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PROCESSES AND EQUIPMENT OF CHEMICAL INDUSTRY

Effect of Diluent Additives on the Rate of Water Purification to Remove Microdrops of Tri-*n*-Butyl Phosphate by Hydrodynamic Heteroadagulation

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Abstract—Effect of diluents on the coarsening of microdrops of tri-*n*-butyl phosphate by hydrodynamic heteroadagulation on a carbon fabric in water was studied.

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The effect of diluents on the extraction equilibrium is a classical example of application of the theory of solutions [1–4]. Diluents are required for performing technological processes under optimal conditions. These substances can provide necessary viscosity and density of the phase of extractive agents, but more frequently, they adjust such extraction parameters as coefficients of element distribution and separation. The list of diluents used in technology and their physicochemical parameters can be found in the handbook [3].

Minor additions of diluents have an insignificant effect on the thermodynamic properties of the extractive systems [1–4]. Any noticeable changes would be expected to occur only in the kinetics of extraction–re-extraction processes. However, the effect of diluents on the extraction kinetics has been insufficiently studied. In [5], data indicating the effect of diluents on the extraction rate of metals with alkylphosphoric acids were reported. Advances in this area can hardly be compared with achievements in the application of the theory of solutions to description of the effect of diluents on equilibrium properties of extractive systems. There is no information about the behavior of microdrops of, e.g., tri-*n*-butyl phosphate (TBP) on solid surfaces. Such microdrops are formed in extraction involving supersaturated phases. The microdrops are adsorbed on walls, baffles, and other immobile members of extraction apparatus, where occurs their hydrodynamic heteroadagulation (HHA) (i.e., hydrodynamic adsorption coagulation).

The formation of microdrops of TBP or TBP mixed with diluents in raffinates is a topical problem of radiochemical industry. Visually, raffinates of this kind look as turbid, long unclarifiable phases. Accumulating at certain places, they constitute a serious danger, which can not only lead to loss of reagents, but even may develop into a nuclear hazard. One of ways to tackle with this phenomenon consists in eliminating the original cause itself, i.e., in removing microscopic TBP drops.

The aim of this study was to determine how minor additives of organic diluents affect the kinetics of purification of the aqueous phase to remove TBP microdrops by hydrodynamic heteroadagulation.

EXPERIMENTAL

The procedure for preparing microscopic TBP drops 0.8–10 μm in diameter was described in most detail in [6–8]. A quasi-stable emulsion of TBP drops was produced with an IKA DI 25 disperser (Germany) at a rotor rotation speed of 8000 rpm. Such a rotation of the rotor was accompanied by imposition of emulsion flow pulsations at a frequency of 1333 Hz. At the same frequency varied pulsations of pressure and shear stresses. Homogeneous TBP solutions with various organic additives were prepared by simple mixing of the diluents and TBP.

It has been shown [1, 5] that the kinetics of the HHA process is described by the Eley–Rideal equation modified by Tarasov for the case of the microdrops. For

the purification (clarification) of the aqueous phase, the equations have the form

$$\Delta_i(t)=A_0^{-1}-A_t^{-1} = k(i)t, \quad (1)$$

$$\Sigma(t) = \ln(A_0/A_t) + \alpha\, b\, (A_t^{-1}-A_0^{-1}) = k_1\, a\, t, \quad (2)$$

where A_0 and A_t are the absorptions of light by the emulsion purified to remove microdrops at the beginning of the adagulation process and at any other instant of time t; $k(i)$, rate coefficient of water purification to remove microdrops (min^{-1}); and t, duration of the purification process (min).

Thus, $\Delta i(t)$ is a dimensionless function whose subscript i relates the quantity to processes occurring at a rotation frequency n_m of the disperser rotor or n_n of the disc mixer of the heteroadagulator.

The reactor for HHA (inner diameter 80 mm, depth 95 mm) was described in most detail in [6]. The same communication reported specific features of how the attachment with a carbon fabric and dampers of turbulent motions induced by mixer discs are assembled and the service life of the carbon fabric. The rotor of the heteroadagulator mixer was constituted by ten Teflon discs whose size was 5 mm smaller than the diameter of the attachment with a fibrous carbon fabric covering the cylindrical wall of the heteroadagulator.

When linearization of the results in the form of $\Delta(t)$ or $\Sigma(t)$ functions [6] was impossible, the degree of purification, $E = 1 - A_t/A_0$, was used. There are linear relationships, found using the KFK photoelectroncalorimeter, between the degree of purification of the aqueous phase, light absorption, and microdrop concentration. For doing so, it is absolutely necessary that the Beer–Lambert law should be obeyed. Commonly, this is the case when the number of microdrops in a frame does not exceed 2000.

The size and number of microdrops were recorded with a Laboval microscope and Nikon Coolpix 4500 camera. The images were processed on a computer by a previously developed software. The overall magnification of the optical system was 384. The diameter of the TBP drops being formed varied within the range 0.8–10 μm.

The substances used in the study were of analytically pure grade, with the exception of TBP and diesel fuel (DF) of technical grade. The physicochemical properties of substances that could affect the HHA kinetics are listed in the table.

Commonly, $\Delta(t)$ functions are linear [6–8], but they had a concave form for TBP. The 1% emulsion of the "oil-in-water" type, obtained under these conditions, was subjected to HHA at a rotation speed n = 1000 rpm of the disc rotor. Under these conditions, the kinetics of the HHA process and its evolution was studied. In this case, the density, viscosity, and refractive index of the substances varied on changing the temperature by 10° only slightly (within 10%), i.e., had almost zero effect on the HHA rate.

Octane is not a practically important TBP diluent because of its low flash point. Naturally, the fire hazard of TBP strongly diluted with octane may be high. The kinetic effects may also be significant even at very small additions of octane. For example, an addition of 1% octane to the TPB phase led to a nearly twofold increase in the initial HHA rate (see Fig. 1a), which was determined

Physicochemical properties of the substances used in the study at 20°C

Substance	Formula	Number of carbon atoms	Density, g cm^{-3}	Viscosity, cP	Refractive index
Chlorobenzene	C_6H_5Cl	6	1.489	0.792	1.525
Octane	C_8H_{18}	8	0.703	0.546	1.397
Decane	$C_{10}H_{22}$	10	0.730	0.920	1.412
Dodecane	$C_{12}H_{26}$	12	0.749	1.492	1.422
Tri-*n*-butyl phosphate	$(C_4H_9O)_3PO$	12	0.975	3.32	1.422
Tridecane	$C_{13}C_{28}$	13	(0.752)[a]	(1.911)	(1.428)
Diesel fuel (solar oil)	nonstoichiometric	up to 30 (17, on average)	0.83–0.93	1.5–6.0	variable

[a]Values obtained in this study are given in parentheses.

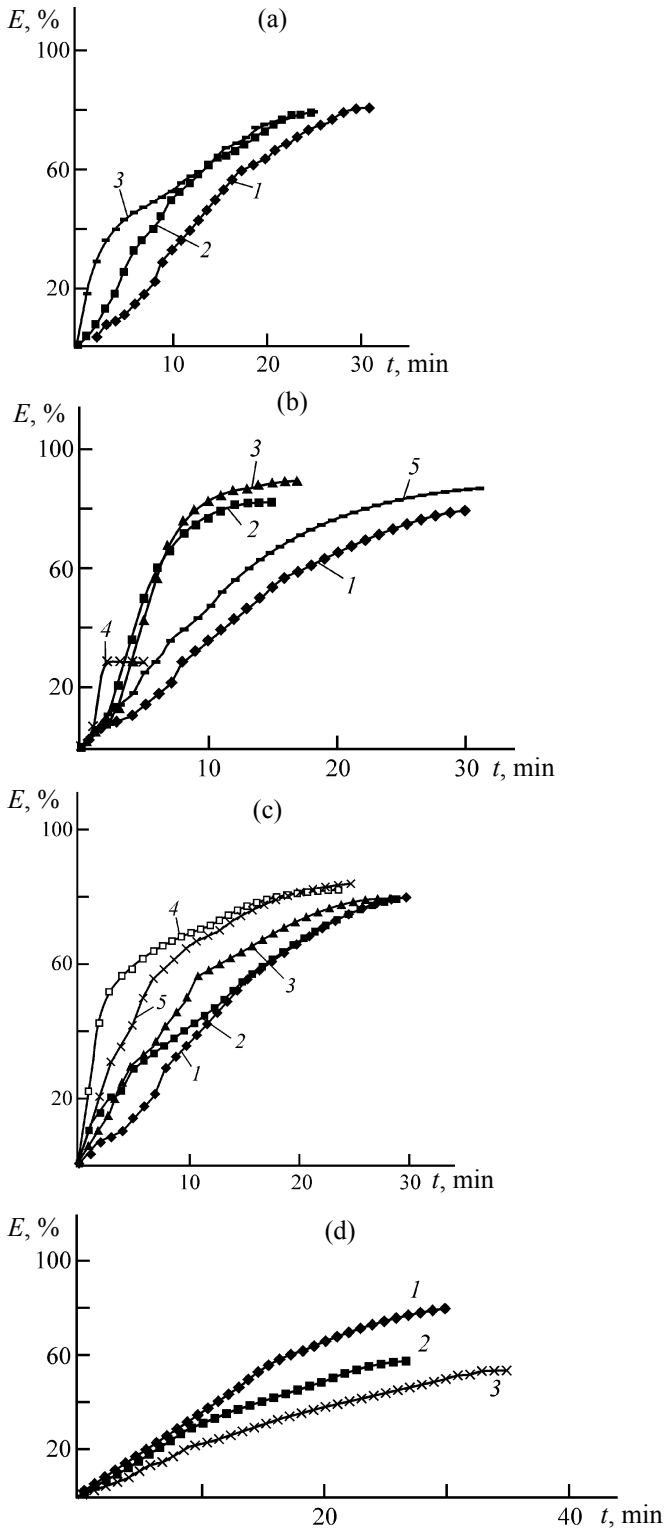

Fig. 1. Degree of purification of the aqueous phase, E, to remove TBP microdrops vs. the purification duration t by the heteroadagulation method at varied content of (a) octane, (b) decane, (c) chlorobenzene, and (d) tridecane additives. Additive content of TBP (%): (a) (*1*) 0, (*2*) 1, and (*3*) 50; (b) (*1*) 0, (*2*) 1, (*3*) 5, (*4*) 10, and (*5*) 50; (c) (*1*) 0, (*2*) 1, (*3*) 5, (*4*) 10, and (*5*) 25; (d) (*1*) 0, (*2*) 1, and (*3*) 10.

as the derivative, i.e., the slope of a tangent to the $E = f(t)$ curve at any t. Effects of this kind are not characteristic of thermodynamic (equilibrium) characteristics of extractive systems.

Upon introduction of 50% octane, a nearly fivefold increase in the initial rate of heteroadagulation was observed, which may be due to a sharp decrease in the viscosity of the mixture. However, as shown below, the viscosity has nearly no effect on the HHA rate. The coarsening rates of microdrops with addition of 1 and 50% octane coincided at $t > 10$ min. These unexpected effects of acceleration of the TBP microdrop coarsening process upon addition of an inert diluent in an amount of 1% require explanation or, at least, consistent hypotheses.

Addition to TBP of another homolog of saturated hydrocarbons, 1% decane, resulted in a sixfold increase in the rate of microdrop coarsening via HHA in 5 min (see Fig. 1b). In this case, the degree of water purification to remove TBP microdrops increased from 14 to 50%, i.e., by a factor of 3.6. A question arises as to how so gigantic effects appear upon so insignificant diluent additives and why the coarsening has an induction period, i.e., occurs with a certain delay in time, as in the case of "autocatalytic" processes. A possible mechanism of water phase purification to remove TBP microdrops consists in that drops become coarser and rapidly float-up or "adhere" to the surface of the carbon fabric. The latter is less probable because a gradual accumulation of the organic phase in the form of "lenses" and macrodrops is observed on the water surface.

Upon a 10% addition of decane to TBP microdrops, the initial coarsening rate of microdrops to sizes at which the drops readily float-up to form lenses and macrodrops on the water surface reached the maximum value. However, the process became unstable in the course of time and the coarsening suddenly terminated, which may be due to full wetting of the carbon fabric surface by the organic phase. Previously, termination of the heteroadagulation was observed upon "forced" rubbing-in of the organic phase at the carbon fabric surface.

The rate of heteroadagulation and microdrop coarsening sharply decreases upon addition of 50% decane to TBP, despite the decrease in the viscosity of the mixture. Consequently, the viscosity is not a decisive factor in the coarsening process. As the process duration increases, the HHA rate upon addition of 50% decane approaches values obtained for "pure" TBP.

In accordance with the homologous series order,

subsequent additions of dodecane and tridecane led, instead of an increase in the HHA rate or a zero influence of admixture addition, to a reverse effect, e.g., to a change of the sign of the process acceleration or to its zero value. An acceleration of the water purification process to remove TBP microdrops was observed upon addition of chlorobenzene.

Addition of 1% chlorobenzene (see Fig. 1c) leads to a nearly threefold increase in the initial coarsening rate of TBP microdrops in water. The strongest effect was observed in the initial period of the HHA process. The purification rate was the highest at a 10% concentration of chlorobenzene in the organic phase.

Addition of dodecane having, similarly to TBP, 12 carbon atoms in its molecule exerted no influence on the HHA rate up to a concentration of 20%. The kinetic curves of heteroadagulation of TBP with dodecane additions coincided with ±7 rel with the kinetic curve for TBP without additives. The physicochemical properties of dodecane (with the exception of viscosity) changed only slightly as compared with the properties of decane (see the table).

With tridecane used as additive, a decrease in the coarsening rate of microdrops of TBP mixtures was observed (see Fig. 1d). The effect of tridecane at a concentration of 1% increased in the course of time: in the initial period, the effect was zero, but after 30 min the process of drop coarsening slowed down. At tridecane concentrations exceeding 10%, the effect was quite insignificant. The maximum decrease in the rate of microdrop coarsening was by about a factor of 2.

A study of the effect of diesel fuel on the coarsening of microdrops of TBP and its mixtures demonstrated that the additive leads to a slower growth of drops. The maximum effect of drop growth deceleration (compared with pure TBP) was observed upon addition of 25% DF. Further increase in the DF concentration had only a slight effect on the HHA rate. As also in the case of tridecane, the effect of deceleration of the microdrop growth became more pronounced in the course of time: before 10 min, there was no effect, but then, a deceleration of the process was observed (the deceleration coefficient was about 2.5), as also upon addition of 25% DF.

The effect of DF on the coarsening of compressor oil drops, observed in [9], coincides with effect of DF addition to tri-*n*-butyl phosphate. Introduction of DF into TBP decelerates (by approximately a factor of 3) the heteroadagulation, similarly to the effect of DF and compressor oil. The average number of carbon atoms in DF is 17.

Thus, the only correlation between the HHA rate and addition of diluents is associated with the number of carbon atoms in the diluent molecule (see the table). The diluent containing less than 10 carbon atoms accelerated the microdrop coarsening, whereas diluents containing 13 carbon atoms and more decelerated this process.

The effects observed are far beyond the experimental errors, which do not exceed 2–4 rel %. However, the coarsening mechanism of TBP microdrops was not conclusively elucidated in this study. Attempts to use such notions as the spreading stress [10] fail to explain the whole set of the relationships obtained. The principal point that cannot be accounted for are the gigantic effects of minor additions of diluents. In their nature, the quantities obtained are not thermodynamic, i.e., do not pertain to the equilibrium state. Methods of thermodynamics of irreversible processes are promising for explaining all the relationships obtained. However, their use gives no way of obtaining information about the kinetic mechanism of the process.

CONCLUSIONS

(1) The coarsening of microdrops of organic solvents occurs via hydrodynamic heteroadagulation on the surface of a fabric made of carbon fibers, a process highly sensitive to presence of minor additions (~1%) of organic diluents. The additives (chlorobenzene, octane, decane) with the number of carbon atoms *C* d” 10, i.e., less than that in TBP lead to a 1.5–6-fold increase in the initial rate of water purification to remove microdrops of tri-*n*-butyl phosphate. Addition of dodecane having the same number of carbon atoms as tri-*n*-butyl phosphate has no effect on the rate of hydrodynamic heteroadagulation up to a concentration of 20%.

(2) Addition of diluents with *C* e” 13 carbon atoms (tridecane, diesel fuel) to tri-*n*-butyl phosphate make the hydrodynamic heteroadagulation slower. Simultaneously, the degree of water purification to remove microdrops of a mixture of tri-*n*-butyl phosphate with diluents decreases by a factor of 1.5–3, compared with purification to remove drops of the extractive agent.

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