JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Activity Coefficients at Infinite Dilution by GLC in Alkanediamines as Stationary Phases

Kamel Khimeche,*,[†] Paolo Alessi,[‡] Abdellah Dahmani,[§] Ireneo Kikic,[‡] and Angelo Cortesi[‡]

[†]UER of Applied Chemistry, Polytechnic Military School (EMP), BP 17 Bordj El-Bahri, Algiers, Algeria

[‡]Department of Chemical, Environmental and Raw Materials Engineering, University of Trieste, Piazzale Europa 1,34127 Trieste, Italy

[§]Laboratory of Thermodynamics and Molecular Modeling, Faculty of Chemistry, University of Science and Technology Houari Boumediene (USTHB), Bab Ezzouar, BP.32 El-Alia, 16111 Algiers, Algeria

ABSTRACT: The infinite-dilution activity coefficients (γ^∞) of paraffins, olefins, chloroparaffins, aromatics, alcohols, ethers, and acetates were measured by medium-pressure gas—liquid chromatography (GLC) in alkanediamines: octane-1,8-diamine, decane-1,10-diamine, and dodecane-1,12-diamine at temperatures from (328.15 to 363.15) K. The present measurements show good agreement with available literature data. The partial molar excess enthalpies at infinite dilution, $\Delta H_i^{E,\infty}$, were calculated from the experimental γ_i^∞ values obtained over the temperature range. In order to determine the different interactions between the solutes and solvents, the linear solvation energy relationship (LSER) or "Abraham method" was applied.

1. INTRODUCTION

Diamines are an important class of compounds in different fields of industry and particularly in the synthesis of a number of polymers.[1−5] Knowledge of the limiting activity coefficients γ^∞ of different solutes in the diamines is important in the rational design of the separation process and provides a useful tool for the optimal choice of the selective solvent. These infinite-dilution activity coefficients are useful for understanding the influence of more than one functional group in the molecule on the thermodynamic properties and nonideality of the mixtures and also for environmental studies because toxic substances are often strongly diluted in the environment. Activity coefficients at infinite dilution, as well as vapor—liquid equilibrium (VLE) and mixing enthalpy data, serve as a database for the further development of liquid theories, in particular group-contribution methods.

Apart from ebulliometry, dilutor techniques, and liquid—liquid chromatography, gas—liquid chromatography (GLC) is a rapid and exact method for experimental determination of activity coefficients at infinite dilution.[6−8]

In this work, CLC was used to characterize diamines and obtain important information about the solvents, which can be advantageously used in a process of extraction. The infinite-dilution activity coefficients for a series of solutes in alkane-α,ω-diamines [octane-1,8-diamine (1,8-ODA), decane-1,10-diamine (1,10-DDA), and dodecane-1,12-diamine (1,12-DDDA)] were determined over the temperature range from (328.15 to 363.15) K. The values of the partial molar excess enthalpies at infinite dilution, $\Delta H_i^{E,\infty}$ were calculated from the experimental γ_i^∞ values obtained over the temperature range. The experimental results obtained were used to characterize the alkanediamines by linear solvation energy relationships (LSERs).

2. EXPERIMENTAL SECTION

A gas—liquid chromatograph (GC 8000, FISONS Instruments) equipped with a thermal conductivity detector was used as the GLC apparatus. The carrier gas (helium) flow rate was measured by means of a calibrated soap bubble flowmeter that was placed at the outlet after the detector. The column temperature was controlled to within ± 0.1 K and measured with an electronic thermometer. The internal pressure gradient was measured to within ± 1 mmHg using a mercury manometer. The outlet pressure P_o was kept at atmospheric pressure.

The operating conditions are summarized as follows: solute injections ranged from (0.1 to 0.2) μL and were considered to be at infinite dilution on the column; stainless steel column (2 m long, 4 mm i.d.); support, (80 to 100) mesh Chromosorb W (Carlo Erba) acid-washed and silanized, quantitative ratio of support to stationary phase = 3/1 by mass; internal pressure gradient, (350 to 450) mmHg; column temperature range, (328.15 to 363.15) K. At each temperature, values of the dead time t_o were measured by using air as a nonretainable component.

The solutes injected were paraffins, olefins, aromatic hydrocarbons, alcohols, ethers, and acetates. They were purchased from Fluka, Merck, Carlo Erba, and Aldrich. Purification of the solutes was not necessary because of the separation properties of the chromatographic process. Two of the stationary phases used, 1,8-ODA (purity > 99 %) and 1,10-DDA (purity > 98 %), were supplied from Aldrich. The 1,12-DDDA (purity > 98 %) was purchased from Fluka. Solvents were used without further purification.

The accuracy of the activity coefficients at infinite dilution is ± 2 %; this value was evaluated by taking into account the errors in the measurements of the experimental quantities (retention time, inlet and outlet pressures, amount of stationary phase, flow rate of the carrier gas, and temperature).

Special Issue: Kenneth N. Marsh Festschrift

Received: June 24, 2011
Accepted: September 9, 2011
Published: October 04, 2011

Table 1. Experimental Activity Coefficients at Infinite Dilution, γ^{∞}, and Specific Retention Volumes, V_g°, for the Solutes in the Solvent 1,8-ODA at Different Temperatures

	T/K = 328.21		T/K = 338.23		T/K = 343.19		T/K = 348.25	
solute	γ^{∞}	log V_g°	γ^{∞}	log V_g°	γ^{∞}	log V_g°	γ^{∞}	log V_g°
n-pentane	3.79	1.37	3.68	1.27	3.63	1.22	3.61	1.16
n-hexane	4.03	1.80	3.83	1.68	3.76	1.62	3.72	1.56
n-heptane	4.36	2.20	4.09	2.07	4.00	2.00	3.95	1.93
n-octane	4.73	2.60	4.40	2.45	4.24	2.38	4.13	2.30
n-decane	5.47	3.40	4.82	3.22	4.58	3.14	4.36	3.05
1-pentene	2.82	1.42	2.70	1.33	2.66	1.28	2.65	1.23
1-hexene	3.18	1.83	2.94	1.72	2.85	1.67	2.77	1.62
1-heptene	3.59	2.21	3.21	2.10	3.03	2.05	2.93	1.99
1-octene	3.94	2.60	3.38	2.49	3.16	2.43	3.00	2.37
1-decene	4.24	3.43	3.58	3.28	3.33	3.20	3.14	3.13
methanol	0.28	2.92	0.32	2.70	0.34	2.59	0.37	2.47
ethanol	0.38	3.05	0.41	2.83	0.42	2.73	0.44	2.62
propan-1-ol	0.57	3.25	0.58	3.02	0.59	2.92	0.61	2.80
butan-1-ol	0.67	3.60	0.68	3.36	0.68	3.24	0.69	3.13
1-chlorobutane	1.88	2.27	1.65	2.18	1.55	2.13	1.48	2.09
1-chloropentane	2.71	2.55	2.13	2.49	1.92	2.45	1.73	2.42
hexyl chloride	3.86	2.84	2.73	2.80	2.38	2.77	2.02	2.75
dichloromethane	0.66	2.21	0.55	2.12	0.53	2.07	0.51	2.03
carbon tetrachloride	2.07	2.20	1.66	2.14	1.51	2.12	1.37	2.09
ethyl acetate	1.08	2.46	0.95	2.39	0.90	2.35	0.86	2.31
propyl acetate	1.29	2.82	1.08	2.73	1.00	2.68	0.93	2.63
butyl acetate	1.51	3.15	1.25	3.04	1.14	2.99	1.05	2.93
benzene	1.80	2.31	1.67	2.19	1.62	2.13	1.59	2.07
toluene	2.39	2.64	2.17	2.51	2.11	2.44	2.08	2.38
ethylbenzene	2.07	3.11	1.86	2.97	1.77	2.90	1.72	2.83
diethyl ether	3.52	1.38	3.41	1.27	3.37	1.22	3.36	1.17
dibutyl ether	8.79	2.61	7.79	2.45	7.42	2.38	7.18	2.30

Table 2. Experimental Activity Coefficients at Infinite Dilution, γ^{∞}, and Specific Retention Volumes, V_g°, for the Solutes in the Solvent 1,10-DDA at Different Temperatures

	T/K = 338.20		T/K = 348.15		T/K = 353.22	
solute	γ^{∞}	log V_g°	γ^{∞}	log V_g°	γ^{∞}	log V_g°
n-pentane	4.33	1.12	4.02	1.04	3.90	1.00
n-hexane	4.96	1.49	4.55	1.40	4.41	1.35
n-heptane	5.05	1.90	4.64	1.78	4.46	1.73
n-octane	5.24	2.29	4.78	2.16	4.55	2.10
n-decane	5.59	3.08	5.03	2.91	4.78	2.83
1-pentene	3.23	1.18	2.98	1.11	2.88	1.07
1-hexene	3.37	1.59	3.06	1.50	2.92	1.46
1-heptene	3.43	1.99	3.10	1.89	2.97	1.84
1-octene	4.09	2.33	3.65	2.21	3.45	2.16
1-decene	4.34	3.12	3.82	2.97	3.57	2.89
methanol	0.55	2.38	0.63	2.16	0.68	2.05
ethanol	0.60	2.58	0.68	2.36	0.72	2.24
propan-1-ol	0.62	2.89	0.73	2.65	0.77	2.53
butan-1-ol	0.72	3.25	0.77	3.01	0.82	2.88
1-chlorobutane	2.38	1.94	2.12	1.85	2.01	1.81
1-chloropentane	2.94	2.27	2.43	2.20	2.24	2.16
hexyl chloride	3.46	2.62	2.81	2.53	2.54	2.49
dichloromethane	1.19	1.71	1.09	1.64	0.98	1.61
carbon tetrachloride	2.25	1.94	2.05	1.84	1.98	1.79
ethyl acetate	1.16	2.25	0.95	2.19	0.87	2.16
propyl acetate	1.39	2.54	1.11	2.48	0.99	2.45
butyl acetate	1.50	2.88	1.17	2.81	1.03	2.78
benzene	1.72	2.10	1.61	1.99	1.58	1.93
toluene	2.52	2.37	2.23	2.27	2.13	2.21
ethylbenzene	1.97	2.87	1.78	2.73	1.72	2.67
diethyl ether	3.84	1.15	3.69	1.05	3.64	1.00
dibutyl ether	7.94	2.37	7.50	2.21	7.39	2.12

3. THEORETICAL BASIS

3.1. Calculation of Limiting Activity Coefficients. The specific retention volume V_g° at 1 atm and 273 K was calculated according to the literature[9−13] and by means of the following equation:

$$V_g^{\circ} = \left(\frac{J_3^2 F_m}{W}\right)\left(\frac{P_o - P_{H_2O}}{P_o}\right)\left[\frac{273}{(T_m/K)}\right](t_r - t_0) \qquad (1)$$

where F_m is the flow rate of the carrier gas (in $m^3 \cdot s^{-1}$) at the ambient temperature T_m (in K), W (in kg) is the mass of the stationary phase, P_{H_2O} (in Pa) is the vapor pressure of water at T_m, t_r (in s) is the retention time of the solute, t_0 (in s) is the retention time of the unretained solute, and J_3^2 is the James−Martin pressure-correction factor, given by

$$J_3^2 = \left(\frac{3}{2}\right)\frac{[(P_i/P_0)^2 - 1]}{[(P_i/P_0)^3 - 1]} \qquad (2)$$

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

$$\ln \gamma_2^{\infty} = \ln\left[\frac{(273K)R}{P_2^0 M_1 V_g^0}\right] - \left[\frac{(B_{22} - V_2^0)P_2^0}{RT_{exptl}}\right] \qquad (3)$$

where R is the gas constant (8.3147 $J \cdot mol^{-1} \cdot K^{-1}$), P_2^0 (in Pa) is the vapor pressure of the solute at the experimental temperature T_{exptl} (in K), M_1 in ($kg \cdot mol^{-1}$) is the molar mass of the stationary phase, B_{22} (in $m^3 \cdot mol^{-1}$) is the second virial coefficient of the solute at T_{exptl}, and V_2^0 (in $m^3 \cdot mol^{-1}$) is the molar volume of the solute at T_{exptl}. The correction for gas-phase nonideality, given by the second term on the right-hand side of eq 3, was included to enable us to determine accurately the values of the limiting activity coefficients, as indicated by Young[14] in his review of the use gas chromatography for the determination of thermodynamic properties. The vapor pressure values P_2^0 were calculated using the Antoine equation from constants obtained from the literature.[15,16] The coefficients B_{22} were calculated as suggested by Beattie and Bridgeman[17] using the empirical formula

$$B_{22} = V_c[0.461 - 1.158(T_c/T) - 0.503(T_c/T)^3] \qquad (4)$$

The necessary critical properties and molar volumes were either collected from or estimated according to the methods recommended by Reid et al.[16]

Table 3. Experimental Activity Coefficients at Infinite Dilution, γ^{∞}, and Specific Retention Volumes, V_g°, for the Solutes in the Solvent 1,12-DDDA at Different Temperatures

	T/K = 348.25		T/K = 353.15		T/K = 358.25		T/K = 363.21	
solute	γ^{∞}	log V_g°	γ^{∞}	log V_g°	γ^{∞}	log V_g°	γ^{∞}	log V_g°
n-pentane	4.76	0.90	4.74 (4.90)[a]	0.85	4.68	0.80	4.63 (4.48)[a]	0.76
n-hexane	4.86	1.30	4.81 (4.95)[a]	1.25	4.74	1.19	4.69 (4.53)[a]	1.14
n-heptane	5.21	1.67	5.13 (5.05)[a]	1.60	5.04	1.54	4.97 (4.66)[a]	1.48
n-octane	5.54	2.03	5.43	1.96	5.27	1.89	5.19	1.83
n-decane	6.11	2.76	5.89	2.68	5.74	2.58	5.60	2.51
1-pentene	4.21	0.89	4.05 (3.97)[a]	0.86	3.89	0.82	3.75 (3.71)[a]	0.79
1-hexene	4.28	1.29	4.12 (4.06)[a]	1.25	3.93	1.21	3.80 (3.78)[a]	1.17
1-heptene	4.44	1.67	4.22 (4.18)[a]	1.63	4.08	1.57	3.88 (3.94)[a]	1.53
1-octene	4.83	2.02	4.53	1.97	4.33	1.92	4.11	1.87
1-decene	5.05	2.78	4.80	2.70	4.47	2.64	4.24	2.57
methanol	0.77	2.01	0.84 (0.89)[a]	1.90	0.92	1.78	1.01(0.96)[a]	1.67
ethanol	0.83	2.20	0.89 (1.08)[a]	2.09	0.95	1.97	1.03(1.11)[a]	1.86
propan-1-ol	0.93	2.48	0.98 (0.94)	2.36	1.04	2.25	1.09(1.02)[a]	2.14
butan-1-ol	1.08	2.79	1.10	2.68	1.12	2.57	1.16	2.46
1-chlorobutane	2.71	1.68	2.63 (2.53)[a]	1.63	2.56	1.58	2.46 (2.44)[a]	1.53
1-chloropentane	3.08	2.03	2.91 (2.66)[a]	1.98	2.73	1.93	2.68 (2.61)[a]	1.87
hexyl chloride	4.50	2.26	4.27	2.19	4.11	2.13	3.94	2.07
dichloromethane	1.33	1.47	1.23	1.45	1.12	1.44	1.05	1.41
carbon tetrachloride	2.37	1.71	2.28	1.66	2.06	1.65	1.98	1.60
ethyl acetate	1.36	1.96	1.29 (3.39)[a]	1.92	1.22	1.88	1.15(2.89)[a]	1.84
propyl acetate	1.55	2.26	1.45 (2.97)[a]	2.21	1.35	2.17	1.26(2.86)[a]	2.13
butyl acetate	1.69	2.58	1.57	2.53	1.46	2.48	1.37	2.43
benzene	2.08	1.81	2.07 (2.08)[a]	1.75	2.06	1.69	2.04(2.03)[a]	1.62
toluene	2.60	2.13	2.51 (2.29)[a]	2.08	2.42	2.02	2.33(2.20)[a]	1.96
ethylbenzene	2.50	2.52	2.47	2.44	2.42	2.37	2.39	2.30
diethyl ether	4.45	0.90	4.37	0.86	4.33	0.81	4.25	0.77
dibutyl ether	8.93	2.06	8.47	1.99	7.90	1.94	7.45	1.88

[a] From ref 22.

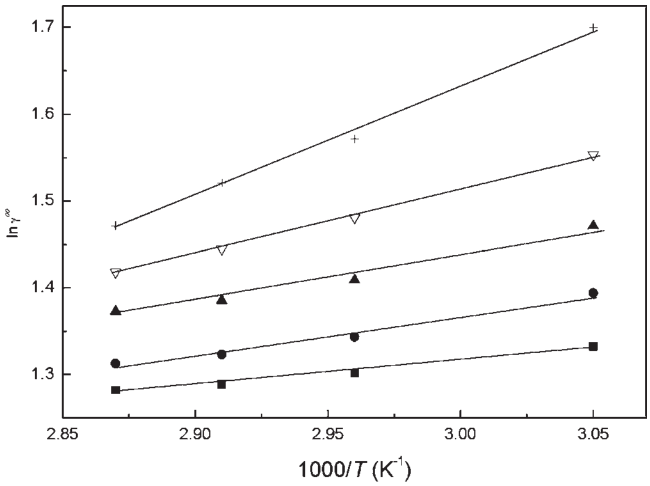

Figure 1. Experimental activity coefficients at infinite dilution for alkanes in the solvent 1,8-ODA as a function of temperature: ■, pentane; ●, hexane; ▲, heptane; ▽, octane; +, decane; —, linear regression.

The partial molar excess enthalpy at infinite dilution, $\Delta H_i^{\mathrm{E},\infty}$, can be directly obtained according to the Gibbs–Helmholtz equation:

$$\left(\frac{\partial \ln \gamma_i^{\infty}}{\partial(1/T)}\right)_{p,x} = \frac{\Delta H_i^{\mathrm{E},\infty}}{R} \tag{5}$$

The value of $\Delta H_i^{\mathrm{E},\infty}$ informs us about the fundamental interactions between the solute and the solvent.

With the V_g° data, the partial molar enthalpy of dissolution of the solute at infinite dilution in the solvent, $\Delta H_i^{\mathrm{dis}}$, can be calculated from the slope of the plot of ln V_g° versus $1/T$ as follows:

$$\left(\frac{\partial \ln V_g^{\circ}}{\partial(1/T)}\right)_{p,x} = -\frac{\Delta H_i^{\mathrm{dis}}}{R} \tag{6}$$

The molar enthalpy of vaporization is given by the relation

$$\Delta H_i^{\mathrm{vap}} = \Delta H_i^{\mathrm{E},\infty} - \Delta H_i^{\mathrm{dis}} \tag{7}$$

3.2. Abraham Correlation.

The experimentally obtained specific retention volumes V_g° were used to determine the different interactions between the solutes and the stationary phases. These interactions were characterized using the Abraham

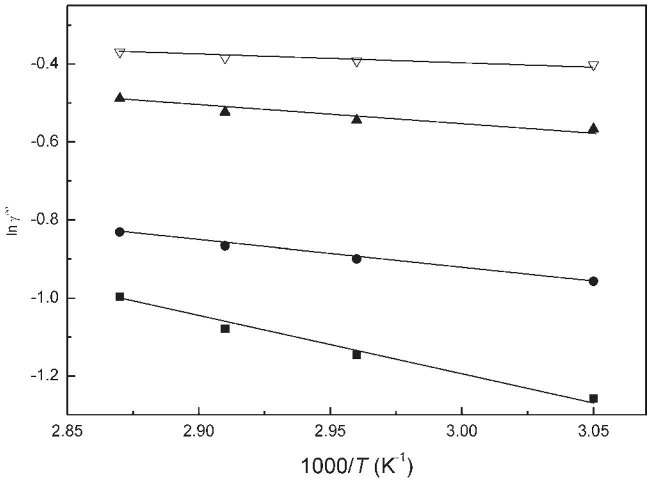

Figure 2. Experimental activity coefficients at infinite dilution for alcohols in the solvent 1,8-ODA as a function of temperature: ■, methanol; ●, ethanol; ▲, propanol; ▽, butanol; —, linear regression.

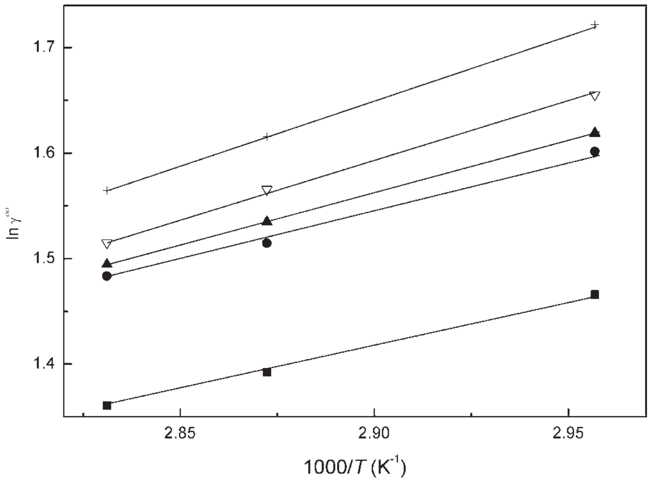

Figure 3. Experimental activity coefficients at infinite dilution for alkanes in the solvent 1,10-DDA as a function of temperature: ■, pentane; ●, hexane; ▲, heptane; ▽, octane; +, decane; —, linear regression.

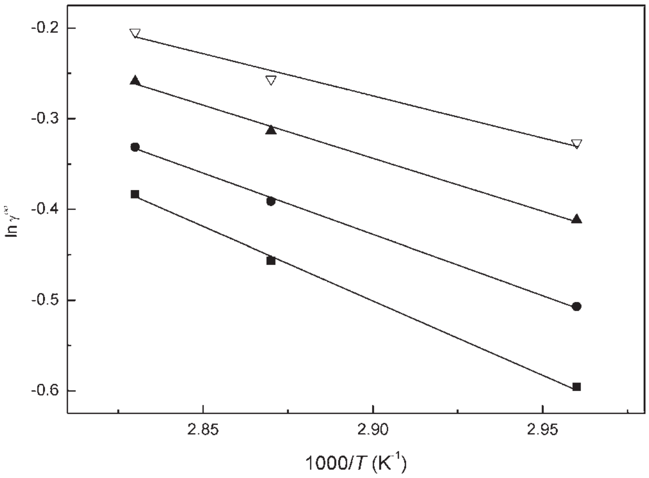

Figure 4. Experimental activity coefficients at infinite dilution for alcohols in the solvent 1,10-DDA as a function of temperature: ■, methanol; ●, ethanol; ▲, propanol; ▽, butanol; —, linear regression.

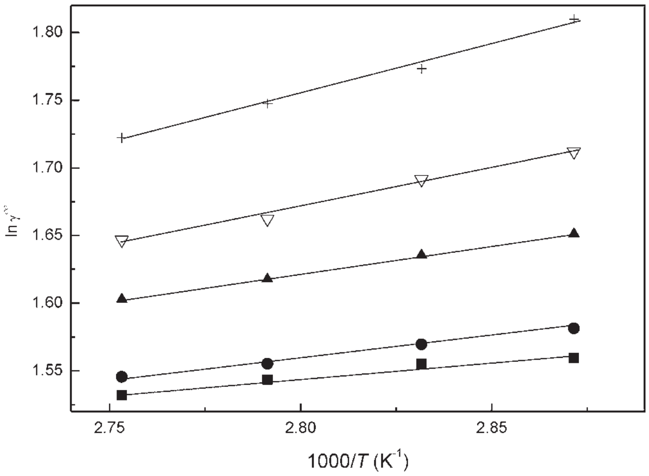

Figure 5. Experimental activity coefficients at infinite dilution for alkanes in the solvent 1,12-DDDA as a function of temperature: ■, pentane; ●, hexane; ▲, heptane; ▽, octane; +, decane; —, linear regression.

method[18] or LSER, which is given by

$$\log V_g^\circ = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l\log L^{16} \tag{8}$$

Each term in this equation is assigned to a solute–solvent interaction. In this equation, five parameters characterize the solutes properties:[19–21] R_2 is the polarizability parameter, which expresses the interaction capacity of the solute through the pair of π electrons; π_2^H is the dipolarity parameter of the solute; α_2^H is the acidity due to solute's hydrogen bond; β_2^H is the basicity due to the solute's hydrogen bond; and L^{16} is the Oswald solubility coefficient of the solute in hexadecane at 298 K. The constants *c*, *r*, *s*, *a*, *b*, and *l* were calculated by meaning of eq 8 using experimentally determined $\log V_g^\circ$ values. These constants characterize the solute–solvent interactions and describe the stationary phase behavior: *c* is the correlation constant; *r* reflects the solute–solvent interaction through the pair of π and n electrons; *s* characterizes the polarizability of the stationary phase; *a* characterizes the interactions of acidic solutes through hydrogen bonding and thus measures the basicity of the stationary phase; *b* characterizes the interactions of basic solutes through hydrogen bonding and thus measures the acidity of the stationary phase; *l* is assigned to the solute–solvent dispersive forces and the effect of formation of cavities within the stationary phase (association of the effect of cave formation and dispersive interactions).

4. RESULTS AND DISCUSSION

Infinite-dilution activity coefficients of various types of solutes were determined for 1,8-ODA at four temperatures in the *T* range (328.21 to 348.25) K, for 1,10-DDA at three temperatures in the *T* range (338.20 to 353.22) K, and for 1,12-DDDA at four temperatures in the *T* range (348.25 to 363.21) K. Tables 1 to 3 report the values of the activity coefficients at infinite dilution and specific retention volumes for the solutes in the three diamines studied.

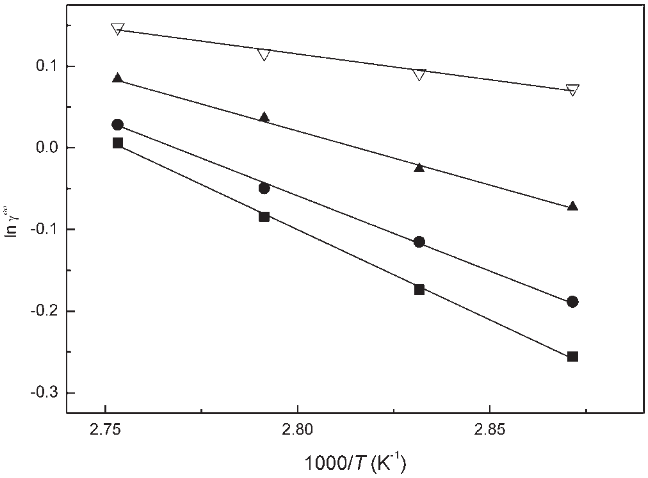

Figure 6. Experimental activity coefficients at infinite dilution for alcohols in the solvent 1,12-DDDA as a function of temperature: ■, methanol; ●, ethanol; ▲, propanol; ▽, butanol; —, linear regression.

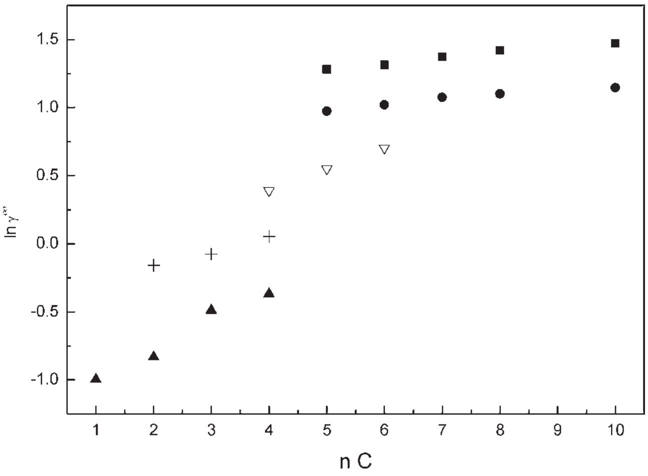

Figure 7. Variation of experimental activity coefficients for the solutes in the solvent 1,8-ODA according to the number of carbon atoms at $T = 348.25$ K: ▲, alcohols; +, acetates; ▽, chloroalkanes; ●, olefins; ■, alkanes.

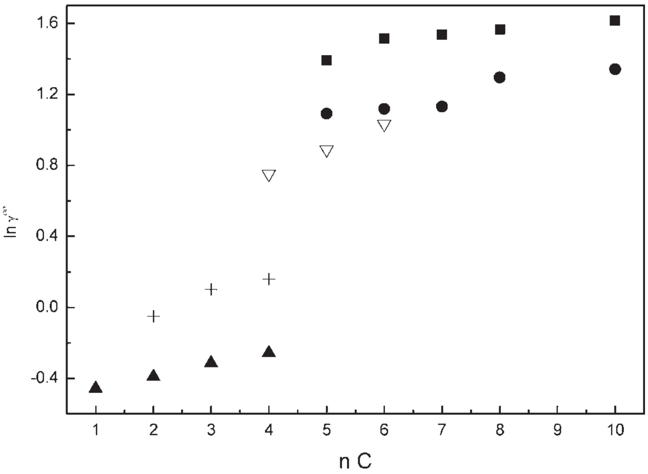

Figure 8. Variation of experimental activity coefficients for the solutes in the solvent 1,10-DDA according to the number of carbon atoms at $T = 348.25$ K: ▲, alcohols; +, acetates; ▽, chloroalkanes; ●, olefins; ■, alkanes.

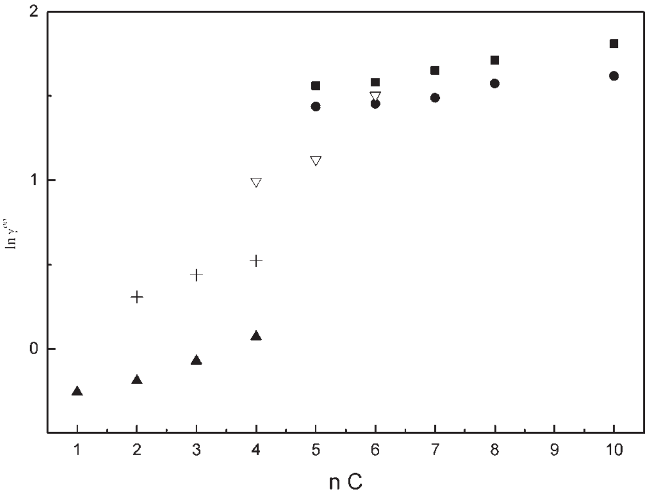

Figure 9. Variation of experimental activity coefficients for the solutes in the solvent 1,12-DDDA according to the number of carbon atoms at $T = 348.25$ K. ▲, alcohols; +, acetates; ▽, chloroalkanes; ●, olefins; ■, alkanes.

A comparison with literature data is possible only for the stationary phase 1,12-DDDA. As shown in Table 3, the present values compare well with the data given in literature.[22]

The γ^{∞} values for alkanes, alkenes, chloroalkanes, acetates, aromatics and ethers decrease as the temperature increases, while those for the alcohols increase as the temperature increases. As can be seen in Figures 1 to 6, for alkanes and alcohols in 1,8-ODA, 1,10-DDA, and 1,12-DDDA, a linear relationship between the natural logarithm of the activity coefficient and the reciprocal of the absolute temperature is often observed over a limited temperature interval for all of the solutes investigated.

The large experimental values of γ^{∞} ($\gamma^{\infty} > 1$) for the alkanes and alkenes in the solvents are probably due to the significant difference in the chemical natures, particularly the polarities, of the solutes and the alkanediamines, which explains their weak solubility. The values of γ^{∞} show high solubility of the alcohols and acetates in all of the diamines. Alcohols are the only compounds that show activity coefficients less than 1 in the stationary phases; this justifies the presence of specific interactions. The more the activity coefficient is lower than unity ($\gamma^{\infty} < 1$), the better is the solvent's absorption capacity.[23] In general, the γ^{∞} values for alkanes, alkenes, chloroalkanes, acetates, and alcohols in the alkanediamines rank in the following order: alcohols < acetates < chloroalkanes < alkenes < alkanes.

The limiting activity coefficient increases with increasing the number of carbon atoms in the molecule, as can be seen in Figures 7 to 9. This can be explained by the increase in the hydrophobic character of the solute with increasing chain length. This behavior has been observed in other stationary phases.[24−27]

The graphs of $\ln \gamma^{\infty}$ versus the reciprocal of the absolute temperature permit the determination of the partial molar excess enthalpy at infinite dilution, $\Delta H_i^{\mathrm{E},\infty}$, for different solutes. The values of $\Delta H_i^{\mathrm{E},\infty}$ reported in Table 4 allow the determination of γ^{∞} at temperatures other than those reported in this work.

Table 4. Values of $\Delta H^{E,\infty}$, ΔH^{dis}, and ΔH^{vap} in the Solvents 1,8-ODA and 1,12-DDDA As Determined Using Equations 5 to 7

	1,8-ODA			1,12-DDDA			lit
	$\Delta H^{E,\infty}$	ΔH^{dis}	ΔH^{vap}	$\Delta H^{E,\infty}$	ΔH^{dis}	ΔH^{vap}	ΔH^{vap}
solute	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
n-pentane	2379	−22064	24.44	1957	−22311	24.27	25.79[a]
n-hexane	3829	−24825	28.65	2527	−25890	28.42	28.85[a]
n-heptane	4626	−28501	33.12	3390	−29519	32.91	31.77[a]
n-octane	6267	−31423	37.69	4686	−32401	37.09	34.41[a]
n-decane	10483	−36592	47.07	6009	−41159	47.17	51.42[a]
1-pentene	2911	−20528	23.43	8101	−15081	23.18	25.47[a]
1-hexene	6305	−21523	27.82	8374	−19215	27.59	30.61[a]
1-heptene	9526	−22756	32.28	9114	−22899	32.01	35.49[a]
1-octene	12559	−24315	36.87	11058	−25473	36.53	34.07[a]
1-decene	13868	−32191	46.05	12315	−33313	45.63	50.43[a]
methanol	−11788	−47087	35.29	−18189	−54016	35.83	35.21[a]
ethanol	−5721	−44883	39.16	−14919	−53614	38.70	38.56[a]
propan-1-ol	−3405	−46738	43.33	−11080	−54264	43.20	41.44[a]
butan-1-ol	−1416	−49754	48.34	−5204	−53117	47.91	49.72[a]
1-chlorobutane	11284	−19053	30.34	6502	−23668	30.17	30.39[a]
1-chloropentane	20530	−14047	34.58	9972	−24441	34.41	33.15[a]
hexyl chloride	29406	−9707	39.11	8150	−30779	38.93	35.67[a]
dichloromethane	7695	−18611	26.31	16760	−9283	26.04	28.06[a]
carbon tetrachloride	18698	−10870	29.57	13212	−15877	29.09	29.82[a]
ethyl acetate	10777	−16096	26.87	11763	−19535	31.30	31.94[a]
propyl acetate	15148	−20819	35.97	14626	−21018	35.64	33.92[a]
butyl acetate	16521	−23196	39.72	14754	−24027	38.78	36.28[a]
benzene	5918	−24890	30.81	1233	−29806	31.04	30.72[a]
toluene	6762	−28050	34.81	7557	−27024	34.58	33.18[a]
ethylbenzene	8624	−30023	38.65	3411	−34599	38.01	35.57[a]
diethyl ether	2147	−22549	24.70	2998	−21380	24.38	26.52[a]
dibutyl ether	9472	−32219	41.69	12767	−28309	41.08	44.97[a]

[a] From ref 30.

Table 5. Abraham Parameters for the Solvents Studied at Different Temperatures; R^2 is the Correlation Coefficient

solvent	T/K	c	r	s	a	b	l	R^2
1,8-ODA	328.21	−0.131	−0.647	1.605	4.506	−0.471	0.729	0.947
	338.23	−0.181	−0.743	1.774	4.209	−0.623	0.707	0.946
	343.19	−0.203	−0.791	1.853	4.063	−0.695	0.696	0.944
	348.25	−0.230	−0.848	1.944	3.926	−0.776	0.686	0.943
1,10-DDA	338.20	−0.424	−0.379	1.338	3.825	−0.128	0.730	0.938
	348.15	−0.430	−0.493	1.506	3.443	−0.271	0.698	0.929
	353.22	−0.436	−0.558	1.595	3.262	−0.346	0.684	0.924
1,12-DDDA	348.25	−0.567	−0.494	1.412	3.461	−0.251	0.691	0.937
	353.15	−0.574	−0.531	1.460	3.297	−0.298	0.676	0.937
	358.25	−0.581	−0.558	1.514	3.114	−0.349	0.660	0.937
	363.21	−0.591	−0.591	1.550	2.925	−0.375	0.647	0.936

The increase in γ^{∞} with increasing temperature for the alcohols results in negative values of the partial molar excess enthalpies at infinite dilution, which is characteristic of an exothermic association between the alkanediamines and alcohols that is certainly due to hydrogen bonds. As cited in the literature,[28] the OH···N bond between unlike molecules is stronger than the OH···O and NH···N bonds present in the self-associated alcohols and amines. In all of the other solutes, the $\Delta H_i^{E,\infty}$ values are positive, probably as a result of dissociation of the diamines in the presence of alkanes, alkenes, chloroalkanes, acetates, aromatics, and ethers.

The small values of γ^{∞} for acetates reflect the competition between attractive association of the compounds and dissociation

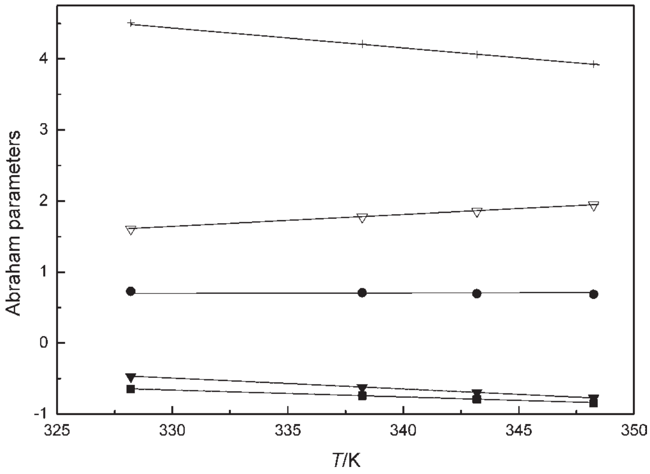

Figure 10. Evolution of the Abraham parameters with temperature for 1,8-ODA: ■, *r*; ▽, *s*; +, *a*; ▼, *b*; ●, *l*; —, linear regression.

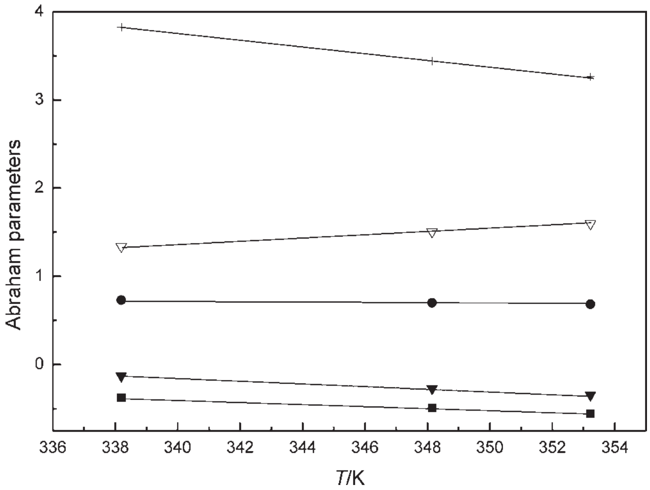

Figure 11. Evolution of the Abraham parameters with temperature for 1,10-DDA: ■, *r*; ▽, *s*; +, *a*; ▼, b; ●, *l*; —, linear regression.

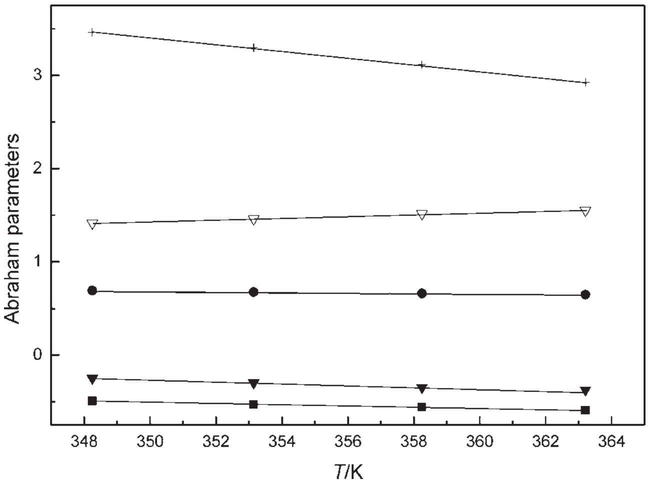

Figure 12. Evolution of the Abraham parameters with temperature for 1,12-DDDA: ■, *r*; ▽, *s*; +, *a*; ▼, *b*; ●, *l*; —, linear regression.

of each of the polar or polarizable pure compounds. The dissociation effect is dominant, and the activity coefficients are relatively small but larger than unity.[29] This is also reflected in the large positive values of $\Delta H_i^{E,\infty}$, which are characteristic of an endothermic dissociation during mixing. Most of the enthalpies of vaporization of the solutes available in the literature[30] agree well with the experimental values given in Table 4.

Another aim of the investigation was the calculation of different interactions between the solutes and the solvents using the Abraham method. The results are presented in Table 5, which gives for each stationary phase the Abraham parameters corresponding to eq 8 along with the correlation coefficients (R^2).

The small values of *b* (hydrogen-bond acidity) relative to the values of *a* show the basic character of the diamines, which act as hydrogen-bond-acceptor bases (significant *a* parameter). This basicity decreases as a function of the chain length of the alkyldiamines. The high values of *s*, ranging from 1.34 to 1.99, can be explained by the polarity of the diamines. On the basis of the *s* parameter, the polarizabilities of the stationary phases increase in the order 1,12-DDDA < 1,10-DDA < 1,8-ODA. The small values of *r* indicate the small interaction capacity through the pairs of π and n electrons.

For the three alkyldiamines, the evolution of the Abraham parameters with temperature is linear (Figures 10 to 12). This result is interesting, since it allows the temperature interval for the prediction of γ^{∞} to be broadened.

■ CONCLUSION

With the help of the GLC technique, infinite-dilution activity coefficients for paraffins, olefins, chloroparaffins, aromatics, alcohols, acetates, and ethers in alkane-α,ω-diamines (octane-1,8-diamine, decane-1,10-diamine, and dodecane-1,12-diamine) have been measured over the temperature range (328.15 to 363.15) K. The experimental results agree well with available literature data. Thermodynamic data relative to these mixtures are not easily available.

The results show the great solubility of the alcohols in the alkanediamines. Furthermore, the temperature dependence of the limiting activity coefficients was verified using experimental $\Delta H_i^{E,\infty}$ data.

The different interactions between the solutes and solvents were calculated using the Abraham method. This method, which involves linear solvation energy relationships, seems to be the most efficient method of calculating the interactions and allows the prediction of γ^{∞} for other solutes not studied in this survey. The temperature dependence of the Abraham parameters allows the temperature interval for the prediction of γ^{∞} to be broadened.

The activity coefficients at infinite dilution determined in this work can be used to predict the phase-separation properties of alkanediamines and mixtures of organic compounds under different conditions.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kamel.khimeche@yahoo.fr.

■ REFERENCES

(1) Konin, C.; Delmotte, A.; Larno, P.; Van Mele, B. Influence of polymerization conditions on melt crystallisation of partially aliphatic polyimides. *Polymer* **1998**, *39*, 3697–3702.

(2) Nagata, M. Novel regular network polyimide films from mellitic acid and aliphatic and aromatic diamines or diisocyanates. *Polymer* **1995**, *36*, 2657–2662.

(3) Diaf, A.; Beckman, E. J. Thermally reversible polymeric sorbents for acid gases. III. CO_2-sorption enhancement in polymer-anchored amines. *React. Funct. Polym.* **1995**, *27*, 45–51.

(4) Aresta, M.; Dibenedetto, A.; Quaranta, E. Reaction of Aromatic Diamines with Diphenylcarbonate Catalysed by Phosphorous Acids: A New Clean Synthetic Route to Mono- and Dicarbamates. *Tetrahedron* **1998**, *54*, 14145–14156.

(5) Prasad, R. N.; Gupta, N. Template synthesis of Mn(II) complexes of tetraazamacrocycles derived from diaminoalkanes and 3,4-hexanedione or benzil. *J. Serb. Chem. Soc.* **2003**, *68*, 455–461.

(6) Knoop, C.; Tiegs, D.; Gmehling, J. Measurement of γ^∞ Using GLC. 3. Results for the stationary phases 10-nonadecanone, *N*-formylmorpholine, 1-pentanol, *m*-xylene and toluene. *J. Chem. Eng. Data* **1989**, *34*, 240–247.

(7) Kojima, K.; Zhang, S.; Hiaki, T. Measuring methods of infinite dilution activity coefficients and a database for systems including water. *Fluid Phase Equilib.* **1997**, *131*, 145–179.

(8) Gruber, D.; Langenheim, D.; Moollan, C.; Gmehling, J. Measurement of activity coefficients at infinite dilution using gas-liquid chromatography, 7. Results for various solutes with *N*-methyl-2-piperidone as stationary phase. *J. Chem. Eng. Data* **1998**, *43*, 226–229.

(9) Kikic, I.; Alessi, P.; Cortesi, A. Activity coefficients of hydrocarbons in polycarbonate by gas chromatography. *Fluid Phase Equilib.* **2000**, *169*, 117–125.

(10) Alessi, P.; Kikic, I.; Papo, A.; Torriano, G. Gas Chromatographic Characterisation of Phosphate Esters. *J. Chem. Eng. Data* **1978**, *23*, 29–33.

(11) Alessi, P.; Cortesi, A.; Napoli, M.; Conte, L. Activity coefficients at infinite dilution of organic solvents in hydrofluoroparaffins. *J. Fluorine Chem.* **1995**, *72*, 43–47.

(12) Desty, D. H.; Swanson, W. T. Gas—liquid chromatography—some selective stationary phases for hydrocarbon separations. *J. Phys. Chem.* **1961**, *65*, 766–774.

(13) Laub, R. J.; Pecsoc, R. L. *Physicochemical Application of Gas Chromatography*; Wiley: New York, 1978.

(14) Morton, D. W.; Young, C. L. Infinite dilution activity coefficients of C_2—C_8 hydrocarbons in alkylcyclohexanes. *J. Chem. Thermodyn.* **1998**, *30*, 143–151.

(15) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: London, 1986.

(16) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(17) Beattie, J. A.; Bridgeman, O. C. A New Equation of State for Fluids. I. Application to Gaseous Ethyl Ether and Carbon Dioxide. *J. Am. Chem. Soc.* **1927**, *49*, 1665–1667.

(18) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. Hydrogen bonding: XVI. A new solute solvation parameter, π_2^H, from gas chromatographic data. *J. Chromatogr.* **1991**, *587*, 213–228.

(19) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. Hydrogen Bonding. Part 14. The Characterisation of Some N-Substituted Amides as Solvents: Comparison with Gas—Liquid Chromatography Stationary Phases. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1851–1857.

(20) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. Hydrogen Bonding. Part 13. A New Method for the Characterisation of GLC Stationary Phases. The Laffort Data Set. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1451–1460.

(21) Mutelet, F.; Rogalski, M. Using temperature gradient gas chromatography to determine or predict vapor pressures and linear salvation energy relationship parameters of highly boiling organic compounds. *J. Chromatogr., A* **2003**, *988*, 117–126.

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

(23) Dahmani, A.; Khimeche, K.; Alessi, P.; Kikic, I. Presented at the 23rd European Symposium on Applied Thermodynamics (ESAT 2008), Cannes, France, May 29—June 1, 2008.

(24) 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.

(25) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic properties of mixtures containing ionic liquids. Activity coefficients at infinite dilution of polar solvents in 4- methyl-*n*-butylpyridinium tetrafluoroborate using gas—liquid chromatography. *J. Chem. Thermodyn.* **2002**, *34*, 1341–1347.

(26) Letcher, T. M.; Whitehead, P. G. The determination of activity coefficients of alkenes, alkynes, and cycloalkanes at infinite dilution with polar solvent tetrahydrothiophene-1,1-dioxide (sulpholane) using a g.l.c technique at T = 303.15 K and T = 313.15 K. *J. Chem. Thermodyn.* **1996**, *28*, 843–849.

(27) Letcher, T. M.; Naicker, P. K. Activity coefficients of hydrocarbon solutes at infinite dilution in 1,4-dicyanobutane from gas liquid chromatography. *J. Chem. Thermodyn.* **2000**, *32*, 1627–1634.

(28) Rao, D. N.; Naidu, P. R. Excess volumes of ethylenediamine + an alcohol. *J. Chem. Thermodyn.* **1981**, *13*, 691–694.

(29) Kozłowska, M. K.; Letcher, T. M.; Domanska, U. The determination of activity coefficients at infinite dilution using g.l.c for hydrocarbons in furfural at T = 278.15 K and T = 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 561–565.

(30) *CRC Handbook of Chemistry and Physics*, 89th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2008; Section 6.