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Excess molar enthalpies of *n*-alkanols or isomeric alkanols + *N*,*N*-dimethylethanolamine at 298.15 K [☆]

Huai-Yu Yang [a], Jian-Ping Zhao (J.P. Chao) [b], Hong-Ping Li [c], Ming Dai [c,*],

[a] *Institute of Corrosion and Protection of Metals, Academia Sinica, Shengyang 110015, People's Republic of China*
[b] *Chemistry Department, Memorial University of Newfoundland, St. John's, NF, A1B 3X7, Canada*
[c] *Research Laboratory of Solution Chemistry, Henan Institute of Chemistry, Zhengzhou 450003, People's Republic of China*

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Abstract

Excess molar enthalpies H^E measured at 298.15 K with a Picker flow microcalorimeter are reported for methanol+, ethanol+, *n*-propanol+, *n*-butanol+, *n*-pentanol+, *n*-hexanol+, iso-propanol+, iso-butanol+, *sec*-butanol+ and *tert*-butanol + *N*,*N*-dimethylethanolamine. The experimental results have shown that for the binary mixtures containing one of the *n*-alkanols (C_1–C_6), excess molar enthalpies are all negative over the entire composition range and increase with lengthening of the alkyl chain of the alkanol. For the mixtures containing an isomeric alkanol, excess molar enthalpies for each isomeric butanol are negative, but for iso-propanol H^E values are positive except for the mixtures approaching the pure alkanol. Based on our experimental results, a brief discussion is given in terms of molecular interactions.

Keywords: Alkanol; Dimethylethanolamine; Excess molar enthalpy

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1. Introduction

Alcohols are strongly self-associated and the properties and structures of binary mixtures containing an alcohol have been the subject of considerable interest. As is

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* Corresponding author.

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well known, the thermodynamic properties of mixtures of an alcohol with a polar compound depend upon the degree of association of each component in the pure state, the structure breaking ability of the components and possible hydrogen bonding interaction between unlike molecules [1]. As a part of the investigation, we have previously studied excess molar enthalpies of (an alkanol + a polar or nonpolar solvent) [2–5].

Ethanolamine is a bifunctional organic compound having hydroxyl and amino groups. Molecules of ethanolamine can form self-associates through intramolecular and intermolecular interactions and also cross-associates with various molecules having polar groups [6]. Excess molar enthalpies and volumes of binary mixtures of ethanolamine with an alcohol have been studied [7]. In this work, we have investigated further the excess molar enthalpies of *N*,*N*-dimethylethanolamine + an alkanol (CH_3OH to $C_6H_{13}OH$) or branched alkanol, and present the results with a brief discussion.

2. Experimental

Excess molar enthalpies H^E were measured with a Picker flow microcalorimeter at 298.15 K and under atmospheric pressure. The principle of the apparatus and operating procedure have been described previously [8]. The performance of the calorimeter was checked regularly by determining the excess molar enthalpies of some thoroughly investigated test mixtures. The results obtained with $x = 0.5$ mixtures agree to within 1% with those of Grolier [9]. All measurements were made at an average temperature of 298.15 ± 0.0005 K.

All alkanols were the same as those used in the previous work [3] and *N*,*N*-dimethylethanolamine was from Shanghai Chemical Co. (analytical grade) and purified by fractional distillation. The density of the purified *N*,*N*-dimethylethanolamine was measured with a Paar DMA 602 digital densimeter; its value ($0.87954\ \mathrm{cm^3\ mol^{-1}}$) at 298.15 K agrees with that reported in the literature [10].

3. Results and discussion

The excess molar enthalpies H^E for the ten binary mixtures $(xC_nH_{2n+1}OH + (1-x)(CH_3)_2NC_2H_4OH)$ for $n = 1, 2, 3, 4, 5$ and 6 and $(x\text{iso-}C_3H_7OH$ or $x\text{iso-}C_4H_9OH$ or $x\textit{sec-}C_4H_9OH$ or $x\textit{tert-}C_4H_9OH + (1-x)(CH_3)_2NC_2H_4OH)$ are listed in Table 1. Excess molar enthalpies of these mixtures are plotted as functions of the alkanol composition in Figs. 1 and 2. For the mixtures studied here, no data at 298.15 K could be found in the literature.

The experimental data of H^E were fitted to a smoothed equation

$$H^E/(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \qquad (1)$$

where x is the mole fraction of alkanols. The values of parameters A_i evaluated by the method of least squares are given in Table 2 along with the standard deviations

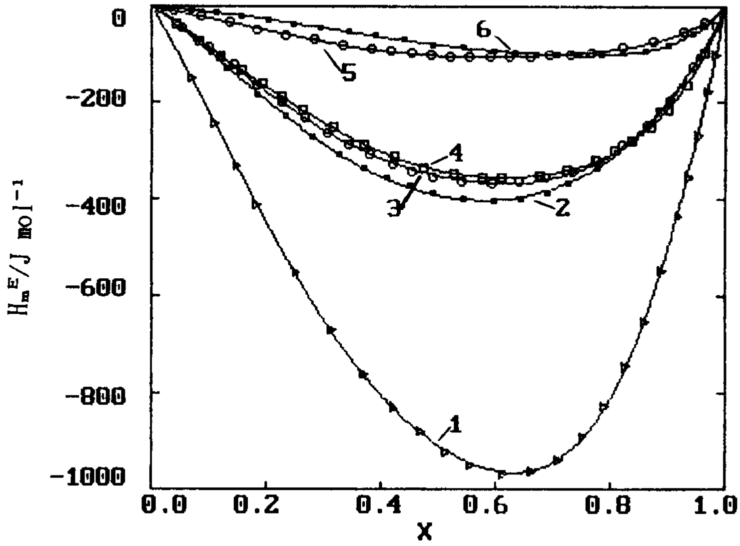

Fig. 1. Excess molar enthalpies of $(xC_nH_{2n+1}OH + (1-x)(CH_3)_2NC_2H_4OH)$ at 298.15 K. Curve 1, methanol; curve 2, ethanol; curve 3, *n*-propanol; curve 4, *n*-butanol; curve 5, *n*-pentanol; curve 6, *n*-hexanol. The curves were calculated from Eq. (1) with coefficients from Table 2.

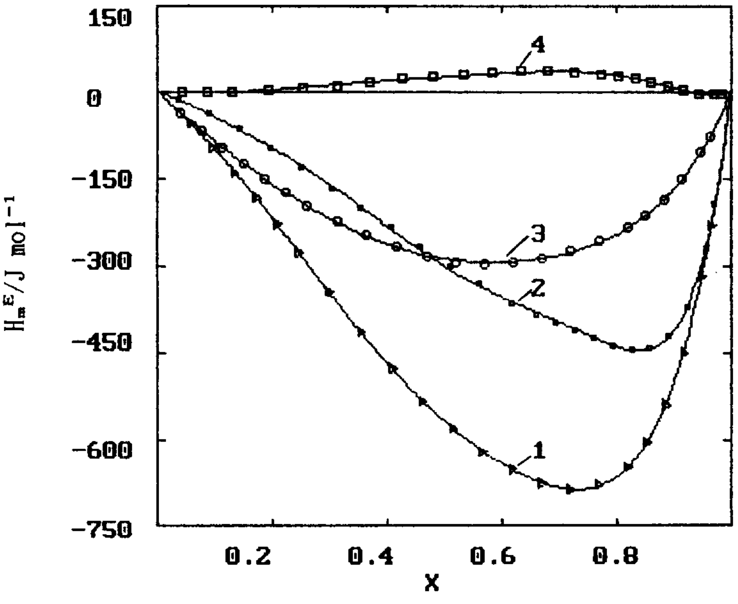

Fig. 2. Excess molar enthalpies of (an isomeric alkanol + *N*,*N*-dimethylethanolamine) at 298.15 K. Curve 1, *sec*-butanol; curve 2, *tert*-butanol; curve 3, iso-butanol; curve 4, iso-propanol.

Table 1

Experimental excess molar enthaplies H^E for an alkanol + N,N-dimethylethanolamine at 298.15 K

x	H_m^E/ (J mol^{-1})	x	H_m^E/ (J mol^{-1})	x	H_m^E/ (J mol^{-1})	x	H_m^E/ (J mol^{-1})
$(1-x)N,N$-Dimethylethanolamine + xMethanol							
0.0682	−147.5	0.3675	−758.9	0.6609	−964.9	0.8878	−548.0
0.1081	−245.2	0.4194	−830.5	0.7074	−939.6	0.9160	−436.1
0.1460	−332.3	0.4674	−880.6	0.7498	−893.4	0.9338	−354.4
0.1821	−412.8	0.5118	−924.1	0.7887	−827.6	0.9507	−269.5
0.2495	−550.7	0.5531	−951.4	0.8244	−745.8	0.9669	−176.8
0.3110	−669.2	0.6097	−972.7	0.8573	−652.9	0.9823	−98.8
$(1-x)N,N$-Dimethylethanolamine + xEthanol							
0.0753	−68.5	0.3250	−306.0	0.5951	−403.8	0.8524	−262.8
0.1030	−96.6	0.3685	−334.5	0.6439	−399.0	0.8835	−217.2
0.1300	−126.1	0.4103	−356.8	0.6901	−387.1	0.9223	−162.0
0.1822	−182.2	0.4502	−373.5	0.7281	−368.0	0.9548	−104.0
0.2320	−229.8	0.4886	−388.0	0.7754	−337.0		
0.2795	−272.2	0.5434	−400.6	0.8097	−303.8		
$(1-x)N,N$-Dimethylethanolamine + xn-Propanol							
0.0545	−42.5	0.3051	−262.2	0.5416	−363.5	0.8210	−289.3
0.0987	−84.3	0.3437	−287.9	0.5917	−366.4	0.8630	−248.4
0.1419	−118.4	0.3814	−309.6	0.6403	−364.3	0.9039	−195.0
0.1841	−164.6	0.4184	−328.3	0.6875	−356.4	0.9436	−123.0
0.2254	−201.0	0.4545	−343.4	0.7333	−342.0	0.9823	−41.0
0.2657	−232.8	0.4900	−354.2	0.7778	−319.5		
$(1-x)N,N$-Dimethylethanolamine + xn-Butanol							
0.0449	−37.3	0.2640	−214.6	0.5758	−356.4	0.8054	−301.8
0.0821	−72.2	0.3173	−252.8	0.6092	−357.6	0.8690	−250.0
0.1190	−102.8	0.3701	−286.1	0.6755	−352.0	0.9005	−214.2
0.1556	−132.4	0.4223	−313.7	0.7246	−341.2	0.9318	−163.9
0.1920	−161.6	0.4740	−334.4	0.7732	−320.7	0.9629	−97.5
0.2281	−188.8	0.5251	−349.2	0.8373	−278.1		
$(1-x)N,N$-Dimethylethanolamine + xn-Pentanol							
0.0385	−9.1	0.3337	−79.3	0.5549	−104.0	0.7652	−95.1
0.0868	−21.0	0.3842	−89.0	0.5895	−105.2	0.8187	−85.6
0.1355	−33.8	0.4180	−93.2	0.6243	−105.0	0.8726	−72.1
0.1846	−46.2	0.4520	−97.2	0.6593	−103.9	0.9270	−51.5
0.2339	−58.1	0.4861	−99.9	0.6944	−101.9	0.9634	−31.8
0.2837	−69.2	0.5204	−102.4	0.7297	−99.2		
$(1-x)N,N$-Dimethylethanolamine + xn-Hexanol							
0.0277	−2.9	0.2945	−43.7	0.5967	−92.6	0.8215	−97.5
0.0700	−7.3	0.3423	−52.7	0.6328	−96.5	0.8610	−91.5
0.1131	−12.8	0.3910	−61.5	0.6694	−99.2	0.9011	−80.0
0.1571	−19.1	0.4408	−69.8	0.7066	−100.6	0.9419	−55.9
0.2020	−26.7	0.4916	−78.0	0.7443	−101.4	0.9625	−39.7
0.2478	−34.9	0.5436	−85.8	0.7826	−100.7		

Table 1 (continued)

x	H_m^E/ (J mol^{-1})	x	H_m^E/ (J mol^{-1})	x	H_m^E/ (J mol^{-1})	x	H_m^E/ (J mol^{-1})
$(1-x)N,N$-Dimethylethanolamine + $x$iso-Propanol							
0.0448	0.14	0.3709	16.4	0.6811	35.1	0.8893	10.8
0.0866	0.64	0.4264	22.8	0.7279	33.4	0.9169	3.6
0.1315	1.6	0.4803	25.2	0.7735	30.4	0.9442	−2.7
0.1941	4.1	0.5327	28.9	0.8032	27.4	0.9710	−4.6
0.2549	7.1	0.5835	31.9	0.8324	23.1	0.9843	−3.1
0.3138	10.9	0.6330	35.2	0.8611	17.7		
$(1-x)N,N$-Dimethylethanolamine + $x$iso-Butanol							
0.0408	−36.4	0.2585	−195.8	0.5708	−295.5	0.8509	−212.9
0.0776	−67.9	0.3118	−223.1	0.6212	−292.7	0.8830	−185.5
0.1143	−97.1	0.3645	−246.5	0.6712	−286.1	0.9148	−149.5
0.1507	−123.9	0.4168	−266.6	0.7208	−274.5	0.9465	−104.1
0.1868	−150.9	0.4686	−282.3	0.7699	−258.2	0.9623	−77.9
0.2228	−174.4	0.5199	−292.4	0.8187	−233.4		
$(1-x)N,N$-Dimethylethanolamine + x*sec*-Butanol							
0.0572	−54.3	0.2987	−343.8	0.6165	−651.5	0.8839	−538.5
0.0951	−95.5	0.3530	−413.9	0.6676	−674.9	0.9164	−448.4
0.1326	−139.5	0.4067	−475.5	0.7184	−685.4	0.9487	−316.2
0.1700	−182.2	0.4599	−532.4	0.7686	−677.6	0.9648	−229.6
0.2071	−227.8	0.5126	−579.9	0.8183	−646.8		
0.2439	−275.2	0.5648	−620.8	0.8512	−604.3		
$(1-x)N,N$-Dimethylethanolamine + x*tert*-Butanol							
0.0361	−13.7	0.3542	−200.6	0.6603	−381.7	0.8580	−439.5
0.0900	−35.9	0.4060	−234.7	0.6936	−395.8	0.8905	−419.9
0.1435	−63.2	0.4575	−267.8	0.7267	−410.5	0.9229	−371.0
0.1967	−96.4	0.5087	−300.1	0.7598	−424.1	0.9551	−270.1
0.2495	−130.8	0.5595	−330.9	0.7927	−435.1	0.9712	−193.5
0.3020	−165.1	0.6150	−362.2	0.8254	−443.3		

$$S = \left[\frac{(H^E_{\text{exp}} - H^E_{\text{calc}})^2}{n-m}\right]^{1/2} \tag{2}$$

with n data points and m parameters.

As can be seen from Fig. 1, excess molar enthalpies for all mixtures containing a normal alcohol are negative over the entire composition range at 298.15 K, and increase in the sequence methanol < ethanol < propan-l-ol < butan-l-ol < pentan-l-ol < hexan-l-ol.

As we know, the alkanols are self-associated through hydrogen bonding interactions, and N,N-dimethylethanolamine is also self-associated mainly through O–H···O owing to the steric effect. The cleavage of hydrogen bonded aggregates upon mixing provides a positive contribution to V^E; the formation of cross-associates between N,N-dimethylethanolamine and alkanol provides a negative contribution.

Table 2
Coefficients A_i of Eq. (1) and standard deviations S

System	A_0	A_1	A_2	A_3	A_4	A_5	S
$(1-x)(CH_3)_2NCH_4OH$							
$+xCH_3OH$	−3642.7	1581.8	−1168.4	1146.8	926.9	−965.7	4.2
$+xC_2H_5OH$	−1572.1	474.3	−86.3	392.7			2.6
$+xn$-C_3H_7OH	−1412.4	527.5	−394.6	389.8	269.9		3.0
$+xn$-C_4H_9OH	−1364.1	526.7	−195.6	558.6	−399.3		1.8
$+xn$-$C_5H_{11}OH$	−408.8	118.3	14.1	255.8	−229.1		1.1
$+xn$-$C_6H_{13}OH$	−318.8	281.6	−127.0	299.2	−244.1		0.7
$+x$iso-C_3H_7OH	102.1	−126.2	133.6	−176.0	−362.3	470.0	1.2
$+x$iso-C_4H_9OH	−1148.9	301.8	−208.9	410.4	−291.7		1.2
$+xsec$-C_4H_9OH	−2273.1	1728.5	−967.9	1617.9	−1050.6		1.5
$+xtert$-C_4H_9OH	−1202.9	1218.6	−312.2	870.9	−2735.3	1890.7	2.9

The actual value of H^E will depend on the balance between these two opposite contributions. It seems that the interaction forces between unlike molecules are stronger as compared to those between like molecules, and therefore H^E values of the binary mixtures studied are negative. Furthermore, the enhancement in interaction between unlike molecules may be due to dipole-induced dipole interaction which is proportional to the polarizability of the alkanol molecule. From the work of Yadav and Yadav [11], the polarizability decreases with increase in number of carbon atoms in the alkanol and the above sequence of H^E value increasing with alkanol can be explained in terms of this evidence.

The excess molar enthalpies of mixtures of *N,N*-dimethylethanolamine with an alkanol are lower than those of ethanolamine with the corresponding alkanol at the same temperature. This is similar to H^E values of ethanolamine or its methyl derivative with water because of the introduction of two methyl groups in the ethanolamine molecule [12].

For the isomeric alkanols, excess molar enthalpies of each of *N,N*-dimethylethanolamine + one of the three isomeric butanols are all negative, but for *N,N*-dimethylethanolamine + iso-propabol H^E values are positive except for those approaching the pure alkanol. The results reveal that the branched chain, the position of hydroxyl group and steric effects are important factors in determining the excess molar enthalpies of these mixtures.

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