*Polish Journal of Chemical Technology, 9, **1**, 43 — 50, 2007, 10.2478/v10026-007-0011-1*

The influence of organic diluents and solvents on the stability of PVC plastisol water dispersions

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The work presents the research, the aim of which is to specify the influence of organic diluents and solvents such as xylene, toluene, n-butyl acetate and butanol as well as cyclohexanone on the stability of water dispersions of the PVC plastisol containing various surface-active agents (SAA). The applied surfactants were characterised by a specific ethoxylation number, molecular mass, the Hildebrand parameter, hydrophilic-hydrophobic balance, surface activity, the limiting viscosity number, the Haller interaction constant, the limiting equivalent conductivity and the Kohlrausch-Onsager equation „b" constant. Basing on the molar refraction and the Hildebrand parameter, the interactions between the plastisol constituents and the constituents of water dispersions of the PVC plastisol were established. The sedimentation tests on the PVC plastisol water dispersions stabilized by various surface-active agents with an organic diluent or solvent added indicated that the addition resulted in the dispergation yield, a reduction in the PVC plastisol molecular size in water dispersion and the increased Huggins interaction constant, showing both surface lyophilisation and higher adsorption of surface-active agents.

Keywords: water dispersions of polymers, surface-active agents (SAA), PVC plastisol.

INTRODUCTION

One of the main trends in the development of contemporary paint and varnish industry is a tendency to reduce or eliminate completely the polar and toxic organic solvents and diluents in the composition of a painting substance. Water dilute paints and powder paints can be rated among the latest and most advanced materials[1, 2].

Water dispersion paints are the lyophobic systems, as a rule thermodynamically unbalanced and unstable. The particles of the constant phase are characterised by an unsaturated surface force system on the developed interfacial separation surface, the automatic reduction of which is related to their aggregation and coagulation. The instability of particles in these systems results from gravity that contributes to their sedimentation. In order to provide the particles with aggregative stability, it is necessary to create adsorptive layers or a double electric layer on their surface that would result in the emergence of electrostatic repulsion as well as solvation and adsorptive-solvation layers. Surface-active agents are used as stabilizers and are able to adsorb on the interface, reducing the interfacial surface free energy. A characteristic feature of the surfactants consists in the fact that its molecules in a solution are more active than the medium molecules. The surface activity of the agents reveals not only with respect to the medium, but also moderates the solution-air interface features. That is why surface-active agents (SAA) include compounds, the molecules of which consist of two parts: polar and non-polar, called hydrophilic and hydrophobic (or lipophilic)[3 – 5].

SAA are often applied to stabilize and control the properties of disperse systems. Surfactants can affect the creation of adsorptive and solvation layers on the surface of the disperse phase particles, particle interaction, rheological and structural properties of the disperse systems. In the SAA solutions and disperse systems co-exist individual molecules and micelles, between which balance is stabilised. There are distinguished several mechanisms of SAA's own micelles formation and of the micelles of the disperse phase particles, depending on the character of the polar group interaction. For ionic SAA, an important role is played by electrostatic interactions. In the water medium, micelles are created due to hydrophobic interactions. In the non-polar liquids hydrogen and coordinate bonds emerge between the polar groups of the SAA molecules, the orientation of which in the micelles is determined by the polarity of the disperse medium. Under these conditions, the micelles can have the forms of globules, ellipsoids, rods, plates and helixes. With the change in the solution concentration, temperature, pH and other conditions, the change in the shape of micelles is also possible[6 – 8].

SAA adsorption layers on the liquid surface reduce surface energy and simultaneously increase the aggregation stability of the disperse system. The structure and the properties of both adsorption and border layers on the solids surface dispersed in the dispersing medium may become an interesting research problem. The actual surface of a solid body is heterogeneous and probably so is the SAA adsorption layer. The first basic monolayer of the adsorbed molecules of the surface active agents is bonded with the atoms of a solid body by physical or chemical interactions, the energy and the properties of which determine the structure of the whole adsorption-solvation layer. The molecular interactions in the adsorption layer form two-dimensional structures, and as far as border layers are concerned, SAA's own micelles are created[3, 6, 9].

The properties of adsorption layers on the particles of solids will depend on the type of the dispersing medium. In many cases they are solvated by solvent molecules, through which the energy of intermolecular interactions, leading to the change of the disperse system stability, is altered. The influence of surface-active agents on the particle interactions was generally explained on the basis of lyophilisation of their surface and an increase in solvation. To explain the stabilizing action of high-molecular surfactants, control agents were introduced, in accordance with which the resistance of the particles moving closer to adsorption layers results from their reduced mobility[10, 11].

However, it is not possible to use one method to specify the dispersion stability degree. The process of stability loss occurs as a result of disperse particle collision affected by Brownian and convection movements. The influence of the SAA molecule structure on the dispersion stability depends on the geometric (form) barrier, i.e., the distance between the already adsorbed emulsifier molecules in the adsorption layer and the proportion of the mass of particular atoms that constitute a polar group with reference to the total mass of non-polar units specified by the hydrophilic and lipophilic balance (HLB). An important role here is played by the energy barrier which determines the minimum resistance of the adsorption layer to external deformation and by the concentration barrier that specifies the number of SAA molecules in a volume unit of the adsorption layer, thus conditioning the presence of a saturated adsorption layer on the surface of the dispersion particle[3, 12, 13].

Dispersion structures are diphase multicomponent systems which are divided into lyophilic, lyophobic and of transitory type. The volume of critical interfacial tension on the border of the disperse phase and the liquid medium is a criterion that includes dispersion into a given type of a colloidal system, which is expressed by dependence[2, 6]:

$$\sigma_{Kr} = (k \cdot T/a^2) \qquad (1),$$

where: a stands for the particle size in the system, k is the Boltzman constant, T is absolute temperature. Polymer constitutes the disperse phase in water systems, and the water with a dissolved stabilizer – the surface-active agent – is the disperse medium.

It should be stressed that currently no specific theory of making, stabilizing and forming films from the disperse substance of transitory and lyophobic types exists. This difficulty stems from the complexity and variety of the processes accompanying polymer dispergation in the liquid phase and their stability necessary for the production of appropriate substance and film[14 – 17].

The preparation of stable water dispersion of the PVC plastisol will allow their application through various methods and as protective films. The purpose of the work was to define the influence of different kinds of surface-active agents on the durability of the PVC plastisol water dispersions. Non-ionic and anionic surface-active agents of various structures and different degree of ethoxylation and hence of different surface activity and different properties were used for dispergation. The research was to characterise the factors that affect the stability of disperse systems and to define the dependencies between the structure parameters and the SAA properties, and the factors that determine the properties of these systems.

EXPERIMENTAL

Materials

Emulsive polyvinylchloride (PVC) in the form of white powder, made in the „Dwory" Chemical Works in Oświęcim, type E-68 Pmbs with K=69.5 number was used to prepare the PVC plastisol. Phthalate di(2-ethylhexyl) (DOP), molecular weight 390, $d^{25}=0{,}982$ [g/cm^3], $n^{20}=1{,}488$; dibutyl sabacate (DBS), molecular weight 314, $d=1{,}436$ [g/cm^3], $n^{20}=1{,}440$; dibutyl phthalate (DBP), molecular weight 278, $d=1{,}046$ [g/cm^3], $n^{20}=1{,}492$ were used as plasticizers. Non-ionic and anionic surface-active agents from different sources and with different ethoxylation numbers were used to stabilize the water dispersions of the PVC plastisol from the following compounds: ethoxylated fatty alcohols, ethoxylated fatty acids, ethoxylated alkylphenols, ethoxylated aliphatic amides and anionic agents. The above-mentioned surface-active agents were produced in the „Rokita" SA Chemical Works in Brzeg Dolny. Their characteristics and basic properties in water solutions are shown in Table 1. The data presented in the table were calculated using tensiometrical, viscometrical and conductometrical methods. The organic diluents and solvents such as xylene, toluene, n-butyl acetate, butanol and cyclohexanone were used in dispersion.

Method of obtaining the PVC plastisol

Plastisol was prepared through careful, mechanical mixing of 100g of PVC-E powder with 120g of DOP plasticizer in a mortar for 8 h. DOP, DBP and DBS were used as plasticizers. After sieving, the sample was deaerated at rest and under lowered pressure (6, 5 Pa, at 22°C) within 72 h. 48 h after having finished the deaeration, the samples were used for the research. The obtained product was homogeneous, without agglomerates of polymer grains. A detailed method of obtaining PVC plastisol has been described in this work[18].

Method of obtaining PVC plastisol water dispersion

10g of PVC plastisol and 1 cm^3 of organic diluent or solvent were put into a homogenizer. Then 50 cm^3 of distilled water, in which an adequate amount of a surface-active agent was dissolved, were added. The tested compositions contained 10 wt.% of the SAA mass fraction (PVC plastisol) in water. Next, the whole was dispergated in a laboratory homogenizer of IKA-Ultra-Turrax T25 type with a mixer arm of IKA-S25N-18G type for 25 minutes. The dispersions prepared in this way were used for further tests.

METHODS

The properties of water solutions of surface-active agents are shown in Table 1.

The Hildebrand solubility parameter for surface-active agents was calculated on the basis of the additivity of cohesion energy density of particular atoms and units that comprise the composition of the compound, and they are listed in the tables of the monograph[19].

The hydrophilic-lipophilic balance value (HLB) was calculated according to the following formula[4, 5, 13]:

$$HLB = 20 \cdot (M_r/M) \qquad (2),$$

where M_r is the total molecular weight of ethoxyl groups, anion or sulphate ones (hydrophilic) in a particle of a surface-active agent, M is the total molecular weight of a surface-active agent. The critical concentration of micelles creation (C_{CMC}) was established by means of experimental methods on the basis of the dependencies between the surface tension and the SAA concentration in water which

Table 1. Kinds of surface-active agents used and some of their properties calculated and determined experimentally

No of surface-active agent	Chemical and trade name	Chemical formula	Hildebrand parameter	HLB	Critical concentration of formed micelles C_{CMC}*10^{-3} [moles/dm^3]	SAA surface activity G*10^{-3} [mN·m·dm^3/mole]	Surfactant limiting viscosity number GLL_{SPC} [cm^3/g]	SAA Haller interaction constant K	SAA limiting equivalent conductivity λ_0 [mS*m^{2}*g^{-1}]	SSA Kohlrausch Onsager's equation constant B	Percentage contents SSA [% weight]
1	Oxyethylated lauryl alcohol (Rokanol L-4)	$C_{13}H_{27}O(CH_2CH_2O)_4H$	7,3	9,4	1,1	59,3	1,45	0,34	130,8	0,78	18,94
2	Oxyethylated saturated fatty alcohol (Rokanol Ł-18)	$C_{19}H_{39}O(CH_2CH_2O)_{18}H$	8,3	14,7	0,2	93,7	0,39	1,01	85,8	0,20	73,01
3	Oxyethylated lauryl alcohol (Rokanol L-25)	$C_{13}H_{27}O(CH_2CH_2O)_{25}H$	8,3	17,0	0,2	12,6	0,54	0,72	292,9	0,40	77,28
4	Oxyethylated rape oil (Rokacet RZ-17)	$(C_{17}H_{33}COO)_3(CH_2CH_2O)_{17}$ (CH_2CHCH_2)	8,3	9,2	0,5	66,1	1,14	0,79	39,8	0,67	95,36
5	Oxyethylated stearic acid (Rokacet S-24)	$C_{16}H_{33}COO(CH_2CH_2O)_{24}H$	8,3	16,0	0,4	73,1	0,60	1,53	11,2	0,92	88,87
6	Oxyethylated glyceride of plant origin (Rokacet R-26)	$(C_{17}H_{33}COO)_3(CH_2CH_2O)_{26}$ (CH_2CHCH_2)	8,3	11,3	0,3	68,1	0,09	10,12	2,8	2,11	98,77
7	Addition product of ethylene oxide to glycerides of plant origin (Rokacet R-33)	$(C_{17}H_{33}COO)_3(CH_2CH_2O)_{33}$ (CH_2CHCH_2)	8,5	11,8	0,22	74,0	0,10	-0,79	18,5	0,07	98,13
8	Adduct of ethylene oxide to nonylphenol (Rokafenol N-5)	$C_9H_{19}C_6H_4(CH_2CH_2O)_5H$	7,7	10,2	0,44	12,1	0,53	-0,32	250,1	1,04	84,01
9	Adduct of ethylene oxide to nonylphenol (Rokafenol N-705)	$C_9H_{19}C_6H_4(CH_2CH_2O)_{7,5}H$	7,3	12,2	0,17	20,1	0,42	-1,38	26,3	0,34	98,02
10	Adduct of ethylene oxide to nonylphenol (Rokafenol N-8)	$C_9H_{19}C_6H_4(CH_2CH_2O)_8H$	7,1	13,1	0,07	51,8	0,32	-0,11	31,6	0,08	85,25
11	Oxyethylated fatty amine (Rokamin SR-8)	$C_{17}H_{35}NH(CH_2CH_2O)_8H$	7,2	11,5	0,11	31,6	0,12	-3,70	30,2	0,07	74,41
12	Oxyethylated ethanolamide (Rokamid MT-17)	$C_{19}H_{39}CONH$ $(CH_2CH_2O)_{17}H$	6,8	14,1	0,09	31,4	0,31	-1,16	44,7	0,11	95,76
13	Sodium salt of sulpho-succinic acid monoester oxyetylated nonylphenol (Sulfobursztynian N-5)	$C_9H_{19}C_6H_6O(CH_2CH_2O)_5$ $COCH_2CH_2COOSO_3Na$	7,1	10,0	0,06	63,7	0,07	2,41	3162,3	0,23	44,97
14	Sodium salt of sulfate adduct of fatty alcohol and ethylene oxide (Sulforokanol L-225/1)	$C_{19}H_{39}O(CH_2CH_2O)_2SO_3Na$	6,9	8,3	0,02	16,37	0,18	2,80	7943,3	0,54	17,64
15	Alkylbenzene sulfonate acid (ABS)	$C_{12}H_{25}C_6H_6SO_3H$	8,6	4,9	0,031	12,0	0,11	9,63	66,8	2,61	92,89

were measured using Du Nouy's tensiometrical balance. The graphically determined minimal value of surface tension corresponds with the value of C_{CMC} [4, 5]. The SAA surface activity (G) in water was calculated on the basis of the following formula[21]:

$$G = (\sigma_{H20} - \sigma_{(CMC)})/C_{CMC} \qquad (3),$$

where: σ_{H2O} is the surface tension of the water, $\sigma_{(CMC)}$ is the limiting surface tension of a surface-active agent solution when its concentration equals C_{CMC}. The limiting viscosity number (GLL_{spc}) of SAA water solutions was determined on the basis of viscosity measurement carried out by the use of Ubbelhod's capillary viscometer. The measurement was taken according to the principle consisting in determining the time of the outflow of a given volume of the solution from the container through the capillary. In order to calculate the viscosity of the solution, the times of the outflow of pure solvent (water) (t_0) and the solution (t) were measured. For the calculations the Poisenielle`s equation was used, and it was assumed that the density of the diluted solution equals the density of the pure solvent. The ratio of the viscosity was calculated on the basis of these assumptions, following the equation[4, 19, 20]:

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \qquad (4),$$

where: η is the viscosity of the solution, η_0 is the viscosity of the solvent (water).

In this case the reduced viscosity number (η_{red}) can be expressed by the following dependence[20]:

$$\eta_{red} = \frac{\eta - \eta_0}{\eta_0 \cdot c} = \left[\frac{\eta}{\eta_0} - 1\right] \cdot \frac{1}{c} = \left[\frac{t}{t_0} - 1\right] \cdot \frac{1}{c} \qquad (5),$$

where c is the concentration of a surface-active agent in the water solution in [g/100cm^3]. In the dependence between the reduced viscosity and the SAA concentration, the value of the limiting viscosity number (GLL_{spc}) (also represented by $[\eta_{SPC}]$ symbol), was established by extrapolation of η_{red} to $c \Rightarrow 0$ concentration. A full range of dependencies between the reduced viscosity and the SAA concentration in water solutions is best described by Haller`s equation[22]:

$$\frac{1}{\eta_{red}} = \frac{1}{[\eta_{spc}]} - k \cdot c \qquad (6),$$

where: $[\eta_{spc}]$ is the limiting viscosity number, c is the concentration of a surface-active agent (SAA) in [g/100cm^3], k – the Haller constant which describes the extent of the interactions between the particles of the surfactant (SAA) and the water.

The electrochemical properties of the SAA water solutions were determined on the basis of conductometrical tests[23]. They consisted in taking the measurements of the electrical conductivity of the SAA solutions in the course of their diluting. Knowing the values of the electrical conductivity of the SAA solutions, the value of their equivalent conductivity was calculated (λ) from the following equation:

$\lambda = (\kappa_{SPC}-\kappa_{H2O})/ c_{SPC}$ (7),

where: κ_{SPC} is the electrical conductivity of the surface-active agent solution with the concentration of c_{SPC}, κ_{H2O} is an electrical conductivity of the solvent (water). Then Kohlrausch-Onsager's equation was used[23, 24]:

$\lambda = \lambda_0 - b\sqrt{c}_{SPC}$ (8)

to establish the value of the limiting equivalent conductivity (λ_0) and b constant. Both constants are empirically determined on the basis of the graphical diagram $\lambda = f(\sqrt{c}_{SPC})$.

The percentage content of the surface-active agents is calculated on the basis of the ratio of the mass that remained after having dried a sample of a surface-active agent on a Petri dish at the temperature of 100°C within 48 hours to the SAA weighed mass:

$P = (m_2/ m_1) \cdot 100\ [\%]$ (9),

where: m_2 is the SAA mass after drying, m1 is the SAA mass weighed on a Petri dish. The results are shown in Table 1. The obtained water dispersions of the PVC plastisols stabilized with different types of surface-active agents were subject to sedimentation, viscometrical and tensiometrical tests. Sedimentation measurements were performed in sedimentation cylinders of 50 cm^3 capacity. They consisted in determining the amount of PVC plastisol in the disperse phase after 14 days of exposure when the state of equilibrium was achieved in the disperse system. The sedimentation measurements make it possible to determine the so-called dispergation capacity which is represented by Wd symbol, and it was calculated according to the following formula:

$W_d = (c_1/c_0) \cdot 100\ [\%]$ (10)

In the above formula c_0 is the theoretical (initial) amount of PVC plastisol in water dispersion in conversion to [g/cm^3], c_1 is the amount of the plastisol determined by taking 10 cm^3 of the disperse phase of a dispersion from the sample and then drying it on a Petri dish at 120°C to get a solid mass in 24 h in [g/cm^3]. The remaining data refer to the viscometrical measurements of the stable disperse phase of the PVC plastisol water dispersion. The limiting viscosity number of the dispersion (GLL_{dysp}) was determined by measuring the viscosity of the disperse phase of the PVC plastisol water dispersion using the Ubbelhod's viscometer. The limiting viscosity number and the Huggins constant were calculated on the basis of viscometrical data and the following relationship[4, 20]:

$\eta_{red} = [\eta_{dysp}] + k_H \times [\eta_{dysp}]^2 \cdot c$ (11),

where: $[\eta_{dysp}]$ is the limiting viscosity number of dispersion particles of the PVC plastisol in water and determines their size, kH is the Huggins constant determining the extent of the interactions between the surface of PVC plastisol particles and the water medium. The Huggins interaction constant can be calculated by transforming formula (11) into the following one:

$k_H = (\eta_{red} - [\eta_{dysp}]) / ([\eta_{dysp}]^2 \cdot c) = (tg\alpha) / [\eta_{dysp}]^2$ (12),

where c is the concentration of the disperse phase expressed in [$g/100cm^3$].

The Hildebrand solubility parameter as a constant value for PVC plasticizers, diluents and solvents was calculated on the basis of the data included in monograph[19] and shown in Table 2. The values of the compound solubility parameter were calculated on the basis of weight additivity of particular constituents in the system. In this case the solubility parameter was calculated in accordance with the following formula:

$\delta = m_1/(m_1+m_2+...m_i) \cdot \delta_1 + m_2/(m_1+m_2+...m_i) \cdot \delta_2 + ... + m_i/(m_1+m_2+...m_i) \cdot \delta_i$ (13),

where: m_1, m_2... m_i are masses and δ1, δ2 … δi are the Hildebrand solubility parameters of particular compound constituents. The value of the miscibility parameter ß was calculated in accordance with the following formula[19]:

$\beta = (\delta_1 - \delta_2)^2$ (14),

where: δ_1, δ_2 are solubility parameters of particular dispersion constituents. The results obtained are shown in Tables 2 and 3.

The value of molar refraction for particular dispersion constituents was calculated on the basis of the Lorentz-Lorenc formula in the form of[24]:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \qquad (15),$$

where: R is a coefficient of molar refraction determining indirectly the polarity of the compound particles, n is a coefficient of light refraction, M is molecular mass, d is the liquid density. The value of the solution molar refraction was calculated on the basis of the total number of molar refractions of particular solution constituents:

$R = M_1/(M_1+M_2+...M_i) \cdot R_1 + ... + M_i/(M_1+M_2+...M_i) \cdot R_i$ (16),

where: M_1, M_2, … M_i are molecular masses of particular constituents that form in the equation a molar fraction of the constituent in the solution, R_1 is molar refraction of this constituent. The results obtained are shown in Table 4.

RESULTS AND DISCUSSION

The formation of a stable disperse system is connected with forming the interface in the polymer particle – disperse medium systems. Under these conditions a transition of a liquid from the disperse medium to polymer particles can be observed, which is related with their limited swelling. On the interface an adsorption layer emerges, which is connected with the concentration of surface-active agents and the reduction in surface tension. In multiconstituent systems the balance of low-particle constituent distribution is gradually stabilised between the polymer phase and the disperse system, as well as the adsorption equilibrium. The phase constitution of the disperse system is determined by its various properties and in particular by aggregative and kinetic stability, rheological characteristics as well as the capacity of forming a film. Considering the above, it may be concluded that the processes occurring in the disperse system volume are strictly interdependent. Thus the control of the disperse system properties consists in establishing the influence of surface-active agents on the processes of mutual interactions between the particles of the disperse phase as

Table 2. Calculated values of the Hildebrand solubility parameter and the miscibility parameter for individual constituents forming the PVC plastisol dispersion

Polymer and plasticizer	Calculated values of the Hildebrand solubility parameter for plastisol constituents $[(cal/cm^3)^{1/2}]$	Calculated values of the Hildebrand solubility parameter for PVC plastisols $[(cal/cm^3)^{1/2}]$	Calculated values of the miscibility parameter $\beta = (\delta_{PVC}-\delta_{plasticizer})^2$
PVC	9,6	–	–
DOP	7,9	8,67	2,89
DBS	9,2	9,38	0,16
DBP	9,4	9,49	0,04

Table 3. Calculated values of the solubility and miscibility parameters for diluents and solvents in the plastisol – the solvent system

Diluents or solvents	Calculated values of the Hildebrand solubility parameter $[(cal/cm^3)^{1/2}]$	Calculated values of the β miscibility parameter in the plasticizer-solvent or solvent-water system			
		DOP	DBS	DBP	Water
Xylene	8,83	0,86	0,14	0,33	212,29
Toluene	8,97	1,15	0,05	0,19	208,23
N-butyl acetate	8,4	0,25	0,64	1	225
Butanol	10,77	8,24	2,47	1,88	159,52
Cyclohexanone	9,26	1,85	0,004	0,02	199,94
Water	23,4	240,25	201,64	196	–

well as their interactions with the disperse medium. One of the methods is binding the surface-active agent from the disperse system with a surface of the disperse phase particles.

Surface-active agents (SAA) reveal the ability to change surface tension on the phase separation border. In diluted water solutions they occur in the form of individual particles. When their number in the solution increases, then under specific conditions the SAA molecule associations called micelles are formed. These are particle groups, which change the physical properties of a solution. The SAA concentration that is relevant to micelle formation is called micelle critical concentration (C_{CMC}). After having exceeded the C_{CMC} value, the SAA particle groups constitute a solid form, in balance with individual particles of the surface-active agents.

Some properties of the surfactants used in the experiment are shown in Table 1. The table presents: ethoxylation number, the calculated molecular weight, the value of the Hildebrand solubility parameter, the value of hydrophilic-lipophilic balance (HLB). The value of the critical concentration of micelles formation, surface activity, the limiting viscosity number, the Haller interaction constant, the limiting equivalent conductivity and Kohlrausch-Onsager's equation constant were calculated.

The PVC emulsion forms with plasticizers dispersions of paste consistence – the so-called plastisols. Through the plastisol gelation at high temperatures homogenous films are produced. The PVC plastisols used for coatings are characterized by appropriate rheological properties, time stability and by sedimentation resistance, etc. The type of polymer and plasticizer, and especially their structures, the shape and size of polymer grains, substantially affect plastisol properties. The phenomenon of sedimentation in plastisols brings about phase heterogeneity and polymer sedimentation. The possibility to modify the PVC plastisol properties by selecting an appropriate plasticizer extends the scope of paste application and influences the disperse system properties. Adding an organic solvent or diluent, the presence of which in the plastisol and its water dispersion substantially changes the system condition, will have even a bigger effect on the PVC plastisol properties.

In Table 2 the calculated values of the Hildebrand solubility parameter and the miscibility parameter for the tested PVC plastisol systems, consisting of PVC and plasticizer are shown. They were calculated in accordance with equations 13 and 14. From the data considered, it might be concluded that particular PVC plasticizers applied differed in terms of the solubility parameter value. The lowest miscibility parameter value is revealed in PVC-DBP system, slightly higher – PVC-DBS system. The aforementioned plastisol systems should theoretically be most stable. The biggest difference was noted in the PVC-DOP system. This system should be least stable. Polymer grains in this system will be solvated to the smallest degree.

Table 3 presents the calculated values of the PVC plastisol miscibility parameter with appropriate diluents and solvents, as well as their water reference. The Calculated values of the Hildebrand solubility parameter for diluents and solvents were also given. Among the already applied diluents and solvents, the lowest value of the miscibility parameter is shown by the PVC plastisol system with DOP in reference to n-butyl acetate, xylene and toluene. On the other hand, the PVC plastisol with DBS is optimally mixed with cyclohexanone, toluene, xylene and n-butyl acetate. The PVC plastisol with DBP is optimally mixed with cyclohexanone, toluene and xylene. Yet, the calculations for water indicated its immiscibility with the PVC plastisol. In this case it is a typical dispersion medium.

In Table 4 the values of molar refraction of the compounds used for the formation of the PVC plastisol dispersion were presented. The value of refraction of particular constituents was calculated in accordance with the Lorentz-Lorenc equation (equation 15) and a formula of the additivity of composition constituents (equation 16). The refraction value was also calculated for the plasticizer systems with organic diluents and solvents and their water compositions. The calculated refraction values indicate high DOP polarity, and the lowest DBS polarity. The above data provide a conclusion that in the plastisol systems with DOP, polymer grains will be solvated to the largest extent. But in the DBS-containing plastisol polymer grains will be solvated at the lowest level. The diluents and solvents used indicate lower refraction values

Table 4. Molar refraction values for individual constituents forming the PVC plastisol dispersion in water stabilized by an anionic and non-ionic surfactant and for the plasticizer-solvent, water-solvent, and the plasticizer-water systems

Diluents or solvents	Constituent molar refraction	DOP R = 114,42	DBS R = 57,63	DBP R = 77,116	Water R = 3,7
Xylene	35,9	112,17	57,13	76,28	3,81
Toluene	30,99	111,95	56,99	76,12	3,8
N-butyl acetate	31,6	112,43	57,12	76,32	3,78
Butanol	22,15	111,21	56,63	75,73	3,78
Cyclohexanone	27,8	111,8	56,9	76,03	3,79
Water	3,7	14,75	10,23	13,58	–

than the plasticizers, which results in the fact that they will solve well. However, they will not form homogenous systems with water. The claims that can be expressed on the basis of the refraction value analysis are qualitatively different from those concluded on the basis of the solubility parameter value analysis and the miscibility parameter. Thus it may be concluded that stable water dispersions of the PVC plastisols can be produced using surface-active agents as stabilizers that will be adsorbed on the surface of the PVC plastisol particles and will reduce their surface energy.

Water dispersions of PVC plastisol stabilized by different surface-active agents underwent sedimentation tests. Gradual destabilization of water disperse system of PVC plastisol in the process of long-lasting sedimentation exposure can be caused by the presence of tiny particles or floccules, which are active centres of slow coagulation. The change in the properties of a disperse system depends on the properties and the state of the SAA particle in the dispersing medium, which is determined, among others, by hydrophilic-lipophilic balance (HLB) and also by hydrophobic interaction of the hydrocarbon part of the SAA molecule with the water medium. Increasing the hydrophobic interaction between the diphilic parts of the SAA molecules in water solutions together with an increase in their concentration will lead to forming the aggregations or micelles, considerably decreasing the SAA effectiveness. Thus the interaction of molecules or ions of surface-active agents with the disperse phase particles is substantially reduced, and those systems will reveal lower stability.

Figure 1 shows water dispersion right after preparation and after 14 days of sedimentation when the state of equilibrium was established.

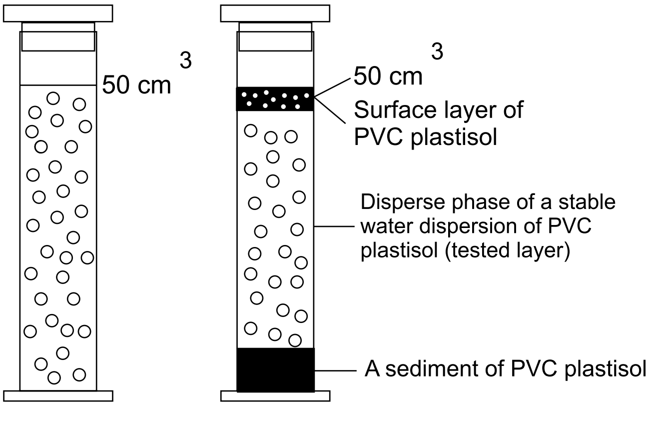

Figure 1. Schematic presentation of the sedimentation process of water dispersions of the PVC plastisol in sedimentation cylinders. Explanations: a – water dispersion of the PVC plastisol right after preparation, b – water dispersion of the PVC plastisol after 14 days of exposure

Sedimentation tests indicated that the state of sedimentation equilibrium corresponds to the separation of the disperse system into three layers. The upper layer is a scum, the structure of which is a foamed PVC plastisol. The medium layer is the proper disperse phase of dispersed PVC plastisol particles in water with adsorptive layers of surface-active agent. The lower layer is the homogenous PVC plastisol. It is an irreversible sediment, which cannot yield a disperse system through intense shaking. The water disperse phase (the medium layer) was analysed. Basing on the test results of the part of the stable water disperse phase of the PVC plastisol, it was concluded that the dependencies between the maximum dispergation efficiency value (W_d) which corresponds to the optimal amount of surface active agent in dispersion and the limiting viscosity number (GLL) as well as the Huggins interaction constant (k_H) can be established. The dependencies considered can be formulated as a general function:

$$W_d/C_{SPC} = f(W_d, GLL, k_H) \tag{17}$$

The charts present some of the experimental data corresponding to the discussed dependencies.

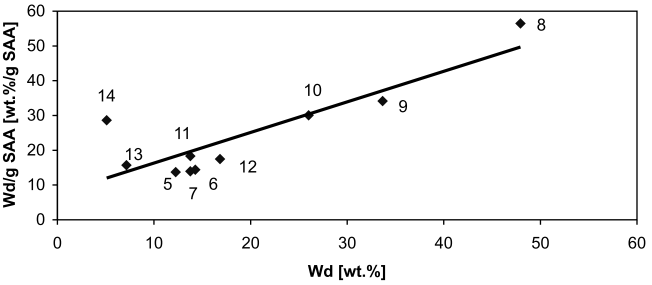

Figure 2. Dependence of dispergation efficiency on the SAA actual content as a function of dispergation efficiency. Dioctyl phthalate was used as the plasticizer, and butanol was added. Explanation: subsequent numbers on the chart correspond to the SAA type given in Table 1

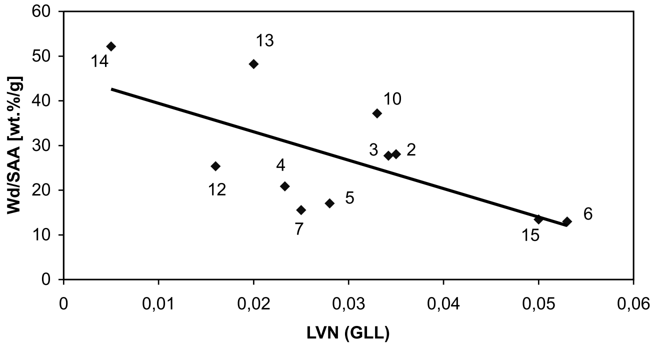

Figure 3. Dependence of dispergation efficiency on the SAA actual content as a function of the limiting viscosity number. Dioctyl phthalate was used as the plasticizer, and xylene was added. Explanation: subsequent numbers on the chart correspond to the SAA type given in Table 1

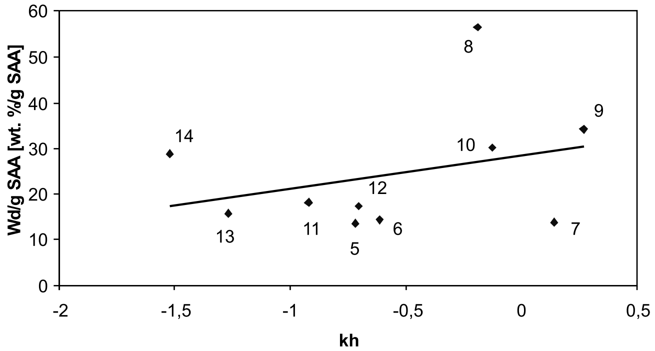

Figure 4. Dependence of dispergation efficiency on the SAA actual content as a function of the Huggins interaction constant. Dioctyl phthalate was used as the plasticizer, and butanol was added. Explanation: subsequent numbers on the chart correspond to the SAA type given in Table 1

On the basis of the measurement point distribution, it is possible to establish general dependencies:

$$W_d/ C_{SPC} = a_{Wd} \cdot W_d + b_{Wd} \qquad (18)$$

$$W_d/ C_{SPC} = a_{GLL} \cdot GLL + b_{GLL} \qquad (19)$$

$$W_d/ C_{SPC} = a_{kh} \cdot k_H + b_{kh} \qquad (20)$$

The values of the constants in the equations are given in Table 5.

The data presented in Table 5 indicate that dispergation efficiency values per unit of the surface active agent at which this system achieved maximum stability and efficiency value renders the task of implementing the organic solvent or diluent necessary. The analysis of the a_{Wd} and b_{Wd} constants indicates higher values when xylene, toluene, n-butyl acetate, butanol and cyclohexanone were used. Thus it can be concluded that a larger amount of surface-active agent will be adsorbed on the surface of dispersion particles that will contain the aforementioned organic compounds. This can affect their polarity. Another factor here may be the size of dispersion particles. The presence of the organic solvent or diluent substantially reduces the particle size, and thus this system becomes more stable, which has been confirmed by the analysis of the a_{GLL} and b_{GLL} constants. This can be also proved by the a_{kh} and b_{kh} data, the positive values of which indicate lyophilisation of the dispersion particle surface, and thus the amount of the adsorbed agent on the dispersion particle surface increases.

CONCLUSION

Water dispersions of the PVC plastisol are, as a rule, unstable aggregation systems. The presence of adsorption layers of surface-active agents on the particle surface conditions the temporary stability of those systems. Various activities can coagulate the dispersion particles and form a firm, homogenous, irreversible PVC plastisol sediment. In this case electrolyte activity is most important.

The presented tests proved that the applied surfactants were characterized by varying the properties calculated and determined on the basis of experiments. This particularly concerned the ethoxylation number, molecular weight, the Hildebrand solubility parameter, hydrophilic-hydrophobic balance, surface activity, the limiting viscosity number, the Haller interaction constant, the limiting equivalent conductivity and „b" constant of the Kohlrausch-Onsager equation. Thus it can be stated that surface-active agents will be adsorbed on the PVC plastisol particle surface in varying amounts, forming layers of varying thickness and properties.

In order to increase the stability of water dispersion systems of the PVC plastisols, organic solvents and diluents such as xylene, toluene, n-butyl acetate, butanol and cyclohexanone were put into the disperse system. The aforementioned compounds differed in terms of calculated molar refraction values and the Hildebrand solubility parameter. It was found out that their interactions with the PVC plastisol constituents – in the form of plasticizers such as dioctyl phthalate, dibutyl phthalate, dibutyl sabacate and PVC – occur differently. The analysis of the calculated refraction values indicates that dioctyl phthalate is the most polar, whereas dibutyl sabacate is the least polar. The lowest value of the miscibility parameter is revealed by a plastisol composition of PVC and dioctyl phthalate with reference to n-butyl acetate, xylene and toluene. The PVC plastisol with dibutyl sabacate is best mixed with cyclohexanone, toluene, xylene and n-butyl acetate. The PVC plastisol with dibutyl phthalate is best mixed with cyclohexanone, toluene and xylene.

Sedimentation tests of the PVC plastisol water dispersions stabilized by various surface active agents with an organic diluent or solvent added showed that the addition resulted in all the cases in the dispergation efficiency increase, particle size reduction expressed by the limiting viscosity number and the increase in the Huggins interaction constant that proves higher lyophilisation of the PVC plastisol particle surface. In this case it is indicative of the increase in the adsorbed amount of the surface-active agent. Xylene and toluene were the most effective added components to the PVC plastisols water dispersions. n-butyl acetate was less effective. Thus the stability period of the PVC plastisol water dispersion can be increased and its application period can be extended.

Table 5. Values of simple equations obtained basing on the dispergation efficiency values, the limiting viscosity number, the Huggins constant basing on the dispergation efficiency values per SAA content

Plastisol	Organic solvent added	W_d/SPC = f(W_d)		W_d/SPC = f(GLL)		W_d/SPC = f(k_H)	
		a_{Wd}	b_{Wd}	a_{GLL}	b_{GLL}	a_{kh}	b_{kh}
PVC/DOP	–	1,12	2,73	-133,13	42,11	-0,35	32,72
	Xylene	0,48	18,2	-635,78	45,78	-0,07	24,16
	Toluene	1,68	-11,34	-38,93	26,57	-0,15	24,76
	N-butyl acetate	0,44	26,45	-154,4	35,34	0,66	23,9
	Butanol	0,88	7,5	-38,92	30,29	7,29	28,41
	Cyclohexanone	0,92	10,82	-245,69	40,99	-1,42	24,0
PVC/DBP	–	0,63	6,87	-32,0	16,36	-0,024	12,82
	Xylene	0,16	8,51	-14,18	10,86	0,06	10,55
PVC/DBS	–	1,58	-7,36	-182,34	54,56	69,2	63,72
	Xylene	0,54	11,86	-143,43	34,03	-0,14	19,61

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