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THERMODYNAMICS OF MIXTURES OF *N*-METHYLPYRROLIDONE WITH HYDROCARBONS AND THEIR HYDROXYL DERIVATIVES

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ABSTRACT

The total pressure data for mixtures of *N*-methylpyrrolidone + hexane, + dodecane, + cyclohexane, + methylcyclohexane, + benzene, + toluene, + propylbenzene, + buthylbenzene, + propanol-1, + hexanol-1, + 4-methylphenol and + 2,4-dimethylphenol are correlated by means of NRTL and UNIQUAC equations. The NRTL equation is found to be more suitable for these systems. Modifications of NRTL equation making allowance for the solvation and association effects are proposed for accurate description of mixtures containing hydroxyl compounds. Better results are obtained with the model considering association only and so the modified NRTL equation is able to describe the excess Gibbs energy with the accuracy achieved in measurements. An attempt to obtain a consistent set of UNIFAC parameters for different mixtures containing *N*-methylpyrrolidone has given unsatisfactory results.

INTRODUCTION

The purpose of the present paper is to find a thermodynamic model suitable to represent, with an accuracy similar to that achieved experimentally, the thermodynamic properties of binary mixtures formed by *N*-methylpyrrolidone (NMP) with aromatic, aliphatic, and naphthenic hydrocarbons or with hydroxyl derivatives of these compounds. Such a model should be suitable for use in computer programs for computation or optimization of azeotropic, extractive or normal distillation.

Present industry imposes very high requirements for the phase equilibrium data used for designing separation processes. This is especially important in the case of close boiling mixtures or deep purification. Distillation is not only a most popular separation process but also the most energy consuming, and its accurate design is necessary to save energy.

Reliable multicomponent vapour–liquid equilibria (VLE) data, in the form of correlating equations, can be directly used in computer programs modeling the separation processes. These programs enable the separation plants to be designed without pilot experiments. Instead of those, a much

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less expensive procedure, consisting of accurate measurements of VLE coupled with proper data reduction procedures, using the thermodynamic equations representing the VLE of the multicomponent systems under consideration, with the accuracy not less than that achieved in direct measurements can be used. Special effort should be made to establish equations suitable for representing thermodynamic properties of multicomponent systems with high accuracy.

APPLICATION OF UNIFAC METHOD

The results of VLE measurements in the investigated systems have been reported previously [1]. Due to its high versatility the UNIFAC method [2] was chosen for correlation. The parameters were computed by reduction of previously published isothermal data [1] by means of the specially modified UNIFAC parameter estimation program of Fredenslund et al. [2] and the 1982 parameter table [3].

The NMP molecule was treated in the computation in the following four different ways:

(1) The whole molecule of NMP was treated as one functional group. (Results are given in Table 1.)

(2) The NMP molecule was divided into three CH_2 groups, one CH_3 group and the N–C=O group. Only the interactions between this last group and other typical groups from the 1982 parameter table were computed. (Results are given in Table 2.)

(3) The NMP molecule was divided into three CH_2 groups and one CH_3–N–C=O group. (Results are given in Table 3.)

(4) The NMP molecule was divided into two CH_2 groups and the CH_3–N–C=O–CH_2 group. (Results are given in Table 4.)

TABLE 1

Values of UNIFAC group-interaction parameters $a_{m,n}$ computed from different systems (NMP treated as one group)

System	Computed parameters			
	a_{NMP,CH_2}	$a_{CH_2,NMP}$	$a_{NMP,OH}$	$a_{OH,NMP}$
NMP + hexane	128.206	197.174	–	–
NMP + dodecane	−69.117	292.306	–	–
NMP + cyclohexane	−81.139	356.252	–	–
NMP + methylcyclohexane	−163.6	477.78	–	–
NMP + propanol-1	39.741	258.105	258.604	−388.59
NMP + hexanol-1	231.303	517.795	155.506	−549.758
NMP + cyclohexanol	110.67	749.5	119.74	−449.63

TABLE 2

Values of UNIFAC group-interaction parameters $a_{m,n}$ computed from different systems (NMP represented as CH_2, CH_3 and N–C=O groups)

System	Computed parameters			
	$a_{N-C=O,CH_2}$	$a_{CH_2,N-C=O}$	$a_{N-C=O,OH}$	$a_{OH,N-C=O}$
NMP + dodecane	5237.333	1497.401	–	–
NMP + cyclohexane	3273.000	1633.301	–	–
NMP + propanol-1	−120.820	849.035	−395.439	−220.637
NMP + cyclohexanol	33.508	809.053	−485.872	757.690

In all computations the difference between measured and calculated total pressures was used as the objective function. To characterize the results the r.m.s. deviations of pressure residuals, $D(\mathrm{P})$, were computed according to the formula:

$$D(\mathrm{P}) = 100\sqrt{\frac{\sum_{i=1}^{n}\left(\frac{P_{\mathrm{exp}_i} - P_{\mathrm{cal}_i}}{P_{\mathrm{exp}_i}}\right)^2}{n-k}} \tag{1}$$

where n is the number of experimental points, k the number of adjustable parameters, P_{exp_i} the measured total pressure and P_{cal_i} the calculated total pressure, both for the point i. The fitting accuracy was similar in all four cases, and the $D(\mathrm{P})$ values for different systems vary from 1 to 2%.

The comparison of results shows that the smallest dependence of the computed values of interaction parameters between the same group pairs from the investigated systems were obtained in the case when the whole NMP molecule was treated as a functional group (Table 1).

However in this case too, the interaction parameters NMP/CH_2 calculated from the systems with hydrocarbons and for the systems with alcohols differ considerably.

TABLE 3

Values of UNIFAC group-interaction parameters $a_{m,n}$ computed from different systems (NMP represented as CH_2 and CH_3–N–C=O groups)

System	Computed parameters			
	$a_{CH_3-N-C=O,CH_2}$	$a_{CH_2,CH_3-N-C=O}$	$a_{CH_3-N-C=O,OH}$	$a_{OH,CH_3-N-C=O}$
NMP + dodecane	42.992	622.222	–	–
NMP + cyclohexane	−43.232	537.493	–	–
NMP + propanol-1	−19.432	201.529	−43.059	−356.905
NMP + cyclohexanol	344.423	117.513	−157.216	183.664

TABLE 4

Values of UNIFAC group-interaction parameters $a_{m,n}$ computed from different systems (NMP represented as CH_2 and CH_3-N-C=O-CH_2 groups)

System	Computed parameters			
	$a_{CH_3-N-C=O-CH_2,CH_2}$	$a_{CH_2,CH_3-N-C=O-CH_2}$	$a_{CH_3-N-C=O-CH_2,OH}$	$a_{OH,CH_3-N-C=O-CH_2}$
NMP + dodecane	−38.788	458.712	–	–
NMP + cyclohexane	72.697	706.338	–	–
NMP + propanol-1	3951.998	−36655.4	33.348	−8092.367
NMP + cyclohexanol	64.553	108.362	−57.645	141.145

TABLE 5

Computed values of NRTL and UNIQUAC equation parameters and relative r.m.s. deviation of objective function (eqn. (1))

System	T (K)	NRTL				UNIQUAC		
		$g_{12} - g_{22}$ [a]	$g_{21} - g_{11}$ [a]	α	D(P)	$g_{12} - g_{22}$ [a]	$g_{21} - g_{11}$ [a]	D(P)
NMP + hexane	333.15	5039.80	5803.50	0.44	0.42	−25.56	2139.53	2.67
	343.15	5656.52	6028.01	0.45	0.73	112.09	2019.78	2.85
NMP + dodecane	393.15	6233.32	1366.12	0.23	0.60	−114.43	1903.34	0.61
NMP + cyclohexane	333.15	−2746.59	9567.13	0.12	0.67	−657.06	2838.80	0.81
	353.15	−3787.90	10793.88	0.11	0.76	−770.48	2960.77	0.96
NMP + methylcyclohexane	353.15	−3580.67	10685.48	0.10	0.99	−936.04	3273.98	1.17
	373.15	−4114.17	11210.90	0.10	0.88	−999.68	3294.36	0.91
NMP + benzene	333.15	−5777.89	8897.07	0.20	0.99	−2638.43	5085.90	1.70
	353.15	−6201.86	9770.64	0.20	0.92	−2711.27	5205.15	2.30
NMP + toluene	363.15	−6197.13	10999.53	0.18	0.89	−2392.70	4416.88	1.60
	383.15	−5568.15	9518.60	0.20	0.93	−2478.06	4614.66	1.41
NMP + propylbenzene	353.15	−946.04	3929.19	0.20	0.44	−1336.70	2601.44	0.71
	373.15	−2356.51	5645.43	0.20	0.78	−1440.51	2789.18	0.82
NMP + butylbenzene	353.15	251.17	3243.94	0.20	1.70	−1136.04	2560.65	2.10
	373.15	−840.23	4113.04	0.20	0.68	−1350.22	2778.43	0.71
NMP + propanol-1	353.15	−6511.98	−5585.89	−0.78	1.30	−369.49	−978.64	2.90
NMP + hexanol-1	353.15	7698.06	−5909.57	0.20	2.92	6762.81	−3280.51	3.37
	393.15	11256.13	−7772.28	0.20	0.77	9080.24	−3831.21	2.67
NMP + cyclohexanol	393.15	−3636.11	2849.43	0.30	0.54	6818.41	−3485.86	2.20
NMP + 4-methylphenol	393.15	−15609.04	3606.98	0.07	4.60	−3615.94	537.10	5.55
NMP + 2,4-dimethylphenol	393.15	−10690.71	−1273.07	0.07	3.09	−3184.92	646.97	3.40

[a] J mol^{-1}.

This leads to the conclusion that the UNIFAC method can be used only to correlate already available experimental results and is unable to predict with reasonable accuracy the VLE in the mixtures containing NMP.

APPLICATION OF LOCAL COMPOSITION MODELS

For correlation of the measured VLE data the Redlich–Kister, NRTL and UNIQUAC equations were used. The Redlich–Kister equation was chosen as a flexible and versatile polynomial type equation. The results of this correlation have been reported previously [1]. NRTL and UNIQUAC are equations suitable for representing both liquid–liquid and vapour–liquid equilibria. Among the systems investigated, those with aliphatic and naphthenic hydrocarbons exhibit immiscibility gaps and those with hydroxyl derivatives represent negative deviations.

The computed values of equation parameters together with the r.m.s. deviations of pressure (D(P)) calculated according to formula (1) are given in Table 5. The analysis of the D(P) values shows that the poorest correlation results were obtained with the UNIQUAC equation. In addition, UNIQUAC predicts two liquid phases for the system with hexane at 333.15 and 343.15 K at which temperatures the system is homogeneous. The Redlich–Kister and NRTL equations show better performance. The correlation leads to homogeneous systems for the NMP + hexane. The disadvantage of Redlich–Kister is its inability to predict multicomponent mixtures. The advantage of the NRTL equation obtainable is the ability to represent properties of dilute solutions due to the possibility of adjustment of its α constant.

The results obtained by means of the NRTL equation although better than for other equations cannot be considered satisfactory. The biggest deviations of the objective function were obtained for systems containing hydroxyl compounds (alcohols and phenols). The description of all other systems is considerably better and the correlation accuracy is of the same order of magnitude as the accuracy of measurement.

MODIFICATIONS OF THE NRTL EQUATION

The good results obtained by means of the NRTL equation for correlation of the NMP–hydrocarbon systems prove that this equation can describe properly not only the interactions between NMP and a hydrocarbon but also the self association of NMP.

The modifications introduced into the NRTL equation were carried in a manner which enabled the description of the solvation and association of

hydroxyl compounds. For this purpose the model of ideal association of the Mecke–Kempter type as introduced by Treszczanowicz [4] was used.

In this model the activity coefficients of the associating component (component 1) are described by the equation

$$\ln \gamma_1 = (\ln \gamma_1)_{K_A = K_B = 0} + \ln\left(\frac{x_A}{x_A^o}\right) \tag{2}$$

and the activity coefficient of the non-associating component (component 2) by the equation

$$\ln \gamma_2 = (\ln \gamma_2)_{K_A = K_B = 0} + \ln x_B \tag{3}$$

where $(\ln \gamma_i)_{K_A = K_B = 0}$ represents the activity coefficient of component i in the liquid phase when association or solvation do not occur. The hypothetical mole fraction of the associated component x_A and of the solvated component x_B are calculated according to the formulae

$$x_A = \frac{-x_1 + 2K_A x_1 + K_B x_2 + \sqrt{(x_1 - K_B x_2)^2 + 4K_A K_B x_1 x_2}}{2x_1 K_A (K_A - 1)} \tag{4}$$

$$x_A^o = \frac{1}{K_A - 1} \tag{5}$$

$$x_B = \frac{1 - (1 + K_A)x_A}{1 + (K_B - K_A)x_A} \tag{6}$$

where x_1 is the mole fraction of the associating component and x_2 the mole fraction of the non-associating component.

The activity coefficients of the associating component (hydroxyl derivative) $(\ln \gamma_1)_{K_A = K_B = 0}$ (eqn. (2)) and non-associating component $(\ln \gamma_2)_{K_A = K_B = 0}$ (eqn. (3)) are calculated from the NRTL equation. On this assumption the following equation for the activity coefficient of the associating component is obtained.

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_2 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} \right] + \ln\left(\frac{x_A}{x_A^o}\right) \tag{7}$$

and for the non-associating component (NMP)

$$\ln \gamma_2 = x_1^2 \left[\frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} \right] + \ln x_B \tag{8}$$

where

$$G_{ij} = \exp(-\alpha \tau_{ij}) \tag{9}$$

TABLE 6

Computed constants of NRTLSOL and NRTLMK equation constants and relative r.m.s. deviations of objective function (eqn. (1)) (for NRTL D(P) values for constants are given in Table 5)

System	T (K)	NRTLSOL			NRTLMK		NRTL
		K_A	K_B	D(P)	K	D(P)	D(P)
NMP + propanol-1	353.15	1552.85	−1.5878	1.17	−0.1048	1.00	1.30
NMP + hexanol-1	353.15	11010.29	−16.5400	2.31	−0.3186	1.38	2.92
	393.15	986.68	−2.5231	0.53	−0.1129	0.48	0.77
NMP + cyclohexanol	393.15	568.05	−1.8188	0.52	−0.0905	0.48	0.54
NMP + 4-methylphenol	393.15	7814.43	−12.5667	3.24	−0.2189	2.36	4.60
NMP + 2,4-dimethylphenol	393.15	368.43	−0.9376	3.02	0.1892	2.65	3.11

and

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT} \tag{10}$$

α and $(g_{ij} - g_{jj})$ are adjustable parameters. Equations (2) and (3) introduced in this way possess two more adjustable parameters (K_A and K_B) than the previously used original NRTL equation. As the solvation reaction has been introduced into this equation the name NRTLSOL is used to identify this modification. Results of correlations by means of the NRTLSOL equation are given in Table 6. It is hard to give any physical meaning to these results. The improvement of the total pressure residuals and its r.m.s. deviations is only marginal. The values obtained for K_A of the association reaction are large positive numbers, while K_B (constant of the solvation reaction) values are small and negative. This leads to the conclusion that the influence of association of the hydroxyl derivative on the correlation results is much bigger than that of solvation. The NRTL equation itself gives a good description not only of the association of NMP but also of the solvation of NMP with hydroxyl derivatives. This conclusion is confirmed by the satisfactory description by the NRTL equation of the systems with hexanol-1 and with cyclohexanol at temperatures as high as 393 K (when the association of hydroxyl compound should not be important) while the same description of this system at 353 K is poor. The value of K_A computed at this temperature is high.

This result leads to the conclusion that for a proper description the NRTL equation, with an additional term describing the association of hydroxyl compounds, should be satisfactory.

For this purpose a grouping of the NRTL equation and the Mecke–Kempter equation [5] is proposed. This equation makes allowance only for the association of hydroxyl compounds, K being the constants of the association reaction.

The equation bears the following form for the activity coefficient of the associating component

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} \right] + \frac{1+K}{K} \ln\left(\frac{1+K}{1+KZ_A} \right) - Z_B \tag{11}$$

and for the activity coefficient of the non-associating components

$$\ln \gamma_2 = x_1^2 \left[\frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} \right] - \frac{r_{21}}{K} \ln(1 + KZ_A) + r_{21} Z_A \tag{12}$$

where

$$r_{ij} = \frac{V_i^1}{V_j^1} \tag{13}$$

$$Z_A = \frac{r_{21}}{x_1 + r_{21} x_2} \tag{14}$$

and

$$Z_B = \frac{r_{21} x_2}{x_1 + r_{21} x_2} \tag{15}$$

V_i^1 being the molar volume of pure liquid 1, and Z the volume fractions.

This modification called NRTLMK has only one adjustable constant more than the NRTL equation. The results of the correlation are significantly better than with the NRTL and NRTLSOL equations. Constant K, due to the values obtained, can be regarded only as an adjustable parameter. It has no physical meaning but the good results of correlation justified such a modification of the NRTL equation.

CONCLUSIONS

For the systems under consideration the UNIFAC method cannot be used as a procedure for predicting their thermodynamic properties with an accuracy similar to that achieved experimentally. The parameters obtained for the same pairs of groups differed considerably when computed from different systems, and it was impossible to find reasonable mean values for them. The results of correlation by means of UNIQUAC, NRTL and Redlich–Kister equations were not satisfactory for systems with associating hydroxyl compounds.

The best results for correlation similar to experimental accuracy for all systems with NMP were obtained by means of the NRTLMK equation. This

equation has four adjustable parameters for systems with hydroxyl compounds, while for all other systems this is reduced to three parameters and the NRTL equation. The equation, due to its mathematical form, is suitable for representing the VLE in systems containing NMP or speaking more generally, for the systems containing components which associate and coassociate.

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