3 \tag{3}$$

where r_c and r_a refer to the ionic radii of the cation and the anion respectively at the sixth coordination, and N, the Avogadro's number. In Table 1, the calculated values are shown. The relations between the logarithmic solubilities ($\log S$) and $(\delta_1 - \delta_2)^2$ are demonstrated in Fig. 2. As is shown in Fig. 2, these plots give an excellent straight line.

In Fig. 3, the plots between $\log S$ and the reciprocal of the dielectric constants ($1/\varepsilon$) are shown for comparison. Although a fairly good correlation is observed in the range of high polarity, no relationship holds in the low-polarity range.

In conclusion, the regular solution theory could be applied to the ion-pair systems by estimating the δ_1 values from the lattice energies of the ionic crystal. However, the slopes of the plots could not be discussed here because of the lack of data.

References

1) T. Takamatsu, This Bulletin, **47**, 1285 (1974).

2) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry, 2, Organic Solvents," Wiley-Interscience, New York (1970).

3) R. B. Heslop and P. L. Robinson, "Inorganic Chemistry," Elsevier Publishing Co., Amsterdam (1960), p. 92.