Polymer Vol. 39 No. 11, pp. 2241–2245, 1998
© 1998 Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

PII: S0032-3861(97)00523-5

Evidence of hydrogen bonding during sorption of chloromethanes in copolymers of chloroprene with methyl methacrylate and methacrylic acid

Yu. P. Yampolskii* and G. N. Bondarenko
A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Pr. 29, 117912, Moscow, Russia
(Received 16 June 1997)

Sorption of chloromethanes (CH_2Cl_2, $CHCl_3$, and CCl_4) in copolymers of chloroprene with methyl methacrylate and methacrylic acid was studied using inverse gas chromatography and infra-red (i.r.) spectroscopy. The chromatographic study showed that introduction of ester and carboxylic side groups into main chains resulted in a selective increase of the solubility coefficient of chloroform and methylene dichloride, the solutes capable to form hydrogen bonds with proton acceptors in polymer. Heats of formation of hydrogen bonds were determined by comparison of the partial molar heats of mixing in these systems and in reference systems where hydrogen bonding is excluded. The shifts of maxima of i.r. bands belonging to CH_2Cl_2 and $CHCl_3$ and to C–O bonds of the copolymers confirmed the formation of hydrogen bonds. The variation of the solubility coefficients and the shifts of absorption bands indicated that hydrogen bonds formed by methylene dichloride are somewhat stronger than those formed by chloroform. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: chloroprene copolymers; hydrogen bonds; thermodynamics)

INTRODUCTION

Specific interactions in transport and sorption of small molecules in polymeric membranes can impart additional permselectivity and possibly permeability to a polymeric membrane material. Enhanced permselectivities of membranes in facilitated transport processes may serve as an evident manifestation and a benefit of this phenomenon[1]. Although it is usually accepted that facilitated transport involves chemical reactions between a diffusing particle and fixed or mobile carriers within the membrane, whereas the solution-diffusion transport in common polymeric membranes is accompanied only by weak, van der Waals type interactions, in many cases it is difficult to establish a sharp boundary between these two extremities. Dipole–dipole and dipole–quadrupole interactions were assumed to take part in sorption and transport of such molecules as CO_2[2–4] and SO_2[5]. The role of specific interactions, or in this case, hydrogen bonding, is especially well documented for sorption and transport of water in polymers[6].

Frequently, evidence of specific interactions is sought and found in indirect manner, e.g. unusually high permselectivity of transport, unexpected position of sorption isotherms and so on. Direct observations of specific interactions between a solute and reactive sites in polymers are very scarce in the literature (see for example refs[7,8]). Study of them by observation of behaviour of both solute and polymer counterparts of the interactions may be useful as a first step in search for materials marked with enhanced permselectivity and maybe suitable for facilitated transport with fixed carriers.

In the present work, sorption of methylene dichloride and chloroform in copolymers of chloroprene, methyl methacrylate and methacrylic acid was studied using inverse gas chromatography (IGC) and infra-red (i.r.) spectroscopy, in the latter case by measuring the shifts of spectral bands corresponding to solutes and polymers.

EXPERIMENTAL

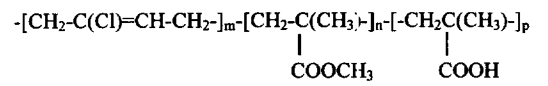
The inverse gas chromatographic study was carried out using an LKhM 8MD instrument. Details on column preparation, determination of polymer content on solid carrier, and corrections introduced in evaluating sorption parameters have been described elsewhere[9,10]. The polymers were deposited on the surface of the Chromaton-W solid carrier. The content of polymer phase was in the range 7–13 wt%. The length of the columns used was 1.2–2.0 m, their inner diameter 3 mm. Special experiments showed that the specific retention volume V_g did not depend on the content of polymer on the carrier, the flow rate of carrier gas (helium) in the range 3–8 ml min^{-1} and the size of solute sample. It could be concluded therefore, that V_g values measured by IGC and solubility coefficients determined therefrom, are characteristic for bulk sorption in polymers, and contributions of surface adsorption are negligible. In other words, they correspond to initial parts of sorption isotherms or infinite dilution conditions.

I.r. spectra of sorbed methylene dichloride and chloroform and of copolymers swollen in these solutes were obtained using a Specord-M-82 instrument in the range of wave numbers 400–4000 cm^{-1}.

---

* To whom correspondence should be addressed

The chemical structure of the random copolymers studied are shown below:



$$-[CH_2\text{-}C(Cl)\text{=}CH\text{-}CH_2\text{-}]_m\text{-}[CH_2\text{-}\underset{COOCH_3}{C}(CH_3)\text{-}]_n\text{-}[\text{-}CH_2\underset{COOH}{C}(CH_3)\text{-}]_p$$

Their preparation by means of emulsion polymerization has been described elsewhere[11]. The following notation will be used for different compositions of the copolymers in this paper: polychloroprene, PCP ($m = 1$, $n = p = 0$), dual copolymer, DCP ($m = 0.85$, $n = 0.15$, $p = 0$), triple copolymers, $TCP_{1.5}$ ($m = 0.837$, $n = 0.148$, $p = 0.015$), TCP_8 ($m = 0.782$, $n = 0.138$, $p = 0.08$). The glass transition temperature (T_g) of PCP as determined by differential scanning calorimetry (d.s.c.) was equal to −40°C, and those of the copolymers varied from −28°C to −23°C, i.e. all the materials studied were in rubbery state. Polybutadiene (PB) of SKD type was also used as the 'reference' solvent in determination of the heats of hydrogen bonding in the copolymers by means of IGC.

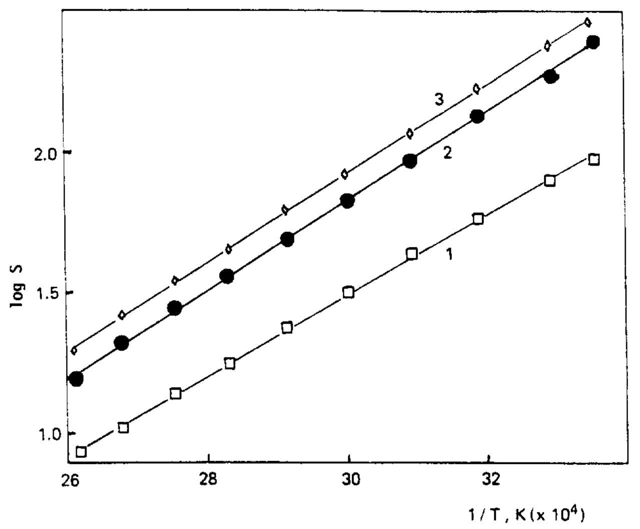


Figure 1 Temperature dependence of solubility coefficients(cm^3(STP)/cm^{3}atm) for chloromethanes in PCP (1, CH_2Cl_2; 2, $CHCl_3$; 3, CCl_4)

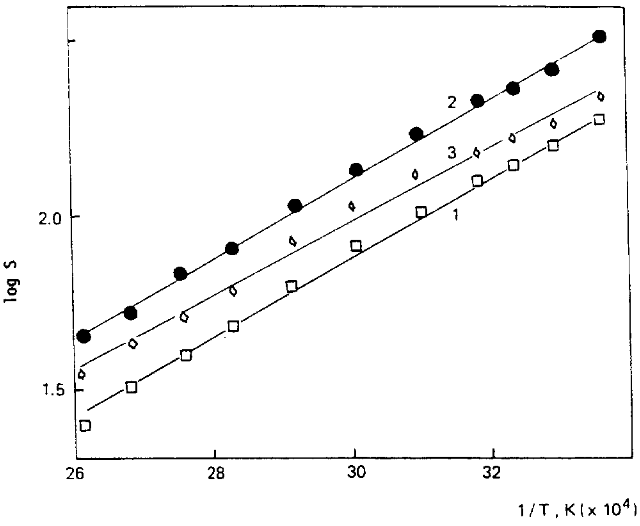


Figure 2 Temperature dependence of solubility coefficients(cm^3(STP)/cm^{3}atm) for chloromethanes in DCP (1, CH_2Cl_2; 2, $CHCl_3$; 3, CCl_4)

RESULTS AND DISCUSSION

Inverse gas chromatography

In the temperature range 25–110°C, retention diagrams, or dependence of log V_g *versus* reciprocal temperature, of methylene chloride, chloroform, and carbon tetrachloride, the latter being used as a reference solute, were obtained in PCP, PB and the three copolymers. The solubility coefficients S can be determined[12] *via* the specific retention volume:

$$S = (V_g/\rho p_o)\exp[p_o/RT(2B_{11} - V_1)J] \qquad (1)$$

where B_{11} is the second virial coefficient, ρ is the density of the polymer, V_1 is the molar volume of the solute, and J is the correction for pressure drop along the column.

Figures 1 and 2 show temperature dependencies of the solubility coefficients in PCP and the copolymer DCP. In these and other cases the dependencies are linear showing that no phase transitions occur in the temperature range studied. A positive slope of the lines indicates that heats of sorption ΔH_s are negative what is characteristic for sorption of organic vapours in polymers. The values of ΔH_s are given in *Table 1*.

Table 1 Heats of sorption ΔH_S, kJ mol^{-1}

Polymer	Solute		
	CCl_4	$CHCl_3$	CH_2Cl_2
PB	32.2	31.0	29.7
PCP	30.1	30.6	27.6
DCP	20.1	22.2	22.2
$TCP_{1.5}$	27.6	29.7	28.9
TCP_8	29.7	30.6	18.8

The sequence of variation of the solubility coefficients for the series CH_2Cl_2, $CHCl_3$, CCl_4 in PCP is in agreement with the changes of boiling points (T_b) or critical temperatures (T_c) of the solutes. It is known[13,14] that, for gas (vapour)–polymer systems without specific interactions, the solubility coefficients increase with increased T_b or T_c values. A variation of the S values for solutes with different T_c values is but a manifestation of the dependencies of S on Lennard-Jones energy parameter ϵ/k of gases, the value being linearly related to T_c and T_b and can serve as a measure of intensity of van der Waals interactions of various solutes with a given polymer. Hence, one can assume that sorption of the chloromethane series considered in PCP is not accompanied by marked specific interactions. It should be mentioned that the same order of the solubility coefficients for the CH_2Cl_2–$CHCl_3$–CCl_4 series was observed in polybutadiene[9].

A different order of variation of the solubility coefficients was observed for the copolymers of chloroprene. *Figure 2* shows that solubility coefficients of chloroform in DCP are larger than those of carbon tetrachloride in spite of much higher boiling point of the latter. The same regularity was observed for triple copolymers as can be seen from *Table 2*. It is evident that the introduction of ester and carboxylic side groups into hydrocarbon main chain does not result, in the case of carbon tetrachloride, in significant variation of the S values. On the other hand, solubility coefficients of $CHCl_3$ and CH_2Cl_2 increase significantly for the copolymers. It can be assumed that changed sequence of variation of the S values for the chloromethane series or the increase in S in the cases of $CHCl_3$ and CH_2Cl_2 are due to appearance of carbonyl containing side groups in the copolymers. It can be explained by additional interactions with proton donor

Table 2 Solubility coefficients S (cm^3(STP)/cm^3·cmHg) in triple copolymers

Copolymer	Solute	$T = 298$ K	$T = 323$ K	$T = 353$ K	$T = 383$ K
TCP$_{1.5}$	CH_2Cl_2	2.06	0.86	0.38	0.14
	$CHCl_3$	3.95	2.01	0.71	0.33
	CCl_4	3.32	1.70	0.67	0.32
TCP$_8$	CH_2Cl_2	1.67	0.79	0.30	0.13
	$CHCl_3$	3.92	1.54	0.67	0.26
	CCl_4	3.73	1.45	0.64	0.28

Table 3 Excess heats of mixing for chloromethanes ΔH_m (kJ mol^{-1})

Polymer	CH_2Cl_2	$CHCl_3$	CCl_4
PB	0.10	0.08	0.08
PCP	0.22	0.30	0.98
DCP	1.68	1.47	4.64
TCP$_{1.5}$	0.77	1.67	3.36
TCP$_8$	1.30	0.52	3.75

Table 4 Strength of hydrogen bonds in chloroprene copolymers $\Delta(H_m)_{A-B}$ (kJ mol^{-1}) estimated with carbon tetrachloride as the model solute

H-donor	PCP	DCP	TCP$_{1.5}$	TCP$_8$
PB as 'reference' solvent				
$CHCl_3$	−0.68	−3.2	−1.7	−3.2
CH_2Cl_2	−0.78	−3.0	−2.6	−2.5
PCP as 'reference' solvent				
$CHCl_3$	–	−2.6	−1.0	−2.6
CH_2Cl_2	–	−2.2	−1.8	−1.7

solutes, namely CH_2Cl_2 and $CHCl_3$, which could take place in the presence of ester and carboxylic groups. Such interactions or hydrogen bonding between these compounds and proton acceptors like acetone or dioxane are well known in liquid solutions[15].

Hydrogen bonding should be reflected in heats of sorption. However, since heats of sorption from vapour phase can be presented as a sum

$$\Delta H_s = \Delta H_c + \Delta H_m \tag{2}$$

where absolute values of heats of condensation ΔH_c are usually much larger than partial molar heats of mixing ΔH_m at infinite dilution in rubbers[10], the former can mask the effect of hydrogen bonding which should be exhibited in the latter. However the analysis of partial molar heats of mixing for different solutes allows to make an assessment of the strength of hydrogen bonds in polymer–solute systems. The partial molar heat of sorption is defined as

$$\Delta H_m = Rd[\ln(a_1/w_1)^\infty]/d(1/T) \tag{3}$$

where $(a_l/w_l)^\infty$ is the activity coefficient of a solute in a polymer, which can be found by the equation[12]

$$\ln(a_1/w_1)^\infty = \ln[(273R/V_g p_o M) - p_o(B_{11} - V_1)/RT], \tag{4}$$

where M is the molecular mass of the solute.

It was proposed[16] that energy of hydrogen bonding in solutions can be estimated, if the correction for hydrogen bonding in pure solute was taken into account. It can be done provided the partial molar heat of mixing at infinite dilution is known for a solvent which is totally unable to form hydrogen bonds, e.g. aliphatic hydrocarbon. The same approach is applicable, as has been shown by DiPaola-Baranyi *et al.*[17], to sorption in polymers.

Formation of hydrogen bonds in polymers usually takes place simultaneously with other interactions between solutes and polymers. A concentrations of the sites capable to hydrogen bonding can be low, as is the case in the copolymers studied, and therefore non-hydrogen bonding interactions such as dispersion forces and dipole–dipole interactions should be taken into account. Arnett *et al.*[18] considered various contributions to the measured thermodynamic parameters of sorption in liquid phase. They proposed to correct for non-specific interactions by choosing a suitable model solute and a reference solvent, for which the same sorption parameters were determined. Accordingly, an estimate of hydrogen bonding contribution can be obtained from

$$(\Delta H_m^{hb})_{A-B} = (\Delta H_m^A - \Delta H_m^M)_{Base} - (\Delta H_m^A - \Delta H_m^M)_{Ref} \tag{5}$$

where A, B, and M refer to 'acid' (proton donors or chloromethanes), 'base' (proton acceptors or oxygen containing groups in polymer), and model solute, respectively. In this study, carbon tetrachloride served as the model solute, whereas polybutadiene was used as the 'reference' solvent. The partial molar heats of mixing are presented in *Table 3*, whereas the estimates of hydrogen bonding contributions are given in *Table 4*.

It can be seen that 'strength' of hydrogen bonds formed by chloroform and methylene dichloride is approximately the same in all the copolymers. This seems to be an unexpected result because the former is often considered as a stronger proton donor. At any rate heats of hydrogen bonding of chloroform in liquid phase is somewhat higher[19] than those of methylene dichloride[19–21]. It is noteworthy also that very weak hydrogen bondings are observed even in absence of ester or carboxylic groups, i.e. in the case of PCP. This can be related to the fact that chlorine atoms carry weak positive charge and are capable therefore to form hydrogen bonds with proton donors as it takes place in vapours of hydrogen chloride. However, hydrogen bondings are so weak in PCP that they do not disturb the order of variation of the solubility coefficients in the series CH_2Cl_2 to $CHCl_3$ to CCl_4. On the other hand, it should be noted that the 'strength' of hydrogen bonds in these systems is rather low, even for the systems including basic, oxygen containing sites.

Alternatively, PCP instead of PB could be chosen as a 'reference' solvent. Such a selection would not be very accurate for assessment of hydrogen bonding, because PCP behaves also as a weak 'base', however it gives an idea of the direct contributions of methyl methacrylate and methacrylic acid moieties into formation of hydrogen bonds. Corresponding data are also shown in *Table 4*.

Let us compare the hydrogen bonding contributions found with those observed in other polymers or in liquid phase. DiPaola-Baranyi *et al.*[17] has determined the same parameters for different solutes in poly(vinyl acetate) and

Table 5 Strength of hydrogen bonds in solutions ΔH_{A-B} (kJ mol^{-1})

Base	$CHCl_3$ H-donor	CH_2Cl_2 H-donor	Ref.
Benzene	−7.1	−7.1	19
Toluene	−9.2	−8.4	19
Dioxane	−9.2	−5.4	19
Dimethyl ether	−10.0	–	21
Dioctyl ether	−10.0	−6.3	20

Table 6 Changes in i.r. spectra for polymer–$CHCl_3$ systems

Type of vibration	Pure polymer (cm^{-1})	Liquid $CHCl_3$ (cm^{-1})	Polymer–$CHCl_3$ (cm^{-1})
–C–O–	980	–	990
	1105	–	1120
	1125	–	1155
–C = O	1710	–	1730^a
	1730	–	
–C = C–	1650	–	1680
Cl_3C–H	–	3040	3030^b

^{a}A broad band with the maximum at 1730 cm^{-1}

^{b}A strong increase in intensity of this band was observed

ethylene-vinyl acetate copolymer with the vinyl acetate content of 18% w/w. For chloroform, the common solute of ref.[17] and this work, the $(\Delta H_m^{hb})_{A-B}$ values were equal to −5.4 and −4.2 kJ mol^{-1}, respectively. Therefore, the decrease in concentration of oxygen containing groups leads to a reduction of hydrogen bonding contribution into the heat of sorption or mixing. The content of methyl methacrylate and methacrylic acid comonomers in the materials studied in the present work is much lower, hence the results for vinyl acetate polymers are obviously in qualitative agreement with the values given in *Table 4*.

Table 5 gives some literature data on hydrogen bonding in solution with participation of the same proton donors as in this work. The 'strength' of hydrogen bonds in liquid phase is somewhat higher than in polymers. However, in all the cases they can be considered as rather weak bonds, much weaker, for example, than those formed by water or methanol, for which corresponding values are in the range 13–26 kJ mol^{-1}[22,23].

I.r. spectroscopy

I.r. spectra of the samples of DCP and $TCP_{1.5}$ swollen in liquid methylene dichloride and chloroform were studied. A comparison was made with the maxima positions and, to some extent, intensity of the bands in pure polymers and liquid solvents. Equilibrium sorption was achieved after overnight storage of films having thickness about 10 μm inserted in liquid phase. It amounted to about 15 %w/w of chloroform and 8% w/w of methylene dichloride in both DCP and $TCP_{1.5}$.

In the i.r. spectra of the films swollen in $CHCl_3$, intensive bands corresponding to the solute at 680, and 760–800 cm^{-1} (ν_{C-Cl} and $\delta_{Cl-C-Cl}$) and 1220 cm^{-1} ($\delta^{+}_{H-Cl-Cl}$), and 3030 cm^{-1} (ν_{C-H}) are observed in addition to the bands characteristic for the polymers (*Table 6*). The latter band belonging to stretching vibrations of the C–H bonds in $CHCl_3$ is much more intensive than in liquid chloroform and is shifted somewhat (10 cm^{-1}) to longer wave regions if compared with the spectrum of liquid chloroform.

The spectra of the polymers swollen in chloroform also reveal some changes in comparison with the spectra of pure polymers. A significant shift (10–30 cm^{-1}) to shorter waves is observed for all the absorption bands, which can be assigned to stretching vibrations of C–O bonds and are situated at 950–1200 cm^{-1}. According to the theory of vibration spectra[24], single C–O bonds are revealed in the bands which are hardly characteristic and due to it are shown in the spectra as poorly resolved broad bands at 950–1300 cm^{-1}. In the case of the copolymers studied in this work, three bands can be considered as intrinsic, namely the bands at 980, 1105, and 1125 in the initial copolymers, and bands at 990, 1120, and 1155 cm^{-1} in the materials sorbed $CHCl_3$ (*Table 6*). A combination of these two effects, which can be observed in the spectra of the sorbed films, namely (1) strong increase in the intensity of the bands and (2) a shift of stretching C–H vibrations in chloroform and a shift to shorter waves of the absorption C–O bands of the copolymers, is an unambiguous indication of weak interactions, obviously hydrogen bonding, which take place between the solute ($CHCl_3$) and polar groups in the polymer. A similar interaction between hydrogen of chloroform and chlorine of the main chain of polychloroprene cannot be excluded as well. There are some indirect indications of it. First, inverse gas chromatographic studies proved some, though very weak hydrogen bonding with PCP, i.e. in the absence of ester and carboxyl groups. Secondly, a shift of stretching C = C vibrations (1650 cm^{-1} in initial polymer and 1680 cm^{-1} in the films sorbed chloroform, as well as methylene chloride) can be interpreted as an evidence of such an interaction. Unfortunately, the stretching C–Cl bands of the polymers cannot be observed due to overlapping with similar bands of the solutes, however, the pattern of the spectra at 500–650 cm^{-1} (deformation vibrations at the angles with C–Cl bonds) is changed drastically after sorption. All this indicates some interaction between C–Cl bonds of the polymers and the solutes.

A pattern of the absorption bands corresponding to stretching C = O vibrations is also changed after sorption of $CHCl_3$: two bands at 1710 and 1730 cm^{-1} are seen in the spectrum of the initial copolymer, whereas one rather broad band with the maximum at 1730 cm^{-1} can be observed for the film containing sorbed $CHCl_3$. An appearance of small splitting 1710 – 1730 cm^{-1} in the spectrum of the initial polymer can be considered as an evidence of some ordering (like crystallinity), which is destroyed after contact with the solute. On the other hand, an absence of any shift of C = O bonds in the films sorbed $CHCl_3$ evidences that the interaction between chloroform and this bond is either too weak to be observed or is absent at all.

The results of the spectral study of the films with absorbed methylene dichloride are very similar and, in some aspects, even more dramatic. Thus, the shift of ν_{C-O} bands in the polymer at 1015, 1130, 1170 cm^{-1}, is expressed even better than in the case of sorption of chloroform. For the $\nu_{C=O}$ bands a marked shift to higher frequencies can be noted, such as that this band is situated at 1750 cm^{-1} instead of 1730 cm^{-1} as in the case of sorption of chloroform (see *Table 7*). The bands corresponding to stretching vibrations of C–H bonds of sorbed methylene dichloride are strongly split: 2990, 3000, 3020, and 3070 cm^{-1} instead of two bands at 3050 and 2986 cm^{-1} in pure liquid CH_2Cl_2. All this can be interpreted as evidence of stronger interaction of CH_2Cl_2 and polymer, if compared with sorption of $CHCl_3$.

At present, only a hypothesis can be advanced to explain this result. It is accepted[15] that the strongest hydrogen bonds are formed when the angle between 'acid', proton, and 'base' is equal to 180° or the complex has the linear

Table 7 Changes in i.r. spectra for polymer–CH_2Cl_2 systems

Type of vibration	Pure polymer (cm^{-1})	Liquid CH_2Cl_2 (cm^{-1})	Polymer–CH_2Cl_2 (cm^{-1})
–C–O–	980	–	1015
	1105	–	1130
	1125	–	1170
–C = O	1710	–	1750
	1730		
–C = C–	1650	–	1680
Cl_2HC–H	–	2986	2990
	–	3050	3000
			3020
			3070

structure. Therefore only one hydrogen atom in the CH_2Cl_2 molecule can participate in hydrogen bonding, whereas the other is too far from the oxygen atom. Since electron density shifts from the hydrogen atom (or its acidity) in chloroform should be stronger than in methylene dichloride, it will be only natural to expect an opposite situation, i.e. stronger interaction with chloroform. A possible explanation of this controversy can be achieved if one assumes that nonlinear complexes are formed in the case of methylene dichloride, in contrast to linear ones when chloroform forms hydrogen bonds. Thus according to Luck[25] the dimers of cyclohexane-oxims have a structure of substituted four-member cycles formed by two hydrogen bonds. In these dimers the angle of hydrogen bonding θ is equal to 49°. Probably for such configuration of hydrogen bonding a decrease in local interaction energy is compensated by doubling of the hydrogen bonds formed.

Qualitatively, very similar results were obtained for the copolymer TCP_8 with sorbed chloroform and methylene dichloride. However the presence of noticeable quantities of methacrylic acid in the material makes the ν_{C-O} and $\nu_{C=O}$ much more complicated, because of which these results are not considered here.

It would be very attractive to deduce energy of the formation of hydrogen bonds proceeding from the spectral shifts of corresponding bands. Indeed such correlation have been considered[15] in the literature. However, as Iogansen[26] has demonstrated, these correlations are often nonlinear, and hence the estimates, which can be made are very approximate. The only although qualitative conclusion which can be made here is that hydrogen bonds formed by CH_2Cl_2 are stronger than the ones formed by $CHCl_3$.

CONCLUSIONS

Thus, the comparison of the i.r. spectra of pure components—both the polymers containing ester and carboxyl groups and the solutes ($CHCl_3$ and CH_2Cl_2), and of the films containing these solvents, agrees with an assumption of formation of hydrogen bonds during sorption and transport of these molecules in chloroprene copolymers. It is noteworthy that a good agreement between independent results of IGC and i.r. spectroscopy was achieved: in both cases evidence of somewhat stronger hydrogen bonds formed by CH_2Cl_2 was obtained. In the IGC experiment they were reflected in larger changes of the solubility coefficients of CH_2Cl_2, i.r. spectroscopy revealed larger shifts of spectral lines. Although a level of variation of the solubility coefficient due to hydrogen bonding, the heats of their formation in the systems investigated, and spectral shifts observed are not very large, this result seems to demonstrate that even not very large concentrations of proton acceptors can cause significant variation in thermodynamic parameters of interaction during sorption and transport. Possibly it would be more rewarding in future to look for the systems with stronger donor–acceptor interactions.

REFERENCES

1. Cussler E. L., in *Polymeric Gas Separation Membranes*, ed. D.R. Paul and Yu. P. Yampolskii. CRC Press, Boca Raton FL, 1994, p. 273.
2. Shah, V. M., Hardy, B. J. and Stern, S. A., *J. Polym. Sci, Part B: Phys.*, 1993, **31**, 313.
3. Fulton, J. L., Yee, G. G. and Smith, R. D., *J. Amer. Chem. Soc.*, 1991, **113**, 8327.
4. Yampolskii, Yu. P., Bespalova, N. B., Finkelshtein, E. Sh., Bondar, V. I. and Popov, A. V., *Macromolecules*, 1994, **27**, 2872.
5. Volkov V. V., Doctor of Science Degree Thesis, TIPS, 1993.
6. Rowland S.P., ed., *Water in Polymers*. ACS Symposium Series, Washington DC. 1980.
7. Fried, J. R. and Li, W., *J. Appl. Polym. Sci.*, 1990, **41**, 1123.
8. Kazarian, S. G., Vincent, M. F., Bright, F. V., Liotta, C. L. and Eckert, C. A., *J. Amer. Chem. Soc.*, 1996, **118**, 1729.
9. Ovsepyan R. M., Candidate of Science Degree Thesis, TIPS, 1990.
10. Yampolskii Yu. P. and Durgaryan S. G., in *Chromatography and Thermodynamics*, ed. R. Stryjek and Yu. Yampolskii. IChF, Acad, Sci. Poland, Warsaw, 1986.
11. Gevorkian A.V., Yegiyan E.S., Nazarian L.N. and Ovsepyan R.M., Avt. Svid. SSSR, N 901271, 1982.
12. Braun, G. -M. and Guileet, J. E., *Adv. Polym. Sci.*, 1976, **21**, 107.
13. Van Amerongen, G. J., *Rubber Chem.Technol.*, 1964, **37**, 1065.
14. Michaels, A. S. and Bixler, H. J., *J. Polym. Sci.*, 1961, **50**, 393.
15. Joesten M. D. and Schaad L. J., *Hydrogen Bonding*. Marcel Dekker, New York, 1974.
16. Murakani, S. and Fujishiro, R., *Bull. Chem. Soc. Japan*, 1966, **39**, 720.
17. DiPaola-Baranyi, G. and Guillet, J. E., *Makromol. Chem.*, 1980, **181**, 215.
18. Arnett, E. M., Joris, L., Mitchell, E., Murty, T. S., Gorrie, T. M. and Schleyer, P. V. R., *J. Amer. Chem. Soc.*, 1970, **92**, 2365.
19. Johnston, M. D., Casparo, F. P. and Kuntz, I. D., *J. Amer. Chem. Soc.*, 1969, **91**, 5715.
20. Sheridan, J. P., Martire, D. E. and Tewari, Y. B., *J. Amer. Chem. Soc.*, 1972, **94**, 3294.
21. Kearns, E. R., *J. Phys. Chem.*, 1961, **65**, 314.
22. Herson, B. and Swenson, C. A., *J. Phys. Chem.*, 1973, **77**, 2401.
23. Becker, E. D., *Spectrochim. Acta*, 1961, **17**, 436.
24. Sverdlov L.M., Kovner M.A. and Krainov E.P., in *Kolebatel'nye Spektry Mnogoatomnnykh Molekul*. Nauka, Moskva, 1970, p. 426.
25. Luck, W. A. P., *Ber. Bunsengenes Phys. Chem.*, 1961, **65**, 355.
26. Iogansen A. V., in *Vodorodnaya Svyyaz*. Nauka, Moskva, 1981.