

STRUCTURE-DRIVEN RHEOLOGICAL OPTIMIZATION OF POLYVINYL CHLORIDE WITH ECO-FRIENDLY PLASTICIZERS BASED ON PETROCHEMICAL RAW MATERIALS

I. N. Vikhareva

South Ural State University, Chelyabinsk, Russia

ABSTRACT

Polyvinyl chloride (PVC) is one of the most widely used polymers, including oil and gas industry. At the same time, plasticizers play a key role in ensuring the flexibility, elasticity and processability of flexible PVC compositions for the manufacture of seals, hoses, cable insulation and protective coatings. This study evaluates the effect of symmetrical esters of azelaic and sebacic acids with ethoxylated butanol and phenol as alternative plasticizers on the processability of PVC compositions. It was found that dibutoxyethyl sebacate, dibutoxyethyl azelate, diphenoxyethyl sebacate and diphenoxyethyl azelate provide a higher melt flow index compared with industrial dioctyl phthalate at temperatures ≥ 165 °C, which indicates a decrease in melt viscosity and improved processability. Dibutoxyethyl sebacate exhibited the highest effectiveness: at 175 °C, its value exceeded that of dioctyl phthalate by 58%. According to thermodynamic analysis, the activation energy of viscous flow is dominated by the enthalpy component, with its maximum observed at approximately 165 °C, due to a change in the molecular flow regime. These data indicate the prospects of the esters under study as highly efficient and environmentally friendly plasticizers for PVC used in the oil industry, enabling the manufacture of more durable and reliable materials.

Keywords: polyvinyl chloride; plasticizer; azelate; sebacate; rheology; melt; viscous flow; activation energy; entropy.

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1. Introduction

Plasticizers are one of the most important groups of additives that determine the processability, flexibility and durability of polyvinyl chloride (PVC) products [1-4]. For decades, phthalic acid esters (phthalates) have remained the classic PVC plasticizers, due to their high compatibility with the polymer and favorable performance characteristics. However, the proven toxicity of phthalates, their tendency to migrate from the material and accumulate in the environment, as well as the potential danger to human health have led to stricter global regulatory requirements (REACH, RoHS, etc.) and have stimulated an active search for safe alternatives [5-6]. For oil and gas applications, where equipment may come into contact with hydrocarbon media and be subjected to significant mechanical loads [7-9], the problem of plasticizer migration is particularly critical, as it directly affects the durability and reliability of products.

For these reasons, the main focus was on the creation and use of effective plasticizers with low toxicity, resistance to migration and biodegradability. Dicarboxylic acid esters occupy a leading position as promising alternatives for phthalates, providing excellent flexibility at low tempera-

tures, which is especially important for use in the oil and gas industry as sealing elements, flexible hoses for liquid and gas transport, cable insulation used on drilling rigs and platforms, as well as protective coatings for equipment operating in aggressive environments [10-11]. In addition, adipic acid esters exhibit an improved environmental profile, which ensures a reduced risk to health and the environment both during product operation and at the disposal stage [12, 13]. Dicarboxylates such as di(2-ethylhexyl) adipate (DEHA), di-n-butyl adipate (DBA), di(butoxyethyl) adipate are currently widely used. They have found application in important areas, including food packaging, medical products, soft films for agriculture, interior solutions [14, 15]. For the oil and gas industry, the key requirement is to maintain the stability of properties during prolonged contact with hydrocarbons and over a wide temperature range.

Of particular interest are alkoxyated esters, which exhibit additional biodegradability, providing accelerated decomposition of products after use under natural conditions [16]. A key approach to addressing global plastic waste problems and achieving materials with a longer, environmentally friendly life cycle is the development of plasticizers that are highly functional in use but rapidly decompose at the end of their service life.

Despite the advantages, the widespread introduction of

E-mail: vikharevain@susu.ru

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dicarboxylic acid esters requires the resolution of several key scientific and practical problems. Controlling the rheological behavior of plasticized PVC compounds is essential as these properties affect the material's performance under different processing techniques, its ease of processing, the quality of the final product, and even uniformity of the plasticizer distribution within the PVC matrix [16-19]. For the production of oil and gas products, such as profiled seals or cable sheaths, optimal melt fluidity ensures accurate mold filling and the absence of internal stresses in the finished product [20-21].

The task of controlling the melt viscosity of PVC is complicated by the fact that the effects of mixtures of plasticizers and lubricants on compatibility with PVC and the rheology of the composition are difficult to predict theoretically and require mandatory experimental verification [22, 23]. This is due to the fact that traditional equilibrium thermodynamics does not take into account the kinetic aspects of component mixing and the actual processing conditions, such as deformation rates and complex temperature-time profiles.

Accordingly, the pursuit of alternative plasticizers based on dicarboxylic acids reflects both a shift toward environmentally friendly additives and the emergence of a new generation of versatile PVC compositions that deliver desired characteristics with minimal ecological impact. This article examines the effect of symmetrical esters of azelaic and sebacic acids and ethoxylated butanol and phenol on the processability of PVC compositions. The main purpose of the work is to deepen the understanding of the relationship between the chemical structure of esters, the peculiarities of their interaction with PVC macromolecules at the molecular level, and the resulting rheological behavior of the material during processing, including relevant to the oil and gas sector.

2. Materials and methods

Materials

Suspension polyvinyl chloride from Bashkir Soda Company Caustic JSC (Sterlitamak, Russia) was used as the polymer matrix. Commercial dioctyl phthalate (DOP) from JSC Kamtex-Khimprom (Perm, Russia) was used as a reference plasticizer (acid value ≤ 0.07 mg KOH/g, saponification number ≤ 289 mg KOH/g, volatile content $\leq 0.1\%$, flash point ≥ 205 °C). Tribasic lead sulfate (TBLS) from Baerlocher GmbH (Ingolstadt, Germany) was employed as a stabilizer (lead content 89%, pH 7.0–7.5, ash $\geq 95\%$). Azelaic acid ($\geq 99.5\%$, m.p. 106.5 °C), sebacic acid ($\geq 99.7\%$, m.p. 134.7 °C), butoxyethanol (purity $\geq 99.5\%$, density 0.900–0.904 g/cm³ at 20 °C, water content $\leq 0.1\%$, b.p. 169–172 °C), and 2-phenoxyethanol (purity $\geq 99.0\%$, density 1.102–1.107 g/cm³ at 25 °C, water content $\leq 0.1\%$) were obtained from commercial sources.

Synthesis method

Synthesis of esters. The target esters – dibutoxyethyl azelate (DBEAz), dibutoxyethyl sebacate (DBES), diphenoxylethyl azelate (DPEAz), and di phenoxylethyl sebacate (DPES) – were synthesized via two-step esterification (fig. 1). A reactor equipped with a reflux condenser, thermometer, and Dean-Stark trap was charged with the aliphatic diacid, the first alcohol, and a *p*-toluenesulfonic acid catalyst. The mixture was heated to boiling, and the reaction progress was monitored by collecting the theoretical amount of water. After completion of the first stage, the second alcohol was added dropwise, and the reaction continued until water evolution

ceased. The crude product was washed sequentially with 5% alkali solution, water, and saturated brine, dried over sodium sulfate, filtered, and stripped of residual solvent.

Characterization of plasticizer

Acid and ester numbers were determined by titrating an alcoholic plasticizer solution with KOH in the presence of phenolphthalein.

The refractive index (*n*) of esters was measured on a refractometer.

The density of esters was measured using a general purpose densimeter.

The mass fraction of volatile compounds in ester can be determined by evaluating the evaporation rates of its constituents.

IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer (450–3700 cm⁻¹, 4 cm⁻¹ resolution, 20 scans) using KBr pellets.

Preparation of PVC compounds

PVC formulations were mixed in a two-stage laboratory mixer (TGHK 5) for 60 min. The base composition (in mass parts) was: PVC – 100, total plasticizer – 100, TBLS – 1. A plasticizer blend was used with a DOP : ester weight ratio of 5 : 1 (i.e., 83.3% DOP and 16.7% ester).

Methods of analysis

The melt fluidity index (MFI) was determined by capillary viscometry using an IIRT-AM plastimeter (capillary length 0.008 m, diameter 0.00209 m; piston diameter 0.00948 m). Tests were conducted at 160–175 °C under a 49 N load. Approximately 4–5 g of the PVC compound was loaded into the preheated barrel, held under load for 5 min, and then extruded. At least five extrudate segments were collected at equal time intervals, cooled, and weighed with an accuracy of ± 0.0001 g. MFI (g/10 min) was calculated as to (1):

$$MFI_{T,P} = m \cdot 600 / t \quad (1)$$

where *m* = average segment mass (g), *t* = cutting interval (s). The low weighing error ensures negligible impact on calculated thermodynamic parameters.

3. Results and discussion

Esters were synthesized via the esterification reaction (table 1).

Table 2 summarizes the main characteristics of the synthesized esters. All products were pale-yellow oily liquids with low acid numbers and minimal volatile content – desirable properties for PVC thermal stability and durability. IR spectra confirmed ester formation: aliphatic C-H stretches

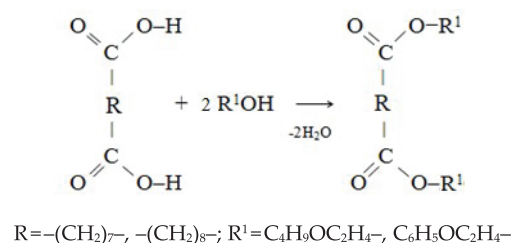


Fig. 1. The scheme of ester synthesis

Table 1

The formulas of esters	
Ester	The structural formula
DBEAz	$\text{BuO}(\text{CH}_2)_2\text{OCO}(\text{CH}_2)_7\text{CO}_2(\text{CH}_2)_2\text{OBu}$
DBES	$\text{BuO}(\text{CH}_2)_2\text{OCO}(\text{CH}_2)_8\text{CO}_2(\text{CH}_2)_2\text{OBu}$
DPEAz	$\text{PhO}(\text{CH}_2)_2\text{OCO}(\text{CH}_2)_7\text{CO}_2(\text{CH}_2)_2\text{OPh}$
DPES	$\text{PhO}(\text{CH}_2)_2\text{OCO}(\text{CH}_2)_8\text{CO}_2(\text{CH}_2)_2\text{OPh}$

Table 2

Key characteristics of the synthesized symmetric esters					
Indicators	Ester				DOA
	DBEAz	DBES	DPEAz	DPES	
Density, g/cm ³	0.989	0.971	-	-	0.9270
Refractive index	1.4548	1.446	-	-	1.4470
Acid number, mg KOH/g	0.2	0.2	0.1	0.1	0.07
Ester number, mg KOH /g	281	270	253	245	300
Molecular weight, calculated	388	402	428	442	370
Mass fraction of volatile substances, %, max	0.2	0.2	0.1	0.1	-
Yield, %	85.4	86.8	84.6	86.5	-

Table 3

Test results of PVC compositions containing symmetric esters				
Plasticizer	MFI (T=160 °C), g/10 min	MFI (T=165 °C), g/10 min	MFI (T=170 °C), g/10 min	MFI (T=175 °C), g/10 min
DBEAz	0.6	2.4	10.5	25.4
DBES	1.2	2.7	12.3	28.6
DPEAz	0.4	1.6	5.8	15.0
DPES	0.6	2.0	7.2	18.6
DOP	0.4	1.1	9.4	18.1

at ~2850–2960 cm⁻¹; for aromatic derivatives, additional aromatic ring bands at ~1250 and ~1625 cm⁻¹. Absence of O-H (3200–3600 cm⁻¹) and carboxylic C=O (1685–1687 cm⁻¹) bands indicated reaction completion and product purity.

The production of esters was confirmed by IR spectra. Aliphatic diesters have characteristic bands in the regions of ~2850–2960 cm⁻¹ (C-H). For aromatic derivatives, additional characteristic bands of the aromatic ring are present at ~1250, ~1625 cm⁻¹. The absence of bands in the regions of 3200–3600 cm⁻¹ (O-H) and 1685–1687 cm⁻¹ (C=O acids) is a key indication of the completion of the esterification reaction and the purity of the product.

The synthesized target esters present as transparent, pale-yellow oily liquids. These compounds exhibit low acid numbers and minimal volatile content – parameters critically important for PVC applications due to their direct impact on thermal stability and product service life. A low acid number inhibits the catalytic promotion of PVC dehydrochlorination, the primary thermal degradation mechanism, thereby preserving material performance. Concurrently, minimal volatile content reduces additive migration dur-

ing use, preventing surface defects such as blooming and further extending service life. The optimization of these parameters aligns with the development of highly stable polymer systems.

The influence of the structure, physicochemical characteristics of synthesized plasticizers, and their thermodynamic compatibility with PVC on the complex of rheological properties of PVC with partial substitution of DOP has been studied. The experiments were carried out in the temperature range of 160–175 °C under a constant load of 49 N. PVC compositions with an industrial analog of DOP were used as a reference sample (table 3).

The results of testing the rheological properties of PVC compositions plasticized with symmetric esters revealed the following patterns. For all the plasticizers studied, a significant increase in the melt fluidity index (MFI) was observed with an increase in temperature from 160 to 175 °C, which indicates a decrease in melt viscosity and an improvement in material fluidity upon heating.

Dibutoxyethyl sebacate produced the highest MFI values at all studied temperatures, demonstrating its greatest effectiveness in reducing PVC melt viscosity and improving recyclability, especially under high-temperature conditions (175 °C).

Diphenoxyethyl sebacate and diphenoxyethyl azelate esters containing the phenoxy moiety showed lower MFI values compared to their butoxyl analogues. Bulk phenoxy groups in the ether structure have greater resistance to melt flow compared to butoxyl groups.

Sebacates of DBES, DPES showed a higher MFI values than the corresponding azelates of DBEAz, DPEAz, especially at 170 and 175 °C. This may be due to the longer aliphatic chain of sebacic acid compared to azelaic acid.

When compared with the industrial plasticizer DOP, it was found that at low processing temperatures (160 and 165 °C), most of the new plasticizers exhibited MFI values equal to or higher than DOP.

The Arrhenius equation is widely used to model the viscosity of polymers during their viscous flow, for example, during extrusion, injection molding, calendaring. The transformation of the equation leads to the following formula (2) [24–27]:

$$\ln \eta = \ln A + (E_a / (R \cdot T)) \quad (2)$$

where E_a – activation energy of viscous flow; η – effective viscosity; A – the pre-exponential multiplier is a constant related to the properties of a material at an infinitely high temperature, Pa·sec; R – universal gas constant, $R=8.314 \text{ kJ}/(\text{mol}\cdot\text{K})$; T – thermodynamic temperature, K.

The angle of inclination of the straight line reflects the value of the activation energy (E_a), which is an energy barrier. This barrier must be overcome by molecules (or segments of macromolecules in the case of polymers) for irreversible flow (shear) to occur. Eyring's theory is widely used to describe the flow of liquids, particularly structured ones (such as polymer melts) [28–30]. According to this, flow is the process of «jumping» molecules or polymer segments from one equilibrium position to another through this barrier. Both collision theory and Eyring's transition state theory interpret such a leap as overcoming the difference in Gibbs free energy (ΔG) between the initial state and the transition state (activated complex) (3):

$$k = k_B \frac{T}{h} \cdot e^{-\Delta G/RT} = k_B \frac{T}{h} \cdot e^{\Delta S/R} \cdot e^{-\Delta H/RT} \quad (3)$$

where κ – transmission ratio; k_B – Boltzmann's constant, $1.38 \cdot 10^{-23}$ J·K; T – thermodynamic temperature, K; h – Planck's constant, $6.626 \cdot 10^{-34}$ J·sec; ΔG – Gibbs energy of viscous flow activation, J/mol; ΔH – enthalpy of activation of viscous flow, J/mol; ΔS – entropy of viscous flow activation, J/(mol·K).

A comparison of equation (3) with the Arrhenius equation, demonstrates that the parameter E_a in the latter is the enthalpy component of the barrier ($E_a \equiv \Delta H$), and the pre-exponential factor A contains the entropy contribution: $A \propto \exp(-\Delta S/R)$ [31-33]. Polymers are characterized by the dependence of viscosity on the jump rate constant: $\eta \propto (1/k)$. This leads to equation (4):

$$\ln A = \ln \frac{h}{k_B T} - \frac{\Delta S}{R} \quad (4)$$

Based on equations (2-4) for each temperature range of the dependence curves processing, thermodynamic criteria for the viscous flow of PVC compositions were calculated using the developed esters and basic PVC compositions at constant shear stress. The obtained parameter values are shown in the table 4.

The investigation of the activation parameters of viscous flow (enthalpy ΔH , entropy ΔS , Gibbs energy ΔG) revealed various effects of the synthesized esters on the molecular kinetic aspects of the flow of PVC compositions.

Figure 2 shows the patterns of changes in the activation energy of the flow of PVC melts containing DBEAz, DPEAz, DBES and DPES esters in comparison with the basic PVC composition with DOP plasticizer.

Evaluating the morphology of the dependence curves enables characterization of the viscous flow rheology for all investigated PVC blends. A common hallmark is a peak appearing on the temperature dependence curves of the activation energy (ΔH). The maximum extreme corresponds to PVC, plasticized with DOP. This is a consequence of a change in the molecular mechanism of plasticized PVC flow under the studied viscous flow conditions. At low temperatures, viscous flow is mainly caused by local jumps of polymer chain segments within their «tubes» (reptational motion). The energy barrier (ΔH) is associated with the local bond stretching and overcoming the short-range order.

In the intermediate temperature range (165 °C), the system approaches a region of more intense softening or the beginning of a flow plateau. Here, not only the local movement of the segments is required to activate the flow, but also the cooperative restructuring of larger sections of chains or even the temporary destruction of weak physical grid nodes (plasticizer chains, residual crystallites, entanglement). The cooperative movement requires the simultaneous overcoming of multiple intermolecular interactions, this leads to an increase in the enthalpy barrier (ΔH). At the same time, the entropy contribution (ΔS) increases, as the transition state in such a cooperative movement is less ordered.

At a high temperature (170 °C), thermal energy is sufficient to effectively break temporary bonds and significantly increase the free volume. The movement of the chains becomes more independent and fluid-like. The energy barrier (ΔH) decreases again, since it takes less cooperative effort to activate the elementary act of flow, and thermal energy easily overcomes the remaining local barriers. The entropy barrier (ΔS) also decreases, as the overall disorder of the system is higher, and the transition state does not require such a significant additional loss of order.

Table 4 Thermodynamic activation parameters for the viscous flow of plasticized PVC				
Activation parameter	Plasticizer			
	DBEAz	DBES	DPEAz	DPES
160 °C				
ΔH , kJ/ mol	434.6	263.7	479.4	424.3
ΔS , J/(mol·K)	720.2	321.6	787.5	867.5
ΔG , kJ/ mol	122.2	124.2	137.0	48.5
165 °C				
ΔH , kJ/ mol	471.8	501.8	452.0	466.7
ΔS , J/(mol·K)	807.0	868.3	732.8	756.6
ΔG , kJ/ mol	118.6	122.9	132.8	136.5
170 °C				
ΔH , kJ/ mol	291.8	289.4	342.4	353.6
ΔS , J/(mol·K)	397.3	379.5	479.4	502.1
ΔG , kJ/ mol	114.9	118.4	129.4	133.0

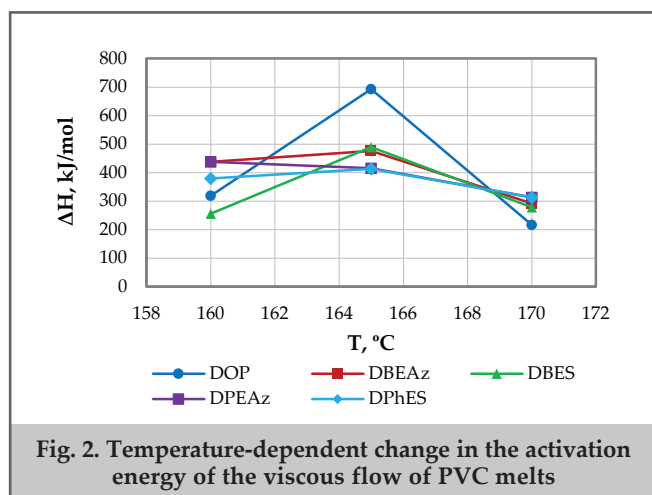


Fig. 2. Temperature-dependent change in the activation energy of the viscous flow of PVC melts

4. Discussions

Rheological concepts form the basis of calculations in the design equipment for plastics processing. Rheological models and equations of state are used in engineering assessments of the operability of polymer materials and composites in structures. Rheological methods control the technological properties of polymers such as the melt index characterizing the fluidity of thermoplastics, and to optimize their processing conditions. In rheological testing of thermoplastic materials, the key measurement is the melt fluidity, which provides important information on the polymer behavior in technological processes. For the oil and gas industry, where mass production of products such as insulation for marine cables, seals for flange connections or flexible pipelines is required, the stability and predictability of the rheological properties of raw materials directly affect the production efficiency and quality of the final product.

In practice, the melt flow index (MFI) offers a fairly reliable and widely used way to assess processability, allowing the processor to set the temperature range that ensures the necessary conditions for the polymer composition's processing [34-36] and to determine the main technological processing method.

The primary evaluation of a polymer or composition begins with defining the boundaries of the fluid state region, followed by an examination of the rheological characteristics within that state. Thermoplastic melts exhibit the properties of elastically viscous bodies and behave like abnormally viscous (non-Newtonian) fluids that do not obey Newton's law; their viscosity is not a constant value, but significantly depends on the rate of deformation, temperature, pressure, and other factors [37].

The response of materials to applied forces is described by their rheological (or structural-mechanical) properties, which define the connection between the imposed stress and the resulting deformation or the speed at which this deformation occurs [38-39]. These properties, manifested by mechanical action, are determined by the material composition, its internal structure, the nature of the interactions between its constituent particles or molecules, as well as their physico-chemical state, i.e., the type of structure formed [40-41].

For all PVC compositions with the studied plasticizers, an exponential increase in MFI is observed in the range of 160-175 °C. This is a typical behavior for polymer melts associated with thermal dilution. An increase in temperature increases the kinetic energy of PVC chains and plasticizer molecules, leading to an increase in the free volume of the system and a reduction in the activation energy of the viscous flow. As a result, a significant decrease in melt viscosity and an increase in MFI are observed. The high melt flow parameter in the range of standard PVC processing temperatures (165-175 °C) indicates good processability of the material, which is advantageous for the manufacture of complex profiles used, for example, as seals for oil and gas equipment.

The MFI data demonstrate a significant effect of the chemical structure of the plasticizer and temperature on the fluidity of PVC compositions, which is directly related to their thermodynamic compatibility and plasticizing efficiency. At temperatures ≥ 165 °C, all synthesized plasticizers provide higher MFI than the industrial DOP, indicating lower melt viscosity and accordingly, the best technological suitability of PVC compositions for recycling. Effective insertion of plasticizer molecules into the interchain spaces of PVC, accompanied by strong (predominantly dipole-dipole) interactions of their polar ether and carbonyl groups with the polar -Cl groups of PVC, reduces the intermolecular forces acting in the polymer and increases the free volume. This leads to an easy melt flow under load at these temperatures. A decrease in the activation energy of the flow for systems containing these plasticizers confirms their effectiveness. For oil and gas products subject to cyclic loads and exposure to chemical agents, such effective plasticization, which ensures a homogeneous material structure at the processing stage, can positively influence durability and resistance to plasticizer migration upon contact with hydrocarbons.

An increase in the chain length of dicarboxylic acid (azylaic C9 – sebacic C10) contributes to an increase in the MFI composition at all temperatures, regardless of the structure of the alcohol group. From a thermodynamic standpoint, elongation of the aliphatic «bridge» between the ether groups in the plasticizer molecule increases molecular flexibility, facilitating its conformational adaptation between PVC chains. An increase in the nonpolar (hydrophobic) part of the molecule improves interaction with nonpolar sections of PVC and promotes better «dissolution» of the plasticizer in the

polymer, as well as reduces the density of polar groups. This reduces the likelihood of strong intermolecular interactions between the plasticizers themselves, which could reduce their compatibility with PVC. These factors result in a more effective plasticizing effect and higher fluidity of sebacates compared to azelates.

Ethoxylated butanol-based plasticizers provide significantly higher melt fluidity at all temperatures compared to phenoxyethanol-based analogues. The volumetric benzene ring in plasticizers creates a significant steric effect (spatial difficulties), limiting the ability of the plasticizer molecule to penetrate between PVC chains and effectively separate them. The rigidity of the phenolic group ring reduces the flexibility of the plasticizer molecule compared to the linear butyl fragment. Although the phenyl group is less polar than the essential oxygen, its volume and rigidity dominate. Phenyl groups promote the π - π interactions between the plasticizer molecules themselves and reduce their availability for interaction with PVC, impairing compatibility.

The activation energy E_a is determined by the slope of the straight line obtained when $\ln(\eta)$ is plotted against the reciprocal temperature ($1000/T$) in an Arrhenius representation. Within the framework of the Eyring model for viscous polymer flow, E_a corresponds to the activation enthalpy ΔH . The contribution of the activation entropy ΔS is included in the pre-exponential factor A of the Arrhenius equation. The significantly increased values of E_a (and ΔH) for PVC are due to the need to overcome strong dipole-dipole interactions between C-Cl polar groups during chain movement. Plasticizers reduce E_a by weakening these interactions and thereby reducing the enthalpy barrier ΔH of the elementary act of hopping.

The Arrhenius equation is empirical, and the Eyring model gives it a physical interpretation. The strict equality $E_a = \Delta H$ is fulfilled in the Eyring model for viscous flow of polymers at zero viscosity. In the non-Newtonian region (at high shear rates), the apparent E_a may decrease, but its relationship with ΔH remains the primary one. The contribution of ΔS (related to conformational chain changes) is nonzero, but for polar polymers such as PVC, the enthalpy component ΔH of the total thermodynamic barrier ΔG dominates under typical processing conditions. The viscous flow of PVC, characterized by strong intermolecular interactions, requires the breaking of numerous bonds (dipole-dipole, van der Waals). Therefore, the barrier ΔG is determined mainly by ΔH , and rather than by the entropy term $T\Delta S$. Although $\exp(-\Delta S/R)$ depends on temperature, this dependence is weaker (logarithmic) than the exponential dependence of $\exp(\Delta H/RT)$. It is ΔH that makes the main contribution to the strong temperature dependence of viscosity, which is fixed by the parameter E_a [42-45].

The nonlinearity of the graph indicates a change in the molecular mechanism of flow. For PVC, this is typical near the melting temperatures of crystallites or during structural rearrangements in the melt. The analysis of the shape of this curve serves as an important diagnostic tool for rheological behavior [46].

Thus, despite the low content (16.7%) of azelates or sebacates in PVC compounds, these additives have a significant effect on structural transitions, by facilitating chain movement. The maximum ΔH (fig. 1) corresponds to the temperature range in which the plasticized system passes through a certain structural transition, or where the plasticizer effect

on structure loosening and facilitating movement is most pronounced and requires cooperative restructuring. The influence of plasticizers on intermolecular interactions and structural organization varies, as reflected by differences in the absolute parameter values; nevertheless, the characteristic maximum in ΔH is a common feature for all studied plasticizers. Understanding these temperature-dependent processes is important for selecting the modes of processing PVC into products that will subsequently be operated at variable temperatures typical of oil and gas fields.

An analysis of the thermodynamic parameters of the viscous flow of plasticized compositions reveals an obvious enthalpy-entropy compensation: high values of ΔH correspond to high values of ΔS . This is typical for processes in condensed media, where obstructed movement (high ΔH) is accompanied by greater disorganization in the transition state (high ΔS). Despite these changes, the Gibbs activation energy (ΔG), which determines the rate of the process ($k \propto \exp(-\Delta G/RT)$), decreases monotonically with increasing temperature. This is explained by the fact that, in the Gibbs-Helmholtz equation ($\Delta G = \Delta H - T\Delta S$), an increase in temperature more actively increases the «gain» from the entropy term ($-T\Delta S$) especially in the area of maximum ΔS , which leads to a decrease in ΔG .

The effect of small additives of azelates (C9) and sebacates (C10) in a mixture with DOP on the rheology of PVC is explained by the synergistic effect and molecular mecha-

nisms of plasticization, despite the low content (16.7% ether in the mixture). Here are the key reasons:

1. Localization in critical zones: the addition of esters is concentrated in areas with the highest PVC matrix rigidity (e.g., in areas of crystallites or strong dipole interactions), loosening them and facilitating the movement of chains.

2. Cooperative effect: esters «pull apart» PVC chains, reducing the activation energy of the viscous flow (ΔH) for the entire volume. Even a small addition reduces the barrier to cooperative segment realignments.

3. Thermodynamic synergy: The combination of DOP (high compatibility) and esters (flexibility/hydrophobicity) improves the overall mobility of the system. At $T \geq 165^\circ\text{C}$, thermal energy enhances this effect.

In the blend, DOP acts as the primary plasticizer. It greatly reduces intermolecular interactions within PVC by forming dipole-dipole bonds with the $-\text{Cl}$ groups. Additionally, it increases the free volume between PVC chains, facilitating azelate or sebacate molecules penetration into the matrix more easily; stabilizes the system, preventing the stratification of the composition and migration of additives, while maintaining the uniformity of the melt. For oil and gas applications where resistance to hydrocarbon extraction is required, such a stable and homogeneous material structure, achieved through the synergistic action of plasticizers, can be a key factor in improving operational reliability.

Conclusions

The developed symmetrical esters, particularly dibutoxyethyl sebacate and dibutoxyethyl azelate, provide PVC melts with significantly improved fluidity (higher MFI) compared to the industrial plasticizer DOP in the processing temperature range of 160-175 °C. Esters containing a phenoxy moiety (DPES, DPEAz) are less effective in reducing viscosity, but they are superior to DOP at 175 °C.

The structure of the plasticizer directly affects the rheological characteristics of PVC melts. The elongation of the dicarboxylic acid chain (C10 sebacate > C9 azelate) increases melt fluidity by increasing molecular flexibility and providing a favorable entropic contribution. The linear alkyl radical provides higher PT values than the bulk aromatic radical (phenoxyethyl) due to lower steric difficulties, greater molecular flexibility, and the absence of a tendency to associate through π - π interactions.

The most effective plasticizer studied is dibutoxyethyl sebacate, which combines a long chain of diacid (C10) and a flexible linear alkoxy fragment. It provides the highest MFI in the entire temperature range.

The high MFI of containing DBES and DBEAz indicates their excellent manufacturability during processing by extrusion or injection molding within the studied temperature range, which is a consequence of the favorable thermodynamics of mixing. This property makes these compositions promising for the production of oil and gas products (e.g., seals, hoses, insulating shells), where processing stability, molding accuracy, and final mechanical properties are important.

The extreme activation enthalpy of viscous flow (ΔH) with increasing temperature is a consequence of a change in the molecular mechanism of flow of plasticized PVC. In the intermediate temperature range, the dominant mechanism requires the cooperative restructuring of polymer segments and the destruction of temporary structural formations, which requires high energy costs (high ΔH) and is accompanied by significant disorganization (high ΔS). At lower temperatures, the flow is local; at higher temperatures, it is facilitated by thermal motion and an increase in free volume, which reduces ΔH . The main thermodynamic finding is a steady decline in the Gibbs activation energy (ΔG) with increasing temperature, which leads to an increased melt flow rate. The measured temperature dependence of the activation parameters allows optimization of PVC compound processing conditions for the production of articles that retain elasticity and functionality across the wide temperature range typical of oil and gas extraction environments.

Consequently, the eco-friendly plasticizers described herein – based on symmetrical dicarboxylic acid esters – not only reduce PVC melt viscosity and enhance its processability but also, open up opportunities for the development of specialized compositions with specified rheological and operational properties for applications in the oil and gas industry.

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