906 *J. Chem. Eng. Data* **2002,** *47,* 906−910

Measurement of Activity Coefficients at Infinite Dilution Using Gas−Liquid Chromatography. 13. Results for Various Solutes with the Stationary Phases 1-Ethylpyrrolidin-2-one and 1,5-Dimethylpyrrolidin-2-one

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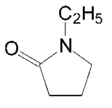
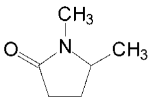
Using gas−liquid chromatography, activity coefficients at infinite dilution ($\gamma_{i,3}^{\infty}$) have been measured for 23 solutes (i) (alkanes, alkenes, cyclic hydrocarbons, aromatic hydrocarbons, ketones, ethers, aldehydes, esters, and halocarbons) in the solvents (3) 1-ethylpyrrolidin-2-one and 1,5-dimethylpyrrolidin-2-one. The measurements were carried out at three temperatures (298.15 K, 308.15 K, and 318.15 K). The obtained $\gamma_{i,3}^{\infty}$ values are compared with data for 1,3-dimethylimidazolidin-2-one, 1-octylpyrrolidin-2-one, pyrrolidin-2-one, and 1-methylpyrrolidin-2-one. The selectivities for benzene and the other organic solutes are presented at three temperatures (298.15 K, 308.15 K, 318.15 K), and the efficacy of the two entrainers for separating benzene from other organic substances is discussed. Furthermore, the experimental data are compared with the results of the modified UNIFAC equation (Dortmund).

Introduction

The activity coefficient at infinite dilution $\gamma_{i,3}^{\infty}$ (limiting activity coefficient) represents an important property, which is used in particular for the selection of selective solvents (e.g. for extraction and extractive distillation) and for the reliable design of thermal separation processes.[1,2] The removal of the last traces of impurities requires the largest separation effort.[1,2] To avoid an oversizing of the distillation column, which would lead to an increase in investment and operating costs, reliable information about the separation factor at infinite dilution is required. Furthermore, more reliable g^E model or group interaction parameters can be obtained by fitting the parameters simultaneously to VLE, H^E, and limiting activity coefficient data.

Activity coefficients at infinite dilution ($\gamma_{i,3}^{\infty}$) can be determined by several methods including the retention time method (gas−liquid chromatography, GLC),[3] ebulliometry,[4] static methods,[5] and the dilutor technique.[6] The latter can also be employed to determine $\gamma_{i,3}^{\infty}$ values in solvent mixtures.[7,8] In this work, activity coefficients at infinite dilution were measured using the GLC technique. Measurements were carried out with the solvents 1-ethylpyrrolidin-2-one (NEP) and 1,5-dimethylpyrrolidin-2-one (DMP), for which little or no literature information is available.


NEP


DMP

Experimental Section

The gas−liquid chromatography technique developed by Everett[9] was used to determine the activity coefficients at infinite dilution; it is described in a previous paper.[10] Stainless steel columns (bore 4.2 mm and length 0.8 to 1.0 m*)* were used for the measurements as opposed to copper columns because of the possible reaction between copper and the amine group. The solid support used was Chromosorb W HP (80/100 mesh) which was loaded with 15% (w/w) or 20% (w/w) of the solvent. A catharometer detector was used with helium as the carrier gas, and the flow rate was maintained constant for each run. The flow rates were within the range 0.66 cm^3/s to 0.79 cm^3/s and were measured using a calibrated soap bubble flow meter. The temperature was controlled to within 0.002 K with a Tronac temperature controller and monitored using a calibrated Hewlett-Packard quartz thermometer.

The purity of the solvents, NEP and DMP, was found to be at least 99.8 mass % (GC analysis of peak areas, TCD detector) and the water content less than 100 ppm (Karl Fischer titration[11]). All precautions were taken to minimize exposure to air, as these two solvents are extremely hygroscopic. Since GLC itself is a separation technique, the results are not influenced by small solute impurities, and therefore the solutes were used without further purification.

The $\gamma_{i,3}^{\infty}$ values for 23 solutes (alkanes, alkenes, cycloalkanes, aromatic hydrocarbons, ketones, ethers, and aldehydes) in the two solvents were measured in the temperature range between 298.15 K and 318.15 K. The experimental conditions (gas flow, solvent loss, etc.) were checked by measuring the retention time of a reference substance (n-hexane) at regular intervals. The determination of $\gamma_{i,3}^{\infty}$ requires the following information: the net retention time of the solute (t_N), the absolute temperature (T), the column inlet and outlet pressures (P_i and P_o), the mass of the

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10.1021/je010318m CCC: $22.00

Table 1. Saturation Fugacity Coefficients, φ_i^s, for the Solutes Investigated at Temperature T

	φ_i^s		
solute i	T = 298.15 K	T = 308.15 K	T = 318.15 K
n-pentane	0.9731	0.9648	0.9552
n-hexane	0.9887	0.9844	0.9790
n-heptane	0.9954	0.9932	0.9903
n-octane	0.9982	0.9971	0.9956
1-pentene	0.9690	0.9600	0.9496
1-hexene	0.9872	0.9824	0.9766
1-heptene	0.9946	0.9921	0.9889
1-octene	0.9979	0.9967	0.9951
cyclohexane	0.9936	0.9909	0.9875
cyclohexene	0.9944	0.9920	0.9889
benzene	0.9946	0.9922	0.9892
toluene	0.9977	0.9966	0.9950
acetone	0.9889	0.9847	0.9794
2-butanone	0.9942	0.9916	0.9883
2-pentanone	0.9972	0.9958	0.9938
diethyl ether	0.9739	0.9655	0.9554
diisopropyl ether	0.9885	0.9840	0.9783
ethyl *tert*-butyl ether	0.9903	0.9864	0.9814
methyl *tert*-amyl ether	0.9937	0.9909	0.9874
methyl *tert*-butyl ether	0.9847	0.9794	0.9728
dichloromethane	0.9847	0.9794	0.9731
acetaldehyde	0.9721	0.9639	0.9545
tetrahydrofuran	0.9921	0.9890	0.9850

solvent on the solid support (m_L) and the carrier gas flow rate (F). The carrier gas flow rate was corrected to take into account the temperature of the bubble flow meter (T_{FM}), the pressure (P_{FM}), and the vapor pressure of water ($P^s_{H_2O}$). From these experimentally determined parameters, the specific net retention volume (V_g°) at 273.15 K was determined.

$$V_g^\circ = \frac{t_N}{m_L} j \frac{273.15F}{T_{FM}} \frac{P_{FM} - P^s_{H_2O}}{P_{FM} + \Delta P} \tag{1}$$

where j ($j < 1$) is the compressibility factor, which is important for the correction of the volume stream according to James and Martin,[12] and m_L is the mass of the solvent.

Equation 2 relates the activity coefficient of the solute at infinite dilution to the measured specific net retention volume (V_g°) at 273.15 K,

$$\gamma_i^\infty = \frac{273.15R}{V_g^\circ P_i^s \varphi_i^s M_L} \tag{2}$$

where R is the general gas constant, M_L is the molar mass of the solvent, and P_i^s is the saturation vapor pressure of the solute. P_i^s was calculated using Antoine constants taken from the Dortmunder Datenbank (DDB).[13] The saturation fugacity coefficient of the solute, φ_i^s, was calculated using the Soave−Redlich−Kwong equation of state following Gmehling and Kolbe.[14] The required critical data and acentric factors were obtained from the DDB. The values for φ_i^s are given in Table 1. The net retention time is equal to the difference between the retention time (t_R) of the solute and the dead time (t_A) (peak caused by air that is injected regularly). The net retention time is a measure of the partition of the solute between the mobile phase (gas/solute) and the stationary phase (solvent). This partitioning is a result of phase equilibrium behavior.

According to Conder and Young,[15] sometimes adsorption effects have to be taken into account and the adsorption at the gas−liquid interface becomes more important with increasing polarity of the solvent. Polar solutes on nonpolar stationary phases lead to adsorption at the gas−liquid interface, and this is often accompanied by adsorption on the solid support. To examine the presence of adsorption effects, the relative amount of stationary phase (liquid loading: 15 to 25 mass %) and the sample volume of the injected solutes (0.02 to 0.5 μL) were varied, but no adsorption effects were observed.

Table 2. Infinite Dilution Activity Coefficients, $\gamma_{i,3}^\infty$, and Partial Molar Excess Enthalpies at Infinite Dilution, $H_i^{E,\infty}$, for Organic Solutes in 1-Ethylpyrrolidin-2-one

	$\gamma_{i,3}^\infty$			
solute i	T = 298.15 K	T = 308.15 K	T = 318.15 K	$H_i^{E,\infty\ a}$ $J\cdot mol^{-1}$
n-pentane	7.15	6.61	6.13	6100
n-hexane	8.40	7.82	7.28	5600
n-heptane	9.94	8.88	8.03	8400
n-octane	11.8	10.5	9.43	8900
1-pentene	4.07	3.91	3.74	3300
1-hexene	4.78	4.49	4.27	4400
1-heptene	5.38	5.13	4.88	3800
1-octene	6.10	5.80	5.58	3500
cyclohexane	5.48	4.98	4.56	7200
cyclohexene	3.06	2.94	2.88	2400
benzene	0.864	0.977	1.09	−9100
toluene	1.12	1.23	1.32	−6600
acetone	1.22	1.21	1.20	700
2-butanone	1.21	1.19	1.16	1600
2-pentanone	1.26	1.26	1.21	1600
diethyl ether	2.86	2.75	2.66	2900
diisopropyl ether	4.70	4.38	4.19	4500
ethyl *tert*-butyl ether	4.00	3.80	3.76	2400
methyl *tert*-amyl ether	3.29	3.12	3.04	3200
methyl *tert*-butyl ether	2.92	2.75	2.74	2400
dichloromethane	0.270	0.298	0.341	−9100
acetaldehyde	1.08	1.13	1.15	−2400
tetrahydrofuran	1.29	1.33	1.38	−2600

[a] Calculated by linear regression from the experimental $\gamma_{i,3}^\infty$ data using eq 3.

Results and Discussion

The values of the activity coefficients at infinite dilution for the investigated solutes in NEP and DMP at three temperatures are listed in Tables 2 and 3. The main source of error in the calculation of the specific net retention volume corrected to 273.15 K (V_g°) is the measurement of the mass of the stationary phase in the column (±2%). In addition, there is a small error in the determination of the difference between the retention time and the dead time.[16] The total error in the determination of the specific net retention volume is about ±2.5%. Taking into account that the Antoine constants, taken from the DDB, used for the calculation of the saturation vapor pressure are also subject to error; the resulting error in $\gamma_{i,3}^\infty$ is ±3%. Measurements with different amounts of stationary phase or different flow rates lead to results within these error bounds.

Figure 1 shows examples of the linear relationship between the natural logarithm of the activity coefficients and the inverse absolute temperature for four different alkanes in NEP. The limiting activity coefficient increases with increasing chain length of the alkanes.

A comparison of $\ln(\gamma_{i,3}^\infty)$ for the different alkenes (1-pentene, 1-hexene, 1-heptene, 1-octene) as a function of inverse temperature in the solvents NEP and DMP is shown in Figure 2. Different temperature behavior of the solutes in these solvents is observed. At 298.15 K the limiting activity coefficients of the alkenes have similar

Table 3. Infinite Dilution Activity Coefficients, $\gamma_{i,3}^{\infty}$, and Partial Molar Excess Enthalpies at Infinite Dilution, $H_i^{E,\infty}$, for Organic Solutes in 1,5-Dimethylpyrrolidin-2-one

	$\gamma_{i,3}^{\infty}$			
solute *i*	$T =$ 298.15 K	$T =$ 308.15 K	$T =$ 318.15 K	$H_i^{E,\infty}$ [a] J·mol^{-1}
n-pentane	6.95	6.77	6.58	2100
n-hexane	8.98	8.31	7.89	5100
n-heptane	9.36	8.98	8.63	3200
n-octane	11.1	10.6	10.1	4000
1-pentene	4.06	4.01	4.00	570
1-hexene	4.76	4.61	4.56	1700
1-heptene	5.29	5.27	5.25	330
1-octene	6.04	6.00	5.95	610
cyclohexane	5.15	4.98	4.83	2545
cyclohexene	3.08	3.05	3.01	930
benzene	0.894	0.956	1.02	−5200
toluene	1.11	1.17	1.24	−4400
acetone	1.05	1.10	1.15	−3500
2-butanone	1.07	1.12	1.16	−3200
2-pentanone	1.14	1.20	1.26	−4100
diethyl ether	2.66	2.66	2.64	290
diisopropyl ether	4.35	4.32	4.29	530
ethyl *tert*-butyl ether	3.81	3.78	3.75	700
methyl *tert*-amyl ether	3.04	2.99	2.93	1500
methyl *tert*-butyl ether	2.70	2.68	2.66	570
dichloromethane	0.243	0.276	0.306	−9000
acetaldehyde	1.04	1.08	1.11	−2700
tetrahydrofuran	1.35	1.38	1.40	−1300

[a] Calculated by linear regression from the experimental $\gamma_{i,3}^{\infty}$ data using eq 3.

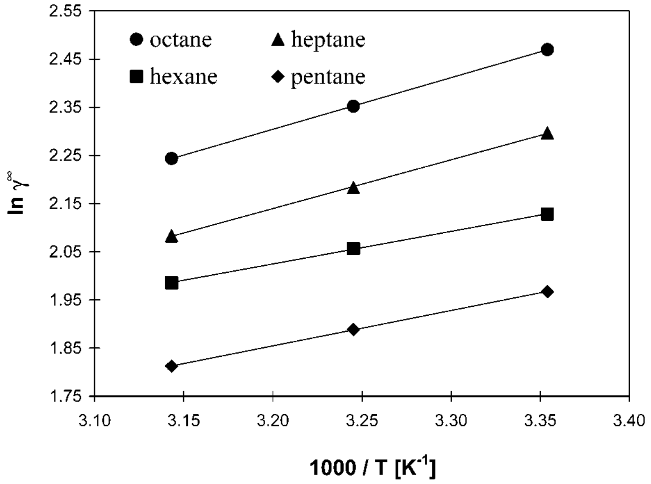

Figure 1. Experimental activity coefficients at infinite dilution $\ln(\gamma_{i,3}^{\infty})$ for alkanes in the solvent 1-ethylpyrrolidin-2-one as a function of inverse temperature: ◆, *n*-pentane; ■, *n*-hexane; ▲, *n*-heptane, ●, *n*-octane; —, linear regression.

values in both solvents. At higher temperatures the difference of the $\ln(\gamma_{i,3}^{\infty})$ values in the solvents increases.

Figure 3 shows a comparison of $\ln(\gamma_{i,3}^{\infty})$ values of *n*-hexane in six solvents with different degrees of alkylation of the pyrrolidinone. The values for $\ln(\gamma_{i,3}^{\infty})$ decrease with increasing degree of alkylation at the nitrogen containing ring system. This phenomenon can be explained as follows. With an increase in the degree of alkylation of the ring system, the hydrophobic nature of the solvent increases. We believe that the scattering of the 1-methylpyrrolidin-2-one (NMP) literature values can be explained by different water contents; however, the authors were not aware of this problem.

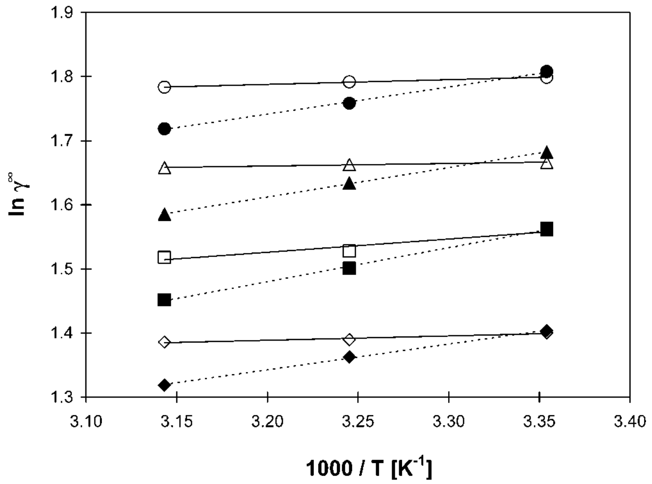

Figure 2. Experimental activity coefficients at infinite dilution $\ln(\gamma_{i,3}^{\infty})$ for four alkenes in the solvents 1-ethylpyrrolidin-2-one (NEP) and 1,5-dimethylpyrrolidin-2-one (DMP) as a function of inverse temperature: ◆, 1-pentene in NEP; ■, 1-hexene in NEP; ▲, 1-heptene in NEP; ●, 1-octene in NEP; ◇, 1-pentene in DMP; □, 1-hexene in DMP; △, 1-heptene in DMP; ○, 1-octene in DMP; - - -, linear regression.

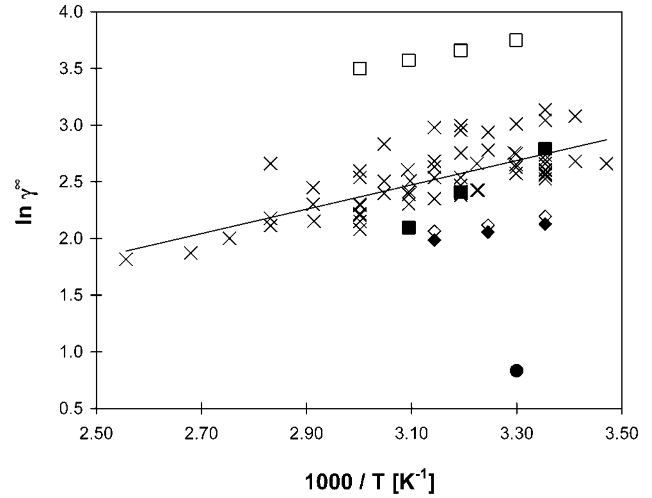

Figure 3. Comparison of $\ln(\gamma_{i,3}^{\infty})$ data from this work with published data of *n*-hexane in different solvents as a function of inverse temperature: ●, 1-octylpyrrolidin-2-one;[26] ◆, NEP (this work); ◇, DMP (this work); ×, 1-methylpyrrolidin-2-one (other authors);[13] □, pyrrolidin-2-one;[20] ■, 1,3-dimethylimidazolidin-2-one;[19] —, linear regression of NMP data.

The choice of the optimal temperature is an important criterion for the application of selective solvents. According to the Gibbs−Helmholtz equation, the values for the partial molar excess enthalpy at infinite dilution ($H_i^{E,\infty}$) can be obtained directly from the slope of a straight line derived from[14]

$$\left(\frac{\partial \ln \gamma_i^{\infty}}{\partial(1/T)}\right)_{P,x} = \frac{H_i^{E,\infty}}{R} \qquad (3)$$

The values for $H_i^{E,\infty}$ calculated by linear regression from experimental $\gamma_{i,3}^{\infty}$ data are shown in Tables 2 and 3. The values for the alkenes are greater than the values for the alkanes and reflect a stronger interaction with NEP and DMP (Tables 2 and 3) due to the double bonds. The values for the aromatic compounds, benzene and toluene, are negative and reflect an even stronger interaction. The values for the polar ketones, aldehydes, and chloro compounds also reflect significant interactions.

Table 4. Selectivities, S_{12}^{∞}, Calculated from Eq 4 for Various Solutes (1) with Benzene (2) at Temperature *T*

	1-ethylpyrrolidin-2-one (NEP) S_{12}^{∞}			1,5-dimethylpyrrolidin-2-one (DMP) S_{12}^{∞}		
solute (1)	T = 298.15 K	T = 308.15 K	T = 318.15 K	T = 298.15 K	T = 308.15 K	T = 318.15 K
n-pentane	8.27	6.77	5.63	7.77	7.08	6.45
n-hexane	9.72	8.00	6.70	10.05	8.70	7.73
n-heptane	11.50	9.08	7.38	10.47	9.39	8.46
n-octane	13.67	10.75	8.67	12.46	11.07	9.87
1-pentene	4.71	4.00	3.44	4.54	4.20	3.92
1-hexene	5.52	4.59	3.93	5.33	4.82	4.47
1-heptene	6.22	5.25	4.49	5.92	5.52	5.14
1-octene	7.06	5.94	5.13	6.76	6.28	5.83
cyclohexane	6.34	5.09	4.19	5.76	5.21	4.73
cyclohexene	3.54	3.01	2.65	3.45	3.19	2.95
toluene	1.30	1.25	1.22	1.24	1.23	1.21
acetone	1.42	1.24	1.11	1.18	1.15	1.13
2-butanone	1.40	1.22	1.07	1.20	1.17	1.14
2-pentanone	1.46	1.28	1.11	1.28	1.26	1.24
diethyl ether	3.31	2.81	2.45	2.98	2.78	2.59
diisopropyl ether	5.43	4.49	3.86	4.86	4.52	4.20
ethyl *tert*-butyl ether	4.62	3.89	3.46	4.27	3.96	3.67
methyl *tert*-amyl ether	3.81	3.20	2.79	3.40	3.12	2.87
methyl *tert*-butyl ether	3.37	2.81	2.52	3.02	2.81	2.61
dichloromethane	0.31	0.31	0.31	0.27	0.29	0.30
acetaldehyde	1.25	1.15	1.05	1.16	1.13	1.09
tetrahydrofuran	1.49	1.36	1.27	1.51	1.44	1.37

Table 5. Selectivity, S_{12}^{∞}, Calculated from Eq 4 for the Solvents for the Example of the Separation Problem Cyclohexane (1)/Benzene (2) at Temperature *T*

	S_{12}^{∞}		
solvent	T = 303.15 K	T = 313.15 K	T = 323.15 K
1,3-dimethylimidazolidin-2-one[19]			5.99
pyrrolidin-2-one[20]	8.73	7.97	7.33
1-methylpyrrolidin-2-one[21]	7.75	7.05	6.48
1-methylpyrrolidin-2-one	7.89[22]	7.37[23]	6.80[24]
1-methylpyrrolidin-2-one + 6% (w/w) water[8]	10.47	9.22	8.35

Table 6. Comparison of Experimental $\gamma_{i,3}^{\infty}$ Data for Different Solutes in the Solvent 1,5-Dimethylpyrrolidin-2-one with Literature Data and Predicted $\gamma_{i,3}^{\infty}$ Values (Using the Modified UNIFAC Equation (Dortmund))

solute	$\gamma_{\text{exp}}^{\infty}$	$\gamma_{\text{lit.}}^{\infty}$	$\gamma_{\text{predicted}}^{\infty\ a}$
n-pentane	6.95 (298.15 K)	7.10 (303.15 K)[25]	6.95 (298.15 K)
1-pentene	4.06 (298.15 K)	3.96 (303.15 K)[25]	3.50 (298.15 K)
benzene	0.894 (298.15 K)		0.891 (298.15 K)
n-hexane	7.89 (318.15 K)		7.56 (318.15 K)
1-octene	5.95 (318.15 K)		6.08 (318.15 K)

[a] Predicted γ^{∞} values using the modified UNIFAC equation (Dortmund).

In Table 4 the selectivity values S_{12}^{∞} are presented; the selectivity is defined[17] as

$$S_{12}^{\infty} = \gamma_1^{\infty}/\gamma_2^{\infty} \tag{4}$$

where γ_1^{∞} is the activity coefficient at infinite dilution of hydrocarbons in NEP or DMP and γ_2^{∞} is the activity coefficient of benzene at infinite dilution in NEP or DMP. The comparison of the solvents for the separation of cyclohexane and benzene (i.e. separation of aliphatics from aromatics) shows that NEP has the best selectivity at 298.15 K. A comparison of the compounds investigated here with other solvents (see Table 5) shows comparable selectivities.

In Table 6, the experimental data for several solutes investigated in this work are compared with published data and predicted $\gamma_{i,3}^{\infty}$ values using the modified UNIFAC equation (Dortmund).[18] There are only a limited number of $\gamma_{i,3}^{\infty}$ values available in the literature. A comparison of these with experimental and predicted data shows good agreement.

Conclusion

Activity coefficients at infinite dilution for 23 solutes in the solvents 1-ethylpyrrolidin-2-one and 1,5-dimethylpyrrolidin-2-one have been measured between 298.15 K and 318.15 K using GLC. This technique has been chosen as it is a fast and reliable method for determining $\gamma_{i,3}^{\infty}$ values.

The selection of the solvents focused on solvents for which no or only limited experimental data were available.

The influence of alkylation group substitution on the solvents was assessed by determining $\gamma_{i,3}^{\infty}$ and S_{12}^{∞} from the solvents 1,3-dimethylimidazolidin-2-one, pyrrolidin-2-one, 1-methylpyrrolidin-2-one, and 1-octylpyrrolidin-2-one.

The accuracy of the group contribution model mod. UNIFAC (Dortmund) was determined by comparing experimental $\gamma_{i,3}^{\infty}$ data with calculated values. This confirms the applicability of the model as a predictive method for the synthesis and design of thermal separation processes.

Acknowledgment

The authors would like to thank the DDBST GmbH for permitting the use of the Dortmund Data Bank.

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Received for review December 5, 2001. Accepted April 3, 2002. The authors would like to thank the “Forschungszentrum Jülich (Bundesrepublik Deutschland)” and the “National Research Foundation (South Africa)” for financial support.

JE010318M