Excess Molar Enthalpies and Vapor−Liquid Equilibrium for *N*-Methyl-2-pyrrolidone with Ketones

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Excess enthalpies (H^E), at ambient pressure and 298.15 K, have been measured by using a solution calorimeter for the binary liquid mixtures of *N*-methyl-2-pyrrolidone (NMP) with ketones, as a function of composition. The ketones chosen in the present investigation were methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and cyclohexanone (CH). The H^E values were measured using a new Parr 1451 solution calorimeter and were negative over the entire mole fraction range for NMP with MEK and were positive for NMP with MIBK or CH. The excess enthalpy data have also been correlated with the Redlich−Kister equation. Furthermore, the vapor−liquid equilibrium (VLE) data were measured at 95.3 kPa for these mixtures, of different compositions, with the help of the Swietoslawski ebulliometer. The experimental temperature−mole fraction ($T-x$) data were used to compute Wilson parameters and then used to calculate the equilibrium vapor-phase compositions. The intermolecular interactions and structural effects were analyzed on the basis of the measured and derived properties.

Introduction

The interaction between solvents with polar groups and the carbonyl carbon group of ketone plays a crucial role in the structural effects, molecular level, and practical applications.[1] The chemical industries have recognized the importance of the thermodynamic properties in design calculations involving chemical separations, heat transfer, mass transfer, and fluid flow. When two or more solvent molecules are associated with one another to form a liquid mixture, it brings about a marked effect on the properties of the resulting system and differences in the intermolecular interactions of the solvents. This fact is well-known as the transport phenomenon and thermophysical properties of mixed solvents. The excess enthalpy (H^E) remains an important probe to use in understanding the interactions and structure of liquid mixtures and also development of industrial processes.[2,3] Vapor−liquid equilibrium (VLE) data are required for design and operation of distillation equipment and for determining the optimal values of parameters in the thermodynamic models.[4,5]

N-Methyl-2-pyrrolidone (NMP) is colorless, is high-boiling, is mobile, has a characteristic odor, and has low viscosity. NMP, known for its low toxicity and solvent power, is rapidly becoming the product for paint strippers, agricultural chemicals, and process solvent applications. On the other hand, NMP is a strongly polar liquid and has the potential for use in the solvent extraction process for separating polar substances from nonpolar substances.[6,7] It is an aprotic solvent with a large dipole moment and a high dielectric constant ($\mu = 4.09$ D and $\varepsilon = 32.2$ at 298.15 K).[8]

Apparently, the thermodynamic properties of highly polar components with the carbonyl carbon group of ketones have been a significant interest area of research for years.[9−12] As part of our research program to explore the thermodynamic properties of various molecular liquids,[13−17] we report here the H^E and VLE measurements for the systems of binary mixtures containing NMP and methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and cyclohexanone (CH). A survey of the literature reveals no studies of H^E and VLE data for these mixtures.

Table 1. Densities *ρ* at 298.15 K and Boiling Point Temperatures (*T*) at 95.3 kPa for Pure Components

	ρ/kg·m^{-3}		T/K	
component	exptl	lit.	exptl	lit.
NMP	1023.40[a]	1023.70[a]	473.3	474.0[g]
	1028.20	1028.25[b]		
MEK	799.71	799.62[c]	352.7	352.7[h]
MIBK	796.33	796.22[d]	390.5	390.6[h]
CH	937.58[e]	937.60[e,f]	428.8	428.8[h]

[a] Ref 18. [b] Ref 19. [c] Ref 20. [d] Ref 21. [e] At 303.15 K. [f] Ref 22. [g] Ref 17. [h] Ref 8.

Experimental Section

Chemicals. All the chemicals used were of analytical grade. NMP (Merck > 99 %) was distilled at low pressure and stored over freshly activated 3 Å molecular sieves.[7] MEK, MIBK, and CH were purified by the methods described earlier.[8] The purity of the samples was checked by measuring densities and boiling points. The densities were measured using a standard bicapillary pycnometer, giving an accuracy of two parts in 10^5. Boiling points were measured using a Swietoslawski-type ebulliometer, giving an accuracy of ± 0.2 K. Good agreement between the measured densities as well as boiling points and literature values[8,17−22] are shown in Table 1. Mixtures of different compositions were prepared gravimetrically by weighing the needed quantities of the pure components, making use of a Mettler balance uncertainty to 0.0001 g. The uncertainty in solution composition was $\pm 1 \cdot 10^{-4}$ in mole fraction.

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Table 2. Experimental Excess Enthalpies for the {x_1Ketone + (1 − x_1)NMP} Solutions at 298.15 K

x_1	H^E/J·mol^{-1}
MEK + NMP	
0.0565	−26.2
0.1162	−45.6
0.1812	−67.3
0.2461	−99.9
0.3104	−128.0
0.3690	−148.6
0.4334	−159.7
0.4841	−167.5
0.5458	−157.6
0.6781	−115.7
0.7324	−86.1
0.7935	−62.0
0.8525	−48.9
0.9112	−24.8
0.9609	−20.1
MIBK + NMP	
0.0508	22.8
0.1052	49.7
0.1632	76.4
0.2234	101.2
0.2858	127.4
0.3815	167.2
0.4258	179.4
0.4787	180.9
0.5346	173.7
0.5990	167.9
0.6712	151.3
0.7536	105.7
0.8369	65.1
0.9192	24.3
CH + NMP	
0.0609	18.0
0.1242	54.2
0.1855	84.3
0.2495	109.0
0.3151	138.5
0.3761	163.5
0.4301	177.9
0.4527	193.0
0.5028	202.7
0.5608	201.2
0.6249	199.6
0.6866	167.3
0.7491	132.5
0.8134	99.2
0.8794	66.0
0.9445	33.4

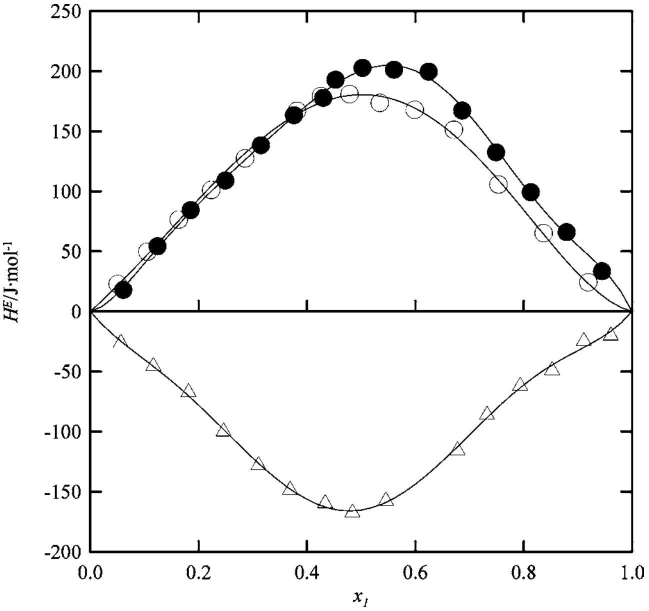

Figure 1. Excess enthalpies H^E at 298.15 K against mole fraction of ketone x_1 for the following binary systems: Δ, MEK + NMP; ○, MIBK + NMP; ●, CH + NMP. Solid lines are calculated by the Redlich−Kister equation with the values of parameters given in Table 3.

Excess Enthalpy Measurements. A new Parr 1451 solution calorimeter was used in the measurements of H^E for the liquid mixtures. More details on the experimental procedure were delineated in our previous papers.[10,13,23] The calorimeter consists of a glass Dewar mixing chamber with a rotating sample cell, a thermistor probe, and a specially designed temperature measuring bridge, all assembled in a compact cabinet. Temperature changes were plotted directly using a strip chart recorder and were read to an accuracy of ± 0.001 K. The two-piece cell which served both as a sample holder and as an agitator consisted of a cell closed with a detachable Teflon disk. Liquid samples were added to the cell from a pipet inserted through the top stem. Excellent thermal insulation was provided by a fully silvered glass Dewar which served as a mixing chamber. The operating principle of this calorimeter was very simple.

In the measurement of excess enthalpies, a known weight of 100 mL of component A is taken into the Dewar vessel, and 20 mL of component B is weighed in a sealed glass rotating cell. Both the components are kept in thermal contact with each other in the Dewar mixing chamber at 298.15 K. After attaining the thermal equilibrium (about 30 min), component B in the rotating cell is mixed with component A in the Dewar vessel by pushing the glass rod. The temperature change accompanying the mixing process is sensed by the thermistor and recorded on the strip chart recorder. These experiments were continued until the concentrations reach (50 to 60) %. This procedure was repeated by taking component A as component B and component B as component A. The excess enthalpy H^E was then measured, knowing the energy equivalent of the system, via the equation

$$H^E = (M_1C_{p1} + M_2C_{p2} + E)\Delta T/n \qquad (1)$$

where M_1 and M_2 are the mass of NMP and ketone and C_{p1} and C_{p2} are the heat capacity (J·g^{-1}·K^{-1}) of NMP and ketone, respectively. E is the energy equivalent of the calorimeter (J·K^{-1}); ΔT is the temperature change (K); and n is the number of moles of mixture. The estimated uncertainty in the measurements of H^E values is ± 1 % and was verified with the measurements over the entire composition range on the standard systems, that is, benzenes with carbon tetrachloride[24] and chlorobenzene[25] with toluene.

VLE Measurements. The VLE measurements were measured in a Swietoslawski-type ebulliometer.[26] The detailed procedure has been delineated in our earlier articles.[4,5] The ebulliometer is connected to a vacuum pump and a dry nitrogen gas cylinder with a closed end manometer in line to enable the measurement and maintenance of the total pressure of the system at 95.3 kPa, by adjusting the opening of the needle valve of the gas cylinder/the opening of the bypass line of the vacuum pump. An open end manometer provided in line is frequently read (along with a Fortin's type barometer), and the needed corrective action of adjusting the opening of the needle valve attached to the gas cylinder or the bypass line of the vacuum pump is performed according to the requirement. The pressure was controlled by a Cartesian driver and was measured with this mercury manometer with an uncertainty of ± 0.13 kPa (1 mmHg). A mercury-in-glass thermometer, calibrated by means of point to point comparison with a platinum resistance thermometer (certified by the National

Table 3. Adjusted Parameters of Equation 2 and the Standard Deviations $\sigma(H^E)$ for the Excess Enthalpies for Mixtures of Ketones with NMP at 298.15 K

system	h_0 / J·mol^{-1}	h_1 / J·mol^{-1}	h_2 / J·mol^{-1}	h_3 / J·mol^{-1}	h_4 / J·mol^{-1}	h_5 / J·mol^{-1}	$\sigma(H^E)^a$ / J·mol^{-1}
MEK + NMP	−660.87	135.88	912.26	−132.61	−796.78		2.7
MIBK + NMP	722.41	9.67	−463.08	−155.38			3.2
CH + NMP	801.84	344.47	−680.16	−1200.64	391.31	1289.92	2.7

[a] $\sigma(H^E) = [\sum_{i=1}^{n}(H^{E(i)}_{\text{exp}} - H^{E(i)}_{\text{cal}})^2/n]^{1/2}$.

Table 4. Adjusted Wilson Parameters and Standard Deviations of the Fit $\sigma(T)$ for the Isobaric Vapor−Liquid Equilibrium Data at 95.3 kPa

system	$(\lambda_{12} - \lambda_{11})/R$ / K	$(\lambda_{12} - \lambda_{22})/R$ / K	$\sigma(T)^a$ / K
MEK + NMP	57.478	−295.86	0.16
NMP + MIBK	68.030	−257.81	0.10
NMP + CH	−409.66	2314.8	0.04

[a] $\sigma(T) = [\sum_{i=1}^{n}(T^{(i)}_{\text{exp}} - T^{(i)}_{\text{cal}})^2/n]^{1/2}$.

Table 5. Constants of the Antoine Equation[a] Determined for Pure Components

component	A	B	C
NMP	7.4159	2572.70	273.15
MEK	6.1844	1259.22	221.76
MIBK	5.9494	1256.45	203.00
CH	6.1033	1495.51	209.56

[a] $\log_{10}(p/\text{kPa}) = A - B/(T/\text{K} + C - 273.15)$.

Institute of Standards and Technology, Boulder, USA) is used to measure the equilibrium temperature to the uncertainty of ± 0.1 K. The thermometer is placed in a thermo well (in the apparatus) whose outer surface is constantly impinged by an equilibrium vapor−liquid mixture. The thermo well contains a small quantity of mercury to provide for good contact.

Each solvent was degassed by magnetic stirring under its vapor pressure before mixing. The boiling points of mixtures of NMP with branched alkanols were determined at 95.3 kPa over the entire range of compositions; mixtures of different compositions were prepared gravimetrically by weighing the needed quantities of the pure components, making use of a Mettler balance uncertainty to 0.0001 g. Boiling points of mixtures were also measured using an ebulliometer, giving the uncertainty of ± 0.2 K. The uncertainty in solution composition was $\pm 4 \cdot 10^{-4}$ in mole fraction. The heating rate is maintained at a level capable of producing a condensate drop rate of 30 drops per minute, following the suggestion of Hala et al.,[26] by carefully adjusting the energy supply to the heater. Equilibrium temperature is recorded, when the steady-state conditions (observation of constant temperature and uniform boiling rate indicated by the maintenance of the chosen condensate liquid drop rate of 30 drops per minute) are observed for at least 30 min.

Results and Discussion

The measured excess enthalpies (H^E) at 298.15 K for NMP with MEK, MIBK, and CH are reported in Table 2 and are graphically represented in Figure 1. The results for each mixture were fitted with the Redlich−Kister equation in the form

$$H^E/\text{J}\cdot\text{mol}^{-1} = x_1(1 - x_1)\sum_{i=0}^{m} h_i(2x_1 - 1)^i \qquad (2)$$

by the method of least-squares. Values of the coefficients h_i and the standard deviation $\sigma(H^E)$ for the fit are given in Table 3. The number of coefficients was determined on the statistical basis.

From Figure 1, it can be seen that the excess enthalpy data for the binary mixtures of NMP with MEK are negative (exothermic) at 298.15 K over the entire range of composition. On the other hand, the positive (endothermic) H^E values have been observed in the mixtures of NMP with MIBK and CH under the same experimental conditions. The exothermic nature of these results is a reflection of the dominance of the strong association between NMP and MEK. The positive excess enthalpies can be ascribed to loss of dipolar association by the addition of one component to the other and the difference in size and shape of the component molecules. The maximum positive H^E values are observed around (0.5 to 0.6) mol fraction of ketone for these binary systems.

NMP is a highly polar but very little hydrogen bonded substance, and it has a large dipole moment ($\mu = 4.09$).[8] This enables it to stabilize molecules and ions through dipole and induced-dipole interactions. Its high electron density on the unscreened oxygen atom enables it to solvate strongly. Meanwhile, owing to the proton-accepting ability of the carbonyl (>CO) group of the ketones is a poorer proton acceptor. The molecules of ketones are dipolar and can be self-associated by dipole−dipole interactions.

The algebraic values of H^E for the systems of NMP with ketones fall in the order:

CH > MIBK > MEK.

The large positive values for the mixtures of NMP with CH (202.7 J·mol^{-1} at $x_1 = 0.5028$) indicate that the contributions due to the break-up of ketone−ketone interactions clearly predominate in the mixture. The negative values for the NMP with MEK mixture compared with the NMP + MIBK mixture evidently show that MEK interacts with NMP more strongly than MIBK.

In the present work, the isobaric $T-x$ measurements were used for data reduction. The model chosen for expressing the composition−temperature dependence of the activity coefficients was the Wilson equation.

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \qquad (3)$$

$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right) \qquad (4)$$

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \qquad (5)$$

and

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left(-\frac{\lambda_{12} - \lambda_{22}}{RT}\right) \qquad (6)$$

where x_1 and x_2 are the mole fractions of ketone and NMP, respectively; γ_1 and γ_2 are the corresponding activity coef-

Table 6. Experimental Boiling Point Temperatures for the {x_1Ketone + (1 − x_1)NMP} Mixtures at 95.3 kPa and the Parameters Calculated (Calculated Boiling Point Temperatures T_{cal}, Vapor-Phase Compositions y_1, and Activity Coefficients γ_1, γ_2)

x_1	T_{exp}/K	T_{cal}/K	y_1	γ_1	γ_2	ΔT^a/K
			MEK + NMP			
0.0000	473.3	473.2	0.0000	0.4317	1.0000	−0.1
0.0725	455.4	455.7	0.4217	0.5513	0.9948	0.3
0.1524	436.4	436.1	0.7063	0.6110	0.9772	−0.3
0.3085	404.9	404.8	0.9204	0.7300	0.9112	−0.1
0.4454	385.9	385.9	0.9712	0.8265	0.8313	0.0
0.5624	374.2	374.3	0.9870	0.8946	0.7568	0.1
0.7199	363.0	363.1	0.9955	0.9592	0.6579	0.1
0.8653	355.7	355.8	0.9987	0.9912	0.5738	0.1
0.9315	353.2	353.2	0.9993	0.9978	0.5386	0.0
1.0000	350.9	350.8	1.0000	1.0000	0.4343	−0.1
			MIBK + NMP			
0.0000	473.3	473.2	0.0000	0.3970	1.0000	−0.1
0.1411	459.3	459.3	0.4195	0.5941	0.9747	0.0
0.3069	437.7	437.5	0.7683	0.7528	0.9028	−0.2
0.6055	407.0	407.0	0.9599	0.9335	0.7408	0.0
0.7287	398.8	398.9	0.9811	0.9713	0.6783	0.1
0.8430	392.9	392.9	0.9919	0.9912	0.6254	0.0
0.9233	389.5	389.5	0.9967	0.9980	0.5914	0.0
1.0000	386.7	386.6	1.0000	1.0000	0.4904	−0.1
			CH + NMP			
0.0000	473.3	473.2	0.0000	1.2041	1.0000	−0.1
0.0729	466.5	466.5	0.2215	1.2248	0.9998	0.0
0.1653	458.9	458.9	0.4281	1.2187	0.9987	0.0
0.2838	450.7	450.6	0.6118	1.2127	0.9961	−0.1
0.4421	441.5	441.4	0.7692	1.2037	0.9922	−0.1
0.6727	431.5	431.4	0.8979	1.1720	1.0138	−0.1
0.7872	428.0	428.0	0.9356	1.1366	1.0963	0.0
0.9024	425.9	425.8	0.9619	1.0760	1.5124	−0.1
0.9505	425.5	425.5	0.9703	1.0405	2.3597	0.0
1.0000	426.3	426.2	1.0000	1.0000	5.7142	−0.1

[a] $\Delta T = T_{cal} - T_{exp}$.

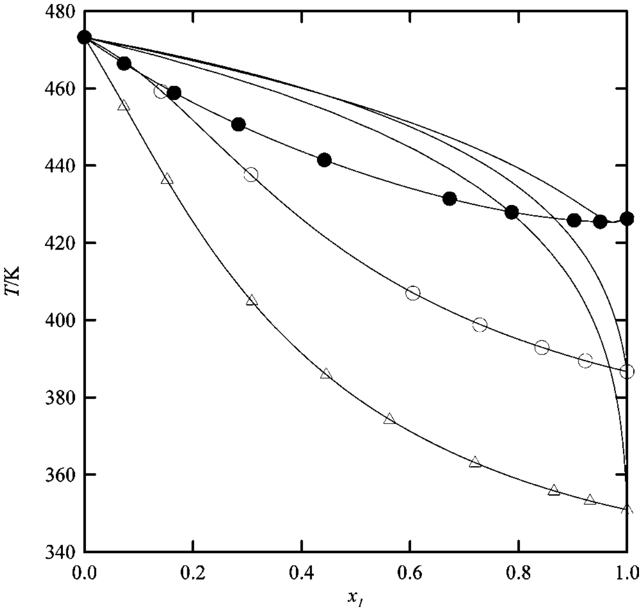

Figure 2. Boiling point temperature fraction at 95.3 kPa against mole fraction of ketone (x_1) for the following binary systems: Δ, MEK + NMP; ○, MIBK + NMP; ●, CH + NMP. Solid lines are calculated by the Wilson equation with the values of parameters given in Table 4.

ficients; and V_1^L and V_2^L are the liquid molar volumes. The ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{12} - \lambda_{22}$) are (to some extent) the temperature-independent Wilson parameters, and λ is the energy of interaction between the molecules designated by the subscripts. The optimum Wilson parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{12} - \lambda_{22}$) were obtained by minimizing the objective function F

$$F = \sum_{i=1}^{n} (T_{exp}^{(i)} - T_{cal}^{(i)})^2 \tag{7}$$

being a sum of squares between experimental and calculated boiling temperatures.

The calculated temperatures $T_{cal}^{(i)}$ were taken as a solution of the following equation

$$p = \sum_{i=1}^{2} p_i^0(T) x_i \gamma_i(T)(\phi_i^0(T)/\phi_i(T))\exp[V_i^L(p - p_i^0(T))/RT] \tag{8}$$

where $p_i^0(T)$ is the vapor pressure of pure component as a function of temperature, here expressed by the Antoine equation, and $\phi_i(T)$, $\phi_i^0(T)$ are fugacity coefficients in the vapor phase for a component in a mixture and in a pure state, respectively. The vapor-phase nonidealities were described by the virial equation of state truncated after the second coefficient with its value estimated by the Hayden−O'Connell correlation.[27] The adjusted Wilson parameters and the standard deviations are presented in Table 4.

Since the description of the isobaric vapor−liquid equilibrium data requires temperature dependencies of the saturated vapor pressures of pure components, they were determined through the direct measurements. The Antoine constants for pure NMP, MEK, MIBK, and CH were obtained by a nonlinear regression of the experimental data and are presented in Table 5.

The measured boiling point temperatures together with the values calculated resulting from the correlation are given in Table 6. The latter values include: calculated boiling point temperatures, vapor compositions, and the activity coefficients for both components. The boiling point temperature versus mole fraction curves are presented graphically in Figure 2. An examination of activity coefficients presented in this study and the excess Gibbs energies calculated on their basis show that all the systems are highly nonideal.

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