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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 organic phosphates☆

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Abstract

Gas chromatographic technique is used to measure the limiting activity coefficients of some aliphatic alcohols (ethanol, 1-propanol, 1-butanol, 1-pentanol), aromatic hydrocarbons (benzene, toluene, *o*-xylene, *p*-xylene, ethylbenzene), ketones (acetone, methylisibutylketone), and an ester (ethylacetate) and chlorobenzene in three organic phosphates (tricresylphosphate, trixylolphosphate, tributylphosphate). The limiting activity coefficient are used to derive the UNIFAC group interaction parameters for 13 new pairs. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Limiting activity coefficient; Organic phosphates; Gas chromatography

1. Introduction

Modern designs of fluid phase separation equipments such as for distillation, liquid extraction, etc., require an accurate mathematical representation of the phase equilibria in multi-component systems. Excellent solution models have been developed in the recent past. Wilson [1] developed equations for both polar and non-polar mixtures. Renon and Prausnitz [2] developed models for polar mixtures which are also valid for immiscible systems. These are followed by the recent developments of group interaction based model for multicomponent systems by Fredenslund et al. [3]. This model, often called the UNIFAC method provides a good representation of the systems containing both the polar and non-polar species and miscible as well as immiscible systems. Limiting activity coefficients are needed for establishing the interaction parameters of the model. Likely errors in the values extrapolated from the conventional vapor–liquid equilibrium data have paved the way to the other simpler, yet reliable means of measuring limiting activity coefficients through the methods such as gas chromatography.

2. Literature review

A rapid method for the determination of reliable vapor–liquid equilibrium data is a permanent need in the industry for screening the solvents to be used for separation by extractive distillation or liquid extraction and for the design of equipments and processes involving these. Hala [4] first suggested the use of gas–liquid chromatography (GLC) as an excellent mean of evaluating the vapor–liquid equilibria. Martin [5] recognised the potentials and applied GLC for the studies on the interaction of a volatile solute with a non-volatile solvent. Kobayashi et al. [6] and Young [7] reviewed the work on GLC techniques exhaustively. Langer et al. [8] have reported the data on a few aromatic hydrocarbons in trixylolphosphate (TXP) at 90°C. Meen et al. [9] reported the limiting activity coefficient data of benzene in aliphatic phosphate tributylphosphate (TBP) at 60°C. Alessi et al. [10] reported limiting activity coefficient data for: aliphatic alcohols (C_1–C_4), benzene, toluene, ethylbenzene and ethylacetate at 25°C, 50°C, 75°C, 100°C and 125°C in TXP and TCP.

Gas–liquid interfacial adsorption is a source of error in the study of solution thermodynamics. Martin [11] is the first to investigate the phenomenon and suggest that when gas–liquid interfacial adsorption contributes to the retention, the

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equation for the net retention volume is

$$V_N = K_R V_L + K_S A_L \quad (1)$$

where K_R is the bulk partition coefficient , V_L the volume of the liquid phase, K_S the liquid surface adsorption partition coefficient and A_L the liquid surface area. The bulk partition coefficient K_R is found by plotting (V_N/V_L) vs. $(1/V_L)$ which is a horizontal line. It is important to note that this equation applies only to the retention data from symmetrical peaks, and as a corollary the absence of peak asymmetry does not preclude the presence of adsorption effects.

Martin [11] studied hydrocarbons (nonpolar) solutes on three stationary phases: n-hexane (non-polar), 1-chloronaphathalene (moderately polar) and 3,3′-thiodipropionitrile (strongly polar) and concluded that liquid surface adsorption occurs for polar stationary phases and does not occur for non-polar ones. He also observed that adsorption contributed to 98% at 1.5% loading and 48% at 25% loading for the same solute. Ashraf et al. [12] studied the interfacial effect of aliphatic alcohols (strongly polar) solutes in a phthalate stationary phase (polar) and established that 30% phthalate loading is required for minimizing the effects due to gas–liquid interfacial adsorption.

3. Experimental

All the chromatographic stationary phases – tricrecylphosphate (TCP), trixylophpsphate (TXP) and tributylphosphate (TBP) employed in the present studies are procured from Anlabs (North Haven, CT, USA). These phase are coated on Chromosorb – W support supplied by Alltech (Arlington Heights, IL, USA). The coated material is then filled into 3 mm i.d. and about 244 cm stainless steel columns, subsequently turned into a spiral shape and fitted into the thermostated oven of the chromatograph maintained at 100°C. Each column is conditioned for 48 h, by passing 99.99% pure IOLAR Grade I nitrogen supplied by Indian Oxygen Limited (Mumbai, India).

In order to obtain precise and accurate results, a Model 5340A microprocessor controlled Hewlett Packard gas chromatograph is used for determining the limiting activity coefficient, using a thermal conductivity detector. All the solutes used in this work are either spectroscopic or analar grade reagents procured from E. Merc (Darmstadt, FRG).

Pure hydrogen gas available locally is used as the carrier gas, after further purification by passing through glass tubed filled with molecular sieves and manganous oxide to remove any traces of moisture and oxygen likely to interfere with the thermal conductivity detection. The carrier gas flow rates are measured by a soap bubble flow meter to an accuracy of 0.05 ml min^{-1}. The flow rates are measured at the ambient temperature. After the attainment of the steady state conditions in the system, 1 μl of solute is injected and its retention time (t_s) is noted. The value of the retention time is accepted only after three successive measurements showed no change. The experiment is then repeated by injecting an inert gas such as methane and its retention time (t_{ir}) is noted.

4. Calculation of the limiting activity coefficients

The specific retention volume (V_g) is calculated using Eq. (2), proposed by Desty and Swanson [13] and discussed in detail by Laub and Pecsok [14], after providing correction to the carrier gas flow rate which is previously measured at the ambient temperature, to the temperature existing inside the column.

$$V_g = \frac{(JF_m/W)(P_o - P_{H_2O})}{P_o[(273/T_m)(t_{sr} - t_{ir})]} \quad (2)$$

where F_m is the flow rate of the carrier gas (m^3 s^{-1}) at the ambient temperature T_m (K), W (kg) the mass of the stationary phase, P_{H_2O} (Pa) the vapor pressure of water at T_m.

J is the James–Martin pressure correction factor given by Eq. (3)

$$J_m = \frac{3}{2}\frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]} \quad (3)$$

where P_i (Pa) is the pressure at the inlet of the column. The activity coefficient (γ_2^∞) of the solute (component 2) at infinite dilution is given by the equation.

$$\ln \gamma_2^\infty = \ln\left(\frac{273R}{P_2 M_1 V_g}\right) - \frac{(B_{22} - 1V_2)P_2}{RT} \quad (4)$$

where R is the gas constant (8.314 J mol^{-1}K^{-1}), M_1 (kg mol^{-1}) the molar mass of the stationary phase (component 1) P_2 (Pa) the vapor pressure of the solute at the experimental temperature T_{Expt} (K), B_{22} (m^3 mol^{-1}) the second virial coefficient of the solute at T_{Expt}, V_2 the molar volume of the solute at T_{Expt}.

The second term on the righ hand side of Eq. (4) takes into account the non-ideality of the gas phase. Since the future usage of the data is to establish the UNIFAC group interaction parameters from γ_2^∞ values alone, these have to be calculated as accurately as possible, therefore the correction for gas phase non-ideality has also been included following the suggestion of Young [7]. The second virial coefficients are calculated as suggested by Hayden and O'Connel [15]. The necessary input properties such as: molar volumes, critical propterties, etc. are found in or estimated in accordance with the methods recommended by Reid et al. [16].

5. UNIFAC parameter estimation

The group contribution method of Fredenslund et al. [3] is followed. In the present studies as the liquid phase(solvent) in the GLC system is non-volatile, it is possible to obtain only one datum: the infinite dilution activity coefficient of the solute in the solvent. In the UNIFAC model, however, the interaction between the functional groups m and n is characterized by two parameters A_{mn} and A_{nm}. Thus there is an apparent problem of having to estimate two parameters from a single piece of information. There are two ways to solve the problem. One is to select the solute and solvent consisting of the pertinent functional groups and determine the two limiting activity coefficients. For instance, in the case of alcohol–alkane interaction, one has to determine the two limiting activity coefficients of a volatile alcohol in a nonvolatile alkane and then determine the limiting activity coefficient of a volatile alkane in a non-violatile alcohol. The second way is to use GLC data of several similar solutes in a single non-volatile solvent. The second approach is used in the present investigation. Several aliphatic alcohols, aromatic hydrocarbons, two ketones, an ester and halogenated benzene are interacted in the GLC column and their limiting activity coefficients are determined at six constant temperatures. Six experimental data points are determined for a majority of solutes to make the UNIFAC parameter estimation meaningful and accurate enough.

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

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} \tag{5}$$

where γ_i is the activity coefficient of the component i of the mixture, γ_i^{C} is the combinatorial part and γ_i^{R} is the residual part. The two parts are evaluated as suggested by Fredenslund et al. [3]. The group volume (R_K) and group area (Q_K) for group K for evaluating the γ_i^{C} are calculated from van der Waals group volume and surface area parameters given in Bondi [17].

An objective function consisting of the experimentally determined infinite dilution activity coefficients and the one calculated using the UNIFAC interaction parameters A_{mn} and A_{nm} of groups m and n of the molecule i are optimized. Many of the UNIFAC interaction parameters are already available in the literature and have been described and listed by Hansen et al. [18]. The available group interaction parameters are incorporated into the present analysis to derive group interaction parameters for the groups which have not been investigated earlier.

The phosphates are split into the indicated groups depending on their structural formulae.

Tricresylphosphate	1 ArO_4, 3 AC, 12 ACH, 3 $ACCH_3$
Trixylolphosphate	1 $ArPO_4$, 3 AC, 9 ACH, 6 $ACCH_3$
Tributylphosphate	1 $AlPO_4$, 9CH_2, 3 CH_3

The functional groups present in the solutes are as follows:

Aliphatic alcohols have

Ethanol	1 CH_3, 1 CH_2, 1 OH
1-Propanol	1 CH_3, 2 CH_2, 1 OH
1-Butanol	1 CH_3, 3 CH_2, 1 OH
1-Pentanol	1 CH_3, 4 CH_2, 1 OH

Aromatic hydrocarbons have

Benzene	6 ACH
Toluene	5 ACH, 1 $ACCH_3$
o-xylene and *p*-xylene	4 ACH, 2 $ACCH_3$
Ethylbenzene Ketones have	5 ACH, 1 $ACCH_2$, 1 CH_3
Acetone	1 CH_3, 1 CH_3-C=O
Methylisobutlyl ketone	1 CH, 1 CH_2, 2 CH_3, 1 CH_3-C=O
Ethyl acetate has	1 CH_2, 1 CH_3, 1 CH_3COO
Chlorobenzene has	5 ACH, 1 ACCl

In the case of aromatic phosphates, TCP and TXP the estimation work is carried out in four different sets. The first set consists of TCP, TXP, aliphatic alcohols and aromatic hydrocarbons. The estimation of the second set is done with TCP, TXP, acetone and methylisobutyl ketone. In the third set, the estimations are carried out with TCP, TXP, ethylacetate. The fourth set consists of TCP, TXP and chlorobenzene. The new UNIFAC parameters estimated in a set are used in the subsequent set if required. Similar grouping is also adopted for TBP. The only difference being the absence of the fourth set, as the data on chlorobenzene with TBP have not been measured.

6. Results and discussion

Phosphate stationary phases are polar in nature, as has been established earlier [12] and the percent loading for all the stationary phases has been maintained at 30%. As the symmetry of the chromatographic peaks is an important criterion for judging the validity of activity coefficient data, 1 μl of the solute in injected to avoid asymmetry. The 30% loading of the stationary phases keeps even the sample size under the Henry's law region. Lower sample sizes of 0.1–0.2 μl produced asymmetric peaks. Alessi et al. [10] also observed the same phenomenon. The retention volume in the present work is calculated from the retention time obtained from the recorder attached to the microprocessor of the gas chromatograph.

The accuracy of the limiting activity coefficients is entirely dependent on two sensitive parameters – flow rate of the carrier gas and the weight of the stationary phase. These two factors are carefully monitored by frequent checking for their constancy.

The limiting activity coefficients of ethanol, 1-propanol, and 1-butanol have been determined by Alessi et al. [10] in the range of 25–125°C at 25°C intervals in TXP and TCP.

Table 1
New UNIFAC group interaction parameters pertaining to aromatic and aliphatic phosphates

Aliphatic phosphate ($AlPO_4$)			Aromatic phosphate ($ArPO_4$)		
Group *m*	Group *n*	A_{mn} (*K*)	Group *m*	Group *n*	A_{mn} (*K*)
CH_2	PO_4	316.7	CH_2	PO_4	312.4
PO_4	CH_2	312.9	PO_4	CH_2	130.7
AC	PO_4	90.0	AC	PO_4	883.4
PO_4	AC	6.1	PO_4	AC	117.8
$ACCH_2$	PO_4	173.2	$ACCH_2$	PO_4	420.8
PO_4	$ACCH_2$	138.6	PO_4	$ACCH_2$	48.9
OH	PO_4	138.4	OH	PO_4	723.1
PO_4	OH	443.2	PO_4	OH	−136.4
CH_3CO	PO_4	83.9	CH_3CO	PO_4	2050.0
PO_4	CH_3CO	−203.1	PO_4	CH_3CO	1550.0
CH_3COO	PO_4	25.4	CH_3COO	PO_4	1786.3
PO_4	CH_3COO	6.9	PO_4	CH_3COO	91.4
			ACCl	PO_4	31.2
			PO_4	ACCl	251.5

The percent average absolute deviation of the present measurements with those of Alessi et al. [10] date is 9% at 50°C and 10% at 100°C in TXP while it is 11% at 50°C and 7% at 100°C in TCP. The reason for the deviations of this order is the probable contribution of adsorption effects more prominently in the work of Alessi et al. who used 25% w/w column loading of the stationary phase and a copper column. In our work 30% w/w column loading of the stationary phase, fixed on the basis of experimentation and stainless steel column have been used.

Langer et al. [8] reported the limiting activity coefficients of benzene, toluene and *o*-xylene in TXP at 90°C. Our measurements deviate from those reported by Langer et al. [8] by 10%. Langer et al. have prepared TXP of 99% purity and used it in their studies while the TXP used by us is procured from Anlabs, North Haven, CT, USA, which is of 99.9% purity. While the other factors contribute similarly, the somewhat lesser purity of the TXP used by Langer et al. and larger absorption effects possible at the gas–liquid interface in the experiments of Langer et al. might have contributed to the differences.

Mean et al. [9] published the limiting activity coefficients of benzene at 60°C which deviate from our data by 7%. The use of a shorter column length by Meen et al., likely to be unable to provide long enough gas–liquid contact and 20% w/w loading used by Meen et al. likely to produce some adsorption effects are believed to be responsible for the deviations.

With the care taken during our experimentation, our measurements are expected to be within +5% of the true values in view of the highest purity substances used and maintenance of the required conditions during the experimentation.

Seven pairs of new UNIFAC parameters are evaluated for the aromatic phosphate group while six pairs of new UNIFAC group interaction parameters are estimated for the case of the aliphatic phosphate. All these parameters are listed in Table 1. The measured values of the limiting activity coefficients for the aliphatic alcohols are given in Table 2, along with the values of the percent deviation (PD) defined as

$$\mathrm{PD} = 100\left[\frac{\gamma^{\infty}_{\mathrm{Expt}} - \gamma^{\infty}_{\mathrm{UNIFAC}}}{\gamma^{\infty}_{\mathrm{Expt}}}\right] \tag{6}$$

and the percent average absolute deviation (PAAD) defined

Table 2
Limiting activity coefficients of aliphatic alcohols in TCP and TXP and percent deviation (PD) and percent average absolute deviation (PAAD) from the values predicted by UNIFAC model

Solute	Solvent	Limiting activity coefficient (PD) at						PAAD
		50°C	60°C	70°C	80°C	90°C	100°C	
Ethanol	TCP	1.39 (7.19)	1.33 (4.51)	1.31 (3.82)	1.32 (6.06)	1.32 (8.33)	1.29 (6.20)	4.02
1-propanol	TCP	1.23 (4.06)	1.14 (−1.75)	1.10 (−4.50)	1.06 (−6.60)	1.03 (−9.71)	1.04 (−6.73)	5.25
1-butanol	TCP	1.35 (18.52)	1.29 (15.50)	1.12 (3.57)	1.05 (−0.95)	1.00 (−5.00)	0.96 (−8.33)	8.64
1-pentanol	TCP	1.27 (18.90)	1.14 (10.53)	1.07 (4.67)	1.02 (0.98)	0.98 (−2.04)	0.94 (−5.32)	8.71
Ethanol	TXP	1.34 (7.46)		1.16 (−5.17)	1.15 (−4.40)	1.06 (−12.3)	1.05 (−11.4)	8.13
1-propanol	TXP	1.30 (−8.46)	1.12 (−0.89)		1.00 (−11.00)		0.95 (−13.68)	8.43
1-butanol	TXP	1.21 (12.40)	1.10 (4.54)	1.00 (−5.00)	0.95 (−9.50)	0.94 (−9.57)	0.92 (−10.87)	8.64
1-pentanol	TXP	1.07 (5.61)	0.98 (−2.04)	0.95(5.30)	0.90(−10.00)	0.86 (14.00)	0.84 (−16.70)	8.92

Table 3
Limiting activity coefficients of aromatic hydrocarbons in TCP, TXP and their percent deviations (PD) and percent average absolute deviations (PAAD) from the values predicted from the UNIFAC model

Solute	Solvent	Limiting activity coefficient (PD) at						PAAD
		50°C	60°C	70°C	80°C	90°C	100°C	
Benzene	TCP	0.64 (−9.37)	0.66 (−9.37)	0.64 (−9.37)	0.66 (−4.45)	0.66 (−4.45)	0.67 (−8.98)	6.66
Toluene	TCP	0.72 (−8.33)	0.70 (−10.0)	0.71 (−10.0)	0.70 (−8.57)	0.70 (−8.57)	0.70 (−7.14)	8.77
o-xylene	TCP	0.79 (−2.53)	0.77 (−5.19)	0.77 (−3.90)	0.74 (−8.11)	0.73 (−8.22)		5.59
p-xylene	TCP	0.86 (4.65)	0.85 (4.70)	0.89 (10.11)	0.80 (0.00)	0.78 (−1.28)	0.77 (−2.60)	3.89
Ethylbenzene	TCP	0.85 (9.63)	0.82 (9.76)	0.82 (9.76)		0.80 (8.75)	0.78 (7.79)	3.89
Benzene	TXP	0.60 (3.33)	0.59 (1.69)	0.59 (1.69)	0.60 (3.33)	0.60 (3.33)	0.61 (3.33)	2.78
Toluene	TXP	0.65 (−4.61)	0.64 (−4.69)	0.64 (−4.69)	0.64 (−4.69)	0.64 (−3.12)	0.64 (−3.12)	4.15
o-xylene	TXP		0.69 (−7.25)		0.71 (−2.82)	0.70 (−4.28)	0.70 (−2.86)	4.30
p-xylene	TXP	0.75 (1.33)		0.72 (−2.78)	0.71 (−2.82)	0.71 (−2.82)	0.71 (−2.82)	2.51
Ethylbenzene	TXP	0.73 (12.50)	0.72 (11.11)	0.71 (9.86)	0.70 (8.57)	0.70 (10.00)	0.71 (7.35)	9.90

Table 4
Limiting activity coefficients of ketones, ethylacetate and chlorobenzene in TCP and TXP and their percent deviation (PD) and percent average absolute deviation (PAAD) from the values predicted by UNIFAC model

Solute	Solvent	Limiting activity coefficient (PD) at						PAAD
		50°C	60°C	70°C	80°C	90°C	100°C	
Acetone	TCP	0.87 (−12.64)	0.89 (−9.00)	0.93 (−3.22)	0.96 (0.00)	0.99 (4.04)	1.01 (6.00)	5.82
Methyl-iso-butylketone	TCP	0.93 (0.00)	0.89 (−4.49)	0.87 (−5.75)	0.87 (−5.75)	0.86 (−6.98)	0.87 (−5.75)	4.78
Ethylacetate	TCP		0.85 (12.94)	0.90 (12.22)	0.93 (12.90)	0.96 (13.54)	1.00 (15.00)	13.32
Chlorobenzene	TCP	0.57 (8.77)	0.56 (5.36)	0.56 (3.57)	0.56 (1.57)	0.56 (0.00)	0.55 (1.87)	3.55
Acetone	TXP	0.82 (1.22)	0.83 (2.41)	0.85 (4.70)	0.86 (6.98)	0.86 (6.98)	0.88 (1.23)	5.42
Methyl-iso-butylketone	TXP	0.84 (7.14)			0.81 (−8.64)	0.81 (2.47)	0.81 (2.47)	5.18
Ethylacetate	TXP		0.86 (−4.65)	0.86 (9.30)	0.86 (−12.8)	0.89 (−12.4)	0.90 (−15.6)	9.11
Chlorobenzene	TXP	0.48 (0.00)	0.49 (−2.04)	0.49 (−5.88)	0.49 (−6.12)		0.50 (−8.00)	4.41

Table 5
Limiting activity coefficients of aliphatic alcohols aromatic hydrocarbons, ketones and ethylacetate in TBP and their percent deviations (PD) and percent average absolute deviations (PAAD) from the values predicted by UNIFAC model

Solute	Limiting activity coefficient (PD) at						PAAD
	50°C	60°C	70°C	80°C	90°C	100°C	
Ethanol	0.50 (12.00)		0.49 (2.04)			0.45 (20.00)	11.35
1-propanol	0.43 (6.98)	0.43 (2.32)	0.42 (4.76)		0.41 (14.63)		7.17
1-butanol	0.46 (−19.56)	0.42 (−7.14)			0.39 (10.20)		12.30
1-pentanol	0.37 (5.40)	0.38 (5.26)	0.36 (−5.55)	0.36 (−8.33)			6.13
Benzene		0.57 (0.00)	0.57 (0.00)	0.57 (0.00)	0.57 (1.75)	0.58 (0.00)	0.35
Toluene	0.64 (0.00)	0.64 (0.00)	0.64 (−1.56)	0.66 (0.00)			0.39
Acetone	0.83 (6.02)	0.83 (6.02)	0.75 (8.23)	0.85 (8.23)	0.85 (8.23)	0.88 (12.50)	8.20
Methyl-iso-butylketone		0.73 (0.00)	0.67 (−8.95)	0.63 (−17.5)	0.62 (−21.0)		11.84
Ethylacetate	0.86 (1.16)	0.84 (0.00)	0.83 (0.00)	0.83 (0.00)		0.81 (0.00)	0.23

as

$$\mathrm{PAAD} = \sum \frac{|\mathrm{PD}|}{n} \tag{7}$$

where n is the number of observations for TCP and TXP.

Table 3 gives the results of the work on aromatic hydrocarbons, while the results for ketones and the other compounds are given in Table 4. The results of the work on TBP are summarized in Table 5.

On the whole, the representation of the limiting activity coefficient data by UNIFAC model is quite good. The group interaction parameter is a measure of the non-ideality involving interaction between each group. The interaction parameters derived in this work can be safely applied to the situations where PO_4 groups are present.

Nomenclature

B_{22}	Virial coefficient of the solute at T_{Expt} ($\mathrm{m^3\,mol^{-1}}$)
F_{m}	Flow rate of the carrier gas ($\mathrm{m^3\,s^{-1}}$)
J	James–Martin correction factor, defined in Eq. (3)

M_1	Molecular weight of the stationary phase (kg mol^{-1})
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	Vapor pressure of the solute at T_{Expt} (Pa)
P_{H_2O}	Vapor 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^2 mol^{-1})
R	Gas constant, 8.314 (J mol^{-1} K^{-1})
R_K	Group volume fraction of group K (cm^3 mol^{-1})
t_{sr}	Retention time of the solute (s)
t_{ir}	Retention time of inert (s)
T_{Expt}	Experimental temperature (K)
T	Ambient temperature (K)
V_g	Specific retention volume (cm^3)
V_N	Net retention volume (cm^3)

Greek symbols

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 UNIFAC model

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