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Inverse Gas Chromatography. 7. Polymer–Solvent Interactions of Hydrocarbon Polymers

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Inverse gas chromatography has been used to generate a comprehensive set of interaction data for 9 hydrocarbon polymers and 43 solvents. The solvents cover a wide range of different chemical families, and the polymers possess increasing amounts of backbone substitution. For each polymer–solvent system, the specific retention volume, the Flory–Huggins interaction coefficient, χ_{12}, and the excess cohesive energy per unit volume, B_{12}, are presented.

Introduction

Inverse gas chromatography (IGC) has been used for the determination of polymer–solvent interaction coefficients since Guillet and co-workers, some 2 decades ago, introduced a method of data analysis based on the use of weight fraction activity coefficients (*1–3*). The IGC technique is relatively rapid, and when appropriate precautions are taken (*4*), it is rather precise. Yet, as far as we are aware, no systematic study has been made to measure the interaction coefficients of many solvents (probes) with a large number of polymers. Although a large number of studies have been made, for example, refs 5–13, there is little consistency between the experimental conditions or probes used, which makes the comparison of results difficult. A systematic study of numerous polymers and their interaction with a large number of probes would help clarify the relations between the chemical structure of the polymer and the probe and their interaction behavior. (Of course, the added advantage of such a comprehensive study is the internal consistency of the results.) This paper is intended as a first step in that direction.

Theory

By combination of standard chromatographic equations (*14*) with the Flory–Huggins theory of polymer solutions (*15*), extended to infinite dilution (*16*), the Flory–Huggins interaction coefficient χ_{12} may be obtained as

$$\chi_{12} = \ln\,(RTv_2/V_g p_1^{\circ} V_1) - 1 + V_1/M_2 v_2 - (B_{11} - V_1)p_1^{\circ}/RT \quad (1)$$

V_g is the specific retention volume of the probe, V_1 is its molar volume, and B_{11} and p_1° are the probe's second virial coefficient in the gas phase and the saturated vapor pressure of the pure probe, respectively. M_2 is the molecular weight of the polymer, and v_2 is its specific volume. R is the gas constant, and T is the temperature of the column. The specific retention volume is determined as

$$V_g = J(t_p - t_m)F/w \quad (2)$$

where w is the weight of the polymer on the column and F is the carrier gas flow rate at the column temperature and at the

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Table I. Physical Data of Polymers

	C28	C32	C36	PP1	PP2	HDMB	PEE	PIB	PVE
density ρ^{20}	0.807	0.812	0.817	0.865	0.855	0.874	0.872	0.914	0.890
density ρ^{100}	0.756	0.761	0.768	0.825	0.816	0.816	0.822	0.859	0.847
$d\rho/dT \times 10^4$	6.40	6.34	6.28			7.21	7.16		7.31
T_g, °C				−26	−26	−26	−4	−68	−30
T_m, °C	61–63	68–70	74–76						
molecular weight	395	451	507		2000				

Table II. Listing of Probes

code	probe	code	probe	code	probe	code	probe
NC3	propane	CC7	cycloheptane	BCL	butyl chloride	THF	tetrahydrofuran
NC4	butane	CC8	cyclooctane	PCL	pentyl chloride	DOX	dioxane
NC5	pentane	CHX	cyclohexene	CLH	chlorohexane	MAC	methyl acetate
NC6	hexane	CHD	cyclohexadiene	CLO	chlorooctane	EAC	ethyl acetate
NC7	heptane	BNZ	benzene	D11	1,1-dichloroethane	PAC	propyl acetate
NC8	octane	TOL	toluene	D12	1,2-dichloroethane	BAC	butyl acetate
NC9	nonane	EBZ	ethyl benzene	MCH	methylchloroform	EOH	ethanol
C10	decane	CL1	methyl chloride	TCE	trichloroethylene	POH	propanol
C11	undecane	CL2	methylene chloride	CLB	chlorobenzene	BOH	1-butanol
CC5	cyclopentane	CL3	chloroform	ACT	acetone	AOH	*n*-amyl alcohol
CC6	cyclohexane	CL4	carbon tetrachloride	MEK	methyl ethyl ketone		

Table III. Specific Retention Volume V_g of Probes at 100 °C

	V_g of various polymers								
code	C28	C32	C36	PP1	PP2	PEE	HDMB	PIB	PVE
NC3	3.96	3.79	3.76	2.76	2.90	2.80	2.38	1.84	2.54
NC4	9.88	9.40	9.10	6.76	7.12	6.66	5.99	4.76	6.37
NC5	22.20	21.57	20.60	14.60	15.73	14.48	13.57	10.54	13.87
NC6	49.22	47.63	45.24	31.68	33.91	30.51	29.12	22.35	29.09
NC7	106.56	102.56	97.18	66.66	71.27	62.77	61.37	46.64	60.17
NC8	228.13	218.57	206.55	138.40	148.50	128.21	127.16	96.02	122.20
NC9	484.92	462.75	435.68	284.15	305.80	259.25	260.85	195.99	246.24
C10	1029.17	981.95	917.36	581.30	629.51	521.44	531.74	397.83	494.37
C11	2166.66	2070.21	1923.79	1185.09	1280.35	1047.15	1090.20	805.33	987.64
CC5	39.46	38.81	37.34	27.92	29.52	27.93	27.15	21.71	28.05
CC6	86.55	84.68	81.24	60.22	64.16	59.63	58.62	45.08	57.92
CC7	243.10	238.84	229.64	165.15	176.38	162.08	164.89	128.61	157.71
CC8	609.06	598.97	576.54	405.52	433.99	394.46	410.95	319.88	381.90
CHX	94.13	92.22	88.33	64.60	68.88	63.93	63.54	49.66	68.63
CHD	82.87	81.87	78.28	55.71	59.30	55.57	55.75	42.68	64.91
BNZ	74.83	73.71	70.96	50.02	53.37	49.53	49.92	38.47	61.84
TOL	171.34	168.32	161.90	109.53	117.08	104.89	109.42	84.89	132.33
EBZ	336.12	330.33	315.65	209.61	224.91	199.88	208.82	161.11	249.85
CL1	5.47	5.21	5.18	3.92	4.24	4.04	3.77	3.13	5.22
CL2	20.65	20.39	19.39	15.25	16.33	15.42	15.07	12.36	21.81
CL3	44.94	44.31	42.49	32.20	34.52	32.50	31.99	25.34	42.63
CL4	77.84	76.18	73.16	52.78	56.20	53.97	53.38	40.44	58.40
BCL	60.36	58.94	56.24	42.16	45.14	40.84	40.56	31.95	48.13
PCL	131.90	128.73	122.79	88.80	95.28	85.21	85.91	67.69	100.75
CLH	281.95	274.91	262.73	183.54	197.62	175.16	178.20	142.17	208.05
CLO	1276.10	1237.43	1176.45	778.78	840.44	723.41	757.36	602.74	853.77
D11	32.10	31.53	30.00	22.91	24.64	23.13	22.61	17.89	29.66
D12	52.40	51.73	49.62	38.46	41.18	37.76	37.82	30.33	53.97
MCH	61.30	59.94	57.36	42.04	44.89	42.38	41.72	31.97	49.02
TCE	98.02	96.77	93.17	67.77	72.38	66.52	68.17	54.21	78.58
CLB	291.16	288.81	277.92	189.82	203.41	184.18	195.50	149.55	234.94
ACT	11.73	11.55	10.81	8.71	9.53	8.29	8.02	6.73	12.50
MEK	27.87	27.29	25.63	20.26	22.01	19.11	18.89	15.59	28.40
THF	45.90	45.09	43.15	33.86	36.48	32.98	33.20	27.71	43.69
DOX	71.43	69.70	66.80	52.70	56.54	49.36	51.27	43.45	75.88
MAC	15.83	15.30	14.48	11.60	12.69	10.84	10.57	8.97	17.46
EAC	29.98	28.94	27.31	21.34	22.97	20.16	19.65	16.13	31.55
PAC	64.69	62.55	58.79	45.05	48.71	42.41	41.22	33.19	64.88
BAC	140.11	135.04	127.43	95.17	103.37	88.44	87.21	70.17	132.53
EOH	7.54	6.78	6.58	4.99	6.06	4.12	3.72	3.40	7.22
POH	18.15	17.78	17.00	13.14	14.45	12.38	12.12	9.81	20.47
BOH	41.78	41.23	39.29	29.55	32.48	27.63	27.82	21.97	45.28
AOH	94.83	92.90	88.22	65.62	71.61	60.34	61.68	48.91	97.92

column outlet. t_p and t_m are the retention time of the probe and of the marker (a noninteracting probe), respectively. j is a correction factor to account for the compressibility of the gas and is given by (*17*)

$$j = (3/2)((P_i/P_o)^2 - 1)/((P_i/P_o)^3 - 1) \qquad (3)$$

where P_i is the column inlet pressure and P_o is the column outlet pressure.

It is common practice in the study of polymers to set the second from last term in eq 1 equal to unity because of the large size of M_2. However, if M_2 is low, then the term should be retained. The probe physical properties, B_{11}, V_1 and $p_1°$,

Table IV. Polymer–Solvent Interaction Coefficients χ_{12} at 100 °C

	χ_{12} of various polymers								
code	C28	C32	C36	PP1	PP2	PEE	HDMB	PIB	PVE
NC3	0.411	0.418	0.395	0.457	0.471	0.431	0.598	0.794	0.506
NC4	0.310	0.322	0.324	0.366	0.380	0.369	0.483	0.646	0.390
NC5	0.273	0.260	0.274	0.347	0.343	0.340	0.416	0.600	0.361
NC6	0.217	0.203	0.219	0.283	0.293	0.303	0.363	0.558	0.328
NC7	0.180	0.168	0.183	0.245	0.263	0.284	0.324	0.526	0.305
NC8	0.153	0.141	0.156	0.217	0.239	0.270	0.299	0.504	0.298
NC9	0.131	0.118	0.134	0.199	0.225	0.264	0.282	0.489	0.296
C10	0.112	0.096	0.112	0.181	0.213	0.260	0.268	0.481	0.296
C11	0.101	0.079	0.096	0.169	0.212	0.260	0.251	0.475	0.301
CC5	0.162	0.145	0.160	0.210	0.210	0.195	0.237	0.406	0.182
CC6	0.126	0.109	0.121	0.166	0.166	0.158	0.191	0.391	0.173
CC7	0.061	0.038	0.050	0.096	0.097	0.094	0.099	0.292	0.120
CC8	0.032	0.004	0.013	0.061	0.065	0.065	0.050	0.245	0.099
CHX	0.146	0.128	0.141	0.215	0.215	0.207	0.229	0.404	0.116
CHD	0.254	0.230	0.244	0.356	0.357	0.340	0.352	0.551	0.163
BNZ	0.388	0.367	0.378	0.510	0.503	0.501	0.508	0.698	0.257
TOL	0.293	0.271	0.279	0.426	0.425	0.447	0.423	0.603	0.194
EBZ	0.279	0.252	0.261	0.402	0.408	0.425	0.402	0.589	0.182
CL1	0.647	0.669	0.653	0.755	0.722	0.712	0.790	0.911	0.434
CL2	0.787	0.771	0.799	0.860	0.839	0.833	0.868	0.998	0.464
CL3	0.527	0.509	0.527	0.608	0.590	0.582	0.611	0.775	0.289
CL4	0.197	0.181	0.193	0.288	0.287	0.248	0.273	0.480	0.147
BCL	0.433	0.418	0.434	0.478	0.476	0.492	0.514	0.681	0.307
PCL	0.341	0.323	0.340	0.388	0.387	0.407	0.420	0.593	0.229
CLH	0.329	0.309	0.325	0.373	0.372	0.397	0.405	0.575	0.225
CLO	0.288	0.265	0.280	0.328	0.339	0.373	0.360	0.532	0.215
D11	0.633	0.617	0.640	0.697	0.681	0.670	0.707	0.871	0.401
D12	0.922	0.901	0.918	0.972	0.957	0.971	0.985	1.134	0.594
MCH	0.294	0.278	0.292	0.366	0.364	0.340	0.370	0.565	0.174
TCE	0.301	0.279	0.287	0.386	0.382	0.385	0.377	0.537	0.197
CLB	0.418	0.388	0.393	0.540	0.538	0.546	0.507	0.703	0.283
ACT	1.669	1.653	1.694	1.716	1.678	1.747	1.795	1.900	1.316
MEK	1.324	1.309	1.344	1.360	1.336	1.399	1.427	1.546	0.982
THF	0.519	0.502	0.520	0.553	0.534	0.561	0.569	0.679	0.258
DOX	1.105	1.095	1.112	1.146	1.131	1.190	1.170	1.262	0.739
MAC	1.323	1.324	1.354	1.370	1.335	1.420	1.460	1.553	0.923
EAC	1.105	1.101	1.130	1.142	1.131	1.179	1.221	1.346	0.711
PAC	0.938	0.929	0.958	0.963	0.956	1.001	1.048	1.191	0.556
BAC	0.824	0.813	0.835	0.840	0.836	0.888	0.924	1.065	0.465
EOH	2.792	2.869	2.874	2.988	2.843	3.177	3.277	3.319	2.597
POH	2.399	2.387	2.403	2.470	2.433	2.502	2.548	2.684	1.980
BOH	2.172	2.148	2.164	2.232	2.203	2.269	2.290	2.449	1.757
AOH	1.942	1.921	1.936	1.989	1.975	2.041	2.049	2.203	1.539

can be calculated or obtained from literature data (*18–24*). We have found it useful in our studies to express the polymer solvent interaction parameter in terms of excess density of cohesive energy, B_{12}, where B_{12} is related to χ_{12} as

$$B_{12} = \chi_{12}RT/V_1 \tag{4}$$

Experimental Section

IGC columns were prepared from 0.25-in.-o.d. copper tubing 150 cm long, which was cleaned with methanol and left overnight in an oven at 110 °C. The support used was 60–80 mesh Chromosorb-W (acid washed and treated with dichlorodimethylsilane). Polymer loadings were 7%, and the carrier gas was nitrogen at a flow rate of 16 mL/min. Samples of high linear alkanes were obtained from Aldrich Chemical Co. and used as supplied; atactic polypropylenes and polyisobutylene were obtained from Scientific Polymer Products Inc. Samples of hydrogenated poly(2,3-dimethyl-1,4-butadiene) and of poly(1,2-butadiene) and its hydrogenated counterpart were kindly provided by Dr. L. J. Fetters. Specific volumes ($v_2 = 1/\rho$) were calculated from the densities at 20 °C and from the expansion coefficients $d\rho/dT$, which were available from the literature, were estimated from several densities at different temperatures, or were determined from group contributions to molar volumes (*24–26*). Where corrections for the molecular weight were necessary, the values used are shown. The glass-transition temperatures, T_g, and values of melting point, T_m, are values either from the suppliers or from the literature. The relevant physical quantities are collected in Table I.

The IGC experiments were performed on a modified Perkin-Elmer Model 3920B gas chromatograph. The signal from the flame ionization detector was converted from analog to digital and processed on a microcomputer via an IEEE-488 board. Signal-to-noise ratios were 5 × 10^4 or better, and retention times were reproducible to ±0.1 s. During the data analysis, we have performed all the necessary corrections (for retention of marker, for retention by support) as described earlier (*4*).

Results

We have determined the polymer–solvent interaction coefficients for three linear alkanes, octacosane, dotriacontane, and hexatriacontane, designated as C28, C32, and C36, respectively (molecular weights were accounted for using the full form of eq 1); two atactic polypropylenes, PP1 and PP2 (the low molecular weight of sample PP2 was accounted for); polyisobutylene, PIB; hydrogenated poly(2,3-dimethyl-1,4-butadiene) (which is more easily thought of as head-to-head polypropylene), HDMB; poly(1,2-butadiene) (which may be considered as poly(vinylethylene)), PVE; and hydrogenated poly(1,2-butadiene) (which may be considered as poly(ethylethylene)), PEE. For each polymer, 43 probes of several different chemical families were measured. Here, we present the specific retention vol-

Table V. Polymer–Solvent Interaction Coefficients B_{12} at 100 °C

	B_{12} for various polymers								
code	C28	C32	C36	PP1	PP2	PEE	HDMB	PIB	PVE
NC3	2.59	2.63	2.49	2.88	2.97	2.71	3.77	5.00	3.19
NC4	1.88	1.95	1.97	2.23	2.31	2.24	2.93	3.93	2.37
NC5	1.52	1.45	1.52	1.93	1.91	1.89	2.32	3.34	2.01
NC6	1.09	1.02	1.10	1.42	1.47	1.52	1.82	2.80	1.65
NC7	0.82	0.76	0.83	1.11	1.19	1.29	1.47	2.39	1.39
NC8	0.63	0.58	0.64	0.90	0.99	1.12	1.23	2.09	1.23
NC9	0.50	0.45	0.51	0.75	0.85	1.00	1.07	1.86	1.12
C10	0.39	0.34	0.39	0.63	0.74	0.91	0.93	1.68	1.03
C11	0.33	0.26	0.31	0.55	0.69	0.84	0.81	1.54	0.97
CC5	1.13	1.01	1.12	1.47	1.47	1.37	1.66	2.84	1.27
CC6	0.78	0.67	0.75	1.02	1.03	0.97	1.18	2.41	1.07
CC7	0.34	0.21	0.28	0.54	0.54	0.53	0.55	1.63	0.67
CC8	0.16	0.02	0.07	0.31	0.33	0.33	0.26	1.25	0.50
CHX	0.96	0.84	0.93	1.42	1.42	1.37	1.51	2.66	0.76
CHD	1.78	1.62	1.72	2.51	2.51	2.40	2.48	3.88	1.15
BNZ	2.91	2.76	2.84	3.83	3.78	3.76	3.81	5.24	1.93
TOL	1.87	1.72	1.77	2.71	2.71	2.85	2.69	3.84	1.24
EBZ	1.55	1.40	1.45	2.23	2.27	2.37	2.24	3.28	1.01
CL1	6.86	7.10	6.92	8.00	7.66	7.54	8.38	9.66	4.60
CL2	8.03	7.86	8.15	8.77	8.55	8.50	8.85	10.18	4.74
CL3	4.65	4.50	4.65	5.37	5.21	5.15	5.39	6.85	2.55
CL4	1.36	1.25	1.33	1.99	1.98	1.71	1.89	3.32	1.02
BCL	2.77	2.67	2.78	3.06	3.04	3.14	3.28	4.35	1.96
PCL	1.90	1.80	1.89	2.16	2.15	2.27	2.34	3.31	1.28
CLH	1.63	1.53	1.60	1.84	1.84	1.96	2.00	2.84	1.11
CLO	1.16	1.06	1.12	1.32	1.36	1.50	1.45	2.14	0.86
D11	4.95	4.82	5.01	5.45	5.32	5.25	5.53	6.81	3.14
D12	7.82	7.65	7.79	8.25	8.12	8.25	8.36	9.63	5.04
MCH	1.96	1.85	1.95	2.44	2.42	2.27	2.47	3.77	1.16
TCE	2.24	2.08	2.14	2.88	2.84	2.87	2.80	4.00	1.47
CLB	2.80	2.60	2.63	3.61	3.60	3.66	3.40	4.71	1.89
ACT	14.84	14.70	15.07	15.26	14.92	15.55	15.96	16.90	11.71
MEK	9.82	9.71	9.97	10.09	9.91	10.39	10.58	11.48	7.29
THF	4.13	4.00	4.14	4.40	4.25	4.47	4.53	5.41	2.06
DOX	9.16	9.08	9.22	9.50	9.37	9.87	9.70	10.47	6.13
MAC	10.88	10.89	11.13	11.27	10.97	11.68	12.00	12.77	7.59
EAC	7.43	7.41	7.60	7.68	7.60	7.93	8.21	9.06	4.79
PAC	5.43	5.37	5.54	5.57	5.53	5.79	6.07	6.89	3.22
BAC	4.20	4.14	4.26	4.28	4.26	4.53	4.71	5.44	2.38
EOH	32.10	33.00	33.06	34.36	32.68	36.57	37.68	38.19	29.89
POH	21.66	21.56	21.71	22.31	21.96	22.63	23.01	24.27	17.90
BOH	16.13	15.95	16.08	16.58	16.36	16.87	17.01	18.20	13.06
AOH	12.22	12.09	12.19	12.51	12.42	12.86	12.89	13.87	9.69

umes, V_g, the Flory–Huggins interaction coefficients, χ_{12}, and the excess cohesive energies per unit volume, B_{12}. All measurements were performed at 100 °C.

In Table II we have listed the probes used in this study. The three-letter code before the probe name identifies the probe in the data tables that follow. Table III contains the specific retention volumes (mL/g) of the probes for each of the polymers, Table IV contains the polymer–solvent interaction parameters χ_{12}, and Table V contains the excess cohesive energy densities B_{12} (cal/mL).

Conclusion

(1) The large number of polymers and solvents used in this study produced an extensive set of data, which should aid in the understanding of the interactions between polymers and solvents based on their chemical structure. We are currently in the process of developing a theoretical model of intermolecular interactions that would account for our results.

(2) The extent of the data shows the usefulness of the IGC technique for gathering rather rapidly (relative to other available techniques) large volumes of data.

(3) Further systems containing polar polymers will be required to establish a complete set of data for the full thermodynamic analysis.

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List of Symbols

B_{11}	virial coefficient of the probe in the gas phase
B_{12}	polymer–probe interaction coefficient (cal/mL)
F	carrier gas flow rate at the column outlet
j	correction factor for compressibility
M_2	molecular weight of polymer
P_i	pressure at column inlet
P_o	pressure at column outlet
p_1^o	saturated vapor pressure of the probe
R	gas constant
T	absolute temperature
t_m	retention time of the marker
t_p	retention time of the probe
V_g	specific retention volume of the probe at the column temperature
V_1	molar volume of the probe
v_2	specific volume of the polymer

w mass of the polymer on the column
ρ density of the polymer
χ_{12} Flory-Huggins interaction parameter

Registry No. C28, 630-02-4; C32, 544-85-4; C36, 630-06-8; PPI, 9003-07-0; PIB, 9003-27-4; PVE, 9003-17-2; NC3, 74-98-6; NC4, 106-97-8; NC5, 109-66-0; NC6, 110-54-3; NC7, 142-82-5; NC8, 111-65-9; NC9, 111-84-2; C10, 124-18-5; C11, 1120-21-4; CC5, 287-92-3; CC6, 110-82-7; CC7, 291-64-5; CC8, 292-64-8; CHX, 110-83-8; CHD, 29797-09-9; BNZ, 71-43-2; TOL, 108-88-3; EBZ, 100-41-4; CL1, 74-87-3; CL2, 75-09-2; CL3, 67-66-3; CL4, 56-23-5; BCL, 109-69-3; PCL, 543-59-9; CLH, 25495-90-3; CLO, 57214-71-8; D11, 75-34-3; D12, 107-06-2; MCH, 71-55-6; TCE, 79-01-6; CLB, 108-90-7; ACT, 67-64-1; MEK, 78-93-3; THF, 109-99-9; DOX, 123-91-1; MAC, 79-20-9; EAC, 141-78-6; PAC, 109-60-4; BAC, 123-86-4; EOH, 64-17-5; POH, 71-23-8; BOH, 71-36-3; AOH, 71-41-0.

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Excess Volumes of Binary and Ternary Mixtures of Water, Methanol, and Ethylene Glycol

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The excess molar volumes of mixtures of water + methanol, water + ethylene glycol, methanol + ethylene glycol, and water + methanol + ethylene glycol have been measured at 283.15, 293.15, and 303 .15 K by using a vibrating tube densimeter. The excess volumes are all negative over the entire composition range.

Introduction

Polyester polymer is produced commercially in a two-step polymerization process, i.e., monomer formation by ester interchange of DMT (dimethyl terephthalate) with glycol or esterification of TA (terephthalic acid) with glycol, followed by polycondensation by removing excess glycol. In the DMT or TA process, methanol and water are produced as byproducts. However, the volumetric properties are very limited even for the binary mixtures composed of water, methanol, and ethylene glycol: water + methanol (*1-3*), water + ethylene glycol (*4*), and methanol + ethylene glycol (*5*). No experimental excess volume data for a ternary system, water + methanol + ethylene glycol, have been reported in the literature.

Table I. Densities ρ of Pure Substances at 283.15, 293.15, and 303.15 K

		$\rho/(\mathrm{g\ cm^{-3}})$	
substances	T/K	this work	lit.
methanol	283.15	0.800 266	0.800 7[a]
	293.15	0.790 004	0.791 29[a]
	303.15	0.782 374	0.781 96[a]
ethylene glycol	283.15	1.119 292	1.120 6[b]
	293.15	1.112 020	1.113 5[b]
	303.15	1.105 825	1.106 35[b]

[a] Reference 6. [b] Reference 7.

The purpose of this investigation is therefore to measure the excess volumes for three binary systems and one ternary system formed by water, methanol, and ethylene glycol at 283.15, 293.15, and 303.15 K.

Experimental Section

The methanol and ethylene glycol were supplied by Aldrich (purity better than 99%) and stored over Linde Type 3A mo-