

Gas-liquid chromatography study of poly(ethylene oxide)-solvent interactions: A molecular approach to solvation mechanisms

Monique Galin

CNRS, Centre de Recherches sur les Macromolécules, 6, rue Boussingault, 67083

Strasbourg Cedex, France

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The heats of solution at infinite dilution, ΔH_s , of more than 40 solvents of widely different structure and polarity (from n-hexane to 2,2,2-trifluoroethanol) in liquid poly(ethylene oxide) PEO, derived from gas-liquid chromatography, were quantitatively analysed within the general framework of linear solvation energy relationships: $-\Delta H_s(\text{kcal mol}^{-1}) = 0.48 \times 10^{24}P + 1.725\mu + 4.29\alpha$, $R(26 \text{ solvents}) = 0.9566$. This linear multiparametric approach allows us to separate the contributions of dispersion-cavitation forces (probe polarizability P), of dipolar interactions (probe dipole moment μ) and of hydrogen bonding (H-bond donating power α of the probe measured by the Taft empirical parameter). It affords reliable values for the heat of H-bonding formation between protic probes and PEO. The potential value of such a correlation analysis as a general strategy to quantify solute-polymer interactions in polar systems at a molecular level is emphasized.

(Keywords: gas chromatography; poly(oxyethylene); polymer-solvent interactions; hydrogen bonding)

INTRODUCTION

The gas-liquid chromatography (g.l.c.) study of the thermodynamics of polymer-solvent interactions in the liquid state at infinite probe dilution has achieved fair success within the last decade^{1,2}. Until now, in most cases, experimental results were readily taken into account within the simple and attractive Hildebrand solubility parameter theory and, on several occasions, g.l.c. has been emphasized as the best method of obtaining accurate values for the polymer solubility parameter over a wide temperature range³. However, this approach has not yet yielded any information on the detailed solvation mechanisms and is quite inefficient in separately ascribing the contributions of the various types of solute-polymer interactions to the observed behaviours. Moreover, it is clearly not valid for very polar systems where strong specific interactions may lead to negative values for the heat of mixing.

The purpose of this work is to try to correlate, in a quantitative way, the heats of solutions ΔH_s for a given solvent-polymer system with the polarity characteristics of the probes in an effort to provide an insight into the solvent-polymer interactions at a molecular level. We focussed our interest on poly(ethylene oxide) (PEO), a representative moderately polar polymer which has some inherent advantages: a high number of reliable experimental studies⁴⁻⁶, the occurrence of specific hydrogen bonding interactions with protic solvents, and our previous analysis of thermodynamics within the Hildebrand solubility parameter concept⁷.

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RESULTS

The thermodynamics of the interactions in the liquid state (70°–150°C) between PEO ($\bar{M}_n \sim 10^4$) and more than 40 solvents covering a wide range of structures and polarity (from n-hexane to 2,2,2-trifluoroethanol) were studied by gas-liquid chromatography as described in a previous communication⁷. Besides our measurements, selected literature data⁴⁻⁶ were also taken into account in order to provide a fairly complete set of experimental data for a more reliable and fruitful discussion.

The retention times were converted to the specific retention volumes corrected to 0°C, V_g° , in the classical way^{1,2}. Heats of solution of the probe in the polymeric phase, ΔH_s , were determined from the temperature dependence of V_g° using the approximate relation:

$$\Delta H_s = -R \frac{\partial \ln V_g^\circ}{\partial (1/T)} \quad (1)$$

The experimental results are given in *Table 1*, together with polarity parameters of the various solvents under study (polarizability P and dipole moment μ measured at 25°C)^{8,9}.

DISCUSSION

A quantitative interpretation of the heats of solution ΔH_s of the various probes in liquid PEO requires determination of the relative contributions of the specific and non-specific solute-polymer interactions in relation to the structural characteristics of the probes.

Table 1 Polarizabilities P , dipole moments μ , hydrogen-bond donating power α of pure solvents and heats of solution $-\Delta H_S$ of solvents-PEO systems

Solvents	$P \times 10^{24} \text{ }^a$ (cm^3) 20°C	μ (Debyes) 25°C	α	$-\Delta H_S$ (Kcal mol $^{-1}$ (± 0.2))			
				this work 70°-120°C	Bonner 5 70°-150°C	Klein 6 70.2°C, 79.2°C	Castello 4 120°C, 140°C
1. n-hexane	11.87	0				6.20	
2. n-heptane	13.71	0		6.36		6.66	
3. n-octane	15.54	0				7.11	
4. n-nonane	17.42	0				8.29	
5. n-decane	19.30	0		8.60		9.25	
6. n-undecane	21.05	0				10.04	
7. n-dodecane	22.92	0		10.9			
8. 1-hexene	11.70	0.34				5.48	
9. 1-heptene	13.54	0.34				6.38	
10. cyclohexane	10.71	0		5.46		5.63	
11. benzene	10.40	0		7.73	7.20	7.81	
12. toluene	12.34	0.37		8.38	8.03	8.67	
13. ethylbenzene	14.17	0.59		8.88			
14. o-xylene	14.21	0.62			8.86		
15. methyl acetate	6.96	1.72				7.27	
16. ethyl acetate	8.83	1.78		7.60			
17. butyl acetate	12.51	1.84			8.80		
18. acetone	6.43	2.68	0.07		6.76	6.83	
19. 2-butanone	8.24	2.70	0.05	8.25	7.57	7.65	
20. diethyl ether	8.93	1.16				5.60	
21. 1,2-dimethoxy-ethane	9.56	1.71		7.97			
22. bis(2-methoxy-ethyl) ether	13.79	1.97		10.50			
23. tetrahydrofuran	7.96	1.80			7.17		
24. 1,4-dioxane	8.61	0.45		8.42		8.71	
25. acetonitrile	4.41	3.44	0.15	8.27	8.31		
26. nitromethane	4.95	3.57	0.23			10.00	
27. pyridine	9.55	2.37		9.28			
28. chloroform	8.32	1.02	0.34	8.80		8.98	
29. carbon tetrachloride	10.24	0			6.73	7.34	
30. 1,2-dichloro-ethane	8.34	1.86			8.31		
31. 1,1,2-trichloro-ethane	10.28	1.50			9.80		
32. water	1.47	1.82	1.13				9.60 b
33. methanol	3.26	1.66	0.98		8.81		
34. ethanol	5.13	1.69	0.85			9.19	
35. 1-propanol	6.90	1.68	0.80	9.30			9.0 b
36. 2-propanol	6.94	1.60	0.78	8.52			
37. 1-butanol	8.76	1.67	0.79		10.00	10.86	
38. 2-butanol	8.78	1.66					8.70
39. 1-pentanol	10.64	1.64					10.96
40. 2-pentanol	10.62	1.62					9.56
41. 1-hexanol	12.56	1.64					11.62
42. 2-hexanol	12.46	1.6					10.30
43. 1-octanol	16.15	1.62					12.62
44. 2,2,2-trifluoro-ethanol	4.80	2.03	1.35	11.48			

$$^a P = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} \frac{3}{4\pi N}$$

b Gray *et al.* data, *Macromolecules* 1975, 8, 326

Because PEO is actually a weak hydrogen bond acceptor (HBA) on its ether functions, hydrogen bonding between the polyether chain and hydrogen bond donor (HBD) probes is expected affording a non-negligible contribution to the total of the polymer-solvent interactions. The derivation of this specific contribution from the crude and readily available ΔH_S values is clearly of major interest. We tentatively follow two complementary strategies, a differential and a linear multiparametric approach, which we shall discuss separately.

Pure base method

This method was first introduced by Martire *et al.* 10 in

g.l.c., developed by Arnett *et al.* 11 in spectroscopy and it was recently adapted by Guillet *et al.* 12 for polymeric systems. It rests essentially upon the assumption that the specific hydrogen bonding interactions between the HBD and the HBA species may be quantitatively estimated by comparison with reference polymer-solvent systems where hydrogen bonding is excluded (NHB probe or polymer). Measurements have to be performed using a NHB model compound M as similar as possible in structure to the HBD probe (same molar volume, shape and polarizability), and also assuming that it does not carry any acidic hydrogen atom. Furthermore, the heats of solution for both the model and the probe have to be

referred to a common apolar inert NHB phase (correction for possible self-association of the HBD probe). Such an approach leads to the following general expression for the enthalpy of hydrogen bond formation:

$$(\Delta H_f)_{\text{HBD-HBA}} = (\Delta H_S^{\text{HBD}} - \Delta H_S^{\text{M}})_{\text{HBA}} - (\Delta H_S^{\text{HBD}} - \Delta H_S^{\text{M}})_{\text{NHB}} \quad (2)$$

which has no theoretical grounds but appears as a convenient approximation. In our case, linear polyethylene seems to be the best inert NHB reference polymer, but the choice of the NHB model compound M is much more ambiguous. According to Martire *et al.*¹⁰, the NHB model compounds of alcohols are selected within the n-alkane series, while Guillet *et al.*¹² have recently preferred the n-alkyl chlorides or the methyl ethers in some cases. It is clear that the thus calculated $(\Delta H_f)_{\text{HBD-HBA}}$ values directly depend on the choice of the model compound which appears to be very critical.

However, as early as 1967, Iogansen *et al.*¹³ proposed the following equation:

$$(\Delta H_f)_{\text{HBD-HBA}} = (\Delta H_S^{\text{HBD}})_{\text{HBA}} - (\Delta H_S^{\text{HBD}})_{\text{NHB}} \quad (3)$$

which does not require the ambiguous use of a model probe M.

We have compared in Table 2 the values of the enthalpies of H-bond formation derived from equations (2) and (3) for three PEO-alcohol systems and for PEO- CHCl_3 , selecting n-alkanes and CCl_4 as NHB models for the probes, respectively. The very good agreement observed in the first case merely reflects the fact that equation (3) is directly derived from the more general equation (2) with the simplifying assumption:

$$(\Delta H_S^{\text{M}})_{\text{HBA}} \simeq (\Delta H_S^{\text{M}})_{\text{NHB}}$$

which actually holds for n-alkanes in PEO and polyethylene (see later). In the same way, the discrepancy observed in the second case arises from the higher enthalpy of solution of CCl_4 in PEO (7.0 kcal mole⁻¹) with respect to PE (6.22 kcal mole⁻¹).

Alternatively, for the PEO-alcohol systems, the use of n-alkyl chlorides instead of n-alkanes as NHB models leads to lower $(\Delta H_f)_{\text{HBD-HBA}}$ values: as we shall see later

the ΔH_f values obtained with n-alkanes as model probes are probably overestimated since they also include a positive dipolar interaction term.

Linear multiparametric approach

According to Karim *et al.*^{14,15}, the heat of solution ΔH_S of a vapour in a solvent may be decomposed in a series of additive terms describing quantitatively and exclusively the contribution of every type of solute-solvent interaction:

$$-\Delta H_S = aP + b\mu + X \quad (4)$$

where P and μ are the solute polarizability and dipole moment, respectively. Besides dispersion and cavitation forces (aP) and dipolar interactions ($b\mu$), X measures any additional enthalpic contribution involving specific probe-polymer interactions. Since hydrogen bonding is of recognized importance in the case of the HBA polyether chain, we found it of more interest to express the X term as a function of the intrinsic hydrogen bond donating power of the HBD probes, measured by an empirical parameter such as the solvatochromic HBD parameter α recently proposed by Taft *et al.*¹⁶

$$-\Delta H_S = aP + b\mu + c\alpha \quad (5)$$

In this linear three parameter relation, P , μ and α are characteristic structural parameters of the probe, while the partial regression coefficients a , b and c are specifically related to PEO. These coefficients allow determination of the respective contributions of the three types of probe-polymer interactions to the total heat of solution ΔH_S . This approach may be better considered within the more general framework of 'Linear Solvation Energy Relationships' which have aroused increased interest in the last few years in physical-organic chemistry¹⁶.

Stepwise least-square linear regression analysis of ΔH_S values versus P , μ and α is illustrated in Figures 1, 2 and 3, emphasizing the specific influence of the three different parameters separately.

Probe polarizability, P. As a characteristic feature, ΔH_S values are linearly correlated with P only within homologous series of probes of identical or similar structure (Figure 1):

Table 2 Enthalpies of H-bond formation (ΔH_f , Kcal mole⁻¹) between protic solvents and PEO or di-n-octyl ether

Solvent	PEO (g.l.c.)			Multiparametric method $-\Delta H_S - aP - b\mu$	$(\text{C}_8\text{H}_{17})_2\text{O}$	
	Pure base method M=RH	M=RCI	Iogansen		calorimetry (ref. 24)	g.l.c. (ref. 23)
Methanol				4.38		4.69
Ethanol				3.81		3.79
1-Propanol				3.00	3.5	3.77
2-Propanol				2.43	3.2	3.78
1-Butanol	4.45	2.76	4.57	3.35	3.5	3.78
2-Butanol				1.63	3.2	3.37
1-Pentanol	4.26	2.73	4.06	3.02		
2-Pentanol				1.60		
1-Hexanol	4.31		4.11	2.81		
1-Octanol				2.06		
2,2,2-Tri-fluoro- Ethanol ^a				5.67	5.85	
Water				5.75		
Chloroform		2.07	2.85	2.98		2.38

^a In $(\text{C}_4\text{H}_9)_2\text{O}$ and $(\text{C}_2\text{H}_5)_2\text{O}$, $\Delta H_f = 5.8$ and 5.1 respectively²⁵

(a) n-alkanes, cyclohexane, 1-hexene and 1-heptene, leading to a straight line passing through the origin as expected:

$$-\Delta H_s = aP \text{ with} \\ a = 0.480 \pm 0.005 \times 10^{24} \text{ kcal mol}^{-1} \text{ cm}^{-3}, \\ R(10 \text{ solvents}) = 0.9990;$$

(b) aromatic hydrocarbons, widely different from the aliphatic hydrocarbons;

(c) ethers, ketones and esters as a common class of single or double bonded oxygen HBA probes;

(d) primary (excluding trifluoroethanol) and secondary alcohols which cannot be considered within the same family.

Probe dipole moment, μ . Figure 2, where the linear plot is forced through the origin, shows that among the aprotic probes ($\alpha=0$) at poor but statistically meaningful correlation may still be drawn only for ethers (except dioxane), esters, ketones and pyridine:

$$-\Delta H_s - aP = b\mu \text{ with } b = 1.725 \pm 0.115 \text{ kcal mol}^{-1} \text{ D}^{-1} \\ R(12 \text{ solvents}) = 0.9606$$

Aromatics (especially benzene) and carbon tetrachloride, however, clearly do not obey the previous linear relation.

Hydrogen bond donating power of the probe, α . In Figure 3, where the linear plot is also forced through the origin, indicates a good correlation for most of the HBA-D or HBD probes, including fairly strong O-H donors such as alcohols (α values are unfortunately not available for alcohols higher than butanol) as well as moderate C-H donors like chloroform, nitromethane and acetonitrile:

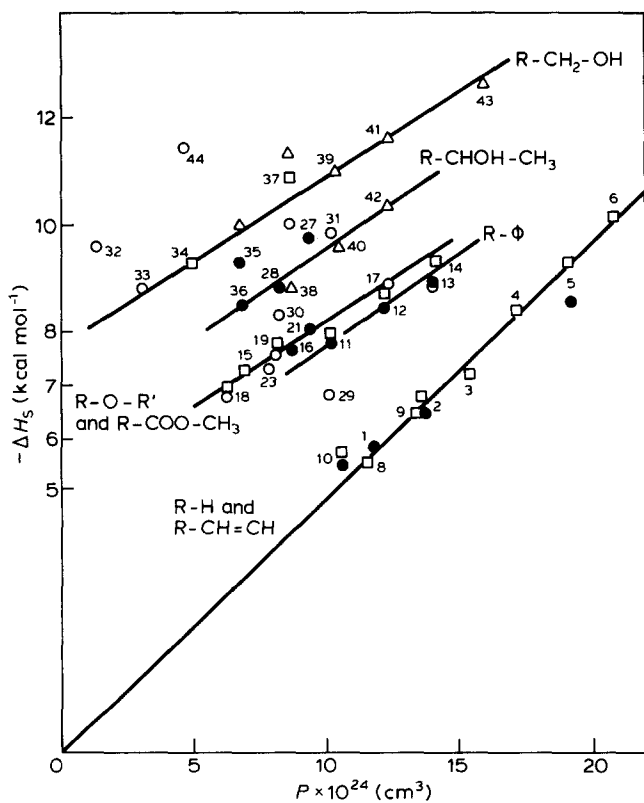


Figure 1 Variations of the heat of solution $-\Delta H_s$ of some homologous series of solvents in PEO versus their polarizability P . (□) Klein 6; (○) Bonner 5; (△) Castello; (●) this work

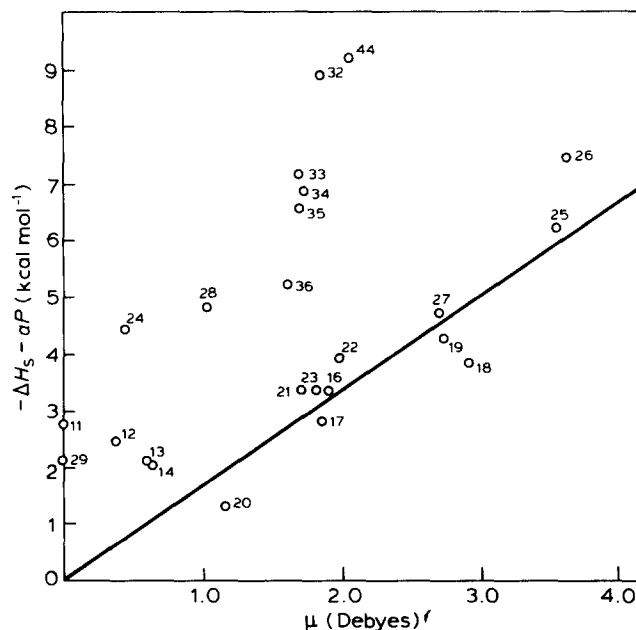


Figure 2 Stepwise linear regression analysis of $-(\Delta H_s + aP)$ values versus the probe dipole moment μ for the various solvent - PEO systems

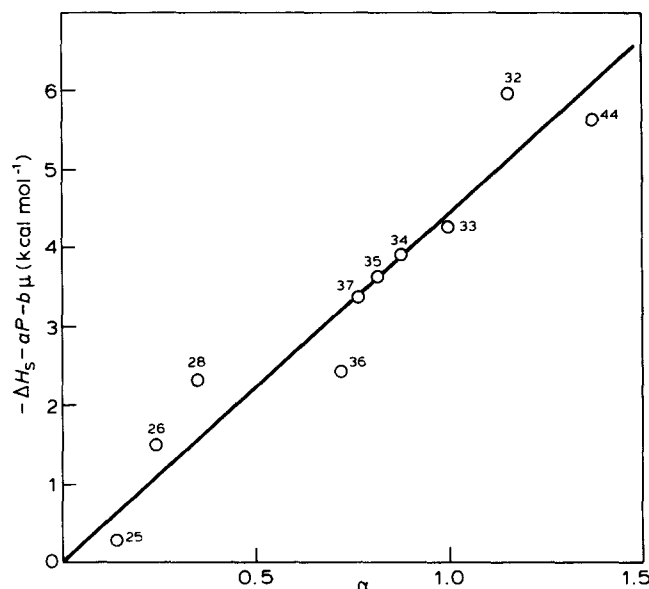


Figure 3 Stepwise linear regression analysis of $-(\Delta H_s + aP + b\mu)$ values versus the probe HBD power α for the protic and amphiprotic solvent - PEO systems

$$-\Delta H_s - aP - b\mu = c\alpha \text{ with } c = 4.29 \pm 0.10 \text{ kcal mol}^{-1} \\ R(9 \text{ solvents}) = 0.9890$$

Excluding aromatic hydrocarbons, carbon tetrachloride and dioxane, the experimental heats of solution of 26 solvents in PEO at 70°C may be thus quantitatively described by the general linear three parameter relationship:

$$-\Delta H_s (\text{kcal mol}^{-1}) = 0.480 \times 10^{-24} P + 1.725 \mu + 4.29 \alpha$$

with a fairly good total regression coefficient R (26 solvents) = 0.9566 (Figure 4). Moreover, statistical analysis of the partial regression coefficients¹⁷ points out that the contributions of dispersion-cavitation (P), dipolar (μ) and hydrogen bonding (α) interactions to the heat of solution of 40, 31 and 29% respectively.

In a similar way, we have considered the heats of solution of a series of solvents in polyethylene, using both literature data for n-alkanes^{18,19}, n-butyl chloride and 2-pentanone¹², and our measurements on n-butyl acetate and three primary alcohols C₄ to C₆ (Table 3). Stepwise linear regression analysis on ΔH_s values leads to the correlation:

$$-\Delta H_s (\text{kcal mol}^{-1}) = 0.495 \times 10^{24} P + 0.95 \mu, \\ R (12 \text{ solvents}) = 0.9807$$

Two features may be noticed:

(1) The very similar values of the P terms for PEO and PE: $a(\text{PEO}) = 0.480$ versus $a(\text{PE}) = 0.495$.

(2) The lack of the α term: $c = 0$ (PE cannot be involved in hydrogen bonding interactions).

This successful multiparametric analysis may be critically discussed from three complementary viewpoints:

(a) The separation of different types of probe-polymer interactions into additive contributions may appear somewhat arbitrary, since they may cooperate in a non-independent way. The lack of sound theoretical grounds for such an approach does not weaken its great versatility as a semi-empirical method which actually finds its justification *a posteriori* by its ability to correlate all the experimental ΔH_s data within a self-consistent framework.

(b) The choice of the empirical parameter to measure quantitatively and exclusively hydrogen-bonding interactions is clearly critical. After a comprehensive analysis of all the available empirical polarity scales within the general framework of linear solvation energy relationships, Taft *et al.*¹⁶ concluded that their solvatochromic α scale of solvent HBD properties is definitely the most reliable, in spite of low accuracy and some ambiguity for weak CH donors. It has to be preferred to the more popular Dimroth-Reichardt E_T parameter or to the Gutman's 'Acceptor Number', AN, which combine both dipolar and hydrogen bonding interactions²⁰.

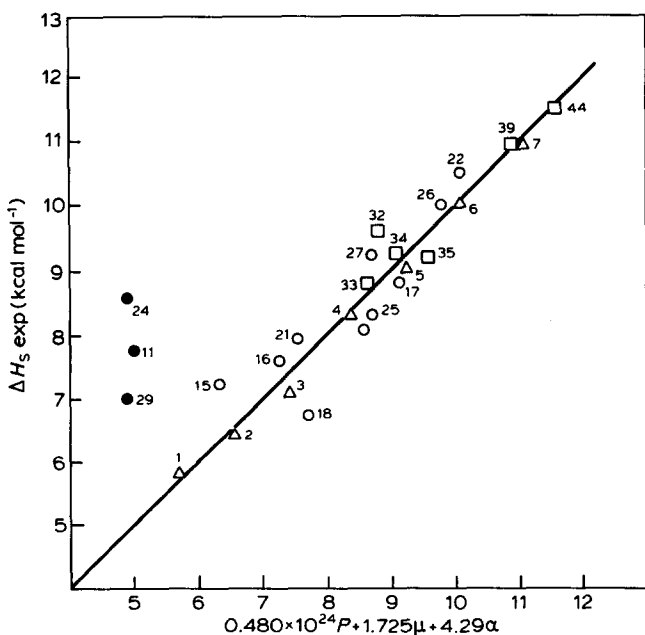


Figure 4 ΔH_s experimental values versus calculated values. Solvents 11 (C₆H₆), 24 (dioxane) and 29 (CCl₄) are excluded from the correlation

Table 3 Heats of solution ($-\Delta H_s$, kcal mol⁻¹) of solvent-PE systems

Solvent	Patterson (ref. 18)	Guillet (refs. 12, 19) work	This
n-Heptane			7.30
n-Octane	7.65		
n-Nonane	8.44		
n-Decane	9.80	9.90	
n-Dodecane	11.51	11.79	
1,1,2-Trichloroethane			6.25
n-Butyl chloride ^a		6.32	
n-Butyl acetate			7.82
2-Pentanone ^b		6.84	
1-Butanol			5.86
1-Pentanol			6.90
1-Hexanol			7.51

^a $P = 10.1$, $\mu = 1.90$

^b $P = 10.0$, $\mu = 2.74$

(c) Finally, the probes which show maximum deviation with respect to the linear multiparametric relation clearly weaken its general validity. As already outlined, this discrepancy may be at last partly explained for some HBD solvents by the uncertainty of their α values. For CCl₄ ($\mu = 0$), benzene ($\mu = 0$) and dioxane ($\mu = 0.45$) however, the experimental ΔH_s values are about 30% higher than the calculated values according to equation (5). Possible charge transfer complexes between the polyether and the two first probes, already put forward in the case of poly(methyl vinyl ether)²¹, may yield an additional contribution to the heat of solution ΔH_s . However, we have no definite explanation for dioxane which shows the weakest μ among the ethers under study.

As a more fundamental critique than the three preceding topics, the true physical meaning of the linear multiparametric correlation $\Delta H_s = f(P, \mu, \alpha)$ may appear somewhat questionable, since the enthalpy of solution is actually a composite thermodynamic parameter

$$\Delta H_s = \Delta H_m^\infty - \Delta H_v$$

where ΔH_m^∞ is the enthalpy of mixing of solute at infinite dilution in the solvent in the condensed state, and ΔH_v the latent heat of vapourization of the solute.

A relation $\Delta H_m^\infty = g(P, \mu, \alpha)$ correlating only the solute solvent interaction term ΔH_m^∞ with polarity parameters of the probe, and excluding the ΔH_v term which is specific for the pure solvent, would be more satisfactory and probably more founded on theoretical grounds. Unfortunately, until now we have not been able to remove this ambiguity which was not noticed by Karim *et al.* in their early^{14,15} and more recent²² works. Nevertheless two important features may be pointed out:

(a) From an experimental viewpoint ΔH_s is the more readily available and the more accurate thermodynamic parameter derived in gas-liquid chromatography. ΔH_m^∞ measurements require the knowledge of the vapour pressure-temperature relationship and the second virial coefficient for every solvent. However, no reliable value for ΔH_m^∞ can be deduced from experimental ΔH_s and known ΔH_v values, since ΔH_v affords in most cases the major contribution to ΔH_s .

(b) In spite of the lack of theoretical ground, the good correlation $\Delta H_s = f(P, \mu, \alpha)$ we observed cannot be purely incidental: it is statistically meaningful since it arises from a sufficiently high number of experimental data. Its value as an empirical forecast method and as a self-consistent

framework in correlating experimental data is worth recognizing.

In calculating the contribution of hydrogen bonding interactions to the heats of mixing ΔH_m^∞ of HBD probes with HBA polymer, we tentatively combined the linear multiparametric approach and the original 'Pure Base Method'. Let us assume that the $\Delta H_s = f(P, \mu, \alpha)$ correlations are of general value for any polymer–solvent system:

—for the HBA polymer under study:

$$\Delta H_s(\text{HBA}) = aP + b\mu + c\alpha$$

—for the reference NHB polymer:

$$\Delta H_s(\text{NHB}) = a_0P + b_0\mu, c_0 = 0$$

The NHB model probes *M* may be easily selected in order to show a zero α value (the most necessary requirement), but, most often, their polarizabilities P' and dipole moment μ' are not strictly identical to that for the HBD probes. Straightforward application of equation (2) leads to:

$$(\Delta H_f)_{\text{HBD-HBA}} = (a - a_0)(P - P') + (b - b_0)(\mu - \mu') + c\alpha$$

This relation clearly emphasizes the drastic influence of the choice of the NHB model probe for the calculation of a reliable value of the actual heat of hydrogen bond formation. $(\Delta H_f)_{\text{HBD-HBA}}$ measures exclusively the hydrogen bonding interactions $c\alpha$ only in the ideal case where the model *M* has exactly the same polarizability and dipole moment as the HBD probe. In the precise system we investigated, and since $\alpha(\text{PEO}) \sim \alpha_0(\text{PE})$, the relative values of the dipole moments of the HBD and model *M* probes are the decisive factors.

With n-alkanes as NHB model probes ($\mu' = 0$) for alcohols, the pure base method leads to rather strongly overestimated $(\Delta H_f)_{\text{HBD-HBA}}$ values of about 1.2 kcal mol⁻¹ since it involves the positive and nearly constant dipolar term $(b - b_0)\mu$ (the fluctuations of the dipole moments around an average value of 1.65 D are quite negligible for all the alcohols under study). However, with n-alkyl chlorides as NHB model probes, $(\Delta H_f)_{\text{HBD-HBA}}$ values are slightly underestimated at about 0.2 kcal mol⁻¹ ($\mu - \mu' \sim 0.3\text{D}$). In a similar way, we may expect CCl₄ ($\mu = 0$) to be a rather bad NHB model of CHCl₃ ($\mu = 1.02\text{D}$). All these conclusions are illustrated by the ΔH_f values related to various alcohol–PEO systems quoted in Table 2.

Moreover, a comparison of the most reliable heats of hydrogen-bond formation, as measured by the $c\alpha$ term, with literature values related to di-n-octyl ether^{23,24} is of special interest. For all the primary alcohols and chloroform, ΔH_f values are very similar for the polymer and di-n-octyl ether. For trifluoroethanol, the strongest hydrogen bond donor, comparison may be extended to other ethers²⁵ and, here again, the similarity of ΔH_f values and their quasi independence with respect to the ether function density of the liquid phase may be outlined: $\Delta H_f = 5.7, 5.8, 5.8$ and 5.1 kcal mol⁻¹ for TFE–PEO, di-n-octyl, butyl and ethyl–ether respectively. In the infinite dilution conditions of g.l.c. experiments, the HBD probe is able to 'sort out' the HBA ether site, offsetting the possible influence of the alkyl moiety. Alternatively, the ΔH_f decrease which occurs when going from primary to secondary alcohols of the same number of carbon atoms is significantly stronger for PEO than for di-n-octyl ether. We have no definite explanation for such a feature, since

the steric and electronic characteristics of the micro-environment in the close vicinity of the HBA oxygen site are probably not too different for PEO and the low molecular weight ether.

CONCLUSION

Quantitative analysis of well ascertained heats of solution at infinite dilution ΔH_s of more than 40 solvents of widely different structure and polarity in liquid poly(ethylene oxide) has been performed within the general framework of linear solvation energy relationships. Least square regression analysis of ΔH_s values versus solvent polarizability P , dipole moment μ and hydrogen bond donating power α (empirical solvatochromic parameter of Taft *et al.*) leads to a statistically good equation which correlates all the experimental data in a self-consistent way:

$$-\Delta H_s = 0.480 \times 10^{24} P + 1.725 \mu + 4.29 \alpha$$

The heats of H-bond formation of HBD solvents at infinite dilution in liquid PEO, which may be thus readily derived, are expected to be more reliable than those calculated according to classical methods which require the use of ideal and elusive NHB model probes.

Finally, we think it reasonable that such a linear multiparametric approach is of general value and that it may be readily extended to any solvent–polymer systems: it would be of special interest to check its versatility and its reliability for HBA probe–HBD polymer systems (using Taft's β parameter to measure the H-bond accepting power of the probes) as symmetric systems of that we investigated.

In spite of the lack of theoretical grounds, general correlations $\Delta H_s = f(P, \mu, \alpha, \beta)$ may afford a useful strategy in analysing solute–polymer interactions at a molecular level. This would be of much use in the important case of polar systems characterized by strong specific interactions where recent studies have clearly shown the limits of the three-dimensional solubility parameter concept^{22,26}.

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