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INFLUENCE OF COMPOSITION AND SOME PHYSICO-CHEMICAL PROPERTIES OF TWO- PHASE LIQUID SYSTEMS ON THE STATIONARY PHASE RETENTION IN A COIL PLANET CENTRIFUGE

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ABSTRACT

The present work is an attempt to correlate the composition and some physico-chemical properties of two-phase systems with the stationary phase retention in a coil planet centrifuge of J-type. Complex liquid systems containing an organic solvent (n-decane or chloroform), an extracting reagent (di-2-ethylhexylphosphoric acid, D2EHPA), water and a mineral salt (ammonium sulphate) are considered.

The extractant additions in the organic phase and the salt additions in the aqueous phase lead to the change of the physico-chemical properties (viscosity, density, interfacial tension) of the liquid system and affect, strongly, the stationary organic phase retention. The influence of the rotation speed on the stationary phase retention for systems based on D2EHPA in chloroform and $(\text{NH}_4)_2\text{SO}_4$ in water has been also investigated.

INTRODUCTION

Countercurrent chromatography (CCC) is currently attracting a great interest of investigators working on the separation and preconcentration of organic and inorganic substances. CCC is based on the retention of either phase (stationary) of a two-phase liquid system in a rotating column, under the action of centrifugal forces, while the other liquid phase (mobile) is being continuously pumped through.¹ A main distinguishing feature of CCC as chromatographic method is the absence of porous or adsorptive matrix for retaining the stationary phase. This feature defines the main advantages of the method, such as: the absence of losses of the substances being separated due to interaction with the sorbent matrix; variety of two-phase liquid system which may be used; easy change from one partition system to another; possibility to change a volume of the sample solution from 0.1 to 1000 mL and more; high preparation capacity provided by a high ratio (up to 0.9) of the liquid stationary phase volume and the total column volume (this ratio is much higher than that for the stationary solid phase used in HPLC).^{2,3}

It should be noted that the problem of column packing is also eliminated in CCC. Besides, the stationary phase is relatively cheap. A few devices providing the retention of the stationary phase in the field of mass forces in the absence of a solid support have been suggested. The most successful one that has gained acceptance is a coil planetary centrifuge.¹

The stationary phase volume retained in a column is characterised by S_f -factor (ratio of the stationary phase volume V_s to the total column volume V_c). The value of S_f is dependent on the parameters of the planetary centrifuge (rotation and revolution radii, tube diameter), on the operation conditions (rotation and revolution speeds, flow rate and direction of pumping of the mobile phase), and on the physico-chemical properties of the two-phase system used. It should be mentioned that the influence of planetary centrifuge parameters and operation conditions on the stationary phase retention are well

studied for simple two-phase liquid systems consisting of water and one or two organic solvents.^{1,4-14} The stationary phase retention is known to increase with increasing the rotation speed and with decreasing the mobile phase flow rate.

For the past few years, the influence of physico-chemical properties of two-phase liquid systems on the stationary phase retention has been under study by different authors.^{1,4-10} Parameters such as polarity of solvents, density and viscosity differences of two phases, settling time of liquid system, and capillary wavelength on the interfacial surface have been considered. A few types of classification of liquid systems on the basis of their physical properties have been proposed. The Ito classification¹ is most frequently used. According to this classification, liquid systems can be divided into three groups: hydrophobic (high values of interfacial tension γ , low values of viscosities η), hydrophilic (low values of γ , high values of η), and intermediate systems. The hydrodynamic behaviour of intermediate systems is governed by β -parameter ($\beta=r/R$, where r and R are rotation and revolution radii of the CCC device, respectively). If β is less than 0.3, intermediate systems are retained in the column like hydrophilic systems, and if β is more than 0.3 they behave like hydrophobic ones. In fact, the hydrodynamic behaviour of hydrophobic and hydrophilic systems is also dependent on the β -values. It can be completely changed if β decreases up to 0.1 (changing the behaviour of hydrophilic systems) and if β increases up to 0.8 (changing the behaviour of hydrophobic systems).⁹ However, apparatus with such low and such high β -values are not used in practice. Thus, Ito's classification can be used for choosing operation conditions (directions and speeds of the column rotation and the mobile phase pumping) needed for the satisfactory retention of the stationary phase. However, the classification described does not consider the S_f -value.

The first attempt to correlate the stationary phase retention and physico-chemical properties of liquid systems was made by Berthod and co-workers.^{4,8,15} According to the data reported, the value of S_f increases linearly with an increase of the density difference between two phases ($\Delta\rho$).

The authors note that they have not managed to find any specific correlation between the densities of two liquid phases, their viscosities and S_f -factor.

For the last ten years, the research group at Vernadsky Institute has been working on the theory of inorganic CCC separations.^{2,3,16-18} The chromatographic behaviour of inorganic compounds, as well as organic compounds, is dependent on the properties of the system used, partition coefficients of substances to be separated and parameters of the planetary

centrifuge operation such as rotation and revolution speeds, direction and speed of the mobile phase pumping, internal diameter of the column, sample volume. However, the systems for inorganic separations are very different from those for organic ones^{2,16,17} as, in most cases, they contain a complexing (extracting) reagent (ligand) in the organic phase and mineral salts and/or acids in the aqueous phase. The complexation process, its rate, and the mass transfer rate are the main factors which determine the separation efficiency. Moreover, the addition of extracting reagents and mineral salts can strongly affect some physico-chemical properties of liquid systems and, consequently, their hydrodynamic behaviour and S_f -factor.

This work is an attempt to correlate composition and some physico-chemical properties of such two-phase systems with S_f -factor. Complex liquid systems containing an organic solvent (n-decane or chloroform), an extracting reagent (di-2-ethylhexylphosphoric acid), water, and a mineral salt (ammonium sulphate) are considered. It should be noted that similar liquid systems, on the basis on one or several organic solvents and aqueous mineral salt solutions, can be used also for organic separation. Thus, the investigation of the hydrodynamic behaviour of such systems is important for both inorganic and organic applications of CCC.

EXPERIMENTAL

Apparatus

Investigations on the stationary phase retention were made with a home-made coil planet centrifuge of J-type (Ito's classification¹) consisting of a planetary centrifuge with a vertical column drum and a peristaltic pump.^{2,3}

The column of the device rotates around its axis and revolves at the same angular velocity around the central axis of the device. The planetary centrifuge model had the following design parameters : revolution radius $R = 85$ mm, rotation radius $r = 35$ mm. The column was made of a Teflon[®] tube with an inner diameter of 1.5 mm and a wall thickness 0.75 mm. The total inner capacity of the column V_c was 17 mL. The rotation speed was varied from 350 to 500 r/min. The mobile phase flow rate F was equal to 1.1 mL/min. The densities were estimated, simply, by weighing a known volume of the liquid phase. A glass capillary viscometer was used for measurements of viscosities of the solutions. A tensiometer (Lauda, Germany) with a thermostated cell was used for measurements of interfacial tension of the systems under investigation by the ring method.¹⁹

Reagents

Di-2 ethylhexylphosphoric acid (D2EHPA, Sigma), containing 95% of the main substance minimum was used. The other chemicals were analytical grade reagents.

CCC Procedure

Before the experiment was begun, the components of the two phase liquid system were stirred and brought into equilibrium for mutual saturation of the phases; the two phases were separated shortly before use; the aqueous phase was used as the mobile phase and the organic one as the stationary phase.

First, the coil column in the stationary mode was filled with the organic phase. After that, while column rotation was started, the aqueous phase was fed to its inlet. The mass force field, which arose during rotation, made it possible to retain a constant volume of the stationary phase V_s while the mobile phase was continuously pumped through.

After equilibrium between the mobile and stationary phases had been established (about 30 min), both phases were removed from the column and their volumes were measured. The mobile phase pumping direction was from head to tail for systems on the basis of n-decane and from tail to head for those on the basis of chloroform.

Measurements of Settling Time

The settling time is the time required for a two-phase solvent mixture to be completely separated into two layers in a unit gravitational field. The method described by Ito and Conway for these measurements was used.²⁰ The two-phase solvent system was first equilibrated in a separatory funnel at room temperature so that it was completely separated into two layers.

A 2-mL aliquot of each phase was introduced into the graduated cylinder, which was then sealed with a glass stopper. The cylinder was gently inverted five times and the time necessary for the solvent system to settle was measured. The experiments were repeated several times to compute the mean values for the settling time.

Table 1

Physico-Chemical Parameters of Solvents and Some Liquid Systems Used

Solvent or Liquid System	ρ g/mL	$\Delta\rho$ g/mL	η cP	$\Delta\eta$ cP	Settling Time, s	γ dyn/cm
H ₂ O	1.00		0.98			
n-decane	0.73		0.92			
chloroform	1.48		0.64			
n-decane/H ₂ O		0.27		0.06	16-18	38.7
chloroform/ H ₂ O		0.48		0.34	10-11	19.8

Table 2

 S_f , ρ , $\Delta\rho$ for D2EHPA in n-Decane - Water Systems*

Stationary Phase	ρ , g/mL	$\Delta\rho$	S_f
n-decane	0.73	0.27	0.18
5% D2EHPA in n-decane	0.74	0.26	0.63
30% D2EHPA in n-decane	0.78	0.22	0.47
50% D2EHPA in n-decane	0.87	0.13	0.38

* $\omega = 350$ r/min, $F = 1$ mL/min.

Measurements of Viscosity

Viscosities were measured using a glass capillary viscometer. The kinematic viscosity ν (in centistokes) was computed using the formula:

$$\nu = k\tau \quad (1)$$

where k is the constant of the capillary tube ($k=0.00832$) and τ is the observed time (in seconds). The dynamic viscosity η (in centipoise) is then obtained from the equation

$$\eta = \nu\rho \quad (2)$$

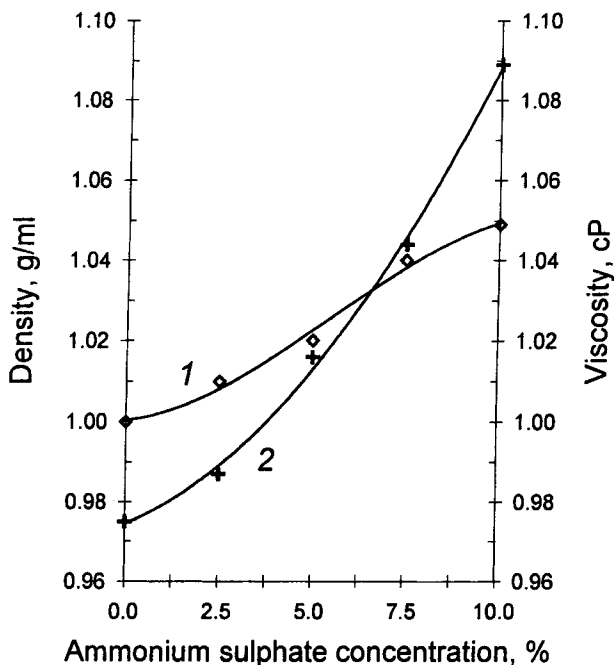


Figure 1. Density (1) and viscosity (2) of $(\text{NH}_4)_2\text{SO}_4$ aqueous solutions.

where ρ is the phase density (in grams per cubic meter). All measurements were performed at $21 \pm 1^\circ\text{C}$. As the relative variation of the viscosity with temperature is typically $1\%/^\circ\text{C}$, the precision of the temperature, $\pm 1^\circ\text{C}$, is sufficient to ensure a high enough accuracy of the viscosity measurements for the purposes of this work.

Measurements of Interfacial Tension

When the interfacial tensions of the systems under investigation were measured, the volumes of upper and lower phases were 20 and 25 mL, respectively. The liquid phases were presaturated and thermostated (25°C).

The interfacial tension γ was calculated with the use of the following expressions.

$$\gamma = F\gamma_{\text{mes}} \quad (3)$$

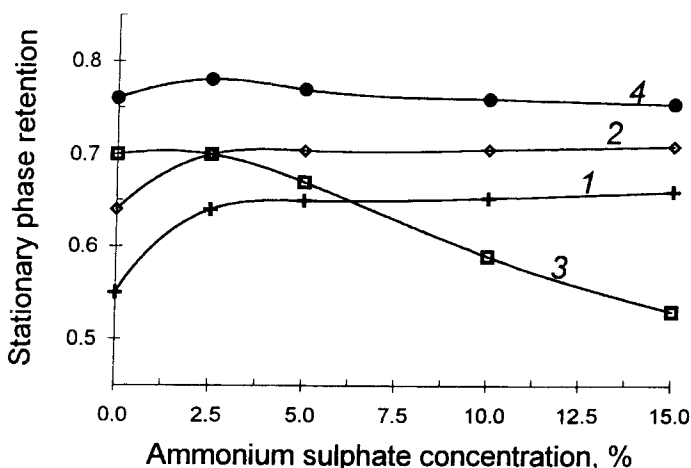


Figure 2. Influence of $(\text{NH}_4)_2\text{SO}_4$ concentration in the mobile aqueous phase on the retention factor. $\omega = 450$ r/min. $F=1.1$ ml/min. Mobile phase: $(\text{NH}_4)_2\text{SO}_4$ (aq). Stationary phase: 1 - n-decane; 2 - 5 % D2EHPA in n-decane; 3 - chloroform; 4 - 5 % D2EHPA in chloroform.

$$\gamma_{\text{mes}} = [m_{\text{et}} H_{\text{mes}} \times 10^3 \times 0.981] / [H_{\text{et}} \times 4\pi \times 0.955] \quad (4)$$

$$F = 0.725 + [4.033 \times 10^{-4} \times \gamma_{\text{mes}} / \Delta\rho + 0.0128]^{1/2} \quad (5)$$

where γ_{mes} - measured interfacial tension, dyn/cm; F - correction factor; H_{mes} - height of the peak obtained by a recorder when the interfacial tension is measured, cm; m_{et} - mass of a standard, g; H_{et} - height of the peak obtained using the same recorder when the standard is weighted, cm; $\Delta\rho$ - density difference between the two phases, g/mL ($\Delta\rho > 0$). Constants correspond to the device parameters.

RESULTS AND DISCUSSION

Changing the Two Phase System Composition

As we have mentioned above, the liquid systems for inorganic separations are very different from those for organic separations because, in most cases, they contain an extracting reagent in the organic phase and mineral components (acids and/or salts) in the aqueous phase; the aqueous phase may also contain some masking agents for better metal separations. This can lead to

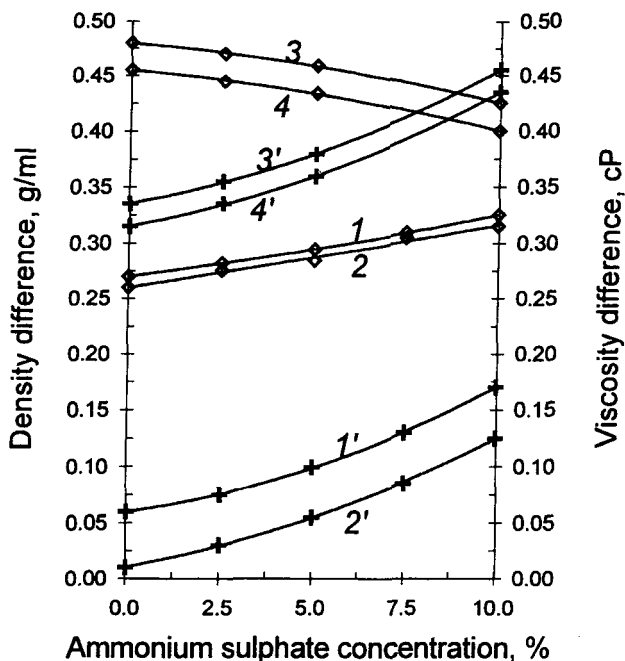


Figure 3. Influence of $(\text{NH}_4)_2\text{SO}_4$ concentration in the mobile aqueous phase on the $\Delta\rho$ (1-4) and $\Delta\eta$ (1'-4') liquid systems. Mobile phase: $(\text{NH}_4)_2\text{SO}_4$ (aq). Stationary phase: 1,1' - n-decane; 2,2' - 5% D2EHPA in n-decane; 3,3' - chloroform; 4,4' - 5% D2EHPA in chloroform.

changes in the physico-chemical properties of the system in general. For our studies, we used two organic solvents (n-decane and chloroform) with different densities (Table 1). According to Ito's classification,¹ these systems are hydrophobic. They are characterised by low values of viscosity, high values of interfacial tension and low values of settling time (several seconds).

The composition and physico-chemical properties of the organic phase were modified by adding an acidic organophosphorus extractant, D2EHPA ($\rho=0.97\text{g/ml}$, $\eta=45.6\text{cP}$);²¹ this extracting reagent has been often used in conventional solvent extraction processes and proved to be a useful extractant for CCC metal separations.²¹ The density and viscosity of the organic phase were varied by changing the amount of D2EHPA in the stationary phase.

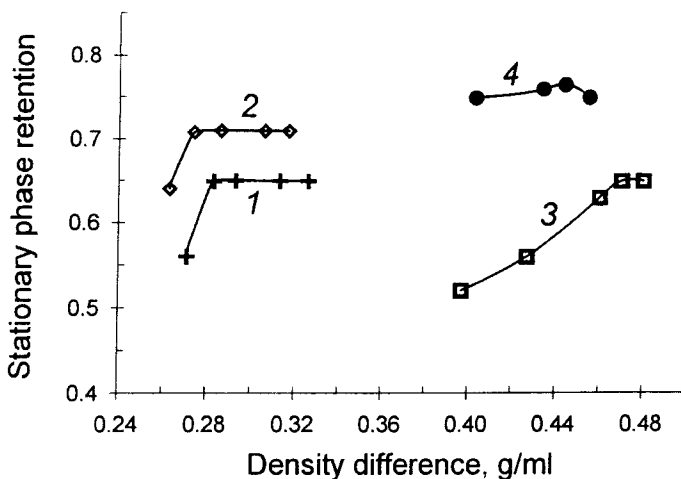


Figure 4. Dependence of stationary phase retention on the density difference between two phases. $\omega = 450$ r/min. $F = 1.1$ ml/min. Mobile phase: $(\text{NH}_4)_2\text{SO}_4$ (aq). Stationary phase: 1 - n-decane; 2 - 5 % D2EHPA in n-decane; 3 - chloroform; 4 - 5 % D2EHPA in chloroform.

A small addition (5%) of D2EHPA in n-decane (n-decane - water system) leads to a considerable increase in the S_f -factor, though the $\Delta\rho$ -values remain practically unchanged. If the D2EHPA concentration in the organic phase is further increased (up to 50%), S_f as well as $\Delta\rho$ begin to decrease (Table 2). The same addition of D2EHPA in the chloroform - water systems also leads to an increase in S_f (S_f increases by 0.28%, see Table 2). It should be noted that the S_f -values for the both systems depend on the rotation speed. This will be discussed below.

In the case of n-decane as solvent, an increase of D2EHPA concentration leads to a considerable increase of the viscosity difference between the phases ($\Delta\rho$ is equal to 0.013 and 0.057 cP for the systems 5% D2EHPA in n-decane - water and n-decane - water, respectively). Chloroform is more viscous than n-decane and the D2EHPA addition to the chloroform-water system is not followed by such a change in the viscosity difference (Table 2).

The D2EHPA addition leads also to a decrease in the interfacial tension for the both systems. In the case of n-decane this change is more considerable (from 38.7 to 19.2 dyn/cm) than in the case of chloroform (from 19.8 to 15.2 dyn/cm).

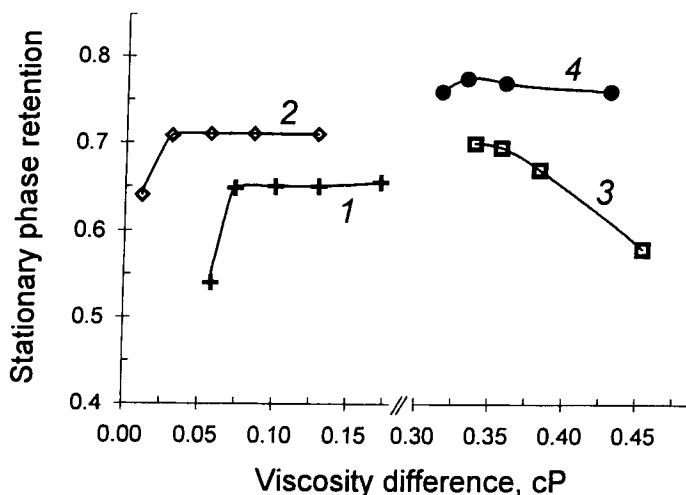


Figure 5. Dependence of stationary phase retention on the viscosity difference between two phases. $\omega = 450$ r/min. $F = 1.1$ ml/min. Mobile phase: $(\text{NH}_4)_2\text{SO}_4$ (aq). Stationary phase: 1 - n-decane; 2 - 5 % D2EHPA in n-decane; 3 - chloroform; 4 - 5 % D2EHPA in chloroform.

The physico-chemical properties of the systems can be changed by varying the aqueous phase composition. Let us consider such changes taking, as example, liquid systems with additions of ammonium sulphate.

The dependencies of the viscosity and density of the ammonium sulphate solution as a function of the salt concentration are shown in Fig. 1. Fig. 2 presents the salt concentration-dependencies of S_f . D2EHPA, 5% in n-decane, and chloroform as well as pure solvents were used as organic phase. It is seen that the dependencies of retention factor on salt concentration (and, consequently, on $\Delta\rho$) for n-decane and 5% D2EHPA in n-decane are quite similar.

In both cases, a relatively small amount of salt (2.5% in the aqueous solution) leads to an increase in the retention factor. The further increase of the salt concentration does not affect the retention of the stationary organic phase in the column.

If chloroform is used as organic phase, increasing the salt concentration results in a decrease in the S_f -factor (Fig. 2, curve 3). For the systems on the basis of 5 % D2EHPA in chloroform, the retention is practically independent of

the salt concentration (Fig. 2, curve 4) and, consequently, on the density difference. The results described show that the viscosities of both phases can be an important factor affecting the retention.

The influence of the salt concentration in the aqueous phase on the values of $\Delta\rho$ and $\Delta\eta$ for the systems used is presented in Fig. 3. It is seen that, in the case of n-decane as organic phase, $\Delta\rho$ and $\Delta\eta$ increase with an increase of the salt concentration. The addition of D2EHPA to n-decane leads to a decrease in $\Delta\rho$ and $\Delta\eta$ for all salt concentrations. If chloroform is used, an increase of the salt concentration results in a decrease of $\Delta\rho$ and an increase of $\Delta\eta$. These data may help to explain quite different hydrodynamic behaviour of n-decane and chloroform-based systems in the column.

$\Delta\eta$ - and $\Delta\rho$ -dependencies of S_f for the systems described are shown in Figs. 4 and 5, respectively. The values of $\Delta\rho$ and $\Delta\eta$ were changed by varying the salt concentration in the aqueous phase. As is seen, $\Delta\rho$ - and $\Delta\eta$ -dependencies are characterised by similar curves. It should be noted that it is possible to attain a constant retention of the stationary phase at different density or viscosity differences between two phases (except for pure chloroform as stationary phase). The results obtained are different from those reported by Berthod.⁴ This may be explained by difference in two-phase liquid systems (systems on the basis of two or more solvents have been investigated in Ref. 4, while we have studied complex liquid systems containing an organic solvent, a viscous extracting reagent, water, and a mineral salt).

The interfacial tension can also be an important factor affecting the hydrodynamic behaviour of the systems investigated.^{1,7} Figs. 6 and 7 show the influence of the salt concentration on the interfacial tension for the n-decane- and chloroform-based systems, respectively. It is seen that the two curves characterising the n-decane - $(\text{NH}_4)_2\text{SO}_4$ (aq) and 5 % D2EHPA in n-decane - $(\text{NH}_4)_2\text{SO}_4$ (aq) systems are very similar. The interfacial tension decreases and then slightly increases with the increasing the salt concentration. However, the value of γ for the n-decane-water system is much higher (38.7 dyn/cm) than that for the 5 % D2EHPA in n-decane-water system (19.8 dyn/cm). According to the results obtained (Figs. 2, 6), high values of the interfacial tension (20 dyn/cm or more) are apparently not favourable for the stationary phase retention.

Two curves for the chloroform-based systems (Fig. 7) are also similar, whereas the dependencies of the retention factor on the salt concentration for these systems are different (Fig. 2).

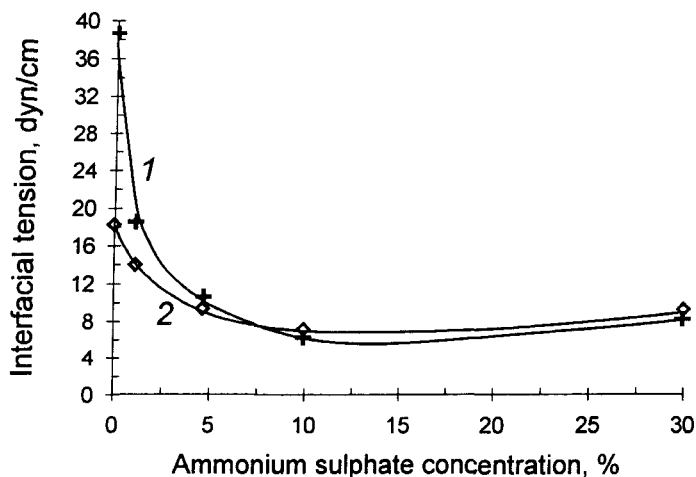


Figure 6. Influence of $(\text{NH}_4)_2\text{SO}_4$ concentration in the aqueous phase on the interfacial tension, for n-decane-based systems. Two phase liquid systems: 1 - n-decane - $(\text{NH}_4)_2\text{SO}_4(\text{aq})$; 2 - 5% D2EHPA in n-decane - $(\text{NH}_4)_2\text{SO}_4(\text{aq})$.

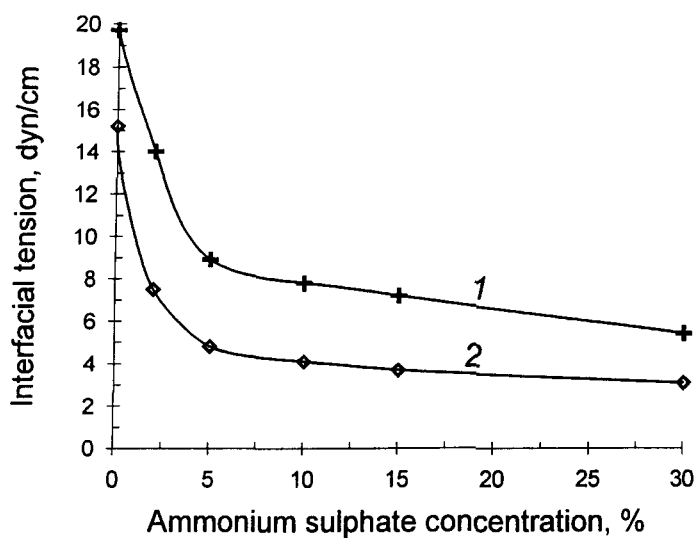


Figure 7. Influence of $(\text{NH}_4)_2\text{SO}_4$ concentration in the aqueous phase on the interfacial tension for chloroform-based systems. Two phase liquid systems: 1 - chloroform - $(\text{NH}_4)_2\text{SO}_4(\text{aq})$; 2 - 5% D2EHPA in n-decane - $(\text{NH}_4)_2\text{SO}_4(\text{aq})$.

Moreover, the retention for the 5 % D2EHPA in the chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq) system is higher and more stable than that for the chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq) system. In this case, the viscosities of two phases may play more important role than the interfacial tension.

Hence, the extractant additions in the organic phase and the salt additions in the aqueous phase lead to a change of the physico-chemical properties ($\Delta\eta$, $\Delta\rho$ and γ) of the liquid system and affect, strongly, the stationary organic phase retention. It should be noted that, in the use of n-decane as organic solvent, the salt concentration in the aqueous phase does not practically influence S_f , the D2EHPA concentration in the organic phase being constant, whereas an increase of the extractant concentration in the organic phase results in a decrease of the S_f -value.

The dependencies observed for the chloroform-based systems are more complicated. If chloroform is used as stationary phase, S_f decreases with an increase in the salt concentration. The addition of D2EHPA in chloroform modifies the system properties. In this case, S_f is practically independent of the salt concentration (Fig. 2). The results presented may be explained by the fact that the chloroform-based systems have a higher $\Delta\eta$ -values in comparison with the n-decane - based systems. For the systems with n-decane, maximum (0.127cP) and minimum (0.057 cP) $\Delta\eta$ -values have been obtained for the 5% D2EHPA in n-decane - 10% $(\text{NH}_4)_2\text{SO}_4$ in water and for n-decane - water systems, whereas in the case of chloroform these values are 0.453 and 0.314 cP for the chloroform - 10% $(\text{NH}_4)_2\text{SO}_4$ in water and 5% D2EHPA in chloroform - water systems, respectively.

Influence of Planet Centrifuge Operation Conditions

As we have mentioned above, the influence of operation conditions on the hydrodynamic behaviour of liquid systems has been considered.^{1,6} The influence of rotation speed ω and mobile phase flow rate F on the retention factor has been investigated on different planet centrifuges. In all cases, S_f increases with increasing ω and with decreasing F . Let us consider the influence of the rotation speed on the stationary phase retention, taking as example chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq) systems. Chloroform and aqueous $(\text{NH}_4)_2\text{SO}_4$ solutions were used as stationary and mobile phases respectively.

As it is seen from Fig. 8, increasing in the salt concentration leads to a decrease in S_f . The less the value of ω , the stronger dependence S_f of on the salt concentration is observed. If the rotation speed is equal to 350 r/min. the

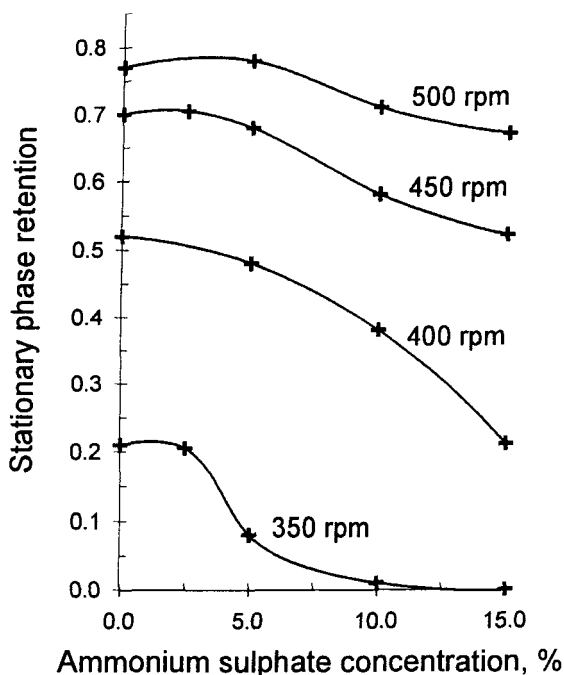


Figure 8. Dependencies of stationary phase retention of the $(\text{NH}_4)_2\text{SO}_4$ concentration in the mobile aqueous phase for different rotation speeds. $F = 1.1$ mL/min. Liquid system: chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq).

retention factor dramatically decreases with an increase in the salt concentration. Whereas, if $\omega = 500$ r/min, a satisfactory retention can be attained for all salt concentrations (from 0 to 15%). Hence, in the case of concentrated salt solutions, high of rotation speeds should be used.

As we have shown above, the addition of D2EHPA to the organic solvent leads to an increase in the retention factor for the all the systems investigated. ω -Dependencies of S_f for different stationary phases and the same mobile phase (water) are presented in Fig. 9. It is seen that a D2EHPA addition favors the stationary phase retention for both chloroform- and n-decane-based systems. However, the minimum value of rotation speed providing the satisfactory retention ($S_f > 0.3$) is dependent on the organic solvent nature. Such S_f values can be achieved for n-decane if $\omega = 350$ r/min, all other conditions being the same, whereas higher rotation speeds (400 r/min or more) are needed for the

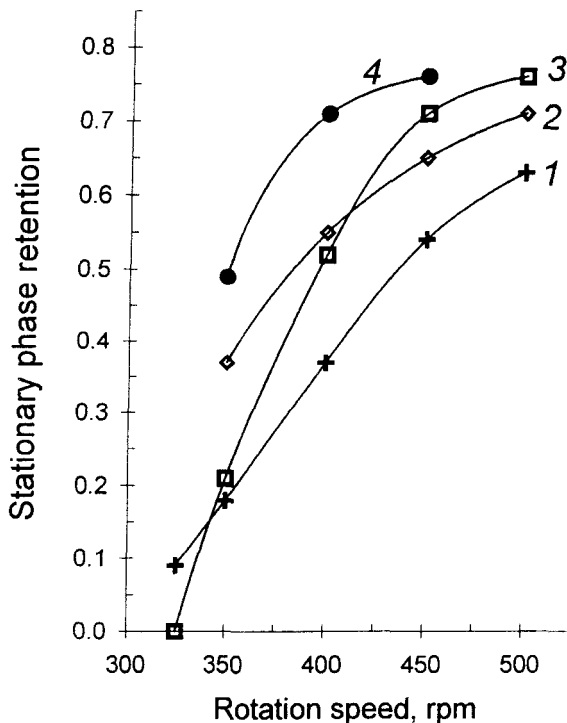


Figure 9. ω -Dependencies of S_f for systems with different organic stationary phases. $F = 1.1$ mL/min. Mobile phase: water. Stationary phase: 1 - n-decane; 2 - 5 % D2EHPA in n-decane; 3 - chloroform; 4 - 5 % D2EHPA in chloroform.

retention of chloroform. The high density of chloroform ($\rho = 1.48$ g/mL) may play a determining role, because the retention of the stationary phase of a higher density can require a higher ω providing a sufficiently strong force field. $\Delta\rho$ -dependencies of S_f for the chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq) and 5% D2EHPA in chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq) systems for different rotation speeds are shown in Fig. 10. The values of $\Delta\rho$ were varied by changing the salt concentration (from 2.5 to 15%) in the aqueous mobile phase. It is seen that an increase of $\Delta\rho$ results in an increase in S_f for the chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq) systems.

If ω is equal to 450 r/min, this dependence is linear. For the 5% D2EHPA in chloroform - $(\text{NH}_4)_2\text{SO}_4$ (aq) system, the retention factor is practically independent of the value of $\Delta\rho$ for all the rotation speeds used (350, 400 and 450 r/min). This phenomenon of the stabilizing retention is needed to be further investigated.

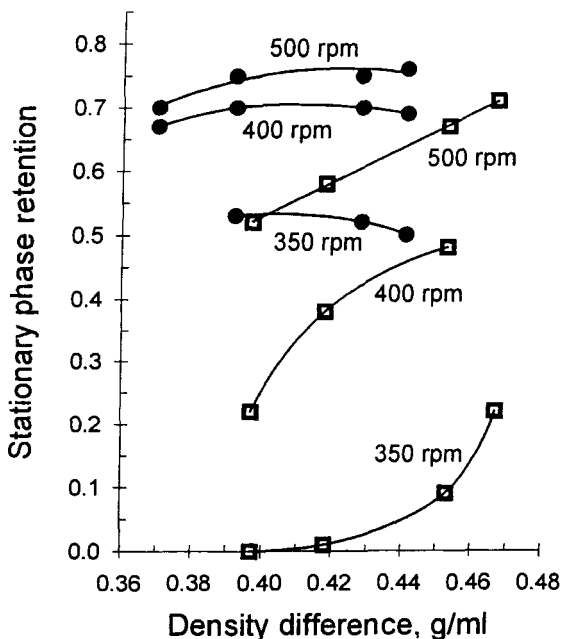


Figure 10. $\Delta\rho$ -Dependencies of S_f for different rotation speeds. $F = 1.1$ mL/min. Mobile phase: $(\text{NH}_4)_2\text{SO}_4$ (aq). Stationary phase: (□) - chloroform; (●) - 5% D2EHPA in chloroform.

CONCLUSIONS

Additions of an extracting reagent (D2EHPA) to the organic phase and additions of a salt to the aqueous phase can lead to changes in the physico-chemical properties ($\Delta\eta$, $\Delta\rho$ and γ) of the liquid system and affect, strongly, the stationary organic phase retention.

In the use of *n*-decane as organic solvent, the salt concentration in the aqueous phase does not practically influence S_f , the D2EHPA concentration in the organic phase being constant, whereas an increase of the extractant concentration in the organic phase results in a decrease of the S_f -value. The dependencies observed for the chloroform-based systems are more complicated.

If chloroform is used as stationary phase, S_f decreases with an increase in the mobile phase composition (salt concentration). The addition of D2EHPA in chloroform modifies the system properties. In this case, S_f is practically

independent of the salt concentration. Therefore, it should be emphasized that it is possible to attain a constant retention of the stationary phase at different density or viscosity differences between two phases (except for pure chloroform as stationary phase). This can be very useful in practice. It should be also noted that high values of interfacial tension (20 dyn/cm or more) are apparently not favourable for the stationary phase retention.

It has been shown that the higher is the rotation speed, the less is the influence of the two-phase system composition on the S'_I -value. Thus, in the case of using of the stationary phase of a higher density, high rotation speed (500 rpm or more) can be required.

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