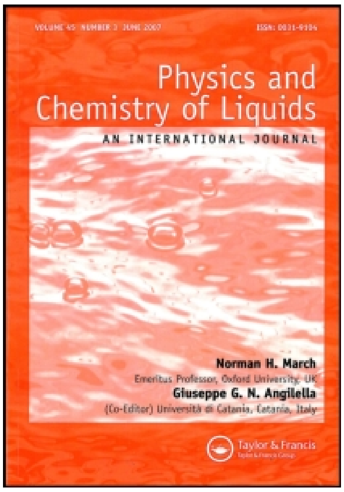

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess molar enthalpies of amides + some alkan-2-OLS at 298.15 K

H. Iloukhani[a]; H. A. Zarei[a]
[a] Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hamadan, Iran

To cite this Article Iloukhani, H. and Zarei, H. A.(2004) 'Excess molar enthalpies of amides + some alkan-2-OLS at 298.15 K', Physics and Chemistry of Liquids, 42: 1, 75 — 79
To link to this Article: DOI: 10.1080/00319100310001613029
URL: http://dx.doi.org/10.1080/00319100310001613029

Physics and Chemistry of Liquids
Vol. 42, No. 1, February 2004, pp. 75–79

EXCESS MOLAR ENTHALPIES OF AMIDES + SOME ALKAN-2-OLS AT 298.15 K

H. ILOUKHANI* and H.A. ZAREI

Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hamadan, Iran

(Received 19 March 2002)

Excess molar enthalpies, H_m^E for the binary systems *N*-methylformamide, *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide + propan-2-ol, and + butan-2-ol have been measured at 298.15 K and atmospheric pressure with a parr 1455 solution calorimeter. All the system present endothermic events and showed maximum positive H_m^E values around 0.40–0.50 mole fraction of amide. The H_m^E values decreased in the order *N*,*N*-dimethylformamide > *N*-methylformamide > *N*,*N*-dimethylacetamide. The excess enthalpies of the above mentioned binary systems, were used to discuss interaction between the alkan-2-ols and amide molecules. The results are interpreted to gain insight into the changes in molecular association equilibria and structural effects in these systems through O···HO hydrogen bonding. The experimental data have been correlated using Redlich–Kister polynomials, and parameters from least-squares analysis have been reported.

Keywords: Excess molar enthalpies; *N*-methylformamide; *N*,*N*-dimethylformamide

1. INTRODUCTION

Estimation of the molecular interaction of binary systems and information to test existing theories of solution may be related to the magnitude of excess thermodynamic properties such as excess molar enthalpies. The thermodynamic properties of binary systems containing polar and self-associated components exhibit significant deviation from ideality, arising not only from the difference in size and shape but also from possible hydrogen-bonding interaction between unlike molecules. Carbonamide–alkanol systems make particularly interesting systems for study because substituents have a marked effect on the association behavior [1–6].

Excess molar enthalpies, H_m^E have been measured for *N*-methylformamide, *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide + propan-2-ol, and + butan-2-ol at 298.15 K. The purpose of this investigation is to study the interactions between alkan-2-ols and amide.

---

*Corresponding author. E-mail: iloukhani@basu.ac.ir

ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100310001613029

2. EXPERIMENTAL SECTION

2.1. Materials

The material used in this study, suppliers, and purities are listed in Table I. *N*,*N*-dimethylformamide showing a stated purity of 99.8% was used as received. Analytical reagent grade *N*,*N*-dimethylacetamide was purified by the standard method of Perria and Armarego [7]. *N*-methylformamide and alkan-2-ols were dried and distilled as described elsewhere [8]. The purities of all the liquid samples were ascertained by the constancy of the density and refractive index. Densities were measured at 293.15 K using a bicapillary pycnometer with an accuracy of five parts in 10^5. Refractive indexes were measured at 293.15 K with an Abbe' refractometer. Water was circulated to the refractometer from a constant-temperature bath at 293.15 K. The accuracy of the refractive index measurement is in the order of ± 0.0002.

Table I also gives the density and refractive index measurements, which agree with values obtained from the literature [8,9].

2.2. Apparatus and Procedure

Mixtures were prepared by weighing the liquids in ground stoppered weighing bottles, taking due precaution to minimize the evaporation losses. All the weighing were performed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

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 calorimeter consists of a silvered glass dewar, a mixing chamber with a rotating sample cell, a thermistor probe, and a built-in, microprocessor-based thermometer for precise temperature measurements. Digital readings are shown on an LED display and fed to outputs for a printer or computer, which are all assembled in a compact cabinet. The two-piece cell serves as both the sample holder and agitator. It is closed with a detachable Teflon disk. The liquid sample can be added to the cell from a pipet inserted through the top stem. Excellent thermal insulation is provided by the fully silvered dewar glass which serves as the mixing chamber. The enthalpy of mixing experiments were conducted in the calorimeter by considering 100 cm^3 of one component as solvent and a mixing of 20 cm^3 of other component as solute. In the subsequent runs 100 cm^3 of the previous solution was taken as the solvent and the pure solute was add to it. These experiments were continued until the concentration reached 50 to 60 vol%. By this method, earlier addition of small error lead to a large error in latter experiments. The temperature measurement can be read to an accuracy

TABLE I Source, purity grades, densities ρ and refractive indices n_D of the pure components at 293.15 K

Component	*Source*	*Purity*/(mass %)	$\rho\,(\text{g cm}^{-3})$		n_D	
			Expt.	*Lit.*	*Expt.*	*Lit.*[a]
N,*N*-dimethylformamide	Merck	99.8	0.94391	0.94397[a]	1.4282	1.42817
N,*N*-dimethylacetamide	Merck	99	0.93651	0.9366[b]	1.4359	1.4356
N-methylformamide	Fluka	99	1.0036	1.005[b]	1.4302	1.4306[b]
Propane-2-ol	Merck	99.5	0.78558	0.78545[c]	1.39730	1.39720[c]
Butane-2-ol	Fluka	99	0.80702	0.8069[c]	1.39731	1.3972[c]

[a][8]; [b]At 298.15 K; [c][9].

of ± 0.0002 K. Because of the limitation of the calorimeter, one is forced to adopt this method to cover the entire concentration range.

Initially, to determine the calorimeter equivalent, it was calibrated with 0.5 g of hydroxy methylaminomethane dissolved in 0.1 mol dm^{-3} hydrochloric acid solution which releases 245.52 J g^{-1} at 298.15 K. 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 [10].

3. RESULTS AND DISCUSSION

The experimental results for the enthalpies of mixing for the binary systems of *N*,*N*-dimethylformamide, *N*-methylformamide, and *N*,*N*-dimethylacetamide + propan-2-ol, and + butan-2-ol at 298.15 K are listed in Table II, together with the

TABLE II Excess molar enthalpies H_m^E and deviation $\delta(H_m^E)$ for the binary systems of amides + alkan-2-ols at 298.15 K

x	H_m^E/(J mol^{-1})	$\delta(H_m^E)$ (J mol^{-1})	x	H_m^E/(J mol^{-1})	$\delta(H_m^E)$ (J mol^{-1})
N,N-Dimethylformamide(1) + propan-2-ol(2)					
0.9078	287.5	0.3	0.4870	1137.2	0.7
0.8006	588.9	− 1.7	0.3911	1159.6	0.9
0.6998	831.7	1.4	0.2937	1083.5	− 0.5
0.6012	1012.5	2.3	0.1967	889.2	0.6
0.4988	1124.0	− 4.0	0.0998	544.0	− 0.2
N,N-Dimethylformamide(1) + butan-2-ol(2)					
0.9052	351.9	0.1	0.4884	1305.6	− 1.4
0.8080	675.5	− 0.7	0.3902	1318.0	− 1.1
0.7093	952.3	0.8	0.2933	1215.8	− 1.5
0.6106	1158.5	− 0.9	0.1957	979.7	1.6
0.5096	1294.8	3.5	0.0985	580.6	− 0.2
N-Methylformamide(1) + propan-2-ol(2)					
0.9022	292.2	− 0.3	0.4721	944.0	3.0
0.8037	535.7	1.6	0.3797	912.2	0.0
0.7043	727.4	1.2	0.2861	803.9	− 0.3
0.6037	851.9	− 11.9	0.1921	612.5	− 0.6
0.5708	902.2	7.3	0.0918	324.4	0.1
N-Methylformamide(1) + butan-2-ol(2)					
0.9029	321.3	− 0.2	0.4794	971.7	2.9
0.8017	590.2	1.5	0.3817	908.0	− 2.4
0.7026	784.3	− 1.1	0.2860	756.7	− 3.0
0.6063	898.6	− 13.9	0.1904	528.3	2.6
0.5767	951.7	13.9	0.0951	245.3	− 0.4
N,N-Dimethylacetamide(1) + Propan-2-ol(2)					
0.8900	169.5	0.23	0.4868	594.7	3.4
0.7920	304.2	− 1.0	0.3973	614.4	− 2.0
0.6909	426.6	0.6	0.2983	593.1	− 0.4
0.5901	524.0	1.1	0.1998	500.4	1.1
0.5002	581.7	− 2.7	0.1042	318.6	− 0.2
N,N-Dimethylacetamide(1) + butan-2-ol(2)					
0.8987	203.0	0.2	0.5016	698.5	− 7.1
0.8020	362.6	− 1.0	0.4009	742.1	− 1.6
0.7012	505.1	0.5	0.2971	702.6	− 2.2
0.6003	621.4	0.1	0.1985	571.7	2.2
0.5019	714.7	9.2	0.0992	326.1	− 36.4

deviation $\delta(H_m^E)$ and shown graphically in Fig. 1. Each set of results was fitted using a Redlich–Kister equation of the type

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

where x is the mole fraction of amide. The coefficients A_r were calculated by a least-square analysis. They are presented in Table III together with the standard deviation $\sigma(H_m^E)$

$$\sigma(H_m^E) = |\zeta/(n-p)|^{0.5} \tag{2}$$

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:

$$\zeta = \sum \delta^2(H_m^E) \tag{3}$$

where $\delta(H_m^E) = H_{m,\mathrm{expt.}}^E - H_{m,\mathrm{calcd.}}^E$.

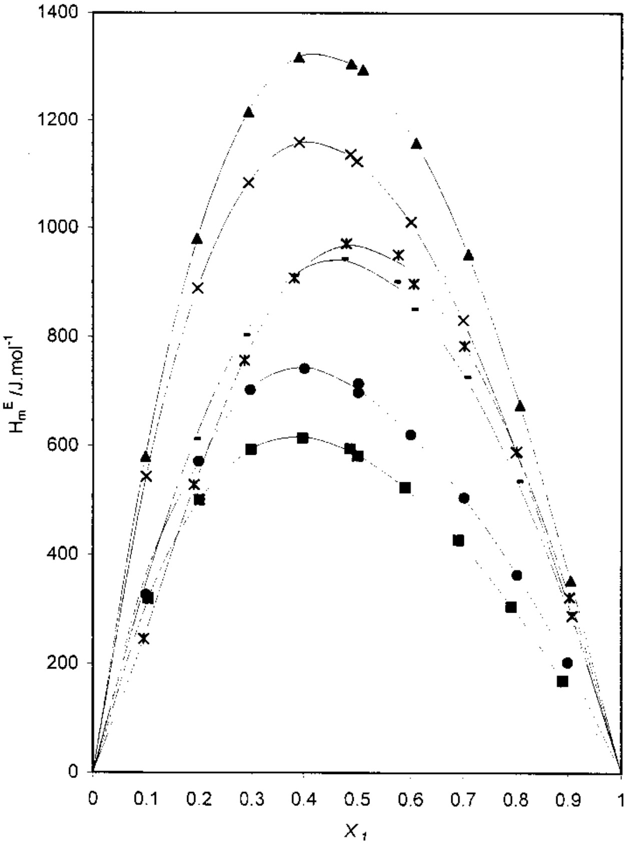

FIGURE 1 Excess molar enthalpies of amides (1) + alkan-2-ols (2) at 298.15 K. Solid curves are calculated from coefficients of Eq. (1) given in Table III. ● Butan-2-ol + *N*,*N*-dimethylacetamide; ■ Propan-2-ol + *N*,*N*-dimethylacetamide; ▲ Butan-2-ol + *N*,*N*-dimethylformamide; × Propan-2-ol + *N*,*N*-dimethylformamide; ⁎ Butan-2-ol + *N*-methylformamide; ▬ Propan-2-ol + *N*-methylformamide.

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

System	A_r	A_2	A_3	A_4	A_5	$\sigma(H_m^E)/(\mathrm{J\,mol^{-1}})$
N,*N*-Dimethylformamide(1) + propan-2-ol(2)	4508.5	−1538.9	436.2	−141.7	−81.3	5.6
N,*N*-Dimethylformamide(1) + butan-2-ol(2)	5196.2	−1513.6	332.7	1.6	−202	5.6
N-Methylformamide(1) + propan-2-ol(2)	3742.3	−611.5	−185.5	394.9	−38.7	11.9
N-Methylformamide(1) + butan-2-ol(2)	3877.1	−143.7	−704.4	987.2	−354	18.9
N,*N*-Dimethylacetamide(1) + propan-2-ol(2)	2338.5	−1059.9	442.3	15.4	−116.3	6.0
N,*N*-Dimethylacetamide(1) + butan-2-ol(2)	2827.0	−1299.4	457.6	640.1	−440.4	11.2

The excess molar enthalpies for all the systems are positive (endothermic) over the entire range of composition of amide at 298.15 K. For these binary systems, the H_m^E values around 0.40–0.50 mole fraction of amide decreased in the order: *N*,*N*-dimethylformamide > *N*-methylformamide > *N*,*N*-dimethylacetamide. When carbonamide and an alcohol are mixed, the main changes that occur in the association equilibria are evidently the rupture of the hydrogen bonds between the alcohol molecules and the dipolar interactions between the amide molecules and the formation of O–H···O=C hydrogen bonds between the alcohol and the amide molecules. A packing effect in the liquid state between chain-like molecules of alkan-2-ols is mainly responsible for the endothermic behavior [11].

References

[1] H. Iloukhani and H.A. Zarei (2002). *Phys. Chem. Liqs.*, **40**(4), 449.
[2] E. Tusel-Langer, J.M. Garcia Alonso, M.A. Villiamanan Olfos and R.N. Lichtenthaler (1991). *J. Solution Chem.*, **20**(1), 153.
[3] H. Iloukhani and H.A. Zarei (2002). *J. Chem. Eng. Data*, **47**, 195.
[4] R. Vijaya Kumer, M. Rao Anand, A. Rajiah and M. Venkateshwara Rao (1995). *J. Chem. Eng. Data*, **40**, 99.
[5] M. Trevor Letcher and G. Gan Redhi (2000). *J. Chem. Eng. Data*, **45**, 57.
[6] H. Iloukhani and J.B. Parsa (2001). *J. Solution Chem.*, **30**(5), 425.
[7] D.D. Perrin and W.L.F. Armarego (1970). *Purification of Laboratory Chemicals*, 3rd Edn. Pergamon press, New York.
[8] J.A. Riddick, W.B. Bunger and T.K. Sakano (1986). *Organic Solvents*. Wiley-Interscience, New York.
[9] A.J. Dean (1973). *Lang's Handbook of Chemistry*, 13th Edn. Mc-Graw Hill Co., New York.
[10] J. Gmehling (1993). *J. Chem. Eng. Data*, **38**, 143.
[11] A. Heintz and R.N. Lichtenthaler (1989). *Ber. Bunsenges. Phys. Chem.*, **81**, 1.