INFLUENCE OF NONIDEALITY OF A TERNARY SOLVENT ON ITS EXTRACTION CHARACTERISTICS

Jana OVEČKOVÁ, Elena GRACZOVÁ and Július SUROVÝ

Faculty of Chemical Technology, Slovak Technical University, 812 37 Bratislava

Limiting selectivities and capacities for various compositions of the mixed solvent ethylene glycol (EG)–diethylene glycol (DEG)–N-methylpyrrolidone (NMP) with respect to toluene have been calculated from limiting activity coefficients of toluene and heptane. The calculations were made for both the ideal and real behaviour of the mixed solvent. The limiting activity coefficients of the model hydrocarbons toluene and heptane in the mixed solvent were calculated from experimentally determined binary coefficients of the Redlich–Kister equation, Wilson's equation as modified by Novák and co-workers, and the NRTL equation.

The greatest problem in the calculation of the extraction characteristics of a mixed solvent is the determination of the thermodynamic properties of the mixed solvent or more specifically, the dependence of the excess Gibbs energy on the composition. This is because extraction is usually carried out at a low temperature for which the dependences of the excess Gibbs energy on the composition for the individual solvent pairs are unknown. The best way to study the extraction characteristics of a solvent is to determine the interdependence of its selectivity and capacity with respect to the component being extracted. If we denote the model hydrocarbons heptane and toluene by subscripts 4 and 5, respectively, then a measure of the selectivity of a solvent towards toluene is the ratio

$$\text{selectivity} = \gamma_4^\infty / \gamma_5^\infty \tag{1}$$

and a measure of the capacity is

$$\text{capacity} = 1/\gamma_5^\infty . \tag{2}$$

Over the past decades, a number of methods have been developed for the experimental determination of limiting activity coefficients[1,2]. Besides these methods, the possibility exists of predicting the γ^∞ from equations for the dependence of the excess Gibbs energy G^E on the composition[3]. In our case, we predicted the limiting activity coefficient of a hydrocarbon in a mixed solvent on the basis of the Redlich–Kister

(R–K) fourth order expansion with binary coefficients, the NRTL equation, and Wilson's equation as modified by Novák and co-workers[4] (W–N).

The relationships for calculating the limiting activity coefficient of heptane in the mixed solvent EG(1)–DEG(2)–NMP(3) are of the forms:

a) Based on the Redlich–Kister fourth order expansion using binary coefficients

$$\ln \gamma_4^\infty = x_1 B_{41} + x_2 B_{42} + x_3 B_{43} - x_1 x_2 B_{12} - x_1 x_3 B_{13} - x_2 x_3 B_{23} +$$
$$+ 2C_{12} x_1 x_2 (x_2 - x_1) + 2C_{13} x_1 x_3 (x_3 - x_1) + 2C_{23} x_2 x_3 (x_3 - x_2) -$$
$$- x_1^2 C_{41} - x_2^2 C_{42} - x_3^2 C_{43} - D_{12} 23 x_1 x_2 (x_1 - x_2)^2 -$$
$$- D_{23}[3x_1 x_3 (x_1 - x_3)^2] - D_{23}[3x_2 x_3 (x_2 - x_3)^2] + x_1^3 D_{41} + x_2^3 D_{42} + x_3^3 D_{43} , \quad (3)$$

where $B_{ij} = B_{ji}$, $C_{ij} = -C_{ji}$, and $D_{ij} = D_{ji}$.

b) Based on Wilson's equation as modified by Novák and co-workers[4]:

$$\ln \gamma_4^\infty = 1 - \ln (x_1 \Lambda_{41} + x_2 \Lambda_{42} + x_3 \Lambda_{43}) - \frac{x_1 \Lambda_{14}}{x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}} -$$
$$- \frac{x_2 \Lambda_{24}}{x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}} - \frac{x_3 \Lambda_{34}}{x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3} +$$
$$+ B_{43} x_3 + B_{41} x_1 + B_{42} x_2 - B_{12} x_1 x_2 - B_{23} x_2 x_3 - B_{13} x_1 x_3 , \quad (4)$$

where $\Lambda_{ii} = \Lambda_{jj} = 1$, $B_{ij} = B_{ji}$, and $B_{ii} = B_{jj} = 0$.

c) Based on the NRTL equation:

$$\ln \gamma_4^\infty = \frac{x_1 \tau_{14} G_{14} + x_2 \tau_{24} G_{24} + x_3 \tau_{34} G_{34}}{G_{14} x_1 + G_{24} x_2 + G_{34} x_3} +$$
$$+ \frac{x_1 G_{41}[\tau_{41}(x_1 + G_{21} x_2 + G_{31} x_3) - (x_2 \tau_{21} G_{21} + x_3 \tau_{31} G_{31})]}{(x_1 + G_{21} x_2 + G_{31} x_3)^2} +$$
$$+ \frac{x_2 G_{42}[\tau_{42}(G_{12} x_1 + x_2 + G_{32} x_3) - (x_1 \tau_{12} G_{12} + x_3 \tau_{32} G_{32})]}{(G_{12} x_1 + x_2 + G_{32} x_3)^2} +$$
$$+ \frac{x_3 G_{43}[\tau_{43}(G_{13} x_1 + G_{23} x_2 + x_3) - (x_1 \tau_{13} G_{13} + x_2 \tau_{23} G_{23})]}{(G_{13} x_1 + G_{23} x_2 + x_3)^2} , \quad (5)$$

where $G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$, and $G_{ji} = \exp(-\alpha_{ij} \tau_{ji})$. Replacing the subscript 4 by 5, we obtain relationships for calculating the limiting activity coefficient of toluene.

RESULTS

The coefficients of the R–K, NRTL and W–N equations for the binary solutions EG(1)–DEG(2), EG(1)–NMP(3) and DEG(2)–NMP(3) were calculated from equilibrium x–y data measured on a differential distillation apparatus and published in our previous paper[5].

For the partially miscible pairs EG(1)–heptane(4), DEG(2)–heptane(4), NMP(3)––heptane(4), EG(1)–toluene(5), and DEG(2)–toluene(5), the three coefficients of the R–K, NRTL and W–N equations were calculated using solubility data published by Feketeová[6] and Medvec[7] (Table I) and the limiting activity coefficient of the respective hydrocarbon in the given solvent. For the given solubility, a trial and error procedure was used to search for such a value of the third parameter for which the limiting activity coefficient calculated from the equation for G^E was equal to the experimentally found value. The limiting activity coefficients of heptane and toluene in EG, DEG and NMP were determined by a modification of the inert gas stripping method[8], and the results are summarized in Table II.

For NMP(3)–toluene(5), a pair miscible over the whole concentration range, the coefficients were calculated from equilibrium P–x data measured by Medvec[7]. So obtained coefficients of the equation for G^E are listed in Tables III to V.

In the case of the R–K equation, it was always possible to find a set of B_{ij}, C_{ij} and D_{ij} $(i = 4, 5; j = 1, 2, 3)$ coefficients which reproduced the experimental values

TABLE I

Miscibility of hydrocarbons (4 — heptane, 5 — toluene) and solvents (1 — EG, 2 — DEG, 3 — NMP)

ij	14	24	34	15	25
x_{ij}	0·00052	0·00055	0·2868	0·0041	0·0160
x_{ji}	0·00159	0·01017	0·3209	0·0239	0·1921

TABLE II

Experimental values of limiting activity coefficients of hydrocarbons (4 — heptane, 5 — toluene) in solvents (1 — EG, 2 — DEG, 3 — NMP)

ij	41	42	43	51	52	53
γ_{ij}^{∞}	611·1	141·5	12·7	46·7	11·3	1·44

of limiting activity coefficient and solubility. Such agreement could not be obtained for the NRTL and W–N equations and the pairs EG(1)–heptane(4) and EG(1)––toluene(5). Here, the experimental values were $\gamma_{41}^{\infty} = 611 \cdot 1$ and $\gamma_{51}^{\infty} = 46 \cdot 7$, while the closest values calculated from the NRTL equation were $\gamma_{41}^{\infty} = 640 \cdot 1$ and $\gamma_{51}^{\infty} = 47 \cdot 3$, and from the W–N equation $\gamma_{41}^{\infty} = 640 \cdot 9$ and $\gamma_{51}^{\infty} = 49 \cdot 1$. As a consequence of this discrepancy, different values of selectivity and capacity of pure solvents with respect to toluene are obtained from the above equations.

Next, Eqs (3), (4) and (5) were used to calculate the limiting activity coefficients, and the selectivity and capacity for various compositions of the mixed solvent were obtained from Eqs (1) and (2) for two cases:

TABLE III

Binary coefficients of the Redlich–Kister (R–K) fourth order expansion

ij	B_{ij}	C_{ij}	D_{ij}
12	$-0 \cdot 0545$	$-0 \cdot 3399$	$-0 \cdot 3029$
13	$-0 \cdot 6554$	$0 \cdot 1836$	$0 \cdot 1967$
23	$-0 \cdot 1596$	$-0 \cdot 1379$	$-0 \cdot 0902$
41	$10 \cdot 5448$	$0 \cdot 5695$	$-3 \cdot 56$
42	$2 \cdot 2191$	$1 \cdot 2869$	$4 \cdot 02$
43	$2 \cdot 2961$	$0 \cdot 0195$	$0 \cdot 265$
51	$4 \cdot 6362$	$0 \cdot 8455$	$0 \cdot 053$
52	$2 \cdot 7721$	$0 \cdot 9174$	$0 \cdot 570$
53	$0 \cdot 5385$	$0 \cdot 2099$	$0 \cdot 0361$

TABLE IV

Coefficients of the NRTL equation

ij	τ_{ij}	τ_{ji}	α_{ij}
12	$-0 \cdot 7573$	$1 \cdot 1669$	$0 \cdot 4365$
13	$-0 \cdot 8143$	$0 \cdot 3114$	$0 \cdot 6$
23	$-1 \cdot 2706$	$0 \cdot 6374$	$-0 \cdot 4794$
41	$5 \cdot 5564$	$2 \cdot 2529$	$0 \cdot 05$
42	$6 \cdot 5976$	$4 \cdot 2822$	$\cdot 0 \cdot 3466$
43	$1 \cdot 7611$	$1 \cdot 6734$	$0 \cdot 4017$
51	$6 \cdot 0421$	$-0 \cdot 4903$	$0 \cdot 05$
52	$3 \cdot 5160$	$1 \cdot 3730$	$0 \cdot 3433$
53	$0 \cdot 9007$	$-0 \cdot 0111$	$0 \cdot 9710$

a) The solvents behave as ideal solutions $\left(B_{ij} = C_{ij} = D_{ij} = 0, \ \Lambda_{ij} = \Lambda_{ji} = 1,\right.$ $\tau_{ij} = \tau_{ji} = 0$, and α has any value different from zero; $i, j = 1, 2, 3$).

b) The solvent pairs EG(1)–DEG(2), EG(1)–NMP(3), and DEG(2)–NMP(3) behave as real solutions.

The R–K equation yields identical values of the limiting solubility for both the real and ideal behaviour of the binary solutions, a result which follows from the structure of the equation (all the terms containing coefficients with subscripts $i, j = 1, 2, 3$ cancel out in the calculation of selectivity, and the relative deviation δ is zero, see Table VI).

TABLE V

Coefficients of Wilson's equation as modified by Novák and co-workers[4] (W–N)

ij	Λ_{ij}	Λ_{ji}	B_{ij}
12	0·3711	1·9086	0
13	0·6778	2·4339	0
23	2·0244	0·4844	0
41	0·9977	0·1395	5·60
42	0·0504	0·00262	0·9664
43	0·2399	0·2002	0·3140
51	0·9846	0·0717	2·95
52	2·4828	0·00197	2·336
53	1·1962	0·2888	—0·1675

TABLE VI

Minimum, maximum and average deviations, δ, between capacities or selectivities of the ideal and real solvents

Equation	Relative deviation δ, %					
	capacity			selectivity		
	δ_{min}	δ_{max}	δ_{aver}	δ_{min}	δ_{max}	δ_{aver}
R–K	1·1	18·3	7·7	0	0	0
W–N	0	5·7	1·9	0·1	2·6	1·3
NRTL	0·5	39·5	18·6	0·2	15·3	4·3

For each pair of selectivities or capacities of the ideal and real solvents, a relative deviation was calculated from

$$\delta = \frac{\left|X^{id} - X\right|}{X} \cdot 100\% \,, \tag{6}$$

where X is the solvent selectivity or capacity. The minimum, maximum and average relative deviations are listed in Table VI. Although it is not an objective of this paper to examine the adequacy of the various equations for G^E (experimental values of selectivity and capacity are not available), it may be concluded, particularly for the solvent capacity, that real behaviour should be considered for binary solutions since the deviations from values for solutions with ideal behaviour may be up to several tens of per cent.

LIST OF SYMBOLS

B	coefficient of the Redlich–Kister (R–K) equation and of Wilson's quation as modified by Novák and co-workers[4] (W–N)
C	coefficient of the R–K equation
D	coefficient of the R–K equation
G	coefficient of the NRTL equation
G^E	excess Gibbs energy
x	mole fraction
X	capacity or selectivity in Eq. (6)
α	coefficient of the NRTL equation
γ^∞	limiting activity coefficient
Λ	coefficient of the W–N equation
δ	relative deviation
τ	coefficient of the NRTL equation

Subscripts

i, j	components
1	ethylene glycol (EG)
2	diethylene glycol (DEG)
3	N-methylpyrrolidone (NMP)
4	heptane
5	toluene

REFERENCES

1. Ferreira P. O., Bastos J. C., Medina A. G.: J. Chem. Eng. Data *32*, 25 (1987).
2. Alessi P., Fermeglia M., Kikic I.: *5th YAI Chemical Engineering Conference, Portoroz, Yugoslavia 1986.*

3. Hála E., Aim K., Boublík T., Linek J., Wichterle I.: *Rovnováha kapalina–pára za normálních a nízkých tlaků*. Academia, Praha 1982.
4. Novák J., Voňka P., Suška J., Matouš J., Pick J.: Collect. Czech. Chem. Commun. *39*, 3593 (1974).
5. Surový J., Graczová E., Ovečková J.: Collect. Czech. Chem. Commun. *54*, 2856 (1989).
6. Feketeová J.: *Thesis*. Slovak Technical University, Bratislava 1986.
7. Medvec E.: *Thesis*. Slovak Technical University, Bratislava 1985.
8. Surový J., Ovečková J., Graczová E.: Collect. Czech. Chem. Commun. *55*, 1457 (1990).

Translated by M. Škubalová.