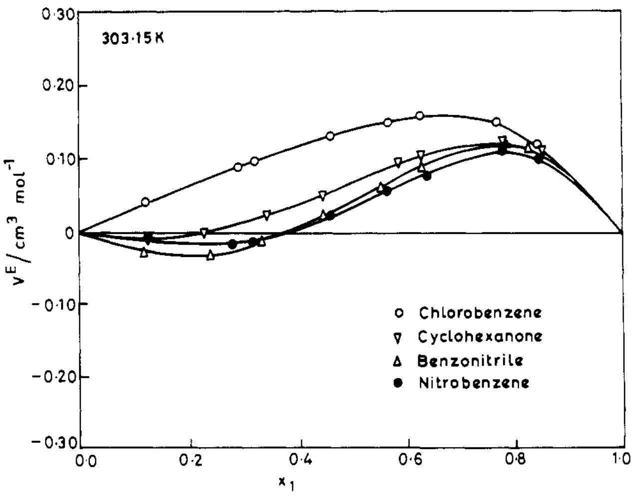

Figure 1. Excess molar volumes V^E as a function of the mole fraction x_1 of methylcyclohexane: points, experimental results; curves, results calculated with eq 1.

Results and Discussion

The V^E data of methylcyclohexane (1) + chlorobenzene (2), + nitrobenzene (2), + benzonitrile (2), or + cyclohexanone (2) are presented as a function of mole fraction x_1 in Table II and Figure 1. The experimental V^E_{exp} data were fitted to an empirical equation of the form

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x_1(1 - x_1)[a_0 + a_1(2x_1 - 1) + a_2(2x_1 - 1)^2] \quad (1)$$

The parameters a_i along with the standard deviations $\sigma(V^E)$

$$\sigma(V^E) = [\sum(V^E_{exp} - V^E)^2/(n - p)]^{1/2} \quad (2)$$

where n is the number of experimental points and p the number of parameters a_i, were evaluated by the least-squares technique and are given in Table II.

The observed V^E values result from the balance of dipole-dipole interactional contributions, leading to expansion in volume, and geometrical packing or free volume effects, leading to contraction in volume.

The curves in Figure 1 show that the excess volumes are positive for chlorobenzene, over the whole range of composition, and change sign for the remaining three systems.

The comparison of V^E data at 303.15 and 313.15 K reveal that the effect of temperature is almost negligible for the investigated mixtures.

Registry No. Methylcyclohexane, 108-87-2; cyclohexanone, 108-94-1; chlorobenzene, 108-90-7; nitrobenzene, 98-95-3; benzonitrile, 100-47-0.

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Received for review July 17, 1990. Accepted May 29, 1991.

Isothermal Vapor–Liquid Equilibria and Excess Volumes for the Systems *n*-Hexane + Ethylbenzene, 2-Methylpentane + *n*-Heptane, and 2-Methylpentane + *n*-Octane

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Vapor–liquid equilibria (VLE) and molar excess volumes have been obtained for *n*-hexane + ethylbenzene, 2-methylpentane + *n*-heptane, and 2-methylpentane + *n*-octane. The VLE data were reduced according to the maximum-likelihood principle. The thermodynamical consistency was verified. The parameters of NRTL, Wilson, and UNIQUAC equations were fitted, and the VLE data were compared with Abdoul group contribution predictions.

Introduction

We recently developed in our laboratory a group contribution model for predicting the thermodynamic properties of mixtures present in petroleum fluids (*1*, *2*). The application of this method to literature vapor–liquid equilibrium (VLE) data showed poor agreement for 2-methylpentane + *n*-octane (*3*), while the 2-methylpentane + *n*-hexane system (*4*) was in good agreement. Our aim was to know whether the discrepancy is due to the inadequacy of the model or to the inaccuracy of experiments. Therefore, we measured isothermal vapor–liquid equilibria for 2-methylpentane + *n*-octane at 328.15 K. We report also VLE data for 2-methylpentane + *n*-heptane at 318.15 and 328.15 K (*5*) and for *n*-hexane + ethylbenzene at 338.15 K. The experimental molar excess volumes of all mixtures at 298.15 K, used to determine the vapor- and liquid-phase compositions, are also reported.

Experimental Section

Materials. *n*-Hexane and *n*-heptane were "Uvasol" reagents from Merck with stated minimum purities of 97 and 99%, respectively. *n*-Octane and ethylbenzene were Fluka "puriss" products with respectively 99.5 and 99% purity. 2-Methylpentane was a 98% "prosynthesis" grade reagent from Merk.

These materials were purified by fractional distillations on a 60 real plates Oldershaw type column. The *n*-hexane was subjected to distillation three times.

The densities of the purified substances were measured with an Anton Paar (DMA-60) densimeter at 298.15 K (Table I). They are in excellent agreement with literature values (*6*).

Apparatus and Procedure. Vapor–liquid equilibrium data were determined at constant temperature in a dynamic still designed by Berro et al. (*7*).

The temperature inside the equilibrium cell was measured by means of a Lauda R42 digital thermometer with a platinum sensor which has a precision of $\sigma_e(T) = 0.01$ K. The pressure was measured by means of a Digiquartz pressure transducer of Paroscientific Inc., Model 215A, calibrated in the pressure range 0–10 MPa. The estimated precision of the pressure measurements is $\sigma_e(P) = 0.01$ KPa.

0021-9568/91/1736-0474$02.50/0

Table I. Densities ρ and Vapor Pressures $P°$ of Pure Components

	ρ(298.15 K)/(g cm^{-3})		$P°$/(kPa)					
			318.15 K		328.15 K		338.15 K	
compounds	this work	lit.	this work	lit.	this work	lit.	this work	lit.
2-methylpentane	0.648 57	0.648 52[a]	60.642	60.680[b]	85.352	85.422[b]		
n-hexane	0.654 86	0.654 81[a]					89.962	89.962[a]
n-heptane	0.679 50	0.679 51[a]	15.328	15.324[a]	23.098	23.094[a]		
n-octane	0.698 51	0.698 49[a]			8.409	8.422[a]		
ethylbenzene	0.862 64	0.862 64[a]					9.170	9.185[a]

[a] Reference 6. [b] Reference 16.

Table II. Experimental Excess Molar Volumes $V^{E°}$ at 298.15 K as a Function of Mole Fraction $x_1°$

n-hexane (1) + ethylbenzene (2)		2-methylpentane (1) + *n*-heptane (2)		2-methylpentane (1) + *n*-octane (2)	
$x_1°$	$V^{E°}$/(cm^3 mol^{-1})	$x_1°$	$V^{E°}$/(cm^3 mol^{-1})	$x_1°$	$V^{E°}$/(cm^3 mol^{-1})
0.0504	−0.020	0.0559	0.001	0.0488	−0.032
0.1273	−0.083	0.1056	−0.014	0.1123	−0.059
0.1891	−0.097	0.1536	−0.029	0.1565	−0.076
0.2544	−0.123	0.1883	−0.036	0.1966	−0.087
0.3240	−0.124	0.2472	−0.045	0.2812	−0.118
0.3514	−0.140	0.2992	−0.052	0.3419	−0.132
0.3932	−0.138	0.3557	−0.054	0.4072	−0.145
0.3906	−0.137	0.3906	−0.060	0.4479	−0.154
0.5044	−0.145	0.4554	−0.063	0.5006	−0.156
0.5383	−0.148	0.5003	−0.065	0.5554	−0.161
0.6107	−0.137	0.5494	−0.068	0.6060	−0.163
0.6545	−0.124	0.5948	−0.068	0.6587	−0.154
0.7017	−0.138	0.6584	−0.066	0.6903	−0.136
0.7455	−0.106	0.7147	−0.059	0.7169	−0.145
0.7899	0.112	0.7509	−0.055	0.7482	−0.130
0.9011	−0.077	0.7989	−0.049	0.7894	−0.120
0.9514	−0.055	0.8497	−0.044	0.8049	−0.115
		0.8979	−0.032	0.8461	−0.089
		0.9563	−0.012	0.9117	−0.067
				0.9178	−0.065
				0.9757	−0.020

Liquid and vapor mole fractions, x_i and y_i, respectively, were determined by densimetric analysis using an Anton paar DMA 60 densimeter equipped with two DMA 601M cells in a flow system as described previously (*7*). The cells were thermoregulated to better than 0.01 K, and the temperature was measured with the same Lauda R42 digital thermometer using another platinum sensor. The inaccuracy of the density measurements proved to be $\sigma_e(\rho)$ = 0.000 01 g cm^{-3}.

The molar excess volumes V^E at 298.15 K were calculated from density data. For density measurements, binary mixtures were prepared by weighing, using the technique described earlier by Berro and Péneloux (*8*) to prevent the partial evaporation of the liquids.

Experimental Results and Data Treatment

Excess Volume Data. The experimental data are collected in Table II. They were fitted by least-squares to a smoothing equation of the type

$$V^E/[x_1(1 - x_1)] = \sum_{j=1}^{m} A_j(2x_1 - 1)^{j-1} \qquad (1)$$

where x_1 denotes the mole fraction of component 1.

The parameters A_j of eq 1 are given in Table III with the values of root mean square deviations of excess volumes $\sigma(V^E)$ and densities $\sigma(\rho)$:

$$\sigma(V^E) = \{\sum_{i=1}^{N}[V_i^{E°} - V^E(x_i°,A)]^2/(N - m)\}^{1/2} \qquad (2)$$

where N is the number of experimental values, denoted by degree symbol, and m the number of A_j parameters. $\sigma(\rho)$ was calculated in a similar way.

Vapor–Liquid Equilibrium Data. The experimental VLE data are listed in Tables IV and V. For the 2-methylpentane + *n*-octane system at the lowest pressures, only P–x results are given. This is due to the fact that, in this range, the vapor-phase composition measurements were not accurate because of partial evaporation of the samples.

The reduction of measured VLE data was performed by using the observed deviation method (*9*). This method permits the simultaneous estimation of the fitting parameters and the experimental inaccuracies. In this method the molar excess Gibbs energies g^E are fitted to a Redlich–Kister polynomial of the form

$$g^E/(RTx_1x_2) = \sum_{j=1}^{m} A_j Y_j \qquad (3)$$

where

$$Y_j = (2j - 1)(2x_1 - 1)^{j-1} \qquad (4)$$

and m is the number of A_j parameters. This number is not fixed in advance but chosen during the reduction procedure as the lowest degree allowing the avoidance of systematic deviations arising from the model. The values of the second virial coefficients estimated by the Hayden and O'Connell method (*10*) to account for vapor-phase nonideality are given in Table VI.

The A_j parameters and the experimental inaccuracies have been obtained by applying the maximum likelihood principle to the objective function S (see Appendix A). Furthermore, the thermodynamic consistency of the measured VLE data was checked by using the weighted root mean square deviation (WRMSD), defined as

$$\text{WRMSD} = [S/(N_l + n - m)]^{1/2} \qquad (5)$$

where N_l and n are the numbers of measured compositions in

Table III. Excess Molar Volumes V^E at 298.15 K, Parameters of Equation 1, Standard Deviations $\sigma(A_j)$, $\sigma(V^E)$ (Equation 2), and $\sigma(\rho)$

		[A_j ± $\sigma(A_j)$]/(cm^3 mol^{-1})		
	j	*n*-hexane (1) + ethylbenzene (2)	2-methylpentane (1) + *n*-heptane (2)	2-methylpentane (1) + *n*-octane (2)
	1	−0.5652 ± 0.0126	−0.2655 ± 0.0042	−0.6268 ± 0.0068
	2	0.0710 ± 0.0458	−0.0784 ± 0.0110	−0.1250 ± 0.0132
	3	−0.2832 ± 0.0658		−0.0661 ± 0.0301
	4	−0.3134 ± 0.1299		
$\sigma(V^E)$/(cm^3 mol^{-1})		0.007	0.003	0.004
$\sigma(\rho)$/(g cm^{-3})		0.000 04	0.000 02	0.000 02

Table IV. Experimental Vapor–Liquid Equilibrium Data, Pressure $P°$, Liquid-Phase Mole Fraction $x_1°$, and Vapor-Phase Mole Fraction $y_1°$, for n-Hexane (1) + Ethylbenzene (2) and 2-Methylpentane (1) + n-Octane (2)

n-hexane (2) + ethylbenzene (1) at 338.15 K			2-methylpentane (1) + *n*-octane (2) at 328.15 K		
$x_1°$	$y_1°$	$P°$/kPa	$x_1°$	$y_1°$	$P°$/kPa
0.158	0.1810	11.027	0.0346		10.952
0.0667	0.4845	16.789	0.0566		12.504
0.1301	0.6507	23.479	0.1171		17.135
0.1933	0.7392	29.544	0.1599		20.278
0.2255	0.7717	32.472	0.2051		23.750
0.2578	0.7971	35.272	0.2468		26.806
0.2973	0.8225	38.542	0.2835		29.554
0.3386	0.8441	41.829	0.3368	0.8303	33.555
0.3606	0.8498	42.810	0.3754	0.8524	36.553
0.3844	0.8642	45.452	0.4084	0.8686	38.981
0.4257	0.8797	48.532	0.4245	0.8764	40.253
0.4471	0.8874	50.211	0.4486	0.8862	42.058
0.4800	0.8970	52.552	0.4958	0.9034	45.648
0.5019	0.9038	54.218	0.5080	0.9079	46.599
0.5161	0.9071	55.130	0.5577	0.9232	50.386
0.5450	0.9151	57.278	0.5575	0.9228	50.421
0.5659	0.9197	58.681	0.6592	0.9481	58.287
0.6231	0.9332	62.758	0.7005	0.9563	61.488
0.6659	0.9421	65.708	0.7439	0.9646	64.877
0.7166	0.9518	69.220	0.7965	0.9733	68.973
0.7621	0.9601	72.367	0.8430	0.9803	72.573
0.8028	0.9672	75.210	0.9131	0.9897	78.120
0.8734	0.9791	80.319	0.9633	0.9957	82.103
0.9067	0.9846	82.740			
0.9578	0.9931	86.598			

the liquid and vapor phases, respectively, and m is the number of polynomial parameters.

The expected value of WRMSD found in this way should be 1 for perfectly consistent data; a value close to 2 would indicate that there are systematic errors of the same magnitude as the random errors in measurements (*7*). Results of the reduction of the VLE data are given in Table VII.

Vapor–liquid equilibrium data were independently fitted to the Wilson (*11*), NRTL (*12*), and modified UNIQUAC (*13*) models; the corresponding expressions are given in Appendix B. The model parameters were estimated by minimizing the objective function S using the experimental inaccuracies estimated during data reduction. The parameters obtained are shown in Table VIII, together with the standard deviations given by

$$100(D(P)/P) = (100/N)\sum_{i=1}^{N}|\Delta P_i|/P_i \tag{6}$$

$$100D(y) = (100/N)\sum_{i=1}^{N}|\Delta y_{1i}| \tag{7}$$

Table V. Experimental Vapor–Liquid Equilibrium Data, Pressure $P°$, Liquid-Phase Mole Fraction $x_1°$, and Vapor-Phase Mole Fraction $y_1°$, for the System 2-Methylpentane (1) + n-Heptane (2)

318.15 K			328.15 K		
$x_1°$	$y_1°$	$P°$/kPa	$x_1°$	$y_1°$	$P°$/kPa
0.0651	0.2133	18.340	0.0564	0.1808	26.615
0.1076	0.3208	20.266	0.1087	0.3060	29.779
0.1558	0.4190	22.445	0.1501	0.3911	32.364
0.1900	0.4773	23.942	0.1868	0.4545	34.609
0.2471	0.5600	26.443	0.2453	0.5388	38.147
0.3594	0.6842	31.492	0.3029	0.6109	41.697
0.3895	0.7113	32.849	0.3522	0.6616	44.731
0.4581	0.7650	35.925	0.3891	0.6959	47.044
0.5005	0.7952	37.860	0.4548	0.7502	51.060
0.5015	0.7949	37.880	0.5002	0.7824	53.917
0.5497	0.8251	40.025	0.5491	0.8139	56.921
0.5998	0.8512	42.241	0.5964	0.8413	59.807
0.6551	0.8797	44.878	0.6598	0.8725	63.664
0.6607	0.8832	45.035	0.6672	0.8780	64.277
0.7162	0.9065	47.568	0.6883	0.8878	65.568
0.7165	0.9074	47.627	0.7036	0.8927	66.388
0.7499	0.9194	49.113	0.7520	0.9146	69.473
0.7976	0.9385	51.349	0.7979	0.9328	72.319
0.8512	0.9560	53.652	0.8451	0.9504	75.271
0.8971	0.9704	55.794	0.8973	0.9687	78.606
0.9470	0.9858	58.163	0.9543	0.9871	82.153

Table VI. Second Molar Virial Coefficients B_{ij} at Temperature T

	T/K	B_{11}/(cm^3 mol^{-1})	B_{22}/(cm^3 mol^{-1})	B_{12}/(cm^3 mol^{-1})
n-hexane (1) + ethylbenzene (2)	338.15	−1353	−2455	−1785
2-methylpentane (1) + *n*-heptane (2)	318.15	−1056	−2434	−1491
	328.15	−997	−2211	−1383
2-methylpentane (1) + *n*-octane (2)	328.15	−997	−3251	−1607

Discussion

Excess volumes of 2-methylpentane + n-heptane (*14*) and n-hexane + ethylbenzene (*15*) systems have already been measured. Our results agree with those of previous investigations to within 0.03% in the central range of concentration.

For vapor–liquid equilibria, alone, the 2-methylpentane + n-octane system has been determined (*3*). Experimental excess Gibbs energies are positive, and the maximum is about 75 J at 313.15 K for $x_1 = 0.5$. If they are calculated by the Abdoul group contribution method (*1*, *2*), they are found to be close to zero.

Table IX shows the standard deviations in pressure and vapor compositions between the experimental VLE data and the values predicted by the Abdoul group contribution method.

Table VII. Results of Vapor–Liquid Equilibrium Data Reduction: Parameters A_j (Equation 3), Estimated Experimental Inaccuracies σ, and Weighted Root Mean Square Deviations (WRMSD)

		$A_j \pm \sigma(A_j)$			
		n-hexane (1) + ethylbenzene (2)	2-methylpentane (1) + *n*-heptane (2)		2-methylpentane (1) + *n*-octane (2)
	j	338.15 K	318.15 K	328.15 K	328.15 K
	1	0.393 94 ± 0.000 72	−0.005 21 ± 0.004 29	−0.004 41 ± 0.001 19	−0.016 61 ± 0.001 47
	2		−0.000 98 ± 0.000 55	−0.003 17 ± 0.000 71	−0.005 65 ± 0.000 79
	3				−0.004 05 ± 0.000 78
$\sigma(\rho)$/(g cm^{-3})		0.000 05	0.000 02	0.000 03	0.000 03
$\sigma(x_1)$		0.0003	0.0007	0.0010	0.0007
$\sigma(T)$/K		0.023	0.010	0.010	0.020
$\sigma(P)$/kPa		0.011	0.009	0.009	0.009
WRMSD		1.82	1.65	1.54	1.46

Table VIII. Parameters of Wilson, NRTL, and UNIQUAC Equations from VLE Data, at Temperatures T, Relative Percentage Standard Deviations in Pressure $100(D(P)/P)$ (Equation 6), and Absolute Standard Percentage Deviation in Vapor Compositions $100D(y)$ (Equation 7)

	n-hexane (1) + ethylbenzene (2)			2-methylpentane (1) + *n*-heptane (2)			2-methylpentane (1) + *n*-octane (2)		
T/K	parameters	$100D(P)/P$	$100D(y)$	parameters	$100D(P)/P$	$100D(y)$	parameters	$100D(P)/P$	$100D(y)$
				Wilson					
318.15				$\Lambda_{12} = 0.539\,15$ $\Lambda_{21} = 1.592\,85$	0.13	0.11			
328.15				$\Lambda_{12} = 0.595\,50$ $\Lambda_{21} = 1.513\,59$	0.19	0.18	$\Lambda_{12} = 0.454\,12$ $\Lambda_{21} = 1.772\,18$	0.25	0.06
338.15	$\Lambda_{12} = 0.814\,73$ $\Lambda_{21} = 0.805\,74$	0.10	0.04						
				NRTL					
318.15				$c_{12}/K = -248.048$ $c_{21}/K = 296.466$ $\alpha = 0.2$	0.13	0.10			
328.15				$c_{12}/K = -234.903$ $c_{21}/K = 272.730$ $\alpha = 0.2$	0.19	0.18	$c_{12}/K = -313.960$ $c_{21}/K = 383.597$ $\alpha = 0.2$	0.19	0.06
338.15	$c_{12}/K = 72.585$ $c_{21} = 66.524$ $\alpha = 0.3$	0.10	0.04						
				UNIQUAC					
318.15				$A_{12}/K = -93.752$ $A_{21}/K = 111.369$	0.13	0.10			
328.15				$A_{12}/K = -86.479$ $A_{21}/K = 100.082$	0.18	0.18	$A_{12}/K = -107.759$ $A_{21}/K = 130.609$	0.21	0.06
338.15	$A_{12}/K = 50.544$ $A_{21}/K = -23.233$	0.10	0.04						

Table IX. Relative Percentage Standard Deviations in Pressure $100(D(P)/P)$ (Equation 6) and Absolute Standard Deviation Percentage in Vapor Compositions $100D(y)$ between Experimental Vapor–Liquid Data and Values Obtained by the Abdoul Group Contribution Predictions

	T/K	100 × $(D(P)/P)$	100 × $D(y)$
n-hexane (1) + ethylbenzene (2)	338.15	0.64	0.20
2-methylpentane (1) + *n*-heptane (2)	318.15	0.29	0.08
	328.15	0.23	0.13
2-methylpentane (1) + *n*-octane (2)	283.15	4.36	1.07[a]
	293.15	3.28	0.81[a]
	303.15	2.50	0.37[a]
	313.15	1.77	0.23[a]
	328.15	0.50	0.10

[a] Reference 3.

Conclusion

The results of the reduction of our vapor–liquid equilibrium data show that they are thermodynamically consistent and that the estimated experimental inaccuracies are perfectly compatible with calibrations and characteristics of the apparatus. The experimental VLE data are equally well described by the Wilson, NRTL, and UNIQUAC models and agree with the Abdoul group contribution predictions.

Appendix A

The T–P–x–y data are reduced by minimizing the objective function S of the form

$$S = \sum_{i=1}^{N} [\Delta P_i/\sigma(P_i)]^2 + \sum_{i=1}^{N} (a_i \Delta P_i + b_i \Delta y_{1i})^2 \qquad \text{(A1)}$$

where

$$\Delta P = P^\circ - P(x_1^\circ, A) \qquad \Delta y_1 = y_1^\circ - y_1(x_1^\circ, A) \qquad \text{(A2)}$$

$$a = -(\delta P\, \delta y_1)/\sigma(P) D^{1/2} \qquad b = \sigma(P)/D^{1/2} \qquad \text{(A3)}$$

$$D = \sigma^2(P)\, \sigma^2(y_1) - (\delta P\, \delta y_1)^2 \qquad \text{(A4)}$$

If the vapor mole fraction is not measured, $a = 1/\sigma(P)$, $b = 0$.

The variances and the covariances are expressed by the following relations:

$$(\sigma(P))^2 = (\sigma_e(P))^2 + (\partial P/\partial x_1)_T^2 (\partial x_1/\partial \rho)_T^2 (\sigma_e(\rho))^2 + (\partial P/\partial T)_{x_1}^{\;2} (\sigma_e(T))^2 \qquad \text{(A5)}$$

$$(\sigma(y_1))^2 = [(\partial y_1/\partial \rho)_T^2 + (\partial y_1/\partial x_1)_T^2 (\partial x_1/\partial \rho)_T^2] (\sigma_e(\rho))^2 + (\partial y_1/\partial T)_{x_1}^{\;2} (\sigma_e(T))^2 \qquad \text{(A6)}$$

$$\delta P\, \delta y_1 = (\partial P/\partial x_1)_T (\partial y_1/\partial x_1)_T (\partial x_1/\partial \rho)_T^2 (\sigma_e(\rho))^2 + (\partial P/\partial T)_{x_1} (\partial y_1/\partial T)_{x_1} (\sigma_e(T))^2 \qquad \text{(A7)}$$

The weighted root mean square deviation is

$$\text{WRMSD} = [S/(N_l + n - m)]^{1/2} \qquad \text{(5)}$$

Appendix B

The parameters given in Table VIII were calculated for the following models:

Wilson

$$g^E/RT = x_1 \ln (x_1 + \Lambda_{12} x_2) + x_2 \ln (x_2 + \Lambda_{21} x_1) \qquad \text{(B1)}$$

NRTL

$$g^E/R = x_1 x_2 [\delta_{21} C_{21}/(x_1 + \delta_{21} x_2) + \delta_{12} C_{12}/(\delta_{12} x_1 + x_2)] \qquad \text{(B2)}$$

where

$$\delta_{21} = \exp(-\alpha C_{21}/T) \qquad \delta_{12} = \exp(-\alpha C_{12}/T) \qquad \text{(B3)}$$

and α values were kept constant.

UNIQUAC

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \qquad (B4)$$

$$g^E(\text{combinatorial})/RT = x_1 \ln\left(\frac{\phi_1}{x_1}\right) + x_2 \ln\left(\frac{\phi_2}{x_2}\right) + \frac{z}{2}\left[q_1x_1 \ln\left(\frac{\theta_1}{\phi_1}\right) + q_2x_2 \ln\left(\frac{\theta_2}{\phi_2}\right)\right] \qquad (B5)$$

$$g^E(\text{residual})/RT = -q_1x_1 \ln(\theta_{1'} + \theta_{2'}\delta_{21}) - q_2x_2 \ln(\theta_{2'} + \theta_{1'}\delta_{12}) \qquad (B6)$$

$$\phi_1 = x_1r_1/(x_1r_1 + x_2r_2)$$

$$\theta_1 = x_1q_1/(x_1q_1 + x_2q_2)$$

$$\theta_{1'} = x_1q_{1'}/(x_1q_{1'} + x_2q_{2'}) \qquad (B7)$$

$$\delta_{21} = \exp(-A_{21}/T) \qquad \delta_{12} = \exp(-A_{12}/T) \qquad (B8)$$

with $z = 10$.

For *n*-hexane

$r = 4.50 \qquad q = q' = 3.86$

For 2-methylpentane

$r = 4.50 \qquad q = q' = 3.85$

For *n*-heptane

$r = 5.17 \qquad q = q' = 4.40$

For ethylbenzene

$r = 4.50 \qquad q = q' = 3.51$

For *n*-octane

$r = 5.85 \qquad q = q' = 4.94$

Glossary

A_j	parameters of polynomial model
A_{ij}	parameters of UNIQUAC model (K)
B_{ij}	molar second virial coefficients (cm^3 mol^{-1})
C_{ij}	parameters of NRTL model (K)
g	Gibbs energy (J mol^{-1})
m	number of polynomial parameters A_j
N	total number of measurements, eqs 2, 6, and 7
N_l	number of measurements of liquid-phase compositions, eq 5
n	number of measurements of vapor-phase compositions
P	total vapor pressure (kPa)
R	gas constant (J K^{-1} mol^{-1})
r	pure component volume parameter
q,q'	pure component area parameter
S	objective function
T	temperature (K)
V_i	molar volume of component *i* (cm^3 mol^{-1})
x_i	liquid mole fraction of component *i*
y_i	vapor mole fraction of component *i*

Greek Letters

α	parameters of NRTL model
θ	area fraction of UNIQUAC model
Λ_{ij}	parameters of Wilson model
ρ	density of pure liquid or liquid mixture (g cm^{-3})
σ_e	experimental inaccuracy
σ	root of resulting variance
ϕ	segment fraction of UNIQUAC model

Superscripts

E	excess property
°	experimental value

Subscripts

1,2,*i*	molecular species

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Received for review July 16, 1990. Revised March 27, 1991. Accepted July 19, 1991.