

The behavior of poly(n-decyl methacrylate) in homologous series of n-alkanes: A method for prediction of its application as viscosity index improver in motor oils and its miscibility with polymethylene

S. AQEEL, D. LATH AND E. LATHOVÁ

Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic

ABSTRACT

Dilute solutions of poly(n-decyl methacrylate) in homologous series of n-alkanes have been studied. The measurements of viscosity-temperature dependence of poly(n-decyl methacrylate) in n-alkanes (as a model solvent for paraffinic oils) were applied for model calculation of the specific viscosity as a function of temperature and molecular weight. Exchange parameters of poly(n-decyl methacrylate) in n-alkanes have been determined according to Flory's theory and were applied to predict the mixing of polymethylene with poly(n-decyl methacrylate). The positive energy of mixing signifies mutual incompatibility of these polymers.

Keywords: dilute solution properties; miscibility of blends; poly(n-decyl methacrylate); viscosity index improver.

INTRODUCTION

One reason for using polymeric additives in lubricating oils is to obtain a product that has better viscosity-temperature characteristics than a comparable pure mineral oil. The viscosity of the oil at engine working temperature should be high enough and at the same time low enough for easy engine ignition at low temperature.

Poly(n-alkylmethacrylates) have been studied as viscosity index improvers in motor oils by Herold & Wolf (1983), Maderek & Wolf (1988), and Müller (1978), who have reported that polymethacrylates exhibit an intrinsic viscosity that increases uniformly with increasing temperature. Jordan *et al* (1978) demonstrated that the entropy of activation for viscous flow largely controlled the effect of temperature on the flow behavior of polymethacrylate and polyacrylate blends in mineral oil.

There is considerable current interest, both academic and industrial, in the study of polymer-polymer interaction and the causes of polymer compatibility

or incompatibility. Simple binary interaction models, applied by ten Brinke *et al* (1983) and Paul & Barlow (1984) provide a way to rationalize these effects through the concept of intramolecular interactions. Cowie & Lath (1988) demonstrated the usefulness of a quantitative interaction parameters database in searching for miscible blends from homopolymers and copolymers made of different monomers.

Another way is the calculation of thermodynamic mixing functions according to the procedure outlined by Flory *et al* (1968). These functions, being inaccessible to direct measurements, can give useful information for a better understanding of the incompatibility of polymers.

In this paper we present an analysis of the influence of polymer additives on the temperature dependence of viscosity of lubricating oils on the basis of the interaction parameters of the polymer with n-alkanes. In addition, this paper presents a study of mixing poly(n-decyl methacrylate) (PDMA) with polymethylene (PM) using determined thermodynamic parameters of PDMA in n-alkanes.

THEORY

For description of the concentration dependence of specific viscosity, η_{sp} , in polymer solution, the equation by Frind & Schramek (1955) was chosen:

$$\eta_{sp} = [\eta]c[(1 + k_H/m)[\eta]c]^m. \quad (1)$$

Its derivation with temperature, expressing parameters according to the intrinsic viscosity $[\eta]$ theory and rearranging according to Lath *et al* (1996), gives:

$$\frac{d \ln \eta_{sp}}{dT} = K_1 \frac{d \ln (1/2 - X_1)}{dT} + K_1 \frac{d \ln (v_{sp,2}^2/V_1)}{dT} + K_2 \frac{d \ln \bar{r}_0^2}{dT} + K_3 \frac{d n c}{dT}. \quad (2)$$

In Equations (1) and (2), c is concentration gd^{-1} , k_H is the Huggins constant, m is the structure parameter ($m = 2$), \bar{r}_0^2 is the polymer mean-square end-to-end distance in unperturbed state, $V_{sp,2}$ is the polymer specific volume, V_1 is the molar volume of the solvent, X_1 is the interaction parameter, and K_1 to K_3 are functions of the viscosity expansion factor, α_η .

In the following discussion, the members on the right-hand side of Equation (3) are marked as P_1 to P_4 . The parameter $d \ln (1/2 - X_1)/dT$ depends on the interaction between the polymer and solvent and is expressed by the relation

$$d \ln (1/2 - X_1)/dT = (K_1/T)(1/2 - X_1)^{-1} \quad (3)$$

where K_1 is the Flory enthalpic parameter.

The interrelationship of X_1 and K_1 parameters with the characteristics of pure components in solutions A and B is formulated by Delmas *et al* (1962) as

$$X_1 = (Ar_A/RT) + (BT/Rr_A), \text{ and} \quad (4)$$

$$K_1 = (Ar_A/RT) - (BT/Rr_A), \quad (5)$$

where $r_A = \frac{1}{2}(n + 1)$, n is the number of carbon atoms in the main chain of the solvent molecule, and R is gas constant.

A study of the viscometric behavior of polymers in homologous series n -alkanes made it possible to determine the polymer-solvent interaction parameters. Exchange terms of the enthalpy and entropy of mixing $X_{1,2}$ and $Q_{1,2}$ can be evaluated from these parameters at theta conditions according to the theory of Flory (Flory 1965, Eichinger & Flory 1968) and applying the following relations:

$$X_1 = \frac{p_1^* V_1}{RT\tilde{v}_1} \left[\frac{\bar{X}_{1,2}(S_2)^2}{p_1^*} + \frac{1}{2} A^2 \alpha_1 T \right], \quad (6)$$

$$X_1 = \frac{p_1^* V_1}{RT\tilde{v}_1} (1 + \alpha_1 T) \left[\frac{X_{1,2}(S_2)^2}{p_1^*} - \frac{2}{3} A^2 \alpha_1^2 T^2 \right], \quad (7)$$

$$A = \left(1 - \frac{T_1}{T_2} \right) \frac{p_2}{p_1} - \frac{X_{1,2}}{P_1} \frac{S_2}{S_1}, \text{ and} \quad (8)$$

$$\bar{X}_{1,2} = X_{1,2} - \tilde{v} T Q_{1,2}, \quad (9)$$

where $X_{1,2}$ represents the exchange enthalpy, $Q_{1,2}$ the exchange entropy, $\bar{X}_{1,2}$ the exchange interaction parameter, α_1 the thermal expansion coefficient of solvent and V_1 the molar volume of solvent. S_2/S_1 is the ratio of surface areas per unit characteristic volume of pure components.

The reduced volumes \tilde{v} , reduced temperatures \tilde{T} , and the characteristic parameters v^* , T^* and p^* have been calculated from the thermal expansion coefficient α and the thermal pressure coefficient γ through use of relations described by Flory (1965):

$$\tilde{p} = \frac{p}{p^*}, \quad (10)$$

$$\tilde{v} = \frac{v}{v^*}, \quad (11)$$

$$\tilde{T} = \frac{T}{T^*}, \quad (12)$$

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}}, \quad (13)$$

$$\tilde{v}^{1/3} = 1 + \frac{\alpha T}{3(1 + \alpha T)}, \text{ and} \quad (14)$$

$$P^* = \gamma T \tilde{v}^2. \quad (15)$$

EXPERIMENTAL

Poly(n-decyl methacrylate) was supplied by Röhm GmbH, (Darmstadt, Germany) and the ratio of molecular weights of the polymer ($M_w/M_n = 2.62$) was determined by gel-permeation chromatography in tetrahydrofuran using a viscosity corrected “universal calibration curve”.

Polymer was fractionated by the method of fractional precipitation, combined with lowering the temperature from 30°C to room temperature using toluene-methanol as solvent-non-solvent system. The molecular weight of fractions was determined viscometrically in tetrahydrofuran using the established Mark-Houwink equation $[\eta]^{30} = 4.56 \times 10^{-5} M^{0.73}$ (Xu *et al* 1984).

The polymer solutions were prepared within the concentration range 0.1 to 0.8 gdl⁻¹. The solution viscosities were measured in an Ubbelohde dilution viscometer and intrinsic viscosities were determined by the usual extrapolation of the η_{sp}/c vs. c dependence to zero using the Huggins equation (Huggins 1942).

RESULTS AND DISCUSSION

Viscosity index improver

For the viscosity index improver to be effective, its intrinsic viscosity should increase with temperature. The temperature coefficient of the oil's viscosity is negative, and the applied polymer additives must lower its absolute value, which means that the temperature coefficient of the viscosity of solutions of polymer additives in lubricating oils should be positive. Figure 1 presents the intrinsic viscosity of the polymer solution in n-alkanes as a function of temperature. As can be seen, the solubility of the polymer increases with decreasing molecular weight of the solvent and increasing temperature.

The parameters A and B for the system PDMA - n'alkanes were determined from experimental data (θ , K_1) by means of Equations (4) and (5) at θ -conditions ($T = \theta$, $X_1 = 1/2$) and are summarized in Table 1.

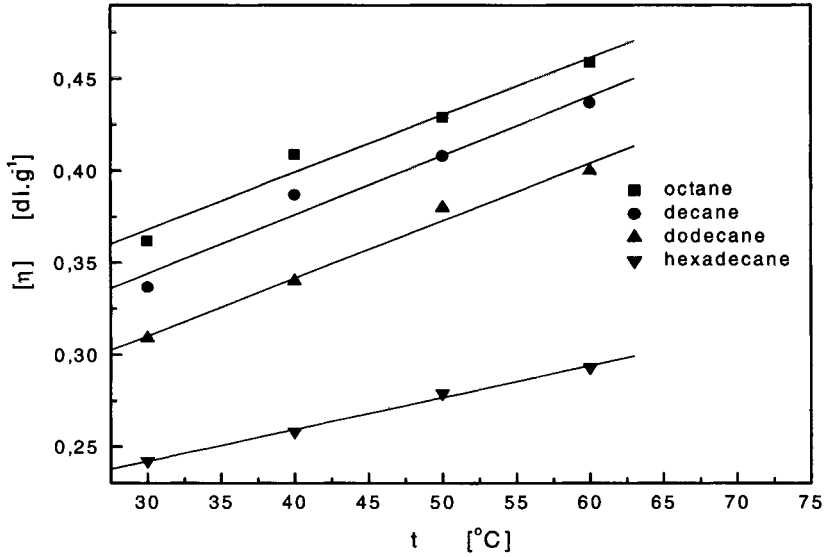


Fig. 1. Relation between intrinsic viscosity and temperature for poly(*n*-decyl methacrylate) in *n*-alkanes ($M = 250 \times 10^3$)

Table 1. Thermodynamic parameters of poly(*n*-decyl methacrylate) in *n*-alkanes.

Solvents	Heptane	Octane	Decane	Dodecane	Hexadecane
θ [K]	267	269	279	284	289
K_1	0.225	0.231	0.260	0.267	0.269
A [$J \text{ mol}^{-1}$]	200.8	181.5	160.5	139.4	108.9
$B \times 10^3$ [$J \text{ K}^{-2} \text{ mol}^{-2}$]	17.1	18.7	19.7	22.2	28.2

The temperature coefficient of unperturbed dimensions for PDMA ($2.4 \times 10^{-3} \text{ K}^{-1}$) was taken from the literature according to Tobolsky *et al* (1961). Model calculations of the viscosity-temperature dependence as a function of additive molecular weight and solvent thermodynamic quality (in the system PDMA - *n*-dodecane) were carried out and the results are summarized in Tables 2 and 3.

Table 2. Model calculation of $d \ln \eta_{sp} / dT$ values for PDMA in *n*-dodecane, dependence on molecular weight.

α_η	$P_1 \times 10^3$	$P_2 \times 10^3$	$P_3 \times 10^3$	$P_4 \times 10^3$	$d \ln \eta_{sp} / dT \times 10^3$
1.2	5.11	0.042	3.14	-1.498	6.80
1.4	15.05	0.123	2.93	-1.498	16.61
1.6	20.36	0.167	2.86	-1.498	21.89
1.8	23.22	0.190	2.79	-1.498	24.71
2.0	24.83	0.204	2.73	-1.498	26.28

Table 3. Model calculations of $d\ln \eta_{sp}/dT$ values for PDMA in n-dodecane, dependence on solvent thermodynamic quality.

ΔT	$P_1 \times 10^3$	$P_2 \times 10^3$	$P_3 \times 10^3$	$P_4 \times 10^3$	$d\ln \eta_{sp}/dT \times 10^3$
10	48.96	0.121	2.93	-1.518	50.49
30	15.05	0.123	2.93	-1.489	16.61
50	7.96	0.125	2.93	-1.462	9.55
100	2.89	0.129	2.93	-1.397	4.55
150	1.23	0.132	2.93	-1.339	2.95

These calculations have shown that the $d\ln \eta_{sp}/dT$ values are increasing with increasing molecular weight (Table 2) and decreasing with improving solvent thermodynamic quality (Table 3). The comparison of the numerical values for P members in Equation (2) has shown that in the studied system, in addition to members P_1 and P_4 , the P_3 member also contributes significantly (especially for low molecular weights). For higher α_η values and shorter distances from the θ -temperature (lower ΔT values), the influence of P_3 and P_4 members is less important and the $d\ln \eta_{sp}/dT$ value is unambiguously positive.

According to these results the polymer should have a high molecular weight and its interaction with solvent should be thermodynamically favorable in order to give a positive $d\ln \eta_{sp}/dT$ and consequently high values of the viscosity index.

Equation of state data and characteristic parameters

The parameters v^* , T^* and p^* for n-alkanes were evaluated from the densities, α_1 and γ_1 values according to Orwoll & Flory (1967), and for PDMA were obtained from α_2 and γ_2 values according to Krevelen (1976) by use of Equations 10-15. The value of S_2/S_1 was estimated according to the procedure described by Orwoll & Flory (1967) and Eichinger & Flory (1968). The molecular surface area for n-alkanes has been calculated by ascribing them the form of a cylinder having a radius of 2.49 Å and a height given by $l^* = 1.32 + 1.19n$ in Å, where n is the number of carbon atoms in the n-alkane molecule. A cylinder with a length of 2.49 Å approximates the polymer segment and its radius was calculated from the characteristic volume of the monomer unit.

The thermal pressure coefficient of polymer γ_2 , can be expressed according to Manzini & Crescenzi (1974) as

$$\gamma_2 = \frac{1}{T} \left(\frac{\sum n_i a_i}{V_u} \right)^2, \quad (16)$$

where V_u is the molar volume of the monomer unit and a_i are parametric values characteristic of a given atom or atomic grouping of which there are n_i per molecule.

Calculated values of the characteristic parameters are given in Table 4. The exchange enthalpy parameter $X_{1,2}$ and exchange entropy parameter $Q_{1,2}$ of PDMA in *n*-alkanes were found to decrease with an increase in length of alkane molecules (Figure 2 and 3). This dependence can be described by the following empirical equations:

$$X_{1,2} = (X_{1,2})_{\infty} + \frac{K_x}{r^2}, \text{ and} \quad (17)$$

$$Q_{1,2} = (Q_{1,2})_{\infty} + \frac{K_Q}{r^2} \quad (18)$$

where $r = n + n_e$, n is the number of carbon atoms in *n*-alkane molecule, and the value of n_e lies in the interval 1.1-1.2 (Orwoll & Flory 1967). By extrapolation of the exchange parameters $X_{1,2}$ and $Q_{1,2}$ to infinite molecular weight of *n*-alkanes (polymethylene), we obtain the values of exchange parameters for the system PM-PDMA.

Table 4. Characteristic parameters of PDMA in *n*-alkanes

Solvents	\tilde{v}_2	T_2^* [K]	P_2^* [J cm ⁻³]	S_2/S_1	γ_2 [J cm ⁻³ K ⁻¹]
Heptane	1.145	6918	528.3	0.349	0.361
Octane	1.146	6932	528.7	0.358	0.358
Decane	1.151	7020	534.7	0.371	0.345
Dodecane	1.153	7068	535.8	0.380	0.339
Hexadecane	1.156	7102	538.3	0.392	0.332

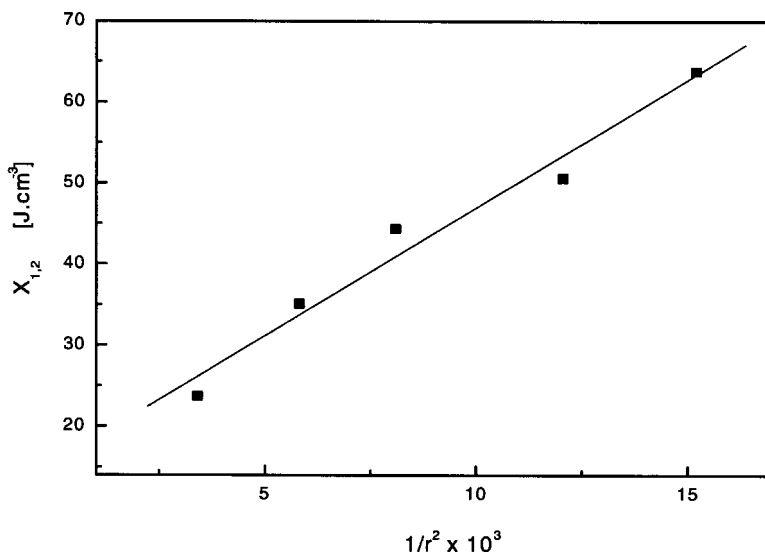


Fig. 2. Empirical correlation of the exchange term $X_{1,2}$ with the length of alkane molecules.

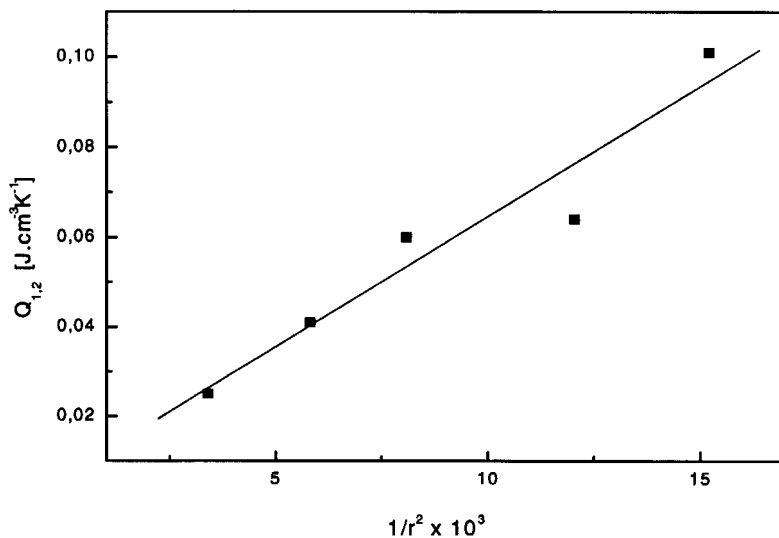


Fig. 3. Empirical correlation of the exchange parameter $Q_{1,2}$ with the length of alkane molecules.

Thermodynamics of PM-PDMA mixing

Prediction of mixing PM with PDMA was carried out according to the procedure of Flory *et al* (1968) and the characteristic parameters of PM are taken from that paper at 100°C. The mixing functions were calculated on the basis of following relations:

$$\Delta H_M = \nu_{sp}^* \left\{ \phi_1 P_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \phi_2 P_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1}) + \left(\frac{\phi_1 \Theta_2}{\tilde{v}} \right) (X_{1,2})_\infty \right\}, \quad (19)$$

$$\Delta S_M = -3\nu_{sp}^* \left\{ \left(\frac{\phi_1 P_1^*}{T_1^*} \right) \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left(\frac{\phi_2 P_2^*}{T_2^*} \right) \ln \frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right\} + \phi_1 \Theta_2 (Q_{1,2})_\infty, \quad (20)$$

$$\Delta G_M = \Delta H_M - T\Delta S_M, \quad (21)$$

$$\Theta_2 = 1 - \Theta_1 = \phi_2 \{ \phi_2 + \phi_1 (S_2/S_1) \}, \quad (22)$$

$$\phi_2 = 1 - \phi_1 = w_2 \nu_{sp,2}^* / (w_{sp,1} + w_2 \nu_{sp,2}^*), \quad \text{and} \quad (23)$$

$$\nu_{sp}^* = w_1 \nu_{sp,1}^* + w_2 \nu_{sp,2}^*. \quad (24)$$

Here the symbols Θ_i , ϕ_i and w_i stand for site fractions, segment fractions and weight fractions, respectively, and ν_{sp}^* is the characteristic volume for 1g of mixture.

Characteristic parameters for PM and PDMA are summarized in Table 5, where PM is component (1) and PDMA is component (2).

Table 5. Characteristic parameters of PM and PDMA

Polymer	$\tilde{\nu}$	T^* [K]	ν_{sp}^* [cm ³ g ⁻¹]	ρ^* [J cm ⁻³]
PM (1)	1.224	7010	1.013	473.0
PDMA (2)	1.195	7738	0.8248	575.4

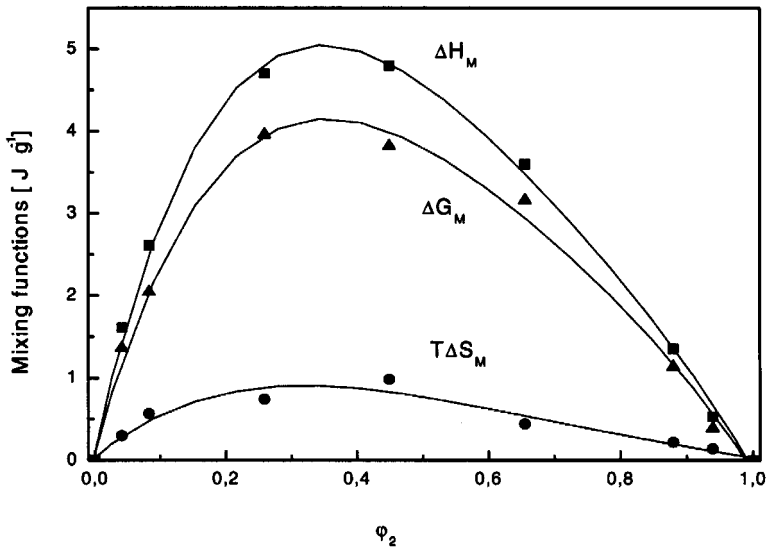


Fig. 4. Thermodynamic mixing functions for PM and PDMA

Calculated values of the thermodynamic mixing functions for the mixture of PM and PDMA are shown in Figure 4. The enthalpy of mixing is positive. The entropy is also positive, but its value is smaller than enthalpy. The resulting positive free energy of mixing ΔG_M signifies mutual incompatibility of these polymers.

CONCLUSION

Temperature dependence of intrinsic viscosities of poly(*n*-decyl methacrylate) in *n*-alkanes was used for the characterization of PDMA as viscosity index improver in lubricating oils and for the prediction of its miscibility with

polymethylene. The performed analysis characterizes the influence of all individual parameters on the temperature dependence of the specific viscosity of polymer additive solutions and can be applied as a useful guide for the selection of additives used as viscosity index improvers in motor oils.

Thermodynamic parameters, obtained from viscometric data of PDMA in n-alkanes were exploited for the determination of the exchange mixing terms for the system PDMA-PM. Both calculated contributions to the free energy of mixing are unfavorable and make the studied polymers incompatible.

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السلوك الخاص بعديد (n-decyl methacrylate) في المتسلسلة (n) الكانات :
طريقة مبتكرة للتنبؤ بمدى تطبيق ذلك في تحسين مؤشر ومعامل اللزوجة
الخاص بزيت المحركات وتأثير امتزاجه بمادة عديد الميثيلين

عقيل ، لاث ولاثوفا

معهد البلمرات، أكاديمية سلوفاك للعلوم، براتسلافا، جمهورية سلوفاكيا

خلاصة

استخدمت في هذه الدراسة محاليل مخففة من عديد (n-decyl methacrylate) واللائكانات. تم أخذ القياسات الخاصة باللزوجة المعتمدة على الحرارة لهذا العديد (كنموذج لمذيب خاص للزيت الشمعي) وأنه قد تم تطبيق ذلك في استنباط نموذج حسابي خاص باللزوجة النوعية بدلالة الحرارة والأوزان الجزيئية. وأنه وفقاً لنظرية Flory تمت دراسة المؤثرات المختلفة الخاصة بهذا العديد على المتسلسلة المتماثلة الخاصة باللائكانات ومن ثم تم تطبيق ذلك على توقع امتزاجه مع عديد الميثيلين. وتفيد الطاقة الموجبة للمزج على عدم التوافق المتبادل لتلك اللدائن.