Partial Molar Heats of Mixing of Small Molecules with Polymers by Gas Chromatography

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Received September 12, 1977

ABSTRACT: Partial molar heats of mixing ($\Delta \overline{H}_1^\infty$) of small molecule probes have been determined with a variety of synthetic polymers by the gas chromatographic method. For normal alkanes from C_8 to C_{14}, $\Delta \overline{H}_1^\infty$ is of the order of a few hundred calories for solution in polyethylene, polypropylene, and poly(1-butene). The inclusion of minor amounts of polar groups such as ketone or ester carbonyl in polyethylene has a negligible effect on the heat of mixing. With more polar substrates such as polystyrene, poly(methyl acrylate), poly(vinyl chloride), or poly(*N*-isopropylacrylamide) the values of $\Delta \overline{H}_1^\infty$ are substantially greater, ranging from 1 to 4 kcal mol^{-1}. Factors involved in the determination are discussed.

The magnitude of experimentally measured retention volumes from gas chromatography experiments with polymer stationary phases is related both to the volatility of the probe and, more importantly, to the polymer–probe interaction. It is thus possible to compute polymer–solute interactions since extensive tabulations of solute volatilities are usually available. Considering the relative ease with which retention volumes can be determined, gas chromatography has become an important route in the measurement of activity coefficients and partial molar heats of mixing which are obtained from the temperature dependence of the activity coefficients.

This paper presents partial molar heats of mixing of small molecule probes (*n*-alkanes and butyl alcohol) with a variety of synthetic polymers of differing polarities.

Experimental Section

Materials. The normal alkanes were of reagent grade and were used without further purification. Octane and dodecane were obtained from BDH Laboratories, decane and tetradecane from Eastman Kodak, and hexadecane from J. T. Baker Chem. Co. Butyl alcohol (ACS certified) was obtained from Fisher.

Polymers. Polystyrene (anionic) ($\overline{M}_w$ = 120 000, $[\eta]$ = 0.575) and poly(methyl acrylate) ($\overline{M}_w$ = 200 000, $\overline{M}_n$ = 63 200) were obtained from Polymer Corp. and Aldrich, respectively.

The origin and characterization of the other polymers have been previously reported.[2-5]

Columns. The polymers were first dissolved in a suitable solvent and deposited onto an inert chromatographic support by slow evaporation of the solvent (with gentle stirring and heating). After vacuum drying for ca. 48 h with slight heating, the chromatographic support was packed with the aid of a mechanical vibrator into 0.25 in. o.d. copper columns. The weight of the stationary phase was determined by calcination using suitable blank corrections.

Column parameters are described in Table I.

Instrumentation

Measurements on polyethylene, polypropylene, poly(1-butene), poly(ethylene–vinyl acetate) (18% w/w vinyl acetate) and poly(*N*-isopropylacrylamide) were carried out on a Hewlett-Packard 5750 gas chromatograph. Details of experimental procedures were as described in previous publications.[2,6]

Measurements on polystyrene, poly(methyl acrylate), poly(vinyl chloride), and poly(ethylene–carbon monoxide) (10.5% w/w CO) were carried out on a Hewlett-Packard 5840A gas chromatograph equipped with a dual flame ionization detector. Prepurified nitrogen was used as the carrier gas. Methane was used as a noninteracting marker to correct for "dead" volume in the column. The net retention time (0.01 min time base) was determined from the positions of the peak maxima for methane and for the probe molecule at each temperature. Pressures at inlet and outlet of the column, read from a mercury manometer (±0.05 mmHg), were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. The oven temperature was measured with a Hewlett-Packard quartz thermometer.

The solute molecules, including a small amount of methane marker, were injected manually with a 10 μL Hamilton syringe (<0.01 μL).

To check the precision of the retention data from the HP5840A GC, specific retention volumes for *n*-decane and *n*-dodecane on high-density polyethylene (linear Marlex 6050) were compared to the literature values which had been previously obtained on the same column.[7] Retention volumes were reproduced to within 1 to 2% of the literature values.

The alkanes were, in general, characterized by symmetrical elution peaks, exhibiting sample size independent retention volumes.

Data Reduction

Specific retention volumes, V_g, were computed from the relation[8]

$$V_g = (t_R F / w_L) J_2^3 (760/P_o) \qquad (1)$$

where t_R is the net retention time, F is the flow rate at 273.16 K (760 mm), w_L is the mass of polymer, and J_2^3 is given by the relation[9]

$$J_n^m = (m/n)\{[(P_i/P_o)^n - 1]/[(P_i/P_o)^m - 1]\} \qquad (2)$$

where $m = 3$, $n = 2$, and P_i and P_o are the inlet and outlet pressures.

Solute vapor pressures were computed from the Antoine equation

$$\log p_1^0 = A - B/(t + C) \qquad (3)$$

where p_1^0 is the solute vapor pressure in mmHg, t is the temperature (°C), and A, B, and C are constants taken from standard sources.[10]

Solute densities were obtained from various sources, including the compilation of Orwoll and Flory,[11] International Critical Tables,[12] and Timmermans' compilation.[13] If density data for a solute were not available in the required temperature range, then data from lower temperatures were extrapolated to the required range. Second virial coefficients (B_{11}) were computed from[14]

$$B_{11}/\overline{V}_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \qquad (4)$$

where $\overline{V}_c$ and T_c are critical volumes and temperatures, T is the temperature (°K), and n is the number of carbon atoms of the *n*-alkane.

Weight fraction activity coefficients $(a_1/w_1)^\infty$ at infinite

0024-9297/78/2211-0224$01.00/0

Table I
Stationary Phases and Column Parameters[a]

	Packing and column				
Polymer	Solvent	Inert support	Loading, %	Mass polymer, g	Length, in.
Polystyrene	Benzene	Chromosorb G, AW, DMCS, 70/80	5.55	0.5554	36
Poly(methyl acrylate)	Toluene	Chromosorb G, AW, DMCS, 70/80	4.87	0.4556	36
Poly(ethylene–CO) (89.5% w/w:10.5% w/w)	Xylene	Chromosorb G, AW, DMCS, 70/80	9.87	0.4408	16
Poly(vinyl chloride)	Tetrahydrofuran	Chromosorb G, AW, DMCS, 70/80	11.1	0.4571	15
Polyethylene (high density) (Marlex 6050)	Xylene	Chromosorb G, AW, DMCS, 70/80	6.88	0.4058	20.5
Polyethylene (high density) (Marlex 6050)	Xylene	Chromosorb G, AW, DMCS, 70/80	6.95	0.3256	17.0
Polypropylene (Eastman)	Xylene	Chromosorb G, AW, DMCS, 70/80	7.57	0.4037	19.5
Polypropylene (Eastman)	Xylene	Chromosorb G, AW, DMCS, 70/80	6.59	0.3685	22

[a] Column characteristics of the other stationary phases have been described previously; see ref 2–5.

dilution were then calculated from the following relationship:[15]

$$\ln (a_1/w_1)^\infty = \ln (273.16R/p_1^0 V_g M_1) - p_1^0(B_{11} - V_1)/RT \qquad (5)$$

where V_1 and M_1 are the molar volume and molecular weight of the probe molecule and R is the gas constant.

Results and Discussion

Activity coefficients were computed for normal alkanes (C_8–C_{16}) on a variety of synthetic polymers above their T_g (eq 5). The results of these computations, in which corrections for vapor phase nonideality were taken into account, were tabulated together with the corresponding specific retention volumes and temperatures (13 to 20 experimental points).[16]

Since the partial molar heat of mixing ($\Delta\bar{H}_1^\infty$) of the solute at infinite dilution in the polymer is given by

$$\Delta\bar{H}_1^\infty = R\partial \ln (a_1/w_1)^\infty/\partial(1/T) \qquad (6)$$

the excess heats of mixing were computed from the slope of the best straight line through a plot of the logarithm of the activity coefficient vs. the reciprocal of the absolute temperature, as determined by a linear least-squares analysis. Partial molar heats of mixing of selected systems are summarized in Table II. Uncertainty limits given refer to the (σ) error in the slope as given by the least-squares program. This method of calculating $\Delta\bar{H}_1^\infty$ values diminishes errors which are inherent in the experimental determination of activity coefficients (such as errors in w_L and F).

Values of $\Delta\bar{H}_1^\infty$ for n-C_{14} on high-density polyethylene, poly(1-butene), and polypropylene represent the average of four determinations (duplicate determinations on two different columns of similar percent loading). Partial molar heats of n-octane in low-density polyethylene, polyethylene wax, and poly(ethylene–vinyl acetate) and for n-C_{10} and n-C_{12} in polypropylene were extracted from previously published retention data.[2–5]

The main criticism directed toward determination of thermodynamic quantities by GC has been to question whether true thermodynamic equilibrium is achieved. Recent contributions,[17–19] including comparisons with static data, indicate the reliability of the method. A detailed outline of the proper procedure required to perform such determinations has recently been given by Young.[20]

Table II
Partial Molar Heats of Mixing of Selected Systems

Polymer	Solute (probe)	Temp range, °C	$\Delta\bar{H}_1^\infty$, cal/mol
LD polyethylene	n-Octane	110–143	325 ± 30
Polyethylene wax	n-Octane	110–136	245 ± 35
Poly(ethylenevinyl acetate)	n-Octane	92–120	390 ± 15
Poly(ethylene–CO)	n-Octane	110–140	258 ± 57
Polypropylene	n-Decane	175–210	−145 ± 40
	n-Dodecane	175–210	−145 ± 40
	n-Tetradecane	180–210	196 ± 150
HD polyethylene	n-Tetradecane	180–210	324 ± 60
Poly(1-butene)	n-Tetradecane	180–210	145 ± 50
Poly(vinyl chloride)	n-Dodecane	130–160	3403 ± 76
Polystyrene	n-Decane	168–218	966 ± 150
	n-Dodecane	168–218	1000 ± 64
	n-Tetradecane	168–218	1143 ± 35
	n-Hexadecane	168–218	1370 ± 36
Poly(methyl acrylate)	n-Octane	88–112	2676 ± 88
	n-Decane	78–108	3215 ± 60
	n-Dodecane	88–112	3379 ± 34
	n-Tetradecane	88–112	4120 ± 39
Poly(N-isopropylacrylamide)	n-Butyl alcohol	139–176	1800 ± 200

An examination of the results in Table II reveals that the absolute error remains constant for many of the systems. However, the relative error is much larger for nearly athermal mixing (polymer–solvent) than it is for highly endothermic mixing (polymer–nonsolvent), e.g., relative error decreases from ca. 25 to 2.5% for an error of 50 cal on $\Delta\bar{H}_1^\infty$ of 200 and 2000 cal, respectively.

In order to obtain reliable excess heats of mixing by the GC method, correction for vapor phase nonideality of the probe should be made. The importance of this correction factor, especially for nearly athermal mixing, is illustrated by the results in Table III. Table III presents the temperatures, specific retention volumes, solute vapor pressures, activity coefficients (corrected and uncorrected), and the correction factors for gas phase nonideality (eq 5) for n-octane on poly-

Table III
Activity Coefficients for *n*-Octane in Poly(ethylene–carbon monoxide) and *n*-Hexadecane in Polystyrene

Temp, °C	V_g, cm^3/g	p_1^0, mmHg	$(a_1/w_1)^\infty_{cor}$	$(a_1/w_1)^\infty_{uncor}$	$-p_1^0/RT \times (B_{11} - V_1)$
		n-Octane–Poly(ethylene–CO)			
108.08	58.64	453.90	5.84	5.60	0.040
110.06	55.40	482.38	5.82	5.58	0.042
112.05	52.17	512.43	5.83	5.58	0.041
114.05	49.36	544.10	5.82	5.58	0.041
116.06	46.94	577.48	5.77	5.50	0.048
118.07	44.11	612.46	5.80	5.52	0.050
120.08	41.71	649.09	5.80	5.51	0.052
122.09	40.08	687.42	5.72	5.41	0.054
124.08	37.65	727.11	5.76	5.45	0.056
126.09	36.03	769.01	5.71	5.38	0.058
128.09	33.62	812.55	5.80	5.46	0.061
130.08	32.41	857.77	5.71	5.36	0.063
132.08	30.41	905.18	5.79	5.42	0.065
134.08	29.60	954.61	5.65	5.28	0.068
136.08	27.60	1006.12	5.76	5.37	0.070
138.08	26.79	1059.77	5.65	5.25	0.073
		n-Hexadecane–Polystyrene			
167.85	237.08	22.37	14.28	14.19	0.006
172.87	197.32	27.34	14.05	13.95	0.007
177.90	165.89	33.22	13.77	13.65	0.008
182.92	139.54	40.13	13.58	13.44	0.010
187.95	119.42	48.21	13.22	13.07	0.011
192.97	100.45	57.60	13.18	13.01	0.013
198.01	86.28	68.51	12.92	12.73	0.015
203.06	74.20	81.12	12.72	12.50	0.017
208.09	64.77	95.53	12.40	12.16	0.019
213.15	55.37	112.11	12.39	12.12	0.021
218.20	48.28	130.96	12.19	11.90	0.024

(ethylene–carbon monoxide) and for *n*-hexadecane on polystyrene. The magnitude of the correction factor becomes significant for vapor pressures greater than 50 mmHg. The partial molar heats derived from the uncorrected activity coefficients are 593 cal/mol for *n*-octane on poly(ethylene–carbon monoxide) and 1521 cal/mol for *n*-hexadecane on polystyrene, respectively. This represents an error of 336 cal/mol (57% relative error) and 151 cal/mol (10% relative error), respectively.

The temperature dependence of this correction term can therefore be quite large. One cannot infer from this, however, that any excess heat of mixing determined by the present method is necessarily in error. In fact, the reliability of any such determination depends ultimately on the accuracy of computations of virial coefficients and their temperature dependence. Although the absolute uncertainties on $\Delta\overline{H}_1^\infty$ may be slightly larger than those quoted in Table II (which were obtained by a linear least-squares analysis of the data), the heats of mixing determined in the present study represent the correct magnitude of the phenomenon.

Strictly speaking, an additional correction term should be added to eq 5 in the calculation of activity coefficients, namely $(P_oJ_3^4/RT)(2B_{13} - V_1)$ where B_{13} is a cross second virial coefficient. Unlike B_{11}, B_{13} is dependent on both the nature of the carrier gas and pressure of the column (P_o is outlet pressure). This factor can thus be minimized by operating at low column pressures and using a light carrier gas, such as helium. Braun and Guillet[3] have shown that this factor contributes ca. 20 cal/mol to $\Delta\overline{H}_1^\infty$ when $P_oJ_3^4$ equals 1 atm and N_2 is the carrier gas. This added uncertainty has not been included in the error estimates in Table II. Owing to the scarcity of experimental and computed cross virial coefficients, together with the lesser magnitude of this third term, this correction factor is often omitted in GC data treatment.[9,21]

The magnitude of the experimental heats of mixing for *n*-alkanes on polyethylene, polypropylene, and poly(1-butene) is in good agreement with other studies of polymer–solvent systems; reported values fall in the range of 0 to 400 cal/mol.[22]

The inclusion of minor amounts of polar groups such as ketone (10.5% w/w) or ester carbonyl (18% w/w) in polyethylene has a negligible effect on the heat of mixing within the experimental uncertainty.

The polymer solutions so far discussed are to be considered as polymer–solvent systems (activity coefficients 3–5), at least in the temperature range studied. Such systems, quite extensively investigated by static methods, are characterized by small excess heats of mixing. It is to be anticipated that a different behavior would be recorded for polymer nonsolvent systems. Due to the experimental difficulties with insoluble materials, little attention has been devoted to such systems using conventional techniques. However, the GC method can be applied with ease.

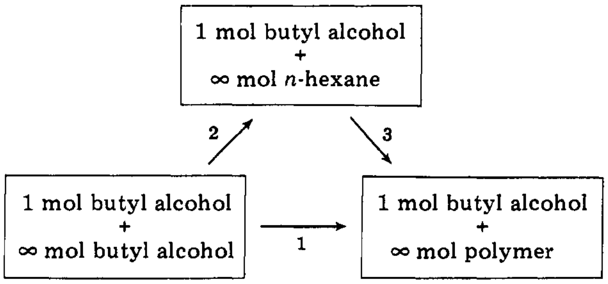
In contrast to the polymer–solvent systems studied, very large activity coefficients (10 to 100) were determined for nonsolvents in polymers. The partial molar heats of mixing of alkanes with more polar substances (poly(vinyl chloride), polystyrene, and poly(methyl acrylate)) are substantially greater, ranging from 1 to 4 kcal/mol.

$\Delta\overline{H}_1^\infty$ values obtained by static sorption methods are sparse and only a very few studies by the more facile GLC route have been reported for polymer–nonsolvent systems.[23] Very large activity coefficients were also observed in such cases.

The *n*-Butyl Alcohol–Poly(NIPAM) System. Virial coefficients for *n*-butyl alcohol were taken from literature sources.[24–26] As expected for a polymer–solvent system, small activity coefficients (ca. 3) were obtained in the temperature range investigated. Poly(*N*-isopropylacrylamide) (poly(NIPAM)) is soluble only in solvents capable of hydrogen bonding.

The magnitude of the partial molar heat of mixing (determined above T_g), +1.8 kcal/mol, is somewhat of a surprise. Endothermic heats of mixing are characteristic of polymer–nonsolvent systems (C_{16}–PS, C_{12}–PVC, etc.) while the formation of polymer–(good) solvent solutions is exothermic or athermal. In view of the strong polymer–solute interactions, a negative heat of mixing would have been expected.

It should be noted, however, that the excess heat of mixing is a measure of the difference between polymer–solute interactions and solute–solute interactions in the pure state. It is well known[27,28] that alcohols are strongly associated liquids, being both hydrogen bond donors and acceptors. A positive heat of mixing obtained for such a solute merely indicates that hydrogen bonding is stronger in the pure liquid (solute) than in the polymer–solute solution. The amount of heat required to break *n*-butyl alcohol–*n*-butyl alcohol hydrogen bonds is thus larger than the heat evolved in the formation of *n*-butyl alcohol–poly(NIPAM) hydrogen bonds. It has been shown by Murakami and Fujishiro[29] that it is possible to evaluate the energy of hydrogen bond interactions between donors and acceptors in solution by correcting for hydrogen bonding in the pure solute. The latter quantity is obtained experimentally from the heat of mixing of the solute in a nonpolar solvent, which represents the heat required to break the hydrogen bonds in the pure solute. One then has the following scheme as applied to *n*-butyl alcohol,[29]



where step 3 involves the interaction of the nonassociated solute with the polymer while steps 1 and 2 are the experimentally measurable heats of mixing. Murakami and Fujishiro, by correcting for the heat of mixing at infinite dilution of *n*-butyl alcohol in *n*-hexane, 5.5 kcal/mol, determined energies of interaction of hydrogen-bonded systems in good agreement with calorimetric and spectroscopic measurements.[28,29] By application of this scheme to the present system, the interaction between nonassociated *n*-butyl alcohol and poly(NIPAM) was found to be −3.7 kcal/mol. This is consistent with a strong polymer–solute interaction, as expected.

Although the magnitude of the polymer–solute interaction can be determined for *n*-butyl alcohol–poly(NIPAM), little insight into the hydrogen bond formation in such a system is yet possible, since both the *n*-butyl alcohol and poly(NIPAM), through its amide group, are hydrogen bond donors as well as acceptors. It is expected, however, that the GLC route can be of future interest for studying more specific hydrogen-bond formations, e.g., between solute donor and polymer acceptor.

There is little doubt that additional experiments would be required to account fully for the exceptional features exhibited by poly(NIPAM). The present study has shown, however, that hydrogen bond interactions between solute and stationary phase polymer can be evaluated. By correcting for the extent of hydrogen bonding in the pure solute, the actual extent of polymer–probe interaction can be derived. Of particular interest in the case of poly(NIPAM) would be the investigation with more specific solute molecules, such as exclusive hydrogen bond acceptors.

Acknowledgments. The authors wish to acknowledge the generous financial support of this work by the National Research Council of Canada. Fellowship support from the Canada Council (to J.-M.B.) and the National Research Council of Canada (to G.DiP.-B.) is also gratefully acknowledged.

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