Corrected Densities and Revised Coefficients for Diffusion of Various Dialkyl Phthalate Plasticizers in PVC

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Received June 4, 1991; Revised Manuscript Received June 10, 1991

Introduction

In recent articles in this journal,[1,2] we have reported a simple but effective mass-uptake technique for measuring diffusion coefficients (D) of plasticizers and other penetrants into amorphous, rubbery polymers, particularly PVC. In these initial articles, the technique was applied specifically to diffusion of the family of dialkyl phthalate plasticizers in PVC, since these are by far the most important class of vinyl plasticizers.

The mass-uptake method involves measurement of the time-dependent cumulative plasticizer absorption of molded PVC disks exposed to a given plasticizer under isothermal conditions. As described previously,[1] for diffusion into both ends of a flattened cylinder (i.e. a disk) of cross section q, D is given by

$$D = \pi s^2/[16q^2(c_0 - c')^2 t] \tag{1}$$

Here, s is the mass of imbibed plasticizer, c_0 is the external plasticizer concentration (its bulk liquid density), and c' is the initial plasticizer concentration within the sample. The latter, if nonzero, is readily calculated, assuming no volume change upon mixing (weak polymer-plasticizer interactions), from the initial weight fraction of plasticizer (w_1), c_0, and the density of PVC (taken to be 1.36 g/mL at 90 °C).

When plasticizer mass uptake is plotted vs $t^{1/2}$, a linear relationship with slope, m, should result for constant D, from which D may be extracted using the following equation:

$$D = \pi m^2/[16q^2(c_0 - c')^2] \tag{2}$$

In our initial article,[1] bulk liquid densities of the plasticizers were measured dilatometrically at various temperatures and fitted to a linear volume expansion equation of the form

$$\frac{1}{\rho_T} = \frac{1}{\rho_{25}}(1 + \alpha\Delta T) \tag{3}$$

where ρ_T is the density (g/mL) at a given temperature; ρ_{25}, the density at 25 °C; α, the temperature coefficient of volume expansion (expansion coefficient); and ΔT, the temperature difference (T − 25 °C). Since our papers appeared, we have had occasion to remeasure densities of many of the phthalates, more accurately and over broader temperature ranges, and in this note we wish to report these corrected density data and to revise our earlier reported D's.

Experimental Section

All phthalate plasticizers were generously supplied by Exxon Chemical Co., Performance Products Group, Intermediates Technology. Table I lists each phthalate and its acronym used herein.

Table I
Phthalate Plasticizers Investigated

model *n*-alkyl phthalates	commercial phthalates
di-*n*-hexyl phthalate (DNHxP)	di-2-ethylhexyl phthalate (DOP)
di-*n*-octyl phthalate (DNOP)	diisodecyl phthalate (DIDP)
di-*n*-nonyl phthalate (DNNP)	diundecyl phthalate (DUP)
di-*n*-decyl phthalate (DNDP)	undecyl dodecyl phthalate (UDP)

Table II
Corrected Densities and Expansion Coefficients for Various Dialkyl Phthalates

phthalate	expansion coefficient: $\alpha_{25} \times 10^4$, °C^{-1}	density: $\rho_{25°C}$, g/mL
DNHxP	7.89	1.001
DNOP	7.77	0.982
DNNP	7.74	0.965
DNDP	7.72	0.955
DOP	7.86	0.980
DIDP	7.39	0.936
DUP	7.58	0.950
UDP	7.39	0.953

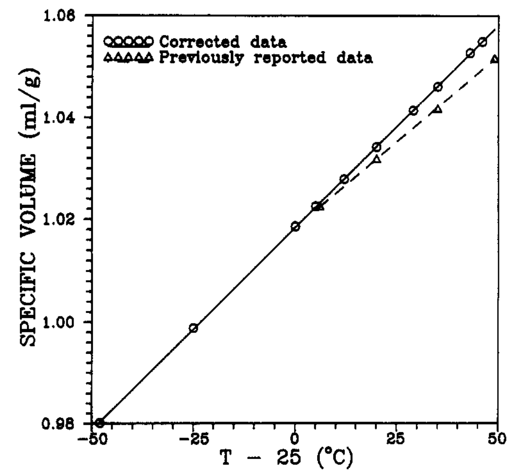

Figure 1. Representative volume expansion plots for DNOP.

Model di-*n*-alkyl phthalate plasticizers (hexyl, octyl, nonyl, and decyl) were provided as essentially pure compounds. Diisodecyl phthalate (DIDP) is a C_{10} phthalate carrying between two and four randomly placed methyl branches per alkyl moiety. Undecyl dodecyl phthalate (UDP) is a mixed ester composed of C_{11}, C_{12}, and C_{13} alkyl moieties (average C_{12}) carrying two to four randomly placed methyl branches each. Diundecyl phthalate (DUP) is a C_{11} phthalate of nearly linear structure (<0.5 methyl branches per alkyl moiety).

Densities and expansion coefficients of the phthalates were measured by charging an accurately determined mass of plasticizer to a dilatometer (Ace Glass cat. no. 6282) immersed in a constant temperature bath and recording the volume after equilibration at several different temperatures.

Results

In Table II are listed the densities at 25 °C and expansion coefficients for all of the phthalate plasticizers for which we have obtained corrected data. In general, these expansion coefficients apply within the temperature range 25-85 °C, although some were measured over much broader ranges. The major difference in the corrected data is that the values for the expansion coefficients are 15-20% higher than previously reported.[1] The corrected data show, as did the previous data, that phthalate density goes down as the length of the alkyl chain increases. The corrected data also show that branching in the alkyl chain causes a slight decrease in density as compared to a normal phthalate of equal carbon number; the previously reported

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Table III
Diffusion Coefficients of Pure Dialkyl Phthalates into Initially Unplasticized PVC

plasticizer	T, °C	D, cm^2/s
DNHxP	60	7.76×10^{-9}
	70	9.97×10^{-9}
	80	1.53×10^{-8}
	85	2.24×10^{-8}
	90	3.03×10^{-8}
	95	5.38×10^{-8}
	100	8.28×10^{-8}
DNOP	70	1.40×10^{-9}
	80	2.13×10^{-9}
	85	3.73×10^{-9}
	90	5.62×10^{-9}
	95	9.74×10^{-9}
	100	1.82×10^{-8}
DNNP	80	1.37×10^{-9}
	90	4.35×10^{-9}
	100	7.09×10^{-9}
DNDP	80	1.98×10^{-10}
	90	5.94×10^{-10}
	100	2.76×10^{-9}
DOP	60	1.71×10^{-10}
	65	3.52×10^{-10}
	70	5.41×10^{-10}
	75	8.41×10^{-10}
	78	1.02×10^{-9}
	80	1.32×10^{-9}
	83	1.69×10^{-9}
	85	2.25×10^{-9}
	88	2.98×10^{-9}
	90	4.06×10^{-9}
	93	5.65×10^{-9}
	95	7.04×10^{-9}
	98	9.41×10^{-9}
	100	1.13×10^{-8}

data showed exactly the opposite effect of branching, and it was noted[1] that this was contrary to expectations. The corrected data agree quite well with values found in the literature; for example, it is reported that for DOP,[3] $\alpha = 7.8 \times 10^{-4}$ °C^{-1} (our value 7.9×10^{-4} °C^{-1}), and for DIDP,[4] $\alpha = 7.4 \times 10^{-4}$ °C^{-1} (our value 7.4×10^{-4} °C^{-1}).

Figure 1 depicts a corrected and an earlier[1] volume expansion plot for a representative phthalate, DNOP. It will be noted that the present volume data was collected over a very broad range of temperatures, including subambient, and that the expansion coefficient is essentially constant over this entire range. The measurements were made by equilibrating the plasticizer at the lowest temperature and recording the volume, then raising the temperature and recording the volume, and so on. After reflecting upon the possible reasons for the decrepancy between present and earlier data, we surmise that the earlier measurements were taken too rapidly, without allowing sufficient time for thermal equilibration at each higher temperature. The present volumes were recorded only after it was established without doubt that the phthalates plasticizer had reached constant volume.

Table IV
Diffusion Coefficients of Mixed-Isomer Phthalates in PVC at 90 °C

phthalate	w_1	c'	D, cm^2/s
DIDP	0.0	0.0	4.99×10^{-10}
	0.089	0.116	1.64×10^{-9}
	0.16	0.205	6.17×10^{-9}
DUP	0.0	0.0	3.39×10^{-10}
	0.089	0.116	1.76×10^{-9}
	0.16	0.206	4.52×10^{-9}
UDP	0.0	0.0	2.60×10^{-10}
	0.089	0.116	7.52×10^{-10}
	0.16	0.206	9.63×10^{-9}

The corrected densities, when applied to our original mass-uptake data,[1,2] lead to revised experimental diffusion coefficients which are listed in Table III for n-alkyl phthalates and DOP and in Table IV for mixed-isomer phthalates. The D's in Table III are all for diffusion into essentially unplasticized PVC; however, in Table IV, D's for the commercial, mixed-isomer phthalates are reported at 0, 10, and 20 phr initial plasticization (i.e., $w_1 = 0, 0.089$, and 0.16, respectively). For most of the phthalates, the D's were revised upward by only several percent compared to our previously reported data; only for the case of DIDP was the correction appreciable, about 10%. All of the conclusions drawn from the previously reported data remain valid, and the activation energies for diffusion reported for DNOP[1] and DOP[2] are unchanged.

Acknowledgment. We gratefully acknowledge the generous support of this work by the Performance Products Group, Intermediates Technology of the Exxon Chemical Co. and the valuable interactions with L. G. Krauskopf and J. R. Hooton.

References and Notes

(1) Storey, R. F.; Mauritz, K. A.; Cox, B. D. *Macromolecules* **1989**, *22*, 289.
(2) Storey, R. F.; Mauritz, K. A.; Cole, B. B. *Macromolecules* **1991**, *24*, 450.
(3) Sears, J. K.; Darby, J. R. *The Technology of Plasticizers*; Wiley: New York, 1982; p 906.
(4) Reference 3, p 907.

Registry No. DNHxP, 84-75-3; DNOP, 117-84-0; DNNP, 84-76-4; DNDP, 84-77-5; DOP, 117-81-7; DIDP, 26761-40-0; DUP, 3648-20-2; UDP, 136806-10-5; PVC, 9002-86-2.