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Determination of Oxygen-Containing Organic Compounds in Aqueous Solutions by Vapor-Phase Extraction and Some Thermodynamic Regularities

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Low-molecular-weight carboxylic acids (C_2 to C_6) and phenols have been isolated from water solutions by vapor phase extraction (VPE). The influence of the molecular structure and the extractant type on the extraction efficiency has been investigated. The suggested model mechanism of VPE is in good agreement with the experimental results and allows quantitative calculations of the changes of Gibbs free energy as a function of the molecular length for the above carbonic acids and of polarity for cresol isomers.

Introduction

Extraction techniques have a fundamental role in the sample preparation stage of analytical investigation, and they quickly develop:[1] the Single-Drop and Microextration, the Hollow-Fiber Membrane Extraction and so on. Unlike liquid extraction (LE), vapor-phase extraction (VPE)[2] allows the use of water-soluble organic liquids. Furthermore, the extractant polarity influences the efficiency of isolation of a target substance.[3] Therefore, VPE compares favorably with gas extraction (GE). On the other hand, the molecular structure of the extractable compound also determines the depth of the process and its partition between the extractant vapor and water solution. The study of such regularities is necessary for understanding the mechanism with the purpose to predict the efficiency and selectivity of VPE.

An extractive mechanism of isolation of organic compounds from water in vapors of organic solvents was suggested when aqueous solutions of low molecular weight acids were being investigated. To explain the results obtained, a kinetic model was proposed based on the existence of equilibrium in the distribution of the extracted components between the vapor and liquid phase. As a result, the mathematical expression for a VPE constant $^*K_{eq}$ is obtained[3]

$$^*K_{eq} = V_L/[(m_o/m_D - 1)\cdot V_D] \tag{1}$$

Here, m_o is the mass of an extracted compound in the initial aqueous solution; m_D is the mass of an extracted compound in the obtained vapor-phase extract, condensate; and V_L and V_D are, respectively, the liquid- and vapor-phase extract volumes after a VPE operation.

The experimentally obtained parameter $^*K_{eq}$ differs from the partition coefficient in a system of liquid–vapor K_{eq} by the factor ρ_D/ρ_V[3]

$$^*K_{eq} = K_{eq}\cdot(\rho_D/\rho_V) \tag{2a}$$

where ρ_V and ρ_D are the vapor density and condensate density, respectively.

The arguments in support of an equilibrium existence between the vapor and liquid phase are that VPE results from static and dynamic modes are almost equal and that technological parameters of a flow VPE correspond to those of equilibrium flow GE.[3]

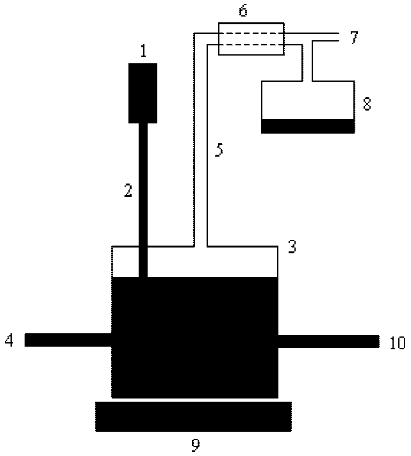

Figure 1. Installation for VPE of organic compounds (VPE-module):[3] 1, the liquid pump for a given extractant; 2, the pipeline; 3, the distilling vessel with the initial liquid specimen; 4, pipeline for the given specimen; 5, the vapor pipeline; 6, the condenser for the condensating extractant vapor with isolable compounds; 7, the branch tube for connection to the compressor or vacuum pump; 8, the receiver VPE condensate; 9, the heater; 10, the exit pipe.

Here we report the results obtained by the application of the Fourier transform IR spectroscopy (FTIR), corroborating the regularity of the VPE mechanism mentioned above.

Experimental Section

Apparatus and Software. Gas chromatograph model-3700 "CHROMATOGRAPH" (Moscow, Russia, under VARIAN license) with a flame ionization detector (FID) was used. The glass column of length 1.25 m and internal diameter of 4 mm with a sorbent 15 % Carbowax 20 M on Chromaton N-AW-DMCS [(0.16 to 0.20) mm] was taken for separation of the extracts. The chromatographic information was collected and processed by a soft-hardware complex "Meta-chrom" made in ≪META-CHROM≫ (Yoshkar-Ola, Russia). The IR spectra of the tested vapor-phase samples were recorded by an FTIR spectrometer "IKAR" (Moscow, Russia) with a resolution of 0.5 cm^{-1} in the gas cuvette with KBr-windows. The cuvette's thickness was 19.3 mm.

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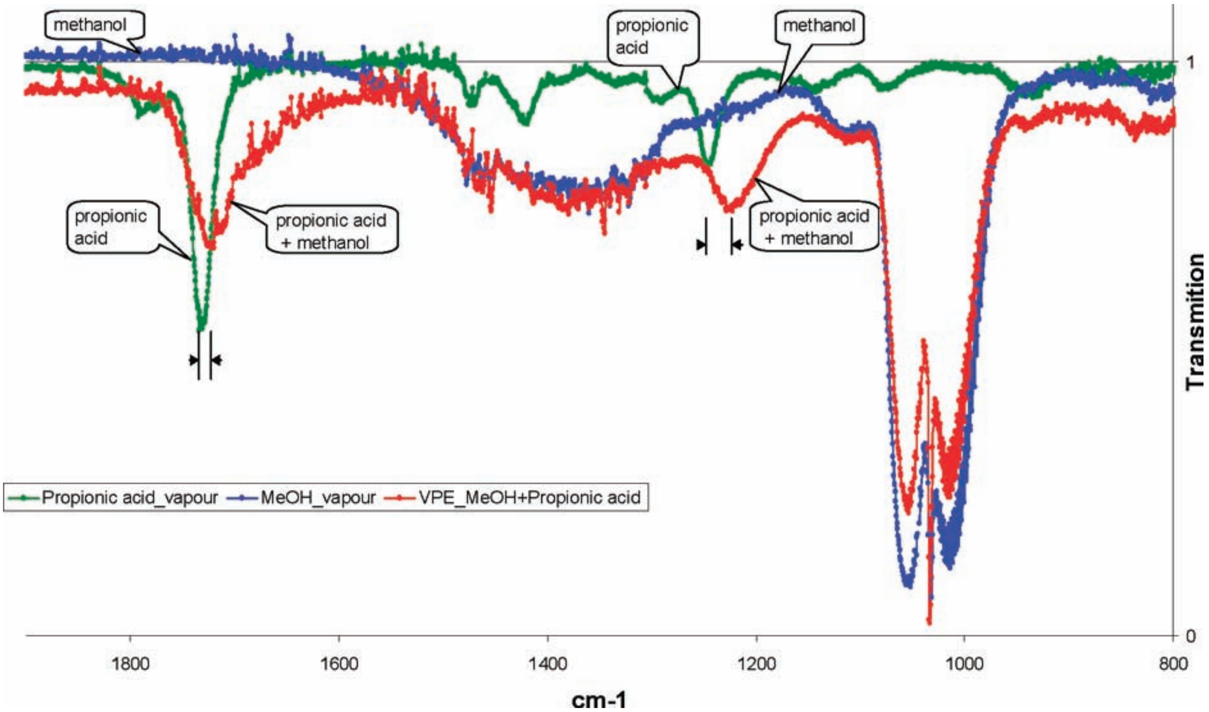

Figure 2. FTIR spectra of saturated vapors at temperature 293 K and pressure 101.1 kPa: green, propionic acid; blue, methanol; red, mixture of propionic acid and methanol.

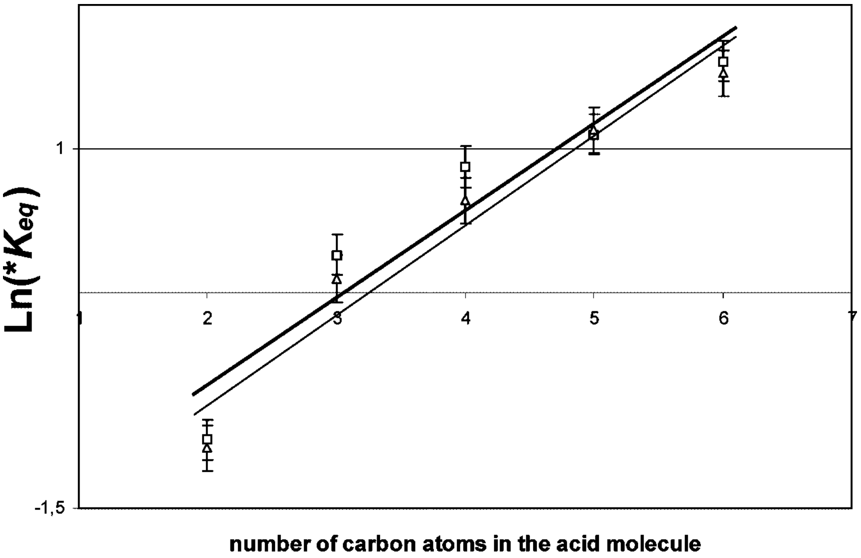

Figure 3. Logarithmic dependence of the factor of vapor-phase extraction $^*K_{eq}$ from the number of carbon atoms in a molecule of a carboxylic acid: □, by the methanol with linear approximation $y = 0.6x - 1.9$, $R^2 = 0.91$; and Δ, ethanol with linear approximation $y = 0.6x - 2.0$, $R^2 = 0.95$.

The vapor-phase extracts of the tested samples were produced by the help of the installation, as depicted in Figure 1. The technique for its usage is described elsewhere.[3]

Chemicals and Materials. The model systems were aqueous solutions of monobasic carboxylic acids and phenolic compounds. Chemically pure acetic, butyric, pentanoic, and hexanoic were purchased from ≪VEKTON≫ (Moscow, Russia). Extra pure propionic acid was purchased from Ferak (Germany). The solutions of phenol, *o*-cresol, *m*-cresol, and *p*-cresol were prepared according to the Russian Federation State standard 7101–94 of ≪EKROS≫ (Moscow, Russia). The following extractants were used: methanol from a biochemical set ≪Na 130≫ from Lachema (Czech Republic), pharmaceutical ethanol, 95 % (Armavir, Russia), and trichloromethane and carbon tetrachloride from ≪VEKTON≫ (Moscow, Russia).

Results and Discussion

The mechanism of liquid extraction (LE) from aqueous solutions of organic substances is known to be based on the replacement of water molecules with the extractant molecules in the hydrated sphere of the extracted compound.[4] New associates are formed between the molecules of the extracted compound and the organic solvent. Taking this into account, VPE was studied by the method of IR spectroscopy, as a phenomenon of extraction of isolated substances from water by an organic solvent vapor.

Figure 2 represents the IR spectra of saturated vapors of propionic acid and methanol, as well as of their mixture. From this figure, we notice that the IR spectrum of the mixture of methanol and propionic acid cannot be obtained by a simple

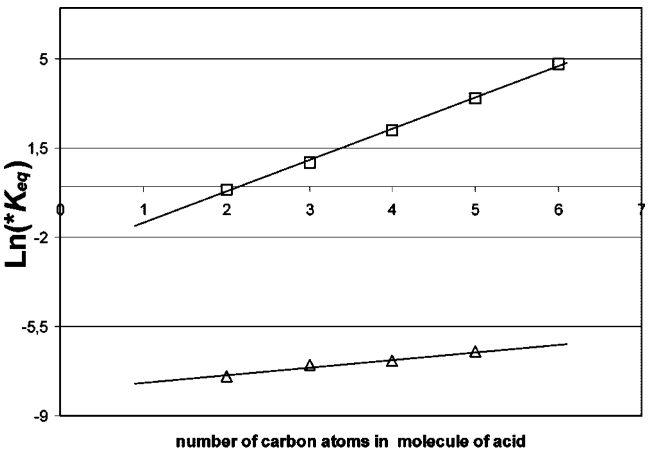

Figure 4. Logarithmic dependence of a partition coefficient of organic acids K_{eq} from the number of carbon atoms in the acid molecule during: □, the liquid extraction by hexanol-1 from water at 293 K with linear approximation $y = 1.2x - 2.7$, $R^2 = 1.00$; Δ, the gas extraction by nitrogen from water at 363 K with linear approximation $y = 0.3x - 8.0$, $R^2 = 0.98$. Initial data for a plotting of those graphs are taken from refs 6 and 7.

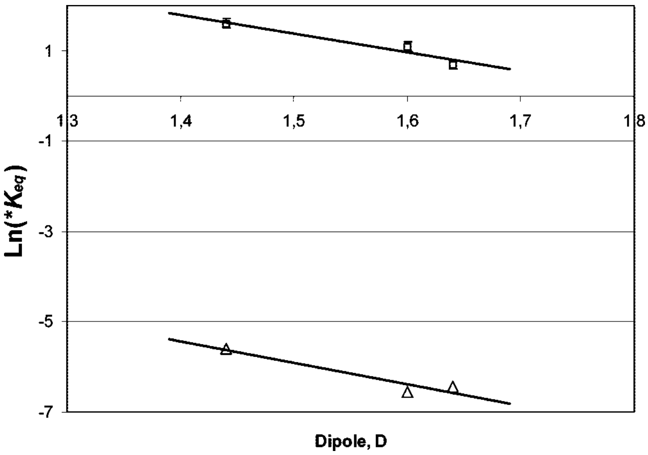

Figure 5. Logarithmic dependence of extractive parameters from a dipole moment of a cresol molecule during: □, the vapor phase extraction by ethanol from water at 368 K and 101.1 kPa with linear approximation $y = -4.2x + 7.7$, $R^2 = 0.93$; Δ, gas extraction by nitrogen from water at 363 K with linear approximation $y = -4.7x + 1.2$, $R^2 = 0.91$. The partition coefficients for a plotting of the gas extraction graph are taken from ref 7, and dipole data are from ref 8.

addition of the corresponding IR spectra of the individual compounds. Moreover, the mixing of saturated vapors of methanol and propionic acid is accompanied by the long-wave shifts of the maxima of absorption of the C=O bond at 1730 cm^{-1} and of CO−OH at 1245 cm^{-1}, respectively, by (5 and 20) cm^{-1}. These two resonances are widened too in comparison with the spectrum of the acid. The observed effects suggest that a molecular association of the target compound, i.e., propionic acid, with molecules of the extractant, methanol, takes place in the vapor phase. An indirect proof of such a suggestion are the literature data[5] that report the gas-phase dimers for acetic and butyric acids formed by hydrogen bonding. Such a dimerization is accompanied by similar changes in the IR spectra of the organic acids.[5]

A theoretical model of the VPE mechanism[3] is based on the existence of equilibrium between the vapor and the liquid. On the other hand, from the thermodynamic point of view, there is the equality of the chemical potentials in the liquid μ_L and vapor μ_V phases (temperature and pressure are constant; at T, p = const) under the conditions of the extraction equilibrium for each isolated component of the mixture

$$\mu_L = \mu_V \tag{2b}$$

$$\mu_L^{o} + RT\ln(a_L) = \mu_V^{o} + RT\ln(a_V) \tag{3}$$

Here, μ_L^{o} and μ_V^{o} are the molar chemical potentials of an extractive compound in the liquid and vapor phases, respectively, and a_L and a_V are its activity in the liquid and vapor phases.

After appropriate rearrangements, eq 3 can be transformed into the known expression for a constant of extraction equilibrium

$$RT\ln(a_V) - RT\ln(a_L) = RT\ln(a_V/a_L) = RT\ln(K_{eq}) = \mu_L^{o} - \mu_V^{o} = -\Delta G^{o} \tag{4}$$

$$\ln(K_{eq}) = -\Delta G^{o}/RT \tag{5}$$

Here, ΔG^{o} is the molar Gibbs energy change during the procedure of the VPE; $K_{eq} = a_V/a_L$ is the partition coefficient of the target compound between the vapor and the liquid throughout the VPE. Under conditions of small concentrations, $C_V \approx a_V$ and $C_L \approx a_L$, and C_V and C_L are the appropriate concentrations of the target compound in the vapor and condensed phases.

As mentioned above,[3] the value of the *K_{eq}, and consequently of the K_{eq}, depends on the molecular structure of the compound isolated by VPE. The interconnection between the physicochemical parameters of the extraction and the molecular structure enables additional information about the VPE mechanism to be obtained. For example, during the liquid−liquid extraction study, it is established that the partition factor of a substance between two phases depends on the compound solubility in the contacting phases, interfacial tension, permittivity, etc.[4] Information for understanding the extraction mechanism was obtained during the study of dependence of the extraction parameters on the molecular structure in a homologous series.

The investigation of the extraction process in a homologous series allows characterization of intermolecular interactions, which are the basis of the investigated mass migration through the interface. Indeed, having presented the obtained results for carboxylic acids C_2 to C_6 as a function of a logarithm ln(*K_{eq}) of the number of carbon atoms in the acid molecule, a linear dependence was established. Such linearity was earlier obtained for the LE of acids by 1-hexanol.[4,6] From Figure 3, it follows that under VPE of these acids by methanol and ethanol, the slopes (so-called homologous difference) are almost equal. At the same time, this parameter essentially differs from those obtained from the liquid and gas extractions of these compounds from water (Figure 4), and its value is intermediate. A bigger change of Gibbs free energy during migration of the compound from one phase into another (i.e., a bigger slope) with extension of an extracted compound molecule by one $-CH_2-$ group, with LE being opposite to GE, is obviously due to the fact that in a condensed phase the smaller intermolecular spacing leads to more significant interaction forces than in a gas. The energy effect, i.e., the intensity of the increase of the extraction constant with growth of a molecule length of an extracted compound by one $-CH_2-$ group, is more in the LE case than in the cases of VPE and GE. For the same reason, the Gibbs free energy change in these homologous series is more for VPE than for GE (Figures 3 and 4).

Thus, the results of the experiments testify that a vapor is no longer a liquid and not yet a gas. The molecules of an extracted compound in the vapor phase make contact with a smaller amount of extractant molecules than during the LE. On the other

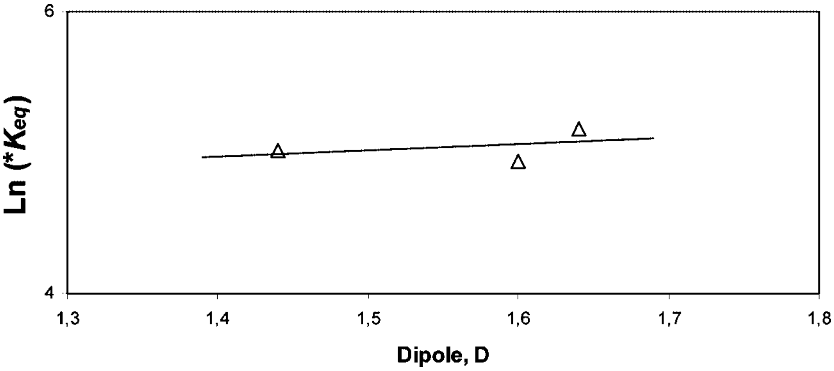

Figure 6. Logarithmic dependence of a partition coefficient from the dipole moment of the cresol molecule during the liquid extraction by hexanol-1 from water at 293 K with linear approximation $y = 0.5x + 4.3$, $R^2 = 0.16$. The partition coefficients for a plotting of this graph are taken from ref 6, and dipole data are from ref 8.

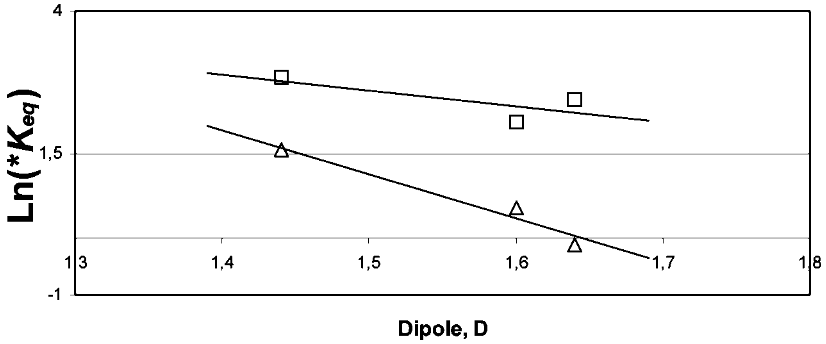

Figure 7. Logarithmic dependence of a partition coefficient from the dipole moment of the cresol molecule during the liquid extraction from water at 293 K: □, by chloroform with linear approximation $y = -2.8x + 6.8$, $R^2 = 0.55$; Δ, carbon tetrachloride with linear approximation $y = -7.7x + 12.7$, $R^2 = 0.96$. The partition coefficients for a plotting of those graphs are taken from ref 6, and dipole data are from ref 8.

hand, in the vapor phase they are less free than the molecular behavior in the gas phase. For GE, the dependence of molecular migration efficiency from a liquid into a gas with an increase of molecular mass is not expressed sharply in a homologous series. The slope of the graph has a small value.

According to eq 2a, the VPE parameter $^*K_{eq}$ experimentally obtained differs from the partition coefficient K_{eq} by a factor ρ_D/ρ_V. Then

$$\ln(^*K_{eq}) = \ln(K_{eq} \cdot \rho_D/\rho_V) = \ln(K_{eq}) + \ln(\rho_D/\rho_V) \quad (6)$$

$$\ln(K_{eq}) = \ln(^*K_{eq}) - \ln(\rho_D/\rho_V) \quad (7)$$

Therefore, in the transition from $^*K_{eq}$ to the partition coefficient of the target compound between the vapor and water media K_{eq} under a VPE by methanol and ethanol, the type of the dependence of extraction parameters in a homologous series of C_2 to C_6 organic acids does not actually vary. The graph only shifts on the ordinate axis by the value of $-\ln(\rho_D/\rho_V)$. Moreover, the intersection point of the graph with the ordinate axis for VPE approaches the corresponding point of intersection of the graph, obtained by GE of these acids with nitrogen (Figure 4).

Thus, for a homologous series of low aliphatic acids, it is established that with the increase of molecular mass (the number of $-CH_2-$ groups in the molecule) the efficiency of the VPE from water solutions by alcohols increases; i.e., the extractive constant $^*K_{eq}$ increases. This trend, although with a different intensity, is identical to all reviewed heterogeneous systems: a liquid−liquid (LE), liquid−vapor of extractant (VPE), and liquid−gas (GE).

According to eq 5 and the data available for the slopes of correlation of $\ln(^*K_{eq})$ from the number of carbon atoms in the acid molecule (Figures 3 and 4), it is possible to evaluate the changes of the Gibbs free energy with the growth of molecular length by one $-CH_2-$ group for the three methods of extraction of C_2 to C_6 acids. With an allowance made for temperature conditions of extraction, the following values for ΔG^o (negative value) were obtained: VPE by methanol or ethanol ($T \approx 368$ K) is in the range –(1900 to 2000) $J \cdot mol^{-1}$, GE by nitrogen ($T = 363$ K) is approximately -900 $J \cdot mol^{-1}$, and LE by hexanol-1 ($T = 293$ K) is approximately -3000 $J \cdot mol^{-1}$.

However, with the increase of the molecular length in a homologous series of C_2 to C_6 acids, the polarity also changes simultaneously. For example, the dipole moment of the molecule of acetic acid is 1.74 D and of butyric already is 0.93 D.[8] It would be interesting to evaluate the contribution into the general energy of the phenomenon VPE, ΔG^o, introduced by the polarity of a molecule $\Delta G^o{}_{dip}$. This polarity effect has been studied with cresol isomers, whose molecules have the same mass but different polarity. The graph $\ln(^*K_{eq})$ with dipole moment of the cresol molecule at the VPE by ethanol is presented in Figure 5. From the graph, it follows that the higher the molecular polarity the lower the efficiency of extraction. Its linearity is satisfactory and gives a negative value for the slope of the graph, −4.2. From comparison of the graphs in Figure 5, it is visible that the slopes of the graphs for VPE and GE coincide on the sign and vary a little bit by value. Therefore, the decrease of an extraction constant with the increase of molecular polarity of the extracted compounds has approximately identical intensity for both VPE and GE.

From Figure 6, it is visible that for LE by aliphatic alcohols the similar dependence of extraction parameters on polarity of the cresol molecule is badly approximated to a straight line and has a more complex type slope. The slope of the graph $\ln(K_{eq})$ vs dipole moment of the cresol molecule is smaller in magnitude.

This confirms that the molecular polarity of the extracted compound is not the determining factor in transboundary transport of the cresols in the case of LE by aliphatic alcohols C_6 to C_8 from water.[6] At the same time, there is a general tendency for all three alcohols: the transition from the least polar *ortho*-cresol to the most polar *para*-isomer is accompanied by a small increase of the extraction constant.[6] On the other hand, the use of such hydrophobic extractants, such as carbon tetrachloride or chloroform, in LE of the cresols results in a change in the nature of this relationship (Figure 7). The slope of the graph becomes negative and has an already noticeable magnitude, as is the case of VPE. Using the obtained results for VPE (Figure 5) and the literature data (Figure 7) for the extraction of the cresols from water for the change of the Gibbs free energy $\Delta G^{o}_{\text{dip}}$ with the increase of the isolated compound polarity by 1 D, identified by eq 5, we got the following (positive values): for VPE by ethanol ($T \approx 368$ K) is about 13000 $\text{J} \cdot \text{mol}^{-1}$, for GE by nitrogen ($T \approx 363$ K) is approximately 14 200 $\text{J} \cdot \text{mol}^{-1}$, and for LE by a tetrachloromethane ($T \approx 293$ K) is approximately 18 800 $\text{J} \cdot \text{mol}^{-1}$.

Conclusions

IR spectroscopy of the intermolecular interaction in a vapor phase between the extractant and the extracted compound confirms the validity of the hypothesis about the extractive mechanism of the studied phenomenon. The suggested model, correlations between VPE efficiency and the molecular structure of the target compounds, has allowed us to obtain some thermodynamic characteristics of this process. The regularities have been established by the example of extraction of the organic acids and the cresol isomers that will allow further calculations and predictions of the extraction parameters of VPE for different organic compounds.

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