Thermochimica Acta, 156 (1989) 129–136
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC AND SPECTROSCOPIC PROPERTIES OF 2-PYRROLIDINONES. 4. EXCESS MOLAR VOLUMES OF 2-PYRROLIDINONE + BENZYL ALCOHOL, + 1,4-DIOXANE, + HEXAMETHYLPHOSPHORTRIAMIDE, AND *N*-METHYLBENZENESULPHONAMIDE + HEXAMETHYLPHOSPHORTRIAMIDE AT 303.15 AND 323.15 K

PÄIVI PIRILÄ-HONKANEN and PIRKKO RUOSTESUO

Department of Chemistry, University of Oulu, SF-90570 Oulu (Finland)

(Received 18 April 1989)

ABSTRACT

Excess molar volumes were determined for 2-pyrrolidinone + benzyl alcohol, + 1,4-dioxane, + hexamethylphosphortriamide, and *N*-methylbenzenesulphonamide + hexamethylphosphortriamide mixtures at 303.15 and 323.15 K. The excess volumes are negative over the whole mole-fraction range for all the mixtures. The results are discussed comparing the volume behaviour of these amides in various solvent mixtures with the IR and NMR spectroscopic results of the studied and related compounds.

INTRODUCTION

2-Pyrrolidinone and *N*-methylbenzenesulphonamide are interesting compounds because of their two competitive interaction centres: basic carbonyl or sulphonyl and acidic NH groups. They are also of great importance as model compounds for pharmacologically interesting compounds.

We have continued a study on the thermodynamic and physical properties of binary liquid mixtures containing amide as one of the components. Excess molar volumes at 303.15 and 323.15 K have been measured previously for 2-pyrrolidinone with acetone, dimethyl sulphoxide, 2-propanol, dichloromethane and water [1] and for *N*-methylbenzenesulphonamide with 1,2-dichloroethane, benzyl alcohol, 2-propanol, dimethyl sulphoxide, 1,4-dioxane and acetone [2]. In addition to these studies, we have measured excess molar volumes for *N*-methylmethanesulphinamide, *N*,*N*-dimethylmethanesulphinamide, *N*,*N*-dimethylbenzenesulphinamide and dimethyl sulphoxide with carbon tetrachloride, 1,4-dioxane and benzyl alcohol [3–5]. The systems were selected with a view to studying the molecular interactions occurring in these binary mixtures.

0040-6031/89/$03.50

EXPERIMENTAL

2-Pyrrolidinone (purum, Fluka AG, Buchs, Switzerland) was purified by distillation above CaO and was preserved over molecular sieves 4A [6]. *N*-Methylbenzenesulphonamide was prepared from benzenesulphonyl chloride and methylamine in anhydrous ether at −10 °C. The amide was purified by distillation and preserved above molecular sieves 4A [7]. 1,4-Dioxane (pro analyse, Merck, Darmstadt, F.R.G.) was refluxed for 12 h with an HCl–water mixture under a nitrogen atmosphere. It was then refluxed twice with sodium, distilled above sodium and preserved above molecular sieves 4A [8]. Benzyl alcohol (puriss. p.a. Fluka AG) was purified by distillation above CaO and preserved over molecular sieves 4A. Hexamethylphosphortriamide (für die Spektroskopie, Merck AG) was purified by distillation and preserved over molecular sieves 4A.

Densities were measured at 303.15 and 323.15 K with a digital density meter DMA 40 (Anton Paar K.G., Granz, Austria) with a reproducibility of within ±0.0001 g cm^{-3}. The density (ρ) of a liquid depends on the square of the period (T) of vibration of the sample tube according to the equation

$$\rho = A(T^2 - B) \tag{1}$$

where A and B are the calibration constants. Distilled water and air were used to obtain the constants.

RESULTS AND DISCUSSION

Experimental densities of the compounds are given in Table 1 with some literature values. Excess molar volumes for the binary mixtures of amide and

TABLE 1

Densities of the pure components at 303.15 and 323.15 K

Compound	ρ (g cm^{-3})			
	$T = 303.15$ K		$T = 323.15$ K	
2-Pyrrolidinone	1.1032	1.1032 [a]	1.0871	1.0875 [a]
N-Methylbenzenesulphonamide	1.2573	1.2569 [b]	1.2419	
1,4-Dioxane	1.0222	1.0221 [c]	0.9998	0.9961 [c]
Benzyl alcohol	1.0376	1.0396 [d]	1.0221	1.0242 [d]
Hexamethylphosphortriamide	1.0157	1.01592 [e]	0.9988	

[a] Ref. 9.
[b] Ref. 10.
[c] Ref. 11.
[d] Ref. 12.
[e] Ref. 13.

TABLE 2

Excess molar volumes (V^E) of amide–solvent mixtures at 303.15 and 323.15 K

Amide	Solvent	x_1	V^E (cm^3 mol^{-1})	
			303.15 K	323.15 K
2-Pyrrolidinone	1,4-Dioxane	0.0000	0.0000	0.0000
		0.0579	−0.0731	−0.0853
		0.1266	−0.1233	−0.1665
		0.1900	−0.1500	−0.2071
		0.2952	−0.1766	−0.2592
		0.3496	−0.1966	−0.2777
		0.3881	−0.2093	−0.2961
		0.4877	−0.2105	−0.2950
		0.5567	−0.2002	−0.2883
		0.6533	−0.1902	−0.2660
		0.7399	−0.1646	−0.2313
		0.8122	−0.1180	−0.1666
		0.8977	−0.0747	−0.0974
		0.9299	−0.0490	−0.0678
		1.0000	0.0000	0.0000
	Benzyl alcohol	0.0000	0.0000	0.0000
		0.0496	−0.0751	−0.0190
		0.1264	−0.1498	−0.1214
		0.1753	−0.2163	−0.1835
		0.2840	−0.2844	−0.2517
		0.3611	−0.3161	−0.2898
		0.4929	−0.3442	−0.3193
		0.5911	−0.2945	−0.2750
		0.6655	−0.2577	−0.2343
		0.7404	−0.2083	−0.1809
		0.8757	−0.0997	−0.0716
		0.9216	−0.0839	−0.0589
		1.0000	0.0000	0.0000
	Hexamethylphosphortriamide	0.0000	0.0000	0.0000
		0.1223	−0.2370	−0.2557
		0.1920	−0.3931	−0.4443
		0.3282	−0.5418	−0.6152
		0.4160	−0.6254	−0.6919
		0.5256	−0.6798	−0.7481
		0.6206	−0.6741	−0.7415
		0.7212	−0.5946	−0.6458
		0.8290	−0.1963	−0.2291
		0.9255	−0.0856	−0.0921
		1.0000	0.0000	0.0000
N-Methylbenzenesulphonamide	Hexamethylphosphortriamide	0.0000	0.0000	0.0000
		0.1125	−0.5284	−0.5722
		0.2090	−0.9066	−0.9846

TABLE 2 (continued)

Amide	Solvent	x_1	V^E (cm^3 mol^{-1})	
			303.15 K	323.15 K
N-Methylbenzene-sulphonamide	Hexamethylphosphortriamide	0.3486	−1.4198	−1.4922
		0.4169	−1.5235	−1.6164
		0.4850	−1.6754	−1.7870
		0.6990	−1.4630	−1.5023
		0.7276	−1.4674	−1.4740
		0.7697	−1.1968	−1.2589
		0.8989	−0.3844	−0.3723
		1.0000	0.0000	0.0000

solvent at 303.15 and 323.15 K are listed in Table 2 and presented graphically in Figs. 1 and 2. The experimental excess molar volumes (V^E) were calculated by using the relation

$$V^E = \left(\frac{x_1 M_1 + x_2 M_2}{\rho_{12}}\right) - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \tag{2}$$

where x_1 and x_2 are the mole fractions of the amide and the solvent

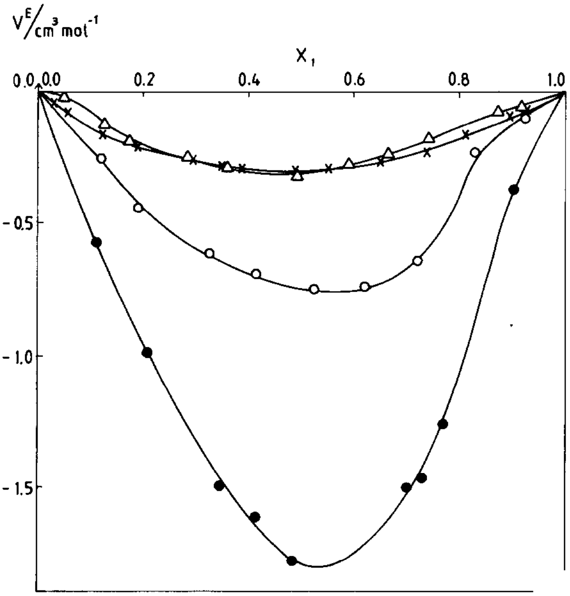

Fig. 1. Excess molar volumes as a function of mole fraction of the first component for the mixtures: (×) 2-pyrrolidinone–1,4-dioxane, (△) 2-pyrrolidinone–benzyl alcohol, (○) 2-pyrrolidinone–hexamethylphosphortriamide and (●) *N*-methylbenzenesulphonamide–hexamethylphosphortriamide at 303.15 K.

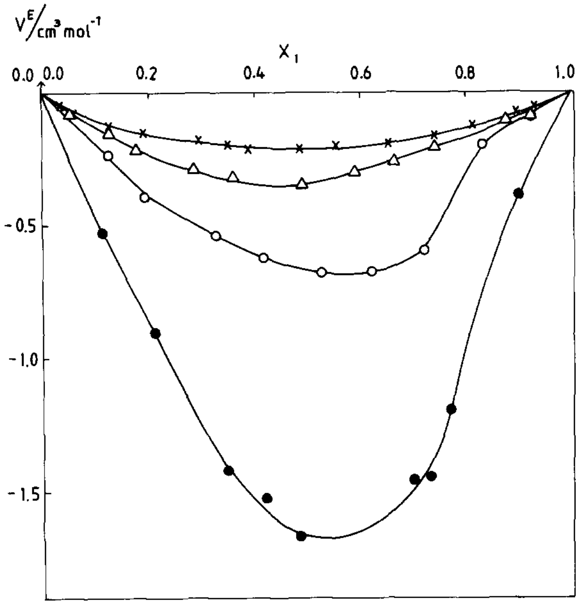

Fig. 2. Excess molar volumes as a function of mole fraction of the first component for the mixtures: (×) 2-pyrrolidinone–1,4-dioxane, (△) 2-pyrrolidinone–benzyl alcohol, (○) 2-pyrrolidinone–hexamethylphosphortriamide and (●) *N*-methylbenzenesulphonamide–hexamethylphosphortriamide at 323.15 K.

respectively. M_1 and M_2 are the molar masses of the components, and ρ_1, ρ_2 and ρ_{12} are the densities of the pure components and the mixture respectively. The excess molar volumes were fitted to the smoothing equation

$$V^E(\mathrm{cm^3\ mol^{-1}}) = x_1(1 - x_1) \sum_{k=0}^{n} A_k(1 - 2x_1)^k \tag{3}$$

where $k = 0, 1, \ldots, n$ and x_1 is the mole fraction of the amide. The parameters A_k were evaluated by the method of the least squares and are given in Table 3 along with the standard deviations. The standard deviation $\sigma(V^E)$ was defined by the equation

$$\sigma(V^E) = \left[\Sigma\left(V^E_{\mathrm{obs}} - V^E_{\mathrm{calc}}\right)^2/(N - M)\right]^{1/2} \tag{4}$$

where N is the number of experimental points and M is the number of parameters.

The V^E data exhibited negative deviation in all the studied systems over the entire mole-fraction range and at both temperatures. Both 2-pyrrolidinone and *N*-methylbenzenesulphonamide have two competitive interaction centres: an acidic NH group and a basic carbonyl or sulphonyl group. The oxygen atom of the carbonyl group or sulphonyl group acts as an electron donor and the NH group as an electron acceptor. Which centre is

TABLE 3

Parameters of eqn. (3) and the standard deviation $\sigma(V^E)$ for amide–solvent mixtures at 303.15 and 323.15 K

Amide	Solvent	T (K)	A_0 cm^3 mol^{-1}	A_1 cm^3 mol^{-1}	A_2 cm^3 mol^{-1}	A_3 cm^3 mol^{-1}	A_4 cm^3 mol^{-1}	A_5 cm^3 mol^{-1}	$\sigma(V^E)$
2-Pyrrolidinone	1,4-Dioxane	303.15	−0.831	+0.002	−0.198	−0.380			0.005
		323.15	−1.189	−0.048	−0.154	−0.369			0.004
	Benzyl alcohol	303.15	−1.338	−0.393	+0.640	+0.169	−0.782		0.008
		323.15	−1.231	−0.134	+0.594	−1.774	+0.037	+2.764	0.007
	Hexamethylphosphortriamide	303.15	−2.710	+1.613	−0.172	−9.381	+3.475	+9.667	0.036
		323.15	−2.978	+1.596	−0.599	−9.931	+4.525	−10.655	0.033
N-Methylbenzenesulphonamide	Hexamethylphosphortriamide	303.15	−6.744	+2.275	+0.385	−4.356	+4.482		0.036
		323.15	−7.047	+1.360	+0.578	+0.608	+4.205	−6.873	0.032

the most active, depends on the composition of the binary mixture. Therefore if lactams and sulphonamides are *N*-unsubstituted or *N*-monosubstituted it is possible that different self-associated species exist in various solution mixtures in addition to competitive interaction species between unlike molecules. Benzyl alcohol also self-associates through hydrogen bonding, and 2-pyrrolidinone as well as *N*-methylbenzenesulphonamide might disturb the alcohol structure and cause the breaking of hydrogen bonds [2].

The results show that the deviation of V^E from ideal behaviour is smallest and of the same order of magnitude for 2-pyrrolidinone–1,4-dioxane and 2-pyrrolidinone–benzyl alcohol systems. 1,4-Dioxane is weakly basic and benzyl alcohol is weakly acidic. The oxygen atoms of 1,4-dioxane act as proton acceptors and the OH proton of benzyl alcohol acts as a proton donor in hydrogen bonding. Therefore, the oxygen atom of 1,4-dioxane can interact with the NH proton of 2-pyrrolidinone and the OH proton of benzyl alcohol with the oxygen atom of the carbonyl group. Both these kinds of interactions are weak and of the same order of magnitude according to IR spectroscopic studies [14,15]. Therefore, the weakly basic 1,4-dioxane and weakly acidic benzyl alcohol to a certain extent disturb the self-association of the 2-pyrrolidinone molecules. The interaction between the unlike molecules is greater, however, as the V^E values are negative for both 2-pyrrolidinone–1,4-dioxane and 2-pyrrolidinone–benzyl alcohol mixtures. According to our NMR spectroscopic results, 1,4-dioxane changes the NMR chemical shift of the oxygen atom of neat 2-pyrrolidinone 6 ppm to higher frequency and that of benzyl alcohol 8 ppm to lower frequency [16]. These results support the above discussion as well as the fact that the V^E values change with temperature in opposite directions in 2-pyrrolidinone–1,4-dioxane and 2-pyrrolidinone–benzyl alcohol mixtures.

Hexamethylphosphortriamide is a dipolar, aprotic solvent with a high dielectric permittivity ($\epsilon^{20} = 30.54$) [17], a high dipole moment ($\mu = 5.39$ D) [17] and excellent solvent properties. It has some interesting biological properties: it is a model compound for the study of certain anti-cancer (cytostatic) drugs and the general mechanism of chemosterilation. The oxygen atom of the PO group of hexamethylphosphortriamide is a very efficient proton acceptor, e.g. toward OH protons such as in alcohols [15]. The proton-donating abilities of NH proton donors are similar to those of OH protons of ordinary alcohols [18]. Therefore the hydrogen bonding of hexamethylphosphortriamide with 2-pyrrolidinone markedly exceeds that of 1,4-dioxane, in agreement with the markedly more negative V^E values for 2-pyrrolidinone–hexamethylphosphortriamide systems compared with 2-pyrrolidinone–1,4-dioxane systems.

The deviation of V^E from ideal behaviour is greatest for *N*-methylbenzenesulphonamide–hexamethylphosphortriamide mixtures. This result reflects the fact that the hydrogen bonding of the NH proton of *N*-methylbenzenesulphonamide with hexamethylphosphortriamide is markedly greater than that of 2-pyrrolidinone. The self-association of NH proton-containing sulphonamides is also clearly greater than that of 2-pyrrolidinone [9,18–21]. Alternatively, it is clear that hexamethylphosphortriamide as a strong electron donor is very effective in breaking the hydrogen bonds between sulphonamide molecules. The results for *N*-methylbenzenesulphonamide–hexamethylphosphortriamide mixtures show, however, that the structure-making effects due to hydrogen bonding or other association possibilities exceed the structure-breaking effects, because the excess volumes are clearly negative for all these binary solution mixtures.

ACKNOWLEDGEMENT

Financial support from the Jenny and Antti Wihuri and the Magnus Ehrnrooth Foundations is gratefully acknowledged.

REFERENCES

1 P. Pirilä-Honkanen and P. Ruostesuo, J. Chem. Eng. Data, 32 (1987) 303.
2 T. Mattila, P. Ruostesuo, V. Rukajärvi, P. Pirilä-Honkanen and S. Kurkisuo, Thermochim. Acta, 132 (1988) 235.
3 P. Ruostesuo and T. Mattila, Thermochim. Acta, 104 (1986) 153.
4 P. Ruostesuo and T. Mattila, J. Chem. Eng. Data, 32 (1987) 241.
5 P. Ruostesuo and S. Kurkisuo, Thermochim. Acta, 109 (1987) 377.
6 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, London, 1966.
7 R.M. Moriarty, J. Org. Chem., 30 (1965) 600.
8 K. Hess and H. Frahm, Ber. Dtsch. Chem. Ges., 71 (1983) 2627.
9 J. Jadzyn, J. Malecki and C. Jadzyn, J. Phys. Chem., 82 (1978) 2128.
10 J.W. Vaughn and P.G. Sears, J. Phys. Chem., 62 (1958) 184.
11 J. Timmermans, Physico-Chemical Constants of Binary Systems in Concentrated Solutions, Interscience, New York, 1960, Vol. IV, pp. 12, 13.
12 M. Rafiqul Islam and S.K. Quadri, Thermochim. Acta, 115 (1987) 335.
13 L. Pikkarainen, Finn. Chem. Lett., (1983) 147.
14 P. Ruostesuo and S. Tolonen, unpublished results, 1980.
15 R. Kuopio, A. Kivinen and J. Murto, Acta Chem. Scand., 30 (1976) 1.
16 P. Ruostesuo, P. Pirilä-Honkanen and L. Heikkinen, J. Phys. Org. Chem., 2 (1989), in press.
17 J.E. Dubois and H. Viellard, J. Chim. Phys., 62 (1965) 699.
18 M.D. Joesten and L.J. Schaad, Hydrogen Bonding, Marcel Dekker, New York, 1974.
19 L. Pikkarainen, Acta Univ. Oul., A98 (1980) Chem. 10.
20 J.A. Walmsley, E.J. Jacob and H.B. Thompson, J. Phys. Chem., 80 (1976) 2745.
21 J.A. Walmsley, J. Phys. Chem., 82 (1978) 2031.