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Ternary Liquid–Liquid Equilibria of Water, Ethanol, and Oleic Acid

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Equilibrium concentration data are presented for the system water–oleic acid–ethanol using a commercial grade solvent. The components and physical properties of the solvent are reported as well as the densities of the equilibrated aqueous and organic phases. The concentration data are shown to be well represented by the NRTL model for predicting liquid–liquid equilibria. Since the organic fluid is shown to give good separation and is not harmful to the growth cycle of *Saccharomyces cerevisiae*, these results are useful for designing in situ, extractive fermentation processes.

Introduction

It is well-known that alternative energy resources can significantly alleviate the demand and consumption of the world's petroleum supplies. Of the many choices of alternate energy forms, gasohol has several advantages because it utilizes a renewable resource, provides another economic route for current agricultural products, and can be utilized directly in current internal combustion engines with little or no adjustments.

However, the production of pure or high-concentration ethanol suitable for motor vehicle use is an economically sensitive process (*1*), mainly because the current fermentation step produces only a dilute aqueous concentration due to end-product inhibition. In order to concentrate the ethanol, traditional distillation processes are frequently used but are very energy intensive. Recently, work has been reported on the use of liquid–liquid extraction to selectively remove ethanol from water (*2*), and some workers have also tried to combine the fermentation and extraction process in one vessel but toxicity of the organic phase has been a major problem (*3*).

Whether combined with fermentation or conducted in a separate vessel, the equilibrium condition between the organic and aqueous phase is a very important aspect of the liquid–liquid extraction process. Four desirable characteristics for a solvent are as follows: (1) a high capacity for ethanol, (2) a high selectivity for ethanol over water, (3) a low solubility in water, and (4) a low toxicity to yeast. The last parameter can be important even for separate liquid–liquid extraction vessels because viable yeast could be used for recycle fermentation. The capacity for ethanol can be described by the equilibrium distribution coefficient, which is the ratio of the mole fraction of ethanol in the solvent to that in the aqueous phase at equilibrium. It is desirable to have a high distribution coefficient to minimize the quantity of solvent required to extract a given amount of ethanol. The ability to selectively remove ethanol over water may be described by the relative selectivity, which is the ratio of the equilibrium distribution coefficient for ethanol over that for water. A high selectivity is desired to reduce any further concentration step needed to remove water from ethanol. Finally, the solubility of the solvent in the water should be low so as to minimize solvent losses and reduce the chances of solvent toxicity to the yeast.

In this work, we report the results of a commercial grade, oleic acid extract to selectively remove ethanol from water. Fatty acids and oleic acid in particular are reported to be a valuable nutrient source for yeast used in membrane synthesis (*4*).

Equilibrium Modeling

The prediction of equilibrium conditions between two liquid phases composed of dissimilar, polar species is one of the most difficult thermodynamic problems. The distribution coefficient for each species i between phase I and phase II is defined as

$$K_{Di} = X_i^{\mathrm{I}}/X_i^{\mathrm{II}} = \gamma_i^{\mathrm{II}}/\gamma_i^{\mathrm{I}} \tag{1}$$

Once accurate distribution coefficients are known it is then easy to express the relative selectivity for any species i compared to another species j via

$$RS_{ij} = K_{Di}/K_{Dj} \tag{2}$$

Many correlations for activity coefficients are available in the literature, but for dissimilar polar species the most accurate semiempirical correlation is known to be the UNIQUAC equation of Abrams and Prausnitz (*5*). However the earlier, nonrandom, two-liquid (NRTL) approach of Renon and Prausnitz (*6*) has also been shown to be a good quantitative approximation. In the NRTL approach, the derivation considers the binary interactions between molecules i and j based on the local mole fraction concept. The NRTL expression for phase I for three species is

$$\ln \gamma_i^{\mathrm{I}} = \frac{\sum_{j=1}^{3} \tau_{ji} G_{ji} X_j^{\mathrm{I}}}{\sum_{j=1}^{3} G_{ji} X_j^{\mathrm{I}}} + \sum_{j=1}^{3} \left[\frac{X_j^{\mathrm{I}} G_{ij}}{\sum_{k=1}^{3} G_{kj} X_k^{\mathrm{I}}} \left(\tau_{ij} - \frac{\sum_{k=1}^{3} X_k^{\mathrm{I}} \tau_{kj} G_{kj}}{\sum_{k=1}^{3} G_{kj} X_k^{\mathrm{I}}} \right) \right] \tag{3}$$

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$$\tau_{ij} = A_{ij}/RT$$

$$\tau_{ii} = A_{ii} = 0$$

$$\alpha_{ij} = \alpha_{ji}$$

There is an identical equation for phase II activity coefficients.

For three species, the NRTL model has nine adjustable parameters (all the A and α coefficients). However, frequently α parameters are set equal to constant, known values (dependent on molecular species) without a great loss of accuracy. Those parameters represent the tendency of species i to be distributed in a random fashion and can vary between 0 (completely random) to 1. A value of 0.2 is frequently chosen for mostly saturated hydrocarbons with polar species (*7*). The A parameters represent the differences between interaction energies between unlike and like molecule pairs.

Although several methods for estimating A parameters exist (such as making two experimental measurements at "infinite" dilution), in this work their values were determined by least-squares minimization of the error function

$$F = \sum_{r=1}^{N} \sum_{i=1}^{3} \left[1 - \left(\frac{K_{Di}^{\mathrm{CALC}}}{K_{Di}^{\mathrm{EXPT}}} \right)_r \right]^2 \tag{4}$$

where N is the total number of experimental data points measured at each temperature. This evaluation was performed with the computer software package called "Chemtran" marketed

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Table I. Manufacturer's Specifications for Ethanol (ρ = 0.788 g cm^{-3}; 20 °C)

substance	purity/(mg L^{-1}) average	purity/(mg L^{-1}) maximum
water	500	900
acids (as acetic)	9	15
esters (as ethyl acetate)	9	15
aldehydes (as acetaldehyde)	4	7
higher alcohols (as isobutyl alcohol)	15	40
nonvolatiles	7	20

Table II. Properties of Commercial Oleic Acid

A. Composition

fatty acid	weight fraction	fatty acid	weight fraction
myristic ($C_{14}H_{28}O_2$)	2.2	oleic ($C_{18}H_{34}O_2$)	74.7
myristoleic ($C_{14}H_{26}O_2$)	2.0	linoleic ($C_{18}H_{32}O_2$)	2.7
palmitic ($C_{16}H_{32}O_2$)	2.5	linolenic ($C_{18}H_{30}O_2$)	0.5
palmitoleic ($C_{16}H_{30}O_2$)	10.1	eicosenoic ($C_{20}H_{38}O_2$)	0.7
stearic ($C_{18}H_{36}O_2$)	0.4	others	4.2

B. Mean Molecular Weight = 282.5

C. Density and Viscosities

t/°C	ρ/(kg m^{-3})	η/cP	t/°C	ρ/(kg m^{-3})	η/cP
20	892.8	34.8	45	874.8	13.8
30	885.8	23.6	60	868.3	8.8

Table III. Equilibrium Mole Fractions, X_i, and Densities, ρ, for Water (1) + Ethanol (2) + Oleic Acid (3)

	aqueous phase			oleic acid phase		
t/°C	X_2	X_3	ρ/(kg m^{-3})	X_2	X_1	ρ/(kg m^{-3})
20	0.003 74	0.000 03	996.5	0.007 05	0.014 06	893.4
	0.018 21	0.000 04	990.2	0.034 65	0.015 90	893.0
	0.037 12	0.000 06	983.5	0.071 31	0.017 09	892.3
	0.075 72	0.000 10	971.8	0.199 30	0.022 53	890.1
30	0.003 44	0.000 09	993.9	0.007 79	0.018 99	886.6
	0.017 38	0.000 12	987.6	0.039 99	0.021 15	886.3
	0.036 64	0.000 15	980.0	0.085 73	0.025 65	885.6
	0.072 65	0.000 20	969.1	0.212 11	0.031 97	883.4
45	0.003 29	0.000 18	988.5	0.009 48	0.027 79	875.7
	0.014 13	0.000 19	984.9	0.042 13	0.032 68	875.5
	0.016 73	0.000 20	982.3	0.050 57	0.033 38	875.4
	0.019 71	0.000 20	980.0	0.059 01	0.037 83	875.0
	0.034 18	0.000 23	975.5	0.104 30	0.038 51	874.7
	0.058 77	0.000 28	967.0	0.196 73	0.042 10	873.0
	0.065 97	0.000 29	963.9	0.231 46	0.047 08	872.5
	0.076 77	0.000 30	960.0	0.277 55	0.051 91	871.8
60	0.003 08	0.000 29	981.3	0.009 82	0.052 19	869.3
	0.015 93	0.000 31	975.4	0.049 99	0.064 59	869.0
	0.033 42	0.000 35	968.8	0.109 32	0.076 81	868.3
	0.062 28	0.000 42	957.3	0.244 21	0.084 35	866.2

by Chemshare Corp., Houston, TX.

Experimental Section

Anhydrous ethanol (Stanchem Inc., Winnipeg, Canada) was mixed with distilled water in concentrations covering the whole range expected in fermentation broths. The manufacturer's specifications for the purity of the ethanol is shown in Table I. The ethanol solutions were then extracted with a commercial grade oleic acid (Emersol 233 LL, Emery Industries Ltd.) in order to obtain data directly applicable to a pilot-scale fermentation system. The actual fatty acid composition of this fluid was measured on a GC (SPB capillary column, flame ionization detector) and is listed in Table II. Also the measured viscosity (Brookfield coaxial cylinder) and densities (Paar densitometer) are shown. Experiments were performed at temperatures from 20 to 60 °C. A 50-cm^3 aliquot of a solution containing a known amount of ethanol in water was poured into 50 cm^3 of the oleic acid and sealed inside a 250-cm^3 Erlenmeyer flask. The flasks were vigorously shaken at a controlled temperature with a New Brunswick gyrotary water bath shaker (Model G76D). Shaking was continued for 48 h since earlier tests indicated that amount of time was necessary to ensure equilibrium. The fluid was then allowed to settle for 4 h while being held at the required temperature. The two phases were finally separated by decantation and then quickly cleansed by centrifugation before samples were taken for chemical analysis. The GC analysis procedures (including the composition of the oleic acid) were accurate to within ±2% of the measured values. The temperature control on the shaker was accurate to within ±0.2 °C.

Ethanol in water was analyzed by GC capillary chromatography (polymethyl (5% phenyl) siloxane capillary column, FID detector) using isopropyl alcohol as an internal standard. Ethanol in the oleic acid phase was measured by first back-extracting the ethanol into pure distilled water (3 volumes distilled water to every volume of oleic acid) at 30 °C. The water phase was then again analyzed by GC and compared to a standard calibration curve made from oleic acid containing known concentrations of ethanol. The concentration of water in the oleic acid phase was determined by Karl-Fisher titration, and finally the concentration of oleic acid in the water phase was measured by base titration.

Results and Discussion

The compositions in mole fraction and liquid-phase densities are reported in Table III at 20, 30, 45, and 60 °C. The pressure in the laboratory was 95.6 kPa. The molecular weight of the fatty acid, solvent phase was taken at the mean value of 282.5 g mol^{-1}. The results indicate that the mole fraction of ethanol in the solvent phase increases to between twice and four times that in the aqueous phase and concentrations of ethanol and water in the solvent phase increase with temperature at the expense of concentrations in the aqueous phase. The solvent phase is very insoluble in the aqueous phase, but its solubility increases with temperature. The reproducibility of the data shown in Table III was checked by running many duplicate experiments. The maximum deviation for any data point was ±5% of its absolute value.

The best fit NRTL parameters with the nonrandomness parameters fixed and best fitted are listed in Table IV along with

Table IV. NRTL Parameters from Liquid-Liquid Equilibria for Water (1) + Ethanol (2) + Oleic Acid (3)

t/°C	α_{12}	α_{13}	α_{23}	A_{12}[a]	A_{21}[a]	A_{13}[a]	A_{31}[a]	A_{23}[a]	A_{32}[a]	F
					Two Parameter					
20	0.20	0.20	0.20	30.0	0.83	21.5	7.23	8.75	25.4	0.0572
30	0.20	0.20	0.20	26.3	0.15	19.3	6.46	11.7	20.2	0.0526
45	0.20	0.20	0.20	21.3	−0.73	19.6	5.46	16.2	13.3	0.0545
60	0.20	0.20	0.20	23.2	−1.55	19.6	3.89	18.5	13.7	0.0163
					Three Parameter					
20	0.37	0.42	0.31	17.5	9.21	24.4	12.7	16.0	16.3	0.0010
30	0.40	0.40	0.32	13.0	7.78	21.6	11.7	14.7	11.0	0.0089
45	0.40	0.38	0.33	7.72	6.82	20.8	11.1	13.8	5.05	0.0027
60	0.39	0.38	0.29	13.1	7.00	20.2	10.6	15.3	9.66	0.0023

[a] Unit: 10^{-3} J mol^{-1}.

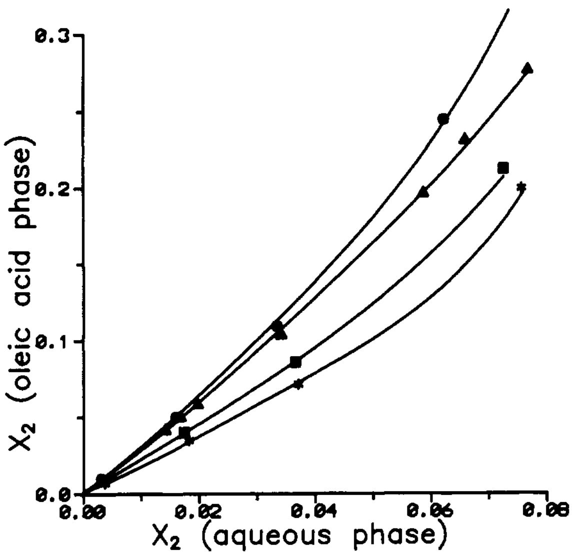

Figure 1. Distribution of ethanol (2) between aqueous and oleic acid phases: (✱) 20 °C; (■) 30 °C; (▲) 45 °C; (●) 60 °C; (—) NRTL equation.

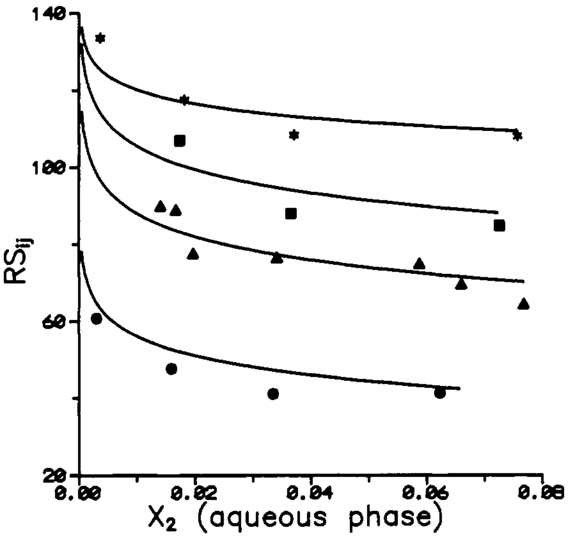

Figure 2. Relative selectivity for ethanol (2) over water (1) in the oleic acid phase: (✱) 20 °C; (■) 30 °C; (▲) 45 °C; (●) 60 °C; (—) NRTL equation.

the values of the minimization objective function. It can be observed that fitting of the nonrandomness parameters reduces the minimum functions by factors from 6- to 100-fold, thereby significantly improving the accuracy. Figures 1 and 2 demonstrate the best fitting results where the experimental data for the distribution of ethanol between phases and the selectivity for ethanol in the organic phases are plotted (respectively) against the NRTL predictions. Since the NRTL method involves a sound thermodynamic basis for modeling equilibrium conditions, this method is preferred to the completely empirical fitting approach. For instance, one is able to extract the values and trends of the differences in interaction energies of molecules in the NRTL approach. Figure 3 depicts the effect of temperature on some of the water/ethanol/oleic acid interaction energies. These values are expected to remain constant with temperature (*7*) and, except for the oil/water values, are seen to remain fairly close to their mean values.

Although not discussed in this paper, we also attempted to fit the UNIQUAC equation to this liquid–liquid system using the same software package. It consistently gave poorer results with larger values of the minimization function being generated. This agrees with the findings of Blanco et al. (*8*) who studied water, acetic acid, and methyl propyl ketone using their own software to calculate the interaction parameters. UNIQUAC has parameters which are much more sensitive to the purity of the species in the liquid phases and is therefore not as suitable as the NRTL model for simulating industrial type solvents.

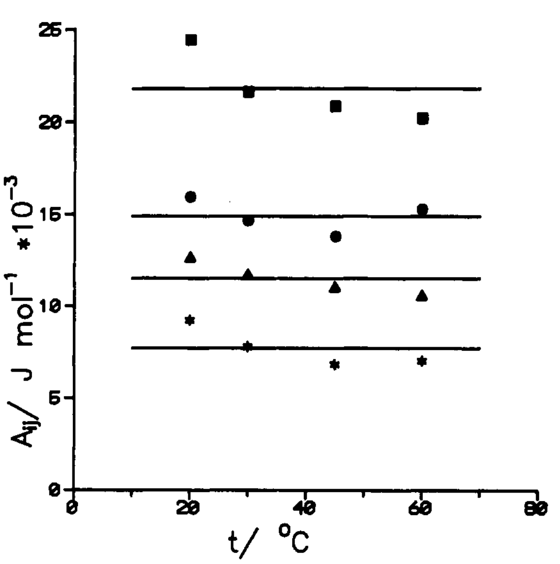

Figure 3. Effect of temperature on interaction energy differences for water (1) + ethanol (2) + oleic acid (3): (✱) A_{23}; (■) A_{21}; (▲) A_{31}; (●) A_{13}; (—) mean values.

Although Figure 1 shows the distribution coefficient is over 1 on a mole fraction basis, on a mole concentration basis the aqueous phase always contains more ethanol than the oleic acid phase. In fact, the molar ethanol concentration in the aqueous phase was from 5 to 10 times higher than in the oleic acid phase. This is still somewhat better extraction than observations made by Roddy and Coleman (*9*) for long-chained alkanes. However, for pure extraction efficiency reasons, data on superior solvents exist (*2*), but oleic acid shows far greater promise as a fluid for in situ extraction without harming and in fact even benefitting the ethanol fermentation pathway of *Saccharomyces cerevisiae*. Further, Figure 2 shows that at the cooler fermentation temperatures the relative selectivity for ethanol remains at approximately 100, thereby minimizing the need for further separation of water from ethanol. These results are important in this regard since they represent the first published data for such a fluid.

Nomenclature

A = difference in interaction energies (J mol^{-1})
F = minimization objective function (eq 4)
G = parameter in eq 3
K_D = distribution coefficient
R = gas constant (J mol^{-1} K^{-1})
RS = relative selectivity factor
T = temperature (K)
X = mole fraction
α = nonrandomness parameter
τ = parameter in eq 3
γ = activity coefficient
η = viscosity (cP)

Registry No. Ethanol, 64-17-5; oleic acid, 112-80-1.

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Solubility of Aromatic Hydrocarbons in Water and Sodium Chloride Solutions of Different Ionic Strengths: C_2-Substituted Benzenes

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The solubilities of ethylbenzene and 1,2-, 1,3-, and 1,4-dimethylbenzene in aqueous sodium chloride solutions having ionic strengths ranging from 0 to 5.00 mol dm^{-3} have been determined at 298.15 K. The solubilities were determined by headspace analysis using a multiple-injection interrupted-flow (MIIF) technique. The values for the Henry's law constants and aqueous/vapor partition coefficients for the compounds in the solutions studied are also given. Correlations between the measured aqueous solubilities and molar volume, molecular surface areas, and a simple group contribution model are given. Extrapolation of the correlations is used to estimate the aqueous solubilities of the tri- and tetramethylbenzenes, which are liquids at 298.15 K.

Solubility data for organic compounds in aqueous solutions as a function of ionic strength is needed in the solution of many industrial and environmental problems. Recently, we have been studying the components of the connate water which makes up the geopressured reservoirs found along the Louisiana and Texas Gulf coast. These hot, brine reservoirs, a possible future energy source, are usually saturated with natural gas—mostly methane and other light alkanes. They also contain a spectrum of aromatic compounds that range from benzene to alkyl-substituted anthracenes. The concentration of these aromatic compounds has been found to be a dynamic variable of the production of some reservoirs (*1*). We have been attempting to construct models of the reservoir which are consistent with the aromatic compounds concentration dynamics. As part of this program we have measured the solubility of benzene and toluene in NaCl brines having ionic strengths of 0-5.00 mol dm^{-3} (*2*). We present here data on the solubility of ethylbenzene and 1,2-, 1,3-, and 1,4-dimethylbenzene in brines under similar conditions.

Determining solubilities of substances with appreciable vapor pressures can be complicated by the partition of such substances between the solvent and the free gas space above the solvent. A headspace analysis technique, developed earlier (*2*), was used for this study because of its ease of execution and because the technique, rather than being complicated by partition, utilizes it.

Experimental Section

Instrumentation. As in our earlier study, measurements were made using a Varian Model 3700 gas chromatograph equipped with a specially constructed headspace attachment (*3*).

Table I. Molar Solubilities (S), Henry's Law Constants (k), and Partition Coefficients (K_p) for Ethylbenzene in Water and Aqueous Sodium Chloride of Ionic Strength (μ) at 298.15 K

μ/ (mol dm^{-3})	S/ (10^{-3} mol dm^{-3})	k^a/ (10^9 Pa)	K_p^b
0	1.66 ± 0.04	4.24 ± 0.11	3.24 ± 0.08
1	1.01 ± 0.05	6.95 ± 0.35	1.98 ± 0.09
2	0.549 ± 0.023	12.7 ± 0.52	1.07 ± 0.05
3	0.387 ± 0.007	18.0 ± 0.27	0.755 ± 0.014
4	0.202 ± 0.007	28.7 ± 1.1	0.473 ± 0.018
5	0.148 ± 0.015	47.1 ± 4.8	0.289 ± 0.029

[a] $p = kx$ where x = solute mole fraction and p = solute partial pressure in pascals. [b] $K_p = x/y$ where x and y = solute mole fraction in the solution and vapor, respectively.

Table II. Molar Solubilities (S), Henry's Law Constants (k), and Partition Coefficients (K_p) for 1,2-Dimethylbenzene in Water and Aqueous Sodium Chloride of Ionic Strength (μ) at 298.15 K

μ/ (mol dm^{-3})	S/ (10^{-3} mol dm^{-3})	k/ (10^9 Pa)	K_p
0	2.09 ± 0.05	2.39 ± 0.08	5.69 ± 0.16
1	1.17 ± 0.05	4.19 ± 0.19	3.28 ± 0.16
2	0.637 ± 0.004	7.67 ± 0.04	1.70 ± 0.01
3	0.419 ± 0.012	11.6 ± 0.39	1.18 ± 0.03
4	0.241 ± 0.030	20.5 ± 2.8	0.673 ± 0.096
5	0.121 ± 0.021	41.9 ± 4.8	0.341 ± 0.059

Materials. The aromatic compounds used in this study were analyzed by gas chromatography prior to use. One sample of 1,2-dimethylbenzene (Aldrich Gold Label, 99.8%), two samples of 1,3-dimethylbenzene (Baker, 99.60%; Aldrich, 99.8%), and two samples of 1,4-dimethylbenzene (Baker, 99.78%; Aldrich Gold Label, 99.83%) were used without further purification. Samples of 1,2-dimethylbenzene and ethylbenzene (Baker) were fractionally distilled to a purity of 99.80 and 99.40%, respectively, prior to use. Sodium chloride (Baker Analyzed Reagent Grade) was dried at 110 °C prior to use. The deionized water had a conductivity of $<10^{-6}$ (Ω cm)$^{-1}$ at 298.15 K.

Sample Preparation, Analytical Procedure, and Data Reduction. Solubilities are determined from computed values for the solute/solvent system at saturation. The technique employed obtains these values by extrapolation of data such as that shown in Figure 1. The upper curve was determined for samples containing only vapor while the lower is for samples containing solute, solvent, and vapor in the headspace above the liquid. In the latter case, vapor removal disturbs the equilibrium between the hydrocarbon in the vapor and in solution. A multiple-injection interrupted-flow gas chromatographic

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