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Excess molar enthalpies of methyl isobutyl ketone (MIBK) with alkan-1-ols (C_1–C_6) and their correlations at 298.15 K

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Abstract

Excess molar enthalpies, H_m^E of methyl isobutyl ketone + methanol, +ethanol, +propan-1-ol, +butan-1-ol, +pentan-1-ol, and +hexan-1-ol have been measured at 298.15 K and atmospheric pressure with a Parr 1455 solution calorimeter. Excess molar enthalpies, H_m^E values are always positive and increase as the chain length of the alkan-1-ol is increased, showing maximum values varying from 882 (methanol) to 1510 J mol^{-1} (hexan-1-ol). The maximum values were observed about 0.5–0.6 mole fraction of methyl isobutyl ketone (MIBK). The experimental results are discussed in terms of intermolecular interactions, particularly hydrogen-bonding interactions between like and unlike molecules. The experimental data were correlated by the Redlich–Kister equation and the two local-composition models (Wilson and NRTL). The correlation of excess enthalpy data in the systems using NRTL model provides good results.

Keywords: Excess enthalpies; Alkan-1-ols; Methyl isobutyl ketone (MIBK); Wilson model; NRTL model

1. Introduction

Thermodynamic data of binary mixtures of an alcohol with a second polar component are necessary for better understanding of hydrogen bonding and for the development and testing of models and theory of associated systems in the liquid state [1–5]. Excess molar enthalpies, H_m^E have been measured for methyl isobutyl ketone (MIBK) + alkan-1-ols (C_1–C_6) at 298.15 K. This study also aims to understand the intermolecular interactions, particular hydrogen-bonding properties, between the MIBK and an alcohol with a different extent of chain length. Experimental values have been fitted to the Redlich–Kister equation to determine the binary coefficients and standard deviation. We also tested the Wilson and NRTL models for excess molar enthalpies, H_m^E to investigate which model gives best correlation of excess enthalpy and to calculate their parameters.

To our knowledge, the excess enthalpy values for all of the methyl isobutyl ketone + alkan-1-ols (C_1–C_6) mixture have not been reported in the literature.

2. Experimental

2.1. Materials

The sources of the liquid components and their purities specified by the manufacturers are summarized in Table 1. These liquids were used without further purification (stated purity ≥ 99%) with exception of hexan-1-ol, which was purified by the standard method of Perrin and Armarego [6].

The purity of solvents was further ascertained by comparing their density at 298.15 K with the corresponding literature values [7]. Densities were measured with an Anton Paar DMA 4500 oscillating U-tube densitometer with a resolution of 5×10^{-5} g cm^{-3}.

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Table 1
Source, purity grades, and densities, ρ of the pure components at 298.15 K

Component	Source	Purity (mass%)	ρ (g cm^{-3})	
			Experiment	Lit.[a]
MIBK	Merck	99	0.79619	0.7961
Methanol	Merck	99.5	0.78650	0.78664
Ethanol	Merck	99.8	0.78515	0.78504
Propan-1-ol	Merck	99.8	0.79951	0.79975
Butan-1-ol	Merck	99.8	0.80575	0.80575
Pentan-1-ol	Fluka	99	0.81088	0.81080
Hexan-1-ol	Merck	98	0.81520	0.81534

[a] Ref. [7].

2.2. Apparatus and procedure

The excess molar enthalpies H_m^E were determined using a Parr 1455 solution calorimeter. The measurements were carried out in an isolated room at 298 K and atmospheric pressure. The detailed procedures and apparatus used have been described in our earlier publications [1–2]. In measurement of excess enthalpies, known weight of 100 ml of component A is taken into Dewar vessel and about 20 ml of component B is weighted 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 component B in the rotating cell is mixed with component A in the Dewar vessel by pushing the glass rod. These experiments were continued until the concentration reached 50–60 vol.%. This procedure was repeated by taking component A as component B and component B as component A. The temperature measurement can be read to an accuracy of ±0.0002 K.

Mole fractions were determined by mass using a digital balance (AB 204-N Mettler) with an accuracy of ±0.0001 g. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$. The performance and reliability of the solution calorimeter was checked by the test mixture cyclohexane + benzene. The excess enthalpies H_m^E agreed within 1% with the reported values [8].

3. Results and discussion

Experimental excess molar enthalpies at 298.15 K of the binary mixtures of methyl isobutyl ketone with alkan-1-ols (C_1–C_6) are reported in Table 2, and are graphically presented in Fig. 1 in the form of H_m^E versus the mole fraction (x_1) of MIBK. All experimental data were fitted by a least squares methods to the Redlich–Kister equation of the type:

$$H_m^E\,(\mathrm{J\,mol^{-1}}) = x(1-x)\sum_{r=1} A_r(2x-1)^{r-1} \qquad (1)$$

where x is the mole fraction of MIBK. The coefficients A_r are the adjustable parameters and in each case the optimum number of coefficients is ascertained from examination of the variation in the standard deviation $\sigma(H_m^E)$ as given by:

$$\sigma(H_m^E) = \left|\frac{\zeta}{n-p}\right|^{0.5} \qquad (2)$$

where n is the number of experimental points and p is the number of adjustable parameters A_r. ζ is the objective function defined as:

$$\zeta = \sum \delta^2(H_m^E) \qquad (3)$$

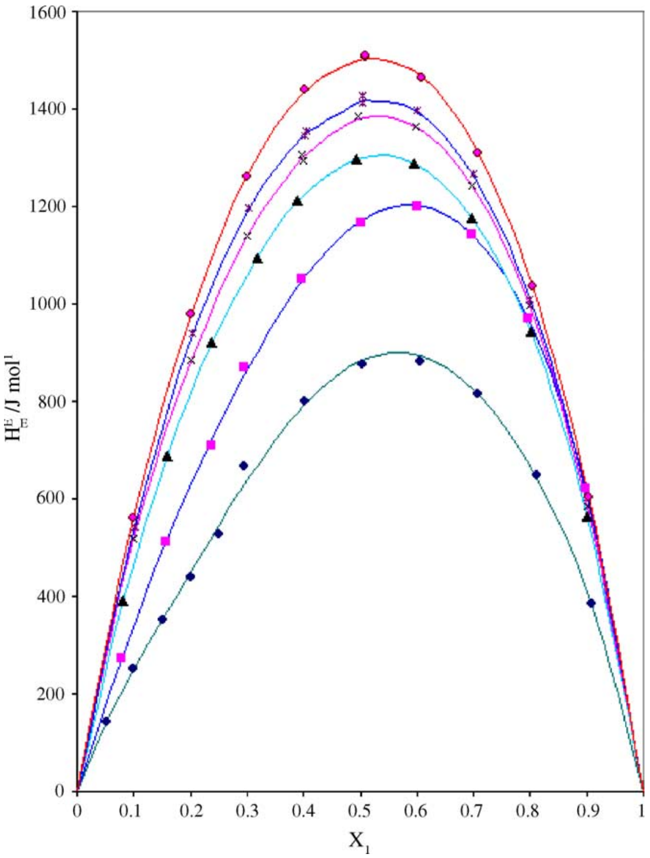

Fig. 1. Excess molar enthalpies of MIBK (1) + Alkan-1ols (2) at 298.15 K. Continuous curve calculated from Eq. (1) with parameters from Table 3. (◆) Methanol, (■) ethanol, (▲) propan-1-ol, (×) butan-1-ol, (✱) pentan-1-ol, (●) hexan-1-ol.

Table 2
Excess molar enthalpies H_m^E for the binary systems of MIBK + alkan-1-ols at 298.15 K

x_1	H_m^E (J mol^{-1})			x_1	H_m^E (J mol^{-1})		
	Experiment	Wilson	NRTL		Experiment	Wilson	NRTL
MIBK (1) + methanol (2)							
0.0523	142.2	154.0	130.5	0.4019	801.3	761.7	785.8
0.0998	252.8	273.6	243.6	0.5037	875.0	832.8	871.5
0.1502	351.1	384.7	356.8	0.6059	882.6	847.2	888.7
0.2002	440.1	481.9	461.5	0.7070	816.1	791.6	823.1
0.2495	527.9	566.5	556.5	0.8119	650.0	638.8	650.2
0.2954	665.7	635.9	636.6	0.9080	383.8	384.4	379.1
MIBK (1) + ethanol (2)							
0.0772	271.4	268.4	269.4	0.5000	1166.3	780.1	1163
0.1571	512.2	445.6	514.5	0.5995	1200.1	778.0	1202.2
0.2369	708.2	572.8	725.6	0.6981	1141.9	721.5	1147.1
0.2947	868.6	643.8	856.8	0.7954	970.3	597.8	972.4
0.3977	1050.2	734.3	1043.9	0.8970	622.2	371.9	616.3
MIBK (1) + propan-1-ol (2)							
0.0797	390.6	273.0	380.0	0.4948	1297	731.1	1298.1
0.1587	686.7	441.7	682.6	0.5955	1286.5	725.3	1288.3
0.2384	920.3	558.9	921.3	0.6981	1176.9	668.4	1176.0
0.3192	1094.9	642.6	1102.0	0.8004	942.3	545.4	942.0
0.3901	1213.3	692.9	1213.1	0.9012	563.4	334.3	561.3
MIBK (1) + butan-1-ol (2)							
0.1005	517.0	319.6	508.3	0.4967	1384.2	704.6	1380.0
0.1998	885.5	499.9	879.9	0.5978	1365.1	694.4	1361.0
0.2999	1137.9	612.0	1143.4	0.6981	1242.7	639.5	1238.4
0.3967	1305.4	676.2	1304.5	0.7978	995.8	527.3	996.3
0.3996	1293.7	677.5	1308.0	0.9006	585.0	325.8	590.3
MIBK (1) + pentan-1-ol (2)							
0.1008	543.2	318.8	539.9	0.5035	1410.6	692.4	1418.7
0.2043	937.9	505.6	936.9	0.6017	1396.3	676.8	1390.4
0.3040	1195.8	612.5	1196.9	0.7007	1266.1	620.4	1261.6
0.4030	1345.6	671.3	1353.8	0.7996	1010.6	511.0	1013.7
0.4035	1355.5	671.5	1354.3	0.9002	603.1	320.6	607.4
0.5030	1427.3	692.4	1418.6				
MIBK (1) + hexan-1-ol (2)							
0.0995	561.4	316.1	560.2	0.5096	1506.5	688.6	1507.2
0.2004	977.4	502.8	976.7	0.6091	1463.0	667.6	1463.4
0.3015	1261.9	612.6	1264.8	0.7086	1310.0	606.7	1307.9
0.4029	1438.0	670.9	1439.1	0.8049	1036.9	498.6	1035.5
0.5082	1510.5	688.6	1507.0	0.903	602.9	313.3	608.0

where

$$\delta(H^E) = H^E_{m,\text{expt.}} - H^E_{m,\text{calc.}}$$

The adjustable parameters A_r and standard deviation, σ are given in Table 3.

The excess molar enthalpies for the all systems are positive (endothermic) over the entire range of composition of MIBK at 298.15 K. For these binary systems, the H_m^E values around 0.50–0.60 mole fraction of MIBK increase in the order: methanol < ethanol < propan-1-ol < butan-1-ol < pentan-1-ol < hexan-1-ol.

Since alkan-1-ols are strongly associated through hydrogen bonding, dilution with a polar solvent, like MIBK, results changes in thermodynamic function which may be due to: (i) the break up of hydrogen bonds with diluent; and (ii) break up dipole–dipole interaction between MIBK molecules which have large dipole moment (13.11 Debye); and (iii) the formation of new species acting as an adduct between the alkan-1-ols and MIBK. The observed positive excess enthalpies of mixing indicate that the dissociation of the associated species of the alkan-1-ols on dilution with MIBK is the dominating force. The value of excess enthalpies indicate that the degree of an association of MIBK + alkan-1-ol is dependent on the alkyl chain length of alkan-1-ol, with the greatest association between the MIBK and the alkan-1-ol with the shortest carbon chain. A packing effect in the liquid state between chain-like molecules of alkan-1-ols (C_1–C_6) is mainly responsible for the endothermic behavior [9].

Table 3
Redlich–Kister equation fitting coefficients A_r in Eq. (1) and standard deviation, $\sigma(H_m^E)$ in Eq. (2) for MIBK (1) + alkan-1-ols (2) at 298.15 K

System	A_r	A_2	A_3	A_4	A_5	$\sigma(H_m^E)$ (J mol^{-1})
MIBK (1) + methanol(2)	3534.9	1106.4	−551.8	24.8	1210.7	43.7
MIBK (1) + ethanol (2)	4677.2	1548.6	502.9	467	704.2	17.1
MIBK (1) + propan-1-ol (2)	5197.3	675	678.2	−25.2	403.3	5.7
MIBK (1) + butan-1-ol (2)	5521.4	624.1	888.3	−193.5	92.1	12.1
MIBK (1) + pentan-1-ol (2)	5674.7	485	1008.5	−68.8	78.5	14.6
MIBK (1) + hexan-1-ol (2)	6022.1	423	903.8	−64.1	−68.1	5.5

4. Correlations

In order to represent excess enthalpy as a function of temperature and composition at constant pressure, some kind of thermodynamic model is required. Typical excess enthalpy models contain parameters that are fitted to experimental data on binary mixtures and then used to predict similar data in a multi component system. In this study two kinds of local composition models (Wilson and NRTL) are tested.

4.1. Wilson equation

The model proposed by Wilson [10] in 1964 is based on the concept of local composition. Wilson recognized that in a mixture with specific interaction the distribution of molecules is not purely random and that non-ideal mixing is associated with this fact. The composition in the immediate vicinity of a molecule of species 1 will not usually be the same as the mean bulk composition. Instead, Wilson suggested that the local composition x_{11} and x_{21} of components 1 and 2 around a molecule of species 1 are given by Boltzman weighted average of the bulk mole fractions.

Accordingly the ratio of the two local compositions is:

$$\frac{x_{21}}{x_{11}}=\frac{x_2\ \exp(-a_{21}/RT)}{x_1\ \exp(-a_{11}/RT)} \tag{4}$$

with a_{21} and a_{11} representing the different interaction energies.

With this relation the following expression for H^E is obtained:

$$\frac{H^E}{x_1x_2}=\frac{\lambda_{12}\Lambda_{12}}{x_1+\Lambda_{12}x_2}+\frac{\lambda_{21}\Lambda_{21}}{\Lambda_{21}x_1+x_2} \tag{5}$$

where $\Lambda_{12}=(V_2/V_1)\ \exp(-\lambda_{12}/RT)$, $\Lambda_{21}=(V_1/V_2)\ \exp(-\lambda_{21}/RT)$, $\lambda_{12}=a_{21}-a_{11}$, $\lambda_{21}=a_{12}-a_{22}$, and $a_{12}=a_{21}$, where V_i is molar volume.

4.2. NRTL equation

In order to take into account the “structure” of the liquid generated by the electrostatic force field of individual molecules, the local composition expression suggested by Wilson is modified [11]:

$$\frac{x_{21}}{x_{11}}=\frac{x_2\ \exp(-\alpha_{21}g_{21}/RT)}{x_1\ \exp(-\alpha_{21}g_{11}/RT)} \tag{6}$$

where g_{21} and g_{11} indicate the different interaction energies. The non-randomness parameter α_{21} is an empirical constant. So for each binary system we used appropriate value of α_{21} which standard deviation could be minimized.

The following expression for H_m^E is obtained with this relation

$$H^E(x)=-x_1x_2\times\left[\frac{Z_1N_1\alpha_{12}\Delta g_{21}-\Delta g_{21}G_{21}N_1-Z_1x_2G_{21}\alpha_{12}\Delta g_{21}}{N_1^2}+\frac{Z_2N_2\alpha_{12}\Delta g_{12}-\Delta g_{12}G_{12}N_2-Z_2x_1G_{12}\alpha_{12}\Delta g_{12}}{N_2^2}\right] \tag{7}$$

where $\Delta g_{21}=g_{21}-g_{11}$; $\Delta g_{12}=\Delta g_{12}-g_{22}$; $G_{21}=\exp(-\alpha_{12}\Delta g_{21}/RT)$; $N_1=x_1+x_2G_{21}$; $N_2=x_2+x_1G_{12}$; $G_{12}=\exp(-\alpha_{12}\Delta g_{12}/RT)$; $Z_1=(\Delta g_{21}/RT)G_{21}$; $Z_2=(\Delta g_{12}/RT)G_{12}$; Δg_{12} and Δg_{21} are the two adjustable parameters remaining, because the randomness parameters α_{21} were taken to be con-

Table 4
Parameters (λ_{21}, λ_{12}, Δg_{21}, Δg_{12})[a] and $\alpha_{12}=\alpha_{21}$ used in Eqs. (5) and (7) for calculating H_m^E derived at 298.15 K

System	λ_{21}	λ_{12}	Δg_{21}	Δg_{12}	α_{ij}	σ	
						Wilson	NRTL
MIBK (1) + methanol (2)	4881.96	1129.84	−994.77	5907.15	0.1	104.3	45.3
MIBK (1) + ethanol (2)	4087.25	2922.19	2081.44	6148.27	0.22	918.2	20.6
MIBK (1) + propan-1-ol (2)	3700.11	3153.65	3617.06	5099.38	0.23	1399.5	10.3
MIBK (1) + butan-1-ol (2)	3538.70	3210.05	4058.27	5300.37	0.22	1780.3	18.8
MIBK (1) + pentan-1-ol (2)	3414.78	3265.47	4512.45	5514.06	0.22	2066.2	16.4
MIBK (1) + hexan-1-ol (2)	3391.57	3325.43	4510.56	5395.62	0.2	2157.6	6.7

[a] Unit: J mol^{-1}.

stant for each binary mixtures studied here. The adjustable parameters λ_{21} and λ_{12} in Wilson equation and Δg_{21}, Δg_{12}, and α_{21} in NRTL equation were obtained by non-linear least square fit and are summarized in Table 4. The H_m^E values from Wilson and NRTL equations are calculated and included Table 2. For all mixtures, good agreement between experimental and calculated results using Redlich–Kister polynomials is obtained. As $H_m^E - x$ curves are symmetric and components are polar, NRTL equation provides to fit the experimental data with good accuracy, whereas in the case of Wilson model deviation appears.

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