The Use of Hydrotropic Solutions for Counter-Current Separations

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The selective dissolving properties of aqueous solutions of hydrotropically active salts* suggest their application as one of the phases in counter-current distribution. However, since hydrotropic activity parallels surface activity (1), such solutions emulsify on shaking with a second solvent; therefore, their use in classical counter-current distribution has been severely limited. Recently, a new variant of an apparatus was realised (2 and 3) following the original proposal of Signer et al. (4) in which shaking the phases is avoided. Such an apparatus has not yet been described in full detail†. In the present paper, the principle of this method will be explained together with an apparatus of our own construction.

A glass tube is separated into cells (see Figure 1) by the insertion of Teflon disks pierced by a small hole through the center. The more dense solvent which serves as the stationary phase is filled into the cells, its final level being lower than the central hole. The less dense solvent is pumped continuously into the first cell, filling it up to the central hole (the direction of flow is indicated by an arrow in Figure 1), and then passes through the hole to the second cell, to the third cell,

etc. Equilibration of the two phases is effected within each cell by rotating the glass tube about its central axis. This rotational movement mixes the two phases and continuously renews their contact surface, leading to equilibration times comparable to those obtained by shaking but without causing foaming. The upper phase is prevented from flowing from one cell to the next without effective mixing by the insertion of smoothly curved stainless steel plates; these also add to the efficiency of the equilibration by longitudinal mixing. Figure 2 shows the whole assembly, the operation of which is described in detail in the experimental part. Essentially, the eluent is pumped through a series of rotating tubes which are parted into cells (in this case, 8 tubes containing 650 cells).

For the application of solutions of hydrotropically active salts in counter-current distribution, a thorough knowledge of their dissolving properties against different classes of substances would be desirable. In the first treatment of hydrotropy, Neuberg (6) investigated the hydrotropic activity of several different salts on a variety of substances by looking at the saturation concentrations. This work only gives information about the solubility of

pure substances, thus taking the pure substance as standard state. More recently, Rath, Rau, and Wagner (1 and 7) investigated the dissolving power of many salts but on only one substance.

We have chosen as standard state the ideal diluted solution in a pure one-component non-polar system [non-polarity is defined as a non-polar substance being only a pure paraffin or mixture of paraffins, C_nH_{2n+2} (8 and 9)]. By equilibrating solutions of given substances in n-heptane with solutions of hydrotropically active salts, the partition coefficient clearly defines the chemical potential of the substance in the salt-solution with respect to the standard state in n-heptane. In

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*In the literature the terms "hydrotropes" and "hydrotropic substances" are used. The definition of a "hydrotrope" should then be: "a substance which changes the solvent properties of water," implying obviously all water soluble substances. We propose to drop these terms and to speak of the "hydrotropic activity" of a substance and of "hydrotropy" for the effect.

†Private communication from Prof. Dr. R. Signer: The apparatus used for separations in ref. (2) and (3) will be described in a forthcoming paper (5).

this way one can even examine substances which are completely miscible with both solvents.

It has been suggested that hydrotropic action arises mainly through interactions of polar parts of the solute with the organic ion of the salt (1 and 7). For this reason two neutral salts were selected, one having a negatively-charged organic ion — potassium-1-octylsulfonate, and the other having a positively-charged ion — trimethyl-1-octyl-ammoniumbromide. The organic part of each salt contains the same, non-polar octyl residue.

Figure 3 shows the logarithms of the partition coefficients K_c plotted against the percentage concentration (in g/100 ml) of the two salts, where K_c is defined in equation 1.

$$K_c = \frac{\text{conc. of the substance in heptane } (g.cm^{-3})}{\text{conc. of the substance in the salt sol. } (g.cm^{-3})}$$

Eq. 1

The same results are shown in Figure 4 but are expressed as K_x against molality, where K_x is defined in equation 2

$$K_x = \frac{\text{mole fraction of the substance in heptane}}{\text{mole fraction of the substance in the salt sol.}}$$
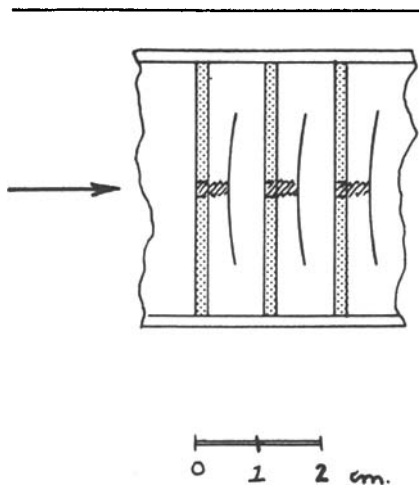
Eq. 2

Neither presentation suggests a

simple interpretation. At low salt concentrations the partition coefficients are more or less constant. For potassium-1-octylsulfonate at about 3% concentration and for trimethyl-1-octylammoniumbromide at 4% concentration, there is an apparent discontinuity in the shape of the curves. A hydrotropic action of the salts begins actually only at higher

concentrations. A possible explanation is that initially the very ordered structure of water is broken down.

In the two figures (3 and 4) the numbered curves belong to the homologuous series of primary alcohols (2:ethanol, 3:propanol, etc., up to 12:dodecanol). The alcohols have lower partition coefficients in

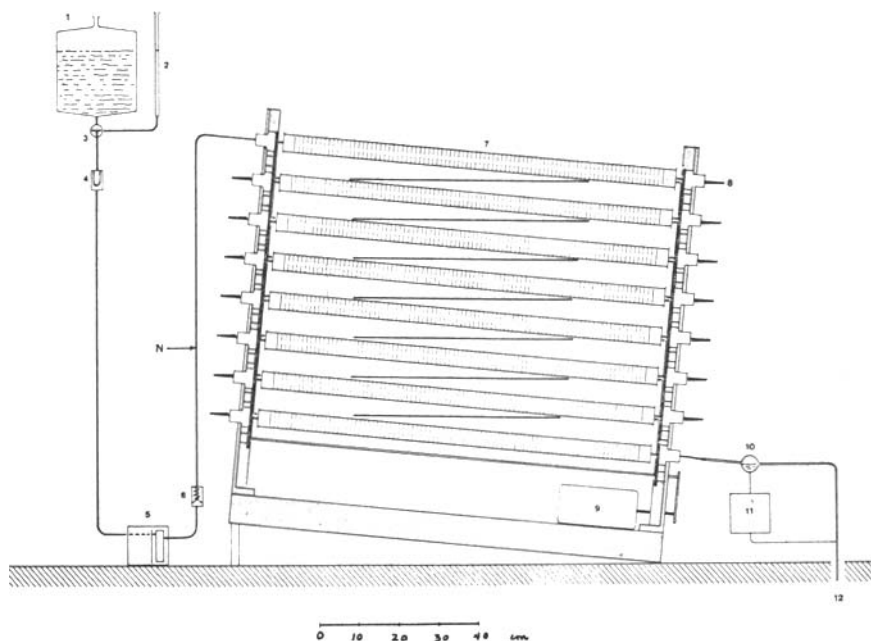Figure 2. Counter-current distribution apparatus showing rotating tube assembly and feed system.
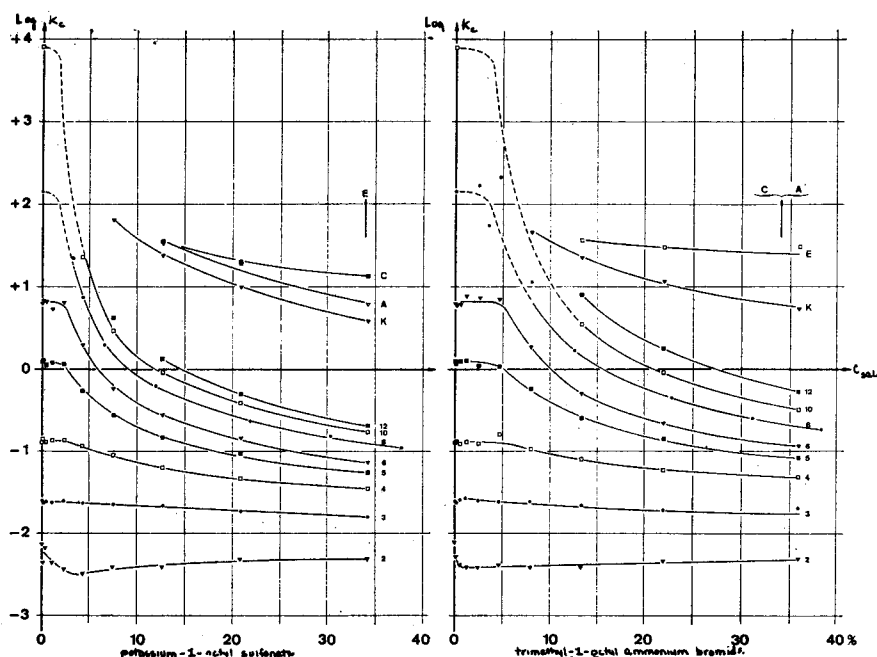
Figure 1. Sectional view of glass counter-current distribution tube showing individual cells.

Figure 3. Partition coefficients as a function of percentage composition.

the solutions of potassium-1-octylsulfonate compared with those of trimethyl-1-octylammoniumbromide. This supports the suggestion of Rath, et al. (7) that in the case of alcohols, one of the main solubilising effects is through hydrogen-bonding to the negatively-charged organic ion (in our case, of the 1-octylsulfonate ion).

Figure 5 shows the logarithms of K_x plotted against the carbon-numbers of the alcohols. This plot is linear for the distribution between heptane and pure water. However, in the case of the distribution between heptane and salt solutions, the lines are curved for the lower alcohols tending to linearity for the higher members, with decreasing slope for increasing concentration of the salt.

To detect further differences between the action of the two salts, four additional compounds of distinctly different types were investigated. These are indicated by capital letters in Figures 3 and 4 (A: 1-octylacetate, C: 1-chlorooctane, E: dipentylether, K: nonanone-(2)). The results for these compounds are difficult to rationalise in any simple scheme. For example, the ketone (K) has a relatively low partition coefficient in both salt solutions. The ether (E) has a preferential solubility in the cationic solvent. Thus, simple arguments might suggest that the acetate (A) which contains both ether and ketone functions should preferentially dissolve in the solutions of trimethyl-1-octylammoniumbromide. However, the contrary is the case.

The results of the present investigation show that the mechanism of hydrotropic action requires much more thorough examination. However, they also show that such solutions are capable of being used as stationary phases for counter-current distribution. The order of the elution would be non-polar substances and substances of low polarity (hydrocarbons), followed by more polar compounds (ethers, esters, aldehydes, ketones, etc.), and finally alcohols. In a homologous series the higher members are eluted first. Preliminary attempts to achieve separations using a solution of potassium-1-octylsulfonate as stationary phase in our counter-current apparatus are promising.

Experimental

Materials

Potassium-1-octylsulfonate was synthesised by the method of Backer (10). Octyl bromide (257 g, 1.33 mole) was heated with an aqueous solution of sodium sulfite (193 g sodium sulfite, 1.54 mole in 750 ml water) in a copper auto-clave at 170°C for 14 hrs. To the resulting hot reaction mixture, sodium chloride (200 g) was added. By cooling the solution the sulfonate could be obtained as a wet crust. The product was freed from water by pressing in a cloth, and the air-dried product was crystallised from absolute ethanol.

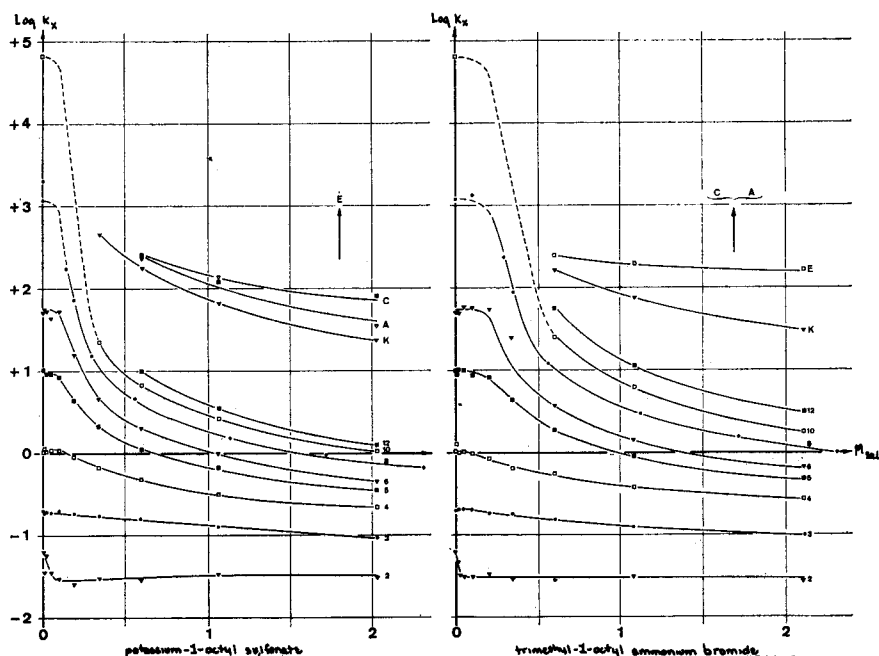An aqueous solution of the sodium sulfonate was filtered onto

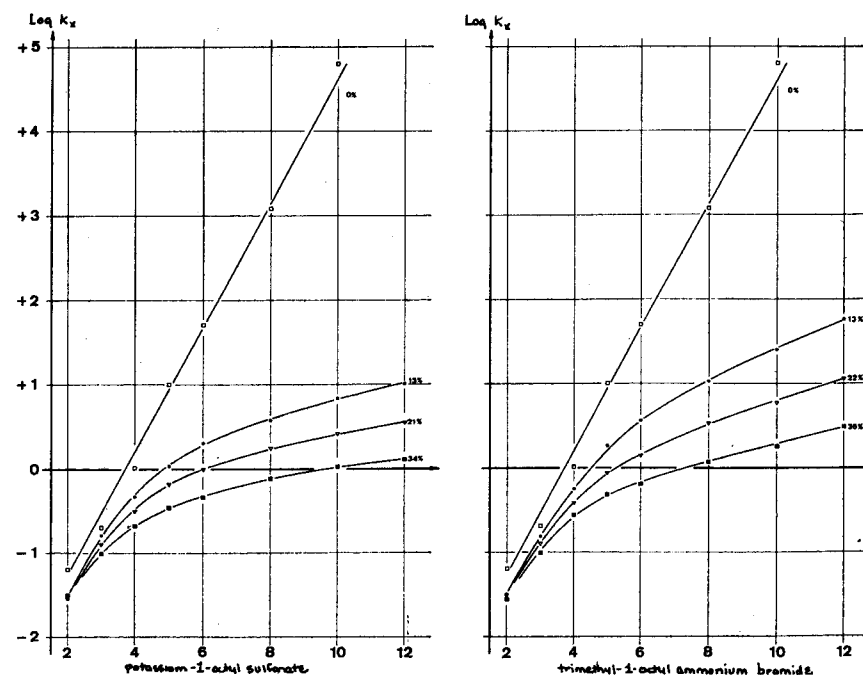Figure 4.   Partition coefficients as a function of molality.

Figure 5.   Partition coefficients as a function of the alcohol carbon number.

an ion exchange column (2000 g Dowex 50 W, 20-50 mesh, prepared as potassium salt). The resulting solution of the potassium sulfonate was evaporated to dryness and the solid product recrystallised from ethanol giving 227 g (75%) potassium-1-octylsulfonate as white crystals.

	C	H	K	
calc	41.35	7.38	16.83	%
found	41.26	7.18	16.85	%

Trimethyl-1-octylammoniumbromide: Octyl bromide (485 g, 2.51 mole) was mixed with trimethylamine (150 g, 2.54 mole) in a pressure flask and was allowed to stand for 72 hrs. at room temperature. The crude crystalline product was recrystallised from acetone giving 393 g (62%) trimethyl-1-octylammoniumbromide (m.p. 221/2°C).

	C	H	N	Br	
calc.	52.38	10.39	5.55	31.68	%
found	52.24	10.45	5.70	31.51	%

Properties of the aqueous solutions of the two salts

Solubility of potassium-1-octylsulfonate: Saturated solutions of this salt were gelatinous and a quantitative value of the saturation concentration could not be obtained. The solubility of the salt was certainly over 47% at 0° and 22°C.

Solubility of trimethyl-1-octylammoniumbromide: Nearly saturated solutions of the salt in water were saturated by pressing through a thermostatted column filled with pills of the salt. Five ml. of the eluent was evaporated to dryness and weighed. Table I shows the saturation concentrations and the densities at different temperatures.

Table I. Saturation concentrations and densities of trimethyl-1-octylammoniumbromide in water.

temp. (°C)	solubility g/100 g solution)	density (g.cm⁻³)
0	69.5	1.0867
5	68.7	1.0827
10	70.5	1.0827
15	70.7	1.0783
20	71.2	1.0746

Densities of aqueous solutions of the two salts: The densities of the solutions were determined in a pyknometer. Tables II and III show the experimental results.

Variance analysis of the results shown in Tables II and III resulted by proving the significance of P_C, P_{CC}, P_{CCC}, P_T, P_{TT}, $P_C P_T$, $P_C P_{TT}$ for potassium-1-octylsulfonate and P_C, P_T, P_{TT}, $P_C P_T$ for trimethyl-1-octylammoniumbromide at the 95% significance level (P_C, P_{CC}, P_{CCC} symbolizing the linear, quadratic, cubic, etc., orthogonal polynominals). Regression equations were calculated with the aid of the significant terms. They allow the calculation of the

Table II. Densities of aqueous solutions of potassium-1-octylsulfonate

concentration (g/g)	temperature (°C)			
	0	20	40	60
0	0.9999	0.9982	0.9922	0.9832
15	1.0426	1.0373	1.0281	1.0179
30	1.0731	1.0652	1.0547	1.0432
45	1.1121	1.1005	1.0888	1.0760

Table III. Densities of aqueous solutions of trimethyl-1-octylammoniumbromide

concentration (g/g)	temperature (°C)			
	0	20	40	60
0	0.9999	0.9982	0.9922	0.9827
16.7	1.0199	1.0147	1.0070	0.9965
33.3	1.0405	1.0327	1.0227	1.0102
50.0	1.0606	1.0492	1.0404	1.0266

Table IV. Concentrations of the aqueous solutions used of potassium-1-octylsulfonate at 20°C

g/g	g/cm³	cm³/cm³	$\frac{gmol}{gmol}$	$\frac{gmol}{g(H_2O)}$	$\frac{cm^3}{cm^3(H_2O)}$	gmol	g/cm³
$\frac{c'}{100}$	$\frac{c}{100}$	$\frac{\alpha}{100}$	$\frac{x}{100}$	$\frac{m}{1000}$	$\frac{\beta}{1000}$	M	d_{20}
0.0000	0.0000	0.0000	0.0000	0.00000	0.000	18.016	0.9982
0.0953	0.0952	0.0635	0.0073	0.00410	0.635	18.031	0.9989
0.4322	0.4322	0.292	0.0336	0.01867	2.928	18.088	1.0001
1.1201	1.1227	0.768	0.0877	0.04874	7.739	18.204	1.0023
2.317	2.330	1.627	0.1835	0.10206	16.539	18.409	1.0060
3.199	3.227	2.285	0.2555	0.14221	23.384	18.564	1.0087
4.269	4.319	3.110	0.3445	0.19189	32.098	18.755	1.0118
6.493	6.609	4.904	0.5354	0.29880	51.569	19.164	1.0178
7.353	7.501	5.633	0.6115	0.34152	59.692	19.327	1.0201
11.527	11.872	9.284	1.0000	0.56065	102.341	20.160	1.0299
12.184	12.567	9.877	1.0632	0.59703	109.595	20.297	1.0314
19.802	20.725	17.014	1.8782	1.06250	205.023	22.042	1.0466
20.839	21.850	17.961	2.0000	1.13279	218.932	22.304	1.0485
28.517	30.216	24.928	3.0000	1.71666	332.055	24.447	1.0626
32.023	34.245	28.047	3.5234	2.02713	389.796	25.569	1.0694
34.958	37.601	30.532	4.0000	2.31278	439.512	26.591	1.0756

density between the experimental limits. The densities as a function of the linear orthogonal polynomials are as follows:

for potassium-1-octylsulfonate:
$$d = 1.04677 + 0.02621\,P_C$$
$$- 0.00070\,P^2_C + 0.00304\,P^3_C$$
$$- 0.00899\,P_T - 0.00106\,P^2_T$$
$$- 0.00209\,P_C P_T$$
$$+ 0.00049\,P_C P^2_T$$

$$\text{Eq. 3}$$

where

$P_C =$	−1.5	−0.5	+0.5	+1.5

| $c' =$ %(g/g) | 0 | 15 | 30 | 45 |

| $P_T =$ | −1.5 | −0.5 | +0.5 | +1.5 |

| $T =$ (°C) | 0 | 20 | 40 | 60 |

for trimethyl-1-octylammoniumbromide:

$$d = 1.01996 + 0.01699\,P_C$$
$$- 0.00868\,P_T - 0.00126\,P^2_T$$
$$- 0.00183\,P_C P_T$$

$$\text{Eq. 4}$$

where

$P_0 =$	−1.5	−0.5	+0.5	+1.5

| $c' =$ %(g/g) | 0 | 16.7 | 33.3 | 50.0 |

| $P_T =$ | −1.5 | −0.5 | +0.5 | +1.5 |

| $T =$ (°C) | 0 | 20 | 40 | 60 |

Concentration data

Knowing the density and the molecular weights, the concentration data in different dimensions can be interconverted. Table IV and V show the interconverted data for the solutions used at 20°C. They were calculated as follows:

c' ($g_{salt}/g_{solution}$): Solutions were prepared by weighing the salt and the water. This concentration is independent of temperature.

Figure 6. Small stoppered glass tube used for equilibration of n-heptane and salt solutions.

c ($g_{salt}/cm^3_{solution}$): $c = c' \cdot d_{20}$

$$\text{Eq. 5}$$

α ($cm^3_{salt}/cm^3_{solution}$): From the density determinations the specific volume $V = 1/d$ can be calculated. The partial volume of the salt which satisfies (6)

$$V = c \cdot V_{salt} + (1 - c) \cdot V_{H2O}$$

$$\text{Eq. 6}$$

can easily be calculated with the aid of the equation 7

$$V_{salt} = V - c' \; (\partial V/\partial c')$$

$$\text{Eq. 7}$$

The volume fraction is then given by

$$\alpha = c \cdot V_{salt}$$

$$\text{Eq. 8}$$

x (g $mole_{salt}$/g $mole_{solution}$): For the mixture of the components a mean molecular weight can be defined which in our case is as follows:

$$\frac{1}{M_{solution}} = \frac{c'_{salt}}{M_{salt}} + \frac{1 - c'_{salt}}{M_{H2O}}$$

$$\text{Eq. 9}$$

Table V. Concentrations of the aqueous solutions used of trimethyl-1-octylammoniumbromide at 20°C

g/g	g/cm³	cm³/cm³	gmol gmol	gmol g(H₂O)	cm³ cm³(H₂O)	gmol	g/cm³
$\dfrac{c'}{100}$	$\dfrac{c}{100}$	$\dfrac{\alpha}{100}$	$\dfrac{x}{100}$	$\dfrac{m}{1000}$	$\dfrac{\beta}{1000}$	M	d_{20}
0.0000	0.0000	0.0000	0.0000	0.00000	0.000	18.016	0.9982
0.1034	0.1031	0.0948	0.0074	0.00410	0.949	18.033	0.9972
0.4692	0.4681	0.431	0.0337	0.01869	4.329	18.095	0.9976
1.2158	1.2139	1.116	0.0878	0.04879	11.286	18.222	0.9984
2.515	2.514	2.306	0.1839	0.10227	23.604	18.447	0.9998
3.501	3.504	3.210	0.2584	0.14383	33.165	18.621	1.0009
4.634	4.644	4.245	0.3458	0.19263	44.332	18.826	1.0021
6.801	6.831	6.223	0.5185	0.28928	66.360	19.230	1.0044
7.981	8.026	7.300	0.6156	0.34383	78.749	19.458	1.0057
12.404	12.533	11.346	1.0012	0.56136	127.981	20.361	1.0104
13.225	13.374	12.097	1.0768	0.60417	137.618	20.538	1.0113
21.493	21.927	19.734	1.9178	1.08530	245.858	22.508	1.0202
22.200	22.664	20.398	1.9972	1.13120	256.245	22.694	1.0209
30.192	31.083	27.944	2.9964	1.71455	387.809	25.035	1.0295
34.759	35.955	32.323	3.6656	2.11208	477.607	26.602	1.0344
36.799	38.146	34.331	3.9925	2.30821	522.789	27.368	1.0366

Table IVa. Concentrations of the substances and markers in n-heptane

substance	concentration (g/100 cm³_sol)	(gmol/l_sol)	marker	concentration (g/100_sol)
ethanol	4.622	1.0	hexane	0.470
propanol-(1)	1.207	0.2	hexane	0.492
butanol-(1)	1.479	0.2	undecane	0.490
pentanol-(1)	1.770	0.2	decane	0.490
hexanol-(1)	2.040	0.2	undecane	0.488
octanol-(1)	2.603	0.2	decane	1.452
decanol-(1)	3.160	0.2	undecane	0.962
dodecanol-(1)	3.720	0.2	tridecane	0.956
dipentylether	3.171	0.2	undecane	1.439
1-chlorooctane	2.980	0.2	undecane	1.449
1-acetoxyoctane	3.458	0.2	dodecane	1.441
nonanone-(2)	2.852	0.2	undecane	1.448

where M's represent molecular weights. The mean molecular weight allows then calculation of the "g moles of the solution."

$$\eta_{solution} = \eta_{salt} + \eta_{H2O} = \frac{w_{solution}}{M_{solution}}$$
Eq. 10

where w is the weight. The mean molecular weights are given in Table IV and V. Knowing the mean molecular weight, the mole fraction of the solution is given by (11)

$$x_{salt} = \frac{c' \cdot M_{soluiton}}{M_{salt}}$$
Eq. 11

m (g $mole_{salt}/cm^3_{H2O}$): The molality of the salt can be calculated as

$$m = M_{salt} \cdot c'/(1 - c')$$
Eq. 12

β (cm^3_{salt}/cm^3_{H2O}): The volume ratio is defined by (13)

$$\beta = (cV_{salt})/[(1 - c) \cdot V_{H2O}]$$
Eq. 13

and can easily be calculated if the function α is known and is given by

$$\beta = \alpha/(1 - \alpha)$$
Eq. 14

Determination of the partition coefficients

Equilibration of the two phases: The substance to be examined was dissolved in the organic phase (n-heptane). 1 ml of this solution of known concentration was placed in a small glass tube (Figure 6), and 1 ml of the salt solution was added together with a small nickel ball. The tube was closed and fixed on an axis which was moving with a rocking motion with a period of 4 RPM under thermostatted water (20.0°C). Thus, the two phases passed over each other and in addition were mixed by the falling movement of the nickel ball.

Experiments have shown that the kinetics of the substance transport from one phase to the other had a half-life of about 20 sec. For security the two phases were equilibrated for 30 min. Finally, the tube was quickly centrifuged at room temperature, and a small part of the heptane phase was taken for gas chromatographic analysis.

Gas chromatographic analysis: All the substances investigated were chosen to be volatile for rapid concentration determination by gas chromatography. In the hydrotropic solutions used, the n-paraffins were practically insoluble. Experiments with n-decane have shown that the partition coefficient of this substance is certainly higher than 1000. Thus, these substances can be used as markers, assuming their concentrations are unchanged during the equilibration experiment. Table IVa shows the concentration of substances in n-heptane as well as those of the markers.

The concentration of the substance was taken as low as possible with the exception of the ethanol. In the latter case the partition coefficients were very low, and an analysis was only possible at higher concentrations. Proof will be given that the concentration chosen can be regarded as ideal diluted.

For the evaluation of the chromatograms a correction factor f (15) has been determined with the aid of the prepared solutions, which allows the calculation of the concentration of the substances from the ratio of the peak-areas (substance/marker). This is given from the chromatograms of the prepared solutions:

$$f = \frac{A_S}{A_M} \cdot \frac{c_M}{c_M}$$
Eq. 15

where A is the peak-area in the chromatogram and c the concentration in g/cm^3.

After equilibration, the n-heptane phases were again chromatographed and the area-ratio determined giving

$$c^*_{s,\alpha} = (A'_S/A'_M) \cdot c_M \cdot 1/f$$
Eq. 16

the index α referring to the heptane phase.

The concentration $c_{s,\alpha}$ would be the correct concentration for infinitely diluted solutions. For more concentrated solutions the substance transport during equilibration is accompanied by a volume change, δV; i.e., the volume of the both phases after equilibration is $V\alpha_{,o} + \delta V$ and $V\beta_{,o} - \delta V$. Supposing that the substance dissolves in both phases without volume con-

traction, then δV is given by

$$\delta V = \frac{V\alpha_{,o}}{d_s} \cdot (c_{s,\alpha,o} - c^*_{s,\alpha})$$
Eq. 17

where $V\alpha_{,o}$ is the volume of the heptane phase before equilibration. The corrected concentration is then given by (18)

$$c_{s,\alpha} = c^*_{s,\alpha} \cdot \frac{1}{1 - (\delta V/V\alpha_{,o})}$$
Eq. 18

The concentration in the salt solution (phase β) was in most cases not determined. It can be calculated if $c^*_{s,\alpha}$ is known:

$$c_{s,\beta} = c^*_{S,\alpha,o} - c^*_{s,\alpha}) \cdot \frac{1}{1/\phi + (\delta V/V\alpha_{,o})}$$
Eq. 19

where ϕ is the phase ratio ($V\alpha_{,o}/V\beta_{,o}$)

Calculation of the partition coefficients: from the above results the partition coefficients can be calculated as:

$$K_c = c_{S,\alpha}/c_{S,\beta}$$
Eq. 20

Tables V and VI show the experimentally determined partition coefficients, K_c, and their logarithms as well as two other partition coefficients (K_m and K_x, see below) with their logarithms, which can be calculated from K_c:

a) if the concentration of the substance is given in mass of substance per mass of solution, the partition coefficient K_m can be calculated:

$$K_m = K_c \cdot (d\beta/d\alpha) = K_c \cdot \frac{d_{solution}}{d_{heptane}}$$
Eq. 21

for the ideal diluted case.

b) if the concentration of the substance is given in mole fraction or mole % the partition coefficient changes into:

$$K_x = K_c \cdot \frac{d_{solution}}{d_{heptane}} \cdot \frac{M_{heptane}}{M_{solution}}$$
Eq. 22

Dependence of the partition coefficients on the substance concentration: Tables VII and VIII show the logarithms of the partition coefficients K_c at different salt concentrations and with different sub-

Table V. Partition coefficients between heptane and aqueous solutions of potassium-1-octylsulfonate

c'	$-\log \gamma$		Ethanol K	log k	Propanol-(1) K	log K	Butanol-(1) K	log K	Pentanol-(1) K	log K	Hexanol-(1) K	log K
0.0000	0.00000	K_c	0.00773	0.888 -3	0.0246	0.391 -2	0.127	0.104 -1	1.242	0.094	6.12	0.787
		K_m	0.0113	0.053 -2	0.0345	0.555 -2	0.185	0.268 -1	1.814	0.259	8.94	0.951
		K_x	0.0628	0.798 -2	0.200	0.301 -1	1.032	0.014	10.09	1.004	49.7	1.696
0.0953	0.03009	K_c	0.00437	0.640 -3	0.0232	0.366 -2	0.141	0.149 -1	1.288	0.110	6.77	0.831
		K_m	0.00639	0.805 -3	0.0339	0.530 -2	0.206	0.314 -1	1.881	0.275	9.90	0.996
		K_x	0.0355	0.550 -2	0.189	0.276 -1	1.145	0.059	10.46	1.020	55.5	1.744
0.4322	0.06011	K_c	0.00668	0.825 -3	0.0241	0.382 -2	0.129	0.111 -1	1.134	0.055	6.57	0.818
		K_m	0.00978	0.990 -3	0.0353	0.548 -2	0.189	0.276 -1	1.659	0.220	9.61	0.983
		K_x	0.0542	0.734 -2	0.195	0.290 -1	1.045	0.019	9.19	0.963	53.2	1.726
1.1201	0.09042	K_c	0.00437	0.640 -3	0.0241	0.382 -2	0.135	0.131 -1	1.212	0.084	5.37	0.730
		K_m	0.00641	0.807 -3	0.0353	0.548 -2	0.198	0.297 -1	1.776	0.250	7.87	0.896
		K_x	0.0353	0.548 -2	0.1945	0.289 -1	1.089	0.037	9.78	0.990	43.4	1.638
2.317	0.12106	K_c	0.00367	0.565 -3	0.0250	0.398 -2	0.136	0.134 -1	1.161	0.065	6.54	0.816
		K_m	0.00540	0.732 -3	0.0368	0.566 -2	0.200	0.301 -1	1.709	0.233	9.62	0.984
		K_x	0.0294	0.469 -2	0.200	0.301 -1	1.088	0.037	9.29	0.968	52.3	1.719
3.199	0.13692	K_c										
		K_m										
		K_x										
4.269	0.15231	K_c	0.00322	0.508 -3	0.0232	0.366 -2	0.116	0.065 -1	0.555	0.744 -1	1.968	0.294
		K_m	0.00477	0.679 -3	0.0343	0.535 -2	0.172	0.235 -1	0.822	0.915 -1	2.91	0.464
		K_x	0.0255	0.406 -2	0.1834	0.263 -1	0.917	0.962 -1	4.39	0.642	15.55	1.192
6.493	0.17672	K_c										
		K_m										
		K_x										
7.353	0.18443	K_c	0.00390	0.591 -3	0.0223	0.349 -2	0.0889	0.949 -2	0.272	0.435 -1	0.574	0.759 -1
		K_m	0.00582	0.765 -3	0.0333	0.522 -2	0.1326	0.123 -1	0.406	0.609 -1	0.856	0.932 -1
		K_x	0.0302	0.480 -2	0.1725	0.237 -1	0.688	0.838 -1	2.10	0.323	4.44	0.647
11.527	0.21409	K_c										
		K_m										
		K_x										
12.184	0.21794	K_c	0.00390	0.591 -3	0.0215	0.332 -2	0.0635	0.803 -2	0.1489	0.173 -1	0.275	0.439 -1
		K_m	0.00588	0.769 -3	0.0324	0.511 -2	0.0957	0.981 -2	0.225	0.352 -1	0.415	0.618 -1
		K_x	0.0290	0.463 -2	0.1600	0.204 -1	0.473	0.675 -1	1.107	0.044	2.05	0.311
19.802	0.25379	K_c	0.00483	0.684 -3	0.0180	0.225 -2	0.0460	0.663 -2	0.0950	0.978 -2	0.140	0.147 -1
		K_m	0.00739	0.869 -3	0.0276	0.441 -2	0.0704	0.848 -2	0.1454	0.162 -1	0.214	0.331 -1
		K_x	0.0336	0.526 -2	0.1251	0.098 -1	0.320	0.505 -1	0.661	0.820 -1	0.974	0.988 -1
20.839	0.25779	K_c										
		K_m										
		K_x										
28.517	0.28357	K_c										
		K_m										
		K_x										
32.023	0.29371	K_c	0.00503	0.702 -3	0.0154	0.187 -2	0.0349	0.542 -2	0.0560	0.748 -2	0.0724	0.860 -2
		K_m	0.00787	0.896 -3	0.0241	0.382 -2	0.0546	0.732 -2	0.0876	0.943 -2	0.1132	0.054 -1
		K_x	0.0308	0.489 -2	0.0944	0.975 -2	0.214	0.330 -1	0.343	0.535 -1	0.444	0.647 -1
34.958	0.30166	K_c										
		K_m										
		K_x										

Table V. (Continued)   Partition coefficients between heptane and aqueous solutions of potassium-1-octylsulfonate

c'	$-\log \gamma$		Octanol-(1)		Decanol-(1)		Dodecanol-(1)		1-Chloro-octane		Octanol-(1)-acetate		Nonanone(2)	
			K	log K	K	log K	K	log K	K	log K	K	log K	K	log K
0.0000	0.00000	K_c	147	2.167	7880	3.896								
		K_m	215	2.332	11500	4.061								
		K_x	1194	3.077	64000	4.806								
0.0953	0.03009	K_c												
		K_m												
		K_x												
0.4322	0.06011	K_c												
		K_m												
		K_x												
1.1201	0.09042	K_c	(250)	(2.398)										
		K_m	(366)	(2.564)										
		K_x	(2020)	(3.305)										
2.317	0.12106	K_c												
		K_m												
		K_x												
3.199	0.13692	K_c	21.9	1.340										
		K_m	32.3	1.509										
		K_x	174	2.241										
4.269	0.15231	K_c	7.45	0.872	23.3	1.368	28.0	1.447						
		K_m	11.02	1.042	34.5	1.538	41.5	1.618						
		K_x	58.90	1.770	184	2.265	221.0	2.344						
6.493	0.17672	K_c	1.94	0.287										
		K_m	2.89	0.461										
		K_x	15.1	1.179										
7.353	0.18443	K_c			2.91	0.464	4.20	0.624	57.5	1.759			65	1.815
		K_m			4.34	0.638	6.27	0.797	85.8	1.934			97	1.987
		K_x			22.5	1.352	32.5	1.512	445	2.648			503	2.701
11.527	0.21409	K_c	0.620	0.792 -1										
		K_m	0.934	0.970 -1										
		K_x	4.64	0.667										
12.184	0.21794	K_c			0.909	0.958 -1	1.35	0.130	34.5	1.538	34.3	1.536	24.0	1.381
		K_m			1.371	0.137	2.04	0.310	52.0	1.716	51.7	1.714	36.2	1.559
		K_x			6.77	0.831	10.05	1.002	257	2.410	255	2.407	179	2.252
19.802	0.25379	K_c			0.381	0.581 -1	0.507	0.705 -1	19.6	1.292	20.4	1.310	9.92	0.997
		K_m			0.583	0.766 -1	0.776	0.890 -1	30.0	1.477	31.2	1.494	15.2	1.181
		K_x			2.65	0.423	3.53	0.547	136	2.134	142	2.152	69.0	1.839
20.839	0.25779	K_c	0.219	0.340 -1										
		K_m	0.336	0.526 -1										
		K_x	1.508	0.179										
28.517	0.28357	K_c	0.151	0.179 -1										
		K_m	0.235	0.371 -1										
		K_x	0.962	0.983 -1										
32.023	0.29371	K_c			0.170	0.231 -1	0.206	0.314 -1	13.5	1.130	6.04	0.781	3.83	0.583
		K_m			0.266	0.425 -1	0.322	0.508 -1	21.1	1.324	9.44	0.975	6.00	0.778
		K_x			1.041	0.018	1.262	0.101	82.8	1.918	37.0	1.568	23.5	1.371
34.958	0.30166	K_c	0.111	0.047 -1										
		K_m	0.175	0.243 -1										
		K_x	0.658	0.818 -1										

Table VI. Partition coefficients between heptane and aqueous solutions of trimethyl-1-octylammoniumbromide

c′	-log γ		Ethanol K	log K	Propanol-(1) K	log K	Butanol-(1) K	log K	Pentanol-(1) K	log K	Hexanol-(1) K	log K
0.0000	0.00000	K_c	0.00773	0.888 -3	0.0246	0.391 -2	0.127	0.104 -1	1.242	0.094	6.12	0.787
		K_m	0.0113	0.053 -2	0.0345	0.538 -2	0.185	0.268 -1	1.814	0.259	8.94	0.951
		K_x	0.0628	0.798 -2	0.200	0.301 -1	1.032	0.014	10.09	1.004	49.7	1.696
0.1034	0.03009	K_c	0.00575	0.760 -3	0.0241	0.383 -2	0.129	0.111 -1	1.150	0.061	5.91	0.772
		K_m	0.00839	0.924 -3	0.0351	0.545 -2	0.188	0.274 -1	1.677	0.225	8.62	0.936
		K_x	0.04659	0.669 -2	0.1953	0.291 -1	1.045	0.019	9.319	0.969	47.89	1.680
0.4692	0.06014	K_c	0.00413	0.616 -3	0.0259	0.413 -2	0.123	0.090 -1	1.246	0.096	6.13	0.787
		K_m	0.00603	0.780 -3	0.0378	0.577 -2	0.179	0.254 -1	1.818	0.260	8.94	0.951
		K_x	0.03337	0.523 -2	0.2092	0.321 -1	0.994	0.997 -1	10.067	1.003	49.52	1.695
1.2158	0.09047	K_c	0.00391	0.592 -3	0.0259	0.413 -2	0.129	0.111 -1	1.246	0.096	7.48	0.874
		K_m	0.00571	0.757 -3	0.9378	0.577 -2	0.188	0.274 -1	1.819	0.260	10.92	1.038
		K_x	0.03139	0.497 -2	0.2080	0.318 -1	1.036	0.015	10.00	1.000	60.06	1.779
2.515	0.12116	K_c	0.00391	0.592 -3	0.0250	0.398 -2	0.123	0.090 -1	1.101	0.042	7.21	0.858
		K_m	0.00572	0.757 -3	0.0366	0.563 -2	0.180	0.255 -1	1.610	0.027	10.54	1.023
		K_x	0.03105	0.492 -2	0.1986	0.298 -1	0.977	0.990 -1	8.744	0.942	57.26	1.758
3.501	0.13749	K_c										
		K_m										
		K_x										
4.634	0.15251	K_c	0.00413	0.616 -3	0.0241	0.382 -2	0.159	0.201 -1	1.074	0.031	6.95	0.842
		K_m	0.00605	0.782 -3	0.0353	0.548 -2	0.233	0.367 -1	1.574	0.197	10.19	1.008
		K_x	0.03222	0.508 -2	0.1880	0.274 -1	1.240	0.093	8.378	0.923	54.21	1.734
6.801	0.17487	K_c										
		K_m										
		K_x										
7.981	0.18482	K_c	0.00391	0.592 -3	0.0241	0.382 -2	0.1045	0.019 -1	0.572	0.757 -1	1.83	0.262
		K_m	0.00575	0.760 -3	0.0354	0.549 -2	0.1537	0.187 -1	0.841	0.925 -1	2.69	0.430
		K_x	0.02961	0.471 -2	0.1825	0.261 -1	0.7915	0.898 -1	4.332	0.637	13.86	1.142
12.404	0.21416	K_c										
		K_m										
		K_x										
13.225	0.21868	K_c	0.00391	0.592 -3	0.0215	0.332 -2	0.0782	0.893 -2	0.250	0.398 -1	0.502	0.701 -1
		K_m	0.00578	0.762 -3	0.0318	0.502 -2	0.1156	0.063 -1	0.370	0.568 -1	0.742	0.870 -1
		K_x	0.02821	0.450 -2	0.1551	0.190 -1	0.5643	0.751 -1	1.804	0.256	3.622	0.559
21.493	0.25512	K_c	0.00460	0.663 -2	0.0189	0.276 -2	0.0574	0.759 -2	0.138	0.140 -1	0.213	0.328 -1
		K_m	0.00686	0.836 -3	0.0282	0.450 -2	0.0856	0.932 -2	0.206	0.314 -1	0.318	0.502 -1
		K_x	0.03055	0.485 -2	0.1255	0.098 -1	0.3812	0.581 -1	0.916	0.962 -1	1.415	0.151
22.200	0.25771	K_c										
		K_m										
		K_x										
30.192	0.28350	K_c										
		K_m										
		K_x										
34.759	0.29620	K_c	0.00483	0.684 -3	0.0171	0.233 -2	0.0475	0.677 -2	0.0834	0.921 -2	0.115	0.059 -1
		K_m	0.00731	0.864 -3	0.0259	0.413 -2	0.0719	0.857 -2	0.1262	0.101 -1	0.174	0.241 -1
		K_x	0.02752	0.440 -2	0.0974	0.989 -2	0.2707	0.432 -1	0.4752	0.677 -1	0.655	0.816 -1
36.799	0.30153	K_c										
		K_m										
		K_x										

c'	-log γ		Octanol-(1) K	log K	Decanol-(1) K	log K	Dodecanol-(1) K	log K	Nonanone(2) K	log K	n-Diamylether K	log K
0.0000	0.00000	K_c	147	1.167	7880	3.896						
		K_m	215	2.332	11500	4.061						
		K_x	1194	3.077	64000	4.806						
0.1034	0.03009	K_c										
		K_m										
		K_x										
0.4692	0.06014	K_c										
		K_m										
		K_x										
1.2158	0.09047	K_c										
		K_m										
		K_x										
2.515	0.12116	K_c	(172)	(2.235)								
		K_m	(251)	(2.400)								
		K_x	(1366)	(3.136)								
3.501	0.13749	K_c	56.4	1.751								
		K_m	82.6	1.917								
		K_x	444.2	2.647								
4.634	0.15251	K_c	(212)	(2.326)								
		K_m	(311)	(2.493)								
		K_x	(1654)	(3.219)								
6.801	0.17487	K_c	31.2	1.494								
		K_m	45.8	1.661								
		K_x	238.8	2.377								
7.981	0.18482	K_c	11.6	1.065					46.6	1.668	36.8	1.566
		K_m	17.1	1.233					68.5	1.836	54.1	1.733
		K_x	87.9	1.944					352.9	2.548	278.7	2.445
12.404	0.21416	K_c	1.65	0.218								
		K_m	2.44	0.387								
		K_x	12.00	1.079								
13.225	0.21868	K_c			3.50	0.544	8.07	0.907	23.2	1.365	34.8	1.534
		K_m			5.18	0.714	11.93	1.077	34.3	1.535	50.6	1.704
		K_x			25.25	1.402	58.23	1.765	167.4	2.223	246.8	2.392
21.493	0.25512	K_c			0.896	0.952 -1	1.72	0.235	11.8	1.072	29.5	1.470
		K_m			1.337	0.126	2.57	0.410	17.6	1.246	44.0	1.643
		K_x			5.951	0.775	11.42	1.058	78.4	1.894	195.9	2.292
22.200	0.25771	K_c	0.443	0.649 -1								
		K_m	0.666	0.823 -1								
		K_x	2.940	0.468								
30.192	0.28350	K_c	0.251	0.399 -1								
		K_m	0.378	0.577 -1								
		K_x	1.513	0.180								
34.759	0.29620	K_c			0.313	0.495 -1	0.536	0.729 -1	5.36	0.729	30.1	1.479
		K_m			0.474	0.676 -1	0.811	0.909 -1	8.11	0.909	45.5	1.658
		K_x			1.783	0.251	3.054	0.485	30.54	1.485	171.5	2.234
36.799	0.30153	K_c	0.182	0.260 -1								
		K_m	0.276	0.441 -1								
		K_x	1.010	0.005								

stance concentrations in the case of octanol-(1).

Variance analysis of the results have shown that within experimental error, there is no significant change in log K especially for concentrations not higher than 0.2 m. Therefore, for all other experiments, the concentration 0.2 m. was chosen as high enough for analysis but low enough to be ideally diluted (see also Table IVa).

Apparatus

Construction and function (see Figure 1 and 2): The eluent is filled into a glass container (1) of internal diameter 20 cm and capacity 5 l. This container is connected through a three-way tap (3) which can be turned in two positions, either allowing the eluent to flow into the line and the burette (2), or (position in Figure 2) connecting only the burette with the line. This second position allows the sample-loading: the burette is emptied by pumping away the eluent and then the substance, diluted with the eluent, is filled into the burette. After loading, the tap is turned to the first position (connecting burette, container, and line).

The eluent passes through a sintered metal filter (4) and to a solution metering pump (5) (Beckman Model 746, 0-20 ml/min) which determines the velocity of the eluent with a precision of about 2%. After the pump is an excess pressure valve giving a back pressure of about ½ atm. At N a slow nitrogen stream (~2-3 ml/min) is pressed into the eluent which then enters the separation tube (7). The tubes can be rotated with the aid of an electric motor (9) with a speed of up to 140 RPM. The separation tubes are connected by small bore stainless steel tubes 3 mm i.d. The whole apparatus is inclined to an extent that both the separation tubes and the connection tubes are descending for the movement of the eluent. After passing through all the tubes, the eluent is led to an overflow (10) where the main stream is collected (12). A bypass from the overflow goes to the detector (11) where the refraction index is measured continuously (Waters liquid chromatography, Model R 4) and is registered on a recorder.

For the description of the separation tubes see Figure 1 and the explanation in part one.

The apparatus can, of course, also be used with a smaller number of separation tubes.

Filling the separation tubes with the two phases: The tube is first placed in a horizontal position and filled completely with a solution of the hydrotropically active salt (or other solvent). By inclining the tube to a given angle, which of course must be higher than the position of the tube in the apparatus, a fraction of the stationary phase flows out. The tube is now placed into the apparatus and filled with the mobile phase without rotating in order to avoid foaming of the solution. After all the tubes are filled with the eluent, they can be rotated and the separation can be started.

Acknowledgment

Table VII. Logarithms of the partition coefficients K_C of octanol-(1) between n-heptane and aqueous solutions of potassium-1-octylsulfonate

initial concentration octanol-(1) (g/100 cm³)	(mole/l)	concentration of the salt (g/100 $g_{solution}$)
		3.2	6.5	11.5	20.8	28.5	35.0
1.3	0.1	1.286	0.202	—0.298	—0.700	—0.816	—0.970
2.6	0.2	1.482	0.370	—0.220	—0.688	—0.842	—0.940
3.9	0.3	1.625	0.403	—0.151	—0.638	—0.822	—0.952
5.2	0.4	1.477	0.460	—0.064	—0.594	—0.794	—0.948

Table VIII. Logarithms of the partition coefficients K_C of octanol-(1) between n-heptane and aqueous solutions of trimethyl-1-octylammoniumbromide.

initial concentration octanol-(1) (g/100 cm³)	(mole/l)	concentration of the salt (g/100 $g_{solution}$)
		3.5	6.8	12.4	22.2	30.2	36.8
1.3	0.1	1.514	1.471	0.176	—0.373	—0.579	—0.725
2.6	0.2	1.891	1.718	0.218	—0.367	—0.615	—0.741
3.9	0.3	1.943	1.483	0.257	—0.328	—0.611	—0.744
5.2	0.4	1.819	1.463	0.285	—0.320	—0.591	—0.748

Literature Cited

1. Rath, H., Rau, J., and Wagner, D., Melliand Textilber. **43**, 718 (1962).
2. Michaelis, W., Schindler, O., and Signer, R., Helv. Chim. Acta **48**, 42 (1965).
3. Arn, H., Grob, E. C., and Signer, R., Helv. Chim. Acta **48**, 851 (1965).
4. Signer, R., Allemann, K., Koehli, E., Lehmann, W., Meyer, H., and Ritschard, W., Dechema Monograph. **27**, 32 (1956).
5. Signer, R., and Arn, H., Helv. Chim. Acta (in press).
6. Neuberg, C., Biochem. Z. **76**, 107 (1916).
7. Rath, H., Rau, J., and Wagner, D., Melliand Textilber. **44**, 969 (1963).
8. Kovats, E. sz., Z. Anal. Chem. **181**, 351 (1961). See also Kovats, E. sz., Advances of Chromatography, Vol. 1, J. C. Giddings and R. A. Keller, editors, M. Dekker, Inc., New York, 1965, p. 229.
9. Kovats, E. sz., and Weiss, P. B., Ber. Bunsenges. Physik. Chem. **69**, 812 (1965).
10. Backer, H. J., Rec. Trav. Chim. **48**, 949 (1929).