

A Study on Molecular Transport of Organic Esters and Aromatics into Viton Fluoropolymers

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ABSTRACT: Molecular transport of organic liquids into Viton fluoropolymers has been investigated by a sorption–desorption gravimetric method. Diffusion coefficients have been calculated from Fick's equation. The sorption–desorption results have been used to calculate the concentration profiles by solving Fick's diffusion equation under suitable boundary conditions. A numerical method based on the finite difference technique was also used to calculate the concentration profiles of liquids as a function of sorption time and thickness of the Viton fluoropolymers. The dependence of sorption, desorption, diffusion, and permeation properties of the liquids on temperature showed a significant effect. The Arrhenius activation parameters have been estimated for diffusion, permeation, and sorption processes. The experimental and calculated results are discussed to study the type and nature of interactions between Viton fluoropolymers and the solvent molecules. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 717–723, 1997

Key words: Vitons, transport, esters, aromatics

INTRODUCTION

Recently, there has been a tremendous impetus in the study of molecular transport of organic liquids into engineering polymers in view of its applications in numerous engineering and industrial areas.^{1–3} For a successful application of polymers in these areas, it is very important to predict their solvent resistivity properties. Among other properties, the most useful ones in such applications is the study of sorption, desorption, diffusion, and permeation of liquids into the target polymeric materials. A great amount of work in this area has been published over the past decades.^{4,5} In most of these studies, liquid transport into solid polymers has been described by the solution–diffusion model and the data for such systems have been analyzed using Fick's equations. However, the nature of the barrier polymer is also an influencing factor while studying such phenomena as sorption, diffusion, and permeation.

In this article we will present some useful transport results for nine organic liquids, namely methyl acetate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, *iso*-amyl acetate, methyl benzoate, ethyl benzoate, benzene, and toluene, into Du Pont's Viton A-201C series fluoropolymer (sample #2094). This polymer is known for its excellent fuel, solvent, and chemical resistivity in addition to outstanding environmental stability over a wide range of temperatures. Viton polymers are not recommended for service in organic environments such as esters, ethers, ketones, certain amines, hot anhydrous hydrofluoric or chlorosulfonic acids, and alkyl phosphate esters. This prompted us to investigate the transport of the above-mentioned liquids with the Viton fluoropolymer. Experiments have been carried out at 25, 44, and 60°C to obtain sorption, desorption, and diffusion parameters. From the sorption data, concentration profiles of liquids into the polymers have been calculated using a numerical method⁶ and also by solving Fick's diffusion equation using the appropriate initial and boundary conditions.⁷

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EXPERIMENTAL

Viton fluoropolymers used⁸ are based on the polymers derived from the copolymerization of vinylidene fluoride, $\text{CH}_2=\text{CF}_2$ (VF_2) and hexafluoropropylene, $\text{CF}_2=\text{CF}-\text{CF}_3$ (HFP) with polymer structure $-(\text{CH}_2-\text{CF}_2)_a-(\text{CF}_2-\text{CF}-\text{CF}_2)_b-$, where the subscripts a and b refer to degree of polymerization of the respective homopolymer. These polymers were prepared by the emulsion polymerization method. The VF_2 monomers with a homopolymer glass transition temperature (T_g) of -40°C and HFP with a homopolymer T_g of 165°C were used to synthesize the copolymer. The low T_g of VF_2 helps to retain the elastomeric characteristics and tends to crystallize with the hydrocarbon portion of the polymer that swells in organic liquids, while the higher T_g HFP portion breaks up crystallinity to give an elastomeric behavior. The fluorine content of the polymers is 66% and the Mooney viscosity, as measured by M1 + 10 at 100°C , is ~ 65 with the weight average molar mass, \bar{M}_w , of 327,000.

The rubber formulations were mixed in a "B" banbury mixer using an upside-down mix procedure. The dry ingredients were preblended before mixing and the polymer was added last. The ram was lowered and the compounds were mixed for 2–2.5 min. The stocks were discharged at an indicated temperature of 93°C and the actual stock temperature was $\sim 121^\circ\text{C}$. The stocks were milled on a 16-inch two-rolled mill for 2 min, sheeted off the mill, and allowed to rest overnight at 24°C before being resheeted on the mill to have samples die-cut for curing. Samples were cured for 10 min at 177°C in an electric press, and the next day they were post-cured at 232°C for 24 h.

Sheets of fluoropolymers were fabricated into 15×15 -cm slabs with the initial thickness rang-

ing from 0.214 to 0.245 cm. The circular disc-shaped samples with a diameter of 1.975 cm were cut from the large sheets using a sharp-edged carbon-tipped steel die. The cut samples were dried in vacuum desiccators over anhydrous calcium chloride at room temperature for at least 24 h before start of the sorption experiments.

The reagent grade methyl acetate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, *iso*-amyl acetate, methyl benzoate, ethyl benzoate, benzene, and toluene (all purchased from s.d. fine Chemicals, India) were used without further purification. Some representative solvent property data are given in Table I.

Sorption (S)–Desorption (D) Experiments

The sorption–desorption, that is, S–D runs, were performed by placing the known dry weights of the cut polymer samples into specially designed screw-tight test bottles containing ~ 15 – 20 cm^3 of the test solvents. At periodic intervals of time (initially these intervals were within 2–3 min), the submerged samples were removed from the test bottles, the surface-adhered liquid drops were removed by slowly pressing them in between smooth filter paper wraps, weighed immediately on a digital Mettler Balance, Model AE 240 (Switzerland) within the precision of $\pm 0.01 \text{ mg}$, and placed back into the test bottles. Since the time required for this operation was $< 30 \text{ s}$, this procedure did not introduce large errors in weight uptake data of the samples. All the samples reached equilibrium sorption within 48 h, which remained steady over an extended period of 3–4 days. After completion of sorption runs, the sorbed samples were placed in a vacuum oven for desorption measurements. The percent weight uptake or loss of the samples were calculated as explained before.^{9–12}

Table I Physical Properties of Esters Used as Penetrants

Liquid	Chemical Formula	Molar Volume ($\text{cm}^3 \text{ mol}^{-1}$)	μ	Solubility Parameter (J cm^{-3}) ^{1/2}
Methyl acetate	$\text{CH}_3\text{COOCH}_3$	79.8	1.72	19.6
Ethyl acetate	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	98.5	1.82	18.6
<i>n</i> -Propyl acetate	$\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}_3$	115.7	1.78	18.0
<i>n</i> -Butyl acetate	$\text{CH}_3\text{COO}(\text{CH}_2)_3\text{CH}_3$	132.5	1.87	17.4
<i>iso</i> -Amyl acetate	$\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	150.3	—	—
Methyl benzoate	$\text{C}_6\text{H}_5\text{COOCH}_3$	125.6	1.94	21.5
Ethyl benzoate	$\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$	144.2	1.99	20.0
Benzene	C_6H_6	89.4	0.00	18.7
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	106.9	0.31	18.2

—, Data not available.

Dimensional changes of the polymer samples at 25°C were monitored by measuring the changes in thickness and diameter during swelling experiments. The thickness (up to the accuracy of ± 0.001 cm) of the samples was measured using a micrometer screw gauge, whereas an increase in the lateral dimensions was measured by means of a vernier caliper.

RESULTS AND DISCUSSION

Sorption results, S , are expressed in mass percent units, which are calculated from the amount of liquid sorbed in a gram per 100 g of the polymer. For desorption experiments, these results represent the loss in weight of the samples. Sorption data presented in Table II show a decrease with increasing temperature for all the esters, whereas an increase in sorption is observed with increasing temperature for benzene and toluene. Among the aliphatic esters, for methyl acetate, ethyl acetate, and *n*-propyl acetate, the values of S between 25 and 44°C differ considerably, whereas at 60°C the S values for these liquids are almost identical, indicating an identical transport mechanism at 60°C. In the case of *n*-butyl acetate and *iso*-amyl acetate, the latter showed lower sorption values than the former at 25 and 60°C, but a reverse tendency is observed at 44°C. Sorption of methyl benzoate and ethyl benzoate are nearly identical at 44 and 60°C, while at 25°C the S values for these liquids are considerably different. For comparative purpose, the sorption results of benzene and toluene are also included in Table II,

wherein it is observed that toluene showed lower sorption values than benzene at all the temperatures. Sorption values at 25 and 60°C for all the liquid-Viton systems are presented in Figure 1. It is observed that the curves are more sigmoidal with the aromatic esters (e.g., methyl and ethyl benzoates) than the aliphatic esters. However, for benzene and toluene, sorption increases slowly, but linearly. With the majority of aliphatic esters, we observe a linear increase in sorption with $t^{1/2}$ being observed at all the temperatures.

The initial sorption results before 55% completion have been fitted to the empirical relationship⁹⁻¹²

$$\frac{M_t}{M_\infty} = Kt^n \quad (1)$$

where M_t and M_∞ are the values of the solvent uptake at time t and at equilibrium time; K is a parameter that depends on the nature of polymer-solvent interactions. The value of the exponent n of eq. (1) is indicative of the type of transport. If $n = 0.5$, then transport follows the Fickian mode. On the extreme side, if $n = 1$, the transport becomes non-Fickian. If n varies between 0.5 and 1, then the transport is classified as anomalous. Least-squares estimation of the values of K at 25, 44, and 60°C and of the average values of n taken over the investigated temperature range are also included in Table II. The values of n show variations from 0.52 to 0.67, indicating the anomalous transport behavior. However, the results of n do not show any dependence on temperature, and hence only the average values are considered. On the other hand, the results of K increase with increasing temperature.

Table II Sorption Coefficients and Estimated Parameter K and Average Values of n for Viton Fluoropolymer with Liquids

Liquid	S (mass %)			$K \cdot 10^2$ (g/g min ^{n})			n
	25°C	44°C	60°C	25°C	44°C	60°C	
Methyl acetate	121.37	120.76 ^a	117.61 ^b	4.07	4.56 ^a	4.71 ^b	0.65
Ethyl acetate	139.50	124.70	116.97	2.97	4.09	5.08	0.66
<i>n</i> -Propyl acetate	145.07	123.75	117.98	2.39	3.84	3.78	0.64
<i>n</i> -Butyl acetate	132.07	115.67	111.42	1.89	2.73	3.42	0.66
<i>iso</i> -Amyl acetate	125.68	120.37	109.92	1.60	2.12	2.47	0.66
Methyl benzoate	62.74	56.43	56.32	0.91	1.55	2.02	0.56
Ethyl benzoate	66.87	57.31	55.54	0.70	1.30	1.64	0.54
Benzene	10.66	13.11	14.71	1.02	1.89	2.51	0.52
Toluene	9.74	11.50	12.73	1.13	1.63	2.45	0.52

Data are from eq. (1).

^a, 40°C.

^b, 50°C.

Generally, the decreasing values of K observed for higher esters support the assumption that lower interactions are possible for these solvents with the polymer chain segments. However, liquid polarity, as manifested by their dipole moment value, μ , and solubility parameter, δ , do not seem to exert any influence on the values of K .

From the sorption data of polymer-liquid systems, we have calculated the relative concentration profiles of liquids developed at different thicknesses of the polymer samples using⁶

$$\frac{C(t,x)}{C_\infty} = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \times \exp\left[-\frac{D(2m+1)^2\pi^2t}{h^2}\right] \times \sin\left[\frac{(2m+1)\pi x}{h}\right] \quad (2)$$

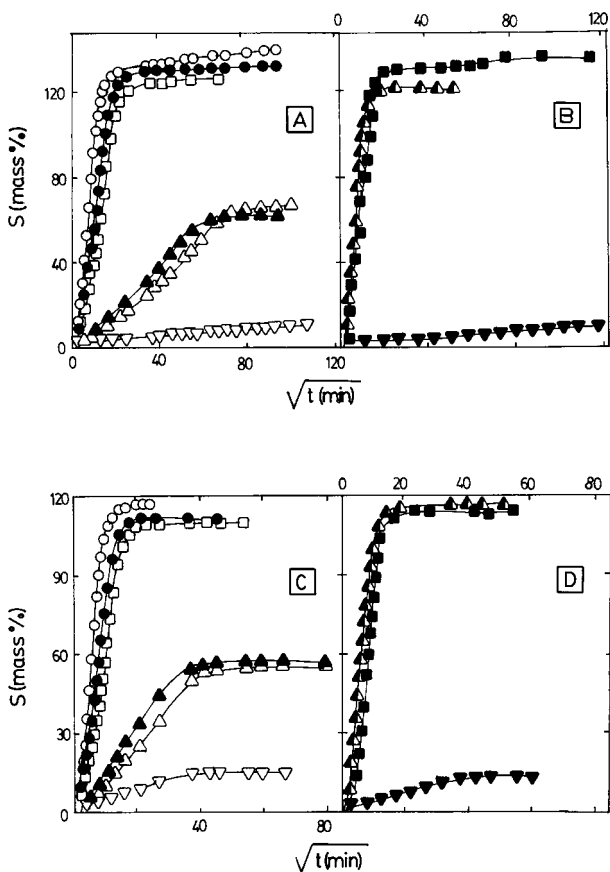


Figure 1 Sorption curves of Viton 2094 fluoropolymer membrane for (A): (○) ethyl acetate, (●) *n*-butyl acetate, (□) *iso*-amyl acetate, (▲) methyl benzoate, (△) ethyl benzoate, and (▽) benzene, and (B): (▲) methyl acetate, (■) *n*-propyl acetate, and (▼) toluene; both (A) and (B) at 25°C; liquids in (C) and (D) are the same as in (A) and (B), but data are presented at 60°C.

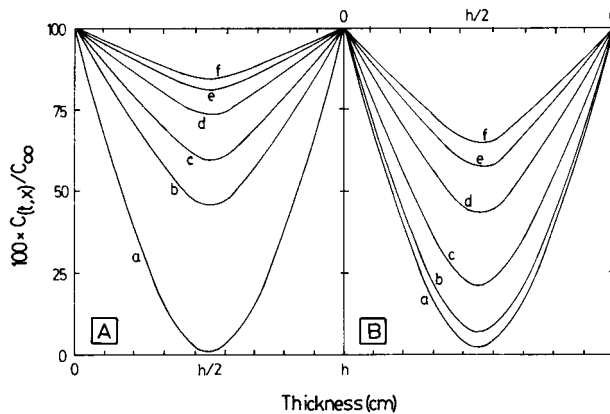


Figure 2 Concentration profiles calculated from eq. (2) for Viton 2094 fluoropolymer membrane for (A) methyl acetate with times (a) 0.5 min, (b) 4 min, (c) 8 min, (d) 20 min, (e) 40 min, and (f) 60 min; and (B) toluene with times (a) 30 min, (b) 40 min, (c) 80 min, (d) 200 min, (e) 400 min, and (f) 600 min at 25°C.

where h is thickness of the polymer sheet and t is sorption time.

Typical liquid concentration profiles calculated at 25°C by using eq. (2) are presented in Figure 2 for methyl acetate and toluene. The C_t/C_∞ values of methyl acetate are considerably higher than those observed for toluene for the same intervals of time.

Liquid concentration profiles were also calculated using the numerical equation based on the principles of finite difference method⁶

$$CN_m = \frac{1}{M} [C_{m-1} + (M-2)C_m + C_{m+1}] \quad (3)$$

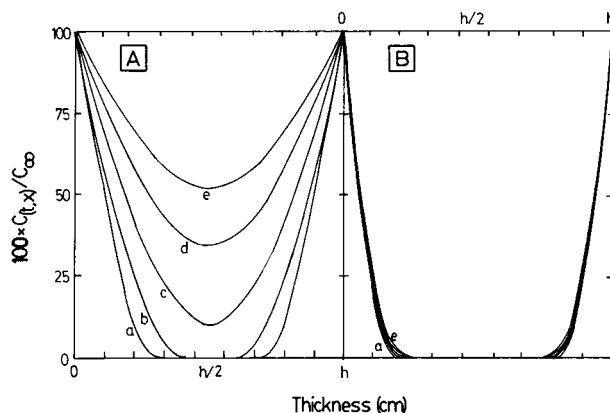


Figure 3 Simulated concentration profiles calculated from eq. (3) for Viton 2094 fluoropolymer membrane with (A) methyl acetate and (B) toluene with times (a) 4 min, (b) 8 min, (c) 20 min, (d) 40 min, and (e) 60 min at 25°C.

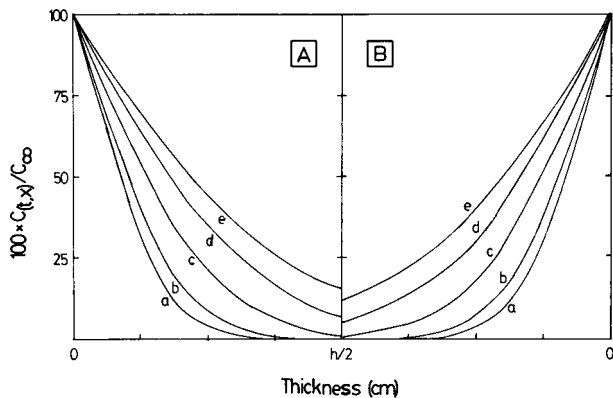


Figure 4 Simulated concentration profiles calculated from eq. (3) for Viton 2094 fluoropolymer membrane with butyl acetate for (A) sorption and (B) desorption at 25°C with the same times given in Figure 3.

where the dimensionless parameter, M is given as

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{1}{D} \quad (4)$$

Concentration profiles calculated by the numerical method for methyl acetate and toluene are given in Figure 3. The concentration profile for the sorption-desorption runs of *n*-butyl acetate is presented in Figure 4. The increase in C_t/C_∞ values with temperature is presented in Figure 5 for *iso*-amyl acetate at 25 and 60°C. At higher temperature, the increase in sorption is indicated by the increase in the values of C_t/C_∞ curves. Comparison of the plots given in Figures 2 and 3 is indicative of the fact that the values of the concentration profiles calculated from eq. (2) are slightly

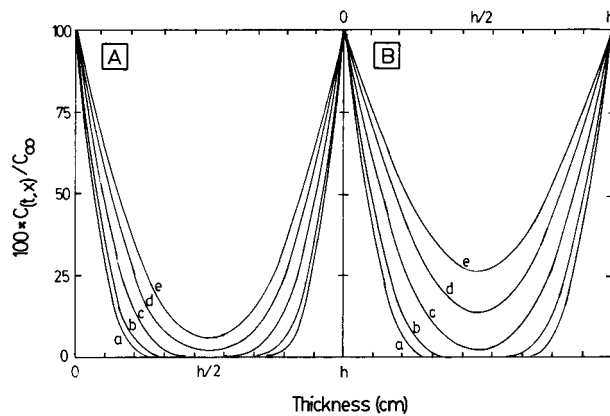


Figure 5 Simulated concentration profiles calculated from eq. (3) for Viton 2094 fluoropolymer membrane with *iso*-amyl acetate (A) at 25°C and (B) at 60°C for the same times given in Figure 3.

smaller than those calculated from eqs. (3) and (4), but the variations of the curves remain almost identical by both the calculations.

Diffusion coefficients, D , of liquids into the polymer matrices are important from considerations of their technological applications. Thus, the values of concentration-independent diffusion coefficients were calculated using the short-time equation⁷

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left(\frac{Dt}{\pi} \right)^{1/2} \quad (5)$$

by fitting the initial sorption results (<55%) as a function of $t^{1/2}$ from the slopes of the sorption plots. These data are presented in Table III.

Table III Diffusion Coefficients (D) of Sorption and Desorption (D_d) and Permeability Coefficients (P) of Viton Fluoropolymers with Liquids

Liquid	$D \cdot 10^7$ (cm ² s ⁻¹)			$D_d \cdot 10^7$ (cm ² s ⁻¹)	$P \cdot 10^7$ (cm ² s ⁻¹)		
	25°C	44°C	60°C	25°C	25°C	44°C	60°C
Methyl acetate	11.71	13.48 ^a	15.84 ^b	41.00	14.21	16.28 ^a	18.63 ^b
Ethyl acetate	8.46	13.46	17.57	22.62	11.80	16.79	20.55
<i>n</i> -Propyl acetate	5.63	7.60	9.97	25.53	8.16	9.41	11.76
<i>n</i> -Butyl acetate	4.25	6.82	8.83	8.96	5.61	7.89	9.83
<i>iso</i> -Amyl acetate	2.83	4.26	5.90	8.67	3.56	5.13	6.48
Methyl benzoate	0.33	0.82	1.51	1.62	0.21	0.46	0.85
Ethyl benzoate	0.22	0.54	0.90	0.14	0.15	0.31	0.50
Benzene	0.18	0.83	2.00	0.13	0.02	0.11	0.29
Toluene	0.14	0.62	1.18	0.11	0.01	0.07	0.15

^a, 40°C.

^b, 50°C.

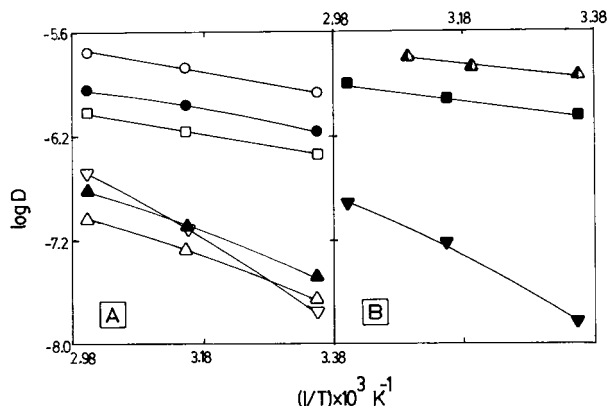


Figure 6 Arrhenius plots of $\log D$ vs. $1/T$ for FA 150P fluoropolymer membrane for the same esters and aromatics given Figure 1.

These data show a systematic decrease with increasing molar volume of the esters from methyl acetate to *iso*-amyl acetate. On the other hand, the values of dipole moments or even the solubility parameter values of the liquids (Table I) do not show much dependence on diffusion data. In between methyl benzoate and ethyl benzoate, the D values of the latter are lower than the former at all the temperatures. A similar tendency is observed with benzene and toluene that is, D of toluene is smaller than benzene. The diffusion coefficients D_d calculated from the desorption experiments at 25°C, also presented in Table III, are higher than the diffusion coefficients of the sorption runs. The results of D_d also show a dependence on the size of the liquids used as penetrants.

Permeability coefficients (P) of the polymer-solvent systems have been calculated using the relation $P = D \cdot S$, and these results are included in Table III. In general, the results of P of the

liquids show a decrease with increasing size of the liquids, a similar pattern observed for diffusion results.

In the present study, the results of D and P show an increase with increasing temperature. In view of this, efforts have been made to calculate the activation energies, E_D and E_P , for the processes of diffusion and permeation using the general form of the Arrhenius equation:

$$X = X_0 \exp(-E_X/RT) \quad (6)$$

where X and X_0 represent D or D_0 and P or P_0 , respectively; E_X refers to E_D for diffusion and E_P for permeation, R is a gas constant, and T is absolute temperature. A representative plot of the dependence of $\log D$ on $1/T$ is displayed in Figure 6. The values of E_D and E_P have been calculated by the method of least-squares by fitting the $\log D$ or $\log P$ results with $1/T$ and these data along with the estimated error values are presented in Table IV. It is observed that for methyl and ethyl benzoates having lower values of D when compared to other esters, both E_D and E_P values are higher than observed for other liquids. For the remaining liquids, the values of E_D and E_P are somewhat lower. On the other hand, for benzene and toluene, E_D values are very small, while the results of E_P are quite large. The $\Delta H_S(E_P - E_D)$ values are negative for all the esters except benzene and toluene, suggesting an exothermic mode of sorption for these liquids. From the swelling data, that is, percent increase in volume, ΔV percent included in Table IV, it is observed that esters seem to produce higher swelling of the polymers when compared to aromatic liquids, for which the values are smaller by an order of magnitude.

Table IV Arrhenius Activation Parameter Values of Viton Fluoropolymers with Liquids

Liquid	E_D (kJ mol ⁻¹)	E_P (kJ mol ⁻¹)	ΔH_S (kJ mol ⁻¹)	$\Delta V\%$
Methyl acetate	9.45 ± 1.66	8.52 ± 1.13	-0.94 ± 0.54	211.99
Ethyl acetate	17.36 ± 1.32	13.16 ± 0.57	-4.18 ± 0.32	225.01
<i>n</i> -Propyl acetate	13.44 ± 0.60	8.38 ± 2.05	-4.97 ± 1.11	290.43
<i>n</i> -Butyl acetate	17.38 ± 1.52	13.26 ± 0.15	-4.09 ± 0.97	247.10
<i>iso</i> -Amyl acetate	17.24 ± 0.81	14.18 ± 0.19	-3.09 ± 0.90	260.86
Methyl benzoate	35.81 ± 0.16	33.27 ± 0.22	-2.64 ± 1.20	92.73
Ethyl benzoate	33.58 ± 2.56	29.09 ± 1.24	-4.49 ± 1.31	106.63
Benzene	57.8 ± 2.70	65.44 ± 3.17	7.64 ± 0.62	28.85
Toluene	51.1 ± 5.86	57.36 ± 7.88	6.34 ± 0.37	24.98

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