ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

OPTIMIZATION OF SEPARATION PROCESSES IN CHROMATOGRAPHY USING LIQUAC MODEL

Nurali Q.Muhamadiev*, Nigina T.Fazlieva, Shuhrat M.Sayitkulov
Department of Natural Sciences, Division of Chemistry, Samarkand State University, Uzbekistan

ABSTRACT

The work is devoted to the evaluation of the process of separation and optimization by column chromatography using LIQUAC model. The possibility of using this approach to the separation of mixture of methyl esters of fatty acid and ether oils by gas-liquid chromatography, as well as cations and ions of iodine from the mixture of electrolytes (from medicinal plants) by ion chromatography. Prediction error makes upto 5-7 %.

Keywords: Chromatography, separation, LIQUAC model, optimization.

INTRODUCTION

It is known, that solutions can be considered as liquid homogeneous systems, consisting minimum of two components. Taking it into consideration chromatographic systems can be considered as solutions of nonelectrolites. But specific features of the solutions formed in gas chromatography, big sizes of molecules of stationary phase specify high-molecular characteristics of such solutions and limit application of known theories of solutions to the system of sorbat – the stationary phase. In the decision of this problem application of methods of structure-group composing, as in these methods are considered not only as geometrical and structural components, but also as energetic parameters of intermolecular interaction is recognized expedient.

MATERIALS AND METHODS

It is known, that the distribution of i component between phases in system of solution-steam (gas) is defined by equation [1].

$$\varphi_i \, Y_i \, P = \gamma_i \, X_i \, P_i^0, \qquad (1)$$

where: φ_i –fugacity; Y_i and X_i – the composition of i component in steam and liquid phases; P - the pressure in the system; γ_i - activity coefficient of i component; P_i^0 - partial pressure of i component, which depends on temperature.

Then the factor of distribution of substances between phases:

$$k = X_i/Y_i = P/\gamma_i \, P_i^0 \qquad (2)$$

In view of equation (2) for gas - chromatographic columns the retention volume will be written as [1]:

$$V_R = V_G + V_L K = V_G + V_L P/\gamma_i \, P_i^0, \qquad (3)$$

where: V_R - retention volume of substance;
V_G - free volume of a column;
V_L - volume of a motionless liquid phase.

As the criterion of the separation process the following value is accepted [6]:

$$R_s = \frac{(\alpha - 1)}{\alpha + 1} \frac{\kappa}{1 + k} \sqrt{\frac{N}{2}} \qquad (4)$$

where: α - selectivity of neighboring components; $\alpha = (t_1^{'}/t_2^{'}), t_1^{'}, t_2^{'}$ - retention time of components; k – retention factor for neighboring components; N - column efficiency. $R_s \geq 0{,}75 \; (\sum R_s \Rightarrow \max)$ has been accepted as a criterion of optimization.

As it is shown from equation (3) the estimation of retention values demands calculation of partial pressure of the components (P_i^0) and activity coefficients (γ_i).

Therefore for the calculation of these values UNIFAC method taking specific features of gas-liquid chromatography into consideration has been used [2]. According to this method:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R + \ln\gamma_i^{FV} \qquad (5)$$

where: $\ln\gamma_i^C$ - combinatory component of activity coefficient;

$\ln\gamma_i^R$ - residual component of activity coefficient;

$\ln\gamma_i^{FV}$ – component of activity coefficient, caused by free volume.

Retention indexes of analyzed substances have been calculated in terms of γ and P by Kovach formula [1]:

$$I=100[(\lg V_L P-\lg\gamma_x P^o_x-\lg V_L P+\lg\gamma_n P^o_n)/(\lg V_L P-\lg\gamma_{n+1}P^o_{n+1}-\lg V_L P+\lg\gamma_n P^o_n)+100n=$$

$$100[\lg(\gamma_n P^o_n/\gamma_x P^o_x)/\lg(\gamma_n P^o_n/\gamma_{n+1}P^o_{n+1})] + 100n \quad (5)$$

Use of UNIFAC model in ion chromatography is limited by specificity of interionic balance, but in LIQUAC model the balance between solutions of electrolytes has been considered [3]. Therefore the opportunity to use the model for the separation of mixtures of ions in ion chromatography is presented in the current work.

It is known, that the activity coefficient of i ion on LIQUAC model is defined by three components, namely [3]:

$$\ln\gamma_i = \ln\gamma_i^{LR} + \ln\gamma_i^{MR} + \ln\gamma_i^{SR} \qquad (1)$$

where: γ_i^{LR} – activity coefficient of i ion in a wide range; γ_i^{MR} – activity coefficient of i ion in a medium range; γ_i^{SR} – activity coefficient of i ion in a narrow range.

In turn:

$$\ln\gamma_s^{LR} = (2AM_s d/(b^3 d_s))[1+b\sqrt{I} - (1+b\sqrt{I})^{-1} - 2\ln(1+b\sqrt{I})] \qquad (2)$$

$$\ln\gamma_s^{MR} = \sum_{ion} B_{s,ion}(I)m_{ion} - \left(\tfrac{M_s}{M_m}\right)\sum_{sol}\sum_{ion}[B_{sol,ion}(I) + IB'_{sol,ion}(I)]x'_{sol}m_{ion} - (M_s)\sum_c\sum_a[B_{ca}(I)+IB'_{ca}(I)]m_c m_a \qquad (3)$$

$$\ln\gamma_s^{LR} = \ln\gamma_s^C + \ln\gamma_s^R \qquad (4)$$

$$\ln\gamma_s^C = 1 - V_s + \ln V_s - 5q_s[1-\frac{V_s}{F_s}+\ln(\frac{V_s}{F_s})] \quad (5)$$

$$\ln\gamma_s^R = q_s[1-\ln(\frac{\sum_i q_i x_i \psi_{is}}{\sum_i q_i x_i}) - \sum_i(\frac{q_i x_i\,\psi_{si}}{\sum_k q_k x_k\,\psi_{ki}})\,] \quad (6)$$

At expression of the activity coefficient through ionic force of the solution:

$$\ln\gamma_j^{LR} = -\frac{z_j^2 A\sqrt{I}}{1+b\sqrt{I}} \qquad (7)$$

$$\ln\gamma_j^{MR} = (M_m)^{-1}\sum_{sol} B_{j,sol}(I)x'_{sol} + \left(\frac{z_j^2}{2M_m}\right)\sum_{sol}\sum_{ion} B'_{sol,ion}(I)x'_{sol}m_{ion} + \sum_{ion} B_{j,ion}(I)m_{ion} + \left(\frac{z_j^2}{2}\right)\sum_c\sum_a B'_{ca}(I)m_c m_a - B_{j,s}(I)/M_s \qquad (8)$$

$$\ln\gamma_j^{SR} = \ln\gamma_j^C - \ln\gamma_j^C(B) + \ln\gamma_j^R - \ln\gamma_j^R(B) \quad (9)$$

$$\ln\gamma_j^C = 1 - V_j + \ln V_j - 5q_j[1-\frac{V_j}{F_j}+\ln(\frac{V_j}{F_j})] \quad (10)$$

$$\ln\gamma_j^R = q_j[1-\ln(\frac{\sum_i q_i x_i \psi_{ij}}{\sum_i q_i x_i}) - \sum_i(\frac{q_i x_i\,\psi_{ji}}{\sum_k q_k x_k\,\psi_{ki}})\,] \quad (11)$$

$$\ln[\gamma_j^C(B)] = 1 - \frac{r_j}{r_s} + \ln(\frac{r_j}{r_s}) - 5q_j[1-\frac{r_j q_s}{r_s q_j} + \ln(\frac{r_j q_s}{r_s q_j})] \quad (12)$$

$$\ln[\gamma_j^R(B)] = q_j(1-\psi_{js} - \ln\psi_{sj}) \qquad (13)$$

$$B_{ij} = b_{ij} + c_{ij}\exp(-I^{1/2} + 0{,}13I) \qquad (14)$$

$$\psi_{ij} = \exp(-a_{ij}/T) \qquad (15)$$

$$\ln\gamma'_j = (\ln\gamma_j^{LR} + \ln\gamma_j^{MR} + \ln\gamma_j^{SR}) - \ln\left(M_s/M_m + M_s\sum_{ion} m_{ion}\right) \quad (16)$$

$$\ln\gamma'_{MX(\pm)} = (1/\nu)(\nu_+\ln\gamma'_M + \nu_-\ln\gamma'_X) \quad (17)$$

$$x_s\gamma_s p_s^{sat} = y_s p \qquad (18)$$

Designations in the equations:

a, b c - interactive parameters of LIQUAC model; c_p - a thermal capacity (j*mole^{-1}*K^{-1}); *G* - Gibbs energy (j*mole^{-1}); *H* - enthalpy (j*mole^{-1}); *M* – molar mass (kg/mole); *m* - molal concentration (mole/kg); *n* - number of moles; *R* - universal gas constant (j*mole^{-1}*K^{-1}); *T* - absolute temperature (K); *x*- number of moles of liquid fractions; *y* - number of moles of steam phase. Indexes: *a* - anion; *c* - cation; i – i^{th} component; j – j^{th} component; *ion* - an ion; *w* - water; *m* - mixture of solutions.

RESULTS AND DISCUSSION

The general schemes of estimation and identification of components of various objects by chromatographic method have been offered. Examples of separation under this general scheme of various samples of complex composition have been shown.

Fatty-acid composition of vegetative and stone oils has been researched on chromatograph "Tsvet-100" using flame – ionization detector under the following conditions of separation: a column of stainless steel with the sizes of 1.5x0.04 m; sorbents: 15 % polyetheleneglycolesuccinate (PEGS) on chromatone A-NW with the sizes of grains 0.250-0.315мм, 15 % lestosyl, 15 % polyethyleneglycoleadipinat (PEGA); the temperature of the evaporator and column has been kept accordingly 225 and 175^{0}C; the charge of gas-carrier-nitrogen - 40 ml/minute. The qualitative composition of methyl ethers has been defined by abovementioned scheme.

The obtained data concerning the content of fatty acids, testify that in all samples of unsaturated acids palmitolein - C (16:1) (41-45 %), of saturated palmitin - C (16:0) (32-39 %) is more than others, and olein C (18:1) 12-17 % have intermediate position. Other acids available in rather smaller quantity. In some samples lynolen acid - C (18:3) is absent. Such acids as C (11:0), C (12:0), C (13:0), C (14:0), C (20:3), C (20:5) enter into the content of samples in very small quantities.

As a result of gas-chromatographic analysis of fatty acids in blood serum of healthy and children with various diseases have been found for children up to 3-years old of healthy and with hypotrophy palmitic - C (16:0), palmitolein - C (16:1), stearin - C (18:0), oleic - C (18:1), linolic - C(18:2), linolenic - C (18:3) and arachidonic - C (20:4) acids. It is shown from these data, that the amount of these acids in organism of healthy children makes relatively: C(16:0)=30,75±0,70; C(16:1)=40,43±0,99; C(18:0)=0,94±0,27; C(18:1)= 14,58±1,23; C(18:2)=10,08±0,93; C(18:3)=1,26±0,40; C(20:4)=1,95±0,46.

For healthy children the ratio of total content of unsaturated fatty acids to saturated in their blood equal to 2:1 is characteristic. At patients with hypotrophy depending on diseases the content of the saturated fatty acids increases and the amount of unsaturated decreases. The ratio of total amount of unsaturated fatty acids to amount of saturated makes for patients of the I degree 1.1:1 for the II degree 0.9:1 and for the III degree 0.75:1. These data are used to diagnose patients with hypotrophy and to increase treatment efficiency in practice.

The analysis of steam phase of vegetable oils has been carried out by gas chromatography method. The content of high volatile components has defined on chromato-mass-spectrometers LKB - 2091 [3].

The feature of the "bouquet" of high volatile compounds of “Chakanda” oils is that its composition includes mainly ethyl ethers of acids.

The composition of an equilibrium steam phase of stone oils, which manufacture is adjusted in Kokand (Uzbekistan) oil - extraction factory has been analyzed by the same way. It is established, that the composition of gas extracts of these oils includes saturated, unsaturated, aromatic, cyclic hydrocarbons, terpenes, alcohols, aldehydes, ketones, complex ethers and other substances.

If the presence of hydrocarbons, terpenes and aldehydes is characteristic for cotton oil, and for the stone oil - hydrocarbons, alcohols, aldehydes, ketones and some complex ethers and the presence of many other complex ethers except the set of above presented substances is characteristic for the “Chakanda” oil. They differ from each other by the number of the substances containing in composition of an extract.

The composition of the whole number of ether oils and products of catalytic reactions and of some other samples has been determined by the method.

Model LIQUAC is used for an estimation of balance of ionite - electrolite system in ion chromatography. As an ionite strong acid cationite KU - 2 and its analogue Amberlet and as cations K^+ and Ca^{2+} have been used. The prepared modeling mixture was passed through the column filled with cationite KU - 2 in n - form. In addition we have also carried out separation and quantitative determination of the iodine ions from herbs [8].

The estimation of an exchange of ions in cationite and their migratory balance was made on the above-stated model. Experimental results were marked from calculation on 5 – 7 %. Definition of the reasons of mistakes and development of methods of their decrease is the purpose of the subsequent researches.

CONCLUSION

The process of separation and optimization by column chromatography using LIQUAC model has been evaluated. The possibility of using this approach to the separation of mixture of methyl esters of fatty acid and ether oils by gas-liquid chromatography, as well as cations and ions of iodine from the mixture of

ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

electrolytes (from medicinal plants) by ion chromatography. Prediction error makes upto 5-7 %.

REFERENCES

[1] Sakodynskii K.I., Brajnikov V.V., Volkov S.A. and etc. Analytical chromatography M.: Chemistry. 1993.
[2] Fredenslund A., Gmehling J., Rasmussen P. Vapor liquid-equlibris using UNIFAC. Amsterdam,Elsevier. 1977.
[3] Muhamadiev N.Q. Elaboration of the methods of identification in gas chromatography applying regression models of retention parameters./Author’s abstract of the dissertation for candidate of chemical sciences. M., 1986. P.22.
[4] Muhamadiev N.Q., Khusainov Kh.Sh., Gulyamova M.T. and etc. Analysis of equilibrium steam phase of sea-buckthorn oil by the method of gaschromato-mass-spectrometer.//DAN UzSSR. 1988. №8. P. 41-42.
[5] Muhamadiev N.Q., Khusainov Kh.Sh. Systematic analysis of the mixtures of organic compounds in gas chromatography. //DAN UzSSR. 1991. №5. P. 42-43.
[6] Muhamadiev N.Q., Khusainov Kh.Sh., Rojenko I.N., Sakodynskii K.I. Structure – group methods in gas chromatographical identification of organic compounds. // DAN UzSSR. 1989. №4. P. 42-44.
[7] Mukhamadiev N.Q., Sayitkulov Sh.M., Ergashev I.M., Khafizov Kh.F., Fayzullaev N.I. Optimization of separation on the basis of UNIFAC parameters and evaluation of the composition of the stationary phase in gas-liquid chromatography.//Chromatographia. 2003. V/57. N 11/12.
[8] Fazlieva N.T., Muhamadiev N.Q., Sayitkulov Sh.M. Study Iodine Amount in Content of Some Medicinal Plants by Ion Chromatography. IJCPS Vol. 3, No. 6, 2014. Pp.91-95.

AUTHOR BIBLOGRAPHY

Nurali Q.Muhamadiev
Dcotor of chemical sciences, professor.

Research interests: physical chemistry of chromatographic processes, methods of separation and identification in chromatography, modeling and oprimization separation processes, food chemistry, chemistry of pathologic processes, computational chemistry, application of information technology achievements to scientific and educational process, chemical synergetics.

Nigina T.Fazlieva
Lecturer

Research interests: physical chemistry of chromatographic processes, methods of separation and identification in chromatography, modeling and oprimization separation processes.

Shuhrat M.Sayitkulov
Candidate of chemical sciences, associate professor

Research interests: physical chemistry of chromatographic processes, methods of separation and identification in chromatography, modeling and oprimization separation processes