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Excess Gibbs Energies and Excess Volumes of 1-Butanol–*n*-Hexane and 2-Methyl-1-propanol–*n*-Hexane Binary Systems

Charles Berro,* Marek Rogalski,[†] and André Péneloux

Laboratoire de Chimie-Physique, Faculté des Sciences de Luminy, 13288 Marseille Cedex 9, France

Isothermal vapor–liquid equilibrium data and excess volumes for 1-butanol and 2-methyl-1-propanol in *n*-hexane were measured. The vapor–liquid equilibrium data were reduced according to the maximum likelihood principle. The parameters of NRTL, Wilson, and UNIQUAC equations were calculated and reported.

Introduction

This study is a continuation of the research program on thermodynamic properties of aliphatic alcohol–alkane systems carried out in the laboratory.

This paper reports the results of measurements on vapor–liquid equilibria for the 2-methyl-1-propanol–*n*-hexane system at 332.53 K and for the 1-butanol–*n*-hexane system at 333.15 K. The excess volumes for both systems are reported, too, at 303.15 and 298.15 K for the former system and at 298.15 K for the latter one.

Materials

n-Hexane was "Lichrosolv" grade reagent from Merck. The starting material contained about 2 mol % of other hydrocarbons substantially affecting its density. This material was purified by three successive fractional distillations on an Oldershaw type, 60 real plates, column.

The 2-methyl-1-propanol and the 1-butanol were Merck products "pro analysis" 99% and 99.5%, respectively. The alcohols were purified by fractional distillations on the column described above.

Gas-chromatographic analysis failed to show any significant impurities. The densities of components are in good agreement with those indicated in the literature (Table I). It is the same for the vapor pressure of the components (Tables II and III).

Table I. Experimental Excess Volume Data

2-methyl-1-propanol (1)–*n*-hexane (2)				1-butanol (1)–*n*-hexane (2) at 298.15 K	
298.15 K		303.15 K			
$x_1°$	$v^{E°}$/(cm^3 mol^{-1})	$x_1°$	$v^{E°}$/(cm^3 mol^{-1})	$x_1°$	$v^{E°}$/(cm^3 mol^{-1})
0.0702	0.135	0.0714	0.163	0.0283	0.079
0.1196	0.193	0.0818	0.179	0.0340	0.080
0.1508	0.209	0.1265	0.220	0.0908	0.114
0.1692	0.214	0.1824	0.252	0.1405	0.130
0.1730	0.216	0.2362	0.269	0.1678	0.135
0.1995	0.231	0.2690	0.278	0.2578	0.133
0.2388	0.246	0.3037	0.278	0.3061	0.121
0.3022	0.237	0.3433	0.273	0.3485	0.108
0.4260	0.211	0.3764	0.266	0.4171	0.078
0.4419	0.213	0.4454	0.243	0.4864	0.047
0.5293	0.177	0.4462	0.241	0.5186	0.026
0.5648	0.152	0.5114	0.217	0.5505	0.019
0.5797	0.143	0.5720	0.184	0.5827	−0.002
0.6202	0.126	0.5996	0.172	0.6216	−0.012
0.6271	0.121	0.6363	0.148	0.6981	−0.034
0.6903	0.087	0.7022	0.107	0.7136	−0.039
0.7062	0.079	0.7349	0.093	0.7265	−0.041
0.8566	0.026	0.7921	0.069	0.7614	−0.042
0.9031	0.014	0.8241	0.053	0.8330	−0.050
		0.8440	0.043	0.8910	−0.041
		0.8514	0.039	0.9256	−0.030
		0.9044	0.022	0.9536	−0.020
		0.9697	0.007		
		0.9704	0.006		

	density at 298.15 K, g cm^3	
	exptl	lit. (*13*)
n-hexane	0.654 88	0.65482
1-butanol	0.805 78	0.8060
2-methyl-1-propanol	0.797 94	0.7978

Apparatus and Procedure

The vapor–liquid equilibrium data were determined by using the recirculating still and the technique described previously (*1*). The temperature of the equilibrium chamber was measured with a C.T.N. thermistor of 10 KΩ at 298.15 K in conjunction with an AOIP 139 Wheatstone bridge. The thermistor was calibrated in the apparatus by consecutive measurements of boiling points of several pure compounds for the pressures ranging from 5 to 100 kPa. The uncertainty of the temperature measurements resulting from this calibration was $\sigma_e(T) = 0.02$ K. The pressure was measured with a fused-quartz Bourdon tube for the range 0–130 kPa. The gauge was calibrated against a precision mercury manometer. The uncertainty of the pressure measurements was estimated to be $\sigma_e(P) = 0.009$ kPa.

Liquid and vapor compositions were determined by densimetric analysis. An Anton Paar DMA 60 densimeter with two DMA 601 M cells was used for density measurements. The measuring cells were thermoregulated to 0.01 K. The resulting uncertainty on the density measurements was $\sigma(\rho) = 0.00001$ g cm^{-3}.

Two methods were applied to sampling equilibrium liquid and condensate from the ebulliometer. In the case of the 2-methyl-1-propanol–*n*-hexane system, the samples of liquid and vapor condensate were withdrawn from the ebulliometer via a silicon rubber septum by using a gas-tight syringe. For the 1-butanol–*n*-hexane system a new, recently published (*2*) technique was used. Compositions of both phases were analyzed continuously in the flow system. The streams of liquid and vapor condensate were drawn from the ebulliometer by using a peristaltic pump and were returned to the apparatus after having been passed through the densimetric cells. Thus, measurements of equilibrium compositions were performed without disturbing the steady state established in the ebulliometer.

Experimental vapor–liquid equilibrium data are given in Tables II and III together with the vapor pressures of pure components and the values of activity coefficients calculated according to the expression

$$\gamma_i° = \frac{P°y_i°}{P_i^s x_i°}\exp\left[\frac{(v_i - B_{ii})(P_i^s - P°) + \delta_{12}(1 - y_i°)^2 P°}{RT}\right] \qquad (1)$$

$$i = 1, 2$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}$$

[†] Present address: Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

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Table II. Experimental Vapor-Liquid Equilibrium Data for the System 2-Methyl-1-propanol (1)-*n*-Hexane (2) at 332.53 K

x_1°	y_1°	P°/kPa	$\ln \gamma_1^\circ$	$\ln \gamma_2^\circ$
0.0000	0.0000	74.764[a]		
0.0204	0.0338	76.159	2.3408	0.0040
0.0364	0.0467	76.505	2.1387	0.0096
0.1124	0.0758	76.376	1.4400	0.0612
0.2303	0.0939	74.903	0.9159	0.1654
0.2922	0.1036	73.886	0.7619	0.2255
0.3562	0.1089	72.652	0.5968	0.2983
0.4346	0.1200	70.831	0.4692	0.3913
0.4816	0.1243	69.587	0.3840	0.4562
0.5142	0.1294	68.481	0.3427	0.5000
0.5508	0.1317	67.356	0.2752	0.5597
0.5818	0.1379	66.184	0.2489	0.6073
0.6268	0.1459	64.129	0.1994	0.6815
0.6673	0.1530	62.117	0.1527	0.7573
0.7383	0.1725	57.355	0.0924	0.8971
0.7413	0.1737	56.942	0.0882	0.9002
0.7680	0.1858	54.591	0.0782	0.9537
0.7875	0.1936	52.768	0.0606	0.9990
0.8031	0.2010	51.034	0.0455	1.0336
0.8577	0.2431	44.152	0.0262	1.1637
0.8778	0.2662	41.055	0.0217	1.2142
0.9002	0.2990	37.096	0.0123	1.2721
0.9273		31.679		
0.9693		21.366		
0.9904		15.309		
1.0000	1.0000	12.042[b]		

$B_{11} = -2642$ cm^3 mol^{-1}
$B_{22} = -1410$ cm^3 mol^{-1}
$B_{12} = -960$ cm^3 mol^{-1} ($k_{12} = 0.15$)

[a] Literature value: P_2^s/kPa = 74.792 (*14*). [b] Literature value: P_1^s/kPa = 12.068 (*9*).

Table III. Experimental Vapor-Liquid Equilibrium Data for the System 1-Butanol (1)-*n*-Hexane (2) at 332.53 K

x_1°	y_1°	P°/kPa	$\ln \gamma_1^\circ$	$\ln \gamma_2^\circ$
0.0000	0.0000	76.284[a]		
0.0088	0.0120	76.776	2.5505	0.0029
0.0164	0.0212	77.063	2.4998	0.0049
0.0312	0.0333	77.317	2.3102	0.0108
0.0563	0.0433	77.129	1.9791	0.0243
0.0978	0.0521	76.717	1.6057	0.0550
0.1291	0.0562	76.363	1.3988	0.0815
0.2151	0.0646	75.054	1.0098	0.1601
0.2937	0.0701	73.660	0.7612	0.2417
0.3160	0.0717	73.251	0.7050	0.2668
0.3597	0.0744	72.354	0.6001	0.3181
0.3905	0.0766	71.857	0.5401	0.3584
0.4251	0.0788	70.951	0.4710	0.4023
0.4742	0.0824	69.679	0.3883	0.4703
0.5114	0.0854	68.501	0.3316	0.5240
0.5628	0.0898	66.676	0.2592	0.6044
0.5928	0.0938	65.350	0.2309	0.6517
0.6017	0.0940	65.018	0.2131	0.6687
0.6238	0.0974	63.868	0.1948	0.7048
0.6668	0.1037	61.611	0.1550	0.7845
0.6911	0.1079	60.018	0.1330	0.8303
0.7257	0.1146	57.327	0.0989	0.8972
0.7810	0.1303	52.066	0.0584	1.0112
0.8378	0.1571	44.943	0.0293	1.1372
0.8785	0.1897	38.345	0.0128	1.2317
0.9125		31.623		
0.9639		18.789		
1.0000	1.0000	8.099[b]		

$B_{11} = -2364$ cm^3 mol^{-1}
$B_{22} = -1410$ cm^3 mol^{-1}
$B_{12} = -924$ cm^3 mol^{-1} ($k_{12} = 0.15$)

[a] Literature value: P_2^s/kPa = 76.357 (*14*). [b] Literature value: P_1^s/kPa = 8.051 (*11*).

The virial coefficients found by the method of Tsonopoulos (*3*) and used in the calculation of the liquid-phase activity coefficients are reported too.

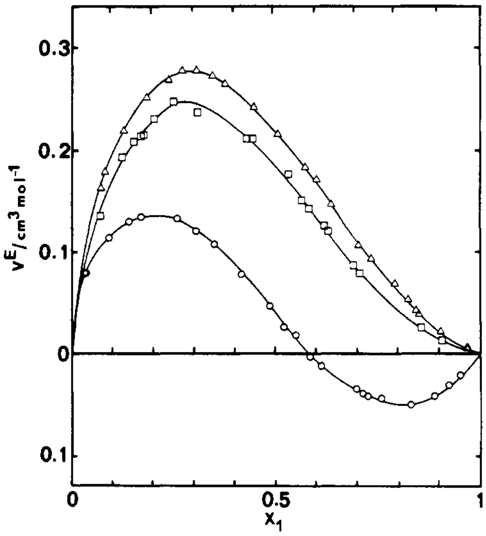

Figure 1. Plot of v^E as a function of composition for the system 2-methyl-1-propanol-*n*-hexane at 298.15 K (□) and 303.15 K (△) and for 1-butanol-*n*-hexane at 298.15 K (○).

T-P-x data only are given for alcohol mole fractions greater than 0.90 in the liquid phase. This is due to the fact that, in this concentration range, measurements of vapor-phase compositions were distorted by partial evaporation during the operations of sampling.

The same densimeters were used to determine the excess volumes of both systems studied. The excess volumes were calculated for the measured densities from mixtures of known composition prepared by weighing, using a special technique preventing the partial evaporation of samples. The experimental data are given in Table I together with the densities of pure components and are presented in Figure 1.

Treatment of the Excess Volume Data

Excess volume calculated from density data were correlated by using the equation proposed by Neau for alcohol-alkane binary systems (*4*):

$$v^E/x_1x_2 = \sum_{j=1}^{m} A_jY_j \tag{2}$$

where

$$Y_j = [x_1 - 1/(1 + Dx_1)]^{j-1}$$

and where x_1 denotes the mole fraction of alcohol.

It is observed that eq 2 fits the measured excess volume data better than commonly used polynomial expansions. The calculations were performed with the value $D = 35$.

The parameters A_j of eq 2 are given in Table IV with the values of the root mean square deviations of the excess volumes and densities:

$$\sigma(v^E) = \{\sum_{i=1}^{N} [v_i^{E\circ} - v^E(x_{1i}^\circ, A)]^2/(N - m)\}^{1/2} \tag{3}$$

where N is the number of experimental values denoted by superscript °. $\sigma(\rho)$ was calculated in a similar way.

Treatment of Vapor-Liquid Equilibrium Data

The reduction of measured vapor-liquid equilibrium data was performed by using the observed deviation method (*5-8*).

The excess Gibbs energy was represented with a Redlich-Kister polynomial:

$$g^E/(RTx_1x_2) = \sum_{j=1}^{m} A_jY_j \qquad Y_j = (2j - 1)(x_1 - x_2)^{j-1} \tag{4}$$

Table IV. Excess Volumes, Parameters of Eq 1, and Values of the Mean Square Deviation in ν^E and in ρ

	2-methyl-1-propanol (1)–*n*-hexane (2)		1-butanol (1)–*n*-hexane (2) at 298.15 K
	298.15 K	303.15 K	
$A_j \pm \sigma(A_j)/(\text{cm}^3\ \text{mol}^{-1})$	1.604 43 ± 0.013 98	1.829 00 ± 0.008 86	1.016 54 ± 0.012 32
	−2.177 78 ± 0.119 73	−2.653 20 ± 0.059 68	−2.131 15 ± 0.098 04
	0.445 64 ± 0.345 97	1.372 29 ± 0.164 46	0.925 21 ± 0.254 36
	0.155 04 ± 0.279 69	−0.466 32 ± 0.133 59	−2.735 42 ± 0.497 15
			4.882 38 ± 1.297 60
			−2.566 90 ± 0.859 16
$\sigma(\rho)/(\text{g cm}^{-3})$	0.00003	0.00001	0.00002
$\sigma(\nu^E)/(\text{cm}^3\ \text{mol}^{-1})$	0.004	0.002	0.002

Table V. Results of Vapor-Liquid Equilibrium Data Reduction

	2-methyl-1-propanol (1)–*n*-hexane (2)	1-butanol (1)–*n*-hexane (2)
$A_j \pm \sigma(A_j)$	1.667 38 ± 0.001 34	1.709 76 ± 0.000 77
	−0.087 10 ± 0.000 70	−0.106 58 ± 0.000 48
	0.048 01 ± 0.001 17	0.048 27 ± 0.000 76
	−0.024 91 ± 0.002 29	−0.024 07 ± 0.001 78
	0.007 16 ± 0.002 68	0.005 42 ± 0.001 78
	0.002 16 ± 0.004 63	−0.003 95 ± 0.003 03
	0.010 91 ± 0.002 04	0.012 67 ± 0.001 32
	−0.011 21 ± 0.003 22	−0.011 74 ± 0.002 03
$\sigma_e(\rho) \pm \sigma(\sigma_e(\rho))/(\text{g cm}^{-3})$	0.00010 ± 0.00001	0.00003 ± 0.00001
$\sigma_e(T) \pm \sigma(\sigma_e(T))/\text{K}$	0.015 ± 0.002	0.019 ± 0.004
$\sigma_e(P)/\text{kPa}$	0.009	0.009
WRMSD	1.07	1.47

where the degree of the polynomial, not fixed in advance, is chosen during the reduction as the lowest degree allowing one to avoid systematic deviations due to the model.

The parameters A_j in eq 4 and the experimental uncertainties on density $\sigma_e(\rho)$ and on the temperature $\sigma_e(T)$ were estimated according to the maximum likelihood principle. The experimental uncertainty on pressure was fixed to the value $\sigma_e(P)$ = 0.009 kPa according to the calibration of the manometer used.

The thermodynamic consistency of experimental results was checked by fitting the vapor-liquid equilibrium data to eq 4 for the appropriate number of parameters. The reduction was performed by minimizing an objective function S, the form of which is given in Appendix A. The weighting factors (expressions 3a and 4a) of the objective function S were calculated with the values of the experimental uncertainties estimated according to the maximum likelihood principle.

The weighted root mean square deviation (WRMSD) found in this way should be equal to 1 for perfectly consistent data; a value close to 2 would indicate that there are systematic errors of the same magnitude as random errors in measurements.

Results of vapor-liquid equilibrium data reduction are given in Table V together with the estimates of experimental uncertainties of density $\sigma_e(\rho)$ and temperature $\sigma_e(T)$.

The vapor-liquid equilibrium data were fitted to UNIQUAC, Wilson, and NRTL models; the corresponding expressions are given in Appendix B. The model parameters were estimated by minimizing the objective function S (expression 1a, Appendix A). They are reported in Table VI together with the values of the standard deviations for the pressure and the vapor composition calculated by using the following expressions:

$$100DP/P = 100\frac{1}{N}\sum_{i=1}^{N}|\Delta P_i|/P_i \tag{5}$$

$$100Dy = 100\frac{1}{N}\sum_{i=1}^{N}|\Delta y_{1i}| \tag{6}$$

In Table VII are reported the NRTL temperature-dependent parameters estimated from the vapor-liquid equilibrium data and heat of mixing data. H^E data used in the study of the 2-methyl-1-propanol–*n*-hexane system were measured by Brown et al. at 298.15 and 318.15 K (*9*); in the case of the 1-butanol–*n*-hexane system, data of Brown et al. at 298.15, 308.15, and 318.15 K (*10*) were used. The heat of mixing data were weighted assuming that experimental uncertainties are equal to $\sigma(H^E) = 0.015H^E$.

Conclusion

The magnitude and the symmetry of the excess Gibbs energy curves are very similar for both systems studied. Replacement of 1-butanol with 2-methyl-1-propanol decreases the excess Gibbs energy by 32 J mol^{-1} for $x_1 = 0.05$.

This difference strongly depends on temperature due to the substantially different values of the heats of mixing for both systems and diminishes at lower temperatures.

Sayegh and Ratcliff (*12*) studied the effect of branching of pentanol on the excess Gibbs energies of mixtures with *n*-hexane. They found that at 298.15 K this effect was small and practically negligible. Small differences in the values of the excess Gibbs energies contrast with important changes of the heats of mixingg due to a branching of an alcohol as is shown by the data of Brown et al. for 1-butanol–*n*-hexane (*10*) and 2-methyl-1-propanol–*n*-hexane (*9*). Important differences are also observed for the excess volumes. The excess volume for the system 1-butanol–*n*-hexane is small and S-shaped; the replacement of 1-butanol with 2-methyl-1-propanol leads to positive and substantially larger values.

Table VI. Parameters of the Most Usual Models Estimated from Vapor-Liquid Equilibrium Data

	2-methyl-1-propanol (1)–*n*-hexane (2)			1-butanol (1)–*n*-hexane (2)		
	parameters	100*DP*/*P*	100*Dy*	parameters	100*DP*/*P*	100*Dy*
NRTL	$C_{21} = 620.327$	0.47	0.20	$C_{21} = 660.383$	0.65	0.12
	$C_{12} = 322.442$			$C_{12} = 300.906$		
	$\alpha = 0.56594$			$\alpha = 0.52897$		
Wilson	$\Lambda_{12} = 0.149399$	0.63	0.21	$\Lambda_{12} = 0.117451$	0.43	0.10
	$\Lambda_{21} = 0.509805$			$\Lambda_{21} = 0.516085$		
UNIQUAC	$A_{21} = 1197.02$	0.92	0.23	$A_{21} = 1301.61$	0.40	0.08
	$A_{12} = -195.82$			$A_{12} = -196.58$		

Table VII. Temperature-Dependent NRTL Parameters Estimated from Vapor-Liquid Equilibrium and Heat of Mixing Data

	2-methyl-1-propanol (1)-*n*-hexane (2)	1-butanol (1)-*n*-hexane (2)
C_{21}	$764.880 - 2.4844(T - 273.15)$	$739.850 - 1.2368(T - 273.15)$
C_{12}	$345.960 - 0.4611(T - 273.15)$	$302.150 + 0.0540(T - 273.15)$
α	$0.54128 + 0.000357(T - 273.15)$	$0.51315 + 0.000340(T - 273.15)$
$100DP/P$	0.44	0.67
$100Dy$	0.19	0.12

Appendix A

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

$$S = \sum_{i=1}^{N} (a_i \Delta P_i + b_i \Delta y_{1i})^2 \qquad (1a)$$

where

$$\Delta P = P^\circ - P(x_1^\circ, A) \qquad \Delta y_1 = y_1^\circ - y_1(x_1^\circ, A) \qquad (2a)$$

$$a = -\overline{\delta P \delta y_1}/\sigma(P) D^{1/2} \qquad b = \sigma(P)/D^{1/2} \qquad (3a)$$

$$D = \sigma^2(P)\,\sigma^2(y_1) - \overline{\delta P \delta y_1}^2 \qquad (4a)$$

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:

$$\sigma^2(P) = \sigma_2{}^2(P) + (\partial P/\partial x_1)_T{}^2 (\partial x_1/\partial \rho)_T{}^2 \sigma_e{}^2(\rho) + (\partial P/\partial T)_{x_1}{}^2 \sigma_e{}^2(T) \qquad (5a)$$

$$\sigma^2(y_1) = [(\partial y_1/\partial \rho)_T{}^2 + (\partial y_1/\partial x_1)_T{}^2 (\partial x_1/\partial \rho)_T{}^2]\sigma_e{}^2(\rho) + (\partial y_1/\partial T)_{x_1}{}^2 \sigma_e{}^2(T) \qquad (6a)$$

$$\overline{\delta P \delta y_1} = (\partial P/\partial x_1)_T (\partial y_1/\partial x_1)(\partial x_1/\partial \rho)_T{}^2 \sigma_e{}^2(\rho) + (\partial P/\partial T)_{x_1} (\partial y_1/\partial T)_{x_1} \sigma_e{}^2(T) \qquad (7a)$$

The weighted root mean square deviation is

$$\mathrm{WRMSD} = [S/(N + n - m)]^{1/2} \qquad (8a)$$

Appendix B

The parameters given in Tables VI and VII were calculated for the following models:

NRTL

$$g^E/R = x_1 x_2 \left(\frac{\delta_{21} C_{21}}{x_1 + \delta_{21} x_2} + \frac{\delta_{12} C_{12}}{\delta_{12} x_1 + x_2} \right) \qquad (1b)$$

where

$$\delta_{21} = \exp(-\alpha C_{21}/T) \qquad \delta_{12} = \exp(-\alpha C_{12}/T) \qquad (2b)$$

UNIQUAC

$$g^E = g^E(\text{combinational}) + g^E(\text{residual}) \qquad (3b)$$

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln \frac{\theta_1}{\Phi_1} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2} \right) \qquad (4b)$$

$$\frac{g^E(\text{residual})}{RT} = -q_1 x_1 \ln (\theta_1' + \theta_2' \delta_{21}) - q_2 x_2 \ln (\theta_2' + \theta_1' \delta_{12}) \qquad (5b)$$

where

$$\Phi_1 = x_1 r_1/(x_1 r_1 + x_2 r_2)$$

$$\theta_1 = x_1 q_1/(x_1 q_1 + x_2 q_2) \qquad (6b)$$

$$\theta_1' = x_1 q_1'/(x_1 q_1' + x_2 q_2')$$

$$\ln \delta_{21} = -A_{21}/T \qquad \ln \delta_{12} = -A_{12}/T \qquad (7b)$$

with $z = 10$. For *n*-hexane

$$r = 4.5 \qquad q = q' = 3.86$$

For 1-butanol and 2-methyl-1-propanol

$$r = 3.45 \qquad q = 3.05 \qquad q' = 0.88 \qquad (8b)$$

Wilson

$$g^E/RT = -x_1 \ln (x_1 + \Lambda_{12} x_2) - x_2 \ln (x_2 + \Lambda_{21} x_1) \qquad (9b)$$

Glossary

A_i	parameters of polynomial model
A_{ij}	parameters of UNIQUAC model
B_{ij}	second virial coefficients
C_{ij}	parameters of NRTL model
H^E	excess enthalpy
k_{12}	characteristic binary constant used in the calculation of the second virial cross-coefficient
m	number of polynomial parameters A_i
N	total number of measurements
n	number of measurements of vapor-phase compositions
P	total vapor pressure
P_i^s	saturated vapor pressure of pure component i
S	objective function
T	temperature
v_i	molar volume of component i
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i

Greek Letters

α	parameter of NRTL model
γ_i	activity coefficient of component i
Λ_{ij}	parameters of Wilson model
ρ	density of a pure liquid or liquid mixture
σ_e	experimental uncertainty
σ	root of resulting variance

Superscripts

E	excess property
$\circ$	experimental measured value

Subscripts

1, 2	molecular species (1 normally refers to alcohol, and 2 to alkane)

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