1446 *J. Chem. Eng. Data* **2002,** *47,* 1446−1452

Densities, Excess Molar Volumes, and Excess Molar Enthalpies of (*N*-Methyl-2-pyrrolidinone + Ketone) at T = 298.15 K

Urszula Domańska* and Joanna Łachwa

Warsaw University of Technology, Faculty of Chemistry, Physical Chemistry Division,
Noakowskiego 3, 00-664 Warsaw, Poland

Trevor M. Letcher

University of Natal, Department of Chemistry and Applied Chemistry, Durban 4041, South Africa

The densities have been measured at 298.15 K and atmospheric pressure for nine binary mixtures of *N*-methyl-2-pyrrolidinone with + 2-propanone or + 2-butanone or + 2-pentanone or + 3-pentanone or + cyclopentanone or + 2-hexanone or + 4-methyl-2-pentanone or + 4-heptanone or + 5-nonanone using a vibrating-tube densimeter. The excess molar volumes have been calculated from measured values of densities. The excess molar enthalpies have been measured at 298.15 K and atmospheric pressure for two mixtures of *N*-methyl-2-pyrrolidinone + 4-heptanone or + 5-nonanone using flow calorimetry. The experimental results have been correlated and compared with the results from the Flory−Benson−Treszczanowicz (FBT) theory and from the extended real associated solution (ERAS) theory. The results are discussed in terms of the intermolecular association.

Introduction

Continuing research into the thermodynamic excess functions and the thermodynamics of phase equilibria of mixtures containing *N*-methyl-2-pyrrolidinone (NMP),[1−19] we present here excess molar volumes and excess molar enthalpies for (NMP + ketone). The compound NMP is a heterocyclic, polar solvent used for the extraction of low molecular weight aromatic compounds from petroleum feedstock.[20] The knowledge of the excess molar properties of a solvent in some organic liquids is useful in predicting the solution behavior in other organic liquids.[21]

In this paper we report excess volumes V_m^E and excess enthalpies H_m^E of the NMP with some ketones. The Flory−Benson−Treszczanowicz (FBT) theory[22,23] and the extended real associated solution (ERAS)[24,25] theory were used to correlate the experimental data. The FBT model has been applied to describe simultaneously V_m^E and H_m^E of mixtures containing only one self-associating component (NMP). The cross-association constant in the mixture was assumed to be equal to zero.

Experimental Section

Herein are reported the Chemical Abstracts Service registry numbers and the sources of the chemicals: *N*-methyl-2-pyrrolidinone (872-50-4, Aldrich), 2-propanone (67-64-1, POCH), 2-butanone (78-93-3, Aldrich), 2-pentanone (107-87-9, Aldrich), 3-pentanone (96-22-0, Aldrich), cyclopentanone (120-92-3, PROLABO), 2-hexanone (591-78-6, Aldrich), 4-methyl-2-pentanone (108-10-1, Merck), 4-heptanone (123-19-3, Janssen Chimica, 98%), and 5-nonanone (502-56-7, Janssen Chimica). The chemicals were dried over type 0.4-nm molecular sieves (SERVA, Heidelberg, F.R.G.) and purified by fractional distillation. After the distillation all compounds were checked by GLC analysis and no significant impurities (less than 0.003 mass %) were found. Analysis using the Karl-Fisher technique showed that the impurity in each of the solvents was less than 0.02 mol %. The density of the compounds were measured as a test of purity.

Table 1. Physical Constants of Pure Compounds at T = 298.15 K: d, Density; V_{mol}, Molar Volume; α, Cubic Expansion Coefficient; κ_T, Isothermal Compressibility

	d^{exp}	d^{lit}	V_{mol}	$\alpha \times 10^4$	$\kappa_T \times 10^4$
component	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	K^{-1}	MPa^{-1}
N-methyl-2-pyrrolidinone	1.02851	1.02804[a]	96.43[a]	8.37[a]	8.42[b]
2-propanone	0.78510	0.78547[c]	74.05[d]	14.6[d]	13.30[d]
2-butanone	0.80085	0.79992[e]	90.16[f]	13.1[f]	11.52[f]
2-pentanone	0.80191	0.80145[g]	107.47[g]	10.2[g]	10.82[g]
3-pentanone	0.80994	0.80945[c]	106.41[h]	12.0[h]	10.73[h]
cyclopentanone	0.95712	*i*	*i*	*i*	*i*
2-hexanone	0.80697	0.80698[g]	124.12[g]	11.1[g]	9.97[g]
4-methyl-2-pentanone	0.79612	0.79625[g]	125.79[g]	11.4[g]	11.00[g]
4-heptanone	0.81106	*i*	140.79	10.5[j]	9.32[j]
5-nonanone	0.81739	*i*	174.02	9.5[j]	8.38[j]

[a] From ref 3. [b] From ref 7. [c] From ref 27. [d] From ref 28. [e] From ref 29. [f] From ref 30. [g] From ref 31. [h] From ref 32. [i] Not found. [j] Extrapolated from values of other ketones C_3−C_6.

An Anton Paar DMA 602 vibrating-tube densimeter thermostated at T = (298.15 ± 0.01) K was used to determine the densities. The densimeter's calibration was performed at atmospheric pressure using doubly distilled and degassed water, specially purified benzene (CHEMIPAN, Poland, 0.999), and dried air. The vibrating-tube temperature was measured by an Anton Paar DM 100-30 digital thermometer and was regulated to within better than ±0.01 K. The temperature was stabilized using a UNIPAN 60 thermostat and 202 temperature control system (UNIPAN, Poland). Mixtures were prepared by

---

* To whom correspondence should be addressed. E-mail: Ula@ch.pw.edu.pl.

10.1021/je020068p CCC: $22.00

Table 2. Experimental Excess Molar Volumes V_m^E for {*x* NMP + (1−*x*) RCOR′} Systems at 298.15 K

x	V_m^E / $cm^3 \cdot mol^{-1}$	$\delta V_m^E \times 10^{-3}$ / $cm^3 \cdot mol^{-1}$	x	V_m^E / $cm^3 \cdot mol^{-1}$	$\delta V_m^E \times 10^{-3}$ / $cm^3 \cdot mol^{-1}$	x	V_m^E / $cm^3 \cdot mol^{-1}$	$\delta V_m^E \times 10^{-3}$ / $cm^3 \cdot mol^{-1}$
x NMP + (1−*x*) 2-Propanone								
0.0239	−0.097	−5	0.4480	−0.738	−2	0.7108	−0.527	−6
0.1176	−0.386	−1	0.4882	−0.719	5	0.7730	−0.426	5
0.1832	−0.532	−1	0.5323	−0.706	−5	0.8804	−0.243	2
0.2536	−0.636	4	0.5791	−0.661	7	0.9118	−0.186	−1
0.3553	−0.724	−1	0.6310	−0.623	−5			
x NMP + (1−*x*) 2-Butanone								
0.0104	−0.034	−6	0.2653	−0.514	−7	0.7898	−0.366	−8
0.0193	−0.053	0	0.3474	−0.572	3	0.8553	−0.267	−7
0.0861	−0.222	−5	0.4669	−0.599	6	0.8963	−0.190	3
0.1564	−0.356	−1	0.5740	−0.563	10	0.9896	−0.016	5
0.2201	−0.455	−2	0.6959	−0.476	−3			
x NMP + (1−*x*) 2-Pentanone								
0.0740	−0.177	−3	0.4124	−0.570	−3	0.7483	−0.400	5
0.1141	−0.245	9	0.4756	−0.570	5	0.8339	−0.291	0
0.2034	−0.399	0	0.5382	−0.564	0	0.9067	−0.174	0
0.2394	−0.452	−8	0.6213	−0.528	−6	0.9631	−0.068	4
0.3338	−0.526	5	0.6799	−0.480	−4			
x NMP + (1−*x*) 3-Pentanone								
0.1497	−0.238	6	0.6212	−0.456	6	0.9169	−0.142	−7
0.2798	−0.401	−4	0.7495	−0.357	0	0.9735	−0.053	−9
0.4524	−0.497	−3	0.7567	−0.346	3			
0.5322	−0.497	−3	0.8481	−0.235	1			
x NMP + (1−*x*) Cyclopentanone								
0.0340	−0.0162	0	0.4752	−0.0993	1	0.8281	−0.0474	−1
0.1086	−0.0470	0	0.5088	−0.0961	2	0.8656	−0.0375	−1
0.2353	−0.0778	4	0.5643	−0.0890	5	0.9234	−0.0232	−2
0.2968	−0.0978	−6	0.6922	−0.0718	3	0.9460	−0.0172	−2
0.3628	−0.1012	−3	0.7899	−0.0601	−5	0.9887	−0.0022	1
x NMP + (1−*x*) 2-Hexanone								
0.1977	−0.299	10	0.5222	−0.465	0	0.8318	−0.250	0
0.3143	−0.417	−4	0.5916	−0.451	−5	0.8927	−0.171	−1
0.3615	−0.447	−7	0.6663	−0.402	5	0.9740	−0.049	−5
0.4813	−0.466	2	0.7560	−0.330	3			
x NMP + (1−*x*) 4-Methyl-2-pentanone								
0.0231	−0.055	9	0.3232	−0.601	−4	0.7175	−0.519	2
0.0892	−0.228	2	0.4381	−0.662	−1	0.7595	−0.465	2
0.1450	−0.350	−3	0.4862	−0.664	1	0.8260	−0.370	−7
0.2022	−0.443	5	0.5597	−0.645	4			
0.2655	−0.541	−4	0.6546	−0.587	0			
x NMP + (1−*x*) 4-Heptanone								
0.1989	−0.246	3	0.5755	−0.378	4	0.8288	−0.225	−3
0.2961	−0.326	0	0.5789	−0.377	4	0.9001	−0.149	−8
0.3849	−0.379	−9	0.6117	−0.370	1	0.9233	−0.116	−5
0.4588	−0.393	−5	0.6772	−0.340	2			
0.5060	−0.389	2	0.7511	−0.286	6			
x NMP + (1−*x*) 5-Nonanone								
0.2348	−0.140	6	0.5276	−0.221	−6	0.7037	−0.182	3
0.3643	−0.189	4	0.5404	−0.220	−6	0.7795	−0.149	6
0.4331	−0.207	1	0.5814	−0.216	−4	0.8931	−0.087	1
0.4729	−0.213	−1	0.6591	−0.200	−2	0.9475	−0.035	11

mass, the error in mole fraction being estimated as less than 5×10^{-5}. The method of determining excess molar volumes has been described elsewhere.[26] The densities, d, of the pure liquids determined here were compared to the literature values in Table 1. The estimated standard uncertainty, u_i, in the excess molar volume V_m^E is less than ±0.005.

A Thermometric 2277 thermal activity monitor in flow mode, driven by two LKB peristaltic pumps, was used to determine H_m^E at $T = 298.15$ K. The temperature was accurate to within ±0.01 K and was monitored by a calibrated quartz thermometer fixed in the cell compartment. The experimental procedure has been detailed previously.[33] The estimated error in the excess enthalpy H_m^E and mole fraction x is less than ±2% and ±0.1%, respectively. The accuracy of the method was verified with a test on (hexane + cyclohexane).[34] The experimental results agreed with the literature data to within ±5 J (2%) in the worst case.

Excess Molar Functions

The V_m^E values are given in Table 2 and H_m^E values are given in Table 3, together with the deviations δV_m^E and δH_m^E, respectively, calculated from the smoothing equation

$$\delta Z_m^E = Z_m^E - x(1 - x)\sum_{r=0}^{r=3} X_r(2x - 1)^r \qquad (1)$$

where x is the mole fraction of the NMP and Z_m^E is either $V_m^E/(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ or $H_m^E/(\mathrm{J \cdot mol^{-1}})$. The values of the pa-

Table 3. Experimental Excess Molar Entalpies H_m^E for {x NMP + (1−x) RCOR′} Systems at 298.15 K

x	H_m^E / J·mol^{-1}	δH_m^E / J·mol^{-1}	x	H_m^E / J·mol^{-1}	δH_m^E / J·mol^{-1}	x	H_m^E / J·mol^{-1}	δH_m^E / J·mol^{-1}
			x NMP + (1−x) 4-Heptanone					
0.3064	184.0	−1.7	0.4912	225.2	−1.1	0.6728	176.7	−8.8
0.3568	205.4	0.7	0.5865	213.9	−0.5	0.7144	168.9	0.5
0.4217	223.1	2.5	0.6192	206.5	1.1	0.8727	74.4	0.3
			x NMP + (1−x) 5-Nonanone					
0.2365	179.0	3.0	0.4086	306.3	−3.9	0.7544	358.3	5.4
0.2638	202.3	3.5	0.4906	356.5	−1.2	0.8089	309.8	0.2
0.3400	262.0	1.6	0.6545	386.1	−4.1			
0.3719	281.4	−3.1	0.7027	379.9	1.3			

Table 4. Coefficients, X_r, for Eq 1 and Standard Deviation, σ, Calculated According to Eq 2, A_r, for the Excess Molar Volume and B_r for the Excess Molar Enthalpy for {x NMP + (1−x) RCOR′} Systems at 298.15 K

system	A_0	A_1	A_2	$\sigma \times 10^3$ / cm^3·mol^{-1}
NMP +				
2-propanone	−2.876	0.904	−0.244	5
2-butanone	−2.404	0.423		6
2-pentanone	−2.291	0.287		5
3-pentanone	−1.990	0.059	0.235	6
cyclopentanone	−0.395	0.109		3
2-hexanone	−1.871	0.127		5
4-methyl-2-pentanone	−2.659	0.200		5
4-heptanone	−1.564			5
5-nonanone	−0.857	−0.080		6

system	B_0	B_1	B_2	σ / J·mol^{-1}
NMP +				
4-heptanone	904.4	−56.8	−351.5	2.4
5-nonanone	1448.0	898.3		3.5

rameters X_r refer to volumes (A_r) or enthalpies (B_r) and have been determined using a method of least-squares. The parameters are given in Table 4 for V_m^E and H_m^E together with the standard deviations σ

$$\sigma = \{\sum_{i=1}^{n}(Z_{m,expt}^E - Z_{m,calc}^E)_i^2/(n-k)\}^{1/2} \qquad (2)$$

where n is the number of experimental points and k is the number of coefficients.

The V_m^E is negative for all the mixtures over the entire composition range. This could be due to the packing effect and the association between NMP and the ketone. The minimum of V_m^E occurs over the mole fraction range $0.4 < x < 0.5$. The excess molar volume data increases in the following order: 2-propanone < 4-methyl-pentanone < 2-butanone < 2-pentanone < 3-pentanone < 2-hexanone < 4-heptanone < 5-nonanone < cyclopentanone. The largest negative V_m^E results were observed for the (NMP + 2-propanone). The minimum of the experimental curve is skewed toward the low concentrations of NMP. The V_m^E (min) value was −0.736 cm^3·mol^{-1} for $x = 0.4239$. The V_m^E (at $x = 0.5$) data increases with increasing the normal ketone chain length (see Figure 1).

The comparison of the excess molar volumes for the mixtures of NMP with three different isomers of pentanone (see Figure 2) has shown that the better packing effect and the association effects A−B are stronger for a nonsymmetrical chain ketone (2-pentanone) compared with those of a symmetrical chain (3-pentanone). The V_m^E (0.5) value was −0.573 cm^3·mol^{-1} and −0.498 cm^3·mol^{-1} for 2-pentanone and 3-pentanone, respectively. The smallest V_m^E results were observed for the (NMP + cyclopentanone) system. The minimum of the V_m^E curve was −0.101 cm^3·mol^{-1} for $x = 0.4348$. This reflects a small deviation from additivity in the mixture containing two cyclic compounds.

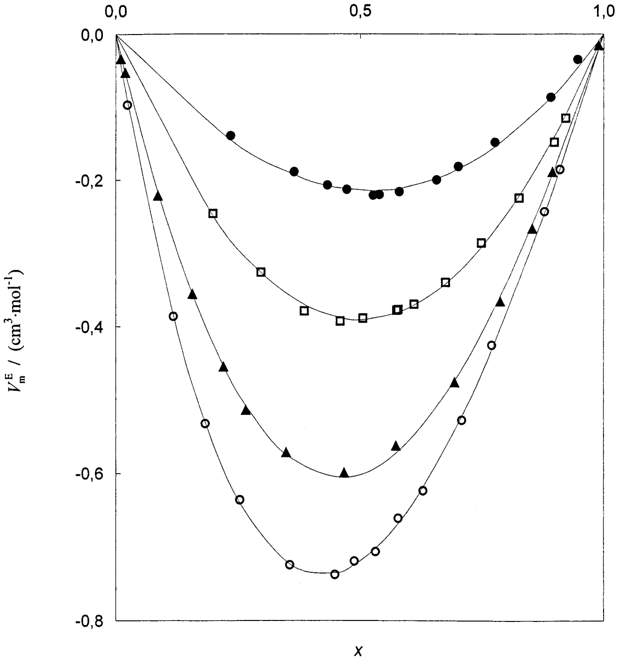

Figure 1. Excess molar volume V_m^E for a binary mixture of x NMP + (1−x) (○) 2-propanone, or (▲) 2-butanone, or (□) 4-heptanone, or (●) 5-nonanone at 298.15 K. Solid lines are calculated by the Redlich−Kister equation.

A similar effect is observed during the comparison between a branched chain ketone and the straight chain ketone (see Figure 3). The V_m^E (min) value was − 0.468 cm^3·mol^{-1} (for $x = 0.50$) and − 0.666 cm^3·mol^{-1} for ($x = 0.4823$) for 2-hexanone and 4-methyl-2-pentanone, respectively. More negative excess molar volume, observed for a branched chain ketone, would seem to indicate that a more organized packing effect and stronger co-association A−B is present in mixtures containing a branched chain ketone.

The two, measured H_m^E curves are positive. The H_m^E (max) increases with increasing ketone chain length (see Figure 4), an order similar to the V_m^E values. The H_m^E (0.5) value was 226.1 J·mol^{-1} and 362.0 J·mol^{-1} for 4-heptanone and 5-nonanone, respectively. For 5-nonanone the maximum is shifted toward higher concentration of the NMP. This skewness reflects the dominance of self-association of the NMP at low concentration of a long-chain ketone in the mixture. No H_m^E data were found in the literature on mixtures containing short-chain ketones. No measure-

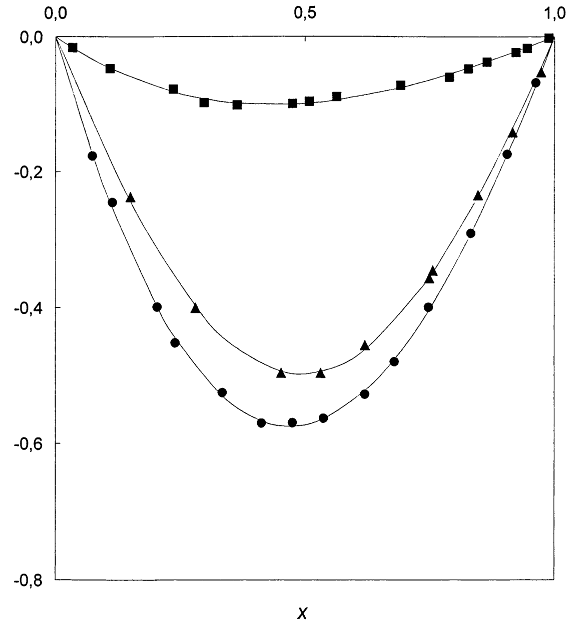

Figure 2. Excess molar volume V_m^E for a binary mixture of x NMP + $(1-x)$ (●) 2-pentanone, or (▲) 3-pentanone, or (■) cyclopentanone at 298.15 K. Solid lines are calculated by the Redlich–Kister equation.

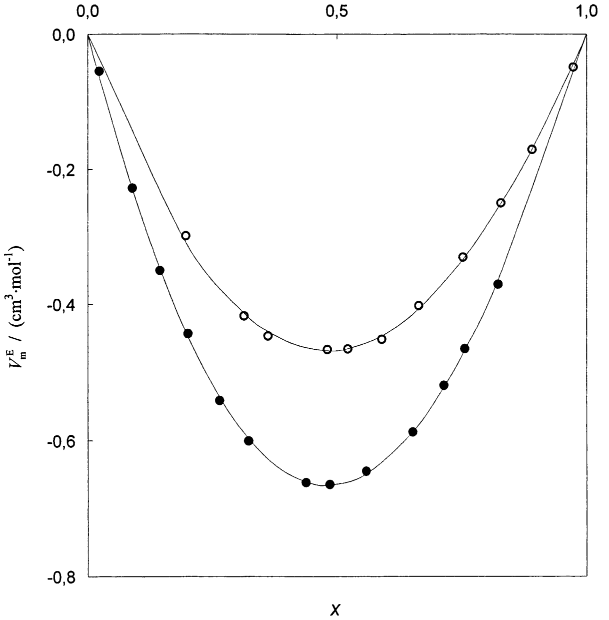

Figure 3. Excess molar volume V_m^E for a binary mixture of x NMP + $(1-x)$ (○) 2-hexanone, or (●) 4-methyl-2-pentanone at 298.15 K. Solid lines are calculated by the Redlich–Kister equation.

ments were done on these mixtures in this work, as the ketones react with the tubing of the peristaltic pumps because they react with the tubing of the calorimeter.

The overall magnitude of H_m^E(max) is a result of the positive effect due to the breakdown of the weak NMP self-association and weak ketone–ketone molecules interaction. These results indicate that the cross-association is weaker than the self-association.

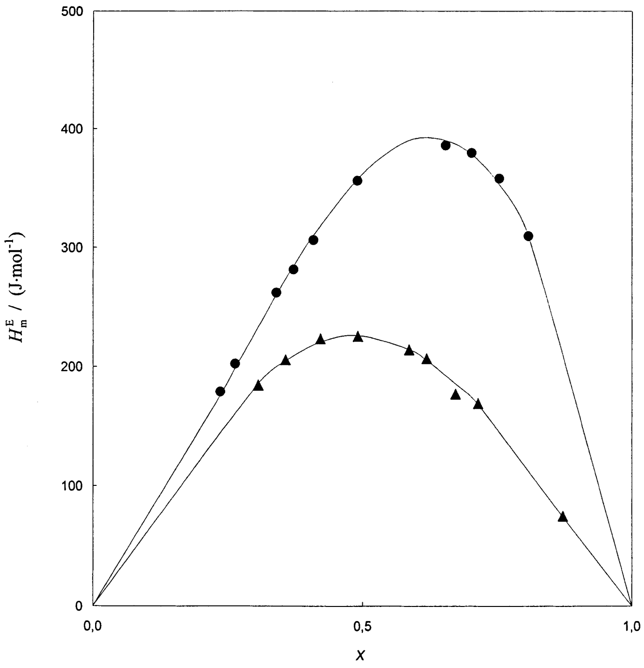

Figure 4. Excess molar volume H_m^E for a binary mixture of x NMP + $(1-x)$ (▲) 4-heptanone or (●) 5-nonanone at 298.15 K. Solid lines are calculated by the Redlich–Kister equation.

Table 5. Characteristic Parameters of Pure Components: V^*, T^*, p^* and Reduce Volume $\tilde{v}$ from the FBT Model at 298.15 K

component	V^* cm^3·mol^{-1}	T^* K	p^* J·cm^{-3}	$\tilde{v}$
NMP	79.5	5796	436	1.213
2-propanone	55.5	4335	583	1.335
2-butanone	68.9	4555	580	1.308
2-pentanone	85.9	5175	440	1.252
3-pentanone	82.7	4754	553	1.287
2-heksanone	97.7	4946	535	1.270
4-methyl-2-pentanone	98.6	4879	503	1.276
4-heptanone	111.9	5094	532	1.258
5-nonanone	140.6	5383	518	1.237

Table 6. Exchange Interaction Coefficient X_{AB} for the Equation of State Contribution and Summary of Calculations for Mixtures of NMP with a Ketone at the Equimolar Concentration Using the FBT Model

system	V_m^E(exp) cm^3·mol^{-1}	H_m^E(exp) J·mol^{-1}	X_{AB} J·cm^{-3}	V_m^E(calc) cm^3·mol^{-1}	H_m^E(calc) J·mol^{-1}
NMP +					
2-propanone	−0.719		−68.9	−0.719	−466.8
2-butanone	−0.601		−60.0	−0.601	−251.4
2-pentanone	−0.573		−35.3	−0.573	351.3
3-pentanone	−0.498		−46.2	−0.498	87.5
2-hexanone	−0.468		−40.4	−0.468	276.3
4-methyl-2-pentanone	−0.665		−45.6	−0.665	159.6
4-heptanone	−0.391	226.1	−24.7	−0.246	689.2
5-nonanone	−0.214	362.0	−10.5	−0.076	1148.9

Flory–Benson–Treszczanowicz Model

The FBT model has been applied first to the excess volumes of binary systems formed by mixing a polar substance base with an alkane or cycloalkane.[24,25] The excess volumes are described as sums of two contributions. One arises from self-association of the NMP base and is evaluated according to the Mecke–Kempter continuous association model.[35] The other comprises equation of state and interaction effects, which are treated according to the Flory theory. The chemical contribution arises from self-association of NMP. The value of $\Delta v_A^* = -0.2$ cm^3·mol^{-1}, $K_{298.15} = 0.58$, and the enthalpy of hydrogen bonding $\Delta H_A^* = -23.6$ for NMP were developed earlier.[7] The value of $\Delta v_B^* = 0$, $K_B = 0$, and $\Delta H_B^* = 0$ for each of the six ketones

Table 7. Adjusted Binary ERAS Model Parameters Characterizing Mixture Properties: Enthalpy ΔH^*_{AB}, Volume Δv^*_{AB}, and Constant of Cross-Association K_{AB}, Exchange Interaction Coefficient X_{AB} for the Equation of State Contribution, and Summary of Calculations for Mixtures of NMP with Ketone at the Equimolar Concentration

system	K_{AB}	ΔH^*_{AB} / kJ·mol^{-1}	Δv^*_{AB} / cm^3·mol^{-1}	X_{AB} / J·cm^{-3}	V^E_m(calc) / cm^3·mol^{-1}	H^E_m(calc) / J·mol^{-1}
NMP +						
2-propanone	1.0	−17.9	−7.4	7.5	−0.720	−252.1
2-butanone	1.0	−17.9	−7.0	7.0	−0.598	−83.8
2-pentanone	1.0	−17.9	−4.9	6.9	−0.577	0.4
3-pentanone	1.0	−17.9	−6.1	6.8	−0.502	44.3
2-hexanone	1.0	−17.9	−5.7	6.0	−0.469	180.9
4-methyl-2-pentanone	1.0	−17.9	−6.8	7.0	−0.672	249.4
4-heptanone	1.0	−17.9	−4.8	3.0	−0.388	222.8
5-nonanone	1.0	−17.9	−3.0	1.0	−0.220	359.1

were assumed to be equal to zero, which means no self-association compounds were shown.

The physical contribution was evaluated using the Flory formula[36−38]

$$V^E_{\text{phys}} = (x_1V^*_1 + x_2V^*_2)[\tilde{v} - (\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)] \qquad (3)$$

where $\tilde{v}$, $\tilde{v}_1$, and $\tilde{v}_2$ are the reduced volumes of the mixture and the pure components. Application of the Flory theory requires equation of state parameters for the pure components. Values for the present systems are summarized in Tables 1 and 5.

A comparison of the predicted and the experimental excess properties for (NMP + 4-heptanone or + 5-nonanone) mixtures shows that the FBT model is not able to describe the excess functions for the straight-chain symmetrical ketone (see Figures 5 and 6). For these systems, V^E_m and H^E_m values, calculated by FBT, are however of the same sign as the experimental values. A comparison between the predicted and experimental values for $x = 0.5$ for two ketones is presented in Table 6, together with predicted H^E_m for the systems not measured here. For cyclopentanone mixtures, no FBT calculations were possible because the pure component parameters, cubic expansion coefficient, and isothermal compressibility were not known. Finally, it should be noted that estimates of excess molar volumes and enthalpies, based on the interchange energy parameters, obtained from the present analysis of excess molar volumes, generally exhibit relatively large deviations from the experimental results due to the importance of contributions from other structural effects, such as interstitial accommodation and conformational changes.

ERAS Model

The ERAS model[23,24] combines the real associated solution model with a free volume contribution using Flory's equation of state.[36−38] A special property of the ERAS theory is its ability to predict simultaneously H^E_m, V^E_m, and G^E_m of mixtures with self- and cross-associations. Experimental data of the excess properties for NMP + alcohol mixtures are described almost quantitatively by adjusting a few interaction parameters such as van der Waals interaction parameters, association constants, bonding enthalpies, and bonding volumes.[7,15]

The version of the ERAS model, related to mixtures consisting of one associating component (NMP) and intermolecular association NMP−ketone, has been used to describe the experimental V^E_m and H^E_m data for the mixtures (NMP + ketone). Application of the ERAS theory to the mixtures containing a weakly self-associating component together with a cross-association, that is, (NMP + ketone), was described previously for the mixtures of (1-alkanol + 1-alkene or 1-alkyne).[39] The equations obtained for the thermodynamic excess functions are split into two additive terms, which arise from the hydrogen-bonding effects (the so-called "chemical" contribution) and from nonpolar van der Waals interactions, which accounts for the free volume effects between unlike molecules (the "physical" contribution).

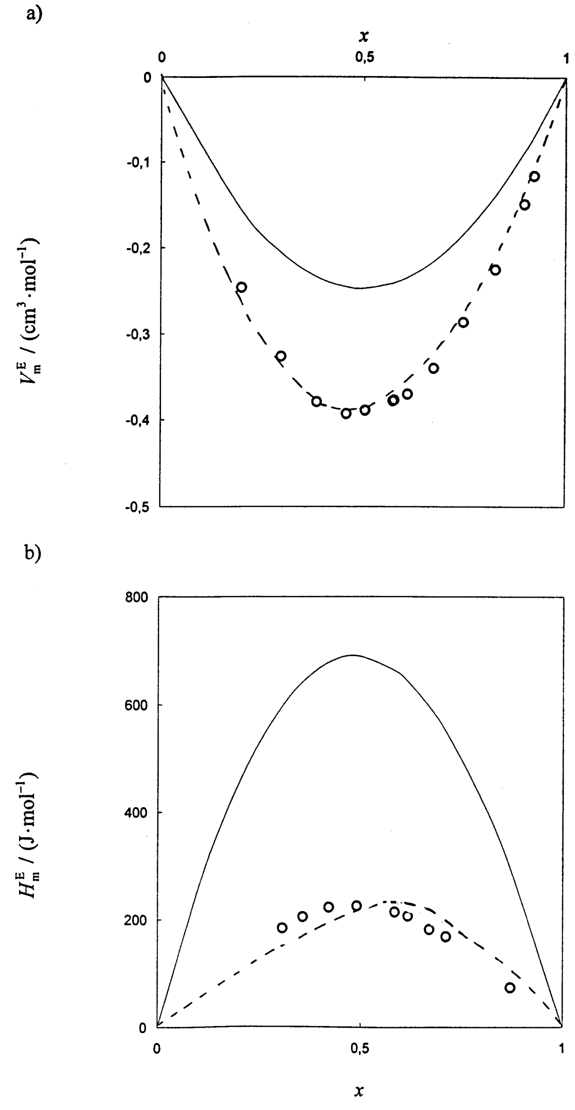

Figure 5. Excess molar functions, V^E_m(a) and H^E_m(b), for a binary mixture of x NMP + (1−x) 4-heptanone at 298.15 K. (○) Experimental results; (—) calculated data from FBT model; (- - -) calculated data from ERAS model.

The parameters required for the calculation of the excess properties of NMP−ketone mixtures are evaluated in the

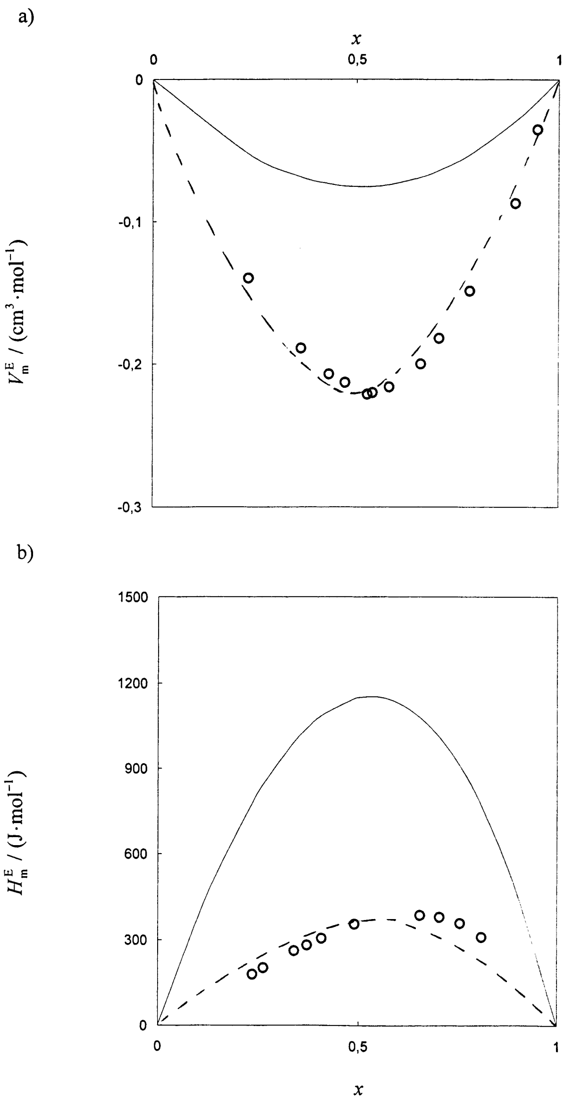

Figure 6. Excess molar functions, V^E_m(a) and H^E_m(b), for a binary mixture of x NMP + (1−x) 5-nonanone at 298.15 K. (○) Experimental results; (—) calculated data from FBT model; (- - -) calculated data from ERAS model.

following way. The value of Δv^*_A, K_A, and the enthalpy of hydrogen bonding ΔH^*_A for NMP are the same as in FBT calculations. Thermal expansion coefficients α and isothermal compressibilities κ_T of the pure substances were used from literature sources and are given in Table 1. The K_A values at other temperatures can be easily calculated by the relationship[39]

$$K_A(T) = K_{A,298.15K} \exp\left\{\frac{\Delta H^*_A}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \quad (4)$$

The characteristic parameters V^* and p^*, obtained from the experimental data, are very similar to those obtained from the FBT model. The unknown parameters, the volume changes being a result of the A−B interaction, Δv^*_{AB}, the cross-association constant, K_{AB}, and enthalpy, ΔH^*_{AB} , and binary interaction coefficient, X_{AB}, have been obtained from a simultaneous adjustment to experimental data of H^E_m and V^E_m at x = 0.5 for two ketones: 4-heptanone and 7-nonanone. All binary ERAS model parameters and the results of prediction for the equimolar compositions using the ERAS model are presented in Table 7.

V^E_m and H^E_m curves, calculated by the ERAS model for (NMP + 4-heptanone or 7-nonanone) mixtures, show good agreement with the experimental data at the equimolar concentration. The characteristic skewing of all V^E_m curves toward low NMP concentration is well described by this model (see Figures 5 and 6). For all systems the V^E_m and H^E_m curves, as calculated by the ERAS model, are better represented than those by the FBT model. Some deviations in the symmetry of the predicted curves are, however, observed.

Conclusions

All the excess molar volumes reported in this work are large and negative, as was observed for the mixtures of NMP with ethers.[17] The deviations of V^E_m from ideality are about 30% of those observed for ethers. These negative effects are most likely to be due to packing effect changes in the "molar free volume" of NMP and ketone in the mixing process. From the experimental and calculated values of V^E_m and H^E_m one may expect much stronger A−B interactions between NMP and short-chain ketone molecules.

Better organized packing effect and stronger co-association A−B are observed for unsymmetrical and branched chain ketones.

A comparison of the calculated and the experimental excess properties for (NMP + ketone) mixtures shows that the ERAS model is better than the FBT model in describing excess properties for the mixtures discussed in this work (see Table 7), especially for the mixtures containing the longer chain ketones.

Literature Cited

(1) Macdonald, D. D.; Dunay, D.; Hanlon, G.; Hyne, J. B. Properties of the *N*-Methyl-2-pyrrolidinone−Water System. *Can. J. Chem. Eng.* **1971**, *49*, 420−423.

(2) Chen, G.; Knapp, H. Densities and Excess Mole Volumes for Sulfolane + Ethylbenzene, Sulfolane + 1-Methylnaphthalene, Water + *N,N*-Dimethylformamide, Water + Methanol, Water + *N*-Formylmorpholine, and Water + *N*-Methylpyrrolidone. *J. Chem. Eng. Data* **1995**, *40*, 1001−1004.

(3) Al-Mashhadani, A. M. A.; Awwad, A. M. Excess Molar Volumes of an Aromatic Hydrocarbon + *N*-Methylpyrrolidone at 298.15 K. *Thermochim. Acta* **1985**, *89*, 75−80.

(4) Letcher, T. M.; Naicker, P. K. Excess Molar Enthalpies and Excess Molar Volumes of Mixtures Containing *N*-Methyl-2-pyrrolidinone and an Aromatic Hydrocarbon at T = 298.15 K and p = 0.101325 MPa. *J. Chem. Thermodyn.* **1999**, *31*, 1585−1595.

(5) Awwad, A. M.; Allos, E. I.; Kanbour, F. J. Thermodynamic Properties of Binary Mixtures Containing *N*-Methylpyrrolidone. *J. Chem. Thermodyn.* **1985**, *17*, 635−639.

(6) Awwad, A. M.; Al-Mashhadani, A. M. A.; Tawfeek, E. A. Excess Volumes of (*N*-Methylpyrrolidone + Isoalkanol) at 298.15 K. *J. Chem. Thermodyn.* **1986**, *18*, 131−133.

(7) Letcher, T. M.; Domańska, U.; Mwenesongole, E. Excess Molar Volumes of (*N*-Methyl-2-pyrrolidone + an Alkanol or a Hydrocarbon) at 298.15 K and the Application of the Flory-Benson-Treszczanowicz and the Extended Real Associated Solution Theories. *Fluid Phase Equilib.* **1998**, *149*, 323−337.

(8) Letcher, T. M.; Whitehead, P. G. H^E_m and V^E_m of the Polar Solvents *N*-Methyl-2-pyrrolidinone (C_5H_9NO), or *N,N*-Dimethylformamide (C_3H_7NO), or Dimethyl Sulphoxide (C_2H_6SO) with 1-Hexyne, or 1-Heptyne, or 1-Octyne at T = 298.15 K, and Application of the ERAS Theory. *J. Chem. Thermodyn.* **1999**, *31*, 1537−1549.

(9) Liu, X.; Su, Z.; Wang, H.; Zhong, X. Excess Molar Volumes of (a Polar Liquid + an Aromatic Hydrocarbon) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1996**, *28*, 277−283.

(10) Dohnal, V.; Roux, A. H.; Hynek, V. Limiting Partial Molar Excess Enthalpies by Flow Calorimetry: Some Organic Solvents in Water. *J. Solution Chem.* **1994**, *23*, 889−900.

(11) Gmehling, J.; Meents, B. Excess Enthalpy. *N*-Methyl-2-pyrrolindinone−Cyclohexane System. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1992**, *3*, 210−213.

(12) Gustin, J.-L.; Renon, H. Heats of Mixing of Binary Mixtures of *N*-Methylpyrrolidone, Ethanolamine, *n*-Heptane, Cyclohexane,

and Benzene by Differential Fow Calorimetry. *J. Chem. Eng. Data* **1973**, *18*, 164−166.

(13) Malanowski, S.; Bittrich, H. J.; Lempe, D.; Reinhardt, K.; Wustling, J.-U. Liquid−Liquid Equilibria in Binary Mixtures of *N*-Methylo-α-pyrrolidone and Saturated Hydrocarbons. *Fluid Phase Equilib.* **1994**, *98*, 163−171.

(14) Fuchs, R.; Krenzer, L.; Gaube, J. Excess Properties of Binary Mixtures Composed of a Polar Component and an Alkane. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 642−649.

(15) Letcher, T. M.; Łachwa, J.; Domańska, U. The Excess Molar Volumes and Enthalpies of (*N*-Methyl-2-pyrrolidinone + an Alcohol) at 298.15 K and the Application of the ERAS Theory. *J. Chem. Thermodyn.* **2001**, *33*, 1169−1179.

(16) Letcher, T. M.; Domańska, U.; Łachwa, J. The Excess Molar Enthalpies of (*N*-Methyl-2-pyrrolidinone + mono-, di-, or Trichlorobenzene) at 298.15 K. *J. Chem. Thermodyn.* **2001**, *33*, 1399−1404.

(17) Domańska, U.; Łachwa, J.; Letcher; T. M. The Excess Molar Volumes, and the Excess Molar Enthalpies of (*N*-Methyl-2-pyrrolidinone + an Ether) at Temperature 298.15 K. *J. Chem. Thermodyn.*, in press.

(18) Domańska, U.; Łachwa, J. Solid−Liquid Equilibria of Binary Mixtures containing *N*-Methyl-2-pyrrolidinone and Long Chain *n*-Alkanols at Atmospheric Pressure. *Fluid Phase Equilib.* **2002**, *198*, 1−14.

(19) Domańska, U.; Łachwa, J. Solid−Liquid Equilibria of *N*-Methyl-2-pyrrolidinone and Alcohol at Atmospheric Pressure. *J. Chem. Thermodyn.*, in press.

(20) Ferreira, P. O.; Barbosa, D. Medina, A. G. Phase Equilibria for the Separation of Aromatic and Nonaromatic Compounds Using Mixed Solvents. Part I. The System *n*-Heptane−Toluene−*N*-Methylpyrrolidone/Monoethyleneglycol. *Fluid Phase Equilib.* **1984**, *15*, 309−322.

(21) Reid, R. C.; Prausnitz, J. M. *The Properties of Liquids and Gases*; McGraw-Hill: New York, 1986.

(22) Treszczanowicz, A.; Benson, G. C. Excess Volumes of Alkanol + Alkane Binary Systems in Terms of an Association Model with a Flory Fontribution Term. *Fluid Phase Equilib.* **1985**, *23*, 117−135.

(23) Treszczanowicz, A.; Benson, G. C. Excess Volumes of Cycloalkanol + Cycloalkane Binary Systems in Terms of an Association Solution Theory with a Flory Equation of State Contribution. *Thermochim. Acta* **1991**, *179*, 39−47.

(24) Heintz, A. A New Theoretical Approach for Predicting Excess Properties of Alkanol/Alkane Mixtures. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 172−181.

(25) Funke, H.; Wetzel, M.; Heintz, A. New Applications of the ERAS Model. Thermodynamics of Amine + Alkane and Alcohol + Amine Mixtures. *Pure Appl. Chem.* **1989**, *61*, 1429−1439.

(26) Letcher, T. M.; Lucas, The Excess Volumes of Decahydronaphthahlene + Cyclopentane, + Cyclohexane, + Cycloheptane and + Cyclooctane at Two Temperatures. A. *Fluid Phase Equilib.* **1982**, *8*, 301−308.

(27) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Method of Purification*; Wiley: New York, 1986; Vol. 2.

(28) Malhotra, R.; Woolf, L. A. Thermodynamic Properties of Propanone (Acetone) at Temperatures from 278 K to 323 K and Pressures up to 400 MPa. *J. Chem. Thermodyn.* **1991**, *23*, 867−876.

(29) Lee, L.; Chuang, M. Excess Volumes of Cyclohexane with 2-Propanone, 2-Butanone, 3-Pentanone, 4-Methyl-2-pentanone, 1-Propanol, and 2-Propanol and Ethanoic Acid +1-Propanol Systems. *J. Chem. Eng. Data* **1997**, *42*, 850−853.

(30) Malhotra, R.; Woolf, L. A. Thermodynamic Properties of Butan-2-one at Temperatures from 278 K to 338 K and Pressures from 0.1 MPa to 280 MPa; Predictions for Higher Ketones. *J. Chem. Thermodyn.* **1992**, *24*, 1207−1217.

(31) Malhotra, R.; Woolf, L. A. Volumetric Measurements of Liquid Pentan-2-one, Hexan-2-one, and 4-Methylpentan-2-one at Temperatures from 278.15 K to 338.13 K and Pressures in the Range from 0.1 MPa to 386 MPa. *J. Chem. Thermodyn.* **1996**, *28*, 1411−1421.

(32) Malhotra, R.; Price, W. E.; Woolf, L. A. Thermodynamic Properties of Pentan-3-one at Temperatures from 278 K to 338 K and Pressures from 0.1 MPa to 380 MPa. *J. Chem. Thermodyn.* **1993**,

(33) Letcher, T. M.; Scoones, B. W. H. The Excess Enthalpies of Bicyclohexyl + a Cycloalkane and + an *n*-Alkane at Two Temperatures. *J. Chem. Thermodyn.* **1982**, *14*, 703−706.

(34) Ferhat-Hamida, Z.; Philippe, R.; Merlin, J. C.; Kehiaian, H. V. Thermodynamic Properties of Binary Mixtures Containing Thiaalkanes. Excess Enthalpies of *n*-Thiaalkane + *n*-Alkane Mixtures. *J. Chim. Phys., Phys. Chim. Biol.* **1979**, *76*, 130−136.

(35) Kehiaian, H.; Treszczanowicz, A. Thermodynamics of Chemically Reacting Mixtures. Excess Free Enthalpy of Athermal Associated Mixtures of the Mecke-Kempter ype. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1968**, *16*, 445−449.

(36) Flory, P. J. Statistical Thermodynamics of Liquid Mixtures. *J. Am. Chem. Soc.* **1965**, *87*, 1833−1835.

(37) Abe, A.; Flory, P. J. The Thermodynamic Properties of Mixtures of Small, Nonpolar Molecules. *J. Am. Chem. Soc.* **1965**, *87*, 1838−1842.

(38) Orwoll, R. A.; Flory, P. J. Equation of State Parameters for Normal Alkanes. Correlation with Chain Length. *J. Am. Chem. Soc.* **1967**, *89*, 6822−6825.

(39) Letcher, T. M.; Mercer-Chalmers, J.; Schnabel, S.; Heintz, A. Application of ERAS Model to H_m^E and V_m^E of 1-Alkanol + 1-Alkene and 1-Alkanol + 1-Alkyne Mixtures. *Fluid Phase Equilib.* **1995**, *112*, 131−149.

Received for review April 19, 2002. Accepted July 3, 2002. Support from the Polish Committee for Scientific Research (Grant 7 TO9B 09521) is acknowledged by the authors U.D. and J. Ł T. M. Letcher wishes to thank the University of Natal, Durban, and N.R.F. (South Africa) for financial help.

JE020068P