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ON THE POSSIBILITY OF APPLYING THE UNIFAC APPROACH TO PREDICTING INFINITE DILUTION ACTIVITY COEFFICIENTS OF SOLUBLE COMPOUNDS IN COMPLEX HIGH BOILING MIXTURES

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Леа МАРИПУУ, Яак АРРО, Хиндрек ТАМВЕЛИУС. О ВОЗМОЖНОСТИ ПРИМЕНЕНИЯ МЕТОДА УНИФАК ДЛЯ ПРЕДСКАЗАНИЯ ПРЕДЕЛЬНЫХ КОЭФФИЦИЕНТОВ АКТИВНОСТИ РАСТВОРЕННЫХ В СЛОЖНЫХ ВЫСОКОКИПЯЩИХ СМЕСЯХ СОЕДИНЕНИЙ

In a previous paper [1] data on infinite dilution activity coefficients (γ^∞) of organic compounds (test compounds) in high boiling shale oils were estimated using inverse gas chromatography (IGC). While the γ^∞ values depend upon the nature of the interaction between the test compound and the molecules of oil on the one hand and the oil components themselves on the other, a set of different test compounds affords a spectrum of γ^∞ which characterizes the oil investigated. These spectra of γ^∞ are very useful to compare thermodynamic properties of different high boiling oils and mixtures. However, the application of IGC to investigating high boiling oils could be more effective if it were possible to compare the γ^∞ values from IGC experiment with those calculated on the basis of liquid phase composition. One of the methods used for this purpose is the UNIFAC approach [2]. Recently, the latter has been successfully applied to calculating hydrogen solubility in coal-derived liquids [3].

In this paper, an attempt is made to use the UNIFAC method to predict γ^∞ of volatile organic compounds in high boiling artificial mixtures which contain, like kukersite shale oil, strongly interacting compounds, i. e. phenols and ketones. In IGC experiments, these mixtures served as liquid phases.

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The mixture named M20 consisted of tridecane, *cis*-5-decene, decalin, α-pinene, isoamylbenzene, 1-methylnaphthalene, acenaphthene, farnesyl acetate, butyl phenyl ether, 5-nonanone, 4-methylcyclohexanone, camphor, valerophenone, 1,3-diphenyl-2-propanone, xanthone, 4-hydroxybenzophenone, 2-propylphenol, 2,6-ditert-butyl-4-methylphenol, 5-indanol, and allylphenol. The mixture named M4 consisted of 1-methylnaphthalene, butyl phenyl ether, valerophenone, and 4-propylphenol. The calculated structural group contents found on weight basis in the artificial mixtures are shown in Table 1.

Table 1

Structural group content of artificial mixtures, mol %

Group	M20	M4	Group	M20	M4
CH_3	14.4	7.7	AC	7.5	12.8
CH_2	26.3	12.8	$ACCH_3$	0.7	2.6
CH	3.7	—	$ACCH_2$	3.9	2.6
C	3.2	—	OH*	3.0	2.6
CH_2=CH	0.9	—	CH_2CO	3.9	2.6
CH=CH	0.4	—	CH_2O	0.4	2.6
CH=C	1.7	—	CH_3COO	0.4	—
ACH	29.6	53.7			

* Alcoholic OH used with an AC group instead of a phenolic OH (ACOH).

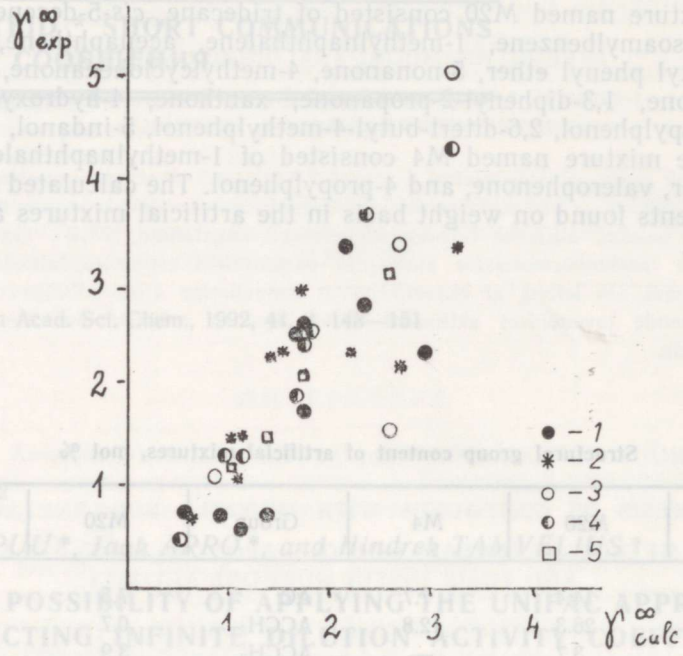
Table 2

Predicted and experimental infinite activity coefficients of test compounds in artificial mixtures M20 and M4 at 298 K

Test compound	M20		M4	
	γ^{∞}_{exp}	γ^{∞}_{calc}	γ^{∞}_{exp}	γ^{∞}_{calc}
Hexane	2.96	1.65	3.41	2.06
1-Hexene	2.33	1.36	2.58	1.66
Methyl-cyclopentane	2.29	1.38	2.57	1.63
Ethyl ether	0.99	0.95	0.73	1.28
Acetone	0.98	1.05	0.65	1.01
Methyl alcohol	2.17	2.63	2.35	2.91
Chloroform	0.70	0.56	0.81	0.52
Acetonitrile	2.36	2.16*	1.74	1.68*
Nitromethane	3.33	3.19*	2.83	2.26
Ethyl acetate	1.09	0.98	0.77	0.86
Water	9.90	22.55**	15.28	11.57

* Interaction parameters from [4].

** 16.97 by using interaction parameters from [4].



The γ^{∞} values of test compounds estimated by IGC versus those calculated in M20 and M4 by UNIFAC: *1* — M4, *2* — M20, *3* — 2-propylphenol, *4* — butyrophenone, *5* — butyl phenyl ether.

The retention volumes of test compounds were measured with a modified LHM-8MD gas chromatograph. Three stainless steel columns (1.0× ×0.004 m) filled with "Inerton" AW-HMDS (0.315—0.400 mm) support impregnated with a 13—15% artificial mixture were thermostated with a precision of 0.1 K in the temperature range 287—303 K. The columns were weighed every day with an accuracy of 0.1 mg and the actual weight for calculations was found by interpolation. The total liquid phase loss per day was less than 1%. The flow rate of helium as carrier-gas was 1.0—1.1 ml/s. All the materials were purchased from Reakhim, USSR. For other details of IGC experiment and calculations see [5]. The UNIFAC procedure described in [2] was used to calculate the γ^{∞} values of test compounds in mixtures M20 and M4. The interaction parameters were taken from [6].

The estimated and calculated γ^{∞} values for both mixtures, M20 and M4, presented in Table 2 are in satisfactory agreement. The best fit has been found for polar compounds. Only for water and alkanes the calculated γ^{∞} values are lower than the experimental ones. The same trend has been observed elsewhere, for example in 4-propylphenol [7].

The Figure shows the γ^{∞} values obtained in different high boiling liquids. It follows that the UNIFAC approach is useful in predicting the γ^{∞} values of organic compounds dissolved in complex mixtures as well as in pure substances. The only problem is how exactly the structural group content of an unknown mixture can be estimated.

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