Equilibrium Composition of 1-Butanol-Water-Alkali Hydroxide System and Distribution of the Base

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Equilibrium compositions of 1-butanol–water–MOH systems were studied at 25 °C, where MOH represents LiOH, NaOH, and KOH. Water and 1-butanol were determined by means of gas chromatography and the bases by titration. Apparent distribution ratio K_{obs} (molality of MOH in the aqueous phase/molality of MOH in the 1-butanol phase) was dependent on the concentration of base. A considerable amount of water was transferred from 1-butanol to the aqueous phase giving rise to an increase of base concentration. This suggests that the variation of K_{obs} depends principally on the variation of solvent composition. K_{obs} was expressed semi-empirically, considering the activity coefficients calculated by Miller's equation and also the change in the standard free energy resulting from the variation in solvent composition. Decrease of 1-butanol in the aqueous phase with the base concentration obeyed the salting-out equation. The calculated salting-out coefficients were: LiOH 0.176, NaOH 0.192, and KOH 0.184. These values are correlated to Gurney's unitary entropy. The results were compared with those previously obtained for alkali halides.

Solvent extraction of inorganic species was reviewed by Marcus,[1] a good summary being given by Marcus and Kartes.[2] There are a few theoretical treatments on extraction including a thermodynamical treatment by Dyrssen *et al.*[3] and Friedman and Haugen,[4] and a regular solution treatment by Skytte-Jensen.[5]

The authors investigated the change of solvent composition with salt concentration for the distribution of alkali halides between the 1-butanol and aqueous phases at atmospheric pressure and room temperature.[6-10] The relation between solvent composition and distribution ratio or salting-out coefficient was described. It was found that the changes in distribution ratio accompanied by the change of solvent composition could be classified into two groups; one showing a decrease of distribution ratio with an increase of salt concentration and the other an increase of distribution ratio. The greater the change of distribution ratio, the greater the change of solvent composition. Namely, the water transfer from 1-butanol to the aqueous phase increased with an increase of salt concentration. As to 1-butanol, the increase of it in the 1-butanol phase and the decrease in the aqueous phase were observed.

A semi-empirical treatment of distribution was made by using Miller's equation for the activity coefficient and also by assuming that the standard free energy depends linearly on the mole fraction of water in the 1-butanol phase.[9] It was found that the decrease of 1-butanol in the aqueous phase is represented by the salting-out equation, the decrease being correlated to Gurney's unitary partial molar entropy.[10] This study was undertaken to examine the applicability of the above treatment to the 1-butanol–water–alkali hydroxide systems.

Experimental

Reagents. *Lithium Hydroxide, Sodium Hydroxide, Potassium Hydroxide, and 1-Butanol*: Chemicals of reagent grade were used without purification. Conductivity water was prepared by passing distilled water through a mixed bed of ion exchange resins. The specific conductance was less than 2×10^{-7} ohm^{-1} cm^{-1}.

Procedure. 100 ml of aqueous and 1-butanol solutions of known composition were shaken mechanically in a thermostat for one hour at 25±0.1 °C and then let to stand in the thermostat for one hour. Distribution equilibrium was reached within 15 min. A portion of each solution was taken for analysis.

Analysis. The method has been described.[7] Solvents were analyzed by gas chromatography, and alkali hydroxide by titration with standard hydrochloric acid using phenolphthalein. A mean of three determinations was taken. The solvent was separated from the base by vacuum distillation for avoiding attachment of the base to gas chromatography detector. *t*-Butanol was added to the sample, separated into two phases on removal of base in order to bring about a single phase. Analysis was then carried out. For molality and wt % calculation, density of the solution was determined with a pycnometer (10 ml).

Various stationary liquids for analyzing a water–alcohol mixture have been reported.[11] We found that cetyl alcohol containing a small amount of triethanol amine gave a satisfactory result. The packing column had a support with 60—80 mesh cellite containing stationary liquid (20 wt%). The column was 100 cm long and made of a ϕ 6 mm stainless steel tube bent into a U shape. This was installed in a HITACHI KGL-2A type gas chromatography apparatus equipped with a thermal conductivity detector. Conditions of operation were: Column temperature 95 °C, carrier gas

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[1] Y. Marcus, *Chem. Rev.*, **62**, 139 (1963).

[2] Y. Marcus and A. S. Kertes ,"Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience (1969), p. 575.

[3] D. Dyrssen, J. O. Liljenzin, and J. Rydberg, "Solvent Extraction Chemistry," North-Holland Publishing Company (1967), p. 195.

[4] H. L. Friedman and G. R. Haugen, *J. Amer. Chem. Soc.*, **76**, 2060 (1954); H. L. Friedman, *J. Phys. Chem.*, **59**, 161 (1955); H. L. Friedman and G. R. Haugen, *ibid.*, **67**, 1757 (1963).

[5] Ref. 2, p. 517.

[6] N. Yui, Y. Kurokawa, Y. Takamura, and M. Maeda, *Nippon Kagaku Zasshi*, **87**, 1138, 1143 (1966).

[7] N. Yui, Y. Kurokawa, and Y. Otomo, *ibid.*, **88**, 273 (1967).

[8] N. Yui, Y. Kurokawa, M. Sono, and T. Hiramoto, *ibid.*, **89**, 483 (1968).

[9] N. Yui and Y. Kurokawa, *ibid.*, **89**, 487 (1968).

[10] N. Yui and Y. Kurokawa, *ibid.*, **88**, 276 (1967).

[11] S. Musha and T. Nishimura, *Bunseki Kagaku*, **14**, 803 (1965); W. T. Casazza and R. J. Stelenkamp, *J. Gas Chromatog.*, **3**, (8), 253 (1965).

(He) flow rate 50 ml/min, bridge current 180 mA and output signal 16 mV. A peak ratio was adopted for the analysis, since a linear relation holds between the peak ratio of solvent and its weight ratio, when the peak of 1-butanol is kept constant. A different method was used for the analysis of the aqueous phase to avoid tailing of the water peak. Weighed toluene and sodium chloride as salting-out agent were added to a weighed sample with shaking, causing the separation into two layers. The toluene phase containing the salted-out 1-butanol was analyzed by gas chromatography. Water was determined by subtracting the amounts of solute and 1-butanol from the total amount.

Results and Discussion

Mutual solubilities of the 1-butanol–water system in the absence of alkali hydroxide are given in Table 1.

Table 1. Mutual solubilities of 1-butanol and water at 25 °C

	Aqueous phase	1-Butanol phase
Water	92.69 (98.12)	20.36 (51.24)
1-Butanol	7.31 (1.88)	79.64 (48.76)

wt% (mol %)

Our result is consistent with those of Butler *et al.*,[12] and Hill and Malisoff.[13] The equilibrium composition of the system in the presence of alkali hydroxide is given in Tables 2—4, where *m* denotes molality, suffixes *a* and *b* indicate the aqueous and 1-butanol phases, respectively. The apparent distribution ratio K_{obs} is defined by $m_{\text{a}}/m_{\text{b}}$. Its determination is restricted to the system in the liquid-liquid distribution region. No determination was carried out in the vicinity of saturated solution and in higher concentration of lithium hydroxide for the sake of precision (particularly aqueous phase). We see that as the base concentration increases, in the 1-butanol phase the amount of water decreases and that of 1-butanol increases, and in the aqueous phase 1-butanol decreases. The behavior of each base shows the same trend as in the case of alkali halides.[6-8]

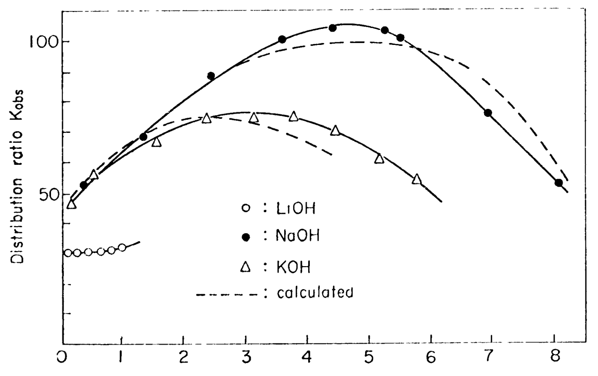

Fig. 1. Distribution ratio of base *vs.* molality in the aqueous phase at 25 °C.

The plots of K_{obs} against m_{a} are shown in Fig. 1. The distribution ratio of lithium hydroxide is almost constant at 31—33. At a higher concentration the same behavior as in sodium hydroxide and potassium hydroxide is expected. The ratios for sodium hydroxide and potassium hydroxide reach maximum at around 5 m_{a} and 3 m_{a} respectively, and then decrease. With the increase of base concentration the base tends to go into the 1-butanol phase. At a low concentration, the base might undergo primary solvation with water molecules even in the 1-butanol phase and secondary solvation with 1-butanol or more water molecules through primary solvation shell. The hydrated base may form bonds with an appreciable portion of 1-butanol molecules and the butanol phase loses its availability for extracting more base. Thus K_{obs} increases with the increase of base concentration. However, at a higher concentration any change in solvation and increase of ionic association might occur. The base might undergo primary solvation with both water and 1-butanol molecules, and is extracted to a greater extent into the 1-butanol phase, making K_{obs} decrease. The m_{a} at the maximum of K_{obs} is not identical with m_{a} at the minimum of activity coefficient in the aqueous phase.[14] A ternary diagram for the 1-butanol–water–sodium hydroxide system is given in Fig. 2. **A** indicates two liquid phases and one solid one, **B** one liquid and one solid phase in the aqueous region, **C** and **D** homogeneous phases. Oblique lines are the tie lines and the region is the range of separation of two liquids. An exact comparison of the results with the iso-butanol–water–sodium hydroxide system by Fritzche can no tbe made, but they seem to show a similar trend.[15]

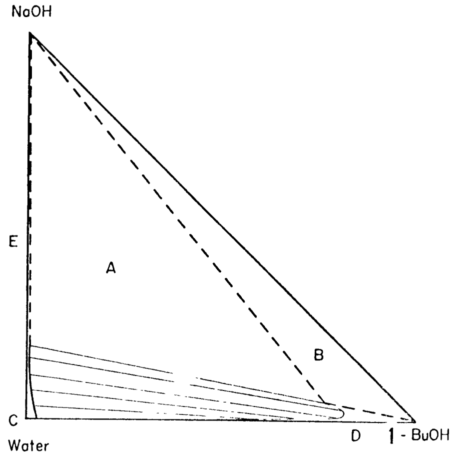

Fig. 2. Ternary diagram for 1-butanol–water–NaOH system at 25 °C, mol %.

The amounts of transfer of 1-butanol and water were determined. 50 mol of 1-butanol and 100 mol of water were taken. Alkali hydroxide was added to the latter and the resulting change of distribution of solvents between the two phases was determined. The result

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[12] J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, *J. Chem. Soc.*, **1933**, 674.

[13] A. E. Hill and W. M. Malisoff, *J. Amer. Chem. Soc.*, **48**, 918 (1926).

[14] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solution," Reinhold Publishing Co. (1964), pp. 498, 161.

[15] R. H. Fritzche and D. L. Stockton, *Ind. Eng. Chem.*, **38**, 737 (1946); H. Stephen and T. Stephen, "Solubilities of Inorganic and Organic Compounds Vol. 2," Pergamon Press (1964), pp. 85, 86.

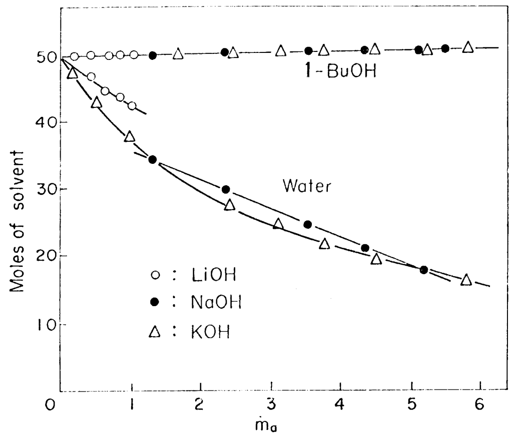

Fig. 3. The change of solvent with base concentration for the butanol phase.

of calculation is shown in Fig. 3. The number of moles of 1-butanol in the 1-butanol phase 49 is almost constant, but transfer of a greater amount of water took place from 1-butanol to the aqueous phase. The decrease of 1-butanol in the aqueous phase appears to be due to the salting-out effect but can not be attributed apparently to the salting-out effect.

Distribution Ratio. Alkali halides can be classified into two groups according to their distribution ratio between 1-butanol and water phases: (a) chlorides, fluorides and bromides which show a significant variation of ratio with the salt concentration, and (b) iodides which show no variation.[9] A semi-empirical treatment was made by assuming that the standard free energy of salt changes linearly with the mole fraction of water in the 1-butanol phase and Miller's equation is applicable to the calculation of activity coefficient. A reasonable agreement was obtained between calculated and observed values. Assuming the equilibrium in which electrolyte is completely dissociated in 1-butanol phase and also in the aqueous phase, we obtain

$$M_b^+ + OH_b^- \overset{K}{=} M_a^+ + OH_a^- \tag{1}$$

where the subscripts a and b refer to the aqueous and 1-butanol phases, respectively. Thus, the equilibrium constant K is obtained as

$$K = \frac{a_a{}^+ \cdot a_a{}^-}{a_b{}^+ \cdot a_b{}^-} = \frac{(\gamma_\pm)_a{}^2}{(\gamma_\pm)_b{}^2} K_{obs}^2 \tag{2}$$

where a: activity, γ: mean activity coefficient. It follows that

$$K_{obs} = \frac{(\gamma_\pm)_b}{(\gamma_\pm)_a} \exp\left\{\frac{(\mu_\pm^0)_a - (\mu_\pm^0)_b}{2RT}\right\} \tag{3}$$

where $\mu_\pm{}^\circ$: the standard free energy term in chemical potential. Thermodynamic relations have been derived for the distribution of salts between the two phases, assuming that the salts in the organic phase are completely associated. However, this is not always valid in the phase with higher dielectric constant or high water content. Hesford and Mckay reported that perchloric acid is largely ionized when extracted into TBP alone.[16] Conductivity measurements on the 1-butanol phase containing alkali halides indicate that the salts are appreciably dissociated.[17] Friedman and Haugen showed that alkali perchlorates are strong electrolytes in the nitromethane phase.[18]

The standard free energies of transfer of various alkali halides from 1-butanol to aqueous phase were calculated, by assuming Eq. (1) and by applying the modified Born's equation proposed by Stokes.[19] The distribution ratio is independent of the concentration of the salts only in the case of complete immiscibility of phases and non-existence of any interaction between the salts and solvents. Dependency of K_{obs} on concentration might result from variation of activity coefficients and that of solvent composition with salt concentration. Solvent composition changes considerably with the addition of alkali hydroxide (Tables 2—4). Identification of the butanol phase containing a large amount of salt with one containing no salt is no longer valid. We assume that the standard free energy term in chemical potential of salt changes linearly with the mole fraction of water in the 1-butanol phase. Thus

$$\{(\mu_\pm^0)_a - (\mu_\pm^0)_b\}/2RT = -A_1 N_b + A_2 \tag{4}$$

where N_b: mole fraction of water in the 1-butanol phase, A_1, A_2: adjustable parameters empirically determined. The variation of solvent composition in the aqueous phase which was considerably less than that

TABLE 2. LiOH–WATER–1-BUTANOL

1-Butanol phase				Aqueous phase				K_{obs} (m_a/m_b)
LiOH	m_b	Water	1-BuOH	LiOH	m_a	Water	1-BuOH	
0.02	(0.0037)	50.61	49.37	0.23	(0.122)	98.08	1.69	32.9
0.03	(0.0062)	49.99	49.98	0.36	(0.193)	98.02	1.62	31.2
0.06	(0.0130)	48.49	51.44	0.76	(0.407)	97.75	1.49	31.3
0.09	(0.0196)	47.07	52.84	1.15	(0.619)	97.45	1.40	31.6
0.12	(0.0256)	46.78	53.10	1.54	(0.838)	97.23	1.23	32.7
0.15	(0.0306)	45.94	53.91	1.88	(1.03)	97.00	1.12	33.6

Equilibrium composition (mol %) at 25°C, m in parenthesis is molality

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16) E. Hesford and H. A. C. Mckay, *J. Inorg. Nucl. Chem.*, **13**, 156 (1960).

17) M. Nakayama, Y. Kurokawa, and N. Yui, This Bulletin, **46**, 1027 (1973); Y. Kurokawa and N. Yui, *Technology Reports Tohoku Univ.*, **37**, 153 (1972).

18) H. L. Friedman and G. R. Haugen, *J. Amer. Chem. Soc.*, **76**, 2060 (1954).

19) Y. Kurokawa and N. Yui, *Nippon Kagaku Zasshi*, **87**, 1135 (1966).

Table 3. NaOH–water–1-butanol

1-Butanol phase				Aqueous phase				K_{obs}
NaOH	m_b	Water	1-BuOH	NaOH	m_a	Water	1-BuOH	(m_a/m_b)
0.03	(0.0052)	45.22	54.75	0.52	(0.276)	97.78	1.70	52.7
0.09	(0.0184)	40.78	59.13	2.27	(1.25)	96.80	0.93	68.1
0.13	(0.0258)	37.30	62.57	4.08	(2.32)	95.39	0.54	89.9
0.19	(0.0341)	32.82	66.99	5.94	(3.47)	93.74	0.32	102
0.23	(0.0403)	29.09	70.68	7.19	(4.27)	92.56	0.25	106
0.32	(0.0521)	24.37	75.32	8.88	(5.38)	90.94	0.17	103
0.54	(0.0854)	19.89	79.58	10.95	(6.80)	88.93	0.13	79.6
0.89	(0.1410)	18.43	80.68	12.66	(8.02)	87.23	0.11	56.9
2.11	(0.3480)	18.71	79.18	14.86	(9.65)	85.03	0.11	28.3
4.42	(0.7556)	22.09	73.50	16.68	(11.87)	83.22	0.10	14.7

Table 4. KOH–water–1-butanol

1-Butanol phase				Aqueous phase				K_{obs}
KOH	m_b	Water	1-BuOH	KOH	m_a	Water	1-BuOH	(m_a/m_b)
0.01	(0.0029)	48.95	51.03	0.27	(0.142)	98.10	1.63	49.0
0.04	(0.0082)	46.23	53.73	0.86	(0.464)	97.77	1.36	56.6
0.08	(0.0153)	42.80	57.12	1.68	(0.918)	97.27	1.05	60.0
0.12	(0.0238)	46.11	59.77	2.87	(1.59)	96.35	0.78	67.0
0.18	(0.0327)	35.32	64.51	4.20	(2.39)	95.22	0.58	73.1
0.23	(0.0412)	32.81	66.96	5.30	(3.06)	94.26	0.44	74.3
0.29	(0.0502)	29.28	70.43	6.35	(3.73)	93.32	0.33	74.2
0.37	(0.0637)	27.80	71.83	7.46	(4.44)	92.27	0.27	69.7
0.48	(0.0820)	26.24	73.27	8.48	(5.08)	91.13	0.39	61.9
0.63	(0.105)	24.15	75.21	9.45	(5.75)	90.33	0.22	54.6

in the 1-butanol was neglected. Dielectric constants of the 1-butanol phase change a great deal with the presence of water. These values for the calculation of the theoretical slope were estimated from those for pure water and 1-butanol assuming that the dielectric constant of the 1-butanol–water mixture is given by a linear function of the weight fraction analogous with the behavior of ethanol–water mixture.

Of the theories on the activity coefficient of salt, those of Robinson-Stokes[20] and Miller[21] are useful. Miller's theory has no solvent activity term, and is convenient for computation. He derived an equation for the molality activity coefficient in terms of the hydration number n and ion size a. We assumed that the ions solvate water molecules selectively, both in the 1-butanol and aqueous phases. Thus, for calculation of γ in the two phases, the hydration number and ion size parameters given by Miller[21] were used. Water molecules are much smaller in size than 1-butanol molecules in the solution. More water than 1-butanol dipoles can pack around a cation to form its primary solvation shell.[22] Thus, the energy of the primary solvation by water is greater than that of 1-butanol. This means that the cation carries its primary water shell with it, and then in the 1-butanol phase undergoes further solvation of the hydrated species by 1-butanol. The following semi-empirical equations were obtained for K_{obs} as

$$\text{NaOH: } K_{obs} = (\gamma_\pm)_b/(\gamma_\pm)_a \exp(-6.60N_b+7.30) \qquad (5)$$

$$\text{KOH: } K_{obs} = (\gamma_\pm)_b/(\gamma_\pm)_a \exp(-9.34N_b+8.45) \qquad (6)$$

The values obtained by means of these equations are given in Fig. 1. The agreement between the calculated and observed values is reasonable. Parameters A_1 and A_2 were determined to fit K_{obs} by combining Eqs. (3) and (4). Theoretically, A_1 should be equivalent to A_2. However, it is not as is evident from the calculation for alkali halides.[9] The errors resulting from the calculation of activity coefficient and the inadequacy of assumption at high concentration are included in A_1 and A_2. This treatment might not be always applicable to other extraction systems. But it is thought to be advisable to investigate the treatment of the two liquid phase system accompaning a great change of solvent composition.

Salting-out Coefficient. The decrease of 1-butanol in the aqueous phase by the addition of salt follows the Setchenow equation[23,24]

$$\log f = \log S^0/S = kc \qquad (7)^{25)}$$

where f is the activity coefficient of non-electrolyte, S^0 and S are the solubility of non-electrolyte in pure water (mol/l) and in salt solution (mol/l), respectively, k is the salting-out coefficient and c is the concentration

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[20] R. H. Stokes and R. A. Robinson, *J. Amer. Chem. Soc.*, **70**, 1870 (1948).

[21] D. G. Miller, *J. Phys. Chem.*, **60**, 1296 (1956).

[22] R. M. Diamond, *ibid.*, **63**, 659 (1959).

[23] Ref. 14, p. 531.

[24] F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

[25] It is assumed that the activity coefficient of 1-butanol in a saturated aqueous solution is unity.

of salt in mol/l. In general, the salting-out effect is influenced by the kind of non-electrolyte, but not by concentration and temperature. The values of k determined by means of Eq. (7) are as follows: LiOH 0.176, NaOH 0.184, KOH 0.192. The data of alkali halides and alkali hydroxides are well represented by Eq. (7), and this linear relation holds up to the salt concentration of one mole. On comparing the coefficients of alkali hydroxides with those of alkali halides, we see that the values are larger found for the latter. The values of k decrease in the order $\mathrm{LiOH}<\mathrm{NaOH}<\mathrm{KOH}$, similar to that for alkali halides.[10] The above order is virtually the same for other non-electrolytes. In the case of alkali metal cations, the order of salting-out is generally $\mathrm{Cs}<\mathrm{Rb}\simeq\mathrm{Li}<\mathrm{K}<\mathrm{Na}$ and for the anion $\mathrm{I}<\mathrm{Br}<\mathrm{Cl}<\mathrm{F}$.[24] The small or highly charged ions which are strongly hydrated show a greater salt effect. There are, however, exceptions such as lithium and hydrogen ions. It is well-known that the tendency for complex ion formation between cation and non-electrolyte is greater for lithium ion.[26]

The relation of k to Gurney's unitary entropy will be discussed. The standard free energy change per mole for transfer of 1-butanol from a solution in pure water to one in which electrolyte is added is given by multiplying Eq. (7) by RT.[27] Combining the latter and the thermodynamic relation we have [10,27]

$$2.3kc = \Delta H/RT - \Delta S/R \tag{8}$$

where ΔH, temperature slope, is small and almost of the same order as for the alkali hydroxides and alkali halides studied, ΔS being dominant. Gurney succeeded in correlating many properties of electrolytes using the partial entropy of salts. He showed that entropy of salts in water contained a constant or a cratic term depending not on the species of particles but only on the number of particles that have been mixed.[28] Subtracting the cratic term 8 e.u. from the observed partial molal entropy, he obtained the values as a unitary term which should be characteristic of ion. Higgins correlated salting-out coefficient with unitary entropy, assuming that all the cations beyond lithium behaved as if they were protons.[5] However, his assumption appears to be oversimplified. Without using it we compared unitary entropies for salts against the corresponding salting-out coefficients and consequently obtained three linear relationships, Li, K, and an other ion group.[10] It is interesting to see to what extent our approach could be applied to the problem of alkali hydroxides. Considerable deviation from lineality were seen for hydroxides as shown in Fig. 4. This might be due to specific interaction between hydroxides and 1-butanol, and to significant difference between temperature effects on salting-out coefficients of alkali halides and alkali hydroxides. The situation may be more complicated than this classification implies.

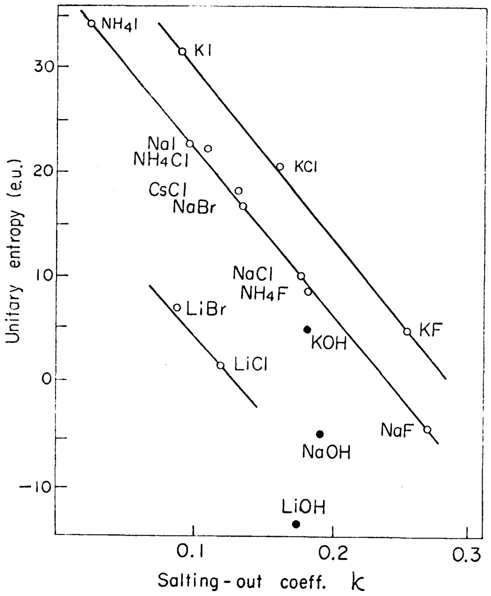

Fig. 4. Unitary entropies *vs.* salting-out coefficients at 25 °C

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26) E. E. Schrier and E. B. Schrier, *J. Phys. Chem.*, **71**, 1851 (1967).

27) C. E. Higgins, W. H. Boldwin, and B. A. Soldna, *ibid.*, **63**, 113, 118 (1959).

28) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc. (1953), pp. 89, 97.