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Contributions of additional group interaction parameters through limiting activity coefficient measurements on aliphatic alcohols, aromatic hydrocarbons, ketones and an ester in tetrahydroxyethylethylenediamine and tetraethylene pentamine

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Abstract

Gas chromatographic method has been used to measure the limiting activity coefficient of some aliphatic alcohols (ethanol, 1-propanol, 1-butanol and 1-pentanol), aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene and *p*-xylene), ketones (acetone and methylisobutylketone), ethylacetate and chlorobenzene in tetrahydroxyethylethylenediamine (THEEDA) and tetraethylpentamine (TEPA). The measurements involving THEEDA have been used to derive UNIFAC group interaction parameters for seven new pairs, while ten pairs of new group interaction parameters have been derived from the measurements on TEPA. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Limiting activity coefficient; Amines; Gas chromatography

1. Introduction

A reliable knowledge of the infinite dilution activity coefficient is important for the selection of selective solvents for extraction, extractive distillation, etc., for fitting the excess Gibbs energy models, and in the establishment of group interaction parameters. Several investigators, like Fredenslund et al. [1], Zakarian et al. [2], Kikic et al. [3] and Alessi et al. [4], have used infinite dilution activity coefficient to predict the UNIFAC group interaction parameters. We [5–8] measured the infinite dilution activity coefficients of both the components of the binary mixtures of volatile systems and established, through Wilson model, that the infinite dilution activity coefficients can be utilised to describe satisfactorily the vapour–liquid equilibria in the whole composition range.

Tetrahydroxyethylethylenediamine (THEEDA) and tetraethylenepentamine (TEPA) — two important amines — are likely to be of value in the separation of alcohols, aromatic hydrocarbons, ketones, esters, halogenated hydrocarbons, etc., but have not been evaluated for their performance as solvents so far. This investigation on the limiting activity coefficients of some aliphatic alcohols, aromatic hydrocarbons, ketones, an ester and a halogenated compound, noted in the abstract, through gas chromatographic technique, and their application in the proposal of contributions to the UNIFAC group interaction parameters for some additional groups, has been taken up.

2. Literature review

Published works on the measurement of limiting activity coefficients through gas chromatographic technique on similar systems by Martin [9], Martire [10] and Ashraf et al. [11] provided the necessary background to finalise the methodology for the present set of experiments. Martin [9] studied hydrocarbon solutes on three stationary phases: hexadecane (nonpolar), 1-chlorophthalne (moderately polar) and β, β-thiododipropionitrile (strongly polar) and concluded that gas–liquid surface adsorption occurs for polar stationary phases and does not occur for nonpolar

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stationary phases. He also observed that adsorption contributed to the retention time by 98% for 1.5% column loading and 48% for 25% column loading. Martire [10] observed that, with certain solutes and polar solvent systems, on which the solute activity coefficients are around unity, liquid surface effects do occur. Ashraf et al. [11] suggested a higher solvent loading to have a check on the effects of adsorption, particularly when polar solvents are used for interaction studies. Based on the experiences of the previous investigators, and present verification, the solvent loading for both the amines has been fixed at 30% in the present work.

3. Experimental

The two stationary phases — THEEDA and TEPA — have been procured from Analabs (North Haven, CT, USA). The phases are coated on Chromosorb-W support material, supplied by Alltech (Arlington Heights, IL, USA). The Chromosorb-W is dried to a constant weight prior to its coating with the stationary phases. The coated material is filled in clean and dry stainless steel columns of 3 mm i.d. and about 244 cm length. The weight of dry empty columns is determined prior to the filling. The columns filled with the stationary phases coated on the support material are turned into spiral shape and fitted into the thermostated oven of model 5840A microprocessor-controlled Hewlett Packard gas chromatograph. Each column is conditioned by passing 99.99% pure IOLAR Grade I nitrogen, supplied by Indian Oxygen (Mumbai, India). The conditioning is done for 48 h, keeping the oven temperature at 100°C. The weights of the column are then determined, from which the weights of the stationary phases can be evaluated. It is ensured that the weights of the stationary phase remain constant throughout the experiment, by weighing at the beginning and at the end of the experiment, after evaporating all the solvent present. Thermal conductivity detector is used as the sensing element for the present set of experiments.

The carrier gas used for these experiments is pure hydrogen, locally available, passed through tubes packed with molecular sieves and manganese oxide to remove traces of moisture and oxygen that are likely to interfere with the functioning of the thermal conductivity detector.

The inlet pressure is measured by means of a mercury manometer, attached to the inlet of the stationary phase, while the outlet pressure is measured by means of a barometer, procured from Hagemann, FRG, to an accuracy of ±0.5 mm Hg. The pressure-drop across the column is generally 50–60 mm Hg. A soap bubble flow meter, capable of measuring the flow rates to an accuracy of 0.05 ml/min, is used to measure the flow rate of the carrier gas. After the attainment of steady state conditions, 1 μl of the solute is injected and its retention time (t_r) noted. The retention-time value is accepted only when three consecutive measurements show no change. The experiment is repeated with an inert gas, such as methane, and the retention time (t_o) recorded.

All the solutes used in the present studies are spectroscopic or analar grade reagents procured from E. Merck (Darmstadt, FRG).

4. Calculation of limiting activity coefficients

Eq. (1), proposed by Desty and Swanson [12] and discussed in detail by Laub and Pecsok [13], is used for the calculation of the specific retention volume V_g^o

$$V_g^o = \left(\frac{JF_m}{W}\right)\left[\frac{(P_o - P_{H_2O})}{P_o}\right]\left(\frac{273}{T_m}\right)(t_r - t_o) \tag{1}$$

where F_m is the flow rate of the carrier gas (m^3/s) at the ambient temperature T (K), W (kg) is the mass of the stationary phase, P_{H_2O} (Pa) is the vapour pressure of water at T_m, J is the James-Martin pressure-correction factor, given by

$$J = \left(\frac{3}{2}\right)\frac{\left[(P_i/P_o)^2 - 1\right]}{\left[(P_i/P_o)^3 - 1\right]} \tag{2}$$

where P_i (Pa) and P_o (Pa) are the pressures at the inlet and outlet of the column, respectively. The activity coefficient of the solute (component 2) at infinite dilution γ_2^∞ is given by

$$\ln\gamma_2^\infty = \ln\left[\frac{273R}{P_2^o M_1 V^o}\right] - \left[\frac{(B_{22} - V_2^o)P_2^o}{RT_{\mathrm{Expt}}}\right] \tag{3}$$

where R is the gas constant (8.3147 J/mol K), P_2^o (Pa) is the vapour pressure of the solute at the experimental temperature T_{Expt} (K), M_1 (kg/mol) is the molar mass of the stationary phase (component 1), B_{22} (m^3/mol) is the second virial coefficient of the solute at T_{Expt}, and V_2 is the molar volume (m^3/mol) of the solute at T_{Expt}. The correction for gas phase non-ideality, given by the second term on the right-hand side of Eq. (3), is included, as indicated by Young [14] in his review on the use of gas chromatography for the determination of thermodynamic properties, to enable us to determine accurately the values of limiting activity coefficients. The method proposed by Hayden and O'Connel [15] is used for the calculation of the second virial coefficient (B_{22}). The necessary critical properties and molar volumes are either collected from, or estimated, according to the methods recommended by Reid et al. [16].

5. UNIFAC parameter estimation

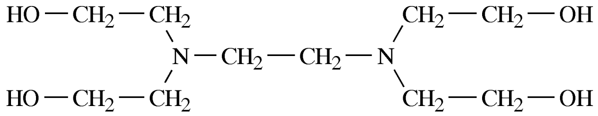
The procedure suggested by Fredenslund et al. [17] is followed. The group volume (R_k) and group area (Q_k)for evaluating the combinatorial part of the activity coefficient are calculated from the Van der Waals group volume and surface area parameters given in Bondi [18]. In the case of larger groups, these parameters are obtained by summing up the values for smaller groups which constitute the larger groups. The liquid phase (solvent) in the gas–liquid chromatographic system is non-volatile, and it is possible to obtain only one datum — the limiting activity coefficient of the solute in the solvent. In the UNIFAC method, however, the interaction between functional groups m and n is characterised by two parameters A_{mn} and A_{nm}. Thus, there is an apparent problem of having to estimate two parameters from one piece of information. The problem is usually circumvented in two ways. One method is to select the solute and solvent consisting of the pertinent functional groups and conduct the experiments on the set of solutes and solvents. For instance, in the case of alcohol–alkane interactions, one has to determine the limiting activity coefficient of a volatile alcohol in a non-volatile alkane and subsequently determine the limiting activity coefficient of a volatile alkane in a non-volatile alcohol. The second method is to determine the limiting activity coefficient of a number of similar solutes in a single non-volatile solvent. In the present work, the second approach is followed, where several aliphatic alcohols, aromatic hydrocarbons, an ester and a chlorinated compound are studied in each non-volatile solvent.

According to the UNIFAC model, the activity coefficient has a combinatorial contribution due to the size and shape of the molecules, and a residual contribution due to the energetic interaction, expressed as

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{4}$$

where γ_i is the activity coefficient of the component i in the mixture. $\gamma_i^C$and γ_i^R are its combanatorial and residual parts, respectively. An objective function comprising of experimentally determined i and that calculated using the UNIFAC model is then minimised using Nelder–Mead technique. During minimisation of the objective function, the UNIFAC parameters, A_{mn} and A_{nm}, of the molecule i are evaluated. Many pairs of UNIFAC parameters have been established in the literature, and a large enough description and compilation is given by Hansen et al. [19]. Whenever parameters listed by Hansen et al. [19] occur in the present systems, the contributions have been incorporated for estimating the UNIFAC group interaction parameters for new groups not reported in the literature. In the present analysis, the two amines are split into the following groups, based on their structural formulae.

THEEDA



has two $N(CH_2)_3$, four CH_2 and four OH groups.

TEPA

$H_2N–CH_2–CH_2–NH_2–CH_2–CH–NH_2$
$–CH_2–CH–NH_2–CH_2–CH–NH$

has two NH_2CH_2 and three $NH(CH_2)_2$ groups.

The solutes have the following groups:

Ethanol: one CH_3, one CH_2 and one OH;
1-Pentanol: one CH_3, two CH_2 and one OH;
1-Butanol: one CH_3, three CH_2 and one OH;
1-Pentanol: one CH_3, four CH_2 and one OH;
Benzene: 6 ACH;
Toluene: 5 ACH and one ACCH;
Ethylbenzene *o*-xylene and *p*-xylene: four ACH and two $ACCH_3$;
Acetone: one CH_3 and one CH_3-C=O;
Methylisobutylketone: one CH, one CH_2, two CH_3 and one CH_3-C=O;
Ethylacetate: one CH_2, one CH_3, and one CH_3-C=O; and
Chlorobenzene: 5 ACH and one ACCl.

In the case of THEEDA, a new group, $N(C_2H_3)$, is identified during the present work. If the molecule is split into the groups, as identified by Bondi [18], it has groups like four CH, ten CH_2 and two aliphatic N groups. If the UNIFAC parameters are estimated with reference to the splitting suggested by Bondi [18], then the data fitting for all the systems is poor, whereas the data fitting in the case of the present studies employing the contributions of the newly proposed group, $N(C_2H_3)$, is good. All the solutes possess the groups identified by Bondi [18], and the contributions to the groups proposed by him have been used, along with the contributions to the newly identified groups proposed in the present work, in the calculation of limiting activity coefficients from the UNIFAC model. The details of the UNIFAC interaction parameters involving the systems with THEEDA are given in Table 1. The experimentally determined limiting activity coefficients of different compounds are compared with the predictions from the UNIFAC model in Tables 2–4. The percent deviation (PD), given by

$$PD = 100\frac{(\gamma_{Expt}^{\propto} - \gamma_{UNIFAC}^{\propto})}{\gamma_{Expt}^{\propto}} \tag{5}$$

Table 1
New UNIFAC group interaction parameters pertaining to the groups present in tetrahydroxyethylethylenediamine (THEEDA)

Group m	Group n	A (m, n)
CH_2	$N(CH_2)_3$	419.8
$N(CH_2)_3$	CH_2	55.3
OH	$N(CH_2)_3$	2072.2
$N(CH_2)_3$	OH	1152.6
ACH	$N(CH_2)_3$	452.0
$N(CH_2)_3$	ACH	363.5
$ACCH_2$	$N(CH_2)_3$	352.1
$N(CH_2)_3$	$ACCH_2$	126.4
ACCl	$N(CH_2)_3$	157.8
$N(CH_2)_3$	ACCl	113.6
CH_3CO	$N(CH_2)_3$	2600.0
$N(CH_2)_3$	CH_3CO	2700.0
CH_3COO	$N(CH_2)_3$	2900.0
$N(CH_2)_3$	CH_3COO	2700.0

Table 2
Limiting activity coefficients of aliphatic alcohols in THEEDA, percent deviation (PD) and percent average absolute deviation (PAAD) of the values predicted by the UNIFAC model[a]

Solute	Limiting activity coefficient at						PAAD
	50°C	60°C	70°C	80°C	90°C	100°C	
Ethanol	1.19 (21.85)	1.06 (13.25)	1.00 (9.00)	0.97 (7.22)	0.94 (5.32)	0.92 (4.35)	10.16
1-Propanol	–	1.30 (7.69)	1.24 (4.03)	1.21 (3.30)	1.19 (3.36)	1.14 (0.88)	3.85
1-Butanol	2.31 (27.27)	1.78 (7.86)	1.61 (0.62)	1.45 (−6.21)	1.47 (−3.40)	1.41 (−2.84)	8.03
1-Pentanol	2.54 (0.79)	2.07 (−6.76)	1.92 (−13.0)	1.81 (16.67)	1.75 (−17.1)	1.70 (−17.1)	11.91

[a] Numbers in parentheses are the values of PD defined by Eq. (5).

Table 3
Limiting activity coefficients of aromatic hydrocarbons in THEEDA, percent deviation (PD) and percent average absolute deviation (PAAD) of the values predicted by the UNIFAC model[a]

Solute	Limiting activity coefficient at						PAAD
	50°C	60°C	70°C	80°C	90°C	100°C	
Benzene	6.48 (14.04)	5.49 (4.55)	5.29 (14.00)	4.88 (4.10)	4.69 (5.54)	4.47 (5.82)	8.01
Toluene	9.25 (18.38)	7.76 (8.63)	7.19 (7.23)	6.52 (3.37)	4.47 (−1.89)	4.14 (−12.1)	8.60
o-Xylene	11.65 (13.48)	10.12 (6.52)	9.03 (5.87)	8.92 (5.94)	7.91 (7.84)	7.69 (2.47)	7.02
p-Xylene	–	11.50 (17.39)	10.54 (19.35)	8.43 (0.47)	7.23 (−9.68)	6.28 (−19.4)	13.26
Ethylbenzene	11.49 (−16.2)	10.78 (−14.84)	10.59 (−8.69)	9.85 (−8.93)	9.13 (−0.98)	–	9.92

[a] Numbers in parentheses are the values of PD defined by Eq. (5).

Table 4
Limiting activity coefficients of acetone, methylisobutylketone, ethylacetate and chlorobenzene in THEEDA, percent deviation (PD) and percent average absolute deviation (PAAD) of the values predicted by the UNIFAC model[a]

Solute	Limiting activity coefficient at						PAAD
	50°C	60°C	70°C	80°C	90°C	100°C	
Acetone	3.92 (7.14)	3.55 (27.60)	3.06 (18.95)	2.56 (5.86)	2.65 (11.32)	2.49 (8.03)	13.15
Methylisobutylketone	10.26 (24.37)	8.41 (13.20)	7.52 (5.85)	6.24 (−8.33)	5.68 (−14.18)	5.78 (−7.78)	12.27
Ethylacetate	8.26	7.22	6.25	5.64	5.37	–	9.10
Chlorobenzene	5.66 (4.42)	4.71 (−6.16)	4.59 (−1.31)	4.32 (−0.23)	4.22 (3.55)	–	3.13

[a] Numbers in parentheses are the values of PD defined by Eq. (5).

and the percent average absolute deviation (PAAD), given by

$$\mathrm{PAAD} = \frac{\Sigma|\mathrm{PD}|}{n} \tag{6}$$

where n is the number of data points, are also included in the tables. The results for the systems involving TEPA are presented in Tables 5–8.

6. Discussion

As noted in Section 1, our earlier work on binary mixtures of volatile solutes [5–8], wherein the VLE data predicted from the infinite dilution activity coefficients alone through Wilson model are shown to compare well with the VLE data measured by conventional methods, like measuring t-x, t-x-y, etc., over the whole composition range, encouraged us to undertake the present study, in which the infinite dilution activity coefficients are utilised to derive group interaction parameters of the NRTL model, for use in the prediction of phase equilibria for design purposes.

Table 5
UNIFAC group interaction parameters pertaining to the groups present in tetraethylenepentamine (TEPA)

Group m	Group n	A (m, n)
CH_2	$NH(CH_2)_2$	−1032.9
$NH(CH_2)_2$	CH_2	615.0
OH	$NH(CH_2)_2$	−575.4
$NH(CH_2)_2$	OH	1054.8
NH_2CH_2	$NH(CH_2)_2$	−1266.3
$NH(CH_2)_2$	NH_2CH_2	643.3
ACH	$NH(CH_2)_2$	−106.1
$NH(CH_2)_2$	ACH	405.8
$ACCH_3$	$NH(CH_2)_2$	−725.9
$NH(CH_2)_2$	$ACCH_3$	253.2
ACCl	$NH(CH_2)_2$	140.7
$NH(CH_2)_2$	ACCl	−227.1
CH_3CO	NH_2CH_2	192.8
NH_2CH_2	CH_3CO	734.6
CH_3CO	$NH(CH_2)_2$	−1087.3
$NH(CH_2)_2$	CH_3CO	769.1
CH_3COO	NH_2CH_2	143.8
NH_2CH_2	CH_3COO	674.0
CH_3COO	$NH(CH_2)_2$	−1066.6
$NH(CH_2)_2$	CH_3COO	705.0

Table 6
Limiting activity coefficients of aliphatic alcohols in TEPA, percent deviation (PD) and percent average absolute deviation (PAAD) of the values predicted from the UNIFAC model[a]

Solute	Limiting activity coefficient at						PAAD
	50°C	60°C	70°C	80°C	90°C	100°C	
Ethanol	2.02 (33.67)	1.70 (28.23)	1.27 (0.00)	1.08 (−132.89)	1.04 (−15.38)	0.98 (−19.38)	10.4
1-Propanol	–	2.20 (21.09)	1.70 (13.02)	1.46 (0.68)	1.17 (18.80)	1.09 (22.93)	17.0
1-Butanol	–	3.16 (39.24)	2.03 (10.34)	1.52 (13.80)	1.50 (10.00)	1.31 (21.61)	18.8
1-Pentanol	–	3.43 (30.32)	2.21 (−1.36)	1.67 (−25.75)	1.55 (−27.74)	1.45 (28.96)	22.8

[a] Numbers in parentheses are the values of PD defined by Eq. (5).

Table 7
Limiting activity coefficients of aromatic hydrocarbons in TEPA, percent deviation (PD) and percent average absolute deviation (PAAD) of the values predicted by the UNIFAC model[a]

Solute	Limiting activity coefficient at						PAAD
	50°C	60°C	70°C	80°C	90°C	100°C	
Benzene	13.26 (40.42)	8.90 (14.49)	9.67 (24.09)	7.06 (−0.28)	5.61 (21.92)	4.61 (43.38)	24.1
Toluene	21.89 (47.65)	13.59 (20.82)	11.47 (11.59)	–	7.23 (25.03)	–	26.3
o-Xylene	22.81 (31.48)	18.53 (22.56)	14.43 (8.32)	10.01 (−22.28)	8.16 (39.24)	9.11 (16.14)	23.3
p-Xylene	21.17 (26.17)	17.29 (17.00)	14.14 (6.44)	11.41 (−7.27)	9.38 (−21.11)	7.55 (−40.13)	19.7
Ethylbenzene	28.30 (42.54)	17.18 (12.26)	15.42 (9.21)	11.25 (−15.91)	7.93 (−66.33)	7.28 (−56.87)	33.9

[a] Numbers in parentheses are the values of PD defined by Eq. (5).

Table 8
Limiting activity coefficients of acetone, methylisobutylketone, ethylbenzene and chlorobenzene in TEPA, percent deviation (PD) and percent average absolute deviation (PAAD) of the values predicted by the UNIFAC model[a]

Solute	Limiting activity coefficient at						PAAD
	50°C	60°C	70°C	80°C	90°C	100°C	
Acetone	15.50 (28.52)	10.51 (8.56)	9.62 (12.68)	6.22 (−19.13)	5.56 (−25.18)	5.33 (−10.69)	17.5
Methylisobutylketone	–	23.4 (10.81)	20.68 (14.75)	–	10.96 (−18.61)	9.29 (−20.45)	16.2
Ethylacetate	37.39 (41.50)	–	–	11.03 (23.48)	9.46 (−35.83)	9.08 (−14.54)	28.8
Chlorobenzene	9.87 (43.33)	7.27 (25.45)	5.05 (4.36)	4.16 (−23.08)	3.66 (36.34)	3.18 (52.83)	30.9

[a] Numbers in parentheses are the values of PD defined by Eq. (5).

Attempts to predict the infinite dilution activity coefficients by means of group interaction parameters for all the groups, as given in Hansen et al. [19], and attempts to propose alternate values for the characteristic groups present in the amines as resolved by them, yielded a poor representation. The two-fold effort involved

1. using the groups as well as group interaction parameters given by them, and
2. deriving revised group interaction parameter values for the same groups based on the present set of measurements.

As the results of both the approaches are unsatisfactory, a set of new groups has been identified and the interaction parameters involving the newly identified groups have been proposed.

Comparisons shown in Tables 2–4 and 6–8 indicate that there is generally good agreement between the calculated and experimental values of the limiting activity coefficients. Although it is not possible to explain the reasons for the behaviour, the following general remarks are in order.

In the case of systems involving THEEDA as the solvent:

1. for aliphatic alcohols (Table 2), the limiting activity coefficients lie between 0.92 and 2.54, and show a decrease with temperature;
2. for aromatic hydrocarbons (Table 3), the limiting activity coefficients lie between 4.22 and 11.65, and decrease significantly with temperature;
3. for acetone, methylisobutylketone ethylacetate and chlorobenzene (Table 4), the limiting activity coefficients are in the range 2.49–10.26, and the decrease with temperature is also prominent.

In the case of systems involving TEPA as the solvent:

1. for aliphatic alcohols (Table 6), the limiting activity coefficients lie between 0.98 and 3.43, and decrease with temperature;

2. for aromatic hydrocarbons (Table 7), the limiting activity coefficients lie between 3.18 and 28.30, and decrease significantly with temperature;
3. for acetone, methylisobutylketone, ethylacetate and chlorobenzene (Table 8), the limiting activity coefficients vary between 5.33 and 37.39, and the decrease with temperature is also considerable.

There is some order in the values of the infinite dilution activity coefficients for the classes of the organic compounds studied.

Limiting activity coefficients of the systems involving THEEDA show the following pattern:

- for normal aliphatic alcohols, the limiting activity coefficients increase with increase in the number of carbon atoms;
- for aromatic hydrocarbons, the limiting activity coefficient increases with alkyl substitution, with no clear pattern for the effect due to the position of substitution;
- for ketones, the limiting activity coefficient is higher for higher molecular weight compounds.

Systems involving TEPA also show the same general trends.

While the overall representation by the UNIFAC model, with the newly proposed group interaction parameters coupled with the already published ones, is quite good, the representation for a few systems is only satisfactory, and the worst represented ones are: *p*-xylene with THEEDA and ethylacetate with TEPA.

7. Conclusion

In conclusion, it can be recommended that:

1. the information on the infinite dilution activity coefficient data can be directly used for design purposes, for the systems studied, and interpolation, or limited extrapolation, may be reliable to obtain data on related systems.
2. the newly proposed group interaction parameters of the NRTL model provide a means of a more accurate representation of the systems containing the groups identified, compared to the schemes already published in the literature, and may serve as a guide in identifying and deriving group interaction parameters for characteristic types of molecules.

Appendix A. Nomenclature

B	virial coefficient of solute at T_{expt} (m^3/mol)
F_{m}	flow rate of the carrier gas (m^3/s)
J	James-Martin correction factor, defined by Eq. (3)
M_1	molecular weight of the stationary phase (kg/mol)
n	number of observations
P_{i}	pressure at the inlet of the column (Pa)
P_{o}	pressure at the outlet of the column (Pa)
P_2^{o}	vapour pressure of the solute at T_{Expt} (Pa)
$P_{\mathrm{H_2O}}$	vapour pressure of water at T_{Expt} (Pa)
PAAD	percent average absolute deviation, defined in Eq. (7)
PD	percent deviation, defined in Eq. (6)
Q_{K}	group area fraction of group K (cm/mol)
R	gas constant (8.314 J/mol K)
R_{K}	group volume fraction of group K (cm^3/mol)
t_{r}	retention time of the solute (s)
t_{o}	retention time of inert
T_{Expt}	experimental temperature (K)
T_{m}	ambient temperature (K)
γ_2^∞	limiting activity coefficient of the solute
$\gamma_{\mathrm{Expt}}^\infty$	experimental value of the limiting activity coefficient
$\gamma_{\mathrm{UNIFAC}}^\infty$	limiting value of the activity coefficient calculated from the UNIFAC model

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