

Table II. Solubilities at 25 °C and Enthalpies of Solution

Substance	Solubility at 25 °C		ΔH_d , kJ/mol	ΔH_{tr} , kJ/mol	ΔH_{fus} , kJ/mol	$\Delta H_{tr} + \Delta H_{fus}$, kJ/mol	T_{tr} , °C	T_{fus} , °C
	$10^3 x_2$	g/100 g of PE						
C ₁₉ H ₄₀	681 ± 8	730 ± 9	57.5 ± 0.3	13.8	45.8	59.6	22.8	32.0
C ₂₄ H ₅₀	98 ± 2	47 ± 1	83.1 ± 0.8	31.3	54.9	86.2	48.1	50.9
C ₂₈ H ₅₈	22.1 ± 0.6	11.4 ± 0.3	99.3 ± 0.7	35.4	64.6	100.0	58.0	61.2
C ₃₂ H ₆₆	5.4 ± 0.2	3.1 ± 0.1	109.0 ± 0.8	?	?	115.8	63.5	70.2
C ₃₆ H ₇₄	0.99 ± 0.05	0.64 ± 0.03	128.5 ± 1.1	9.9	88.8	129.2	72.1	75.9
				30.5			73.8	

the denominator (law of ideality of dilute solutions). H_2^E is zero for an ideal solution, and if ΔH_{fus} is treated as a constant, eq 2 may be integrated to yield the well-known relation

$$\ln x_2 = (\Delta H_{fus}/R)(1/T_{fus} - 1/T) \quad (3)$$

For substances with a first-order transition point we have, for $T < T_{tr}$

$$\ln x_2 = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_{fus}} - \frac{1}{T} \right) + \frac{\Delta H_{fus} + \Delta H_{tr}}{R} \left(\frac{1}{T_{tr}} - \frac{1}{T} \right) \quad (4)$$

If we calculate the solubilities at 25 °C from eq 4, we find the following values for x_2 at 25 °C: C₁₉H₄₀, 0.655; C₂₄H₅₀, 0.069; C₂₈H₅₈, 0.0143; C₃₂H₆₆, 0.0021; C₃₆H₇₄, 0.000 55. From these values we see that the assumptions made in deriving eq 4 are not fulfilled for the actual systems. We arrive at the same conclusion from a comparison of the values of ΔH_d and $\Delta H_{fus} + \Delta H_{tr}$ in Table II. The causes for nonideality of the systems are (1) the nonvanishing of H_2^E and (2) the important excess entropy of mixing large and small molecules. The latter effect is accounted for by the Flory–Huggins theory (6, 10), whereas the

former seems more difficult to treat theoretically. In addition, the variation of ΔH_{fus} with temperature influences the solubility. We may conclude that the solubilities follow an equation of the form (3) or (4), but with the enthalpies and transition temperatures replaced by slightly different values.

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Gas Chromatographic Characterization of Phosphate Esters

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The gas chromatographic technique was employed in order to characterize four phosphate esters, which are at present used as plasticizers for plastic materials. The four phosphate esters were employed as stationary phases, while 22 organic compounds (hydrocarbons, alcohols, and acetates) were employed as GLC solutes. The investigation was carried out over a large range of temperatures. The four esters were classified according to Novak's polarity scale. Their insertion in the analogous classification for phthalate, adipate, and sebacate esters resulted in a 14-term polarity scale which suggests a new scientific criterion for the selection of the most suitable plasticizer to be used with polymeric systems.

At present, gas chromatography is considered one of the most suitable techniques for the determination of thermodynamic properties, such as activity coefficients, which provide useful indications among the components of liquid mixtures. On this basis, in the present study four phosphate esters were charac-

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terized by GLC. The present work is the continuation of the investigations started (1–3, 5, 6, 10) with a series of phthalate, adipate, and sebacate esters. These classes of compounds are widely employed as plasticizers for plastics, varnishes, etc. (13), to which they impart flexibility and shock resistance at reasonable prices.

Theory

The relationship which correlates the specific retention volume, V_g , with gas chromatographic quantities is the following (8)

$$V_g = \frac{F}{W_s} j \frac{P_o - P_{H_2O}^0}{760} \frac{273}{T_o} (t_R - t_a) \quad (1)$$

where j is the James–Martin factor (9) defined as

$$j = \frac{3(P_i/P_o)^2 - 1}{2(P_i/P_o) - 1} \quad (2)$$

Activity coefficients at infinite dilution, γ_i^∞ , are calculated by means of the following equation (7)

$$\ln \gamma_i^\infty = \ln \frac{273R}{V_{g,i} P_i^0 M_s} - \frac{B_{ii} P_i^0}{RT} \quad (3)$$

Table I. Physical Properties of the Stationary Phases

Stationary phase	State	Mol wt	Density (at 20 °C)	Bp, °C	Viscosity, cP
Triphenyl phosphate	Solid (mp 49 °C)	326.29	1.185	220 (11 mmHg)	
Tricresyl phosphate	Liquid	368.29	1.16–1.17	295 (13 mmHg)	175 (at 20 °C)
Triisobutyl phosphate	Liquid	410.46	1.13–1.14	285–295 (20 mmHg)	112 (at 25 °C)
Tri-2-ethylhexyl phosphate	Liquid	434.65	0.926	220 (5 mmHg)	14 (at 20 °C)

Equation 3 is usually applied when solute-carrier gas interactions and pressure effects within the column can be neglected.

Coefficients B_{ii} are determined using the empirical formula proposed by Beattie and Bridgeman

$$B_{ii} = V_c [0.461 - 1.158(T_c/T) - 0.503(T_c/T)^3] \quad (4)$$

If the temperature dependence of γ_i^∞ is known, the excess partial molar enthalpy at infinite dilution, $\bar{H}_i^{E,\infty}$, and the excess partial molar heat at infinite dilution, $\bar{C}_{p,i}^{E,\infty}$, defined as $\bar{C}_{p,i}^{E,\infty} = (\partial \bar{H}_i^{E,\infty} / \partial T)_p$, can be determined. In this manner the variation of γ_i^∞ with temperature can be described by the following equation (10)

$$\ln \gamma_i^\infty = -(\bar{C}_{p,i}^{E,\infty}/R) \ln T + (A/R)(1/T) + B \quad (5)$$

where $\bar{C}_{p,i}^{E,\infty}$ is supposed constant with T .

Experimental Section

A thermal conductivity chromatograph Fractovap Model B (Carlo Erba) was used as GLC apparatus. The carrier gas flow rate was measured by means of a soap-film meter. The column temperature was controlled to within ± 0.2 °C and measured by an electronic thermometer (Avo Comark). The internal pressure gradient was measured to within ± 1 mm Hg by a mercury manometer. The outlet pressure was atmospheric. The quantities of solutes injected were 0.2 μ L; to this aim a 5- μ L Hamilton syringe was employed. The operating conditions are summarized as follows: carrier gas, pure hydrogen; carrier gas flow rate, 20–40 cm^3/min ; copper column (2-m long, 4-mm internal diameter); support, 60–80 mesh Chromosorb W (Carlo Erba) acid washed and silanized with 1,1,1,3,3,3-hexamethylsilazane (Merck) (17), quantitative ratio of support to stationary phase = 3:1 (by weight); internal pressure gradient, 250–270 mmHg; column temperature range, 50–145 °C (for triphenyl phosphate, 35–125 °C); solutes injected, paraffins, olefins, cycloparaffins, aromatic hydrocarbons, alcohols, and acetates (Fluka, BDH); stationary phases, phosphate esters, namely, triphenyl phosphate (TPP), tricresyl phosphate (TCP), triisobutyl phosphate (TXP), and tri-2-ethylhexyl phosphate (TOP) (Koch Light, Novaria, Albright & Wilson, Union Carbide).

The physical properties of the four stationary phases examined are reported in Table I.

Results and Discussion

The elution peaks were only slightly asymmetric (this also confirms the infinite dilution). For this reason and owing to the fact that (1) the stationary phases studied are not very polar compounds, (2) a silanized support was employed, and (3) a 25% liquid loading was used, the experimental data are reasonably unaffected by appreciable adsorption phenomena.

Retention times were estimated according to a criterion proposed by the authors in a previous paper (4). This method permits the construction of the ideal elution peak starting from gas chromatographic quantities. It is based on the following procedure. The initial retention time (anti-Langmuir isotherm) or the final retention time (Langmuir isotherm) is measured. The peak width, W_{b0} , at infinite dilution is determined. To this end, the quantity τ is introduced; it is defined as

$$\tau = W_{b0}/2t_R \quad (6)$$

where W_b is the peak width at finite concentration and t_R is the total retention time. The limiting value τ_0 (at infinite dilution) is calculated. So, the corrected retention time, t_{R0} , can be determined as follows

$$t_{R0} = t_R(1 + \tau_0) \quad (\text{anti-Langmuir isotherm}) \quad (7)$$

$$t_{R0} = t_{Rf}(1 - \tau_0) \quad (\text{Langmuir isotherm}) \quad (8)$$

It has been seen experimentally that τ_0 is independent of the solute-solvent pair, temperature, and flow rate. It only depends on the column length. (For columns 2 m long $\tau_0 = 0.05$.)

Subsequently specific retention volumes were calculated with eq 1.

The investigation was carried out at five temperatures.

As a perfectly linear correlation was found (by plotting the $\ln V_{g,i}$ of the solutes vs. $1/T$), the values of $V_{g,i}$ at 25 °C could be determined by extrapolating experimental data obtained in the operative range of temperature. In order to verify the validity of experimental data, the $\ln V_{g,i}$ of solutes of homologous series were plotted vs. the number of carbon atoms; a linear correlation was found, with the exception of the first terms of the classes of alcohols and acetates. For TPP some tests were carried out below its melting point. The results obtained were surprisingly in optimum agreement with those extrapolated (see Figure 1). This could be due to the fact that there are only minor differences in the behavior and physical properties between the solid and liquid phase. In fact, the density of solid TPP is similar to that of the other liquid plasticizers.

Activity coefficients at infinite dilution were calculated by means of eq 3, in which the coefficients B_{ii} were evaluated with eq 4 and vapor pressures with the Antoine equation using the Antoine constants tabulated in ref 14. The values of $\ln \gamma_i^\infty$ at 25, 50, 75, 100, and 125 °C are reported in Tables II–V. The results obtained show that the natural logarithms of activity coefficients at infinite dilution do not vary linearly either with $1/T$ (see Figure 2) or with the number of carbon atoms within each homologous class of solutes. In particular, the following effects can be observed. (a) The γ_i^∞ of all solutes generally increase in the order TOP < TXP < TCP < TPP; all solutes injected in TCP and TXP show similar values of γ_i^∞ ; the values of γ_i^∞ in TPP are generally higher than unity; the values of γ_i^∞ in TOP are generally lower than unity. (b) By comparing solutes of different homologous classes but having similar boiling points it can be noted that the γ_i^∞ generally increase in the order: aromatics < acetates < alcohols < cycloparaffins < olefins < paraffins with the only exception being TOP, for which the γ_i^∞ of the acetates are similar to those of paraffins and olefins. (c) The γ_i^∞ generally increase with increasing number of carbon atoms within each homologous class, except for alcohols and acetates, where no substantial regularities could be noticed. (d) By plotting the $\ln \gamma_i^\infty$ vs. $1/T$ it can be seen that the $\ln \gamma_i^\infty$ generally increase with $1/T$. Minima in the $\ln \gamma_i^\infty$ vs. $1/T$ curves were found in some cases, i.e., for paraffins, olefins, cycloparaffins, and *n*-propyl and *n*-butyl alcohols in TOP, for 1-pentene in TPP, for acetates in TPP and TCP, for *n*-propyl and *n*-butyl acetates in TXP and TOP, and for aromatics in all the liquid phases examined. The presence of minima in the $\ln \gamma_i^\infty$ vs. $1/T$ curves might be due to experimental errors, which, under optimum operating conditions, are generally of about 2–5%, or also to specific solute-solvent interactions. Assuming that the trend of $\ln \gamma_i^\infty$ with T is described by eq 5, a

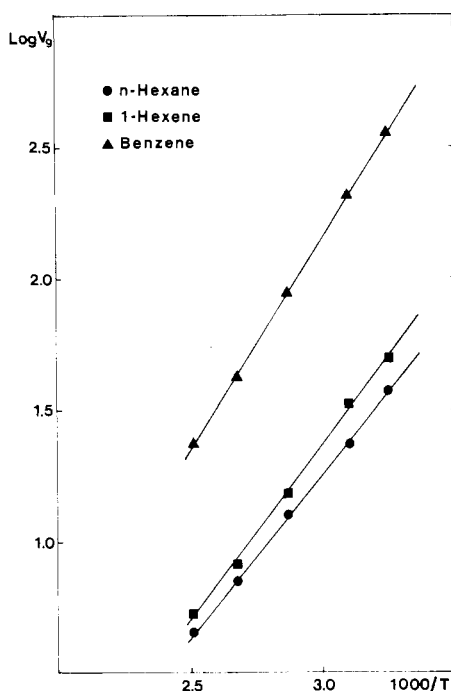


Figure 1. Decimal logarithms of specific retention volumes in triphenyl phosphate vs. $1/T$.

Table II. Natural Logarithms of Activity Coefficients at Infinite Dilution in Triphenyl Phosphate

Solute	$\text{Ln } \gamma_i^\infty$				
	25 °C ^a	50 °C	75 °C	100 °C	125 °C
<i>n</i> -Pentane	1.72	1.52	1.40	1.30	1.23
<i>n</i> -Hexane	1.96	1.72	1.57	1.44	1.36
<i>n</i> -Heptane	2.17	1.90	1.72	1.57	1.48
<i>n</i> -Octane	2.38	2.06	1.86	1.69	1.58
1-Pentene	1.08	0.99	0.97	0.94	0.95
1-Hexene	1.39	1.24	1.17	1.10	1.08
1-Heptene	1.67	1.46	1.34	1.24	1.19
1-Octene	1.94	1.67	1.50	1.36	1.28
Cyclohexane	1.41	1.16	1.01	0.88	0.79
Methylcyclohexane	1.65	1.41	1.26	1.13	1.05
Ethylcyclohexane	1.83	1.57	1.41	1.27	1.18
Benzene	0.01	-0.05	-0.05	-0.05	-0.02
Toluene	0.23	0.16	0.16	0.16	0.19
Ethylbenzene	0.34	0.26	0.26	0.26	0.30
Methyl alcohol	0.78	0.51	0.34	0.18	0.08
Ethyl alcohol	0.91	0.64	0.46	0.30	0.19
<i>n</i> -Propyl alcohol	0.94	0.63	0.45	0.30	0.22
<i>n</i> -Butyl alcohol	1.13	0.74	0.54	0.38	0.31
Methyl acetate	0.19	0.07	0.03	-0.01	-0.01
Ethyl acetate	0.23	0.14	0.12	0.11	0.13
<i>n</i> -Propyl acetate	0.28	0.19	0.19	0.19	0.23
<i>n</i> -Butyl acetate	0.38	0.30	0.31	0.31	0.36

^a The data at 25 °C are extrapolated.

mathematical explanation can be given to the above-mentioned effect; in fact, in the $\text{Ln } \gamma_i^\infty$ vs. $1/T$ curve obtained according to eq 5 there is a minimum when $T = -A/C_{p,i}^{E,\infty}$. Therefore, the temperature dependence of γ_i^∞ was evaluated using eq 5 and, applying the least-squares method, the experimental data were found to fit the theoretical equation (5) satisfactorily (see Figure 2). The constants of eq 5 and the mean squares deviations (MSD) are reported in Tables VI-IX.

For a deeper insight into their properties the four phosphate esters studied were classified according to a polarity scale based on a criterion proposed by Novak (12), which states that the polarity of a stationary phase can be determined on the basis

Table III. Natural Logarithms of Activity Coefficients at Infinite Dilution in Tricresyl Phosphate

Solute	$\text{Ln } \gamma_i^\infty$				
	25 °C ^a	50 °C	75 °C	100 °C	125 °C
<i>n</i> -Pentane	1.02	0.86	0.77	0.70	0.66
<i>n</i> -Hexane	1.24	1.04	0.93	0.83	0.78
<i>n</i> -Heptane	1.44	1.21	1.07	0.95	0.88
<i>n</i> -Octane	1.63	1.36	1.19	1.05	0.97
1-Pentene	0.93	0.71	0.56	0.43	0.35
1-Hexene	1.04	0.81	0.68	0.56	0.49
1-Heptene	1.11	0.90	0.78	0.67	0.61
1-Octene	1.17	0.97	0.86	0.76	0.72
Cyclohexane	0.70	0.53	0.44	0.36	0.32
Methylcyclohexane	1.06	0.83	0.68	0.54	0.46
Ethylcyclohexane	1.22	0.96	0.80	0.66	0.58
Benzene	-0.20	-0.31	-0.34	-0.38	-0.37
Toluene	-0.16	-0.24	-0.24	-0.24	-0.21
Ethylbenzene	-0.10	-0.15	-0.10	-0.08	-0.01
Methyl alcohol	0.65	0.35	0.15	-0.02	-0.14
Ethyl alcohol	0.68	0.41	0.25	0.09	-0.01
<i>n</i> -Propyl alcohol	0.65	0.35	0.18	0.04	-0.03
<i>n</i> -Butyl alcohol	0.78	0.41	0.22	0.08	0.02
Methyl acetate	-0.09	-0.19	-0.21	-0.23	-0.21
Ethyl acetate	-0.05	-0.13	-0.13	-0.15	-0.12
<i>n</i> -Propyl acetate	0.03	-0.06	-0.06	-0.07	-0.03
<i>n</i> -Butyl acetate	0.16	0.06	0.08	0.08	0.08

^a The data at 25 °C are extrapolated.

Table IV. Natural Logarithms of Activity Coefficients at Infinite Dilution in Triisobutyl Phosphate

Solute	$\text{Ln } \gamma_i^\infty$				
	25 °C ^a	50 °C	75 °C	100 °C	125 °C
<i>n</i> -Pentane	1.07	0.85	0.71	0.58	0.50
<i>n</i> -Hexane	1.21	0.98	0.84	0.72	0.64
<i>n</i> -Heptane	1.33	1.09	0.95	0.83	0.76
<i>n</i> -Octane	1.44	1.19	1.05	0.93	0.86
1-Pentene	0.63	0.48	0.39	0.32	0.28
1-Hexene	0.80	0.63	0.54	0.46	0.42
1-Heptene	0.95	0.76	0.66	0.57	0.53
1-Octene	1.07	0.87	0.77	0.68	0.64
Cyclohexane	0.69	0.50	0.38	0.28	0.23
Methylcyclohexane	0.83	0.64	0.53	0.43	0.38
Ethylcyclohexane	1.04	0.80	0.67	0.55	0.48
Benzene	-0.34	-0.44	-0.46	-0.48	-0.47
Toluene	-0.14	-0.25	-0.27	-0.30	-0.29
Ethylbenzene	-0.05	-0.17	-0.19	-0.22	-0.21
Methyl alcohol	0.66	0.35	0.14	-0.05	-0.19
Ethyl alcohol	0.78	0.46	0.24	0.04	-0.10
<i>n</i> -Propyl alcohol	0.69	0.35	0.15	-0.02	-0.11
<i>n</i> -Butyl alcohol	0.77	0.37	0.17	0.01	-0.06
Methyl acetate	0.06	-0.10	-0.19	-0.26	-0.29
Ethyl acetate	0.13	-0.03	-0.09	-0.14	-0.15
<i>n</i> -Propyl acetate	0.10	-0.03	-0.06	-0.09	-0.07
<i>n</i> -Butyl acetate	0.14	0.03	0.01	0.00	0.03

^a The data at 25 °C are extrapolated.

of the value of the excess partial molar Gibbs free energy of a methylene group, $\Delta G^E(\text{CH}_2)$, defined as follows

$$\Delta G^E(\text{CH}_2) = -RT(d \ln (V_{g,i} P_i^0)/dn) \quad (9)$$

The mean values of $\Delta G^E(\text{CH}_2)$ in the temperature range investigated were determined for all phases (see Table X). The following sequence of increasing polarity could be determined: TOP < TXP < TCP < TPP. For the calculation of $\Delta G^E(\text{CH}_2)$ retention data of paraffins were employed.

By adding the $\Delta G^E(\text{CH}_2)$ values obtained in this work for phosphate esters to the analogous data available in the literature (1, 3) for phthalate, adipate, and sebacate esters the scale given in Table X was obtained. An examination of the sequence of Table X shows that phosphate esters are generally characterized

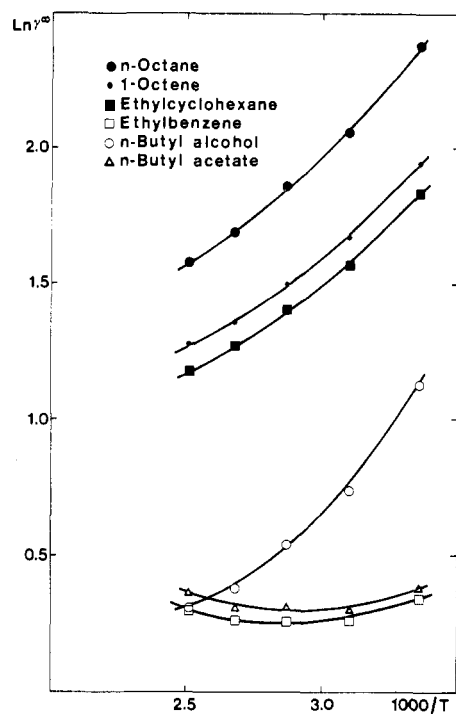


Figure 2. Natural logarithms of activity coefficients at infinite dilution in triphenyl phosphate vs. $1/T$.

Table V. Natural Logarithms of Activity Coefficients at Infinite Dilution in Tri-2-ethylhexyl Phosphate

Solute	$\text{Ln } \gamma^\infty$				
	25 °C ^a	50 °C	75 °C	100 °C	125 °C
<i>n</i> -Pentane	-0.21	-0.28	-0.28	-0.29	-0.27
<i>n</i> -Hexane	-0.12	-0.19	-0.20	-0.21	-0.18
<i>n</i> -Heptane	-0.04	-0.13	-0.14	-0.15	-0.12
<i>n</i> -Octane	0.01	-0.08	-0.09	-0.10	-0.06
1-Pentene	-0.39	-0.43	-0.43	-0.43	-0.40
1-Hexene	-0.25	-0.32	-0.32	-0.33	-0.30
1-Heptene	-0.15	-0.23	-0.24	-0.26	-0.23
1-Octene	-0.05	-0.16	-0.18	-0.20	-0.17
Cyclohexane	-0.28	-0.39	-0.42	-0.46	-0.46
Methylcyclohexane	-0.21	-0.30	-0.32	-0.35	-0.34
Ethylcyclohexane	-0.13	-0.23	-0.24	-0.27	-0.24
Benzene	-0.72	-0.78	-0.79	-0.80	-0.77
Toluene	-0.60	-0.66	-0.65	-0.65	-0.61
Ethylbenzene	-0.54	-0.62	-0.61	-0.61	-0.56
Methyl alcohol	-0.50	-0.64	-0.69	-0.76	-0.78
Ethyl alcohol	-0.54	-0.66	-0.71	-0.77	-0.78
<i>n</i> -Propyl alcohol	-0.67	-0.82	-0.84	-0.87	-0.84
<i>n</i> -Butyl alcohol	-0.65	-0.85	-0.89	-0.90	-0.85
Methyl acetate	0.03	-0.17	-0.27	-0.36	-0.41
Ethyl acetate	0.01	-0.16	-0.23	-0.31	-0.33
<i>n</i> -Propyl acetate	-0.10	-0.24	-0.29	-0.33	-0.32
<i>n</i> -Butyl acetate	-0.16	-0.28	-0.29	-0.31	-0.28

^a The data at 25 °C are extrapolated.

by higher values of polarity than other esters. These values are associated with the phosphoric group and the presence of a long-chain, saturated, esterifying alcohol lowers the polarity value to the range of the values of the corresponding phthalate, adipate, and sebacate esters; in the family of 2-ethylhexyl esters an influence of the acidic group can be observed. Of the phthalates, diisodecyl phthalate, which has the longest hydrocarbon chain esterifying alcohol, is located at the lowest polarity level, whereas the presence of benzyl alcohol increases the

Table VI. Constants of Equation 5 and Mean-Squares Deviations for Triphenyl Phosphate

Solute	$-\bar{C}_{p,i} E^\infty / R$	A/R	B	10^4 (MSD)
<i>n</i> -Pentane	4.44	2100	-30.66	4.81
<i>n</i> -Hexane	5.28	2520	-36.55	9.34
<i>n</i> -Heptane	5.98	2870	-41.54	5.79
<i>n</i> -Octane	6.99	3340	-48.65	4.96
1-Pentene	4.33	1640	-29.12	9.76
1-Hexene	4.99	2090	-34.04	38.70
1-Heptene	6.03	2640	-41.54	3.89
1-Octene	6.77	3100	-47.03	1.64
Cyclohexane	5.15	2500	-36.29	22.78
Methylcyclohexane	5.21	2500	-36.44	6.24
Ethylcyclohexane	5.54	2670	-38.68	2.16
Benzene	4.78	1670	-32.81	1.34
Toluene	5.29	1860	-36.15	1.93
Ethylbenzene	6.37	2230	-43.41	3.22
Methyl alcohol	4.79	2470	-34.84	4.75
Ethyl alcohol	4.39	2360	-31.99	4.43
<i>n</i> -Propyl alcohol	8.51	3770	-60.20	3.25
<i>n</i> -Butyl alcohol	13.11	5460	-91.88	11.81
Methyl acetate	5.27	2040	-36.69	2.45
Ethyl acetate	5.68	2060	-39.07	1.37
<i>n</i> -Propyl acetate	6.88	2410	-47.02	3.70
<i>n</i> -Butyl acetate	6.78	2350	-46.10	4.48

Table VII. Constants of Equation 5 and Mean-Squares Deviations for Tricresyl Phosphate

Solute	$-\bar{C}_{p,i} E^\infty / R$	A/R	B	10^4 (MSD)
<i>n</i> -Pentane	4.79	2070	-33.23	2.10
<i>n</i> -Hexane	5.44	2410	-37.85	3.03
<i>n</i> -Heptane	5.57	2570	-38.96	3.17
<i>n</i> -Octane	6.79	3110	-47.47	5.68
1-Pentene	4.25	2150	-30.51	1.26
1-Hexene	5.43	2510	-38.31	2.98
1-Heptene	5.16	2360	-36.23	2.26
1-Octene	6.03	2600	-41.91	7.03
Cyclohexane	4.91	2130	-34.44	1.75
Methylcyclohexane	4.39	2220	-31.42	1.95
Ethylcyclohexane	6.11	2850	-43.20	2.19
Benzene	5.24	2000	-36.77	3.24
Toluene	5.35	1890	-36.96	5.18
Ethylbenzene	6.59	2150	-44.86	7.15
Methyl alcohol	5.40	2780	-39.45	1.53
Ethyl alcohol	4.73	2440	-34.44	5.21
<i>n</i> -Propyl alcohol	8.94	3870	-63.26	3.23
<i>n</i> -Butyl alcohol	13.47	5510	-94.45	5.70
Methyl acetate	5.90	2160	-40.98	2.39
Ethyl acetate	5.11	1840	-35.36	4.19
<i>n</i> -Propyl acetate	6.05	2140	-41.65	7.19
<i>n</i> -Butyl acetate	4.91	1750	-33.70	14.56

polarity value to a level comparable with that showed by diethyl phthalate, which has the shortest hydrocarbon chain esterifying alcohol.

The data reported in Table X offer a new tool for the selection of the most suitable plasticizer to be employed with any material, provided the polarity of the latter is evaluated according to the same procedure. So, a new criterion, which gives information on the interactions between plasticizer and polymer on the grounds of thermodynamic data, is made available in addition to the usual standards based upon specific performance requirements, price, and other empirical parameters.

At present, tests are carried out according to Novak's method to evaluate a series of polymers which usually require plasticization.

Table VIII. Constants of Equation 5 and Mean-Squares Deviations for Trixilenyl Phosphate

Solute	$\bar{C}_{p,i}^{E,\infty}/R$	A/R	B	10^4 (MSD)
n-Pentane	4.01	2050	-28.67	8.07
n-Hexane	4.92	2360	-34.77	6.79
n-Heptene	5.99	2730	-41.97	16.53
n-Octane	6.50	2910	-45.34	5.29
1-Pentene	4.19	1850	-29.43	1.87
1-Hexene	4.83	2100	-33.77	3.54
1-Heptene	4.63	2430	-39.26	10.82
1-Octene	6.14	2620	-42.71	12.62
Cyclohexane	5.00	2260	-35.40	1.28
Methylcyclohexane	4.84	2200	-34.14	2.30
Ethylcyclohexane	5.84	2660	-41.16	5.64
Benzene	5.27	1950	-36.91	5.47
Toluene	5.39	2020	-37.65	4.53
Ethylbenzene	5.90	2210	-41.11	5.42
Methyl alcohol	4.08	2400	-30.63	2.27
Ethyl alcohol	4.37	2540	-32.63	2.28
n-Propyl alcohol	9.04	4050	-64.41	3.96
n-Butyl alcohol	13.63	5650	-95.89	9.26
Methyl acetate	5.27	2220	-37.42	0.90
Ethyl acetate	6.69	2620	-46.80	3.21
n-Propyl acetate	7.14	2640	-49.44	3.73
n-Butyl acetate	7.28	2620	-50.11	2.32

Table IX. Constants of Equation 5 and Mean-Squares Deviations for Tri-2-ethylhexyl Phosphate

Solute	$\bar{C}_{p,i}^{E,\infty}/R$	A/R	B	10^4 (MSD)
n-Pentane	4.35	1560	-30.25	3.66
n-Hexane	5.06	1810	-35.05	1.55
n-Heptane	6.10	2180	-42.10	2.44
n-Octane	6.66	2370	-45.86	2.46
1-Pentene	3.84	1320	-26.73	3.53
1-Hexene	4.91	1740	-34.08	2.81
1-Heptene	5.20	1880	-36.10	3.11
1-Octene	6.90	2510	-47.76	3.07
Cyclohexane	4.60	1790	-32.50	3.67
Methylcyclohexane	4.37	1650	-30.62	2.60
Ethylcyclohexane	5.85	2140	-40.63	5.12
Benzene	4.57	1620	-32.20	13.80
Toluene	5.19	1790	-36.19	6.37
Ethylbenzene	7.04	2440	-48.85	3.77
Methyl alcohol	4.19	1770	-30.32	5.06
Ethyl alcohol	4.11	1690	-29.65	14.11
n-Propyl alcohol	8.58	3130	-60.11	14.55
n-Butyl alcohol	13.36	4800	-92.82	11.10
Methyl acetate	5.60	2430	-40.03	4.09
Ethyl acetate	5.66	2340	-40.10	4.78
n-Propyl acetate	7.02	2670	-49.05	3.07
n-Butyl acetate	7.26	2620	-50.35	6.15

Table X. Mean Values of $\Delta G^F(\text{CH}_2)$

Stationary phase	$\Delta G^F(\text{CH}_2)$, cal/mol
Triphenyl phosphate (TPP)	125.4
Tricresyl phosphate (TCP)	116.2
Diethyl phthalate	109.5
Butylbenzyl phthalate	108.6
Diisobutyl phthalate	100.9
Trixilenyl phosphate (TXP)	98.4
Dicyclohexyl phthalate	89.5
Dibutyl phthalate	89.1
Butylethylhexyl phthalate	73.5
Di-2-ethylhexyl phthalate	68.9
Tri-2-ethylhexyl phosphate (TOP)	64.2
Di-2-ethylhexyl adipate	59.7
Di-2-ethylhexyl sebacate	58.6
Diisodecyl phthalate	57.3

Glossary

A, B	constants of eq 5
B_{ii}	virial coefficient of second order of the pure solute i, cm^3/mol
bp	boiling point, $^\circ\text{C}$
$C_{p,i}^{E,\infty}$	excess partial molar heat at infinite dilution of the solute i (cal/(mol deg))
F	carrier gas flow rate, cm^3/s
$\Delta G^F(\text{CH}_2)$	excess partial molar Gibbs free energy of a methylene group, cal/mol
$\bar{H}_i^{E,\infty}$	excess partial molar enthalpy at infinite dilution of the solute i, cal/mol
j	James-Martin factor
M_s	molecular weight of stationary phase
mp	melting point, $^\circ\text{C}$
n	number of methylene groups
P	pressure
P_i	inlet column pressure, mmHg
P_o	outlet column pressure, mmHg
$P_{\text{H}_2\text{O}}^0$	vapor pressure of water at flow meter temperature, mmHg
P_i^0	vapor pressure of the pure solute i (atm)
R	gas constant (= 82.0 ($\text{cm}^3 \text{ atm}$)/(mol deg) in eq 3 and 5; = 1.987 cal/mol in eq 9)
t_a	dead time, s
t_R	retention time, s
t_{Ri}	initial retention time, s
t_{RF}	final retention time, s
t_{R0}	corrected retention time, s
T	temperature, K; column temperature, K (eq 3)
T_c	critical temperature, K
T_0	flow-meter temperature, K
V_c	critical volume, cm^3/mol
$V_{g,i}$	specific retention volume of the solute i at the column temperature T, cm^3/g of stationary phase
W_b	elution-peak width
W_{b0}	elution-peak width at infinite dilution
W_s	Weight of stationary phase, g
Greek letters	
γ_i^∞	activity coefficient at infinite dilution of the solute i
τ	see eq 6
τ_0	see eq 7 and 8

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