CORRELATION OF EQUILIBRIUM DATA FOR MULTICOMPONENT LIQUID–LIQUID SYSTEMS

Milan SOVILJ*, Aleksandar TOLIC and Zoran MAKSIMOVIC

Department of Chemical Engineering
Faculty of Technology, University of Novi Sad, 21000 Novi Sad, Yugoslavia

Liquid–liquid equilibrium studies have been carried out for five multicomponent systems comprising aromatics, paraffins and selected solvents (tetraethylene glycol, sulfolane, dimethyl sulfoxide, *N*-methylpyrrolidone and trimethyl phosphate). The experimental equilibrium data were fitted by empirical correlations suggested by Hand, Othmer–Tobias, Bulatov–Yachmenev and Rod. The best fit was obtained with the relation by Rod. The solvent capacities and selectivities are also compared.

Various organic solvents applied so far to the separation of aromatics from aliphatic hydrocarbon mixtures obtained by treatment of primary naphtha products have been discussed in the literature[1–7]. For a quantitative evaluation of the extraction of aromatics it is important to have available equilibrium values of the systems concerned.

Several methods of equilibrium data correlation for ternary and multicomponent systems have been suggested[8]. Major attention has been focused on the thermodynamic approach to the description of the equilibrium using the relation between the activity coefficients of the components and the phase composition. The NRTL, UNIQUAC and UNIFAC thermodynamic models have proved to be well suited to this. However, those models are primarily designed for vapor–liquid equilibria and are less convenient in the treatment of liquid–liquid equilibria (LLE), as pointed out by Sorensen et al.[9]. Also, the parameters of the models are more difficult to obtain for LLE than for vapor–liquid equilibria.

Since the experimental determination of equilibrium data for multicomponent systems is a very complex procedure, such systems are usually treated as pseudo ternary systems. Reduction of multicomponent systems to pseudo ternary systems can be made on the basis of their chemical similarities[10]. In this paper, the components are classed as aromatics, paraffins, and solvents (the first, second and third components, respec-

---

* The author to whom correspondence should be addressed.

tively). For a description of the equilibrium in such systems, it is convenient to use the empirical correlations developed for ternary liquid–liquid systems.

This work is aimed at correlating equilibrium data for aromatics–paraffins–selected solvent multicomponent liquid–liquid systems at various temperatures. The results can serve as a good basis for calculation of the equilibrium in a simulation of the extraction process. A general comparison of the solvents investigated is also made in terms of their capacities and selectivities.

THEORETICAL

Hand[11] proposed an elegant plot of equilibrium composition data, viz.

$$y_1/y_3 = p(x_1/x_2)^q \ . \tag{1}$$

According to Hand, the result should be reasonably well approximated by a straight line in logarithmic coordinates.

Othmer and Tobias[12] also suggested an empirical corelation which in logarithmic coordinates produces a linear relationship for the equilibrium compositions, viz.

$$(1 - y_3)/y_3 = k[(1 - x_2)/x_2]^r \ . \tag{2}$$

Bulatov and Yachmenev[13] proposed empirical correlations of binodal curves and tie-lines in the form:

$$x_3 = \sum_{m=0}^{5} b_m x_2^m \tag{3}$$

$$y_3 = \sum_{j=0}^{5} c_j y_2^j \tag{4}$$

$$y_3 = g \exp(hx_2) \ . \tag{5}$$

Rod[8] expressed the concentration dependence of distribution coefficients for ternary systems in a semilogarithmic form:

$$\ln K_i = \sum_{n=1}^{3} a_{i,n}(x_1 - x_p)^n \ , \quad i = 1, 2, 3 \ . \tag{6}$$

Using these equations, equilibrium data at elevated temperatures can be obtained by interpolation and extrapolation. A FORTRAN program for all calculations by means of the correlations (*1*) – (*5*) was set up for a Varian Digital Computer; the original program by Rod was used for his correlation.

The experimental equilibrium data for the aromatics–paraffins–selected solvent multicomponent systems can also be used to compare the capacities and selectivities of the solvents. The solvent capacity affects the extraction process. It determines the rate of solvent circulation and consequently the size of the majority of the plant equipment. Moreover, the operating costs are also affected by the amount of heat needed to heat the solvent from the extraction temperature to the distillation temperature. The aromatics distribution coefficient K_1 between the solvent and hydrocarbon phases, which is given by[3]

$$K_1 \equiv y_1/x_1 \tag{7}$$

is a measure of the capacity. The selectivity affects the size of the distillation column and the heat requirements for distillation. The selectivity $S_{1,2}$ for aromatics with respect to paraffins is defined by the following equation:

$$S_{1,2} \equiv (K_1/K_2) = (y_1 x_2/x_1 y_2) \ . \tag{8}$$

EXPERIMENTAL

The equilibrium data for the multicomponent systems were measured in an apparatus as described earlier[14,15]. Paraffins and aromatics obtained from pyrolytic gasoline (Oil Refinery, Pancevo, Yugoslavia) served as the starting components. The paraffins were mixtures consisting of 28.76 wt.% n-paraffins, 70.14 wt.% i-paraffins and 1.10 wt.% benzene. The aromatics, also mixtures, contained 73.68 wt.% benzene and 26.32 wt.% toluene. Tetraethylene glycol with 0.3 wt.% water was used as the solvent to increase the polarity. *N*-Methylpyrrolidone and trimethyl phosphate were used after addition of 3 wt.% water. Sulfolane and dimethyl sulfoxide were solvents of "pure" grade.

Experimental data for the binodal curves were obtained by the turbidity method[16] which was based on the following procedure: Two-phase mixtures with different but constant mass ratios of two components and a variable mass fraction of the third component were heated to transparency and then cooled down to become turbid. The temperature of turbidity and the mass fraction of the third component in the mixtures were mutually plotted for the constant mass ratio of two components. The points of binodal curves at the selected temperatures were determined by interpolation.

The tie-lines were determined by a two-phase equilibrium procedure at a constant temperature. A cathetometer was used to measure the level of the interface in graduated glass test tubes after separation, from which the volumes of the raffinate (light phase) and extract (heavy phase) were determined. The masses of the phases were calculated from their volumes and densities. The two-phase

mixtures were equilibrated at selected temperatures and the aromatic content of the raffinate was determined by gas chromatography whereas the aromatic content of the extract was calculated from mass balance. The plait-point was determined by the method of Bancroft[17].

The temperatures were held constant to within ±0.5 °C and the error of measurement did not exceed ±3%.

RESULTS AND DISCUSSION

The experimental results of phase characterization of the systems investigated under selected conditions were presented in our earlier papers[14,15,18–21].

The experimental equilibrium data for the multicomponent systems were fitted by the empirical correlations suggested by Hand[11] (Eq. (*1*)), Othmer–Tobias[12] (Eq. (*2*)), Bulatov–Yachmenev[13] (Eqs (*3 – 5*)) and Rod[8] (Eq. (*6*)). The fit was assessed in terms of the criterion

$$\delta = \left\{ \left[\sum_{l=1}^{N} (x_{l,i}^{\exp} - x_{l,i}^{\text{calc}})^2 + (y_{l,i}^{\exp} - y_{l,i}^{\text{calc}})^2 \right] / 3N \right\}^{1/2} , \quad i = 1, 2, 3 . \tag{9}$$

The results of comparison of the calculated and experimental equilibrium data are given in Table I.

The δ values for all the four correlations were lowest when using sulfolane as solvent.

The best fit for the majority of systems was obtained using the empirical correlation by Rod[8], whereas the Othmer–Tobias[12] and Hand[11] correlations resulted in larger deviations. The Bulatov–Yachmenev[13] equations gave the best results for the multicomponent system involving tetraethylene glycol as the solvent.

The agreement of the experimental equilibrium data with those obtained by using the Rod[8] correlation is shown graphically in Fig. 1.

The correlations and the corresponding computer program package were applied to the construction of the tie-lines, i.e. to the determination of the equilibrium pairs in the systems investigated. All of the correlations can also be used to predict the equilibrium data if their constants have previously been determined for the given system in conditions in which the correlation is valid.

A correlation of the type shown in Fig. 2 was used to compare the capacities of the solvents at a constant temperature. The capacities of the solvents as a function of the mass fraction of aromatics in the raffinate decrease in order *N*-methylpyrrolidone, trimethyl phosphate, sulfolane, dimethyl sulfoxide, tetraethylene glycol. The capacity of the solvents decreases in the same order with increasing mass fraction of paraffins in raffinate and with increasing mass fraction of solvent in raffinate. This applies to all temperatures used.

The selectivities of solvents in the aromatics–paraffins–solvent systems are compared in Fig. 3. The selectivity as a function of the mass fraction of aromatics in raffi-

nate decreases in order: sulfolane, trimethyl phosphate, *N*-methylpyrrolidone, dimethyl sulfoxide, tetraethylene glycol. The same trend is observed in dependence on the mass fraction of paraffins in raffinate and on the mass fraction of solvent in raffinate. Again, this applies to all temperatures used.

TABLE I
Comparison of experimental and calculated equilibrium data of aromatics–paraffins–selected solvent systems at various temperatures and with different solvents

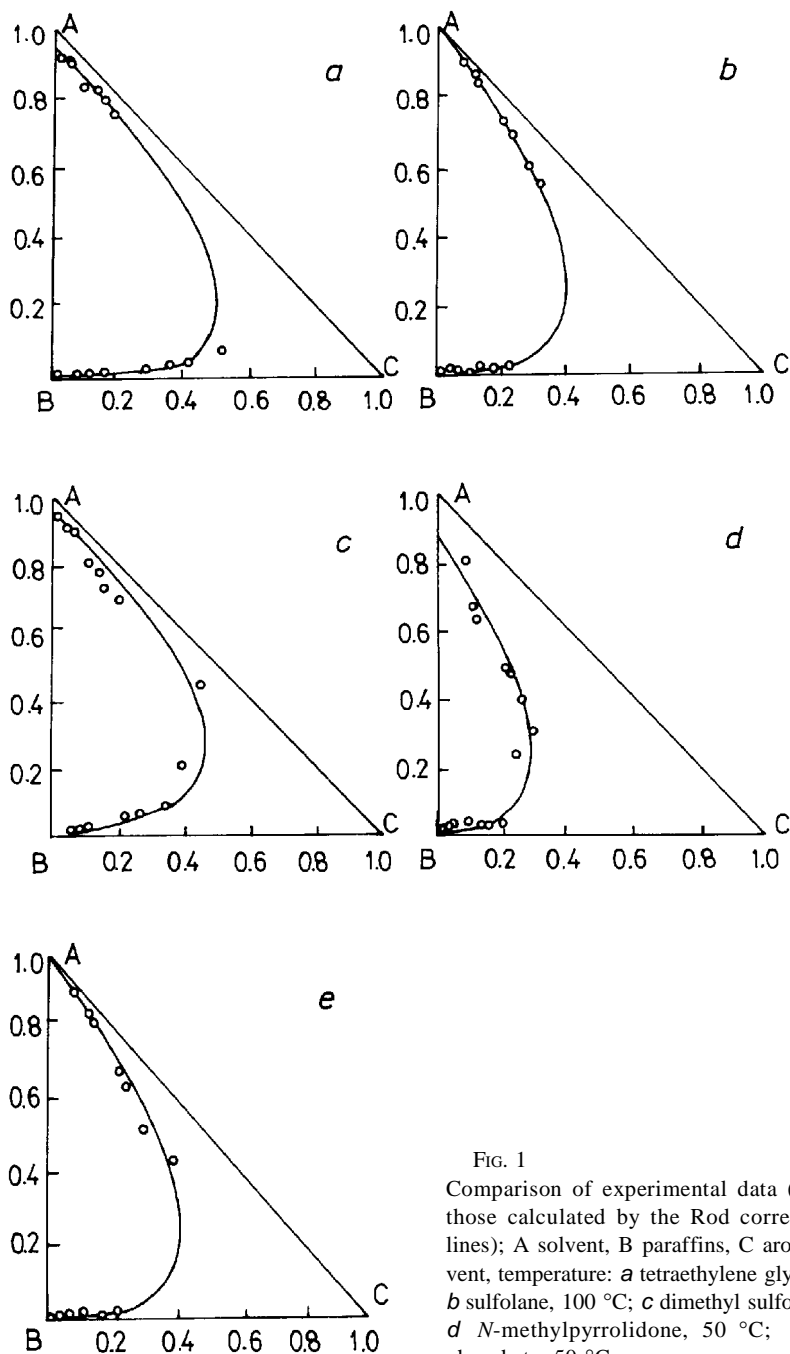| Temperature °C	*N*	Empirical correlations			
		Hand[11]	Othmer–Tobias[12]	Bulatov–Yachmenev[13]	Rod[8]
		δ	δ	δ	δ
		Tetraethylene glycol			
100	7	0.244	0.048	0.009	0.021
115	7	0.267	0.064	0.012	0.010
130	7	0.263	0.081	0.009	0.051
145	7	0.252	0.076	0.008	0.033
		Sulfolane			
100	7	0.075	0.018	0.007	0.002
115	7	0.103	0.021	0.021	0.003
130	7	0.132	0.032	0.004	0.003
		Dimethyl sulfoxide			
90	7	0.221	0.039	0.036	0.052
105	7	0.230	0.052	0.012	0.036
120	7	0.222	0.056	0.036	0.008
135	5	0.255	0.044	0.007	0.006
		N-Methylpyrrolidone			
50	7	0.213	0.062	0.119	0.008
55	7	0.073	0.031	0.018	0.005
60	7	0.175	0.050	0.149	0.006
75	5	0.222	0.138	0.226	0.022
		Trimethyl phosphate			
50	6	0.073	0.022	0.011	0.002
60	6	0.094	0.033	0.082	0.006
70	5	0.182	0.033	0.006	0.002

FIG. 1

Comparison of experimental data (points) and those calculated by the Rod correlation[8] (full lines); A solvent, B paraffins, C aromatics. Solvent, temperature: *a* tetraethylene glycol, 100 °C; *b* sulfolane, 100 °C; *c* dimethyl sulfoxide, 90 °C; *d* N-methylpyrrolidone, 50 °C; *e* trimethyl phosphate, 50 °C

A high selectivity for a desired capacity is the primary requirement for a good solvent. However, increase in solvent capacity is associated with a decrease in its selectivity and vice versa. A compromise must be therefore made. The two parameters can be adjusted by changing the temperature and/or by adding a second component such as water to the solvent.
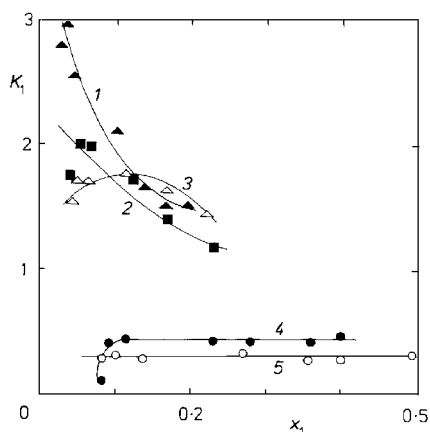

FIG. 2

Comparison of capacities K_1 of solvents in the systems under study. Solvent, temperature: *1* N-methylpyrrolidone, 50 °C; *2* trimethyl phosphate, 50 °C; *3* sulfolane, 100 °C; *4* dimethyl sulfoxide, 90 °C; *5* tetraethylene glycol, 100 °C
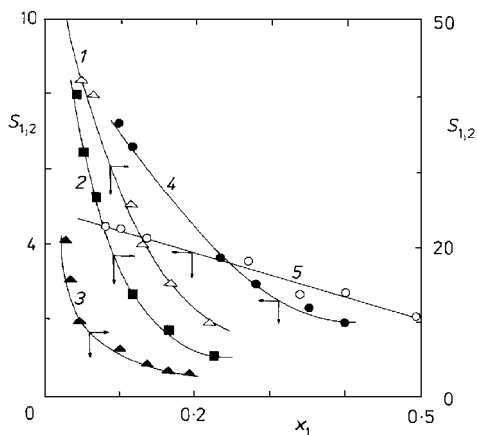

FIG. 3

Comparison of selectivities $S_{1,2}$ of solvents in the systems under study. Solvent, temperature: *1* sulfolane, 100 °C; *2* trimethyl phosphate, 50 °C; *3* N-methylpyrrolidone, 90 °C; *4* dimethyl sulfoxide, 90 °C; *5* tetraethylene glycol, 100 °C

FIG. 4

Comparison of selectivity $S_{1,2}$ and capacity K_1 of the solvents in the extraction of a feed with starting mixture composition: $x_{m,1} = 0.0667$, $x_{m,2} = 0.4333$ and $x_{m,3} = 0.5$. Solvent, temperature: $\triangle$ sulfolane, 100 °C; $\blacksquare$ trimethyl phosphate, 50 °C; $\blacktriangle$ N-methylpyrrolidone, 50 °C; $\bullet$ dimethyl sulfoxide, 90 °C; $\bigcirc$ tetraethylene glycol, 100 °C
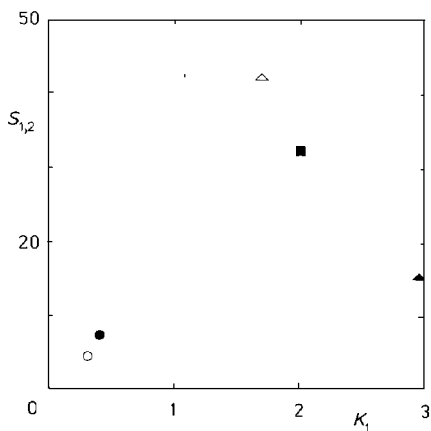
For a comparison of the solvents, their selectivity and capacity data are plotted in Fig. 4 for the same starting mixture composition, viz. $x_{m,1} = 0.0667$, $x_{m,2} = 0.4333$ and $x_{m,3} = 0.5$.

Figure 4 demonstrates that sulfolane has the largest selectivity at a high capacity. This implies that sulfolane is the most suitable solvent for the starting mixtures. Tetra-ethylene glycol and dimethyl sulfoxide, on the other hand, exhibit low capacities and selectivities. These conclusions apply to all starting mixtures.

CONCLUSIONS

When comparing the experimental and calculated equilibrium data, the best agreement for the majority of systems was obtained by using the correlation by Rod[8]. For all the four correlations applied, the best agreement between the experimental and calculated equilibrium data was observed when using sulfolane as solvent.

Comparison of the capacity and selectivity data of the systems investigated revealed that sulfolane has the largest selectivity at a high capacity (for the same starting mixture composition). This implies that from among the solvents tested, sulfolane is best suited to the extraction of aromatics from aromatics–paraffins mixtures.

SYMBOLS

$a_{i,n}$	constants in Eq. (*6*)
b_m	constants in Eq. (*3*)
c_j	constants in Eq. (*4*)
g, h	constants in Eq. (*5*)
k	constant in Eq. (*2*)
K_i	distribution coefficient, Eq. (*7*)
N	number of experimental points
p, g	constants in Eq. (*1*)
r	constant in Eq. (*2*)
$S_{1,2}$	selectivity, Eq. (*8*)
x_i	mass fraction of component i in raffinate
$x_{l,i}$	mass fraction of component i in raffinate
$x_{m,i}$	mass fraction of component i in the starting mixture
y_i	mass fraction of component i in extract
$y_{l,i}$	mass fraction of component i in extract
δ	root mean square deviation, Eq. (*9*)

Subscripts

i	component of the ternary system ($i = 1$ for aromatics, $i = 2$ for paraffins, $i = 3$ for solvent)
j	serial number of coefficient in Eq. (*4*)
l	serial number of experimental or calculated value
m	serial number of coefficient in Eq. (*3*)
n	serial number of coefficient in Eq. (*6*)

Superscripts

calc   calculated value
exp   experimental value

REFERENCES

1. Johanson G. C., Francis A. W.: Ind. Eng. Chem. *46*, 1662 (1954).
2. Somekh G. S., Friedlander B. I.: Hydrocarbon Process. Petr. Ref. *48*, 127 (1969).
3. Moeller E., Hoehfeld G.: *Proc. 7th World Petroleum Congress, Mexico City 1967*, Vol. II, p. 21. Elsevier, London 1967.
4. Renon G., Rimbault G., Jeanjean P.: *Proc. 8th World Petroleum Congress, Moscow 1971*, Vol. IV, p. 197. Applied Science Publishers, Barking 1971.
5. Somekh G. S.: *Proc. Int. Solvent Extraction Conference (ISEC 71), The Hague 1971*, Vol. 1, p. 323. Soc. Chem. Ind., London 1971.
6. Proskuyakov V. A., Gaile A. A.: *Proc. Int. Solvent Extraction Conference (ISEC 74), Lyons 1974*, Vol. 2, p. 1971. Soc. Chem. Ind., London 1974.
7. Grishchenko N. F., Rogozkin V. A., Lastochkina I. I., Golubeva K. V.: Khim. Tekhnol. Topl. Masel *8*, 18 (1974).
8. Rod V.: Chem. Eng. J. *11*, 105 (1976).
9. Sorensen J. M., Magnussen T., Rasmussen P., Fredenslund A.: Fluid Phase Equilib. *3*, 47 (1979).
10. Treybal R. E.: *Liquid Extraction*, p. 463. McGraw-Hill, New York 1963.
11. Hand D. B.: J. Phys. Chem. *34*, 1961 (1930).
12. Othmer D. F., Tobias P. E.: Ind. Eng. Chem. *34*, 693 (1942).
13. Bulatov S. N., Yachmenev L. T.: Teor. Osn. Khim. Tekhnol. *5*, 644 (1971).
14. Perunicic M., Antonicic S., Maksimovic Z., Vojinovic V.: Hemijska industrija *28*, 247 (1974); Chem. Abstr. *81*, 141553 (1974).
15. Maksimovic Z., Tolic A., Perunicic M., Tot F., Kapor M.: Nafta *29*, 158 (1978); Chem. Abstr. *89*, 165851 (1978).
16. Francis A. W.: *Liquid–Liquid Equilibriums*, p. 40. Interscience Publishers, Wiley, New York–London 1963.
17. Ciborovskii J.: *Osnovy protsessov khimicheskoi tekhnologii*, p. 463. Khimiya, Leningrad 1967.
18. Maksimovic Z., Tolic A., Mihaljkovic J., Sovilj M., Vatai G., Kapor M.: Hemijska industrija *33*, 291 (1979); Chem. Abstr. *92*, 44259 (1980).
19. Maksimovic Z., Tolic A., Vatai G., Sovilj M., Teodorovic M., Sinadinovic S.: Proc. Adv. Sep. Sci. (Trieste) *1*, 313 (1978); Chem. Abstr. *91*, 76484 (1979).
20. Maksimovic Z., Tolic A., Sovilj M., Josanov D.: Zbornik radova, Tehnoloski fakultet, Novi Sad *10*, 119 (1979).
21. Maksimovic Z., Tolic A., Sovilj M., Lalic G.: Nafta *12*, 605 (1980); Chem. Abstr. *95*, 121709 (1981).

Translation revised by P. Adamek.