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Micellar Extraction of Carboxylic Acids with Phases of OP-10 Nonionic Surfactant on Heating

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Abstract—Extraction of carboxylic acids from aqueous solutions with phases of OP-10 nonionic surfactant on heating was studied in relation to the concentration and hydrophobicity of the acids. A multiple linear regression equation describing the process was suggested.

An essential step of hybrid analysis methods is concentrating the component to be determined [1], which decreases the detection limit and enhances the selectivity of determination. One of procedures widely used for concentrating organic and inorganic microcomponents is extraction with organic solvents [2]. However, many of the solvents are toxic, which limits their use.

Recovery of substances from aqueous solutions with micellar phases of nonionic surfactants (NSs) on heating is a promising and environmentally safe alternative of traditional extraction processes; it attracts considerable researchers' attention [3–5]. In aqueous solutions, oxygen atoms of polyoxyethylene chains of nonionic surfactants form a system of hydrogen bonds with water molecules. However, when these solutions are heated above a certain temperature (cloud point, T_c), these bonds are broken, and the system separates in two phases [6]. The first phase is the micellar phase of a nonionic surfactant, formed by large hydrated micelles and used for concentrating microcomponents. The second phase is an aqueous solution of a nonionic surfactant with the concentration close to the critical micelle concentration (hereinafter, "water"). However, quantitative data on micellar extraction are virtually lacking. Also lacking are data on the effect of various factors on the recovery of substances with phases of nonionic surfactants. Therefore, we examined in this work the influence exerted by the concentration and hydrophobic properties of carboxylic acids on their micellar extraction. Carboxylic acids are widely used compounds with complexing properties; their hydrophobic properties vary in a wide range. Therefore, carboxylic acids are convenient models for revealing the effect of hydrophilic–hydrophobic properties of acidic compounds on their micellar extraction with phases of nonionic surfactants.

As a nonionic surfactant we chose OP-10, polyoxyethylated alkylphenol with the mean degree of oxyethylation $m = 10–12$. The choice of OP-10 was governed by the high rate, as compared to other nonionic surfactants, of formation of micellar phases on heating and by the compactness and high viscosity of the micellar phase formed.

Extraction in general, and micellar extraction in particular, depends on speciation of the substance to be extracted in aqueous solution. The dissociation equilibrium of carboxylic acids in aqueous-micellar solutions of nonionic surfactants depends on the solution acidity. Furthermore, the protolytic properties of acids are affected by solubilization processes. The strength of carboxylic acids in aqueous-micellar solutions of OP-10 depends on the number of carbon atoms n in the aliphatic radical and varies within 3.8–7.4 pK units [7]. We performed the extraction experiments under the following standard conditions: pH 2.5 for extraction of molecular carboxylic acid species (HA) and pH 11 for extraction of their anions (A^-). At these pH values, the dissociation equilibrium is virtually fully shifted toward the corresponding species for all the examined acids. Also, we studied the micellar extraction of "free" carboxylic acids (without adding a strong acid or base).

First, we found that carboxylic acids affect the cloud point and the volume of the micellar phase (V_{MP}) of OP-10, formed on heating. As seen from Fig. 1, under the experimental conditions the HA form of carboxylic acids with $n > 6$ decreases the cloud point (curve *3*). The volume of the forming micellar phases, however, remains constant. On the other hand, the A^- forms of carboxylic acids, starting from enanthic acid, increase the cloud point.

With respect to the effect of the A^- form on the volume of the forming phase, carboxylic acids can be

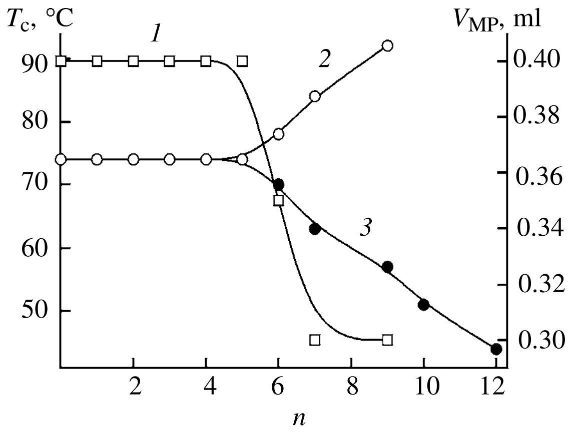

Fig. 1. Influence of the length of the hydrocarbon radical in (*1, 2*) A^- and (*3*) HA forms of monobasic carboxylic acids on the (*2, 3*) cloud point and (*1*) volume of the forming micellar phase of OP-10. C_{NS} 2%, C_{HA} 0.01 M, V_0 10 ml.

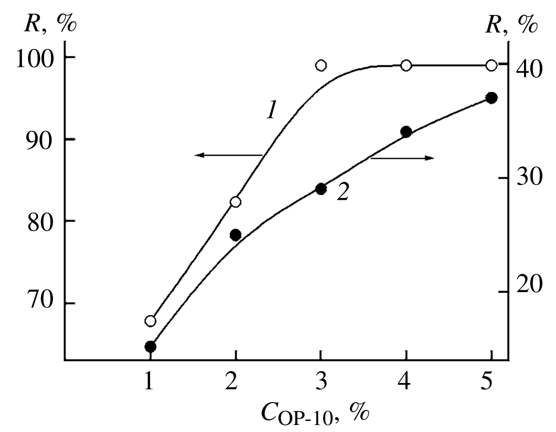

Fig. 2. Degree of recovery of (*1*) caprylic and (*2*) propionic acids as a function of OP-10 concentration in the initial solution. pH 2.5, C_{HA} 0.01 M, V_0 10 ml.

subdivided into three groups. Lower acids ($n \leq 6$) under the experimental conditions did not affect the volume of the forming micellar phase of the nonionic surfactant. In extraction of moderately hydrophobic acids ($6 < n < 9$), the volume of the forming micellar phase of OP-10 decreased with increasing length of the alkyl radical (Fig. 1, curve *1*). With alkaline solutions of higher carboxylic acids ($n \geq 9$), heating to 100°C was not accompanied by turbidization and formation of the micellar phase at all. Such a trend is attributable to hydrophilization of OP-10 micelles with anions of higher carboxylic acids due to formation of mixed micells of the nonionic surfactant and acid anions. As a result, OP-10 micelles become additionally hydrated, which prevents formation of the micellar phase on heating. On the contrary, formation of mixed micelles of OP-10 with the neutral HA form of carboxylic acids weakens the hydration of the micelles, and the cloud point decreases.

With propionic and caprylic acids as examples, we studied how the concentration of monobasic carboxylic acids affects the efficiency of their extraction with OP-10 phases formed from 2% solutions. We found that, as the propionic acid concentration in the initial solution is decreased from 0.1 to 0.005 M, the degree of its extraction monotonically increases from 17.3 to 29.6%. The degree of extraction of more hydrophobic caprylic acid increased from 73.8 to 88.4% as its concentration was decreased from 0.03 to 0.005 M.

Thus, the efficiency of micellar extraction is maximal at a low content of a carboxylic acid. This fact additionally confirms the feasibility of concentrating microcomponents using nonionic surfactant phases.

The degree of recovery of carboxylic acids in micellar extraction depends also on the content of the nonionic surfactant in the initial solution. We found that, as the OP-10 concentration is increased, the volume of the forming micellar phase grows, and the extraction becomes more efficient. For example, as the OP-10 concentration is increased from 1 to 3%, the degree fo recovery of caprylic acid increases by more than 30% (Fig. 2, curve *1*). With 3–5% solutions of OP-10, caprylic acid is extracted into the micellar phase virtually completely ($R > 99\%$). For lower carboxylic acids, the extraction efficiency depends on the OP-10 content less significantly. As seen from Fig. 2, as the OP-10 concentration is increased from 1 to 5%, the degree of recovery of propionic acid increases by 20%, but the extraction is still incomplete (curve *2*).

Taking into account the data obtained, we measured the degree of recovery of some aliphatic monobasic carboxylic acids with OP-10 phases formed from 2% aqueous solutions of the surfactant. As seen from the table, the degree of recovery of carboxylic acids in the neutral (HA) form monotonically grows with increasing number of methylene groups in the hydrocarbon radical. Hydrophilic ($n < 4$) acids are poorly extracted with the micellar phases of OP-10, whereas undecanoic and tridecanoic acids were extracted under the experimental conditions virtually completely ($R > 99\%$). Such a behavior correlates with the solubility of the acids in water: Acids with $n > 9$ are almost insoluble.

With respect to the degree of recovery with the OP-10 phase, carboxylic acid anions can be conventionally subdivided into three groups. Anions of hy-

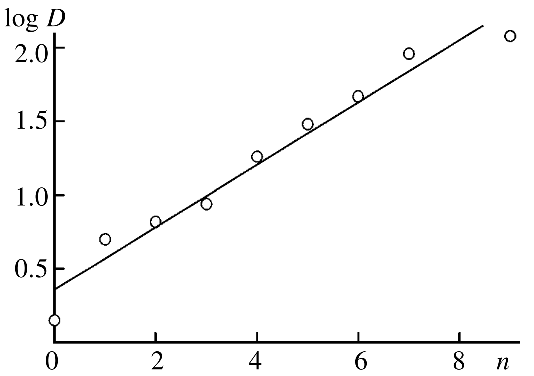

Fig. 3. Correlation between the distribution factor of HA forms of monobasic carboxylic acids in the system water–OP-10 phase and the number of carbon atoms in the aliphatic radical of the acid. pH 2.5, C_{NS} 2%, C_{HA} 0.01 M, V_0 10 ml.

drophilic acids ($0 \le n < 4$) are not extracted with the OP-10 micellar phases. Anions of moderately hydrophobic carboxylic acids ($4 \le n < 7$) partially pass into the OP-10 micellar phase, with the degree of recovery of the A^- forms growing with increasing n but remaining by a factor of 5–10 lower as compared to the degree of recovery of the respective HA forms. In the presence of anions of higher carboxylic acids ($n \ge 9$), the OP-10 micellar phase is not formed at all because of hydrophilization of the micelles.

The degree of recovery of the free acids grows with increasing n, as in the case of the HA forms. However, solutions of free acids contain both HA and A^- species. With increasing n, the strength of the acids decreases and hence the relative content of HA species in OP-10 solutions grows. However, the content of the A^- species in the case of lower carboxylic acids remains significant. Therefore, the efficiency of the micellar extraction of free carboxylic acids depends not only on their hydrophobicity, but also on the degree of their acid dissociation in aqueous-micellar solutions of OP-10.

Degree of recovery (R, %) of monobasic carboxylic acids with OP-10 micellar phases (C_{NS} 2%, C_{HA} 0.01 M, V_0 10 ml)

Acid	n	HA	Free HA	A^-
Formic	0	6.6	8.3	0
Acetic	1	20	6.6	0
Propionic	2	25	25	0
Butyric	3	30	30	0
Valeric	4	48	35	7
Caproic	5	60	56	10
Enanthic	6	70	70	11
Caprylic	7	82	70	25
Capric	9	86	71	[a]
Undecanoic	10	>99	87	[a]
Tridecanoic	12	>99	93	[a]

[a] Micellar phase of OP-10 is not formed.

In the range $0 \le n \le 9$, the logarithm of the distribution factor of HA species is linear in n; the correlation (correlation coefficient R 0.97) is described by Eq. (1) (Fig. 3):

$$\log D = 0.36 + 0.21n. \quad (1)$$

The calculated contribution of the methylene group of the carboxylic acid to $\log D$ is 0.21. The contribution of the terminal methyl group to $\log D$ is assumed to be the same as that of the methylene groups. The free term of Eq. (1) corresponds to the contribution of the carboxy group to $\log D$, i.e., to a first approximation, to $\log D$ of formic acid. However, the calculated (0.36) and experimental (0.15) values of this parameter differ significantly. Therefore, we examined the possibility of describing the distribution of monobasic carboxylic acids in the system water–OP-10 phase by a multiple linear regression equation explicitly taking into account the difference between the methyl and methylene groups in the hydrocarbon radical of acids. The following equation was obtained:

$$\log D = 0.15 + 0.52n_{CH_3} + 0.19n_{CH_2}, \quad (2)$$

where n_{CH_3} is the number of methyl groups, and n_{CH_2}, the number of methylene groups in the hydrocarbon radical. For all the acids except HCOOH, n_{CH_3} was taken equal to unity.

Regression (2) fairly accurately describes the distribution of monobasic carboxylic acids in the system water–OP-10 phase under the experimental conditions. It is characterized by high values of the Fisher test (F 175) and linear correlation coefficient ($R > 0.99$), and also by acceptable mean absolute error of estimation of $\log G$ (MAE 0.063). It should be noted that, according to Eq. (2), the methyl group makes a ~2.5 times greater contribution to $\log D$ than the methylene group. Thus, the approach based on considering different contributions of the methyl and methylene groups to $\log D$ allows substantially more accurate prediction of the distribution factor of carboxylic acids in the system water–nonionic surfactant phase.

Data on distribution factors of carboxylic acids are available for many systems water–organic solvent [8]. The distribution factors that we obtained for carboxylic acids in the system water–OP-10 phase are the closest to those obtained for the system water–nonanol. This fact is in line with many papers in which solubilization of substances with nonionic surfactant micelles is compared to their extraction with higher alcohols [9]. It is also noteworthy that the micellar extraction of propionic acid with the OP-10 phase is characterized by the highest distribution factor as compared to its extraction with polar and nonpolar solvents.

Pavlovskaya *et al.* [8] proposed an additive scheme for describing extraction of aliphatic monobasic acids, based on consideration of an acid as a bifunctional compound containing an aliphatic radical and a carboxy group. The contributions of the methylene and carboxy groups to the Gibbs energy of resolvation of carboxylic acids at their transfer into the OP-10 micellar phase, calculated using this approach, were as follows (kJ mol^{-1}): ΔG_{CH_2} –1.3 and ΔG_{COOH} –4.2. In traditional extraction of carboxylic acids, ΔG_{CH_2} is somewhat lower, from –2.95 to –3.45 kJ mol^{-1}. On the contrary, ΔG_{COOH} in extraction with various organic solvents is much higher as compared to extraction with the nonionic surfactant phases. We believe that the close negative values of ΔG_{CH_2} and ΔG_{COOH} for absolutely dissimilar groups in micellar extraction are due to the biphilic nature of the OP-10 micellar phase. Namely, the micellar phase ensures both hydrophobic solvation of methylene groups and hydrophilic solvation of carboxy groups. Presumably, in micellar extraction of carboxylic acids, the ends of the hydrocarbon radicals are "immersed" in the hydrocarbon core of nonionic surfactant micelles. The methylene groups that are located more closely to the carboxy group are accommodated in the surface oxyethyl layer and are subject to the effect of hydration water. The carboxy group is apparently located on the micelle surface. Comparison of the ΔG_{COOH} values for organic solvents and the OP-10 phase also suggests that the carboxy group is not noticeably dehydrated at its transfer from the aqueous solution to the micellar phase.

Below are the degrees of recovery (R_{H_2A}) and logarithms of the distribution factors ($\log D_{H_2A}$) of the H_2A forms of dibasic carboxylic acids in the system water–OP-10 phase (C_{NS} 2%, C_{H_2A} 0.01 M, V_0 10 ml). It should be noted that neither hydrophilic nor hydrophobic dibasic acids are extracted with OP-10 micellar phases in the form of dianions.

Acid	Adipic	Azelaic	Sebacic
n	4	7	8
R_{H_2A}, %	15	25	77
$\log D_{H_2A}$	0.54	0.81	1.80

Thus, our results show that the charge of carboxylic acid species is the major factor affecting their micellar extraction. For example, the degrees of recovery of monobasic carboxylic acids with $4 \le n < 9$ in the anionic A^- form are by a factor of 5–10 lower compared to the neutral HA form, and dianions of dibasic carboxylic acids are not extracted with OP-10 micellar phases at all. We also found that the micellar extraction of carboxylic acids depends on their hydrophobicity, which, to a first approximation, is quantitatively characterized by the number of methylene groups in the hydrocarbon radical of the acid. As n is increased, the recovery of the acids with the OP-10 phases becomes more efficient. Calculations of the energies of resolvation of the methylene and carboxy groups in micellar extraction of acids revealed a substantial difference between the properties of nonionic surfactant phases and organic solvents.

EXPERIMENTAL

Monobasic and dibasic carboxylic acids were of analytically pure (liquid substances) or pure (solid substances) grade. Solid acids were additionally recrystallized from aqueous ethanol. Working solutions of acids were prepared by dissolving an accurately weighed portion of an acid in aqueous-micellar solutions of the nonionic surfactant. Working solutions of OP-10 were prepared by dissolving accurately weighed portions of the surfactant in distilled water. The acidity of the solutions was measured with a pH-340 pH meter.

Aqueous solutions of OP-10 and carboxylic acids were placed in calibrated 10-ml volumetric cylinders, fixed in a holder, and immersed in a glass water bath. The solution temperature was monitored with thermometers immersed in one of the cylinders and directly in the water bath. The solutions were heated at a rate of ~0.5 deg min^{-1}. When the cloud point was attained, a characteristic opalescence of solutions was observed, followed by further phase separation. After that, the aqueous phase was separated by decanting. The distribution of carboxylic acids was determined by alkalimetric titration of the initial solution and both phases after separation.

From the data obtained, we calculated the degrees of recovery and distribution factors of particular carboxylic acid species. The volume of the forming micellar phase of the nonionic surfactant and the cloud point depended on the OP-10 concentration in the starting solution. As the OP-10 concentration was increased from 0.5 to 5%, V_{MP} increased from 0.1 to 1.8 ml, and T_c decreased from 76 to 68°C.

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