Measurement of Activity Coefficients at Infinite Dilution Using Gas-Liquid Chromatography. 4. Results for Alkylene Glycol Dialkyl Ethers as Stationary Phases

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Because of their properties, alkylene glycol dialkyl ethers are often used as scrubbing liquids. Activity coefficients at infinite dilution (Henry coefficients) are reported for 45 substances (hydrocarbons, halocarbons, esters, nitriles, aldehydes, ethers, furan, pyridine, and water) in 5 alkylene glycol dialkyl ethers (tetraethylene glycol dimethyl ether, tripropylene glycol dimethyl ether, diethylene glycol dibutyl ether, triethylene glycol dibutyl ether, and tripropylene glycol dibutyl ether) in the temperature range between 303 and 343 K. These values were measured with the use of gas-liquid chromatography.

Introduction

In chemical processes solvents are used for multiple purposes. Various techniques for the removal and recycling of components (e.g., solvents) from the resulting air and waste gas streams are available (*1*, *2*).

Solvents may be recovered from air or gas streams more or less completely by scrubbing with a suitable liquid (absorption). The values of the Henry coefficients, H_{ij}, and the activity coefficients at infinite dilution γ_i^∞, of the substances in the scrubbing liquid are required for the selection of the scrubbing liquid and the design of the absorption process.

Among the suggested scrubbing liquids (e.g., silicon oils, dialkyl phthalates, glycol ethers, ...) alkylene glycol dialkyl ethers are especially suitable because of their favorable properties such as low vapor pressure, low toxicity, low viscosity, high chemical stability, and low melting point (*3*). In glycol ethers the Henry coefficients and the activity coefficients at infinite dilution are not only influenced by the number and type of the monomers (ethylene oxide, propylene oxide) but also by the length of the alkyl chains.

In a systematic investigation we have measured activity coefficients at infinite dilution (Henry coefficients) for 45 substances in five different glycol ethers to obtain quantitative information about the influence of the number and type of monomers and alkyl residues.

The results of this work allow the selection of the most suitable glycol ether for a given separation problem and the reliable design of the separation process (absorber, desorber).

Selection of the Experimental Technique for the Measurement of the Activity Coefficient at Infinite Dilution

Different techniques (*4*, *5*) can be applied for the measurement of γ^∞ values (Henry coefficients) of organic substances or water in alkylene glycol dialkyl ethers, e.g., static methods, dilutor technique, and gas-liquid chromatography (GLC).

The measurement of γ^∞ values with a static apparatus (isothermal P-x data) delivers reliable data. However, the static method is not suitable, because the measurement of a great quantity of values (different temperatures, different substances, and various glycol ethers) would involve a tremendous and time-consuming experimental effort for a systematic study.

The measurement using headspace gas chromatography (also a static principle, resulting in isothermal x-y data), already used for systems with similar boiling components (*6*), causes great analytical problems and requires considerable calibration efforts when—as in our case—the components show great vapor pressure differences. Another problem in the use of headspace gas chromatography, especially for the systems investigated in this paper, arises from condensation occurring during sampling. In comparison to GLC measurements using the dilutor technique is much more time consuming.

Gas-liquid chromatography (GLC) was therefore chosen as the most preferable measuring method for the planned investigations. This technique requires the careful preparation of the column and allows the measurement of a great number of γ^∞ values in a rather short time; the reliability of γ^∞ measurements obtained with the help of gas-liquid chromatography has already been demonstrated in a large number of investigations (see e.g. ref 4).

Measurement Procedure

The solid support used for all stationary phases (scrubbing liquids) was Chromosorb P-AW-DMCS (60-80 mesh). The coating of the predried carrier material with the glycol ether was carried out with methanol (solubilizer) in a rotary evaporator. After removal of the solubilizer, the column (length ca. 20 cm, inner diameter 4.1 mm) was carefully filled with the coated solid support and the liquid loading (glycol ethers) was determined gravimetrically. The apparatus used in these investigations was developed in our laboratory. The exact construction of the homemade gas chromatograph, the measurement procedure, the most important equations, and the theoretical background are given in more detail in ref 8. The following five different glycol ethers were examined: $CH_3(OCH_2CH_2)_4OCH_3$ (tetraethylene glycol dimethyl ether), $CH_3(OCH_2CHCH_3)_3OCH_3$ (tripropylene glycol dimethyl ether), $CH_3(CH_2)_3(OCH_2CH_2)_2O(CH_2)_3CH_3$ (diethylene glycol dibutyl ether), $CH_3(CH_2)_3(OCH_2CH_2)_3O(CH_2)_3CH_3$ (triethylene glycol dibutyl ether), $CH_3(CH_2)_3(OCH_2CHCH_3)_3O(CH_2)_3CH_3$ (tripropylene glycol dibutyl ether).

In all cases the purities of the glycol ethers were better than 99.6% (GLC analysis of peak areas, temperature 200 °C, detector FID). Results for 45 different substances (hydrocarbons, alcohols, ketones, chloroaromatics, chloroalkanes, chlorofluoroalkanes, esters, aldehydes, ethers, nitriles, furan, pyridine, and water) were obtained over a temperature range between 303 and 343 K. Since in the case of GLC the

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Table I. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent Tetraethylene Glycol Dimethyl Ether as a Function of Temperature T

solute i	γ_i^∞ 303.15 K	323.15 K	343.15 K	solute i	γ_i^∞ 303.15 K	323.15 K	343.15 K
n-pentane	3.475	3.098	2.779	1,1,2-trichlorotrifluoroethane	1.905[b]	1.817	1.796[f]
n-hexane	4.045	3.593	3.195	1,1,1-trichlorotrifluoroethane[g]	1.652[a]	1.778	1.931
n-heptane	4.785	4.285	3.663	1,2-dichloroethane	0.316	0.380	0.435
cyclohexane	2.745[a]	2.494	2.223	trichlorethylene	0.530	0.573	0.653
methanol	0.942	0.873	0.800	1-chlorobutane	1.066	1.053	1.104
ethanol	1.186	1.137	1.019	methyl formate	0.603	0.641	0.721
2-propanol	1.396	1.241	1.098	methyl acetate		0.766	0.757
isobutanol	1.132	1.027	0.954	ethyl acetate	0.888[b]	0.864	0.858
2-propen-1-ol	0.589	0.645	0.645	*n*-propyl acetate	0.975	0.959	
acetone		0.848	0.830	*n*-butyl acetate	1.051	1.035	1.014
2-butanone	0.859[a]	0.846	0.836	methyl acrylate	0.695	0.723	0.758
benzene	0.694	0.712	0.741[f]	acetonitrile	0.556	0.627	0.667
toluene	0.848[d]	0.858	0.891	acetaldehyde	0.691	0.701	0.713
o-xylene	1.023			isobutyraldehyde	0.891	0.906	0.914
m-xylene	1.080	1.046		diethyl ether	1.461[b]	1.365	1.298
p-xylene	1.183	1.099	1.065	diisopropyl ether	2.170	2.097	2.059
styrene	0.630[a]	0.702[e]	0.728	methyl *tert*-butyl ether	1.520[a]	1.462	1.395
chlorobenzene	0.594[c]	0.624[e]	0.661	tetrahydrofuran	0.804[a]	0.777	0.754[f]
dichloromethane	0.197	0.251	0.304	furan	0.410	0.465	0.566
chloroform	0.157	0.200	0.262	1,4-dioxane	0.742[a]	0.754	0.765[f]
tetrachloromethane	0.818	0.846	0.931	pyridine	0.524	0.536	0.569
trichlorofluoromethane	1.121[a]		1.122	water[h]	1.848[d]	1.686	1.562
1,1,1-trichloroethane	0.721	0.743	0.785[f]				

[a] Exact temperature T = 304.55 K. [b] Exact temperature T = 306.05 K. [c] Exact temperature T = 313.15 K. [d] Exact temperature T = 313.45 K. [e] Exact temperature T = 327.55 K. [f] Exact temperature T = 343.45 K. [g] Calculation with saturation fugacity coefficient φ_i^s = 1. [h] After correction of the observed adsorption effects (*9*).

Table II. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent Tripropylene Glycol Dimethyl Ether as a Function of Temperature T

solute i	γ_i^∞ 303.15 K	323.15 K	343.15 K	solute i	γ_i^∞ 303.15 K	323.15 K	343.15 K
n-pentane	1.535	1.485	1.397	1,1,2-trichlorotrifluoroethane	1.101	1.093	1.090
n-hexane	1.681	1.606	1.482	1,1,1-trichlorotrifluoroethane[a]	0.997	1.070	1.221
n-heptane	1.846	1.738	1.591	1,2-dichloroethane	0.460	0.509	0.529
cyclohexane	1.361	1.287	1.197	trichlorethylene	0.480	0.518	0.559
methanol	1.402	1.352	1.230	1-chlorobutane	0.774	0.794	0.809
ethanol	1.559	1.442	1.275	methyl formate	0.839	0.844	0.848
2-propanol	1.591	1.460	1.253	methyl acetate		0.849	0.848
isobutanol	1.166	1.137	1.030	ethyl acetate	0.840	0.831	0.820
2-propen-1-ol	0.842	0.936	0.922	*n*-propyl acetate		0.909	0.862
acetone	1.082	1.046	0.991	*n*-butyl acetate		0.876	0.864
2-butanone	0.995	0.963	0.926	methyl acrylate	0.777	0.846	0.820
benzene	0.646	0.666	0.669	acetonitrile	1.236	1.268	1.281
toluene	0.753	0.758	0.763	acetaldehyde		0.938	0.960
o-xylene	0.853	0.901		isobutyraldehyde		0.950	0.896
m-xylene	0.863	0.903		diethyl ether	0.887	0.901	0.911
p-xylene	0.851	0.889		diisopropyl ether		1.174	1.132
styrene	0.651	0.710	0.732	methyl *tert*-butyl ether		0.953	0.931
chlorobenzene	0.601	0.651	0.669	tetrahydrofuran		0.673	0.666
dichloromethane	0.273	0.320	0.361	furan	0.483	0.510	0.534
chloroform	0.187	0.237	0.276	1,4-dioxane		0.857	0.818
tetrachloromethane	0.662	0.694	0.703	pyridine	0.660	0.697	0.693
trichlorofluoromethane	0.773	0.784	0.819	water[b]	4.192	3.857	3.031
1,1,1-trichloroethane	0.602	0.638	0.663				

[a] Calculation with saturation fugacity coefficient φ_i^s = 1. [b] After correction of the observed adsorption effects (*9*).

results are not influenced by impurities, commercially available substances were used for the investigations without further purification.

The determination of γ^∞ requires the following information: the net retention time of the solvent, the measuring temperature, column inlet and outlet pressures, the carrier gas flow rate, and the mass of the glycol ether on the carrier material. The net retention time is obtained between the difference of the retention time of the solvent (solvent peak) and the dead time (air peak). The net retention time is a measure of the probability of finding the solvent in the gas (mobile) phase. This probability is determined directly by the phase equilibrium behavior.

The liquid loading of the stationary phase (15–30%) and the sample volumes of the injected substances (0.02–0.5 μL) were varied in order to be able to detect adsorption effects; only in the case of water were these detectable. The method proposed by Jönsson and Mathiasson (*9*) was used to account for the retention caused by adsorption and to obtain the corrected γ^∞ values (based on distribution between the liquid and the vapor phase).

Results and Discussion

Tables I–V contain the results for the five glycol ethers at three different temperatures (303.15, 323.15, and 343.15 K). Because of combinatorial contributions and multifunctional

Table III. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent Triethylene Glycol Dibutyl Ether as a Function of Temperature T

	γ_i^∞				γ_i^∞		
solute i	303.15 K	323.15 K	343.15 K	solute i	303.15 K	323.15 K	343.15 K
n-pentane	1.308	1.218	1.139	1,1,2-trichlorotrifluoroethane	1.029	1.026	0.991
n-hexane	1.412	1.315	1.233	1,1,1-trichlorotrifluoroethane[a]	0.937	1.028	1.105
n-heptane	1.546	1.418	1.322	1,2-dichloroethane	0.368	0.411	0.437
cyclohexane	1.101	1.023	0.956	trichlorethylene	0.392		0.437
methanol	1.392	1.255	1.173	1-chlorobutane	0.702	0.709	0.676
ethanol	1.561	1.364	1.233	methyl formate	0.819	0.787	0.768
2-propanol	1.639	1.411	1.227	methyl acetate	0.847	0.836	0.787
isobutanol	1.177	1.104	0.989	ethyl acetate	0.834	0.828	0.786
2-propen-1-ol	0.842	0.902	0.853	*n*-propyl acetate	0.860	0.844	0.787
acetone	1.040	0.991	0.948	*n*-butyl acetate		0.860	0.784
2-butanone	0.946	0.914	0.881	methyl acrylate	0.753	0.777	0.742
benzene	0.538	0.540	0.545	acetonitrile	1.101		1.115
toluene	0.607	0.608	0.613	acetaldehyde	0.915		
o-xylene	0.698	0.714		isobutyraldehyde	0.880	0.868	
m-xylene	0.701	0.699		diethyl ether	0.832	0.805	0.768
p-xylene	0.697	0.714		diisopropyl ether	1.096	1.071	1.015
styrene	0.500		0.569	methyl *tert*-butyl ether	0.879	0.846	0.828
chlorobenzene	0.473	0.506	0.510	tetrahydrofuran	0.601	0.594	0.579
dichloromethane	0.239	0.253	0.275	furan	0.434	0.446	0.455
chloroform	0.156	0.197	0.233	1,4-dioxane	0.757	0.743	0.708
tetrachloromethane	0.543		0.575	pyridine	0.616	0.626	
trichlorofluoromethane	0.682		0.685	water[b]	3.964	3.588	3.160
1,1,1-trichloroethane	0.514	0.533	0.548				

[a] Calculation with saturation fugacity coefficient $\varphi_i^s = 1$. [b] After correction of the observed adsorption effects (*9*).

Table IV. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent Diethylene Glycol Dibutyl Ether as a Function of Temperature T

	γ_i^∞				γ_i^∞		
solute i	303.15 K	323.15 K	343.15 K	solute i	303.15 K	323.15 K	343.15 K
n-pentane	1.260	1.214	1.142	1,1,2-trichlorotrifluoroethane	1.079	1.042	1.037
n-hexane	1.354	1.280	1.190	1,1,1-trichlorotrifluoroethane[a]	0.988	1.026	1.155
n-heptane	1.454	1.351	1.259	1,2-dichloroethane	0.482	0.518	0.537
cyclohexane	1.091	1.029	0.961	trichlorethylene	0.456	0.478	0.508
methanol	1.757	1.658	1.510	1-chlorobutane	0.765	0.746	0.743
ethanol	1.910	1.715	1.506	methyl formate	1.028	0.997	0.945
2-propanol	1.907	1.693	1.442	methyl acetate	1.004	0.956	0.936
isobutanol	1.387	1.322	1.181	ethyl acetate	0.950	0.916	0.903
2-propen-1-ol	1.086	1.153	1.121	*n*-propyl acetate	0.967	0.921	0.895
acetone	1.242	1.188	1.106	*n*-butyl acetate	0.949	0.916	0.880
2-butanone	1.100	1.064	1.010	methyl acrylate	0.919	0.880	0.872
benzene	0.615	0.620	0.626	acetonitrile	1.549	1.566	
toluene	0.675		0.694	acetaldehyde	1.143	1.070	1.035
o-xylene	0.747	0.778		isobutyraldehyde	1.004	0.972	0.938
m-xylene	0.760	0.786		diethyl ether	0.854	0.826	0.841
p-xylene	0.762	0.773		diisopropyl ether	1.095		1.024
styrene	0.596	0.657	0.683	methyl *tert*-butyl ether	0.885	0.870	0.862
chlorobenzene	0.563		0.611	tetrahydrofuran	0.659	0.655	0.639
dichloromethane	0.277	0.318	0.352	furan	0.525	0.537	0.549
chloroform	0.194	0.238	0.274	1,4-dioxane	0.916	0.910	0.848
tetrachloromethane	0.596	0.614	0.618	pyridine	0.631	0.685	0.706
trichlorofluoromethane	0.729		0.759	water[b]	5.428	4.847	4.303
1,1,1-trichloroethane	0.589	0.596	0.606				

[a] Calculation with saturation fugacity coefficient $\varphi_i^s = 1$. [b] After correction of the observed adsorption effects (*9*).

interactions, negative deviations from Raoults law are often obtained. This behavior can be confirmed from actual experience with glycol ethers in absorption and desorption processes in chemical industry. While negative deviations from Raoults law are desirable for the absorption step, they are very disadvantageous for the regeneration of the scrubbing liquid.

The required saturation fugacity was calculated with the help of the Soave–Redlich–Kwong equation of state and the Antoine equation; the necessary pure component properties were taken from the Dortmund Data Bank DDB (*10*). The vapor pressures P_i^s and the calculated saturation fugacity coefficients φ_i^s used for the evaluation are given in Tables VI and VII. This information, together with the γ^∞ values given in Tables I–V, allows us to calculate the Henry coefficients H_{ij} from the following simplified relation (*11*):

$$H_{ij} \approx \gamma_i^\infty \varphi_i^s P_i^s \qquad (1)$$

Following ref 8 an error of 3% is realistic for the presented systems, while in fact the reproducibility of the data was much better (ca. 1%). The results (in particular the data for water and the different alkanes) clearly show the increase of the hydrophobic character, when ethylene oxide fragments are substituted by propylene oxide fragments and butyl ethers are used instead of the methyl ethers. Thus, the activity coefficients at infinite dilution and the Henry coefficients for the alkanes (*n*-pentane (Figure 1), *n*-hexane, and *n*-heptane) are a factor of 4 smaller in the case of tripropylene glycol dibutyl ether compared with the values for tetraethylene glycol

Table V. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent Tripropylene Glycol Dibutyl Ether as a Function of Temperature T

solute i	γ_i^∞ 303.15 K	323.15 K	343.15 K	solute i	γ_i^∞ 303.15 K	323.15 K	343.15 K
n-pentane	0.875	0.860	0.843	1,1,2-trichlorotrifluoroethane	0.831	0.818	0.813
n-hexane	0.929	0.906	0.884	1,1,1-trichlorotrifluoroethane[a]	0.760	0.803	0.907
n-heptane	1.017	0.967	0.942	1,2-dichloroethane	0.550	0.561	0.572
cyclohexane	0.766	0.739	0.722	trichlorethylene	0.419	0.441	0.461
methanol	1.775	1.643	1.466	1-chlorobutane	0.647	0.642	0.648
ethanol	1.978	1.742	1.520	methyl formate	1.010	0.985	0.926
2-propanol	2.030	1.762	1.496	methyl acetate	0.934	0.908	0.856
isobutanol	1.409	1.313	1.179	ethyl acetate	0.863	0.859	0.821
2-propen-1-ol	1.150	1.245	1.153	*n*-propyl acetate	0.859	0.857	0.843
acetone	1.262	1.181	1.112	*n*-butyl acetate	0.837		0.805
2-butanone	1.066	1.023	0.977	methyl acrylate	0.847	0.859	0.822
benzene	0.540	0.540	0.543	acetonitrile	2.052	1.943	1.828
toluene	0.587	0.593	0.603	acetaldehyde		1.149	1.067
o-xylene	0.659	0.662	0.671	isobutyraldehyde	0.935	0.900	0.893
m-xylene	0.628	0.665	0.666	diethyl ether		0.682	0.674
p-xylene	0.615	0.652	0.658	diisopropyl ether	0.823	0.817	0.810
styrene	0.539	0.604	0.623	methyl *tert*-butyl ether		0.701	0.693
chlorobenzene	0.544	0.561	0.586	tetrahydrofuran		0.546	0.543
dichloromethane	0.300	0.336	0.363	furan	0.471	0.490	0.493
chloroform	0.201	0.239	0.279	1,4-dioxane	0.828	0.824	0.785
tetrachloromethane	0.508	0.517	0.532	pyridine	0.690	0.689	0.677
trichlorofluoromethane		0.585	0.588	water[b]	6.705	5.552	4.455
1,1,1-trichloroethane	0.517	0.528	0.540				

[a] Calculation with saturation fugacity coefficient $\varphi_i^s = 1$. [b] After correction of the observed adsorption effects (*9*).

Table VI. Vapor Pressures P_i^s, kPa, as a Function of Temperature T Used To Calculate the Activity Coefficients Given in Tables I–V

solute i	P_i^s, kPa 303.15 K	323.15 K	343.15 K	solute i	P_i^s, kPa 303.15 K	323.15 K	343.15 K
n-pentane	82.03	159.5	283.9	1,1,2-trichlorotrifluoroethane	54.13	110.0	203.1
n-hexane	24.95	54.04	105.4	1,1,1-trichlorotrifluoroethane	58.87	109.5	174.0
n-heptane	78.05	18.92	40.53	1,2-dichloroethane	13.31	31.07	64.62
cyclohexane	16.23	36.25	72.55	trichlorethylene	11.75	27.97	58.37
methanol	21.86	55.54	125.1	1-chlorobutane	17.03	38.38	77.26
ethanol	10.46	29.49	72.30	methyl formate	93.85	191.6	356.7
2-propanol	7.770	22.93	59.19	methyl acetate	35.85	79.12	156.5
isobutanol	2.276	7.342	20.36	ethyl acetate	16.01	37.96	79.83
2-propen-1-ol	4.872	13.26	33.09	*n*-propyl acetate	5.669	14.82	33.92
acetone	38.01	81.90	159.3	*n*-butyl acetate	2.019	5.829	14.42
2-butanone	15.22	35.54	73.85	methyl acrylate	14.63	34.21	71.74
benzene	15.91	36.18	73.46	acetonitrile	15.16	34.07	69.21
toluene	4.887	12.28	27.17	acetaldehyde	143.4	274.2	481.6
o-xylene	1.182	3.399	8.424	isobutyraldehyde	28.53	62.30	122.3
m-xylene	1.473	4.152	10.12	diethyl ether	85.93	170.3	308.1
p-xylene	1.551	4.337	10.50	diisopropyl ether	24.78	54.31	106.8
styrene	1.249	3.420	8.250	methyl *tert*-butyl ether	40.88	84.91	160.6
chlorobenzene	2.101	5.628	13.22	tetrahydrofuran	26.81	58.61	115.3
dichloromethane	70.64	144.1	267.4	furan	96.42	190.8	344.5
chloroform	32.33	69.26	133.9	1,4-dioxane	6.391	15.91	35.22
tetrachloromethane	18.94	41.62	82.25	pyridine	3.616	9.583	22.15
trichlorofluoromethane	126.6	237.8	411.7	water	4.232	12.31	31.09
1,1,1-trichloroethane	20.63	45.22	89.17				

dimethyl ether, the γ^∞ values for the different *n*-alkanes increasing with the number of carbon atoms in the hydrocarbon chain. However, this does not mean that at the same time the Henry coefficients are also larger, because to a first approximation Henry coefficients are the product of γ^∞ and the saturation vapor pressure (see also eq 1).

The behavior of polar components such as methanol, ethanol, propanol, and water was exactly opposite. Thus, for the polar component water a γ^∞ value of 1.68 in tetraethylene glycol dimethyl ether at 323 K was obtained, while a value of 5.53 was measured in tripropylene glycol dibutyl ether (Figure 2).

In the case of aromatic compounds or other compounds such as ethers, ketones, etc. the dependence on the type of glycol ether used is less strongly pronounced.

The choice of the best temperature for the absorption and desorption processes also requires the knowledge of the temperature dependence of the Henry coefficients (γ^∞ values). For almost all substances the activity coefficients at infinite dilution become more ideal with increasing temperature ($\gamma_i \rightarrow 1$). A decrease of the activity coefficients for components with γ^∞ values > 1 and an increase of the activity coefficients for components with γ^∞ values < 1 was observed with increasing temperature.

A comparison of the obtained γ^∞ values with literature data results in disagreement for water in tetraethylene glycol dimethyl ether. In contrast to our results Schmidt and Ulrich (*7*) observed negative deviation from Raoult's law and an increase of the γ^∞ values with increasing temperature. It is however well known from industrial practice that tetraethylene glycol dimethyl ether/water systems show positive deviation from Raoult's law. Furthermore, it can be shown with the help of the Gibbs–Helmholtz relation and from published excess enthalpy data (*12–14*) that the temperature

Table VII. Fugacity Coefficients at Saturation, φ_i^s, as a Function of Temperature T Used To Calculate the Activity Coefficients Given in Tables I–V

solute i	φ_i^s 303.15 K	φ_i^s 323.15 K	φ_i^s 343.15 K	solute i	φ_i^s 303.15 K	φ_i^s 323.15 K	φ_i^s 343.15 K
n-pentane	0.9691	0.9500	0.9250	1,1,2-trichlorotrifluoroethane	0.9777	0.9620	0.9409
n-hexane	0.9865	0.9754	0.9596	1,1,1-trichlorotrifluoroethane	1.0000	1.0000	1.0000
n-heptane	0.9944	0.9885	0.9793	1,2-dichloroethane	0.9948	0.9898	0.9819
cyclohexane	0.9923	0.9855	0.9753	trichlorethylene	0.9950	0.9899	0.9821
methanol	0.9948	0.9891	0.9795	1-chlorobutane	0.9915	0.9839	0.9725
ethanol	0.9967	0.9922	0.9841	methyl formate	0.9780	0.9625	0.9410
2-propanol	0.9968	0.9921	0.9832	methyl acetate	0.9875	0.9770	0.9616
isobutanol	0.9988	0.9966	0.9922	ethyl acetate	0.9924	0.9849	0.9732
2-propen-1-ol	0.9980	0.9954	0.9904	*n*-propyl acetate	0.9964	0.9921	0.9847
acetone	0.9868	0.9762	0.9610	*n*-butyl acetate	0.9984	0.9961	0.9919
2-butanone	0.9930	0.9863	0.9760	methyl acrylate	0.9934	0.9870	0.9769
benzene	0.9935	0.9875	0.9783	acetonitrile	0.9937	0.9881	0.9795
toluene	0.9972	0.9940	0.9887	acetaldehyde	0.9682	0.9493	0.9254
o-xylene	0.9991	0.9978	0.9953	isobutyraldehyde	0.9882	0.9785	0.9645
m-xylene	0.9988	0.9973	0.9943	diethyl ether	0.9701	0.9506	0.9249
p-xylene	0.9988	0.9971	0.9941	diisopropyl ether	0.9863	0.9750	0.9586
styrene	0.9991	0.9978	0.9955	methyl *tert*-butyl ether	0.9822	0.9690	0.9505
chlorobenzene	0.9987	0.9971	0.9941	tetrahydrofuran	0.9906	0.9827	0.9711
dichloromethane	0.9822	0.9694	0.9519	furan	0.9757	0.9596	0.9383
chloroform	0.9895	0.9810	0.9688	1,4-dioxane	0.9971	0.9939	0.9885
tetrachloromethane	0.9920	0.9851	0.9750	pyridine	0.9983	0.9962	0.9925
trichlorofluoromethane	0.9646	0.9441	0.9183	water	0.9994	0.9985	0.9968
1,1,1-trichloroethane	0.9911	0.9836	0.9724				

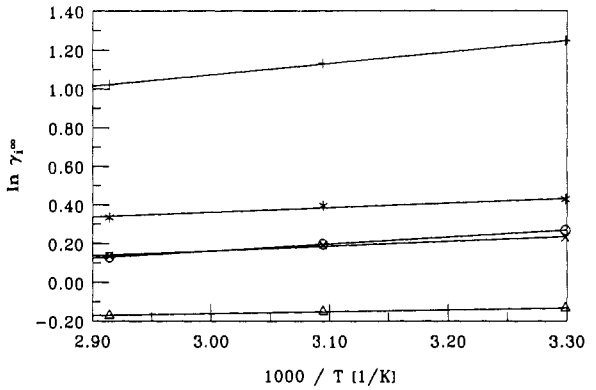

Figure 1. Activity coefficients at infinite dilution, γ_i^∞, for *n*-pentane in the scrubbing liquids as a function of temperature T: +, tetraethylene glycol dimethyl ether; *, tripropylene glycol dimethyl ether; ×, diethylene glycol dibutyl ether; ○, triethylene glycol dibutyl ether; △, tripropylene glycol dibutyl ether.

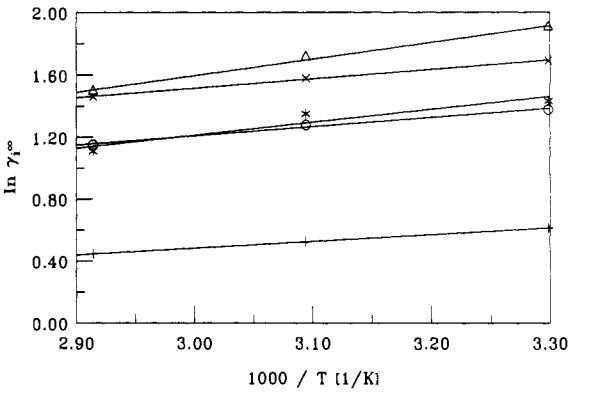

Figure 2. Activity coefficients at infinite dilution, γ_i^∞, for water in the scrubbing liquids as a function of temperature T: +, tetraethylene glycol dimethyl ether; *, tripropylene glycol dimethyl ether; ×, diethylene glycol dibutyl ether; ○, triethylene glycol dibutyl ether; △, tripropylene glycol dibutyl ether.

dependence given in Table I is correct for both the tetraethylene glycol dimethyl ether/water system and for other systems, e.g., tetraethylene glycol dimethyl ether/alkanes. Our own H^E measurements carried out using isothermal flow calorimetry for dichloromethane or benzene with tetraethylene glycol dimethyl ether also confirm the temperature dependence found for these systems.

Conclusion

Gas–liquid chromatography is an ideal technique for the measurement of activity coefficients at infinite dilution, especially when the vapor pressure of the stationary phase is low. This is true not only for the scrubbing liquids used in this work, but also for selective substances commonly used for extractive rectification or the measurement of γ^∞ values in higher alcohols, esters, ... for the further development of group contribution methods. If instead of Henry coefficients (or γ^∞) the separation factor at infinite dilution is required, this value can be directly obtained from the net retention times of the components considered, since the other quantities such as liquid loading or pressure required for the determination of γ^∞ cancel out.

Acknowledgment

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Glossary

y	mole fraction in the vapor phase
x	mole fraction in the liquid phase
γ_i	activity coefficient of component i
γ_i^∞	activity coefficient at infinite dilution of component i
f_i^s	saturation fugacity of component i, kPa
H_{ij}	Henry coefficient of component i in the scrubbing liquid j, kPa
H^E	molar excess enthalpy, J/mol
φ_i^s	fugacity coefficient of component i at saturation state
P_i^s	saturation pressure of component i, kPa
P	total pressure, kPa

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Registry No. *n*-Pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; cyclohexane, 110-82-7; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; isobutanol, 78-83-1; 2-propen-1-ol, 107-18-6; acetone, 67-64-1; 2-butanone, 78-93-3; benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; styrene, 100-42-5; chlorobenzene, 108-90-7; dichloromethane, 75-09-2; chloroform, 67-66-3; tetrachloromethane, 56-23-5; trichlorofluoromethane, 75-69-4; 1,1,1-trichloroethane, 71-55-6; 1,1,2-trichlorotrifluoroethane, 76-13-1; 1,1,1-trichlorotrifluoroethane, 354-58-5; 1,2-dichloroethane, 107-06-2; trichloroethylene, 79-01-6; 1-chlorobutane, 109-69-3; methyl formate, 107-31-3; methyl acetate, 79-20-9; *n*-propyl acetate, 109-60-4; *n*-butyl acetate, 123-86-4; methyl acrylate, 96-33-3; acetonitrile, 75-05-8; acetaldehyde, 75-07-0; isobutyraldehyde, 78-84-2; diethyl ether, 60-29-7; diisopropyl ether, 108-20-3; methyl *tert*-butyl ether, 1634-04-4; tetrahydrofuran, 109-99-9; furan, 110-00-9; 1,4-dioxane, 123-91-1; pyridine, 110-86-1; water, 7732-18-5; ethyl acetate, 141-78-6; tetraethylene glycol dimethyl ether, 143-24-8; tripropylene glycol dimethyl ether, 42769-21-1; diethylene glycol dibutyl ether, 112-73-2; triethylene glycol dibutyl ether, 63512-36-7; tripropylene glycol dibutyl ether, 115702-75-5.