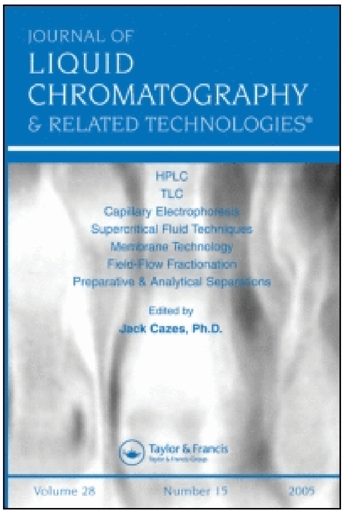

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Retention of the Stationary Phase in a Coil Planet Centrifuge: Effects of Interfacial Tension, Density Difference, and Viscosities of Liquid Phases

P. S. Fedotov[a]; D. Thiébaut[a]
[a] Laboratoire de Chimie Analytique Ecole Supérieure de Physique et de Chimie Industrielles de Paris (E.S.P.C.I.), Paris Cedex, France

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RETENTION OF THE STATIONARY PHASE IN A COIL PLANET CENTRIFUGE: EFFECTS OF INTERFACIAL TENSION, DENSITY DIFFERENCE, AND VISCOSITIES OF LIQUID PHASES

P. S. Fedotov,*,† D. Thiébaut

Laboratoire de Chimie Analytique
Ecole Supérieure de Physique
et de Chimie Industrielles de Paris (E.S.P.C.I.)
10, rue Vauquelin
75231 Paris Cedex 05, France

ABSTRACT

The influence of interfacial tension, density difference and viscosities of immiscible liquid phases on the stationary phase retention in a coil planet centrifuge has been studied. Two-phase liquid systems containing organic solvent (n-decane), extracting reagent (di-2-ethylhexylphosphoric acid), water, surfactant (sodium salt of dodecylbenzenesulphonic acid) and mineral salt (ammonium sulphate) have been considered. Varying concentrations of the system constituents allows selectively changing the interfacial tension, density difference or viscosity, all other conditions remaining the same. It has been shown that these parameters, especially interfacial tension, strongly affect the stationary phase retention. The data obtained are in good agreement with proposed theoretical models.

INTRODUCTION

Interfacial tension, density difference and viscosities of liquid phases are known to be the important physico-chemical parameters affecting the stationary phase retention in countercurrent chromatography (CCC).[1-3] In a previous publication,[4] we have tried to correlate composition and some physico-chemical properties of complex two-phase liquid systems used for CCC inorganic separations with their S_f-factor (ratio of the stationary phase volume V_s to the total column volume V_c). Systems containing organic solvents, a viscous extracting reagent, water, and a mineral salt have been considered.

Similar liquid systems, utilising one or several organic solvents and mineral salt aqueous solutions, can also be used for separation of organic species. Thus, the results reported[4] may be important for both inorganic and organic applications of CCC. However, varying the composition of the systems investigated can lead to a simultaneous change in all the physico-chemical parameters enumerated above. Therefore, some difficulties arise concerning the interpretation of the data obtained.

In the present work, we have investigated the influence of each physico-chemical parameter (interfacial tension γ, density difference between two liquid phases $\Delta\rho$ and viscosity of the organic stationary phase η_{org}) on the stationary phase retention. Two-phase liquid systems containing organic solvent (n-decane), extracting reagent (di-2-ethylhexylphosphoric acid), water, superfactant (sodium salt of dodecylbenzenesulphonic acid) and mineral salt (ammonium sulphate) have been chosen. These systems provide the possibility of selectively changing certain parameters (γ, $\Delta\rho$ or η_{org}), all other conditions being the same.

EXPERIMENTAL

Apparatus

Investigations of the stationary phase retention were made on a CCC device of J-type (Ito's classification[1]) consisting of a planet centrifuge with a horizontal column drum equipped by three multilayer coil columns (Pharma-Tech Research Corp., USA, Model CCC-2000) and a chromatographic pump (Gilson, France, Model 302). Only one coil column made of a Teflon tube with an inner diameter of 1.85 mm was used for our experiments. The total inner capacity of the column was 24 mL. β-Parameter ($\beta = r/R$, where r and R are rotation and revolution radii, respectively) is not a constant value for multilayer

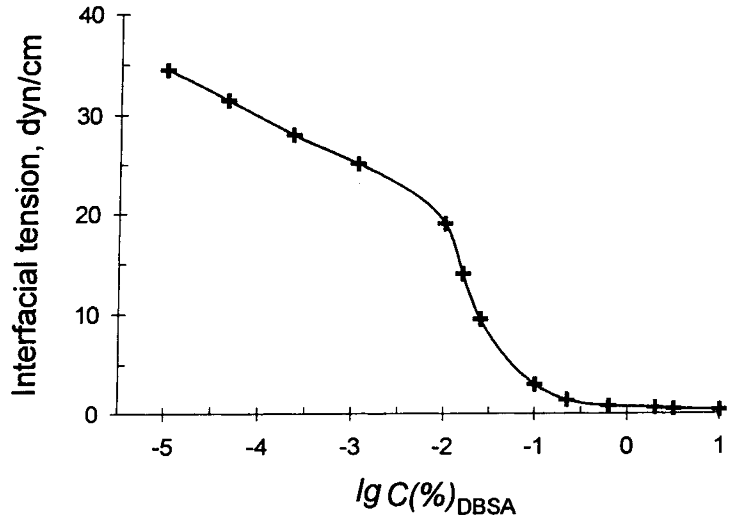

Figure 1. Dependence of interfacial tension on the logarithmic concentration of DBSA in the n-decane - DBSA - water liquid system.

columns. In our case, β varied from 0.38 (internal layer) to 0.53 (external layer). The mobile phase flow rate was equal to 1.0 mL/min. The rotation speed was varied from 400 to 1000 rpm. Apparatus for measurement of physico-chemical parameters of the systems under investigation are described in detail in our previous publication.[4]

Reagents

Di-2-ethylhexylphosphoric acid (D2EHPA, Sigma, 95 % minimum) was used as a cation-exchange extracting reagent. Sodium salt of dodecylbenzenesulphonic acid (DBSA) and other chemicals were analytical grade reagents.

Procedure

The CCC procedure, as well as procedure for the measurement of physico-chemical parameters of the systems used are given in reference [4]. However, it should be mentioned that the aqueous phase was used as the mobile phase and the organic one as the stationary phase. The mobile phase pumping direction was from head to tail. The mobile phase flow rate was equal to 1.0 mL/min.

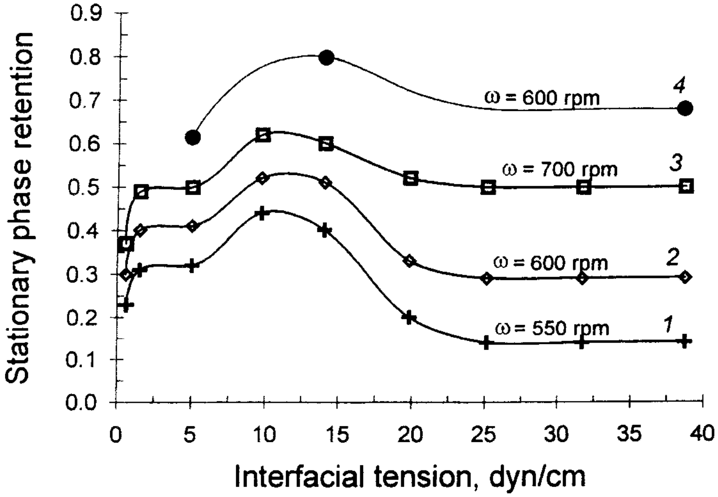

Figure 2. Influence of interfacial tension on the stationary phase retention. Two-phase liquid system: n-decane - DBSA - water. $\Delta\rho$ = 0.27 g/cm^3; η_{org} = 0.92 cP. $\eta_{aq} \approx$ 1.0 cP. ***1-3*** - Stationary phase: n-decane; mobile phase pumping direction - from head to tail; ***4*** - Stationary phase: DBSA in water; mobile phase pumping direction - from tail to head.

Table 1

Surfactant Concentration in the Aqueous Phase and Corresponding Values of Interfacial Tension γ and Capillary Wavelength λ_{cap} for the n-Decane - DBSA - Water Liquid System

C_{DBSA}, %	γ, dyn/cm	λ_{cap}, cm
0	38.7	0.240
5×10^{-5}	31.7	0.217
1×10^{-3}	25.1	0.193
5×10^{-3}	19.8	0.171
0.016	14.0	0.144
0.025	9.7	0.120
0.10	5.0	0.086
2	1.5	0.047
8	0.6	0.029

RESULTS AND DISCUSSION

Changing the Interfacial Tension of the Liquid System

DBSA has been chosen for changing the interfacial tension of the hydrophobic n-decane - water liquid system. This surfactant is soluble in water due to the presence of sulphonic group and is almost insoluble in n-decane. The logarithmic dependence of the interfacial tension on the concentration of DBSA in the aqueous phase is shown in Fig. 1. It is seen that a small addition of the surfactant can strongly affect the interfacial tension of the system under investigation. For example, γ decreases drastically (from 38.7 to 5.0 dyn/cm), whereas the DBSA concentration changes from 0 to 0.1% (0.1% correspond to about 3×10^{-3} mol/l). Thus, adding DBSA to the solvent system provides a considerable decrease in the interfacial tension, all other conditions being the same ($\Delta\rho = 0.27$ g/cm^3, $\eta_{\mathrm{org}} = 0.92$ cP, $\eta_{\mathrm{aq}} = 0.98$ cP). Further increasing the DBSA concentration is followed by a slight decrease in the interfacial tension value; γ attains 0.6 dyn/cm when C_{DBSA} is equal to 8%.

Influence of the Interfacial Tension on the Stationary Phase Retention

Influence of the interfacial tension on the stationary phase retention of the n-decane - DBSA - water liquid system is presented in Fig. 2. The corresponding values of the surfactant concentration are given in Table 1. As is seen from Fig. 2, high values of the interfacial tension (25-40 dyn/cm) are not favourable for the stationary phase retention. If the interfacial tension decreases, S_f increases attaining the highest values for $\gamma = 9\text{-}14$ dyn/cm. Further decreasing the interfacial tension is followed by the decrease in S_f. The most considerable decrease is observed when the interfacial tension value changes from 1.6 to 0.6 dyn/cm.

Thus, the moderate values of the interfacial tension (9-14 dyn/cm) are most favourable for the retention of the organic stationary phase of the system under investigation. Such behaviour of the liquid system seems to be unusual.

Earlier we have estimated the length L of an element of the stationary phase in a rotating coil column.[5] For the hydrophobic systems, it can be written:

$$L \approx \gamma / [\Delta\rho S^{1/2} \omega^2 R] \qquad (1)$$

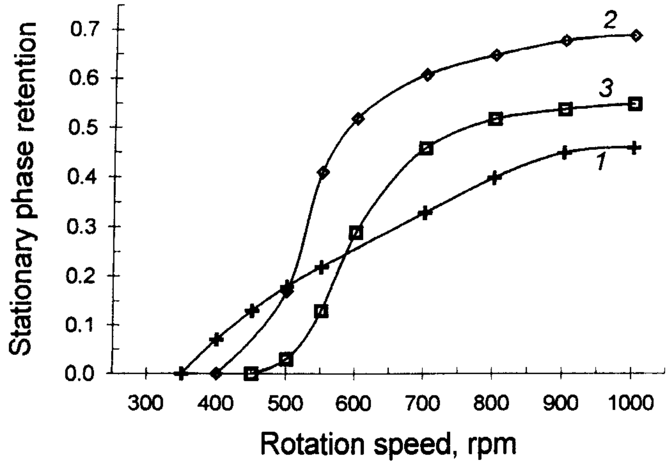

Figure 3. ω-Dependencies of S_f for the n-decane - DBSA - water systems. *1* - C_{DBSA} = 8%, γ = 0.6 dyn/cm.; *2* - C_{DBSA} = 0.025%, γ = 9.7 dyn/cm; *3* - C_{DBSA} = 0%, γ = 38.7 dyn/cm.

where S is the cross section area of a stationary phase element. The S-value is unknown; however, equation (1) may help to understand the observed phenomena. If the interfacial tension is high, the formation of stationary phase elements with high L is possible. That can lead to the hydraulic removing of the stationary phase elements from the column by the mobile phase flow. On the other hand, low values of interfacial tension provide the formation of small stationary phase elements characterising by low L. In this case, the entrainment of the stationary phase elements by the mobile phase flow can occur. Consequently, the moderate values of the interfacial tension lead to the formation of the stationary phase elements with the size which is most favourable for the stationary phase retention.

If γ is less than 1.5 dyn/cm, the system under investigation becomes hydrophilic,[6] the mechanism of the stationary phase retention changes, and S_f-value drastically decreases. Changing the hydrodynamic properties of the liquid system is confirmed by Fig. 3. It is seen that curves 2 and 3 are similar. According to the data reported,[2] such ω-dependencies of S_f are usually observed for hydrophobic systems. Curve 1, characterising the hydrodynamic behaviour of the n-decane - 8% DBSA in water liquid system (γ = 0.6 dyn/cm), is quite different. This curve looks like the major ω-dependencies of S_f for hydrophilic systems.[2]

Table 2

Physico-Chemical Parameters of D2EHPA - n-Decane - $(NH_4)_2SO_4$ Liquid Systems

Liquid System	ρ_{org}	ρ_{aq}	$\Delta\rho$	η_{org}	η_{aq}	$\Delta\eta$	γ	λ_{cap}
	--- g/cm ---			--- cP ---			dyn/cm	cm
1. 50% D2EHPA in n-decane - water	0.85	1.00	0.15	3.34	0.98	2.36	11.5	0.176
2. 50% D2EHPA in n-decane - 10% $(NH_4)_2SO_4$ (aq)	0.85	1.05	0.20	3.34	1.10	2.24	8.6	0.132
3. 50% D2EHPA in n-decane - 20% $(NH_4)_2SO_4$ (aq)	0.85	1.10	0.25	3.34	1.36	1.98	10.1	1.127
4. 50% D2EHPA in n-decane - 30% $(NH_4)_2SO_4$ (aq)	0.85	1.15	0.30	3.34	1.71	1.63	11.3	0.123
5. n-decane - 5% $(NH_4)_2SO_4$ (aq)	0.73	1.02	0.29	0.92	1.02	0.10	9.6	0.115
6. 30% D2EHPA in n-decane - 20% $(NH_4)_2SO_4$ (aq)	0.79	1.10	0.29	1.62	1.37	0.25	9.3	0.114

It should be noted that the higher the rotation speed, the lower is the dependence of the stationary phase retention on the interfacial tension. This fact is also in good agreement with our model. It is seen from expression (1), that the higher the rotation speed, the lower is the L-dependence of γ. In general, the increase in the rotation speed leads to the decrease of L-values. As we have mentioned above, decreasing the length of the stationary phase element can be followed by the decrease in the stationary phase retention. However, high rotation speed, providing a strong centrifugal force field, permits to diminish the entrainment of the stationary phase element by the mobile phase flow and, consequently, favours the stationary phase retention.

It is interesting to note that, if the aqueous and organic phases are used as the stationary and mobile ones, respectively, γ-dependence of S_f is practically unchanged (Fig.2, curve 4, mobile phase pumping direction - from head to tail). Nevertheless, in this case the curve is displaced in the area of high S_f-

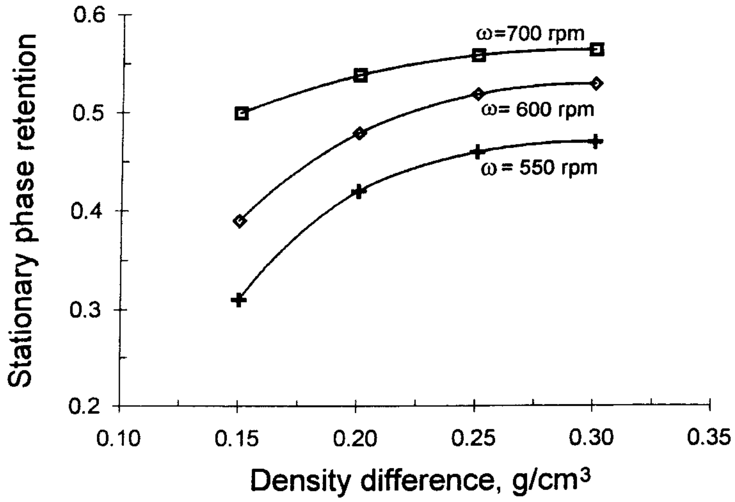

Figure 4. Influence of the density difference between the phases on the stationary phase retention. Liquid system: 50% D2EHPA in n-decane - $(NH_4)_2SO_4$ (aq). Concentration of $(NH_4)_2SO_4$: see Table 2, systems 1-4. $\eta_{org} = 3.34$ cP. $\gamma = 8.6\text{-}11.5$ dyn/cm.

values. Hence, if the heavier aqueous phase is used as the stationary phase, a relatively low value of the rotational speed (600 rpm) is sufficient for attaining high magnitudes of the stationary phase retention (more than 0.6). This phenomenon is needed to be specially studied.

Influence of the Density Difference Between Two Liquid Phases on the Stationary Phase Retention

Varying the concentration of ammonium sulphate in the 50% D2EHPA in n-decane - $(NH_4)_2SO_4$ (aq) system allowed us to change the density difference between two liquid phases from 0.15 to 0.30 g/cm^3, whereas the other parameters (interfacial tension and viscosity of the stationary organic phase) are practically constant (Table 2, systems 1-4). In fact, the interfacial tension varies in the range 8.6-11.5 dyn/cm. However, as we have mentioned above, the stationary phase retention is practically unchanged in this interval of γ-values.

$\Delta\rho$-Dependencies of S_f for different rotation speeds are presented in Fig. 4. It is seen that the stationary phase retention slightly increases with the increase of the density difference from 0.15 to 0.25 g/cm^3, whereas in the range of $\Delta\rho$

from 0.25 to 0.30 g/cm^3 the stationary phase retention is practically independent on the density difference. The influence of the density difference on the interfacial tension decreases in general with the increase of the rotation speed.

The results obtained can be also correlated with expression (1). Relatively high $\Delta\rho$-values (0.25-0.30 g/cm^3) must lead to the moderate length of the stationary phase elements, which is most favourable for the stationary phase retention. The decrease in the density difference is followed by an increase in L-values. Hence, in this case, the hydraulic removal of the stationary phase elements from the column by the mobile phase flow can occur.

As it is seen from the results obtained (Fig. 2, Fig. 4) the dependence of S_f on the interfacial tension is much stronger and complicated than that of the density difference, though $\Delta\rho$ and γ are first order magnitudes in expression (1). However, it should be emphasised that the interfacial tension was varied from 0.6 to 38.7 dyn/cm (in other words, it was increased in about sixty times), whereas the density difference was only varied from 0.15 to 0.30 g/cm^3.

The results obtained are different from those reported by Berthod.[3] This may be explained by the difference in two-phase liquid systems (systems on the basis of two or more solvents have been investigated in reference [3], while we have studied complex liquid systems containing an organic solvent, a viscous extracting reagent, water and a mineral salt.

Influence of the Viscosities of Liquid Phases on the Stationary Phase Retention

Viscosities of the two phases of a liquid system (especially the viscosity of an organic phase) have been reported earlier to affect, strongly, the hydrodynamic behaviour of two liquids in a coil column.[6] For our studies, the viscosities of two liquid phases were varied by changing the concentrations of $(NH_4)_2SO_4$ and D2EHPA in the D2EHPA - n-decane - $(NH_4)_2SO_4$ (aq) system (Table 2, systems 4-6). Choosing the appropriate combination of D2EHPA and $(NH_4)_2SO_4$ concentrations provided the change in viscosity values, other parameters being practically the same ($\gamma = 9.3\text{-}11.3$ dyn/cm, $\Delta\rho = 0.3$ g/cm^3).

The influence of the viscosity of the organic stationary phase (η_{org}) on the S_f-value is shown in Fig. 5. It is seen that S_f increases and then slightly decreases with the increase in η_{org}. Thus, for the system under investigation, the moderate stationary phase viscosities (1.5-2.0 cP) are most favourable for

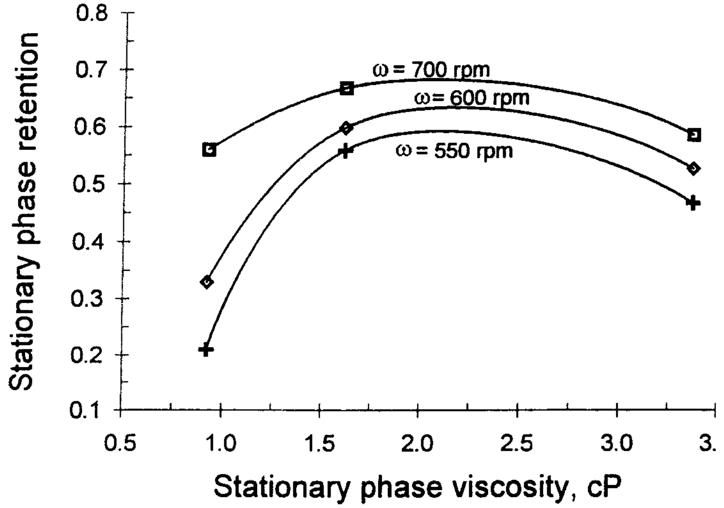

Figure 5. Influence of the organic stationary phase viscosity on S_f. Liquid system: D2EHPA in n-decane - $(NH_4)_2SO_4$ (aq). Concentration of $(NH_4)_2SO_4$: and DBSA: see Table 2, systems 4-6. $\Delta\rho = 0.3$ g/cm^3. $\gamma = 9.3 - 11.3$ dyn/cm.

the stationary phase retention. It should be noted that the aqueous phase viscosity is also varied (see Table 2). So, it is of interest to present the dependence of S_f on η_{org}-η_{aq} (Fig. 6). It is seen that Fig. 5 and Fig. 6 are similar. It should be noted that the stationary phase retention is practically unchanged in the range of η_{org}-η_{aq} from 0.2 to 1.3 cP (η_{org} varies from 1.7 to 3.3 cP), especially if the rotational speed is high (700 rpm). This phenomenon can be useful in practice.

It is not quite clear why low values of the viscosity difference ($|\eta_{org}-\eta_{aq}| < 0.1$ cP) lead to a significant decrease in the stationary phase retention, especially if the rotation speed is relatively low (ω = 550-600 rpm). Maybe, in some cases, the viscosity difference may be, like the density difference, a "moving force" of the retention process.

Classification of the Systems Investigated on the Basis of a Capillary Wavelength

The dynamics of the macroscopic behaviour of the interface between two immiscible liquids is governed by the evolution of waves. The following

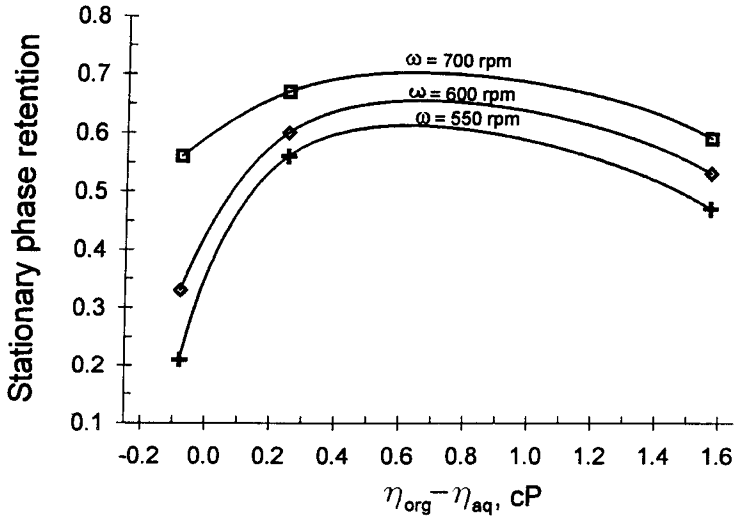

Figure 6. Influence of η_{org}-η_{aq} on the stationary phase retention. Liquid system: see Figure 5. $\Delta\rho$ = 0.3 g/cm^3, γ = 9.3-11.3 dyn/cm.

expression has been proposed for estimating the capillary wavelength λ_{cap}, cm[7]:

$$\lambda_{cap} = 2\pi[\gamma/(\Delta\rho\times981\times100)]^{1/2} \tag{2}$$

Unfortunately, expression (2) does not consider the viscosities of liquid phases. However, it can be useful for classification of the systems investigated. The values of the capillary wavelength are presented in Tables 1 and 2. A correlation between λ_{cap} and the stationary phase retention can be evaluated. As is seen from the data obtained, the values of λ_{cap} in the range from 0.12 to 0.14 cm provide the highest values of the stationary phase retention for both n-decane - DBSA - water and D2EHPA - n-decane - $(NH_4)_2SO_4$ - water liquid systems, the viscosity of the organic stationary phase being the same. Hence, estimating the capillary wavelength may help to choose a system providing a satisfactory retention from several liquid systems with a constant η_{org}.

CONCLUSION

The contribution of interfacial tension, viscosity and density differences in two-phase liquid systems to the stationary phase retention has been estimated.

It has been shown that moderate values of the interfacial tension (9-14 dyn/cm) are most favourable for the retention of the organic stationary phase. In addition, the stationary phase retention slightly increases with the increase in density difference from 0.15 to 0.25 g/cm^3, whereas in the range of $\Delta\rho$ from 0.25 to 0.30 g/cm^3 S_f is practically independent on the value of $\Delta\rho$.

The viscosity difference between two phases can also affect the stationary phase retention. Low values of $|\eta_{org}-\eta_{aq}|$ (< 0.1 cP) lead to a significant decrease in the stationary phase retention.

The results on the influence of γ and $\Delta\rho$ on the stationary phase retention have been correlated with a theoretical model which had been proposed earlier.[5] Experimental data and theoretical expressions are in good agreement.

It should be noted that the higher is the rotation speed, the lower is the dependence of the stationary phase retention on the physico-chemical parameters investigated. This fact is also correlated with our model.

The systems investigated have been classified on the basis of the capillary wavelength. Estimating this value may help to choose a system providing a satisfactory retention from several liquid systems with a constant η_{org}.

Further studies are needed to extend the regularities obtained to other two-phase liquid systems.

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