COMPARISON OF DIFFERENT METHODS
FOR ESTIMATING ACTIVITY COEFFICIENTS IN BINARY MIXTURES
OF HYDROCARBONS

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The accuracy and reliability of a number of different methods for predicting activity coefficients in binary solutions of hydrocarbons was tested. Various modifications of the regular solution model and of the one-parameter Wilson equation and various group-contribution methods were applied to a set of 53 binary mixtures of hydrocarbons of different types. The agreement of the calculated and experimental dependence of activity coefficients on composition was considered. On using the best methods requiring the knowledge of pure component properties only, it is necessary to expect on the average an error of 7% in the value of activity coefficient. When using the group-contribution methods, which employ condensed information on related systems for the prediction, the mean error in the activity coefficient estimation lies about 4%.

The judgement of feasibility of the component separation by distillation and the design of the distillation equipment in petrochemistry require above all the quantitative information on activity coefficients in hydrocarbon mixtures. At the present time there exist a number of different methods enabling their estimation. The aim of this work has been to check the accuracy and reliability of some well-known methods as well as of some of their new modifications with a wider set of systems covering different types of hydrocarbons.

The methods tested can essentially be divided into three groups: The first one consists of the relations being derived from the regular solution model[1]. To estimate activity coefficients only properties of pure components are required in this case. In general these relations can be written in the form

$$\ln \gamma_i = s_i \psi_i^2 A + \ln \gamma_i^{comb} , \tag{1}$$

$$A = c_{11} + c_{22} - 2c_{12} , \tag{2}$$

where

$$\psi_i = s_i x_i / \sum_j s_j x_j \tag{3}$$

is the concentration variable, c_{ii} the cohesive energy density

$$c_{ii} = u_{ii}/s_i \tag{4}$$

and u_{ii} denotes the cohesive energy itself. The individual tested relations differ in the choice of size characteristic of molecule, s_i, in the used rule for estimation of c_{12} and in the chosen expression for the combinatorial contribution $\ln \gamma_i^{comb}$. In this work, altogether 18 different relations of the regular solution type have been tested. For their designation we have used the symbol $RSklm$, where the number k determines the chosen characteristic of molecule size, l the chosen rule for c_{12} and m the expression for the combinatorial term. The molecule size has been characterized by molar volume $(k = 1)$

$$s_i = v_i^L, \tag{5}$$

in terms of parachor[2] $(k = 2)$

$$s_i = \text{const. } [P]^{2/3} \tag{6}$$

or by molecular surface tabulated by Bondi[3] $(k = 3)$

$$s_i = q_i . \tag{7}$$

To estimate c_{12}, partly the geometric mean rule $(l = 1)$

$$c_{12} = (c_{11}c_{22})^{1/2} , \tag{8}$$

that is

$$A = (\delta_1 - \delta_2)^2 , \tag{9}$$

where δ_i is the solubility parameter

$$\delta_i = (c_{ii})^{1/2} , \tag{10}$$

partly the harmonic mean $(l = 2)$

$$c_{12} = 2c_{11}c_{22}/(c_{11} + c_{22}) , \tag{11}$$

that is

$$A = (c_{11} - c_{22})^2/(c_{11} + c_{22}) \tag{12}$$

have been used.

The combinatorial contribution to the activity coefficient has been neglected $(m = 1)$, estimated in terms of the Flory–Huggins equation $(m = 2)$

$$\ln \gamma_i^{comb} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}, \quad \phi_i = v_i x_i / \sum_j v_j x_j \tag{13}$$

or by means of the Guggenheim expression modified recently by Kikic and co-workers[4] $(m = 3)$

$$\ln \gamma_i^{comb} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} q_i \left(\ln \frac{\xi_i}{\theta_i} + 1 - \frac{\xi_i}{\theta_i} \right), \tag{14}$$

$$\xi_i = r_i x_i / \sum_j r_j x_j,$$

$$\theta_i = q_i x_i / \sum_j q_j x_j,$$

where r_i and q_i are the relative volume and surface of a molecule calculated on the basis of the Bondi values.

The cohesive energies have been calculated from the calorimetric data on heats of vaporization[5] according to the approximate relation

$$u_{ii} = \Delta h_i^V - RT \tag{15}$$

for the temperature of 298 K. Even if the cohesive energies and the cohesive energy densities (*i.e.* the solubility parameters, too) are relatively significantly dependent on temperature, their differences are only a weak function of temperature. It can be expected that, owing to the strongly approximate character of relations tested, this temperature dependence can be neglected, which was proved by preliminary calculations. The values u_{ii}, c_{ii} or δ_i used in this work have therefore been evaluated at a fixed temperature (298 K). The data on molar volumes of pure substances have been taken over from the literature[6]. The values of parachors have been determined on the basis of group and structural contributions reported by Reid and coworkers[7].

The second group of methods tested is represented by the methods based on the Wilson equation

$$\ln \gamma_i = -\ln \left(x_i + \Lambda_{ij} x_j \right) + x_j \left(\frac{\Lambda_{ij}}{x_i + \Lambda_{ij} x_j} - \frac{\Lambda_{ji}}{x_j + \Lambda_{ji} x_i} \right), \tag{16}$$

$$\Lambda_{ij} = (v_j^L / v_i^L) \exp \left[-(\lambda_{ij} - \lambda_{ii}) / RT \right]. \tag{17}$$

Altogether four methods of this type have been investigated. Three of these methods estimate the interaction energies between molecules of the same kind, λ_{ii}, on the basis of cohesive energy and the interaction energies between molecules of different kinds, λ_{ij}, are then determined by means of a combination rule. So these

methods employ only information on pure components. In the methods denoted as WIL1 and WIL2, the interaction energies between equal molecules have been calculated according to[8]

$$\lambda_{11} = -(2/z)\,(v_2^L/v_1^L)\,u_{11}\,; \quad v_1 > v_2 \tag{18}$$

$$\lambda_{22} = -(2/z)\,u_{22}\,, \tag{19}$$

and for WIL1

$$\lambda_{12} = (\lambda_{11}\lambda_{22})^{1/2} \tag{19a}$$

or for WIL2

$$\lambda_{12} = 2\lambda_{11}\lambda_{22}/(\lambda_{11} + \lambda_{22})\,. \tag{20}$$

In equation WIL3, the parameters λ_{ii} are calculated according to the relation[9]

$$\lambda_{ii} = -(2/z)\,u_{ii} \tag{21}$$

and the mixed parameter on the basis of the combination rule assuming the harmonic mean of cohesive energies and molar volumes[10]

$$\lambda_{12} = \frac{2c_{11}c_{22}}{c_{11} + c_{22}} \frac{2v_1^L v_2^L}{v_1^L + v_2^L}\,. \tag{22}$$

The fourth tested method starting from the Wilson equation was developed by Gothard and coworkers[11]. These authors expressed the interaction parameters $\lambda_{ij} - \lambda_{ii}$ as generalized functions of the solubility parameter difference. They evaluated altogether six generalized coefficients on the basis of experimental VLE data for a set of hydrocarbon systems chosen.

The last group of methods are the group-contribution methods based on the Solution of Groups concept proposed by Wilson and Deal[12]. The activity coefficient is here expressed in the form

$$\ln \gamma_i = \sum_{j \in i} v_j^{(i)}(\ln \Gamma_j - \ln \Gamma_j^{(i)}) + \ln \gamma_i^{comb}\,, \tag{23}$$

where $v_j^{(i)}$ is the number of groups of type j in the molecule i and Γ_j and $\Gamma_j^{(i)}$ is the activity coefficient of the group of type j in solution or in pure component i, respectively. It is assumed that the group activity coefficients are a function of the group composition and, if need be, of temperature.

Individual group-contribution methods differ above all in the analytical expression describing the concentration and/or the temperature dependence of group activity

coefficients, further in the relation expressing the combinatorial part, in the definition of types of functional groups and in the used values of their geometric characteristics. In this work, the quasichemical model in the transcription by Kehiaian and co-workers[13] (designated as the TOM Project), the UNIFAC model[14] with the original and modified combinatorial term (14) and the ASOG model[15] have been tested. For a detailed description of these methods we refer to the original literature. The number and type of the included interaction parameters needed for the description of hydrocarbon mixtures are listed for single models in Table I. Values of these parameters have been taken over from the original papers; some missing parameters in case of the quasichemical model have been evaluated only in this work (Table II).

RESULTS

The methods mentioned have been tested with a set of 53 binary hydrocarbon systems selected from the compilation by Maczynski[16]. The constants of the Redlich–Kister

TABLE I

Number of adjustable parameters used for estimations for some methods

Method	Altogether	Without temp. dependence	Expressing temp. dependence
GOTHARD	6	6	—
TOM	10	5	5
UNIFAC	12	12	—
ASOG	20	10	10

TABLE II

Group interaction parameters TOM for describing hydrocarbon mixtures ($T_0 = 298.15$)

h_{ij}/RT_0	CH_3 or CH_2	g_{ij}/RT_0		$C{=}C$
		Cyclo-CH_2	Aromatic-CH	
CH_3 or CH_2	—	0.05123	0.2598	0.3181^a
Cyclo-CH_2	0.1533	—	0.2445	
Aromatic-CH	0.5623	0.5619	—	0.1715^c
$C{=}C$	0.2090^b		0.02616^d	—

Adjusted from experimental data: ^{a} g^E 1-heptene + n-heptane[20], ^{b} g^E 1-octene + n-hexane[21], ^{c} g^E benzene + 1-octene[22], ^{d} h^E benzene + 1-octene[23].

polynomial have been taken directly. For the purposes of judgement, the set tested has been divided into 7 subgroups according to the type of hydrocarbons included. The set systems are formed by 35 hydrocarbons. Most of selected experimental data are isothermal ones often for temperatures not too far from 300 K.

TABLE III

Prediction of activity coefficients in binary mixtures of hydrocarbons. Mean integral deviation

Model	Alkane + alkane	Alkane + alkene	Alkane + aromatic	Alkane + cyclo alkane	Aro- matic + aromatic	Aro- matic + alkene	Aromatic + cyclo alkane	Mean	Mean[c]
RS111	0·124	0·052	0·062	0·066	0·034	0·106	0·127	0·082	0·070
RS112	0·075	0·054	0·046	0·071	0·040	0·076	0·132	0·071	0·066
RS113	0·092	0·053	0·097	0·061	0·036	0·149	0·119	0·087	0·080
RS121	0·207	0·052	0·318	0·119	0·034	0·365	0·088	0·169	0·146
RS122	0·146	0·054	0·288	0·112	0·038	0·334	0·090	0·152	0·137
RS123	0·174	0·053	0·346	0·113	0·035	0·408	0·084	0·173	0·155
RS211	0·309	0·051	0·124	0·061	0·036	0·087	0·158	0·118	0·081
RS212	0·203	0·053	0·154	0·058	0·043	0·118	0·162	0·113	0·090
RS213	0·255	0·052	0·082	0·055	0·039	0·060	0·148	0·099	0·068
RS221	0·572	0·050	0·056	0·102	0·036	0·056	0·123	0·142	0·067
RS222	0·466	0·051	0·080	0·070	0·043	0·078	0·128	0·131	0·070
RS223	0·533	0·050	0·063	0·083	0·039	0·064	0·115	0·135	0·065
RS311	0·099	0·052	0·150	0·068	0·031	0·212	0·083	0·099	0·091
RS312	0·056	0·054	0·122	0·065	0·034	0·181	0·086	0·085	0·084
RS313	0·064	0·053	0·191	0·063	0·032	0·255	0·077	0·105	0·102
RS321	0·156	0·052	0·502	0·129	0·037	0·572	0·081	0·218	0·202
RS322	0·078	0·053	0·472	0·104	0·031	0·540	0·078	0·194	0·190
RS323	0·118	0·052	0·545	0·118	0·035	0·615	0·084	0·224	0·213
WIL1	0·199	0·055	0·200	0·038	0·037	0·131	0·200	0·123	0·101
WIL2	0·181	0·055	0·133	0·043	0·036	0·068	0·180	0·099	0·080
WIL3	1·135	0·064	0·117	0·164	0·062	0·055	0·180	0·254	0·098
GOTHARD	0·076	0·087	0·062	0·084	0·053	0·039	0·108	0·073	0·068
TOM	0·096	0·035	0·057	0·026	0·032	0·022	0·043	0·044	0·037
UNIFAC[a]	0·089	0·044	0·042	0·066	0·051	0·021	0·029	0·049	0·042
UNIFAC[b]	0·025[b]	0·036[b]	0·042	0·039[b]	0·051	0·021	0·029	0·035	—
ASOG	0·114	0·046	0·057	0·040	0·036	0·044	0·037	0·053	0·043
RAOULT	0·043	0·053	0·222	0·050	0·036	0·162	0·192	0·108	—
number of systems	8	3	18	6	6	5	7		

[a] Original UNIFAC model, [b] UNIFAC model with the Kikic modification of combinatorial term, [c] Raoult law used for describing the systems of alkane + alkane type.

For the methods tested, the agreement has been judged of the calculated and experimental dependence of activity coefficients on composition. The following criterion has been used

$$\sigma_{\text{integ}} = \left(\sigma^{(1)}_{\text{integ}} + \sigma^{(2)}_{\text{integ}}\right)/2\,, \tag{24}$$

$$\sigma^{(i)}_{\text{integ}} = \left[\int_0^1 \left(\ln \gamma_i^{\text{exp}} - \ln \gamma_i^{\text{calc}}\right)^2 \mathrm{d}x_i\right]^{1/2}. \tag{25}$$

The mean values of this criterion not only over single subgroups of systems but also their averages for the whole set are summarized in Table III for individual methods tested. For comparison also the results calculated on the assumption of ideal behaviour are given.

On the basis of the results obtained it is possible to draw the following conclusions: *1*) The systems of the alkane + alkane type, which are closest to the ideal behaviour, are described comparatively worst. Since the obtained estimates are substantially worse than the approximation of ideal behaviour it is necessary for these systems to prefer, as a matter of course, the Raoult law. The mean deviations $\bar{\sigma}_{\text{integ}}$ (averaged over all types of systems) decrease then markedly. The only successful relation for system of the alkane + alkane type is the Kikic modification of the Guggenheim combinatorial term (*14*) which represents well the usual small negative deviations from ideality due to the different size of alkane molecules. *2*) The group-contribution methods yield the best estimates; the results of single methods are here comparable. The entirely best predictions can be obtained on the basis of the UNIFAC model with the modified combinatorial term thanks to substantial improvement of results for systems of molecules differing markedly in size. *3*) The best estimation method requiring no data on mixture (nor in the form of generalized constants) for predicting is the RS112 method, *i.e.* the volume version of the regular solution in combination with the Flory–Huggins equation and the methods RS221 and RS223 which employ the surface concept and, as a measure of molecule surfaces, parachors and for estimating c_{12}, the harmonic mean rule. *4*) The classical method yielding good results is the original Scatchard–Hildebrand equation for regular solution (RS111). Unlike the recent results of Drahoš[17], this method has been more successful than the Erdös surface modification with parachor[2] (RS211). A reason of this discrepancy might be the use of different criteria and nearly three times smaller tested set of hydrocarbon mixtures in case of the Drahoš work. *5*) From modifications of the one-parameter Wilson equation, the most successful one has been WIL2 (harmonic mean of cohesive energies). *6*) The method by Gothard and coworkers has yielded on the whole satisfactory results. However, it is necessary to consider that it contains six adjusted generalized constants. *7*) The aromatic hydrocarbon–cycloalkane systems are mostly predicted by the RS and WIL methods evidently with lower reliability and accuracy

than other types of systems. For these cases it is possible to recommend[18,19] to adjust the geometric mean rule (8) in the relation RS111 or RS112, or to use the surface modification of regular solution with the Bondi characteristics (Table III). 8) On the whole it is possible to say that on making use of methods with adjustable constants (group-contribution methods), the mean error of 4% in activity coefficients can be taken into account (on the assumption that for the description of the alkane + alkane systems, the Raoult law or the Kikic modification of the combinatorial term is used). When using the best methods employing only information on pure substances, it can be assumed on the average an error of 7% in activity coefficients.

REFERENCES

1. Hildebrand J. H., Prausnitz J. M., Scott R. L.: *Regular and Related Solutions.* Reinhold, New York 1970.
2. Erdös E.: This Journal *21*, 1528 (1956).
3. Bondi A.: *Physical Properties of Molecular Crystals, Liquids and Glasses.* Wiley, New York 1968.
4. Kikic I., Alessi P., Rasmussen P., Fredenslund A.: Can. J. Chem. Eng. *58*, 253 (1980).
5. Majer V.: Unpublished results.
6. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds.* Elsevier, Amsterdam 1950.
7. Reid R. C., Prausnitz J. M., Sherwood T. K.: *The Properties of Gases and Liquids.* McGraw-Hill, New York 1977.
8. Ladurelli A. J., Eon C. H., Guiochon G.: Ind. Eng. Chem., Fundam. *14*, 191 (1975).
9. Schreiber L. B., Eckert C. A.: Ind. Eng. Chem., Process Des. Develop. *10*, 572 (1971).
10. Hiranuma M., Honma K.: Ind. Eng. Chem., Process Des. Develop. *14*, 221 (1975).
11. Gothard F. A., Ciobanu M. F. C., Breban D. G., Bucur C. I., Sorescu G. V.: Ind. Eng. Chem., Process Des. Develop. *15*, 333 (1976).
12. Wilson G. M., Deal C. H.: Ind. Eng. Chem., Fundam. *1*, 20 (1962).
13. Kehiaian H. V., Grolier J. P. E., Benson G. C.: J. Chim. Phys. Physicochim. Biol. *75*, 44 (1978).
14. Fredenslund A., Gmehling J., Rasmussen P.: *Vapor–Liquid Equilibria Using UNIFAC, A Group Contribution Method.* Elsevier, Amsterdam 1977.
15. Kojima K., Tochigi K.: *Prediction of Vapor–Liquid Equilibria by the ASOG Method.* Kodansha-Elsevier, Amsterdam 1979.
16. Maczynski A.: *Verified Vapor–Liquid Equilibrium Data*, Vol. 1. *Binary Hydrocarbons Systems.* PWN, Warszawa 1976.
17. Drahoš J.: This Journal *43*, 805 (1978).
18. Funk E. W., Prausnitz J. M.: Ind. Eng. Chem. *62*, 8 (1970).
19. Huron M. J., Vidal J., Asselineau L.: Chem. Eng. Sci. *31*, 443 (1976).
20. Kudryavtseva L. S., Viit A., Eisen O.: Eesti NSV Tead. Akad. Toim. Keem. Geol. *20*, 292 (1971).
21. Woycicki W.: J. Chem. Thermodyn. *7*, 77 (1975).
22. Vera J. H., Prausnitz J. M.: J. Chem. Eng. Data *16*, 149 (1971).
23. Karbalai Ghassemi M. H., Grolier J. P. E., Kehiaian H. V.: J. Chim. Phys. Physicochim. Biol. *73*, 925 (1976).