JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Infinite-Dilution Activity Coefficients of Volatile Organic Compounds in Cyclic Olefin Copolymers

P. Alessi,[†] A. Cortesi,[†] I. Kikic,[†,*] D. Solinas,[†] N. De Zordi,[‡] and M. Moneghini[‡]

[†]Department of Industrial Engineering and Information Technologies, University of Trieste, Via Valerio 10, 34127 Trieste, Italy

[‡]Department of Chemical and Pharmaceutical Sciences, University of Trieste, Piazzale Europa 1, 34127 Trieste, Italy

ABSTRACT: Infinite-dilution activity coefficients for nine classes of volatile organic compounds (paraffins, olefins, cycloparaffins, aromatics, ketones, nitriles, alcohols, esters, and chlorocompounds) in a series of four cyclic olefin copolymers were determined using an inverse gas chromatography technique with a packed column. Abraham's equation of solvation was used for the evaluation of the different types of interactions between the solvents and polymers. The results are compared with the activity coefficients at infinite dilution obtained for other polymers of similar use.

INTRODUCTION

Knowledge of equilibrium and mass-transfer properties is of considerable importance in a wide variety of manufacturing operations involving polymers, such as polymerization, devolatilization, vacuum/gas stripping, and drying. Accurate measurements of the activity and diffusion coefficients of solvents in polymer melts or solutions are needed. Conventional methods for measuring them have relied on bulk equilibration and gravimetric sorption/desorption experiments. These techniques, however, become very difficult to apply to polymer + solvent systems when the solvent is present in vanishingly small amounts or at temperatures near the glass transition temperature (T_g).[1−5]

Inverse gas chromatography (IGC) has been developed as a fast and reliable technique for the measurement of the activity, particularly in the high-polymer-concentration region. This region is interesting in the polymer industry, particularly in the manufacturing of polymer films and coating/drying operations. Furthermore, the necessity to preserve the environment and human health against volatile residual solvents employed during polymer production and characterization has induced increased interest in activity coefficients at infinite dilution for volatile solvents in polymer melts. Data on activity coefficients at infinite dilution provide more valuable information in terms of molecule−molecule interactions in comparison with those in the finite-solvent-concentration region.

Cyclic olefin copolymers (COCs) are made from ethylene and norbornene; they are amorphous, transparent copolymers characterized by a cyclic olefin structure. The high purity and absence of ionic content in these materials provide high insulation resistance and very low dielectric loss. They also have excellent chemical resistance to many polar solvents and aqueous acids and bases. Moreover, they are recognized as a resin with optical properties comparable to those of poly(methyl methacrylate) acrylic resin (PMMA). They also have superior heat resistance and dimensional stability relative to polycarbonate (PC) and PMMA. COCs have a very high moisture barrier, low water absorption, good resistance to hydrolysis and chemical media, and low density. In addition, they offer high transparency extending into the UV range, low birefringence, adjustable heat deflection temperatures, and high rigidity.

Table 1. Properties of COCs

property	COC 1	COC 2	COC 3	COC 4
MW/g·mol^{-1}	42000	45000	45000	50000
T_g/K	408	408	448	356
% norbornene	50	50	60	37

In this work, the IGC technique was used to determine the activity coefficients of several volatile organic compounds (in the following defined as solutes) in polymers. The retention times of solutes were determined over a variety of flow rates at constant temperature as well as over a variety of temperatures at fixed flow rate. The infinite-dilution activity coefficients of solutes in different types of COCs are reported. Retention volumes were correlated by means of Abraham's equation of solvation.[6]

EXPERIMENTAL SECTION

Materials. All of the volatile organic compounds used in this work were reagent-grade and used without further purification. The adopted solutes were supplied by Aldrich Chemical Co. COC polymers with different properties, designated as COC 1, COC 2, COC 3, and COC 4, were kindly donated by Hoechst (Frankfurt, Germany).

Apparatus. A thermal-conductivity chromatograph (Fractovap model B, Carlo Erba, Italy) was employed. The thermostat stability of the oven was better than 0.05 K and measured using an electronic thermometer (Systemteknik AB S1220). The carrier-gas (helium) flow rate was measured by means of a soap-film meter. The pressure drop in the column was measured to within ± 0.13 KPa using a mercury manometer.

Special Issue: John M. Prausnitz Festschrift

Received: October 28, 2010
Accepted: December 27, 2010
Published: January 21, 2011

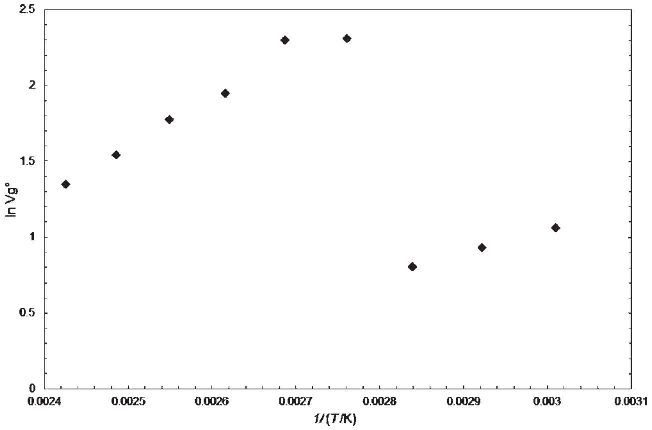

Figure 1. Retention diagram for *n*-hexane in COC 4.

Table 2. Natural Logarithms of the Experimental Retention Volumes (ln V_g°) of COC 1 in Different Organic Solvents at (438, 443, 449, and 457) K

solvent	ln V_g° T/K = 438	T/K = 446	T/K = 449	T/K = 457
n-hexane	0.78	0.69	0.66	0.58
n-heptane	1.43	1.31	1.27	1.16
n-octane	2.01	1.88	1.83	1.70
1-hexene	0.78	0.70	0.67	0.59
heptene	1.39	1.27	1.23	1.12
octene	1.99	1.87	1.82	1.70
cyclohexane	1.69	1.60	1.57	1.48
methylcyclohexane	1.99	1.89	1.86	1.76
ethylcyclohexane	2.67	2.54	2.49	2.37
benzene	1.81	1.68	1.63	1.50
toluene	2.39	2.23	2.18	2.03
ethylbenzene	2.88	2.71	2.65	2.48
methyl ethyl ketone	0.86	0.65	0.57	0.38
diethyl ketone	1.41	1.26	1.20	1.06
methyl isobutyl ketone	1.50	1.39	1.34	1.23
propanol	0.39	0.24	0.18	0.04
butanol	1.14	0.98	0.92	0.77
ethyl acetate	0.62	0.50	0.46	0.34
propyl acetate	1.24	1.12	1.08	0.97
butyl acetate	1.86	1.72	1.67	1.53
tetrahydrofuran	1.36	1.26	1.23	1.13
dibutyl ether	2.39	2.23	2.18	2.03
chlorobutane	1.37	1.25	1.21	1.09
chloropentane	1.97	1.83	1.78	1.64
tetrachloromethane	1.72	1.65	1.62	1.56
chloroform	1.44	1.33	1.29	1.19
propionitrile	0.52	0.36	0.29	0.13
butyronitrile	1.18	1.03	0.98	0.84

Table 3. Natural Logarithms of the Experimental Retention Volumes (ln V_g°) of COC 2 in Different Organic Solvents at (449, 453, 457, and 461) K

solvent	ln V_g° T/K = 449	T/K = 453	T/K = 457	T/K = 461
n-hexane	0.81	0.76	0.72	0.68
n-heptane	1.37	1.32	1.27	1.22
n-octane	1.89	1.85	1.81	1.77
1-hexene	0.76	0.73	0.70	0.66
heptene	1.34	1.29	1.24	1.19
octene	1.87	1.83	1.79	1.75
cyclohexane	1.62	1.59	1.56	1.53
methylcyclohexane	1.94	1.90	1.86	1.83
ethylcyclohexane	2.55	2.51	2.47	2.43
benzene	1.69	1.64	1.59	1.55
toluene	2.24	2.19	2.15	2.11
ethylbenzene	2.69	2.65	2.60	2.56
methyl ethyl ketone	0.55	0.52	0.49	0.47
diethyl ketone	1.28	1.22	1.16	1.10
methyl isobutyl ketone	1.43	1.38	1.33	1.28
propanol	0.36	0.29	0.23	0.16
butanol	0.99	0.96	0.92	0.89
ethyl acetate	0.61	0.55	0.47	0.41
propyl acetate	1.12	1.08	1.05	1.01
butyl acetate	1.71	1.66	1.61	1.57
tetrahydrofuran	1.26	1.22	1.18	1.14
dibutyl ether	2.22	2.17	2.12	2.08
chlorobutane	1.26	1.23	1.21	1.19
chloropentane	1.83	1.80	1.77	1.74
tetrachloromethane	1.60	1.59	1.58	1.56
chloroform	1.32	1.26	1.21	1.15
propionitrile	0.47	0.40	0.33	0.27
butyronitrile	1.06	1.02	0.98	0.93

The measured experimental conditions were the retention time of the solute, the dead time (retention time of air), the carrier flow rate, the column temperature, the flow-meter temperature, the ambient pressure, and the pressure drop in the column. The carrier flow rate ranged from (20 to 40) mL·min^{-1}, and the pressure drop was (4 to 15) KPa. For each of the polymers, the influence of the carrier flow rate was evaluated by extrapolating the retention volume to zero flow rate; no influence of the flow rate was observed for any of the stationary phases. Since the peaks did not show notable asymmetry, retention times were read using the peak maxima.

The uncertainties were estimated to be the following: carrier flow, ± 0.005 mL·s^{-1}; column temperature, ± 0.05 K; soap-film meter temperature, ± 0.1 K; inlet and outlet pressures, ± 0.2 kPa; solvent mass, ± 0.001 g. The effect of these uncertainties on the activity coefficients was estimated to be about 2 %.

Polymer Characteristics. The COC polymers used in this work exhibited different values of physicochemical properties such as molecular weight (MW), T_g, and composition (as % norbornene), as reported in Table 1.

Glass Transition Temperatures. Values of T_g were determined using a differential scanning calorimeter (model TA 4000, Mettler, Greifensee, Switzerland) equipped with a DSC 20 measuring cell. A fixed amount of polymer was placed in a pierced aluminum crucible and heated in hot air at a scanning rate of 10 K·min^{-1} from (303 to 573) K.

Columns. A known amount of polymer was solubilized in chloroform and mixed with a known quantity of silanized Chromosorb (WDMCS, 100/120 mesh), which allows no adsorption on the support. The solvent was then removed by vacuum and

Table 4. Natural Logarithms of the Experimental Retention Volumes ($\ln V_g^\circ$) of COC 3 in Different Organic Solvents at (478, 488, 498, and 508) K

	$\ln V_g^\circ$			
solvent	T/K = 478	T/K = 488	T/K = 498	T/K = 508
n-hexane	0.82	0.69	0.58	0.46
n-heptane	1.28	1.09	0.90	0.72
n-octane	1.75	1.50	1.25	1.01
1-hexene	0.82	0.70	0.59	
heptene	1.18	1.05	0.94	0.85
octene	1.51	1.42	1.32	1.25
cyclohexane	1.58	1.39	1.18	0.99
methylcyclohexane	1.87	1.67	1.47	1.27
ethylcyclohexane	2.42	2.22	2.02	1.82
benzene	1.46	1.36	1.26	1.16
toluene	2.02	1.89	1.74	1.60
ethylbenzene	2.58	2.34	2.11	1.86
methyl ethyl ketone	0.03	−0.07	−0.10	−0.14
diethyl ketone	0.53	0.42	0.33	0.24
methyl isobutyl ketone	1.33	1.17	1.00	0.85
propanol	0.46	0.31	0.17	0.04
butanol	0.90	0.75	0.59	0.46
ethyl acetate	0.52	0.41	0.33	0.24
propyl acetate	1.01	0.86	0.75	0.61
butyl acetate	1.54	1.33	1.12	0.93
tetrahydrofuran	1.06	0.86	0.67	0.46
dibutyl ether	1.98	1.81	1.63	1.46
chlorobutane	1.14	0.94	0.73	0.54
chloropentane	1.69	1.49	1.30	1.10
tetrachloromethane	1.69	1.41	1.14	0.85
chloroform	1.17	1.05	0.91	0.77
propionitrile	0.02	−0.04	−0.11	−0.16
butyronitrile	0.56	0.50	0.43	0.39

Table 5. Natural Logarithms of the Experimental Retention Volumes ($\ln V_g^\circ$) of COC 4 in Different Organic Solvents at (383, 393, 403, and 413) K

	$\ln V_g^\circ$			
solvent	T/K = 383	T/K = 393	T/K = 403	T/K = 413
n-hexane	1.95	1.72	1.54	1.35
n-heptane	2.83	2.49	2.24	2.00
n-octane	3.57	3.22	2.93	2.67
1-hexene	2.01	1.75	1.50	1.29
heptene	2.77	2.47	2.18	1.97
octene	3.50	3.18	2.87	2.59
cyclohexane	3.00	2.75	2.51	2.29
methylcyclohexane	3.42	3.14	2.91	2.68
ethylcyclohexane	4.21	3.92	3.63	3.38
benzene	2.96	2.71	2.49	2.21
toluene	3.73	3.47	3.18	2.90
ethylbenzene	4.39	4.09	3.78	3.48
methyl ethyl ketone	1.57	1.22	0.95	0.69
diethyl ketone	2.64	2.31	2.03	1.79
methyl isobutyl ketone	3.08	2.74	2.46	2.18
propanol	1.64	1.25	0.92	0.63
butanol	2.47	2.10	1.76	1.47
ethyl acetate	2.22	1.92	1.64	1.38
propyl acetate	2.71	2.35	2.03	1.76
butyl acetate	3.37	3.00	2.70<	2.44
tetrahydrofuran	2.41	2.24	2.01	1.73
dibutyl ether	4.04	3.74	3.39	3.08
chlorobutane	2.58	2.26	2.01	1.76
chloropentane	3.37	3.01	2.76	2.51
tetrachloromethane	2.92	2.66	2.44	2.24
chloroform	2.59	2.31	2.10	1.85
propionitrile	1.64	1.25	0.89	0.54
butyronitrile	2.42	2.06	1.73	1.42

nitrogen stripping, and the coated support was fed into a 2 m long, 4 mm internal diameter column. The solvent was further removed once the column was installed using a flow of helium at 353 K for about 24 h. The mass fraction of polymer in the impregnated support was > 0.15 for all of the columns; under these conditions, the effect of adsorption was negligible.[1] Solutes (0.1 μL) were injected with a Hamilton syringe.

Theory. The specific retention volume (V_g°) is given by

$$V_g^\circ = \frac{F}{w_2}\frac{273.15}{T_{\mathrm{fm}}}J_3^2\frac{P_{\mathrm{fm}} - P_{\mathrm{w}}^{\mathrm{S}}}{P_{\mathrm{fm}}(t_{\mathrm{r1}} - t_{\mathrm{a}})} \tag{1}$$

where w_2 is the mass of polymer in the column, t_{r1} and t_a are the retention time of the solvent and the dead time, respectively, F is the carrier gas flow rate, T_{fm} and P_{fm} are the absolute temperature and pressure of the flow meter, respectively, and P_w^S is the vapor pressure of water at T_{fm}. J_3^2 represents the correction factor for gas compressibility inside the column, which is given by

$$J_3^2 = \frac{3}{2}\frac{\left(\frac{P_{\mathrm{i}}}{P_{\mathrm{o}}}\right)^2 - 1}{\left(\frac{P_{\mathrm{i}}}{P_{\mathrm{o}}}\right)^3 - 1} \tag{2}$$

where P_i and P_o are the pressures at the input and exit of the column, respectively.

Many theoretical approaches have been proposed in order to characterize the compounds (often polymers) used as stationary phases in gas−liquid chromatography. Some of them, on the basis of chromatography data for some reference substances, have been used to obtain characteristic parameters of stationary phases. With other approaches, the solute−solvent interactions in both stationary and mobile phases have been investigated. These latter approaches involve the use of a number of parameters (descriptors) that describe the properties of the solute molecule and, for extension, the behavior of the solute molecule in solution. In particular, the present work employed the Abraham solvation equation:[6,7]

$$\log \mathrm{SP} = c + eE + sS + aA + bB + lL \tag{3}$$

where the variable SP can be the partition coefficient of an organic solvent or, as is the case in the present work, the retention volume in gas−liquid chromatography. Each term in the equation refers to some particular solute−solvent interaction. In particular, there are five parameters that represent solute properties:

E is the solute excess molar refractivity relative to an alkane of equivalent volume, and it is obtained from refractive indexes of

Table 6. Abraham Parameters of COC Polymers at Various Temperatures

T/K	c	e	s	a	b	l	AAD/%
			COC 1				
438	−0.762	0.639	−0.037	−0.125	0.079	0.505	1.7
446	−0.838	0.607	−0.012	−0.195	0.012	0.517	1.7
449	−0.859	0.599	−0.006	−0.214	−0.005	0.521	1.8
457	−0.927	0.574	0.010	−0.287	−0.062	0.532	2.8
			COC 2				
449	−0.779	0.523	0.063	−0.077	−0.095	0.508	1.8
453	−0.842	0.514	0.080	−0.156	−0.110	0.524	2.1
457	−0.903	0.506	0.097	−0.234	−0.124	0.539	2.7
461	−0.964	0.497	0.113	−0.311	−0.138	0.555	3.4
			COC 3				
478	−0.722	0.591	−0.086	−0.053	−0.06	0.41	3.8
488	−0.721	0.603	−0.123	−0.107	0.001	0.386	3.0
498	−0.721	0.616	−0.173	−0.192	0.096	0.362	3.1
508	−0.679	0.614	−0.198	−0.244	0.134	0.326	3.0
			COC 4				
383	−0.522	0.498	0.051	−0.228	0.124	0.557	5.8
393	−0.571	0.522	0.006	−0.332	0.132	0.539	5.6
403	−0.624	0.544	0.005	−0.417	0.069	0.519	5.9
413	−0.724	0.526	0.050	−0.430	0.004	0.510	6.2

solutes that are liquid at 293 K and/or from summations over fragments or substructures.[8]

S is the solute dipolarity/polarizability, which can be obtained from gas−liquid chromatographic measurements on polar stationary phases or, more generally, from water/solvent partition.

A and *B* are the solute overall hydrogen-bond acidity and basicity, which are most easily obtained from water−solvent partitions.

L is the solute gas−*n*-hexadecane partition coefficient at 298 K. The numerical values of these descriptors can be calculated on the basis of the molecular structures of the different organic solutes[9] and have been found to contain essentially the same chemical information as the theoretically calculated molecular descriptors of Klamt's COSMO-RS.[10]

The solute descriptors represent the solute effects on various solute−phase interactions; the regression coefficients *c*, *e*, *s*, *a*, *b*, and *l* correspond to the complementary effects of the phase on these interactions:

The *e* coefficient shows the tendency of the phase to interact with solutes through π and electron-pair interactions, and it is usually positive.

The *s* coefficient represents the tendency of the phase to interact with dipolar/polarizable solutes.

The *a* coefficient depends on the hydrogen-bond basicity of the phase (an acidic solute interacts with a basic phase), and the *b* coefficient is a measure of the hydrogen-bond acidity of the phase.

The *l* coefficient is a combination of dispersion forces (which make a positive contribution) and a cavity term (which makes a negative contribution). In general, the dispersion effect is predominant, so the *l* coefficient is often positive. In the case of gases and water, it is negative, so it can also be regarded as a measure of the hydrophobicity of the phase.The coefficients *c*, *e*, *s*, *a*, *b*, and *l* were obtained by fitting the experimental values of the quantity SP (in our case, the retention volume).

Table 7. Mass-Fraction Activity Coefficients at Infinite Dilution [$\Omega(\exp)^\infty$] for COC 1 at (438, 446, 449, and 457) K in Various Organic Solvents

	$\Omega(\exp)^\infty$			
solvent	T/K = 438	T/K = 446	T/K = 449	T/K = 457
n-hexane	15.4	15	14.8	14.4
n-heptane	12.4	12.2	12.1	11.9
n-octane	11.1	10.7	10.6	10.4
1-hexene	14.3	13.9	13.7	13.4
heptene	12.1	11.9	11.8	11.6
octene	10.4	10.0	9.9	9.7
cyclohexane	8	7.7	7.6	7.3
methylcyclohexane	8.8	8.4	8.3	8.0
ethylcyclohexane	6.8	6.6	6.5	6.4
benzene	7.0	7.0	7.0	7.1
toluene	6.5	6.5	6.6	6.6
ethylbenzene	6.2	6.2	6.2	6.3
methyl ethyl ketone	19.1	20.5	21.1	22.6
diethyl ketone	14.4	14.4	14.4	14.4
methyl isobutyl ketone	10.5	10.3	10.2	10.1
propanol	36.6	35.8	35.6	35.0
butanol	24.6	23.8	23.5	22.7
ethyl acetate	18.9	18.8	18.7	18.7
propyl acetate	14.3	13.8	13.7	13.2
butyl acetate	12	11.6	11.5	11.2
tetrahydrofuran	8.8	8.5	8.5	8.3
dibutyl ether	9.2	9.0	8.9	8.8
chlorobutane	9.3	9.2	9.1	9.1
chloropentane	8.3	8.2	8.2	8.2
tetrachloromethane	3.8	3.6	3.5	3.4
chloroform	4.6	4.5	4.5	4.4
propionitrile	53.3	54.5	55.1	56.6
butyronitrile	33.1	32.8	32.6	32.4

In the literature,[11−14] applications of solvation theory for the characterization of polymer−solvent interactions have been extensively reported. Gas-chromatographic retention volumes of the solvents are regressed, and the specific solvation parameters of the polymers, used as stationary phases, are able to reproduce the partition.[13] These parameters can be used for the prediction of the partition and, consequently, of the interactions between other volatile organic compounds and the polymer, provided that the descriptors for these solutes are known.

The specific retention volume can also be used for the calculation of Ω_1^∞, the infinite-dilution mass-fraction activity coefficient of a solvent in a polymer at temperature *T*, as Ω_1^∞ is related to the specific retention volume by the following equation:

$$\ln \Omega_1^\infty = \ln\left(\frac{273.15\cdot R}{M_1 V_g^\circ P_1^{\text{sat}}}\right) - \frac{(B_{11} - v_1^0)P_1^{\text{sat}}}{RT} \qquad (4)$$

where M_1, B_{11}, P_1^{sat}, and v_1^0 are the molecular weight, the second virial coefficient, the vapor pressure, and the molar volume of the solvent at the column absolute temperature *T*, respectively. The

Table 8. Mass-Fraction Activity Coefficients at Infinite Dilution $[\Omega(\exp)^\infty]$ for COC 2 at (449, 453, 457, and 461) K in Various Organic Solvents

	$\Omega(\exp)^\infty$			
solvent	T/K = 449	T/K = 453	T/K = 457	T/K = 461
n-hexane	12.8	12.6	12.5	12.4
n-heptane	11.0	10.9	10.7	10.6
n-octane	10	9.6	9.3	9
1-hexene	12.5	12.2	12.0	11.8
heptene	10.6	10.4	10.3	10.2
octene	9.5	9.1	8.8	8.6
cyclohexane	7.2	7	6.7	6.5
methylcyclohexane	7.7	7.5	7.3	7.1
ethylcyclohexane	6.2	5.9	5.7	5.5
benzene	6.6	6.6	6.5	6.4
toluene	6.2	6.0	5.8	5.7
ethylbenzene	6	5.8	5.5	5.4
methyl ethyl ketone	21.6	20.9	20.1	19.4
diethyl ketone	13.4	13.2	13.0	12.9
methyl isobutyl ketone	9.4	9.3	9.2	9.0
propanol	29.9	29.4	28.9	28.6
butanol	22.1	20.8	19.6	18.6
ethyl acetate	16.0	16.1	16.4	16.5
propyl acetate	13.1	12.7	12.3	11.9
butyl acetate	11	10.6	10.3	10.0
tetrahydrofuran	8.2	8.0	7.9	7.8
dibutyl ether	8.6	8.3	8.0	7.8
chlorobutane	8.7	8.4	8.1	7.8
chloropentane	7.8	7.5	7.2	7
tetrachloromethane	3.6	3.5	3.3	3.2
chloroform	4.4	4.4	4.4	4.4
propionitrile	46	46.1	46.1	46.2
butyronitrile	30.2	29.2	28.2	27.3

Table 9. Mass-Fraction Activity Coefficients at Infinite Dilution $[\Omega(\exp)^\infty]$ for COC 3 at (478, 488, 498, and 508) K in Various Organic Solvents

	$\Omega(\exp)^\infty$			
solvent	T/K = 478	T/K = 488	T/K = 498	T/K = 508
n-hexane	8.9	9.1	9.3	10.1
n-heptane	7.9	8.3	8.9	9.5
n-octane	7.0	7.8	8.6	9.5
1-hexene	8.4	8.6	8.8	
heptene	8.3	8.2	8.1	8
octene	8.4	7.9	7.6	7.1
cyclohexane	5.0	5.4	5.9	6.4
methylcyclohexane	5.3	5.7	6.1	6.6
ethylcyclohexane	4.3	4.5	4.7	5
benzene	5.6	5.4	5.4	5.3
toluene	4.8	4.7	4.7	4.8
ethylbenzene	3.9	4.2	4.6	5.0
methyl ethyl ketone	24.1	23.2	21.4	19.9
diethyl ketone	19	18.3	17.5	16.9
methyl isobutyl ketone	6.9	7.1	7.5	7.8
propanol	16	15.7	15.7	15.6
butanol	13.3	12.9	12.7	12.3
ethyl acetate	12	11.8	11.6	11.4
propyl acetate	9.2	9.2	9.0	9.1
butyl acetate	7.7	8.1	8.5	8.9
tetrahydrofuran	6.9	7.5	8.1	9.0
dibutyl ether	6.4	6.4	6.6	6.7
chlorobutane	6.6	7.2	7.9	8.6
chloropentane	5.7	6.1	6.4	7
tetrachloromethane	2.2	2.6	3.1	3.7
chloroform	3.5	3.6	3.7	3.8
propionitrile	46.5	42.8	39.8	37.1
butyronitrile	30.3	27.4	25.2	22.9

saturation pressures were calculated using the Antoine's equation, the second virial coefficients using the correlation of Hayden and O'Connell, and the liquid molar volumes using the correlation of Yen and Woods.[15]

■ RESULTS AND DISCUSSION

In the ICG technique, the retention mechanism of a solute in a polymer depends on the polymer state: a plot of the logarithm of the retention volume versus the reciprocal of the temperature is called a retention diagram, and in such a plot it is possible to observe the phase transitions of the investigated polymer. For a semicrystalline polymer,[16] three characteristic temperatures can be identified: the glass transition temperature (T_g), the softening temperature (T_s), and the melting temperature (T_m).

In the temperature range below T_g, diffusion of the solute in the polymer bulk phase is precluded, so the retention mechanism involves only surface adsorption. At T_g, solute penetration begins, and the retention volume increases with temperature. Below T_m, retention proceeds by bulk sorption, and the interactions between the polymer and the solute are restricted to the amorphous domains of the stationary phase. For temperatures above T_m, the behavior is linear, corresponding to bulk absorption in the totally amorphous polymer.

Retention diagrams were determined for all of the polymers studied in order to establish the correct range of temperatures to be investigated. A typical retention diagram is presented in Figure 1 for the polymer COC 4 with *n*-hexane as solute. The presence of the characteristic ζ behavior is evident, and the T_g and T_m values correspond approximately to the minimum and maximum, respectively. For each of the polymers, the temperatures chosen for the determination of the retention volume, which were suitable to give correct values of the activity coefficient, were always higher than the T_m value obtained from the retention diagram. In this way, the linearity of the plot of $\ln V_g^\circ$ versus $1/T$ was always satisfactory to better than $\pm$ 0.024 in $\ln V_g^\circ$, which gave an uncertainty of about 3 % in the activity coefficients.

In Tables 2 to 5, the natural logarithms of the retention volumes at different temperatures are reported.

The retention volumes were correlated using the Abraham solvation equation, and the parameters obtained for the different COCs are reported in Table 6 together with the corresponding average absolute deviations (AADs). The *e* and *l* parameters provided the main contributions to the retention volumes and were constant for all of the investigated polymers. In every case, a very small value of the *s* parameter was obtained, indicating that the dipole−dipole interactions of the polymers (constituted by a

Table 10. Mass-Fraction Activity Coefficients at Infinite Dilution [$\Omega(\mathrm{exp})^\infty$] for COC 4 at (383, 393, 403, and 413) K in Various Organic Solvents

	$\Omega(\mathrm{exp})^\infty$			
solvent	T/K = 383	T/K = 393	T/K = 403	T/K = 413
n-hexane	13.5	13.7	13.4	13.4
n-heptane	10.4	11.4	11.5	11.8
n-octane	9.3	9.9	10.1	10.2
1-hexene	11.5	12.1	12.7	13.1
heptene	10.0	10.5	11.2	11.1
octene	8.9	9.3	9.8	10.1
cyclohexane	6.6	6.7	6.8	7
methylcyclohexane	7.0	7.3	7.3	7.3
ethylcyclohexane	5.9	5.9	6.0	6.0
benzene	7.0	7.1	7.1	7.6
toluene	6.3	6.3	6.5	6.8
ethylbenzene	5.9	5.9	6.1	6.3
methyl ethyl ketone	30.1	33.6	35.0	36.7
diethyl ketone	16.0	17.1	17.6	17.7
methyl isobutyl ketone	7.2	7.9	8.3	8.8
propanol	49.2	52.5	54.1	54.5
butanol	36.2	36.5	36.9	36.1
ethyl acetate	11.9	12.7	13.4	14.2
propyl acetate	12.5	13.6	14.4	14.8
butyl acetate	11.5	12.3	12.5	12.4
tetrahydrofuran	8.5	8.5	8.7	9.5
dibutyl ether	8	7.9	8.3	8.6
chlorobutane	8.5	9.2	9.5	10
chloropentane	7.4	8.1	8.1	8.2
tetrachloromethane	3.5	3.6	3.6	3.6
chloroform	4.1	4.4	4.4	4.7
propionitrile	60.3	69.3	78.4	88.4
butyronitrile	38.6	41.5	44.1	47.1

paraffinic chain with olefinic rings) with the polarizable solutes are negligible. The values of the *a* and *b* parameters also had scarce influence on the retention properties.

Mass-fraction activity coefficients were calculated from the retention volumes using eq 4 and are reported in Tables 7 to 10. Nitriles and alcohols showed the largest values of the mass-fraction activity coefficients. Globally, the smallest values were those of the nonpolar or slightly polar solutes.

CONCLUSIONS

Activity coefficients at infinite dilution for common solvents in cyclic olefin copolymers characterized by different physicochemical properties have been measured at different temperatures. This work has highlighted the chemical properties of a series of COCs and demonstrated the difference in the behaviors of polar and nonpolar solvents. In order to compare the results obtained for COCs with those of polymers that are used for similar applications, literature data for polycarbonate have been utilized.[17,18] The interactions between polycarbonate and COCs with nonpolar solvents are similar, while some differences can be seen for polar solutes, particularly nitriles, ketones, and alcohols. These similarities in the behaviors justify the use of these polymers for similar utilizations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ireneo.kikic@dicamp.units.it.

REFERENCES

(1) Newman, R. D.; Prausnitz, J. M. Polymer−Solvent Interactions by Gas−Liquid Partition Chromatography. *J. Phys. Chem.* **1972**, *76*, 1492–1496.

(2) Alessi, P.; Cortesi, A.; Sacomani, P.; Vallés, E. Solvent−Polymer Interactions in Polybutadienes. *Macromolecules* **1993**, *26*, 6175–6179.

(3) Romdhane, I. H.; Danner, R. P. Polymer−solvent diffusion and equilibrium parameters by inverse gas−liquid chromatography. *AIChE J.* **1993**, *39*, 625–635.

(4) Davis, P. K.; Danner, R. P.; Duda, J. L.; Romdhane, I. H. Use of inverse gas chromatography to study binary polymer−solvent systems near the glass transition temperature. *Macromolecules* **2004**, *37*, 9201–9210.

(5) Zhao, C.; Li, J.; Jiang, Z.; Chen, C. Measurement of the infinite dilution coefficients of small molecule solvents in silicone rubber by inverse gas chromatography. *Eur. Polym. J.* **2006**, *42*, 615–624.

(6) Abraham, M. H. Application of solvation equations to chemical and biochemical processes. *Pure Appl. Chem.* **1993**, *65*, 2503–2512.

(7) Abraham, M. H.; Ibrahim, A.; Zissimos, A. M. Determination of sets of solute descriptors from chromatographic measurements. *J. Chromatogr., A* **2004**, *1037*, 29–47.

(8) Platts, J. A.; Butina, D.; Abraham, M. H.; Hersey, A. Estimation of Molecular Linear Free Energy Relationship Descriptors by a Group Contribution Approach. 2. Prediction of Partition Coefficients. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 71–80.

(9) *ADME Boxes*, version 2.2; Pharma Algorithms Inc.: Toronto, ON, 2002.

(10) Zissimos, A. M.; Abraham, M. H.; Klamt, A.; Eckert, F.; Wood, J. A Comparison between the Two General Sets of Linear Free Energy Descriptors of Abraham and Klamt. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 1320–1331.

(11) Abraham, M. H.; Poole, C. F.; Poole, S. K. Classification of stationary phases and other materials by gas chromatography. *J. Chromatogr., A* **1999**, *842*, 79–114.

(12) Abraham, M. H.; Du, C. M.; Osei-Owusu, J. P.; Sakellariou, P.; Shuely, W. J. On the Prediction of Polymer−Probe χ and Ω Values from Inverse Gas-Chromatographic Data. *Eur. Polym. J.* **1994**, *30*, 635–639.

(13) Abraham, M. H.; Balantine, D. S.; Callihan, B. K. Revised linear solvation energy relationship coefficients for the 77-phase McReynolds data set based on an updated set of solution descriptors. *J. Chromatogr., A* **2000**, *878*, 115–124.

(14) Van Noort, P. C. M.; Haftka, J. H.; Parsons, J. R. Updated Abraham Solvation Parameters for Polychlorinated Biphenyls. *Environ. Sci. Technol.* **2010**, *44*, 7037–7042.

(15) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2004.

(16) Braun, J. M.; Guillet, J. E. Study of Polymers by Inverse Gas Chromatography. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1976.

(17) Sadowski, G.; Mokrushina, L. V.; Arlt, W. Finite and infinite dilution activity coefficients in polycarbonate systems. *Fluid Phase Equilib.* **1997**, *139*, 391–403.

(18) Juhr, A.; Kuhlmann, C. Polycarbonate characterization. Master's Thesis, University of Berlin, 1993.