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Solution thermodynamics of some organic solutes in supported liquid film of polyethylene glycol6000 — a gas–liquid chromatographic study

De-Zhi Sun[a,b], Jian Chen[a,c], Wei-Min Lu[a], Xiao-Ming Zheng[a,*]

[a]*Institute of Catalysis, Xixi Campus, Zhejiang University, 34 Tianmushan Road, Hangzhou 310028, PR China*
[b]*Department of Chemistry, Liaocheng Teachers' University, Liaocheng, Shandong 252059, PR China*
[c]*Department of Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, PR China*

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Abstract

The changes of standard thermodynamic functions (ΔH° and ΔS°) for 21 organic compounds dissolved in supported polyethylene glycol-6000 from gas phase have been determined using gas–liquid chromatographic technique. The experimental thermodynamic data have been discussed in the light of interaction between molecules of the solvent and solute. Selective intermolecular forces are believed to be the main cause of PEG selectively dissolving and separating solutes. Selectivity of the PEG is not only observed to polar substances but also to apolar ones such as benzene and cyclohexane. We believe that the macromolecule can adjust its conformation when it receives a solute molecule, so as to more strongly interact with the small molecule. When such strong negative electric groups as carbonyl oxygen atom, nitro group approach ethylene of PEG or strongly positive charged hydrogen atom(s) approach(s) an oxygen atom of PEG, strong intermolecular forces occur and solution heats are large. On the other hand, strongly intermolecular force may be caused by a kind of synergistic interaction between the solvent and solute molecules. In such a case, a solute molecule is attracted by two or more sites on the polymer chain. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polyethylene glycol; Chromatography; Heat of solution; Entropy effect

1. Introduction

Polyethylene glycols (PEGs) are very important macromolecular compounds in both industry and research. They are widely used as stationary phases in chromatographic technology, due to their ability to separate various polar compounds [1,2], as solid-phase cosolvents in triphase catalytic processes [3], as phase transfer catalysts [4], and as additives to change interface activity of surfactants in solution [5]. Recently, effects of PEG on dyeing properties of vinylon fibre [6] and on lactate dehydrogenase [7] have been reported. PEGs have so many uses because of the unique molecular structure. In the long, flexible chain of the PEG molecule, oxygen atoms and ethylene groups alternate. The oxygen atoms are electron donors and have affinity for polar molecules or electron withdrawing groups while the ethylenes are very weak polar groups with affinity for apolar species or very strong electronic donors. In the liquid phase, PEG

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[*] Corresponding author. Tel.: +86-571-8273272; fax: +86-571-8273283.
E-mail address: jmdou@letu.edu.cn (X.-M. Zheng)

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molecules continuously coil due to thermal motion, which gives rise to many possible configurations. This kind of flexibility is of great importance in interactions of PEG with smaller molecules, similar to those of biological receptors with substrates described by Lehn in his Nobel Lecture [8]. The flexibility makes it possible for several ether oxygen atoms and ethylenes of a PEG molecule to distribute in space such that they can interact with a smaller molecule or an ion [9]. Kuhl et al. believe that PEGs can chelate metal cations as 18-crown-6 (18C6) can [10]. It might be a good idea to regard PEGs as a type of host substances which can selectively receive guest substances through intermolecular forces and form supramolecular structures [11]. Interaction between PEG and other substance can certainly cause changes in thermodynamic properties of the system. In the present work, solution enthalpies and entropies have been determined using gas–liquid chromatography, with a polyethylene glycol whose molecular weight is 6000 (PEG6000) as stationary liquid phase and 21 volatile organic substances as solutes. The results discussed in the light of interactions between the solvent and solute molecules.

2. Experimental

2.1. Reagents

All reagents were supplied by Shanghai Chemical Company (Shanghai, China). Analytically pure polyethylene glycol (mean molecular weight 6000, PEG6000) was used as obtained. The 21 solutes including carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), methylene dichloride (CH_2Cl_2), 1,2-dichloroethane (DCE), methanol (MeOH), ethanol (EtOH), 1-propanol (n-C_3H_7OH), 2-propanol (i-C_3H_7OH), 1-butanol (n-C_4H_9OH), acetone, butanone, 2-pentanone, nitromethane ($MeNO_2$), nitroethane ($EtNO_2$), 2-nitropropane (i-$C_3H_7NO_2$), cyclopetanone (CP-one), cyclohexanone (CH-one), tetrahydrofuran (THF), benzene, toluene and cyclohexane (C_6H_{12}) were either chemically or analytically pure liquids. The chemically pure liquids were purified by distillation or reduced pressure distillation. The alcohols, ketones, nitroalkanes and THF were stored above 4 Å molecular sieve so as to remove residual water.

2.2. Preparation of chromatographic column

PEG6000 was dissolved in acetone (A.R.) at 50°C. Then 60–80 mesh 6201 support particles were added to the PEG solution. The mixture was gently stirred for about 2 h, and then the PEG was coated on the support by slowly evaporating acetone. The weight ratio of PEG to the support is 1:10. Then a stainless steel column (length 2.0 m and inner diameter 3.0 mm) was packed with the PEG/support particles. Before being used for determination of retention times, the column was aged for 24 h in flowing highly pure nitrogen (99.999%) at 126°C.

2.3. Determination of retention times

The column was installed in a 2304-A Chromatograph with a thermal conductivity detector (Beijing Analytic Apparatus Factory, Beijing, China). Flow rates (15–30 cm^3/min) were measured with a soap-bubble flow meter. Variation in the flow rate were normally less than 1%. Highly pure nitrogen (99.999%) was used as carrier gas. The inlet and outlet pressures (P_i and P_r) were controlled and measured with the accuracy ±0.5 kPa. The range of (P_i-P_r) was from 20 to 60 kPa. Column temperature was measured with an accurate thermometer. Liquid sample was injected in the column in amounts less than 0.5 μl, so the concentration of the solute is near 0 and the retention time repeatable. Retention times (T_R) were recorded on C-R6A Chromatopac (Shimadzu, Japan) with an accuracy of ±0.001 min. Every retention time used for the calculation of specific volume was the average value of three replicates. Hold-up time (t_M) was the retention time of argon.

3. Results and discussion

3.1. Specific retention volumes (V_g°) and solution thermodynamics

Specific retention volumes were calculated with the literature method [12] (pressure gradient correction factor and the vapor-pressure of water in the soap-bubble flow meter are counted while the non-ideality correction [13] is neglected due to the low inlet pressure). Calculations of the thermodynamic properties of solution were performed with Eqs. (1)–(3) [14]:

$$\Delta G^\circ = -RT\ln\left(\frac{M_1 P^\circ V_g^\circ}{273.2R}\right) \tag{1}$$

$$\Delta H^\circ = RT^2\left(\frac{\partial \ln V_g^\circ}{\partial T}\right) \tag{2}$$

$$T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ \tag{3}$$

where T is column temperature, M_1 is the molal weight of the solvent (PEG6000), and P° is standard pressure (1 atm or 101.325 kPa). Standard changes of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) correspond to the following process:

$$\mathrm{X}\,(\mathrm{gas}, T, P^\circ) = \mathrm{X}\,(\text{solute in PEG}, T, \text{at concentration of standard state}) \tag{4}$$

According to Meyer [14], the standard state of solute X in the stationary phase (PEG) is mole fraction unity, with the solute having molecular interactions characteristic of infinite dilution. Here we use the assumption that X behaves ideally in the gas phase and obeys Henry's Law in the gas–liquid equilibrium state. Because the specific retention volumes are the necessary data for the calculation of thermodynamic properties, we put them in Table 1. When calculating enthalpy changes according to Eq. (2), we found that ln V_g° versus $1/T$ is a linear function (i.e., the correlation coefficient for every solute is larger than 0.995). Therefore Eq. (2) can become ln $V_g^\circ = -(\Delta H^\circ/R)\ (1/T) + C$, where C is an integration constant. Deduced values of ΔH° are collected in Table 2 along with the linear functions and coefficients. $T\Delta S^\circ$ data obtained from Eqs. (1)–(3) are in Table 3 for the purpose of comparison.

3.2. Thermodynamic selectivity of PEG to solute

Specific retention volumes (Table 1) and heats of solution (Table 2) of the solutes are in the same order: cyclohexane<short chain alkyl chloride≈benzene<toluene<alcohols≈chain ketones<nitroalkanes<cycloketones. This shows that substitution groups in the molecules of the derivatives of the hydrocarbons have much to do with the solution properties. We tried to correlate the thermodynamic function changes (ΔH° and ΔS°) with dipolar moments and/or molecular weights of the solutes, but were not successful. If

Table 1
Natural logarithms of specific retention volumes (ln V_g°) of solutes in supported film of PEG6000 (the unit of V_g° is cm^{-3}/g)

Solute	Column temperature (T/K)						
	336.0	344.1	352.2	363.0	373.3	383.1	393.8
CCl_4	2.832	2.552	2.319	2.017	1.790	1.410	1.163
$CHCl_3$	3.557	3.233	2.972	2.671	2.413	1.984	1.706
CH_2Cl_2	2.961	2.698	2.446	2.177	1.808	1.462	1.257
$(CH_2Cl)_2$	4.098	3.793	3.528	3.202	2.989	2.489	2.203
MeOH	3.556	3.237	2.852	2.588	2.150	1.783	1.464
EtOH	3.680	3.436	3.136	2.789	2.428	2.085	1.788
n-C_3H_7OH	4.366	3.971	3.660	3.339	3.175	3.018	2.386
i-C_3H_7OH	3.772	3.396	3.090	2.938	2.573	2.285	2.011
n-C_4H_9OH	5.140	4.712	4.350	3.941	3.527	3.064	2.769
Acetone	3.258	2.965	2.715	2.417	2.078	1.767	1.505
Butanone	3.812	3.474	3.235	2.909	2.668	2.207	1.887
2-Pentanone	4.404	4.035	3.772	3.407	3.138	2.704	2.383
$MeNO_2$	5.069	4.719	4.447	4.079	3.814	3.304	2.983
$EtNO_2$	5.213	4.858	4.574	4.197	3.924	3.404	3.069
i-$C_3H_7NO_2$	5.083	4.731	4.449	4.073	3.803	3.311	2.986
CP-one	5.595	5.231	4.946	4.552	4.289	3.720	3.361
CH-one	6.252	5.842	5.548	5.140	4.853	4.270	3.933
THF	3.386	3.057	2.861	2.530	2.149	1.838	1.516
Benzene	3.437	3.093	2.904	2.550	2.365	1.975	1.635
Toluene	4.188	3.830	3.592	3.231	2.990	2.588	2.285
Cyclohexane	2.251	1.916	1.762	1.354	1.118	0.927	0.508

Table 2
Standard heats of solution ($-\Delta H^\circ$) of solutes in supported film of PEG6000, and the corresponding parameters a, b and correlation coefficients (R) of the linear equation $\ln V_g^\circ = a(1000/T) + b$

Solute	$-\Delta H^\circ$/kJ mol^{-1}	a/K	$-b$	R
CCl_4	31.5	3.792	8.447	0.997
$CHCl_3$	34.7	4.174	8.863	0.998
CH_2Cl_2	33.2	3.989	8.886	0.998
$(CH_2Cl)_2$	35.6	4.282	8.352	0.995
MeOH	39.8	4.793	10.700	0.998
EtOH	37.4	4.496	9.627	0.995
n-C_3H_7OH	36.0	4.330	8.591	0.995
i-C_3H_7OH	32.8	3.941	7.995	0.995
n-C_4H_9OH	43.3	5.211	10.444	0.995
Acetone	33.4	4.023	8.710	0.999
Butanone	35.8	4.302	8.982	0.996
2-Pentanone	37.7	4.538	9.110	0.998
$MeNO_2$	39.2	4.714	8.941	0.997
$EtNO_2$	40.3	4.844	9.183	0.997
i-$C_3H_7NO_2$	39.4	4.741	9.013	0.997
CP-one	41.8	5.033	9.354	0.996
CH-one	43.5	5.234	9.317	0.996
THF	35.3	4.250	9.246	0.998
Benzene	33.0	3.967	8.375	0.996
Toluene	35.5	4.265	8.520	0.998
Cyclohexane	30.8	3.707	8.808	0.997

PEG molecules change their conformation by coiling the long chain when it meets a solute molecule, so that the interaction between them is stronger and more interacting energy is released, PEG might offer different environments of electrostatic and dispersion forces to different solute molecules, and the experimental data could not be explained without considering the configuration of the molecule of PEG. Because standard heat of solution is a positive function of intermolecular force between solvent and solute, we mainly discuss the heat data in the light of intermolecular force.

Firstly, PEG6000 seems to selectively dissolve the apolar compounds benzene and cyclohexane. Retention volume (V_g°) of benzene is larger than that of cyclohexane at lower temperature, but is not so at higher temperature (Table 1). The solution heat of benzene (33.0 kJ mol^{-1}) is 2.2 kJ mol^{-1} larger than that of cyclohexane (Table 2). This indicates that the intermolecular force of PEG with benzene is stronger than that of PEG with cyclohexane. The phenomenon may be relative to polarity of C–H bond, since each hydrogen atom of benzene carries a little more posi-

Table 3
Entropy effect ($-T\Delta S^\circ$/kJ mol^{-1}) of solutes from gas phase dissolving into supported liquid film of PEG6000 at different column temperatures

Solute	T/K						
	336.0	344.1	352.2	363.0	373.0	383.1	393.8
CCl_4	27.3	28.0	28.6	29.4	30.1	31.2	32.0
$CHCl_3$	28.4	29.2	29.9	30.6	31.3	32.6	33.4
CH_2Cl_2	28.6	29.2	29.9	30.6	31.6	32.6	33.4
$(CH_2Cl)_2$	27.8	28.5	29.1	29.9	30.4	31.9	32.7
MeOH	33.6	34.4	35.4	36.0	37.3	38.4	39.4
EtOH	30.8	31.6	32.2	32.9	33.9	34.9	35.8
n-C_3H_7OH	27.5	28.4	29.1	29.9	30.2	30.6	32.5
i-C_3H_7OH	25.9	26.8	27.6	27.9	28.9	29.7	30.5
n-C_4H_9OH	32.6	33.6	34.4	35.4	36.5	37.8	38.7
Acetone	28.0	28.7	29.4	30.1	31.1	32.0	32.8
Butanone	28.8	29.6	30.2	31.0	31.6	32.9	33.9
2-Pentanone	29.1	30.0	30.5	31.4	32.1	33.3	34.2
$MeNO_2$	28.7	29.5	30.0	30.9	31.4	32.9	33.7
$EtNO_2$	29.4	30.1	30.7	31.6	32.2	33.6	34.5
i-$C_3H_7NO_2$	28.9	29.7	30.2	31.1	31.7	33.1	34.0
CP-one	29.9	30.7	31.2	32.1	32.6	34.2	35.2
CH-one	29.7	30.6	31.1	32.0	32.6	34.1	35.0
THF	29.6	30.4	30.8	31.7	32.8	33.7	34.7
Benzene	27.1	27.9	28.3	29.3	29.7	30.9	31.9
Toluene	27.4	28.3	28.8	29.4	30.3	31.4	32.3
Cyclohexane	28.2	29.1	29.5	30.7	31.4	32.1	33.2

tive charge than that of cyclohexane. The solution heat of toluene is 2.5 kJ mol^{-1} larger than that of benzene. This difference may be from two causes. One is the molecule of toluene being slightly heavier than benzene molecule, and the other is that toluene has a small dipolar moment because of the σ–π conjugative effect between the methyl and benzene ring.

Secondly, by comparing the solution heats of the three methyl chlorides (Table 2), it can be found that intermolecular force between $CHCl_3$ and PEG is the strongest and that between CCl_4 and PEG is the weakest. But the order of dipole moments of the solute molecules is: CH_2Cl_2 (1.60 D)>$CHCl_3$ (1.01 D)>CCl_4 (0). This fact shows that although dipolar moments of solute molecules are important when they interact with PEG molecule, the relative strengths of the interactions cannot be decided by dipole moments. The structure of the site on PEG chain to which the solute molecule approach might be more important. Oxygen atoms of PEG are electronic donors. The polarity of the C–H bond of $CHCl_3$ is stronger than that of CH_2Cl_2, and hence the hydrogen atom of $CHCl_3$ can form stronger hydrogen bond with a oxygen atom of PEG. The solution heat of 1,2-dichloroethane (DCE) is larger than that of $CHCl_3$. This can be quite well explained according to literature [15], i.e. both DCE (dipolar moment is 2.06D) and a ethylene of PEG adopt cisoid conformation, and the two chloride atoms of DCE approach the two pairs of hydrogen atoms through electrostatic force. This is a type of synergistic interaction.

Thirdly, solution heats of five low alcohols give us interesting information. The value of $-\Delta H^\circ$ slightly decreases (from 39.8 to 36.0 kJ mol^{-1}) with the molecular chain lengthening from MeOH to n-C_3H_7OH, but that of n-C_4H_9OH abruptly increases to 43.3 kJ mol^{-1}. Specific retention volume of n-C_4H_9OH is also evidently larger than that of n-C_3H_7OH. The phenomena might be interpreted from the formation of hydrogen bond. When the chain (C_nH_{2n-1}–) of a normal alcohol is short, the dispersion force between the chain and PEG cannot offset the rotation of the hydrocarbon chain around the hydroxyl which forms the hydrogen bond with the ether oxygen atom of PEG, and the larger the number of carbon atoms (n) is, the weaker the hydrogen bond becomes. However, butyl may be long enough to have a strong dispersion force with a part (probably ethylene) of PEG molecule when the hydrogen bond is existing. Hence the intermolecular force between n-C_4H_9OH and PEG is another type of synergistic interaction.

Fourthly, solution heats of ketones present two regular trends: (1) $-\Delta H^\circ$ of cycloketone is larger than that of a normal chain 2-ketone if the number of carbons is about the same; (2) $-\Delta H^\circ$ increases about 2 kJ mol^{-1} with hydrocarbon chain lengthening by methylene (–CH_2–). These trends (1) indicate that ketone molecules interact with PEG by orienting the carbonyl oxygen atom to a local part of the PEG molecule. Literature [15] pointed out that the carbonyl oxygen attracts all the four hydrogen atoms of an ethylene in chain of PEG through electrostatic force. The carbonyl oxygen atom of cyclo-ketone is more protrudent than that of chain ketones, so it can more easily approach the ethylene and therefore the interaction between cyclo-ketone and PEG molecules is stronger. The trends (2) might simply come from dispersion force. Additionally, the solution heat of THF (35.3 kJ mol^{-1}) is larger than that of benzene and near to that of butanone, due to oxygen of THF attracting with ethylene of PEG like the ketone oxygen atom doing. But oxygen atom of THF is not so protrudent and so negatively charged as the carbonyl oxygen atom of cyclopentanone (CP-one), and therefore the intermolecular force between PEG and THF is weaker than that between cyclopentone with PEG.

At last, solution heats of the three nitroalkanes are quite large, which is mainly due to the strong interactions of the two oxygen atoms of nitro-group (–NO_2) with the hydrogen atoms of PEG ethylene. It can be found by comparing the $-\Delta H^\circ$ values of methanol and i-propanol with nitromethane and 2-nitropropane, respectively, that interaction of PEG ethylene with nitro-group is as strong as the hydrogen bond between alcohol hydroxyl and PEG oxygen atom, while the interaction between nitro-group and PEG molecule is less weakened by the two methyls bonded to C-2.

3.3. Calorific effect and entropy effect

Usually, calorific and entropy effects of a thermodynamic process can be expressed by enthalpy change and product of entropy multiplying temperature ($T\Delta S$). In our experimental system, equilibrium constant of Eq. (4), $K^\circ = \exp[(T\Delta S^\circ - \Delta H^\circ)/RT]$. $K^\circ \propto V_g^\circ$, i.e. specific retention volume is determined by both calorific effect and entropy effect. ΔH° is decided by intermolecular force, and $T\Delta S^\circ$ by phase change of solute, configuration change of PEG and solute molecules, as well as temperature. The data in Tables 2 and 3 show that all the values of ΔH° and $T\Delta S^\circ$ are negative, but all of the ($T\Delta S^\circ-\Delta H^\circ$) values are positive except that of cyclohexane at the temperature higher than 363 K. Therefore, the process of solute from gas phase to PEG solution is driven by calorific effect or intermolecular force, while the entropy effect partly offsets the driving force. To every solute, ($T\Delta S^\circ-\Delta H^\circ$) becomes larger when the column temperature is lower. At a certain temperature, ($T\Delta S^\circ-\Delta H^\circ$) values of various solutes may have great differences. For instance, at 336 K, ($T\Delta S^\circ-\Delta H^\circ$) values of the nitroalkanes and the two cyclo-ketones are larger than 10 kJ mol^{-1} while that of cyclohexane is only 2.6 kJ mol^{-1}. These differences are the thermodynamic foundation of PEG selectively absorbing and separating solutes. In fact, retention volumes or adjusted retention times are quite sensitive to ($T\Delta S^\circ-\Delta H^\circ$), since molar energy of a motional degree of freedom (0.5RT) is less than 1.16 kJ mol^{-1} at the experimental temperatures.

3.4. Possibility of adsorption

To investigate the possibility of adsorption, we have used the method of literature [16] i.e., determining the variation of retention time (t_R-t_M) with amount of the sample, and found that (t_R-t_M) is almost independent of sample size, provided the injected liquid sample is less than 0.5 μl. In fact, the specific area of the support is only about 5 m^2/g. The estimated thickness of the PEG film on it is about 20 nm, while molecular length of solute is less than 0.8 nm. Hence the opportunity of solute molecule interacting with the support surface is greatly less than that of it with the PEG liquid film, if the concentration of solute in the liquid phase is low. So small size of sample can make adsorption effect negligible.

3.5. About errors

According to literature [16], enthalpy data obtained by chromatography is encouragingly good. If we could determine specific retention volumes at a great many temperatures and V_g versus $1/T$ were an exactly linear function, we could deduce the relative error formula from Eq. (5):

$$\left|\frac{\delta(\Delta H^\circ)}{\Delta H^\circ}\right| \times 100\% = \left(\left|\frac{RT}{\Delta H^\circ}\right|\left|\frac{\delta V_g^\circ}{V_g^\circ}\right|\left|\frac{\delta T}{T}\right|\right)\times 100\% \tag{5}$$

where $|\delta(\Delta H^\circ)/\Delta H^\circ|\times 100\%$ is the relative error of standard enthalpy change or solution heat, $|\delta V_g^\circ/V_g^\circ|\times 100\%$ (<2%, estimated with repeated determining data of retention times) and $|\delta T/T|\times 100\%$ (<0.1%) are relative errors of specific retention volume and temperature, respectively. $|RT/\Delta H^\circ|$ is less than 0.2 due to $|\Delta H^\circ|$of the systems being larger than 5RT. So the relative error of solution heat is less than 0.5%. But we only have gotten retention data at seven temperatures and have to estimate the relative error with the method in our earlier work [17] and $|\delta(\Delta H^\circ)/\Delta H^\circ|\times 100\%$ is about 1%. The relative error of Gibbs free energy is that of specific retention volume. So relative error of entropy effect ($T\Delta S$) is about 3%, according to Eq. (3).

4. Conclusions

Standard thermodynamic properties, ΔH° and $T\Delta S^\circ$ of 21 solutes dissolving in polyethylene glycol6000 liquid film from gas phase have been determined, with the relative errors are about 1 and 3%, respectively. The data are qualitatively explained by considering intermolecular force between solvent and solute molecules. The intermolecular forces are discussed according to molecular structures. Because of its flexible long chain, PEG molecule might be able to adopt such a type of conformation that the interaction of it with the molecule of solute is stronger and more interacting energy could be released. In our experimental systems, there are three types of quite strong intermolecular forces. (1) Electrostatic force between strong electronic donors such as carboxyl oxygen or nitro with ethylene of the PEG. (2) Hydrogen bond involving an oxygen atom of PEG. (3) Synergistic interaction such as the intermolecular force of PEG with butanol.

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