Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 405 (2003) 123–128

thermochimica acta

www.elsevier.com/locate/tca

Excess molar enthalpies of formamide + some alkan-1-ols (C_1–C_6) and their correlations at 298.15 K

H.A. Zarei[*], H. Iloukhani

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

Abstract

Excess molar enthalpies, H^E for the binary systems formamide + 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 Paar 1455 solution calorimeter. All the system present endothermic events and showed maximum positive H^E values around 0.40–0.50 mole fraction of formamide. The H^E values increases in the order: methanol < ethanol < propan-1-ol < butan-1-ol < pentan-1-ol < hexan-1-ol. Experimental showed insolubility of hexan-1-ol in formamide around $x \cong 0.5$ mole fraction of formamide. The excess enthalpies of the above mentioned binary systems, were used to discuss interaction between the alkan-1-ols and formamide 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. In this research work, the thermodynamics models were also tested: NRTL, Wilson models and their parameters were calculated. The correlation of excess enthalpy data in the systems using NRTL model provides good results.

Keywords: Excess enthalpies; Alkan-1-ols; Formamide; Wilson model; NRTL model

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 different in size and shape but also from possible hydrogen-bonding interaction between unlike molecules. Formamide + alkan-1-ols systems make particularly interesting systems for study because substituents have a marked effect on the association behavior [1–5].

Excess molar enthalpies, H^E have been measured for formamide + alkan-1-ols (C_1–C_6) 298.15 K. The purpose of this investigation is to study the interactions between alkan-1-ols and formamide. The excess molar enthalpies at 298.15 K were correlated by the Redlich–Kister equation. We also tested the Wilson and NRTL models for excess molar enthalpies H^E, to investigate which model gives the best correlation of excess enthalpy and to calculate their parameters.

2. Experimental

2.1. Materials

The material used in this study, suppliers, and purities are listed in Table 1. Analytical reagent grade formamide was purified by the standard method of Perria

---

[*] Corresponding author.

E-mail address: zareih@basu.ac.ir (H.A. Zarei).

doi:10.1016/S0040-6031(03)00141-2

Table 1
Source, purity grades, densities ρ and refractive indices n_D of the pure components at 293.15 K

Component	Source	Purity (mass%)	ρ (g cm^{-3})		n_D	
			Experimental	Literature[a]	Experimental	Literature[a]
Formamide	Fluka	99.5	1.0039	1.005[b]	1.4301	1.4306[b]
Methanol	Merk	99.5	0.7912	0.7913	1.3289	1.3284
Ethanol	Merk	99.8	0.7895	0.7894	1.3611	1.3614
Propan-1-ol	Merk	99.8	0.8036	0.8037	1.3851	1.3856
Butan-1-ol	Merk	99.8	0.8098	0.8097	1.3991	1.3993
Pentan-1-ol	Fluka	99	0.8147	0.8148	1.4104	1.4100
Hexan-1-ol	Merk	98	0.8185	0.8186	1.4184	1.4182

[a] [7].
[b] At 298.15 K.

and Armarego [6]. Alkan-1-ols were dried and distilled as described elsewhere [7]. 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 four parts in 10^4. 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 on the order of ±0.0002.

2.2. Apparatus and procedure

Table 1 also gives the density and refractive index measurements, which agree with values obtained from [7,8]. 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^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 LCD 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 50–60 vol.%. By this method a small error in an early addition lead to a larger error in latter experiments. The temperature measurement can be read to an accuracy 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 hydroxymethylaminomethane 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 the solution calorimeter was checked by the test mixture cyclohexane + benzene. The excess enthalpies H^E (J mol^{-1}) agreed within 1% with the reported values [9].

3. Results and discussion

The experimental results for the excess molar enthalpies for the binary systems of formamide with alkan-1-ols at 298.15 K are listed in Table 2, and shown graphically in Fig. 1. Dash line indicates insolubility of hexan-1-ol in formamide around $x \cong$

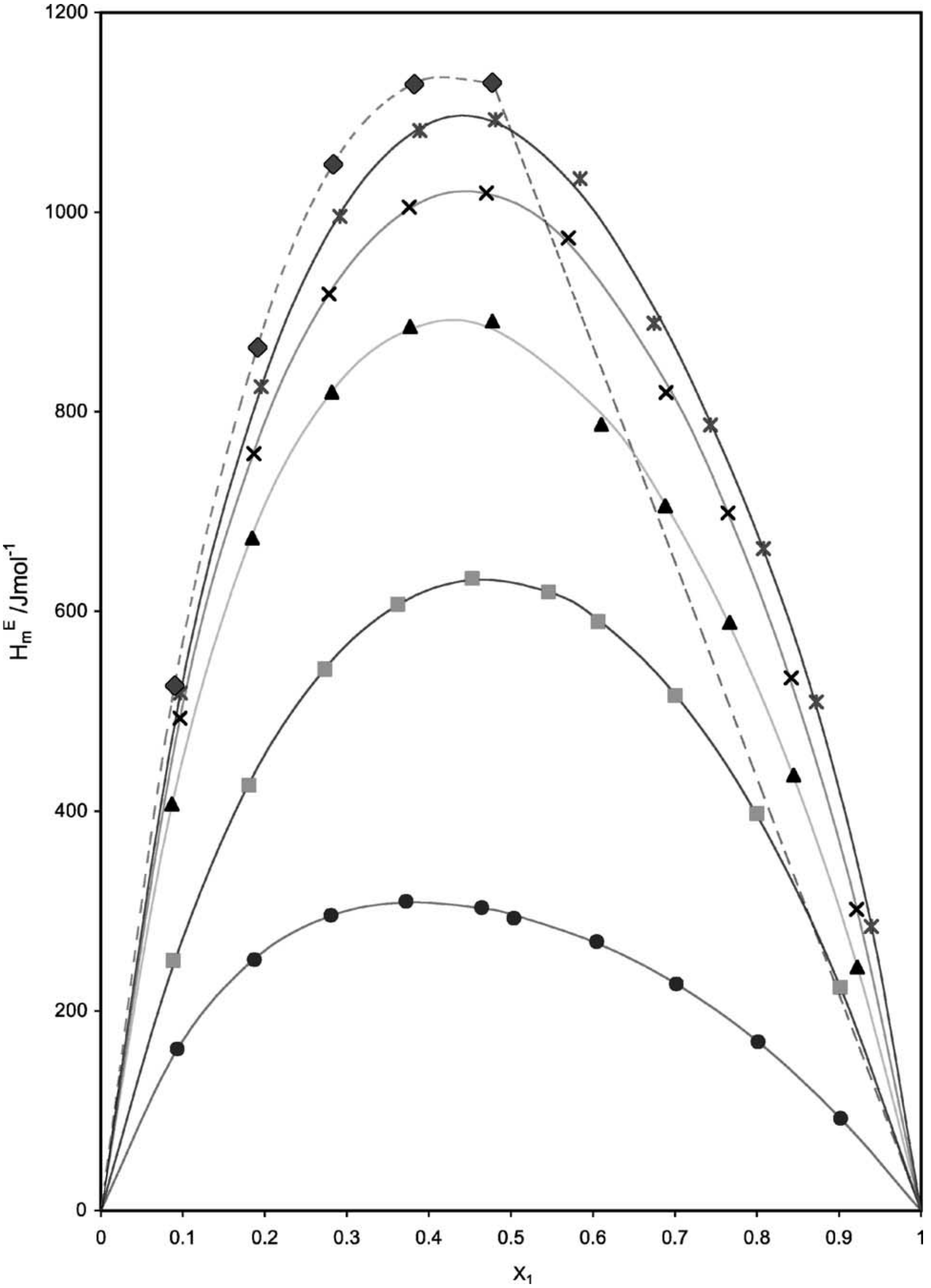

Fig. 1. Excess molar enthalpies of formamide (1) + alkan-1-ols (2) at 298.15 K. Dash line indicates insolubility of hexan-1-ol in formamide about approximately from $x_1 = 0.5$ to 1: (●) methanol; (■) ethanol; (▲) propan-1-ol; (×) butan-1-ol; (✱) pentan-1-ol; (◆) hexan-1-ol.

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

x	H^E (J mol^{-1})			x	H^E (J mol^{-1})		
	Experimental	Wilson	NRTL		Experimental	Wilson	NRTL
Formamide (1) + methanol (2)							
0.0934	161.5	150.5	162.0	0.5036	292.6	303.5	296.5
0.1873	251.2	244.7	251.4	0.6045	269.2	269.1	267.6
0.2806	295.5	296.3	294.9	0.7019	226.8	219.9	225.7
0.3721	309.8	316.0	309.0	0.8013	168.9	156.7	168.4
0.4645	303.4	311.5	303.5	0.9022	92.0	81.6	93.1
Formamide (1) + ethanol (2)							
0.0880	250.1	244.9	247.1	0.5457	619.3	619.8	618.8
0.1808	426.1	425.1	426.6	0.6065	589.4	590.7	590.6
0.2731	542.1	544.1	543.9	0.7001	516.2	515.8	517.0
0.3620	606.9	609.3	607.7	0.8001	397.5	394.4	396.0
0.4524	632.7	633.8	631.9	0.9014	223.7	223.1	223.7
Formamide (1) + propan-1-ol (2)							
0.0867	407.1	321.5	404.3	0.6102	787.0	699.5	796.0
0.1846	673.1	548.9	677.0	0.6883	705.7	636.8	708.3
0.2818	819.5	678.6	821.3	0.7668	588.7	547.9	588.8
0.3772	885.1	739.9	880.2	0.8446	436.1	428.0	435.7
0.4774	890.6	751.3	878.3	0.9223	243.5	260.2	242.2
Formamide (1) + butan-1-ol (2)							
0.0963	493.2	355.4	485.9	0.5701	973.9	770.5	965.2
0.1866	757.9	573.9	762.6	0.6892	819.1	674.8	832.3
0.2781	917.7	711.0	924.1	0.7647	698.5	581.9	703.1
0.3760	1005.0	785.9	1004.2	0.8419	533.5	455.7	528.4
0.4701	1019.0	802.2	1014.0	0.9217	301.5	276.8	294.6
Formamide (1) + pentan-1-ol (2)							
0.0970	518.4	364.4	518.4	0.6744	888.5	739.1	920.6
0.1953	825.0	612.5	832.2	0.7435	786.5	647.5	803.9
0.2913	995.4	762.0	1002.0	0.8081	662.6	544.1	662.3
0.3890	1081.4	838.5	1078.7	0.8725	509.4	414.8	489.9
0.4813	1092.4	853.0	1084.1	0.9396	284.5	237.6	254.7
0.5845	1033.4	812.7	1025.3				
Formamide (1) + hexan-1-ol (2)							
0.0902	526.8	383.3	509.6	0.3818	1128.9	876.2	1135.4
0.1910	865.8	657.8	871.1	0.4778	1130.0	880.9	1120.0
0.2831	1047.6	803.9	1056.0				

0.5–1 mole fraction of formamide. Each set of results was fitted using a Redlich–Kister equation of the type:

$$H^E = x(1-x)\sum_{r=1} A_r(2x-1)^{r-1}, \qquad (1)$$

where x is the mole fraction of formamide. The coefficients A_r were calculated by a least square analysis. They are presented in Table 3 together with the standard deviation $\sigma(H^E)$:

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

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

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

where $\delta(H^E) = H^E_{\text{expt.}} - H^E_{\text{calcd.}}$.

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

System	A_r	A_2	A_3	A_4	A_5	$\sigma(H^E)$ (J mol^{-1})
Formamide (1) + methanol (2)	1186.3	−397.2	440.9	−202.6	−8.4	3.6
Formamide (1) + ethanol (2)	2519.9	−268.3	350.2	−126.4	138.9	3.7
Formamide (1) + propan-1-ol (2)	3500.3	−818.0	784.5	−337.1	485.4	15.0
Formamide (1) + butan-1-ol (2)	4042.6	−728.3	723.1	−335.7	897.6	11.7
Formamide (1) + pentan-1-ol (2)	4330.2	−906.8	579.0	262.5	1467.8	20.1
Formamide (1) + hexan-1-ol (2)	4509.0	−204.6	6033.4	10146.7	7250.9	

The excess molar enthalpies for the all systems are positive (endothermic) over the entire range of composition of formamide at 298.15 K.

For these binary systems, the H^E values around 0.40–0.50 mole fraction of formamide increase in the order: methanol < ethanol < propan-1-ol < butan-1-ol < pentan-1-ol < hexan-1-ol. When formamide 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 formamide molecules and the formation of O–H···O=C hydrogen bonds between the alcohol and the formamide molecules. A packing effect in the liquid state between chain-like molecules of alkan-1-ols is mainly responsible for the endothermic behavior [10].

4. Correlations

The experimental data are compared to data calculated using the Wilson [11] and NRTL [12] equations.

4.1. Wilson equation

In the development of the equation, Wilson conceived that interaction between molecules depends primarily on "local concentrations", which he expressed as volume fractions. These concentrations are defined in probabilistic terms, the Boltzman distribution of energies in a binary mixture that consists of a mixture of molecules of types 1 and 2. In the vicinity of a molecule type 1 the probability of finding another molecules of the same type is p_{11} and the probability of finding the other type is p_{21}. Accordingly the ratio of the two probabilities are:

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

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

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

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

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

To take into account non-randomness in this model the following relation between the local mole fraction x_{11} of molecules 1 and the local mole fraction x_{21} of molecules 2 which are in the immediate neighborhood of molecules 1 is given by:

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

where g_{21} and g_{11} indicate the different interaction energies. The non-randomness parameter a_{21} is an empirical constant.

The following expression for H^E is obtained with this relation:

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

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^E derived at 298.15 K

System	λ_{21}	λ_{12}	Δg_{21}	Δg_{12}	α_{ij}	σ	
						Wilson	NRTL
Formamide (1) + methanol (2)	−36.32	2019.65	1864.49	816.56	0.96	25.9	3.7
Formamide (1) + ethanol (2)	1271.70	2733.86	2474.30	1789.60	0.47	6.2	3.9
Formamide (1) + propan-1-ol (2)	2895.11	4083.95	4689.70	2658.10	0.35	303.1	13.8
Formamide (1) + butan-1-ol (2)	2966.77	4108.98	5101.30	3261.20	0.31	541.6	22.2
Formamide (1) + pentan-1-ol (2)	2979.65	4154.91	5398.38	3587.33	0.29	618.8	45.7
Formamide (1) + hexan-1-ol (2)	2642.4	4845.20	5607.85	1596.91	0.21	633.6	27.3

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

where $\Delta g_{21} = g_{21} - g_{11}$, $\Delta g_{12} = g_{12} - g_{22}$, $G_{21} = \exp(-\alpha_{12}\Delta g_{21}/RT)$, $N_1 = x_1 + x_2G_{21}$, $N_2 = x_2 + x_1G_{12}$, $G_{12} = \exp(-\alpha_{12}\Delta g_{12}/RT)$, $Z_1 = (\Delta g_{21}/RT)G_{21}$, $Z_2 = (\Delta g_{12}/RT)G_{12}$, Δg_{12} and Δg_{21} are the two adjustable parameters remaining, because the randomness parameters α_{21} were taken to be constant 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 nonlinear least square fit and are summarized in Table 4. The H^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^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.

Acknowledgements

The authors wish to thank the university authorities for providing the necessary facilities to carry out the work and Mr. E. Samei for his kind help in preparing the manuscript.

References

[1] H. Iloukhani, H.A. Zarei, J. Chem. Eng. Data 47 (2002) 195–197.

[2] H. Iloukhani, J.B. Parsa, J. Sol. Chem. 30 (5) (2001) 425–433.

[3] E. Tusel-Langer, J.M. Garcia Alonso, M.A. Villiamanan Olfos, R.N. Lichtenthaler, J. Sol. Chem. 20 (1) (1991) 153–161.

[4] M. Vijaya Kumer, A. Rao Anand Rajiah, M. Venkateshwara Rao, J. Chem. Eng. Data 40 (1995) 99–101.

[5] M. Trevor Letcher, G. Gan Redhi, J. Chem. Eng. Data 45 (2000) 57–60.

[6] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon Press, New York, 1970.

[7] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, Wiley/Interscience, New York, 1986.

[8] A.J. Dean, Lang’s Handbook of Chemistry, 13th ed., McGraw-Hill, New York, 1973.

[9] J. Gmehling, J. Chem. Eng. Data 38 (1993) 143–146.

[10] A. Heintz, R.N. Lichtenthaler, Ber. Bunsen-Ges. Phys. Chem. 81 (1977) 921.

[11] G.M. Wilson, J. Am. Chem. Soc. 86 (1964) 127–130.

[12] H. Renon, J.M. Prausnitz, J. Chem. Eng. Sci. 22 (1967) 299.