Thermochimica Acta, 180 (1991) 159–167
Elsevier Science Publishers B.V., Amsterdam

THERMODYNAMICS OF 2-PYRROLIDINONE + *n*-ALKANOL BINARY MIXTURES: ACTIVATION PROPERTIES

B. GARCIA, C.A. HERRERA and J.M. LEAL

Universidad de Valladolid, Departamento de Química Física, Colegio Universitario Integrado, 09001 Burgos (Spain)

(Received 21 August 1990)

ABSTRACT

Based on the Eyring and Andrade equations, activation energies of viscous flow, enthalpies and entropies of mixture as functions of mole fraction, and free energies of activation of mixtures as functions of temperature and mole fraction were determined for binary mixtures of 2-pyrrolidinone + *n*-alkanols. Densities were linearly fitted against $1/T$ for the range 25–60 °C. The presence of well-defined minima in the variation of the activation parameters with composition was a common feature of these binary mixtures.

INTRODUCTION

2-Pyrrolidinone, an amide of the lactams group with *cis*-conformation, has both acid (NH) and basic (CO) groups and exhibits the property of being self-associated; in highly diluted solutions, it dimerises by intermolecular hydrogen bonding [1,2] and at higher concentrations, when disolved in non-polar solvents, spectral and electrical polarisation investigations have indicated the existence of dimers, trimers and higher oligomers [3–5]. Investigations have also been made on the self-association of the gaseous alcohols, of which monomers, dimers and tetramers are known to form [6]. The self-association of alcohols in non-polar solvents has been widely investigated and this phenomenon has been ascribed to intermolecular interactions due to hydrogen bonding [7,8].

Intermolecular interactions in binary liquid mixtures may be interpreted through physical and thermodynamic properties of mixtures. In this work, the activation thermodynamic properties of binary mixtures containing 2-pyrrolidinone + methanol, + ethanol, + 1-propanol, + 1-butanol and + 1-pentanol were calculated as functions of temperature and mole fraction from density and viscosity measurements. An interpretation of these results is made.

0040-6031/91/$03.50

RESULTS AND DISCUSSION

The viscosities of the five binary mixtures investigated are dependent on temperature according to Andrade's equation

$$\ln \eta = \ln A + E/RT \tag{1}$$

where A is the pre-exponential factor and E is the activation energy of viscous flow: E is related to the disruptions in intermolecular forces that make liquid flow possible. In fact, only one third of this energy is necessary for liquid molecules to move from initial equilibrium to intermediate positions of high energy. Table 1 lists the values of E and $\ln A$ for each system, calculated within the range 25–60 °C; E increases with the chain length of the alcohol, as already noted by Saltiel and Sun for *n*-alkanols [9] ranging from 6.27 (*n*-C_5) to 15.21 kJ mol^{-1} (*n*-C_{16}). Values ranging from 12.5 to 21 kJ mol^{-1} have already been reported for cyclic amides such as *N*-methylpyrrolidone, 1,3-dimethyl-2-imidazolidinone, and 1,3-dimethyl-2-oxohexahydropyrimidine [10]. In previous papers, we have also reported values of E and $\ln A$ which follow straight lines, the slopes and ordinates of which were constant for all the binary mixtures investigated [11,12]; this suggested a unique relationship for the variation of viscosity with both temperature and mole fraction because the polynomial function, $\ln A$ versus X, was easily adjustable. In the present work, a linear relationship, common to all mixtures, was only observed at concentrations higher than $X_1 = 0.6$. Deviations from linearity were observed at higher alcohol concentrations ($X_1 < 0.6$) and, except for methanol, minima for E occurred, the position of which depended on the chain length of the alcohol (Fig. 1); these minima may be interpreted as being due to competition between dispersion forces (dipole–dipole interactions) and specific interactions (hetero-associations by hydrogen bonding) whose extent will depend on the nature of the binary mixture and also on mole fractions. The role of acid–base interactions should not be important in these mixtures because $pK_{acid} \simeq 15.5$ for methanol, ethanol and propanol, and $pK_{basic} \simeq 11.31$ for 2-pyrrolidinone [13].

Densities were fitted to the function

$$\rho = a + b/T \tag{2}$$

Table 2 lists the values for a and b as functions of composition. Activation enthalpies, $\Delta H_m^{\neq}$, and activation entropies, $\Delta S_m^{\neq}$, of mixtures were calculated using the equation of Eyring et al. [14]

$$\ln \nu_m M_m = \ln Nh - \Delta S_m^{\neq}/R + \Delta H_m^{\neq}/RT \tag{3}$$

where ν_m is the kinematic viscosity of the mixture (calculated as the quotient of viscosity, η, and density, ρ) and M_m is defined as

$$M_m = \sum_i X_i M_i \tag{4}$$

TABLE 1

Values[a] of E (kJ mol^{-1}) and ln A of eqn. (1) calculated as functions of 2-pyrrolidinone mole fraction (X_1)

2-Py + methanol			2-Py + ethanol			2-Py + 1-propanol			2-Py + 1-butanol			2-Py + 1-pentanol		
X_1	$-\ln A$	E	X_1	$-\ln A$	E	X_1	$-\ln A$	E	X_1	$-\ln A$	E	X_1	$-\ln A$	E
0.0000	4.862	10.523	0.0000	6.112	15.291	0.0000	7.113	19.214	0.0000	7.399	20.642	0.0000	7.763	22.259
0.0998	5.063	11.780	0.0986	5.902	15.085	0.0996	6.707	18.270	0.1017	6.924	19.391	0.1175	7.187	20.667
0.1977	5.210	12.877	0.1993	5.852	15.390	0.1989	6.561	18.132	0.1992	6.696	18.926	0.2056	6.994	20.227
0.2964	5.416	14.136	0.3034	5.910	16.063	0.2999	6.566	18.493	0.3030	6.604	18.930	0.3026	6.902	20.149
0.3979	5.675	15.555	0.3960	6.023	16.864	0.3971	6.548	18.825	0.3989	6.621	19.277	0.3975	6.889	20.345
0.4942	5.952	16.979	0.4924	6.222	17.939	0.4980	6.657	19.564	0.4919	6.544	19.456	0.4934	6.950	20.788
0.5944	6.333	18.709	0.5941	6.452	19.156	0.6003	6.837	20.545	0.5900	6.841	20.618	0.5914	7.083	21.482
0.6912	6.770	20.546	0.6919	6.823	20.749	0.6987	7.091	21.751	0.6941	7.101	21.721	0.6925	7.282	22.421
0.7887	7.251	22.517	0.7963	7.287	22.678	0.8000	7.519	23.448	0.7945	7.437	23.222	0.8010	7.609	23.788
0.8968	7.912	25.047	0.8933	7.863	24.879	0.8907	7.968	25.199	0.8986	7.943	25.184	0.9248	8.179	25.992
1.0000	8.669	27.800	1.0000	8.669	27.800	1.0000	8.669	27.800	1.0000	8.669	27.800	1.0000	8.669	27.800

[a] Linear correlation coefficients were always better than 0.9999.

TABLE 2

Variation[a] of ρ(g cm^{-3}) with temperature according to eqn. (2) (X_1 = 2-pyrrolidinone mole fraction)

2-Py + methanol			2-Py + ethanol			2-Py + 1-propanol			2-Py + 1-butanol			2-Py + 1-pentanol		
X_1	a	b	X_1	a	b	X_1	a	b	X_1	a	b	X_1	a	b
0.0000	90.574	0.483	0.0000	87.888	0.490	0.0000	82.518	0.523	0.0000	78.818	0.542	0.0000	75.511	0.558
0.0998	89.824	0.548	0.0986	84.863	0.544	0.0996	83.396	0.553	0.1017	78.934	0.568	0.1175	76.264	0.581
0.1977	86.378	0.610	0.1993	84.306	0.588	0.1989	82.918	0.587	0.1992	79.020	0.594	0.2056	76.821	0.600
0.2964	83.847	0.660	0.3034	81.612	0.636	0.2999	82.784	0.619	0.3030	79.583	0.621	0.3026	77.699	0.621
0.3979	83.521	0.697	0.3960	82.307	0.666	0.3971	82.132	0.652	0.3989	79.886	0.648	0.3975	77.275	0.647
0.4942	81.864	0.732	0.4924	84.104	0.691	0.4980	81.575	0.685	0.4919	79.891	0.676	0.4934	77.480	0.674
0.5944	82.739	0.754	0.5941	79.756	0.736	0.6003	81.460	0.717	0.5900	79.662	0.706	0.5914	79.129	0.697
0.6912	84.195	0.771	0.6919	83.447	0.751	0.6987	81.236	0.748	0.6941	80.006	0.738	0.6925	78.795	0.730
0.7887	83.094	0.794	0.7963	81.993	0.784	0.8000	81.575	0.776	0.7945	77.218	0.779	0.8010	80.091	0.763
0.8968	82.351	0.815	0.8933	81.544	0.809	0.8907	81.460	0.803	0.8986	80.977	0.801	0.9248	80.897	0.806
1.0000	83.682	0.827	1.0000	83.682	0.827	1.0000	83.682	0.827	1.0000	83.682	0.827	1.0000	83.682	0.827

[a] Linear correlation coefficients were always better than 0.999.

TABLE 3

Activation enthalpies, ΔH_m^* (kJ mol^{-1}), activation entropies, ΔS_m^* (J K^{-1} mol^{-1}), and free energies of activation of mixtures, ΔG_m^* (kJ mol^{-1}), at different temperatures as functions of 2-pyrrolidinone mole fraction, X_1

	X_1	ΔH_m^*	ΔS_m^*	ΔG_m^*				
				298 K	303 K	313 K	323 K	333 K
2-Pyrrolidinone–methanol	0.0000	9.831	−0.374	9.943	9.945	9.949	9.952	9.956
	0.0998	10.882	−0.001	10.882	10.882	10.882	10.882	10.882
	0.1977	12.066	0.906	11.796	11.791	11.782	11.773	11.764
	0.2964	13.383	2.229	12.719	12.709	12.686	12.664	12.642
	0.3979	14.833	3.909	13.669	13.650	13.610	13.571	13.534
	0.4942	16.290	5.802	14.562	14.534	14.475	14.417	14.361
	0.5944	18.031	8.487	15.504	15.462	15.376	15.291	15.210
	0.6912	19.869	11.654	16.398	16.341	16.223	16.107	15.995
	0.7887	21.860	15.268	17.313	17.238	17.084	16.931	16.785
	0.8968	24.409	20.352	18.347	18.247	18.042	17.838	17.643
	1.0000	27.161	26.209	19.354	19.226	18.961	18.699	18.448
2-Pyrrolidinone–ethanol	0.0000	14.339	6.142	12.510	12.480	12.418	12.356	12.297
	0.0986	14.216	4.460	12.887	12.865	12.820	12.776	12.773
	0.1993	14.569	3.979	13.384	13.365	13.324	13.285	13.246
	0.3034	15.303	4.427	13.985	13.963	13.918	13.874	13.831
	0.3960	16.124	5.214	14.571	14.545	14.492	14.440	14.390
	0.5941	18.485	8.559	15.935	15.893	15.807	15.721	15.639
	0.6919	20.064	11.374	16.676	16.620	16.505	16.392	16.282
	0.7963	22.023	15.107	17.523	17.449	17.297	17.146	17.001
	0.8933	24.239	19.733	18.362	18.265	18.066	17.868	17.679
	1.0000	27.161	26.209	19.354	19.226	18.961	18.699	18.448
2-Pyrrolidinone–1-propanol	0.0000	18.337	12.654	14.568	14.506	14.379	14.252	14.131
	0.0996	17.420	9.369	14.630	14.584	14.489	14.396	14.306
	0.1989	17.320	8.272	14.856	14.815	14.732	14.649	14.569
	0.2999	17.710	8.405	15.206	15.165	15.080	14.996	14.915
	0.3971	18.075	8.346	15.589	15.549	15.464	15.381	15.301
	0.4980	18.843	9.333	16.064	16.018	15.924	15.830	15.741
	0.6003	19.849	10.893	16.605	16.551	16.441	16.332	16.228
	0.6987	21.075	13.055	17.187	17.123	16.991	16.861	16.735
	0.8000	22.791	16.643	17.834	17.752	17.584	17.418	17.258
	0.8907	24.558	20.411	18.479	18.379	18.173	17.969	17.773
	1.0000	27.161	26.209	19.354	19.226	18.961	18.699	18.448
2-Pyrrolidinone–1-butanol	0.0000	19.812	13.517	15.786	15.720	15.583	15.448	15.318
	0.1017	18.586	9.798	15.668	15.620	15.521	15.423	15.329
	0.1992	18.147	8.132	15.725	15.685	15.603	15.522	15.444
	0.3030	18.170	7.580	15.912	15.875	15.799	15.723	15.650
	0.3989	18.540	7.940	16.175	16.136	16.056	15.976	15.900
	0.4919	18.739	7.506	16.503	16.466	16.390	16.315	16.243
	0.5900	19.927	10.210	16.885	16.835	16.732	16.630	16.532
	0.6941	21.122	12.585	17.374	17.312	17.185	17.059	16.938
	0.7945	22.590	15.674	17.921	17.845	17.686	17.529	17.379
	0.8986	24.543	20.014	18.582	18.484	18.282	18.082	17.890
	1.0000	27.161	26.209	19.354	19.226	18.961	18.699	18.448

TABLE 3 (continued)

	X_1	$\Delta H_m^{\neq}$	$\Delta S_m^{\neq}$	$\Delta G_m^{\neq}$				
				298 K	303 K	313 K	323 K	333 K
2-Pyrrolidinone–1-pentanol	0.0000	21.469	15.286	16.916	16.841	16.686	16.534	16.387
	0.1175	19.894	10.850	16.663	16.610	16.500	16.391	16.287
	0.2056	19.466	9.510	16.634	16.587	16.491	16.396	16.305
	0.3026	19.404	9.054	16.707	16.663	16.571	16.481	16.394
	0.3975	19.623	9.282	16.858	16.813	16.719	16.626	16.537
	0.4934	20.084	10.125	17.069	17.019	16.917	16.815	16.718
	0.5914	20.787	11.543	17.349	17.292	17.176	17.060	16.949
	0.6925	21.749	13.580	17.705	17.638	17.501	17.365	17.235
	0.8010	23.130	16.682	18.161	18.079	17.911	17.744	17.584
	0.9248	25.357	21.896	18.836	18.728	18.507	18.288	18.078
	1.0000	27.161	26.209	19.354	19.226	18.961	18.699	18.448

where M is the molecular weight of the pure components. Free energies of activation of the mixtures are listed in Table 3, and were defined as

$$\Delta G_m^{\neq} = \Delta H_m^{\neq} - T \Delta S_m^{\neq} \tag{5}$$

Self-association in pure alcohols decreases as the chain length increases, and also decreases for secondary and tertiary alcohols. Enthalpies of formation for hydrogen bondings do not differ significantly for alcohols of lowest molecular weight, and fall around 25 kJ mol^{-1} [15]. Mixing of alcohols with other solvents is accompanied by positive enthalpies of mixture, and produces breaking of the hydrogen bonds as well as certain changes in the interactions among polymer alcohols. Because the dipole moment, μ, of

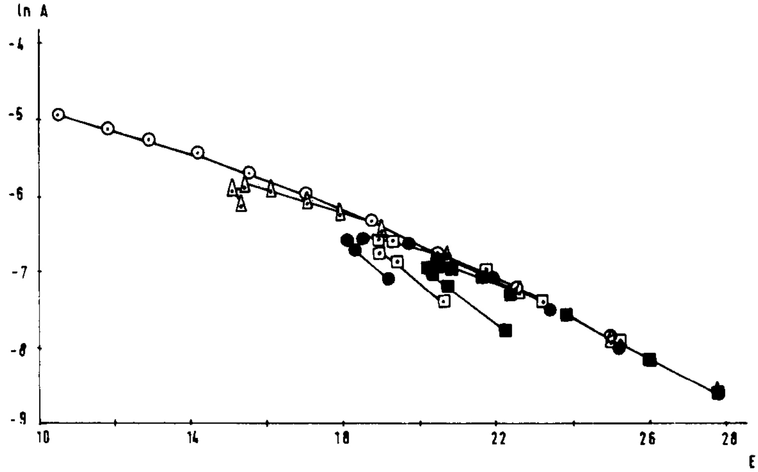

Fig. 1. Plots of ln A vs. E for binary mixtures: 2-pyrrolidinone + methanol, (○); + ethanol, (△); + 1-propanol, (●); + 1-butanol, (□); and + 1-pentanol (■).

TABLE 4

Comparison of measured densities, ρ (g cm^{-3}), and viscosities, η (cP), or pure components with literature values

Temp (°C)	2-Pyrrolidinone		Methanol		Ethanol		1-Propanol		1-Butanol		1-Pentanol	
	Liter.	Calc.	Liter.	Calc.	Liter.	Calc.	Liter.	Calc.	Liter.	Calc.	Liter.	Calc.
Densities												
15	–	–	0.79609 [a]	–	0.79360	–	0.80749 [a]	–	–	–	–	–
20	1.120 [a]	–	0.79129 [a]	–	0.78937 [a]	–	0.80375 [a]	–	0.8098 [b]	–	0.8103 [b]	–
25	1.107 [a]	1.1080	0.76664 [a]	0.7687	0.78504 [a]	0.7850	0.79975 [a]	0.7995	0.8095 [b]	0.8059	0.8115 [a]	0.8109
30	–	1.1034	0.7816 [c]	0.7818	0.7807 [c]	0.7807	0.7955 [c]	0.7956	0.8018 [c]	0.8019	0.8074 [c]	0.8072
40	–	1.0950	–	0.7723	–	0.7721	–	0.7873	–	0.7941	–	0.7997
50	1.087 [a]	1.0869	–	0.7632	–	0.7632	–	0.7789	–	0.7862	–	0.7920
60	–	1.087	–	–	0.75438 [d]	0.7543	0.77064 [d]	0.7706	0.77822 [d]	0.7782	–	0.7844
Viscosities												
15	–	–	0.623 [b]	–	–	–	2.52	–	3.379	–	4.650 [a]	–
20	–	–	0.597 [b]	–	1.200	–	2.256	–	2.948	–		–
25	13.033 [a]	13.0927	0.547 [b]	0.5415	–	1.0600	–	1.8994	–	2.0397	3.347 [a]	3.3952
30	–	10.6983	0.516 [b]	0.5063	1.003	0.9627	1.720 [b]	1.6825	2.300 [b]	2.2266	–	2.9404
40	–	7.4041	0.456 [b]	0.4434	0.834 [b]	0.7968	1.405 [b]	1.3242	1.782 [b]	1.7201		2.2243
50	–	5.3718	0.403 [b]	0.3895	0.702 [b]	0.6632	1.130 [b]	1.0514	1.411 [b]	1.3434	–	1.7033
60	–	4.0633	–	–	0.592 [b]	0.5562	–	0.8454	–	1.0643	–	1.3296

[a] Ref. 17. [b] Ref. 18. [c] Ref. 19. [d] Ref. 20.

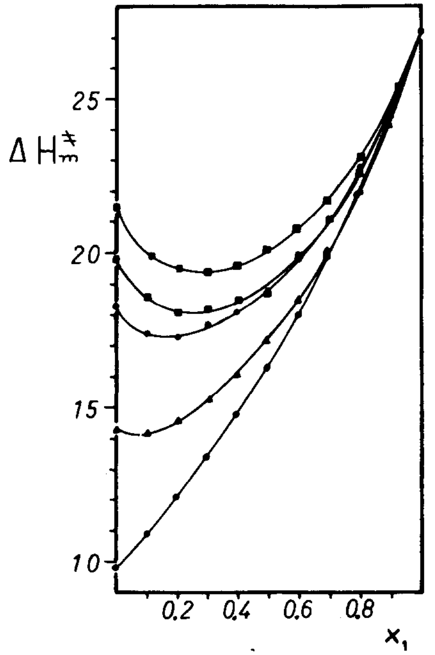

Fig. 2. Plots $\Delta H_m^{\neq}$ vs. X_1 (2-pyrrolidinone mole fraction) for binary mixtures. Symbols as in Fig. 1.

2-pyrrolidinone is 4.0 D, and those of the alcohols range from $\mu = 1.7$ (methanol) to $\mu = 1.64$ D (pentanol), dipole–dipole interactions are very important in these binary mixtures. However, this would result in the values of $\Delta H_m^{\neq}$ being nearly constant for the five mixtures, because the dipole moments of alcohols are very close to each other. Thus, it seems reasonable to suggest that hetero-associations are responsible for the existence of the minima found in $\Delta H_m^{\neq}$ values, as well as for the distinct behaviour observed as the chain length of the alcohols increases. Figure 2 shows the appearance of minima in $\Delta H_m^{\neq}$ versus X_1 plots for all binary mixtures, except 2-pyrrolidinone + methanol.

The equilibrium constant of the activated complexes can be calculated as

$$\Delta G_m^{\neq} = -RT \ln K^{\neq} \tag{6}$$

which is in complete agreement with the results obtained for the excess properties of the same mixtures [16].

EXPERIMENTAL

The pure liquids used were obtained commercially from Merck. 2-Pyrrolidinone and 1-pentanol were purified by vacuum distillation over CaO and the other alkanols were purified by simple distillation over CaH_2. The purity was assessed by GC, the densities and viscosities being compared with those found in the literature (Table 4). Densities were measured with a double-capillary pycnometer calibrated at the five working temperatures, with quantities weighed to within ±0.0001 g. Viscosities were measured with a Cannon–Fenske viscometer calibrated with distilled water at different temperatures, with densities and viscosities taken from the literature [17]. The temperature was kept constant to ±0.01°C with a thermostat, heater and refrigerator. Densities and viscosities were reproducible to ±0.0001 g cm^{-3} and ±0.0004 cp, respectively. Mixtures were prepared by mixing weighed amounts of pure liquids, and care was taken to prevent evaporation.

REFERENCES

1 R. Hopman, Ber. Bunsenges, Phys. Chem., 77 (1973) 52.
2 P. Kedziora, J. Jadzyn and J. Malecki, Wiad. Chem., 29 (1975) 347.
3 J. Jadzyn, J. Malecki and C. Jadzyn, J. Phys. Chem., 82 (1978) 2128.
4 J. Walmsley, J. Jacob and B. Thompson, J. Phys. Chem., 80 (1976) 2745.
5 J. Walmsley, J. Phys. Chem., 82 (1978) 2031.
6 W. Dannhauser, J. Chem. Phys., 48 (1968) 1411.
7 H. Elmgren, J. Chim. Phys., 65 (1968) 206.
8 L.H. Thomas and R. Meatyand, J. Chem. Soc., 1986 (1963).
9 J. Saltiel and P. Sun, J. Phys. Chem., 93 (1989) 6236.
10 J.R. Langan and G.A. Salmon, J. Chem. Eng. Data, 32 (1987) 420.
11 B. García and J.C. Ortega, Thermochim. Acta, 117 (1987) 219.
12 B. García, R. Alcalde and J.M. Leal, unpublished results.
13 A. Albert and E.P. Serjeant, The Determination of Ionization Constants, Chapman and Hall, New York, 1984.
14 H. Eyring, R.E. Powell and W.E. Roseware, Ind. Eng. Chem., 33 (1941) 837.
15 P. Huyskens, J. Mol. Struc., 100 (1983) 403.
16 B. García, C. Herrera and J.M. Leal, J. Chem. Eng. Data, in press.
17 J.A. Riddik, W.B. Bunger and T.K. Sakano, Organic Solvents, Wiley, New York, 1986.
18 Handbook of Chemistry and Physics, CRC Press Inc., Boca Raton, 1987.
19 J. Ortega, J. Chem. Eng. Data, 27 (1982) 312.
20 L. Pikkarainen, J. Chem. Eng. Data, 32 (1987) 429.
21 L. Pikkarainen, J. Chem. Thermodyn., 20 (1988) 481.