Infinite Dilution Activity Coefficient Measurements for 1-Methyl-4-(1-methylethenyl)-cyclohexene as a Green Solvent for Separation

Banzi Patrick Mbatha, Peterson Thokozani Ngema,* Nkululeko Nkosi, and Suresh Ramsuroop*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Infinite dilution activity coefficients for various solutes, which include alkanes, alkenes, alkynes, cycloalkanes, heterocycles, alcohols, aromatics, ketones, ethers, nitrile, and water, in a 1-methyl-4-(1-methylethenyl)-cyclohexene solvent were measured using gas−liquid chromatography at 303.15, 313.15, and 323.15 K. The focus of this study was to assess 1-methyl-4-(1-methylethenyl)-cyclohexene as a green solvent for separation processes. 1-Methyl-4-(1-methylethenyl)-cyclohexene, a nonpolar monoterpene solvent extracted from essential oils of citrus peels, was investigated as an alternative solvent to currently employed conventional organic solvents in separation processes. Through experimental infinite dilution activity coefficients, γ_{13}^{∞}, the values of partial molar excess enthalpy at infinite ($\Delta H_i^{E,\infty}$) were obtained using the Gibbs−Helmholtz equation. The infinite dilution selectivity (S_{ij}^{∞}) and capacity (Δk_j^{∞}) values were calculated from the experimental limiting activity coefficients and were compared with deep eutectic solvents, ionic liquids, and industrial solvents. From this study, it was observed that 1-methyl-4-(1-methylethenyl)-cyclohexene is not suitable to be used as an alternative for separation processes. In addition, activity coefficients at infinite dilution of different organic solutes in hexadecane were measured at various temperatures to validate the reliability and accuracy of gas−liquid chromatography. Finally, the experimental data were modeled using Aspen Plus, compared with experimental data, and found to be in good agreement.

R-Limonene   S-Limonene
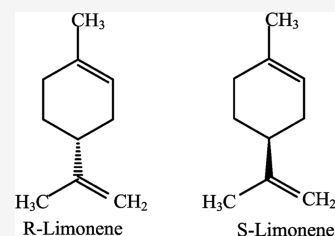
1. INTRODUCTION

The need to replace volatile organic compounds (VOCs) with benign solvents in industrial applications is key in developing more sustainable processes. Petrochemical solvents, usually called traditional solvents, have been widely used in the chemical industry for several years. These solvents are consumed in large quantities due to their availability and low costs. These petrochemical solvents, which are generally obtained via an energy-intensive separation process, can account for more than 50% of the energy costs.[1] These traditional solvents, which generally produce volatile gases, adversely affect the environment by polluting the environment, depleting the ozone layer, posing risks to human health, and are obtained from nonrenewable resources.[2,3] The environmental, sustainability, and health and safety issues related to these traditional solvents have driven the research on developing alternative environmentally friendly solvent processes/systems to replace the use of traditional volatile organics. Some of the alternatives to the traditional solvents that have received extensive attention include ionic liquids (ILs),[4,5] deep eutectic solvents (DESs),[4,6,7] and natural deep eutectic solvents (NADESs).[4] Solvents derived from renewable biological feedstock that are nontoxic and biodegradable are becoming a highly desirable replacement for petrochemical solvents. While these have been identified as potential alternative solvents to VOCs in a wide variety of industrial separation applications, the reduced cost, complexity, and environmental impact of large-scale industrial manufacture of the alternative solvents are necessary precursors for their use.

ᴅ-Limonene (1-methyl-4-(1-methylethenyl)-cyclohexene) is a naturally occurring cyclic monoterpene having the molecular formula $C_{10}H_{16}$. Limonene, a solvent derived from renewable biological feedstock, has been identified as a potential alternative to the traditional solvent due to its biodegradability and low toxicity[8−10] and its performance as a cleaning and degreasing solvent.[7] It is the main component of essential oil extracted from a range of citrus vegetation and is distilled as a clear, colorless, and natural hydrocarbon liquid for technical, pharmaceutical, and food-based uses.[11,12] Furthermore, the extraction and distillation of 1-methyl-4-(1-methylethenyl)-cyclohexene release fewer toxic pollutants and volatile gases. As a result, it has a minimal impact on the environment.[13] Due to its flavor and fragrance, it is widely used in cosmetics, pharmaceuticals, natural medicine, and food.[14]

Activity coefficients at infinite dilution provide incisive information concerning solute−solvent interactions by characterizing the intermolecular interaction behavior of a solute molecule surrounded by the solvent. The activity coefficients at infinite dilution present a better knowledge of the phase equilibrium of high-purity separation processes. Engineers
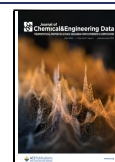
often use this data to design and optimize separation processes of complex mixtures such as close boiling mixtures and mixtures exhibiting azeotropes or limited miscibility. In addition, the activity coefficient data provide valuable information for solvent screening purposes and evaluation of alternative processes. In this case, processes including extractive distillation and liquid−liquid extraction are used when it is not feasible to use ordinary distillation.

The gas−liquid chromatography (GLC) method is used to determine the activity coefficients of solutes, whereby the inner part of the chromatic column is coated with the solvent and solutes are introduced with a carrier gas.[15−18] The net retention times for solutes in the stationary solvent represent the strength of interaction of the solute in the solvent. Direct from the experimental values of γ_{13}^{∞}, the selectivity and capacity factors can be calculated, and they provide critical information on the separation performance of the solvent for separation processes. The high value of selectivity will result in the separation column with a low number of equilibrium stages. Capacity is inversely proportional to the amount of solvent used for extraction. Hence, the lower the capacity, the higher the amount of solvent required for extraction.

In this study, 1-methyl-4-(1-methylethenyl)-cyclohexene is evaluated as a potential solvent for separation processes. There is limited experimental data found in the literature for infinite dilution activity coefficients (IDAC) for 1-methyl-4-(1-methylethenyl)-cyclohexene. The performance of 1-methyl-4-(1-methylethenyl)-cyclohexene is compared with DES, ILs, and industrial solvents for selected nonideal separation cases. This study used separation mixtures such as hexane/hexene, heptane/benzene, ethanol/water, octane/ethylacetate, octane/acetonitrile, octane/thiophene, heptane/pyridine, and octane/pyridine. The experimental infinite dilution activity coefficients are modeled using Aspen Plus software.

2. EXPERIMENTAL SECTION

2.1. Materials. The chemicals used in this study are listed in Table 1 with the suppliers and their purities. The suppliers already purified these analytical grade chemicals, so no purification was required before experiments. The chemical purities listed in Table 1 were verified by analyzing both the refractive index and the density. GC analysis revealed no significant impurities, and the measured refractive indexes and densities agree well with the literature. The properties of D-limonene (1-methyl-4-(1-methylethenyl)-cyclohexene) are listed in Table 2 and graphically illustrated in Figures S1−S3. This solvent was supplied by Sigma-Aldrich (SA). It has two forms of two isomers due to the presence of a chiral center on the fourth atom of carbon in the cyclic ring, as shown in Figure 1.

2.2. Experimental Apparatus and Procedures.
2.2.1. Refractive Index, Density, and Viscosity Measurements. The refractive index of the studied solvent was measured using the Anton Paar Abbemat Refractometer (with an uncertainty of 0.0001). The density of 1-methyl-4-(1-methylethenyl)-cyclohexene was measured using the Anton Paar Density Meter DMA 4100 M (with an uncertainty of ±0.0001). The Abbemat refractometer was directly integrated into the density meter. Table 2 presents the measured values for the refractive index and density at temperatures of 293.15−333.15 K with intervals of 5 K. The recorded measurements are in good agreement with the measurements in the literature.[19]

Table 1. Purity for All Solutes Used in This Study

| compound	supplier	purity (mass fraction)	CAS no.
n-pentane	Merck	≥99.0	109-66-0
n-hexane	Merck	≥99.0	110-54-3
n-heptane	Sigma-Aldrich	≥99.0	142-82-5
n-octane	Fluka	≥99.9	111-65-9
n-nonane	Merck	≥99.0	111-84-2
hex-1-ene	Sigma-Aldrich	≥98.0	592-41-6
hept-1-ene	Flucka	≥98.0	592-76-7
oct-1-ene	Flucka	≥99.5	111-66-0
non-1-ene	Flucka	≥95.0	124-11-8
dec-1-ene	Capital lab	≥98.0	872-05-9
hex-1-yne	Sigma-Aldrich	≥97.0	628-21-7
hept-1-yne	Fluka	≥98.0	628-71-7
oct-1-yne	Fluka	≥98.0	629-05-0
cyclopentane	Fluka	≥98.5	287-92-3
cyclohexane	ACE	≥99.0	11-82-7
cycloheptane	ACE	≥99.9	291-64-5
cyclooctane	Sigma-Aldrich	≥995	292-64-8
ethanol	Sigma-Aldrich	≥99.9	64-17-5
methanol	Macron	≥99.9	67-59-1
propan-1-ol	Lab scan	≥99.5	71-23-8
propan-2-ol	Lab scan	≥99.5	67-63-0
butan-1-ol	Sigma-Aldrich	≥99.0	71-36-3
pentan-1-ol	Sigma-Aldrich	≥99.0	71-41-0
tert-butanol	Sigma-Aldrich	≥99.0	75-65-0
benzene	Sigma-Aldrich	≥99.9	71-43-2
toluene	Sigma-Aldrich	≥99.9	108-88-3
ethylbenzene	ACE	≥99.9	100-41-4
acetone	Sigma-Aldrich	≥99.9	37-64-4
butan-2-one	Sigma-Aldrich	≥99.7	78-93-3
pentan-2-one	Sigma-Aldrich	≥99.0	107-87-9
methylacetate	Capital lab	≥98.0	79-20-9
ethylacetate	ACE	≥99.5	141-78-6
acetonitrile	Sigma-Aldrich	≥99.7	75-05-08
water	Lab purified	≥99.9	7732-18-5
thiophene	Sigma-Aldrich	≥99.9	110-02-1
pyridine	Sigma-Aldrich	≥99.9	100-86-1
m-xylene	Sigma-Aldrich	≥99.9	108-38-3
helium	Afrox-SA	≥99.0	7440-49-7
n-hexadecane	Sigma-Aldrich	≥99.9	544-76-3
1-methyl-4-(1-methylethenyl)-cyclohexene[a]	Sigma-Aldrich	≥97.0	5989-27-5

[a]D-Isomer of limonene was studied.

The viscosity of 1-methyl-4-(1-methylethenyl)-cyclohexene was measured using the Anton Paar AMVn rolling-ball viscometer. Prior to the experimental analysis, ethanol was

Table 2. Experimental Refractive Index (RI), Density (ρ), and Viscosity (μ) of the 1-Methyl-4-(1-methylethenyl)-cyclohexene Solvent as a Function of Temperature, T, at Atmospheric Pressure $p = 101.3 \pm 2$ kPa[a]

	RI		ρ/g·cm^{-3}		μ/mPa·s	
T/K	lit.[19]	exp.	lit.[15]	exp.	lit.[15]	exp.
293.15	1.472		0.845		0.932	0.935
298.15	1.471	1.471	0.841	0.841	0.897	0.895
303.15	1.468	1.468	0.837	0.837	0.816	0.819
308.15	1.481[b]	1.466	0.833[b]	0.833	0.769[b]	0.771
313.15	1.464	1.463	0.829	0.829	0.722	0.728
318.15	1.461[b]	1.461	0.825[b]	0.825	0.684[b]	
323.15	1.459	1.458	0.821	0.821	0.645	
328.15	1.457[b]	1.456	0.817[b]	0.817	0.613[b]	
333.15	1.454	1.454	0.813	0.813	0.580	

[a]Clará et al.[19] [b]Interpolated values, standard uncertainties u are $u(\rho)$ = 1.5 × 10^{-3} g·cm^{-3}, $u(\mu)$ = 0.004 mPa·s, $u(T)$ = 0.01 K, RI = 1.4 × 10^{-3}, and $u(p)$ = 1 kPa of the measured value.
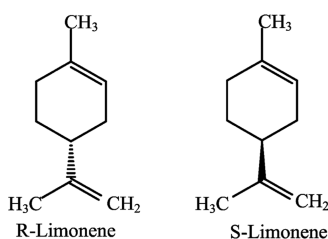
Figure 1. Isomers of 1-methyl-4-(1-methylethenyl)-cyclohexene (Merck, 2015).

used to clean the cell and acetone was used for drying using the automatic Xsample 452 Module. Prior to the viscosity measurements, the water calibration was done at 298.15 K to ensure that the equipment will produce valid results. An uncertainty of 0.004 was obtained. Table 2 presents the measured values for viscosity at temperatures of 293.15–313.15 K with intervals of 5 K. The recorded measurements are in good agreement with the measurements in the literature.[19]

2.2.2. Infinite Dilution Activity Coefficient Measurements. Infinite dilution activity coefficients were measured by gas–liquid chromatography using a Shimadzu GC-2014 gas chromatograph with Chromosorb W-HP (80/100 mesh) as a solid support and dry helium as a carrier gas. The detailed experimental procedure for the GLC technique has been described in previous publications.[15–18] Experiments were undertaken with two different solvent column loadings (27.63 and 33.35 wt %). Each column was made of 0.5 m long stainless steel with an internal diameter of 4.1 mm.[20–23] These columns were washed several times using hot water with soap, rinsed with cold water, and finally flushed with acetone to reduce drying time. Dichloromethane was used to dissolve and evenly distribute all green solvent deposits around the solid support in a solution into the Chromosorb. While gently shaking the mixture, dichloromethane was constantly evaporated using a vacuum pump. Then, the dried mixture was placed in an oven for further drying at a temperature of 333.15 K. The dichloromethane-free mixture was gradually added into the columns until the mixture was equally distributed inside the columns. The gas chromatography (GC) oven temperature was set at T = 333.15 K for more than 4 h until there were no

further changes in the column mass. Before infinite dilution activity coefficient measurements, the carrier gas was allowed to flow for at least 30 min to stabilize the baseline.

The carrier gas flow rates were measured through a calibrated soap bubble flowmeter, which was placed at the end of the thermal conductivity detector (TCD) vent and varied between 10 and 20 mL·min^{-1}. To calculate γ_{13}^{∞}, the carrier gas flow rates were corrected to account for water vapor pressure in the soap bubble flowmeter. The solutes were injected in volumes ranging between 0.2 and 0.3 μL, which fulfilled the requirements of the sample in the column to be at infinite dilution. For each experimental temperature measurement, each solute was injected three times to check the stability of the experimental conditions. The dead time, t_G, was determined using air as an unretained pure component for each temperature in the TDC under the assumption that the solubility effects of air in the stationary phase inside the column are insignificant. The measurement of t_G was repeated at least three times for each temperature to evaluate repeatability.

Three experimental temperatures were used for infinite dilution activity coefficient measurements ranging from 303.15 to 323.15 K, at an interval of 10 K. The injector and detector temperature was specified at a value of T = 523.15 K, which is higher than the boiling point of all organic solutes investigated. The temperature kept solutes entering the column in the gaseous state and liquid state over headspace. The outlet pressure was measured using a digital barometer and was the same as atmospheric pressure, as the end of the column is connected to the atmosphere. The pressure drop measured across the column varied between 4.6 and 9.6 kPa, depending on the oven temperature and the carrier gas flow rate. The investigated solvent has a higher vapor pressure, which causes the column's mass to decrease over time. A reference solute, n-heptane, was injected at regular intervals to lower the uncertainty of the solvent mass in the column. The results for the test systems were found to be within ±3.47% and were found to agree with the literature.[15,24–29]

3. THERMODYNAMIC FUNDAMENTAL

The infinite dilution activity coefficient of solutes was calculated according to the equations developed by Everett 1965, and Cruickshank et al. 1969, through the solute retention.[30]

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3 RT}{V_N P_i^*}\right) - \frac{(B_{i1} - v_1^*)P_i^*}{RT} + \frac{(B_{i2} - v_1^{\infty})J_2^3 P_o}{RT}$$

(1)

where γ_{13}^{∞} is the activity coefficient of solute i at infinite dilution in the stationary phase, n_3 is the number of moles of the solvent, R is the universal gas constant, T is the column temperature, P_i^* is the saturated vapor pressure of solute i, P_o is the pressure at the column outlet, and V_N is the net retention volume of solute obtain in eq 2.[31] The second and third serves as a correctional term from the nonideality of the mobile gas phase at effect pressure. B_{i1} is the second virial coefficient of the solute, B_{i2} is the mixed second virial coefficient of the solute (i) with a carrier gas (2), v_i is the liquid molar volume of the pure solute, and v_i^{∞} is the partial molar volume of the solute in the stationary phase (3) at infinite dilution. P_i^* values were calculated from the Antoine equation with coefficients.[32–34]

Table 3. Infinite Dilution Activity Coefficient for the Selected Solutes in *n*-Hexadecane at T = 298.15−323.15 K and p = 101.3 ± 2 kPa[a,b,c,d,e]

solute	temperature/K	experimental γ_{13}^{∞}	literature γ_{13}^{∞}	R.D%
benzene	298.15	1.093	1.060[26]	3.09
benzene	313.15	1.021	1.006−1.051[27]	1.49
benzene	323.15	0.977	0.932−0.995[28]	1.81
toluene	323.15	0.930	0.941[28]	1.17
n-hexane	313.15	0.91	0.870−0.910[29]	0.55
n-hexane	323.15	0.880	0.860−0.905[27,28]	2.76
cyclohexane	313.15	0.751	0.778[27]	3.47
cyclohexane	323.15	0.725	0.739−0.787[29]	1.89

[a]Standard uncertainties u are $u(p)$ = 1 kPa, $u(\gamma_{13}^{\infty})$ = 1.4, and $u(T)$ = 0.05 K. [b]Tiegs et al.[26] [c]Chien et al.[27] [d]Schult et al.[28] [e]Castells et al.[29]

$$V_{N} = (J_2^3)^{-1} U_o (t_r - t_G) \frac{T_{col}}{T_f} \left[1 - \frac{p_w^o}{P_o} \right] \quad (2)$$

where J_2^3 is the pressure correction term, t_r is the retention time, t_G is the dead time, U_o is the flow rate of helium gas, T_{col} is the column temperature, T_f is the flowmeter temperature, p_w^o is the saturation vapor pressure of water at T_f, and P_o is the pressure at the column outlet. The pressure correction term J_2^3 was given by Everett 1965, as follows

$$J_2^3 = \left(\frac{2}{3} \right) \left[\frac{\left(\frac{p_i}{p_o} \right)^3 - 1}{\left(\frac{p_i}{p_o} \right)^2 - 1} \right] \quad (3)$$

where p_i and p_o are the pressures at the column inlet and the outlet of the GC.

4. RESULTS AND DISCUSSION

The deviation of the result for the hexadecane test system was found to be within ±3.47% and found to agree with literature values,[15,24−29] as shown in Table 3. The experimental values of the infinite dilution activity coefficient for 37 solutes in 1-methyl-4-(1-methylethenyl)-cyclohexene solvent are presented in Tables S1 and S2, at temperatures of 303.15−323.15 K, and an interval of 10 K. Two columns with different solvent loadings were used in this study, and all measured values of γ_{13}^{∞} were averaged, as listed in Table 4 and presented graphically in Figures S4−S8.

The experimental runs were repeated three times at a given temperature to ensure reproducibility. From Figures S4−S8, it was observed that the values of γ_{13}^{∞} were decreasing with the increase in temperature for all solutes. This shows the temperature dependence of the activity coefficients. The activity coefficient at infinite dilution of all solutes decreases with the increase in the alkyl chain length. High values of γ_{13}^{∞} for polar solutes compared to nonpolar solutes with a similar number of carbon atoms were observed, as shown in Table 4. This indicates poor solubility or miscibility of the solute in the solvent. These high values were observed for all polar solutes: alcohols, nitrile, ketones, heterocyclic, ethers, and water. This is attributed to the strong intermolecular forces in the solutes acting between polar molecules such as hydrogen bonds. As a result, weak intermolecular forces are difficult to break down, namely London or dispersion forces acting on the nonpolar solvent. Furthermore, these polar solutes contain elements such as O and N. This creates a weak interaction with the solvent. Therefore, it becomes difficult for a 1-methyl-4-(1-

Table 4. Experimental Average Activity Coefficient at Infinite Dilution, γ_{13}^{∞}, for Various Solutes in the Limonene Solvent as the Stationary Phase at T = 303.1−323.15 K and p = 101.3 ± 2 kPa[a]

solutes (i)	303.15 K	313.15 K	323.15 K
n-pentane	5.704	5.104	4.580
n-hexane	5.578	4.855	4.238
n-heptane	5.431	4.533	3.866
n-octane	5.287	4.433	3.778
n-nonane	5.168	4.304	3.538
hex-1-ene	7.070	6.273	5.420
hept-1-ene	6.602	5.772	5.043
oct-1-ene	6.415	5.351	4.625
non-1-ene	6.044	4.975	4.259
dec-1-ene	5.857	4.717	3.907
hex-1-yne	15.651	14.532	12.898
hept-1-yne	14.555	12.816	11.434
oct-1-yne	13.753	11.425	9.439
cyclopentane	9.794	8.669	7.151
cyclohexane	25.546	22.464	18.817
cycloheptane	29.003	25.660	20.844
cyclooctane	35.643	29.747	24.824
thiophene	24.855	18.955	15.878
pyridine	5.625	4.696	3.891
ethanol	22.072	16.268	12.290
methanol	27.068	20.181	15.571
propan-2-ol	19.431	13.926	10.655
tert-butanol	18.562	12.917	9.820
propan-1-ol	21.003	14.980	11.655
butan-1-ol	18.937	13.240	10.128
pentan-1-ol	17.882	12.325	8.919
ethylbenzene	40.727	32.403	26.766
m-xylene	35.496	29.680	23.084
toluene	24.961	20.414	16.986
benzene	19.851	16.194	12.648
acetone	27.612	18.692	13.274
butan-2-one	24.112	16.150	11.657
pentan-2-one	22.228	14.764	10.771
methylacetate	32.995	26.889	20.842
ethylacetate	30.671	23.738	18.541
acetonitrile	33.321	26.848	21.297
water	341.445	331.147	322.673

[a]Standard uncertainties u are $u(p)$ = 1 kPa, $u(\gamma_{13}^{\infty})$ = 1.4, and $u(T)$ = 0.05 K.

methylethenyl)-cyclohexene solvent to overcome these kinds of bonds or forces; hence, poor miscibility is observed.

The low values of γ_{13}^{∞} signify the greater solubility and miscibility between the solute and the solvent. For the solutes with the same carbon number, the comparison of cycloalkane interactions with their linear alkane counterparts reveals higher values of γ_{13}^{∞} than the straight-chain compounds. High values of γ_{13}^{∞} for the unsaturated alkenes and alkynes when compared with saturated alkanes of the same carbon number were observed. This is because the triple bonds are shorter, stronger, and more polarized than the double bonds, and therefore alkynes have weak interaction with the solvent compared with the alkenes. Compared with straight-chain hydrocarbons and alkenes, higher values of γ_{13}^{∞} were observed for aromatic hydrocarbons. Π-Delocalized electrons may cause this in the benzene ring, which creates weak interaction with the nonpolar solvent. For the nonpolar solutes, the values of γ_{13}^{∞} were lower than polar solutes due to the weak intermolecular forces, namely London or dispersion forces between nonpolar solutes and the solvent. These forces or bonds were broken down easily to form new bonds, indicating that nonpolar solutes have better solubility in the solvent.

Table 5 provides information on the thermodynamics property of partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$. This thermodynamic property provides insights into the interaction between the solutes and the solvent at a reference temperature of 313.15 K. The partial molar excess enthalpies and entropies at infinite dilution were determined from the Gibbs−Helmholtz equation

$$\ln \gamma_{13}^{\infty} = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R} \qquad (4)$$

where R is the universal gas constant; the partial molar excess enthalpy $\Delta H_1^{E,\infty} = Ra$ and the entropy $\Delta S_1^{E,\infty} = -Rb$ at infinite dilution were obtained from the slope and the intercept, respectively, using the Van't Hoff relation.

$$\ln \gamma_{13}^{\infty} = \frac{a}{T} + b \qquad (5)$$

Positive values for enthalpies were observed for all of the solutes in a 1-methyl-4-(1-methylethenyl)-cyclohexene solvent. These positive $\Delta H_1^{E,\infty}$ values imply that the activity coefficient decreases with increasing temperature. This proves that the solubility increases with the temperature increase. Furthermore, positive values of $\Delta H_1^{E,\infty}$ show that the interaction between the solute−solute pairs is lower than the solute−solvent pairs, and when contacted with the solvent, the solutes have an endothermic heat of mixing.

The gas−liquid partial activity coefficients, K_L, for solutes in the 1-methyl-4-(1-ethylethenyl)-cyclohexene solvent are listed in Table 6. The densities were taken between temperatures of 298.15 and 333.15 K, as presented in Table 2. The highest value at T = 303.15 K was observed for dec-1-ene, K_L = 7871.737, and the lowest for acetone, K_L = 3.447 at T = 323.15 K. It was observed that the values of K_L decrease with the increase in temperature, and K_L values increase with the increase in the alkyl chain length.

The values of the measured activity coefficient at infinite dilution listed in Table 4 were used to determine the performance of the solvent for industrial separation processes by determining the selectivity (S_{ij}^{∞}) and capacity (k_j^{∞}) at infinite dilution. This has been widely accepted as the criteria for solvent selection. Selectivity is defined as the preference of the solvent to form a phase with one of the solutes rather than with the other solute. Capacity gives a measure of the amount

Table 5. Coefficients of eq 2, a and b, Correlation R^2, Partial Molar Excess Enthalpies $\Delta H_1^{E,\infty}$ at Infinite Dilution for the Solutes in the 1-Methyl-4-(1-methylethenyl)-cyclohexene Solvent at a Reference Temperature of 313.15 K and p = 101.3 ± 2 kPa^a

solutes (i)	a	b (K)	γ_{13}^{∞}	$\Delta H_1^{E,\infty}$ (kJ·mol^{-1})	R^2
n-pentane	1.11	−1.917	5.104	9.227	0.999
n-hexane	1.5	−3.219	4.855	12.473	0.992
n-heptane	1.715	−3.963	4.533	14.259	0.996
n-octane	1.733	−4.045	4.433	14.406	0.998
n-nonane	1.928	−4.708	4.304	16.029	0.998
hex-1-ene	1.449	−2.807	6.273	12.044	0.99
hept-1-ene	1.597	−3.361	5.772	13.279	0.998
oct-1-ene	1.801	−4.072	5.351	14.972	0.991
non-1-ene	1.801	−4.14	4.975	14.972	0.998
dec-1-ene	1.997	−4.822	4.717	16.606	1.000
hex-1-yne	1.1195	−0.922	14.532	9.308	0.996
hept-1-yne	1.239	−1.407	12.816	10.303	0.998
oct-1-yne	1.916	−3.691	11.425	15.93	0.999
cyclopentane	1.684	−3.252	8.669	14.004	0.999
cyclohexane	1.713	−2.385	22.464	14.239	0.994
cycloheptane	1.828	−2.632	25.66	15.195	0.991
cyclooctane	1.849	−2.519	29.747	15.373	0.999
thiophene	2.155	−3.91	18.955	17.913	0.995
pyridine	1.773	−4.122	4.696	14.744	0.999
ethanol	2.909	−6.5	16.268	24.185	1.000
methanol	3.04	−6.71	20.181	25.275	0.991
propan-2-ol	3.088	−7.218	13.926	25.674	0.998
$tert$-butanol	3.289	−7.928	12.917	27.344	0.997
propan-1-ol	2.978	−6.782	14.98	24.755	0.998
butan-1-ol	3.18	−7.553	13.24	26.441	0.998
pentan-1-ol	3.655	−9.159	12.325	30.384	0.997
ethylbenzene	2.112	−3.261	32.403	17.561	0.999
m-xylene	2.232	−3.772	29.68	18.559	0.993
toluene	1.965	−3.259	20.414	16.335	0.999
benzene	2.149	−4.096	16.194	17.868	0.997
acetone	3.706	−8.903	18.692	30.813	0.999
butan-2-one	3.727	−9.108	16.15	30.985	0.998
pentan-2-one	3.631	−8.882	14.764	30.186	0.998
methylacetate	2.212	−3.794	26.889	18.394	0.997
ethylacetate	2.317	−4.228	23.738	19.262	0.997
acetonitrile	2.284	−4.019	26.848	18.989	0.998
water	0.3	4.845	331.147	2.494	0.995

^{a}Standard uncertainties u are $u(p)$ = 1 kPa, $u(\gamma_{13}^{\infty})$ = 1.4, $u(T)$ = 0.05 K, and $u(\Delta H_1^{E,\infty})$ = 1.5 of reported values.

of solute which the solvent will be capable of entraining. Selectivity and capacity at infinite dilution were calculated using eqs 6 and 7, respectively.

$$S_{ij}^{\infty} = \gamma_i^{\infty}/\gamma_j^{\infty} \qquad (6)$$

$$k_j^{\infty} = 1/\gamma_j^{\infty} \qquad (7)$$

In eqs 6 and 7, i and j are the solutes to be separated from the mixture. The values of the selectivity and capacity for the investigated 1-methyl-4-(1-methylethenyl)-cyclohexene solvent for the different industrial separation problems at T = 313.15 K are presented in Table 7 and graphically illustrated in Figures S9−S12. These separation problems are hexane/hexene, heptane/benzene, octane/thiophene, and octane/pyridine. The obtained results from this experimental work

Table 6. Experimental (Gas and Liquid) Partition Coefficients K_L for the Solutes in the 1-Methyl-4-(1-methylethenyl)-cyclohexene Solvent at a Temperature of 303.15−323.15 K and $p = 101.3 \pm 2$ kPa[a]

solutes (i)	303.15 K	313.15 K	323.15 K
n-pentane	4.518	4.448	4.657
n-hexane	6.144	5.583	5.060
n-heptane	9.778	7.951	6.749
n-octane	20.601	15.059	12.024
n-nonane	53.643	33.330	22.895
hex-1-ene	5.180	4.724	4.528
hept-1-ene	9.410	7.886	6.831
oct-1-ene	20.039	15.350	12.165
non-1-ene	50.913	33.651	23.659
dec-1-ene	150.646	83.231	50.091
hex-1-yne	7.035	5.907	5.346
hept-1-yne	15.615	11.675	9.461
oct-1-yne	33.994	22.582	16.863
cyclopentane	4.380	3.963	3.707
cyclohexane	7.141	6.030	5.408
cycloheptane	20.101	14.640	11.760
cyclooctane	62.805	39.672	27.523
thiophene	11.028	8.684	7.251
pyridine	49.194	33.818	24.924
ethanol	7.419	5.691	4.528
methanol	5.342	4.410	3.727
propan-2-ol	16.985	11.322	7.972
$tert$-butanol	8.535	6.299	4.835
propan-1-ol	52.952	30.008	19.113
butan-1-ol	168.560	84.258	46.439
pentan-1-ol	9.589	6.887	5.359
ethylbenzene	8.841	6.915	5.866
m-xylene	21.508	15.300	11.622
toluene	50.902	32.424	22.506
benzene	57.831	37.803	25.958
acetone	4.408	3.920	3.447
butan-2-one	8.174	6.618	5.583
pentan-2-one	15.687	11.744	9.253
methylacetate	5.134	4.790	4.366
ethylacetate	8.681	6.963	6.137
acetonitrile	5.404	4.824	4.299
water	70.435	51.832	40.470

[a]Standard uncertainties u are $u(p) = 1$ kPa, $u(T) = 0.05$ K, and $u(K_L)$ = 1.6 of reported values.

presented in Table 4 were used to calculate the selectivities and capacities of 1-methyl-4-(1-methylethenyl)-cyclohexene and were compared with deep eutectic solvents, ionic liquids, and industrial solvents from the literature.

The results presented in Table 7 reveal 1-methyl-4-(1-methylethenyl)-cyclohexene as a poor solvent for separation problems of hexane/hexene, heptane/benzene, octane/thiophene, and octane/pyridine. These mixtures cannot be separated since the selectivity is close to 1. Good extraction is observed with a higher capacity value and large selectivity values. The separation of paraffin and olefins yielded promising results for the mixture of n-hexane and hex-1-ene. In this study, the selectivity and capacity were found to be lower than those of $[4C_1NCl]$ + $[Gly]$ $[1:2]$.[35] The azeotropic separation mixture of ethanol/water had lower selectivity than that of $[C_6C_1Pip][NTf_2]$.[36]

The results for the n-octane/thiophene separation problem are satisfactory when compared with other solvents. Low values of selectivity and capacity for the 1-methyl-4-(1-methylethenyl)-cyclohexene solvent are observed. High values for the separation of n-octane/thiophene are $S_{ij}^{\infty}/k_j^{\infty} = 236.28/0.801$,[37] and this shows that $[BMIM][SCN]$ in this comparison performs better than the 1-methyl-4-(1-methylethenyl)-cyclohexene solvent, and the investigated solvent may not be used for desulfurization of the liquid fuel. The separation mixture of heptane/benzene is $S_{ij}^{\infty}/k_j^{\infty} = 0.14/0.03$, and these values are very low when compared with other solvents such as $[BMIM][SCN]$ ($S_{ij}^{\infty}/k_j^{\infty} = 106.2/0.463$).[37] This makes the investigated solvent impossible to be used as a solvent for desulfurization of the liquid fuel.

4.1. UNIFAC Model. The UNIFAC model was used in this study to correlate the experimental infinite dilution activity coefficients for the selected solutes. The detailed calculation procedure for the UNIFAC model has been described in the previous literature.[38] However, in this study, Aspen Plus Tech software, which has a UNIFAC model that follows the prediction method developed by Fredenslund et al.[38] was used to predict the results.

The selected experimental values were compared with those predicted by the UNIFAC model. The values of the infinite dilution activity coefficient reported in this work were found to be in good agreement with the reported literature, as presented in Table 8. The deviation between the experimental and Aspen Plus software values was found to have the highest deviation of 4.65%, as presented in Table 8.

5. CONCLUSIONS

In this study, the infinite dilution activity coefficients of all solutes in a 1-methyl-4-(1-methylethenyl)-cyclohexene solvent were measured by GLC at temperatures between 303.15 and 323.15 K. It was noted that for all solutes, the activity coefficient at infinite dilution decreased with the increase in temperature and decreased with the increase in the alkyl chain length. The thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy at infinite dilution are calculated at $T_{ref} = 313.15$ K, and these parameters were used to characterize the interaction of molecules between the solutes and the investigated 1-methyl-4-(1-methylethenyl)-cyclohexene solvent. It was observed that the single-bond alkyl solutes had a strong interaction with 1-methyl-4-(1-methylethenyl)-cyclohexene due to their low values of infinite dilution activity coefficients. The partial activity coefficient values for the same solute describe the molecular interaction pattern between the solutes and the 1-methyl-4-(1-methylethenyl)-cyclohexene solvent. The investigated 1-methyl-4-(1-methylethenyl)-cyclohexene solvent reveals lower values of selectivity and capacity at infinite dilution for the separation mixtures compared with other DES, ILs, and industrial solvents. Selectivity values of less than 1 symbolize that the 1-methyl-4-(1-methylethenyl)-cyclohexene solvent can be used for extraction but differs in terms of performances for separating mixtures.

The selectivity and capacity for separating hexane/hex-1-ene, heptane/benzene, ethanol/water, and octane/thiophene did not show promising results compared with other DES, ILs, and industrial solvents. The selectivity and capacity for the investigated separation mixtures indicate that 1-methyl-4-(1-methylethenyl)-cyclohexene is not suitable as an extraction solvent compared with other DES, ILs, and industrial solvents.

Table 7. Values of the Selectivity, S_{ij}^{∞}, and Capacity, k_i^{∞}, at Infinite Dilution for Various Separation Problems at a Temperature of T = 313.15 K and p = 101.3 ± 2 kPa[a,b,c,d,e,f,g,h,i]

solvent	hexane/hex-1-ene	heptane/benzene	ethanol/water	octane/thiophene
limonene	0.77/0.159	0.14/0.031	0.05/0.003	0.23/0.213
DES 1; [4C$_1$NCl]:[EG] [1:2][35]	3.04/0.0017	79.32/0.051		
DES 2; [4C$_1$NCl] + [Gly] [1:2][39]	0.78/0.004	33.96/0.018		81.8/0.386
DES 3; [4C$_1$NCl] + [Hdiol] [1:1][15]		31.74/0.813		154/1.307
[C$_6$H$_{13}$OCH$_2$MIM][NTf$_2$][j 40]	1.42/0.460	6.16/1.646	0.39/1.375	7.91/1.745
[BMIM][SCN][j 37]	3.39/0.019	106.2/0.463		236.28/0.801
[C$_5$C$_1$Pip][NTf$_2$][j 36]	1.79/0.185	18.58/1.430	0.36/0.593	28.22/1.608
[C$_6$C$_1$Pip][NTf$_2$][j 36]	1.68/0.223	14.76/1.475	0.35/0.581	20.63/1.612
NMP + 3% (w/w) water[41]	1.97/0.102	16.93/0.714		
NFM + 3% (w/w) water[41]	2.15/0.040	26.67/0.358		
[PMMIM][NTf$_2$][42]		3.74/0.813		
sulfolane[43]		24.05/0.424	1.08/0.355	

[a]Nkosi et al.[35] [b]Nkosi et al.[39] [c]Nkosi et al.[15] [d]Domańska and Marciniak.[40] [e]Domańska and Laskowska.[37] [f]Paduszyński and Domańska.[36] [g]Krummen and Gmehling.[41] [h]He et al.[42] [i]Möllmann and Gmehling.[43] [j]Interpolate; [4C$_1$NCl]:[EG]: tetramethylammonium chloride + ethylene glycol; [4C$_1$NCl] + [Hdiol]: tetramethylammonium chloride + 1,6 hexanediol; [4C$_1$NCl] + [Gly]: tetramethylammonium chloride + glycerol; [BMIM][SCN]: 1-butyl-3-methylimidazolium thiocyanate; [C$_6$H$_{13}$OCH$_2$MIM][NTf$_2$]: 1-hexyloxymethyl-3-methyl-imidazolium bis-(trifluoromethylsulfonyl)-imide; [C$_5$C$_1$Pip][NTf$_2$]: 1-n-alkyl-1-methylpiperidium bis{(trifluoromethyl)sulfonyl}imide; [C$_6$C$_1$Pip][NTf$_2$]: 1-n-alkyl-1-methylpiperdinium bis[(trifluoromethyl)sulfonyl]imides; [PMMIM][NTf$_2$]: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide; NMP: N-methyl-2-pyrrolidone; and NFM: N-formylmorpholine.

Table 8. Comparison of the Experimental, Aspen Plus Software, and the Literature Values of Infinite Dilution Activity Coefficients[a,b,c,d]

solutes (i)	solvent	γ_{13}^{∞}[e]		R.D%	γ_{13}^{∞} lit.	
		exp.	aspen		exp.	aspen
water	limonene	322.673	319.746	0.9	352.1[44]	344.8[44]
acetonitrile	limonene	21.297	20.019	3.65	22.18[45]	20.33[44]
ethanol	limonene	10.05	9.583	4.65	9.79[45]	
					9.13[46]	9.34[46]

[a]lit.: literature. [b]Zapata et al.[44] [c]Ngema et al.[45] [d]Zapata et al.[46] [e]This study.

More investigation of 1-methyl-4-(1-methylethenyl)-cyclohexene must be conducted for future work through measurements of liquid−liquid equilibrium and vapor−liquid equilibrium. Such data would provide useful information and understanding about separating investigated mixtures. The experimental results were found to be in good agreement when compared with the UNIFAC model and the literature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.1c00801.

Viscosity measurements of a 1-methyl-4-(1-methyle-thenyl)-cyclohexene solvent; density measurements of a 1-methyl-4-(1-methylethenyl)-cyclohexene solvent; experimental activity coefficient at infinite dilution, γ_{13}^{∞}, for various solutes in the limonene at T = 303.15−323.15 K and p = 101.3 ± 2 kPa with the solvent column loading n_3 = 4.90 mmol (27.63%); experimental activity coefficient at infinite dilution, γ_{13}^{∞}, for various solutes in the limonene T = 303.15−323.15 K and p = 101.3 ± 2 kPa with the solvent column loading n_3 = 7.60 mmol (33.35%); plot of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for the solutes; and selectivities, S_{12}^{∞} and capacities, k_2, at infinite dilution for 1-methyl-4-(1-methylethenyl)-cyclohexene (PDF)

AUTHOR INFORMATION

Corresponding Authors

Peterson Thokozani Ngema − Department of Chemical Engineering, Thermodynamics Research Group, Durban University of Technology, Durban 4001, South Africa; Email: ngemat@dut.ac.za

Suresh Ramsuroop − Department of Chemical Engineering, Cape Peninsula University of Technology, Bellville 7535, South Africa; orcid.org/0000-0003-2753-796X; Email: RAMSUROOPS@cput.ac.za

Authors

Banzi Patrick Mbatha − Department of Chemical Engineering, Thermodynamics Research Group, Durban University of Technology, Durban 4001, South Africa

Nkululeko Nkosi − Department of Chemical Engineering, Thermodynamics, Materials and Separations Research Group (TMSRG), Mangosuth University of Technology, Durban 4001, South Africa; orcid.org/0000-0002-9151-3359

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jced.1c00801

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

■ REFERENCES

(1) Sholl, D. S.; Lively, R. P. Seven chemical separation to change the world. *Nature* 2016, 532, 435−437.

(2) Wan, P. J.; Hron, R. J.; Dowd, M. K.; Kuk, M. S.; Conkerton, E. J. Alternative hydrocarbon solvents for cottonseed extraction: Plant trials. *J. Am. Oil Chem. Soc.* 1995, 72, 661−664.

(3) Hanmoungjai, P.; Pyle, L.; Niranjan, K. Extraction of rice bran oil using aqueous media. *J. Chem. Technol. Biotechnol.* 2000, 75, 348−352.

(4) Chandran, D.; Khalid, M.; Walvekar, R.; Mubarak, N. M.; Dharaskar, S.; Wong, W. Y.; Gupta, T. C. S. M. Deep eutectic solvents for extraction-desulphurisation: A review. *J. Mol. Liq.* 2019, 275, 312−322.

(5) Pereiro, A. B.; Araújo, J. M. M.; Esperança, J. M. S. S.; Marrucho, I. M.; Rebelo, L. P. N. Ionic liquids in separations of azeotropic systems−A review. *J. Chem. Thermodyn.* 2012, 46, 2−28.

(6) Verevkin, S. P.; Sazonova, A. Y.; Frolkova, A. K.; Zaitsau, D. H.; Prikhodko, I. V.; Held, C. Separation performance of BioRenewable deep eutectic solvents. *Ind. Eng. Chem. Res.* 2015, 54, 3498−3504.

(7) Kabane, B.; Redhi, G. G. Thermodynamic properties and activity coefficients at infinite dilution for different solutes in deep eutectic solvent: 1-butyl-3-methylimidazolium chloride+ glycerol. *J. Mol. Liq.* 2020, 311, No. 113216.

(8) Mamidipally, P. K.; Liu, S. X. First approach on rice bran oil extraction using Limonene. *Eur. J. Lipid Sci. Technol.* 2004, 106, 122−125.

(9) Liu, S. X.; Mamidipally, P. K. Quality Comparison of Rice Bran Oil Extracted with d-Limonene and Hexane. *Cereal Chem.* 2005, 82, 209−215.

(10) Virot, M.; Tomao, V.; Ginies, C.; Visinoni, F.; Chemat, F. Green procedure with a green solvent for fats and oils' determination. Microwave-integrated Soxhlet using Limonene followed by micro-wave Clevenger distillation. *J. Chromatogr. A* 2008, 1196−1197, 147−152.

(11) Toplisek, T.; Gustafson, R. Cleaning with D-limonenes: A substitute for chlorinated solvents. *Precis. Clean.* 1995, 3, 17−20.

(12) Ciriminna, R.; Lomeli-Rodriguez, M.; Demma Carà, P.; Lopez-Sanchez, J. A.; Pagliaro, M. Limonene: A versatile chemical of the bioeconomy. *Chem. Commun.* 2014, 50, 15288−15296.

(13) Pourbafrani, M.; McKechnie, J.; MacLean, H. L.; Saville, B. A. Life cycle greenhouse gas impacts of ethanol, biomethane and limonene production from citrus waste. *Environ. Res. Lett.* 2013, 8, No. 015007.

(14) Uemura, M.; Hata, G.-i.; Toda, T.; Weine, F. Effectiveness of eucalyptol and d-limonene as gutta-percha solvents. *J. Endod.* 1997, 23, 739−741.

(15) Nkosi, N.; Tumba, K.; Ramsuroop, S. Activity coefficients at infinite dilution of various organic solutes in the deep eutectic solvent (tetramethylammonium chloride + 1,6 hexanediol in the 1:1 molar ratio). *S. Afr. J. Chem. Eng.* 2019, 27, 7−15.

(16) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*; McGraw-Hill, 2001.

(17) Letcher, T. M.; Soko, B.; Reddy, P.; Deenadayalu, N. Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid 1-Hexyl-3-methylimidazolium Tetrafluoroborate Using Gas-Liquid Chromatography at the Temperatures 298.15 K and 323.15 K. *J. Chem. Eng. Data* 2003, 48, 1587−1590.

(18) Deenadayalu, N.; Letcher, T. M.; Reddy, P. Determination of Activity Coefficients at Infinite Dilution of Polar and Nonpolar Solutes in the Ionic Liquid 1-Ethyl-3-methyl- imidazolium Bis-(trifluoromethylsulfonyl) Imidate Using Gas Liquid Chromatography at the Temperature 303.15 K or 318.15 K. *J. Chem. Eng. Data* 2005, 50, 105−108.

(19) Clará, R. A.; Marigliano, A. C. G.; Sólimo, H. N. Density, viscosity, and refractive index in the range (283.15 to 353.15) K and vapor pressure of α-pinene, d-limonene,(±)-linalool, and citral over

the pressure range 1.0 kPa atmospheric pressure. *J. Chem. Eng. Data* 2009, 54, 1087−1090.

(20) Reddy, P.; Aslam Siddiqi, M.; Atakan, B.; Diedenhofen, M.; Ramjugernath, D. Activity coefficients at infinite dilution of organic solutes in the ionic liquid PEG-5 cocomonium methylsulfate at T = (313.15, 323.15, 333.15, and 343.15)K: Experimental results and COSMO-RS predictions. *J. Chem. Thermodyn.* 2013, 58, 322−329.

(21) Kersten, B. R.; Poole, C. F. Influence of concurrent retention mechanisms on the determination of stationary phase selectivity in gas chromatography. *J. Chromatogr. A* 1987, 399, 1−31.

(22) Mutelet, F.; Jaubert, J.-N. Measurement of activity coefficients at infinite dilution in 1-hexadecyl-3-methylimidazolium tetrafluor-oborate ionic liquid. *J. Chem. Thermodyn.* 2007, 39, 1144−1150.

(23) Kozlova, S. A.; Verevkin, S. P.; Heintz, A.; Peppel, T.; Köckerling, M. Activity coefficients at infinite dilution of hydro-carbons, alkylbenzenes, and alcohols in the paramagnetic ionic liquid 1-butyl-3-methyl-imidazolium tetrachloridoferrate(III) using gas−liquid chromatography. *J. Chem. Thermodyn.* 2009, 41, 330.

(24) Tumba, K. Infinite dilution activity coefficient measurements of organic solutes in fluorinated ionic liquids by gas-liquid chromatog-raphy and the inert gas stripping method. M.Sc. Thesis, School of Chemical Engineering University of KwaZulu-Natal, 2010.

(25) Tumba, K.; Letcher, T. M.; Naidoo, P.; Ramjugernath, D. Activity coefficients at infinite dilution of organic solutes in the ionic liquid trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide using gas−liquid chromatography at T = (313.15, 333.15, 353.15 and 373.15)K. *J. Chem. Thermodyn.* 2013, 65, 159−167.

(26) Tiegs, D.; Gmehling, J.; Medina, A.; Soares, M.; Bastos, J.; Alessi, P.; Kikic, I. *Activity Coefficients at Infinite Dilution*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt/Main, 1986; Vol. 2.

(27) Chien, C.; Kopecni, M.; Laub, R.; Smith, C. Solute liquid-gas activity and partition coefficients with mixtures of n-hexadecane and n-octadecane with N, N-dibutyl-2-ethylhexylamide solvents. *J. Phys. Chem. A* 1981, 85, 1864−1871.

(28) Schult, C. J.; Neely, B. J.; Robinson, R., Jr.; Gasem, K.; Todd, B. A. Infinite-dilution activity coefficients for several solutes in hexadecane and in n-methyl-2-pyrrolidone (NMP): experimental measurements and UNIFAC predictions. *Fluid Phase Equilib.* 2001, 179, 117−129.

(29) Castells, C. B.; Carr, P. W.; Eikens, D. I.; Bush, D.; Eckert, C. A. Comparative study of semitheoretical models for predicting infinite dilution activity coefficients of alkanes in organic solvents. *Ind. Eng. Chem. Res.* 1999, 38, 4104−4109.

(30) Heintz, A.; Verevkin, S. P. Thermodynamic properties of mixtures containing ionic liquids. 6. activity coefficients at infinite dilution of hydrocarbons, alcohols, esters, and aldehydes in 1-methyl-3-octyl-imidazolium tetrafluoroborate using gas−liquid chromatog-raphy. *J. Chem. Eng. Data* 2005, 50, 1515−1519.

(31) Letcher, T. M. *Activity Coefficients at Infinite Dilution from Gas-Liquid Chromatography*; The Royal Society of Chemistry, 1978; p 2.

(32) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*; McGraw-Hill Education, 2000.

(33) McGlashan, M. L.; Potter, D. J. B. An Apparatus for the Measurement of the Second Virial Coefficients of Vapours; The Second Viral Coefficients of Some n-Alkanes and of Some Mixtures of n-Alkanes. *Proc. R. Soc. London, Ser. A* 1962, 267, 478−500.

(34) Hudson, G. H.; McCoubrey, J. C. Intermolecular forces between unlike molecules. A more complete form of the combining rules. *Trans. Faraday Soc.* 1960, 56, 761−766.

(35) Nkosi, N.; Tumba, K.; Ramsuroop, S. Measurements of activity coefficient at infinite dilution for organic solutes in tetramethylam-monium chloride + ethylene glycol deep eutectic solvent using gas-liquid chromatography. *Fluid Phase Equilib.* 2018, 462, 31−37.

(36) Paduszyński, K.; Domańska, U. Experimental and theoretical study on infinite dilution activity coefficients of various solutes in piperidinium ionic liquids. *J. Chem. Thermodyn.* 2013, 60, 169−178.

(37) Domańska, U.; Laskowska, M. Measurements of activity coefficients at infinite dilution of aliphatic and aromatic hydrocarbons,

alcohols, thiophene, tetrahydrofuran, MTBE, and water in ionic liquid [BMIM][SCN] using GLC. *J. Chem. Thermodyn.* **2009**, *41*, 645−650.

(38) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.* **1975**, *21*, 1086−1099.

(39) Nkosi, N.; Tumba, K.; Ramsuroop, S. Tetramethylammonium chloride + glycerol deep eutectic solvent as separation agent for organic liquid mixtures: Assessment from experimental limiting activity coefficients. *Fluid Phase Equilib.* **2018**, *473*, 98−105.

(40) Domańska, U.; Marciniak, A. Activity coefficients at infinite dilution measurements for organic solutes and water in the 1-hexyloxymethyl-3-methyl-imidazolium and 1,3-dihexyloxymethyl-imidazolium bis(trifluoromethylsulfonyl)-imide ionic liquids—The cation influence. *Fluid Phase Equilib.* **2009**, *286*, 154−161.

(41) Krummen, M.; Gmehling, J. Measurement of activity coefficients at infinite dilution in N-methyl-2-pyrrolidone and N-formylmorpholine and their mixtures with water using the dilutor technique. *Fluid Phase Equilib.* **2004**, *215*, 283−294.

(42) He, Z.-Z.; Li, R.-Q.; Sun, A.-L.; Mu, Z.; Xiao, Y.-L.; Chang, H.-W.; Jiao, Y.-H.; Ge, M.-L. Experimental and theoretical study on infinite dilution activity coefficients of various solutes in ionic liquid 1-propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Chem. Thermodyn.* **2020**, *140*, No. 105894.

(43) Möllmann, C.; Gmehling, J. Measurement of Activity Coefficients at Infinite Dilution Using Gas-Liquid Chromatography. 5. Results for N-Methylacetamide, N,N-Dimethylacetamide, N,N-Dibutylformamide, and Sulfolane as Stationary Phases. *J. Chem. Eng. Data* **1997**, *42*, 35−40.

(44) Zapata, R. B.; Villa, A. L.; de Correa, C. M. Measurement of activity coefficients at infinite dilution for acetonitrile, water, Limonene, limonene epoxide and their binary pairs. *Fluid Phase Equilib.* **2009**, *275*, 46−51.

(45) Ngema, P. T.; Matkowska, D.; Naidoo, P.; Hofman, T.; Ramjugernath, D. Vapor−Liquid Equilibrium Data for Binary Systems of 1-Methyl-4-(1-methylethenyl)-cyclohexene+{Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Pentan-1-ol, or Hexan-1-ol} at 40 kPa. *J. Chem. Eng. Data* **2012**, *57*, 2053−2058.

(46) Zapata, R. B.; Villa, A. L.; Correa, C. Measurement of activity coefficients at infinite dilution for acetonitrile, water, limonene, limonene epoxide and their binary pairs. *J. Chem. Eng. Data* **2005**, *S0*, 1353−1356.

⊞ **Recommended by ACS**

Measurement and Correlation of Vapor–Liquid Equilibrium for Binary Systems of Dimethyl Carbonate with Butyl Butyrate, o-Xylene, and Cyclohexanone at...

Kai Liu, Yinglong Wang, *et al.*

NOVEMBER 06, 2019
JOURNAL OF CHEMICAL & ENGINEERING DATA   READ ☑

Isobaric Vapor–Liquid Equilibria of Binary Mixtures of Diethyl Carbonate with Isopropyl Acetate, sec-Butyl Acetate, or Isoamyl Acetate at 101.3 kPa

Xia Yin, Zhiguo Yan, *et al.*

OCTOBER 04, 2019
JOURNAL OF CHEMICAL & ENGINEERING DATA   READ ☑

Isobaric Vapor–Liquid Phase Equilibrium Measurements, Correlation, and Prediction for Separation of the Mixtures of Cyclohexanone and Al...

Kai Zhang, Yinglong Wang, *et al.*

MAY 22, 2018
JOURNAL OF CHEMICAL & ENGINEERING DATA   READ ☑

Isobaric Vapor–Liquid Equilibria of Binary Mixtures of Diethyl Carbonate with Methyl Acetate, n-Propyl Acetate, or Amyl Acetate at 100.17 kPa

Chaochen Du, Xia Yin, *et al.*

MAY 29, 2019
JOURNAL OF CHEMICAL & ENGINEERING DATA   READ ☑

Get More Suggestions >