Interaction of organic vapours with hydroxypropyl cellulose

Joseph S. Aspler and Derek G. Gray
Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, 3420 *University Street, Montreal, Quebec H3A 2A7, Canada*

(*Received* 10 *February* 1981*; revised* 23 *March* 1981)

The interaction of a number of organic vapours with hydroxypropyl cellulose was measured by gas chromatographic (g.c.) methods. The limiting Flory–Huggins interaction parameters at infinite dilution of vapour in polymer were readily evaluated, but the g.c. data did not provide a route to the solubility parameter for the polymer. The temperature dependence of the g.c. retention volumes for several vapours indicated what may be a glass transition for hydroxypropyl cellulose at ~10°C. Sorption isotherms for acetone, ethanol and tetrahydrofuran were measured with a vacuum microbalance, and the results were compared with theory.

Keywords Chromatographic analysis; gas chromatography; organic vapour; interaction; hydroxypropyl cellulose

INTRODUCTION

As part of the investigation of the solution properties of hydroxypropyl cellulose (HPC), the sorption of a large number of organic probes was measured by inverse g.c. The initial impetus for this work was the discovery that HPC forms lyotropic liquid crystalline mesophases in several organic solvents[1,2].

DiPaola-Baranyi and Guillet[3] recently proposed a method by which the solubility parameter of a polymer, δ_2, could be obtained from inverse g.c. measurements at a single temperature, using the infinite dilution retention of a series of probes. The applicability of the method to HPC was examined. The solubility parameter of a substance, δ, has been defined as[4]:

$$\delta \equiv [(\Delta H_v - RT)/V]^{1/2} \tag{1}$$

where ΔH_v is the heat of vapourization and V the molar volume. This equation was combined with the Flory–Huggins solution theory to yield the interaction parameter as a function of the difference between the solubility parameters of solvent and substrate[4]:

$$\chi_{12} = V_1(\delta_1 - \delta_2)^2/\mathrm{R}T - \beta \tag{2}$$

where β is the correction for the existence of the non-combinatorial entropy of mixing. DiPaola–Baranyi and Guillet rearranged the previous equation to obtain with $\beta = 0$ (Ref 3):

$$\frac{\delta_1^2}{\mathrm{R}T} - \frac{\chi_{12}}{V_1} = \frac{2\delta_2}{\mathrm{R}T}\delta_1 - \frac{\delta_2^2}{\mathrm{R}T} \tag{3}$$

and proposed that a plot of $(\delta_1^2/\mathrm{R}T - \chi_{12}/V_1)$ vs. δ_1 would yield $2\delta_2/\mathrm{R}T$ as slope and $-(\delta_2^2)/\mathrm{R}T$ as intercept. Another version[5] takes advantage of the equation:

$$\Delta\bar{H}_m = V_1(\delta_1 - \delta_2)^2 \tag{4}$$

After suitable rearrangement, the previous equation allows δ_2 to be determined from a plot of $\Delta\bar{H}_m$ vs. δ_1. A δ_2 value of 21.9 $(\mathrm{J\ cm^{-3}})^{1/2}$ for HPC was recently derived from solubility measurements[6].

The gas chromatographic method allows measurements of χ_{12} at very small concentrations of probe in the polymer; the limiting values at infinite dilution are indicated by χ_{12}^∞.

EXPERIMENTAL

The hydroxypropyl cellulose sample (Klucel 'L', Hercules Inc., with nominal $\bar{M}_w = 100\,000$), g.c. apparatus, columns and techniques were the same as those referred to in an earlier paper[7]. Values of χ_{12}^∞, the Flory–Huggins interaction parameter at infinite dilution of the solvent probe in the polymer, were calculated from:

$$\chi_{12}^\infty = \ln\frac{273.2\mathrm{R}v_2}{p_1^0 V_g V_1} - 1 - \frac{p_1^0}{\mathrm{R}T}(B_{11} - V_1) \tag{5}$$

where R is the gas constant, v_2 the specific volume of the polymer, p_1^0 the saturated vapour pressure and V_1 the partial molar volume of the probe at temperature T, V_g the g.c. specific retention volume, and B_{11} the second virial coefficient of the probe vapour.

The volume fraction based activity coefficient, $(a_1/\varphi_1)^\infty$, is related to χ_{12}^∞ by:

$$\ln(a_1/\varphi_1)^\infty = 1 + \chi_{12}^\infty \tag{6}$$

The partial molar heats of mixing at infinite dilution of probe in the polymer were calculated from:

$$\Delta\bar{H}_m^\infty = R\frac{\partial(a_1/\varphi_1)^\infty}{\partial(1/T)} \tag{7}$$

assuming temperature independence of the heat of mixing over the range in question.

0032-3861/82/010043-04$03.00

Table 1 Infinite dilution thermodynamic data at 50.2°C for organic probes

Probe	χ_{12}^{∞}	δ_1 $(\mathrm{J\,cm^{-3}})^{1/2}$	δ_1^2/RT	χ_{12}^{∞}/V_1
Water (a)	1.55	47.06	0.824	0.073
Methanol (a)	0.47	28.96	0.312	0.011
Ethanol (a)	0.38	25.56	0.243	0.006
1-Propanol (a)	0.26	23.95	0.213	0.004
2-Propanol	0.43	24.17	0.217	0.006
1-Butanol	0.26	24.17	0.217	0.003
Acetone	0.38	19.27	0.138	0.005
n-Butyl acetate	0.14	17.22	0.110	0.001
1,4-Dioxane (a)	0.06	19.34	0.139	0.001
Tetrahydrofuran (a)	−0.12	18.62	0.129	−0.002
Diethyl ether	−0.14	15.05	0.084	−0.001
Cyclohexanol (b)	2.31	20.98	0.164	0.021
Cyclohexanone	0.18	20.09	0.150	0.002
Cyclohexane (b)	0.96	16.34	0.099	0.009
Toluene (b)	0.17	17.71	0.117	0.002
n-Heptane (b)	0.10	14.76	0.081	0.001
n-Decane (b)	1.83	18.80	0.143	0.009
Acetic acid (a)	−2.28	25.62	0.244	−0.038
Acetic anhydride (a)	−1.65	20.82	0.161	−0.017
Dimethyl sulfoxide (a)	−0.19	25.77	0.247	−0.003
N,N-Dimethyl formamide (a)	−0.01	29.26	0.319	0.0
Pyridine (a)	−0.42	21.04	0.165	−0.005
Dichloromethane (b)	−0.38	19.78	0.146	−0.006
Chloroform	−0.73	17.99	0.120	−0.009
Carbon tetrachloride (b)	0.45	16.84	0.106	0.004

(a) Forms liquid crystalline mesophase
(b) Non-solvent

RESULTS AND DISCUSSION

Infinite dilution results

Retention volumes were measured at 50±0.2°C for 25 probes of different types. Peaks were extrapolated to zero height, but no correction was made for the effect of gas flow rate, which for a good solvent such as water was small[7]. Values of χ_{12}^{∞} were calculated from equation 5. With water as probe, there was no need to correct for the second virial coefficient, B_{11}. However, the contribution from B_{11} for the organic probes was larger. Since the second virial coefficient changes with temperature, it was especially important to make this correction when retention was being measured as a function of temperature. Where available, values of B_{11} were taken from the literature[8]. For several of the probes, values of B_{11} were calculated using the Bertholet equation[9]:

$$B_{11} = \frac{9}{128}\frac{RT_c}{P_c}\left[1 - \frac{6T_c^2}{T^2}\right] \tag{8}$$

where the value of B_{11} at a temperature T is a function of the critical temperature T_c and the critical pressure P_c. There were several probes for which critical data could not be found. As the probes concerned were only used at a single temperature and have a very low vapour pressure at 50°C, the error can be dismissed.

The vapour pressures of the probes at a temperature T were calculated from the Antoine equation:

$$\log_{10}P = \mathrm{A} + \frac{\mathrm{B}}{T + \mathrm{C}} \tag{9}$$

where A, B and C are constants obtained from the literature[10-14]. For several probes, vapour pressures at different temperatures were fitted to a polynomial function, and desired vapour pressures were interpolated from these functions. The heats of vapourization of the pure probes at a given temperature were calculated from the Clausius–Clapeyron equation[15]:

$$-\frac{\Delta H_v}{2.303RT^2} = \frac{\partial(\log_{10}P)}{\partial(T)} \tag{10}$$

The molar volumes of the probes were calculated from published densities and thermal expansion coefficients[10-14].

Table 1 gives values of χ_{12}^{∞} for the 25 probes. Also shown are values of the probe solubility parameter δ_1 calculated from equation 1 and the quantities δ_1^2/RT and χ_{12}^{∞}/V_1 from equation 3. Heats of mixing at infinite dilution, $\Delta\bar{H}_m^{\infty}$, were calculated from equation 7 using experimental activity coefficients at temperatures above 40°C for 12 probes. Results are shown in *Table 2*. The errors given are the standard deviations of the least squares data.

The infinite dilution data presented in *Tables 1* and *2* show the difficulties in the use of the derivation of DiPaola-Baranyi and Guillet[3] in the calculation of the polymer solubility parameter δ_2. The negative heats of mixing of HPC with most of the probes automatically invalidate the use of that derivation for this polymer. In addition, examination of the two terms on the left hand side of equation 3 shown in *Table 1* reveals that the term δ_1^2/RT is much greater than the experimentally derived term χ_{12}^{∞}/V_1. In fact, insertion of the data in *Table 1* into equation 3 yields a 'value' of δ_2 close to the mean value of all the δ_1's (water omitted).

The data in *Tables 1* and *2* were also examined in order to determine whether any trend exists with regard to the formation of liquid crystalline mesophases. No trend is evident. In fact, it now seems that HPC will form a liquid crystalline mesophase in any solvent in which the necessary high concentration can be achieved[16]. Thus, polymer–solvent interactions are much less important than chain stiffness in mesophase formation[1]. Further correlations will require knowledge of the phase diagrams of the various solvents with HPC.

It may be noted that the values of χ_{12}^{∞} are calculated with the assumption that the combinatorial entropy of mixing is given by the Flory Huggins theory. If the polymer is assumed to be rod-like, then the combinatorial entropy should be ideal. In this case, the corresponding χ values are obtained by subtracting unity from the values listed in *Table 1* (ref 7).

Table 2 Partial molar heats of mixing of organic probes with HPC

Probe	Temperature range (°C)	$\Delta\bar{H}_m^{\infty}$ (kJ mol^{-1})
Water	15–85	−5.7 ± 0.6
Methanol	40–75	−4.4 ± 1
Ethanol	40–75	−1.4 ± 0.7
1-Propanol	40–75	−1.8 ± 0.8
1-Butanol	40–75	−1.9 ± 0.8
Acetone	40–60	−3.1 ± 1.3
1,4-Dioxane	40–85	−0.7 ± 0.6
Tetrahydrofuran	40–100	0.2 ± 0.4
Chloroform	40–70	−4.8 ± 1
Toluene	40–85	0.2 ± 0.6
n-Heptane	45–85	2.6 ± 0.7
n-Decane	40–70	5 ± 2

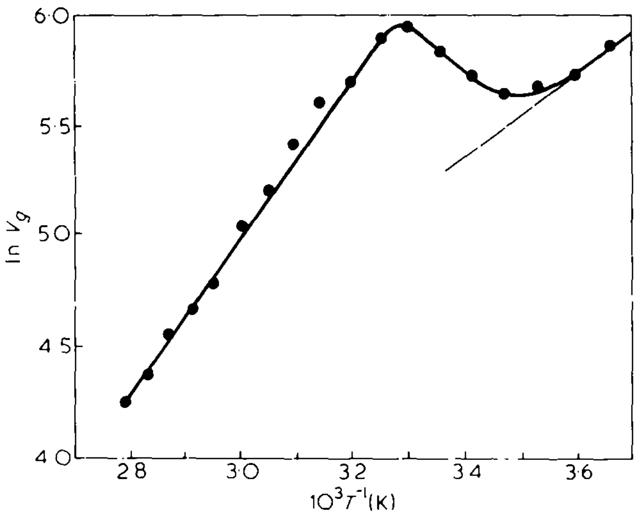

Figure 1 Retention diagram of the log specific retention volume vs. inverse absolute temperature for n-heptane on HPC

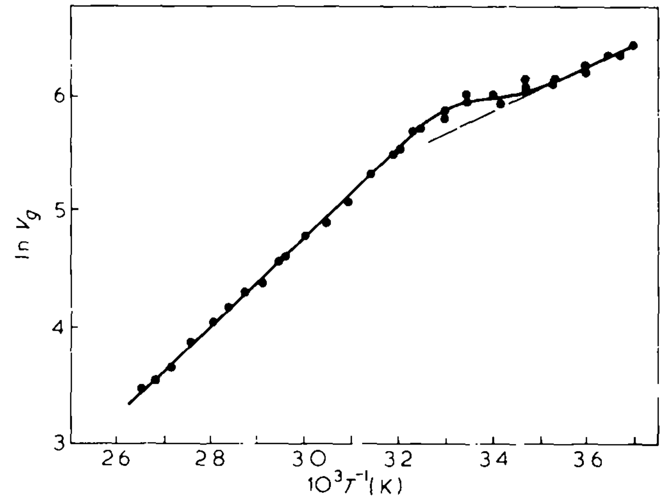

Figure 2 Retention diagram of the log specific retention volume vs. inverse absolute temperature for THF on HPC

Evidence for a glass transition

Figures 1 and *2* show the specific retention volumes at infinite dilution for n-heptane and tetrahydrofuran (THF), respectively a non-solvent and a fair solvent for HPC. A very clear transition temperature can be seen at about 10 C. In g.c. measurements, these Z-shaped curves are characteristic of a glass transition temperature, resulting from a change in retention mechanism from equilibrium surface adsorption below T_g to surface adsorption plus non-equilibrium bulk sorption in the region immediately above T_g. At a temperature sufficiently far enough above T_g, a state of equilibrium bulk sorption plus surface adsorption is reached. As is normal, the glass transition was taken to be the first point of deviation from linearity on the low temperature side of the curve.

The fundamental criterion for detection of a glass transition by inverse g.c. is that the probe be able to mix with the bulk of the polymer above T_g, but only adsorb onto the polymer surface below T_g[17,18]. This behaviour can be seen for n-heptane in *Figure 1* and for THF in *Figure 2*. No sign of a glass transition temperature was seen with good solvents such as water, ethanol, and methanol. This is generally accepted to be the result of the ability of a good solvent to penetrate even the glassy polymer, acting as a plasticizer to lower T_g. A non-solvent, toluene, did not show the glass transition temperature. This probably means that toluene is such a poor solvent that it cannot penetrate the polymer bulk, even above T_g. Discrepancies in the value of T_g from *Figures 1* and *2* may result from similar differences between n-heptane and THF. Further evidence from other techniques for a glass transition is required.

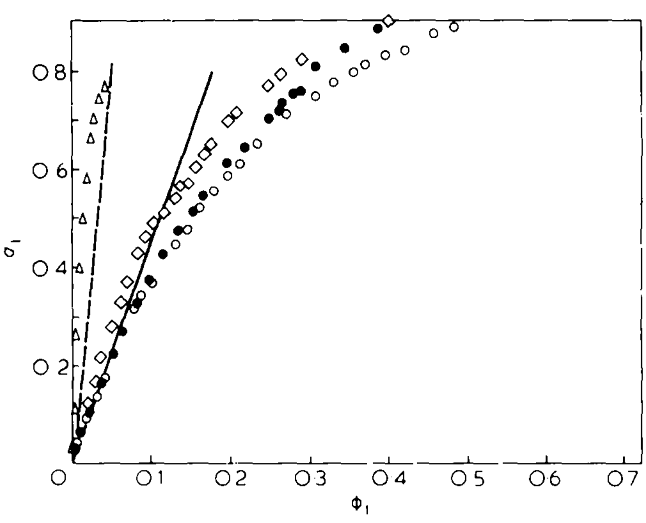

Figure 3 Sorption isotherms on HPC at 25°C; (△) n-decane, measured by inverse g.c.; (◇) acetone, (●) ethanol, and (○) THF measured on the vacuum microbalance apparatus. The solid line and the dotted line were calculated assuming rod-like mixing for ethanol and n-decane, respectively. See text for details

Finite concentration results

Sorption isotherms at 25 C are shown in *Figure 3* for three solvents (acetone, ethanol, and THF), and for one non-solvent (n-decane). The isotherm for n-decane was obtained by inverse g.c., while the others were measured on the vacuum microbalance apparatus[7].

The solid line in *Figure 3* was calculated for ethanol using Flory's equation for the solvent activity over an ordered polymer phase[17], as described previously[7]. The value of the orientation parameter y was taken to be one, indicating perfect orientation of the polymer, while the rod-like interaction parameter χ_R was obtained by subtracting unity from χ'_{12} for ethanol in *Table 1*, after correction to 25 C. The dotted line in *Figure 3* was calculated from the value of χ_R for n-decane.

It can be seen that the calculated solid line fits the ethanol sorption data at low ethanol concentrations. As in the case of water shown previously[7], the system deviates from the ideal rod-like model behaviour at $\varphi \simeq 0.07$, which corresponds to somewhat less than one solvent molecule per HPC unit. The fit between the rod-like molecule theory and the isotherms for the other solvents is poorer. It is possible that a better fit would result if preferential mixing with the side-chain had been considered, following Flory and Leonard[20]. There is also a strong possibility that surface adsorption contributes significantly to the g.c. retention of n-decane and the other hydrocarbons.

ACKNOWLEDGEMENTS

The support of Hercules Incorporated and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. J.S.A. thanks the Pulp and Paper Research Institute of Canada for a scholarship.

REFERENCES

1 Werbowyj, R. S. and Gray, D. G. *Macromolecules* 1980, **13**, 69
2 Tsutsui, T. and Tanaka, R. *Polym. J.* 1980, **12**, 473
3 DiPaola-Baranyi, G. and Guillet, J. E. *Macromolecules* 1978, **11**, 228
4 Hildebrand, J. H. and Scott, R. H. 'The Solubility of Non-Electrolytes', 3rd Edn., Dover Publications Inc., New York, 1964
5 Kawakami, M., Egashira, M. and Kagawa, S. *Bull. Chem. Soc. Jpn.* 1976, **49**, 3449
6 Roberts, G. A. F. and Thomas, I. M. *Polymer* 1978, **19**, 459
7 Aspler, J. S. and Gray, D. G. *Macromolecules* 1979, **12**, 562; Aspler, J. S. *PhD Thesis*, McGill University, Montreal, 1980
8 'The Virial Coefficients of Gases; A Critical Compilation', (Eds. J. H. Dymond and E. B. Smith), Clarendon Press, Oxford, 1969
9 Deshpande, D. D. and Oswal, S. L. *J. Chem. Soc., Faraday Trans. I* 1972, **68**, 1059
10 'Handbook of Chemistry', 10th Edn. (Ed. N. A. Lange), McGraw-Hill Co., New York, 1961
11 'Chemical Engineering Handbook', (Ed. J. H. Perry), McGraw-Hill Co., New York, 1963
12 'International Critical Tables', Vol. III, 1st Edn., McGraw-Hill Co., New York, 1928
13 Reid, R., Prausnitz, J. M. and Sherwood, T. K. 'The Properties of Gases and Liquids', McGraw-Hill Co., New York, 1977
14 'Handbook of Chemistry and Physics', 58th Edn., CRC Press, Inc., West Palm Beach, 1977
15 Barrow, G. M. 'Physical Chemistry', 2nd Edn., McGraw-Hill Book Co., New York, 1966
16 Werbowyj, R. S. and Gray, D. G., unpublished results
17 Smidsrød, O. and Guillet, J. E. *Macromolecules* 1969, **2**, 272
18 Gray, D. G. *Progr. Polym. Sci.* 1977, **5**, 1
19 Flory, P. J. *Proc. Roy. Soc. London, Ser. A* 1956, **234**, 73
20 Flory, P. J. and Leonard, Jr., W. J. *J. Am. Chem. Soc.* 1965, **87**, 2101