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Excess molar enthalpies for binary mixtures of different amines with water

Ruilei Zhang [a,b], Jian Chen [b,*], Jianguo Mi [a,*]

[a] State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
[b] State Key Laboratory of Chemical Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

The isothermal excess molar enthalpies for binary mixtures of different amines with water were measured with a C-80 Setaram calorimeter. The experimental results indicate that the excess molar enthalpy is related to the molecular structure. The experimental excess molar enthalpies were satisfactorily fitted with the Redlich–Kister equation. They were also used to test the suitability of the NRTL model, and the deviations are a little larger than the R–K equation.

1. Introduction

Excess molar enthalpy (H^E) is an essential thermodynamic property of solutions that is used to determine the molecular interactions and macroscopic behavior of fluid mixtures. As one of the major signs of non-ideality for solution, it reflects the change of the interactions for different molecules during the mixing process [1]. Excess molar enthalpy is useful to determine heat loads, and to design distillation units [2]. Therefore, the determination of H^E provides important thermodynamic data necessary for the proper design of the chemical process. Furthermore, excess molar enthalpy can accurately determine the (vapor + liquid) equilibria data within a reasonable range through the Gibbs–Helmholtz equation [3,4]. In addition, excess molar enthalpy has been used to test the feasibility of existing solution theories [5,6].

Alkanolamines and alkylamines are the most common solvents which are extensively used in the removal of acid gas impurities such as carbon dioxide, hydrogen sulfide, and sulfur dioxide (SO_2) from gas streams [7]. There is a constant need for the excess molar enthalpies of alkanolamines and alkylamine with water in order to support the design of absorption and stripping columns. Excess molar enthalpies of (monoethylethanolamine, MMEA, +H_2O), (diethylethanolamine, DEEA, +H_2O), (*n*-propylethanolamine, *n*-PEA, +H_2O), and (2-amino-2-methyl-1-propanol, AMP + H_2O) were studied by Mathonat [8]. Maham reported the excess molar enthalpies of (ethyldiethanolamine, EDEA, +H2O), and (*n*-butyldiethanolamine, *n*-BDEA, +H2O) at T = (298.15, 318.15, and 338.15) K [9]. The molar excess enthalpies for 2-{(2-aminoethyl)amino}ethanol (AEEA), 3-amino-1-propanol (AP), 2-(methylamino)ethanol (MAE), 1-amino-2-propanol (MIPA), and N-N-dimethylethanolamine (DMEA) in water are reported at T = (298.15, 313.15, and 323.15) K [10]. In this work experimental measurements were performed to determine excess molar enthalpies of binary mixtures of ten amines with water at T = (303.15 and 323.15) K, at atmospheric pressure. The measured H^E values were correlated as a function of molar fractions using the Redlich–Kister (RK) equation. The non-random two-liquid model (NRTL) based on the local composition theory was also used to examine the suitability of the model to generate H^E values by correlating the experimental H^E data with solution compositions.

2. Experimental

2.1. Materials

The molecular formula, CAS number, purity and source were reported in table 1. The solution was prepared by ultrapure water, which was taken from the Center 120 FV-S ultrapure water

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* Corresponding authors.
E-mail addresses: cj-dce@mail.tsinghua.edu.cn (J. Chen), mijg@mail.buct.edu.cn (J. Mi).

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TABLE 1
Chemical substances employed in this work.

Component	Abbreviation	Molecular formula	CAS number	Purity (mass fraction %)	Source
Diethanolamine	DEA	$C_4H_{11}NO_2$	111-42-2	99	Sinopharm Chemical
Diethylenetriamine	DETA	$C_4H_{13}N_3$	111-40-0	99	J&KScientific
3,3'-Diaminobispropylamine	DPTA	$C_6H_{17}N_3$	56-18-8	99	J&KScientific
Triethylenetetramine	TETA	$C_6H_{18}N_4$	112-24-3	>97	J&KScientific
N,N,N′,N″,N″-Pentamethyldiethylenetriamine	PMDETA	$C_9H_{23}N_3$	3030-47-5	99	J&KScientific
N,N-Diethylethanolamine	DEEA	$C_6H_{15}NO$	100-37-8	>98	J&KScientific
Dimethylaminopropanol	DMAP	$C_5H_{13}NO$	3179-63-3	99	J&KScientific
Diglycolamine	DGA	$C_4H_{11}NO_2$	929-06-6	98	J&KScientific
Triethanolamine	TEA	$C_6H_{15}NO_3$	102-71-6	99	J&KScientific
2-(2-Aminoethylamino)ethanol	AEEA	$C_4H_{12}N_2O$	111-41-1	99.5	J&KScientific
N-Methyl-N-(N,N-Dimethylaminoethyl)-Aminoethanol	DMEAE	$C_7H_{18}N_2O$	2212-32-0	98	J&KScientific

machine. The resistivity of ultrapure water is 18.2 MΩ · cm at 298.15 K. All reagents, were used as supplied without any further purification.

2.2. Apparatus and procedure

The excess enthalpies were measured directly by a C-80 Setaram calorimeter at atmospheric pressure. A Mettler-Toledo AL 204 digital balance (weighing accuracy ±0.1 mg) was used to weigh the pure component masses. The uncertainties of molar fractions measuring were 0.0002. The C-80 Setaram calorimeter was equipped with membrane mixing cells. The C-80 Setaram calorimeter used calvet type heat-flow for all measurements (Setaram, France). The actual temperatures of each measurement were within ±0.05 K of the stated T = (303.15, and 323.15) K. The uncertainties of measured molar excess enthalpies were 0.02 (K = 2, with 0.95 level of confidence) [11]. Further details regarding the experimental method of calorimeter operation can be found elsewhere [12]. The operating range of the C-80 calorimeter is from ambient temperature to 573.15 K. The calorimeter was calibrated by measuring the phase change temperature of Tin (purity 99.999%), which has a well-known precise transition temperature. The accuracy of the apparatus was verified by determining H^E of DEA + H_2O at 298.15 K and atmospheric pressure. The H^E value for DEA + H_2O at 298.15 K are list in table 2. The results obtained are in good agreement with the previously reported data [13], and the comparison are list in figure 1. The biggest error is 1.0%. The reliability of the apparatus has been described in detail elsewhere [14].

3. Results and discussion

Ten excess molar enthalpies of aqueous solutions of DETA, DPTA, TETA, PMDETA, DEEA, DMAP, DGA, TEA, AEEA, and DMEAE were measured using a C-80 Setaram calorimeter. The excess molar values obtained by calorimetry are listed in tables 3 and 4, and shown graphically in figures 2–9. In all binary systems, x_1 is the molar fraction of water. All of the excess enthalpies are large and negative over the entire range of molar fractions. The curves of excess molar enthalpies vs. composition vary asymmetrically. The maximum negative values are (−6727 J/mol at x_2 = 0.3030), (−6648 J/mol at x_2 = 0.2828), (−6816 J/mol at x_2 = 0.2525), (−4533 J/mol at x_2 = 0.2072), (−2617 J/mol at x_2 = 0.3870), (−2895 J/mol at x_2 = 0.3515), (−2351 J/mol at x_2 = 0.3232), (−1402 J/mol at x_2 = 0.3030), (−4006 J/mol at x_2 = 0.3535), and (−3741 J/mol at x_2 = 0.2500) respectively for mixtures: {DETA (2) + H_2O (1)}, {DPTA (2) + H_2O (1)}, {TETA (2) + H_2O (1)}, {PMDETA (2) + H_2O (1)}, {DEEA (2) + H_2O (1)}, {DMAP (2) + H_2O (1)}, {DGA (2) + H_2O (1)}, {TEA (2) + H_2O (1)}, {AEEA (2) + H_2O (1)}, and {DMEAE (2) + H_2O (1)}. The comparison with available literature data for DEEA [8], TEA [13], and AEEA [10] have been added in figures 2 and 4. Because the literature data are measured at 298.15 K, the measurement H^E value is slightly higher than our work. The result is consistent with the tendency that H^E increase with decreasing the temperature.

TABLE 2
Experimental results of the excess molar enthalpies at 298.15 K and 0.1 MPa.[a]

x_2	H^E/(J · mol^{-1})	x_2	H^E/(J · mol^{-1})
	DEA(2) + water(1)		
0.05035	−546	0.3974	−2053
0.1001	−1115	0.4915	−1947
0.1989	−1714	0.599	−1591
0.2023	−1736	0.7038	−1274
0.2958	−2027	0.795	−932
0.3428	−2066	0.9029	−414

[a] Standard uncertainties $u(x_2)$ = 0.0002, $u(T)$ = 0.1 K, $u(P)$ = 3 kPa and expanded uncertainty $U_r(H^E)$ = 0.02 (the standard coverage factor K = 2, 0.95 level of confidence).

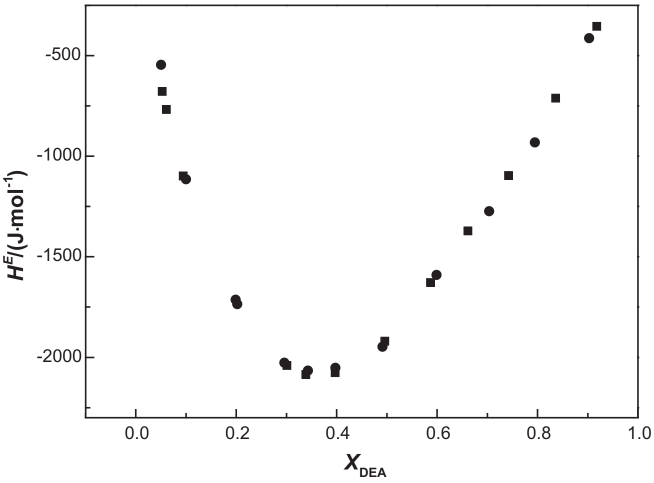

FIGURE 1. Excess molar enthalpy H^E as a function of mole fraction x_2 for the binary mixtures {DEA (2) + H_2O (1)} at 298.15 K. ●, the results of this work; ■, the result of reference [13].

3.1. Correlation with the Redlich–Kister equation

The relationship between H^E and the molar fraction of solute (x_2) can be fitted with the following smoothing function [15–17]

$$H^E = x_2(1 - x_2)\sum A_n(1 - 2x_2)^{n-1}. \tag{1}$$

The fitting parameters A_n are determined by least-squares analysis with all points weighted equally. n is the number of fitted parameters. The value of n is mainly determined by the deviation with which calculations can be made [18].