Thermochimica Acta, 39 (1980) 325—328
© Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THERMODYNAMIC STUDIES OF BINARY MIXTURES CONTAINING A SELF-ASSOCIATED COMPONENT: EXCESS VOLUMES OF TETRAHYDROFURAN + AMIDE MIXTURES

S.K. SURI

Chemistry Department, Indian Institute of Technology, New Delhi 110029 (India)

(Received 7 January 1980)

The thermodynamic properties of binary mixtures containing a self-associated component exhibit a significant deviation from ideality, arising not only from differences in molecular size but also from the changes in the hydrogen bonding between like and unlike molecules. In this laboratory we have been interested in the investigations related to the dependence of each thermodynamic property of the mixture of polar and associated liquids on the nature of component molecules [1—3]. The present paper deals with the excess volumes of binary mixtures of tetrahydrofuran with some amides. The amides are capable of forming strong inter- and intramolecular hydrogen bonding. Tetrahydrofuran was chosen for size and polarity considerations.

EXPERIMENTAL

Fisher (A.C.S. Certified) formamide and dimethylformamide, IR and GC analysed methylformamide supplied by Aldrich, and reagent grade methylpropionamide and butylacetamide supplied by Eastman were purified by drying over anhydrous sodium sulphate and fractionally distilling the solvent under reduced pressure immediately before use. The sample of tetrahydrofuran (A.C.S. Certified) supplied by Fisher was purified according to standard procedures [4]. The densities and refractive indices of the solvents were in close agreement with the accepted literature values [4,5].

The molar excess volumes of mixing, V^E, have been calculated from the experimental density data. The solutions for the density measurements were prepared by weight and corrections for buoyancy were applied. Details of the experimental technique for the preparation of solutions have been described previously [6]. The densities were measured with a vibrating flow densimeter (Sodev., Inc.). Water from a thermostat was circulated through the densimeter module at a flow rate of ~2—3 l min^{-1}. The temperature of the thermostat (298.15 K) was maintained at ±0.001 K using a Tronic precision temperature controller. The densimeter was calibrated with nitrogen gas and degassed ion-exchanged water using densities of Kell [7]. Duplicate studies of densities of liquids and liquid mixtures agreed within 1×10^{-5} g cm^{-3}. An analysis of the experimental uncertainties led to the conclusion that the reported excess volumes of mixing were within ±0.008 cm^3 mole^{-1}.

RESULTS AND DISCUSSION

V^E values for the binary mixtures at 298.15 K are recorded in Table 1 and a graphical representation is given in Fig. 1. The data have been fitted to a smoothing equation

$$V^E(\text{cm}^3\ \text{mole}^{-1}) = X_1(1-X_1)\,[A + B(2X_1-1) + C(2X_1-1)^2 + D(2X_1-1)^3] \qquad (1)$$

where X_1 is the mole fraction of tetrahydrofuran. Values of the parameters A, B, C and D and the standard deviation for the excess volumes, $\sigma(V^E)$, are given in Table 2.

All the binary mixtures studied exhibit contraction on mixing over the entire composition range. The large negative excess volumes for binary mixtures containing formamide indicate that the hydrogen bonding between formamide and tetrahydrofuran is slightly stronger than that in the pure formamide. Substitution of an amidic hydrogen with an alkyl group tends to decrease the volumetric effects. This is due to the decrease in acidic character of the amide and also the steric hindrance caused by the alkyl group resulting in a relatively weaker hydrogen bonding with tetrahydrofuran. The excess volumes for formamide and methyl substituted formamide

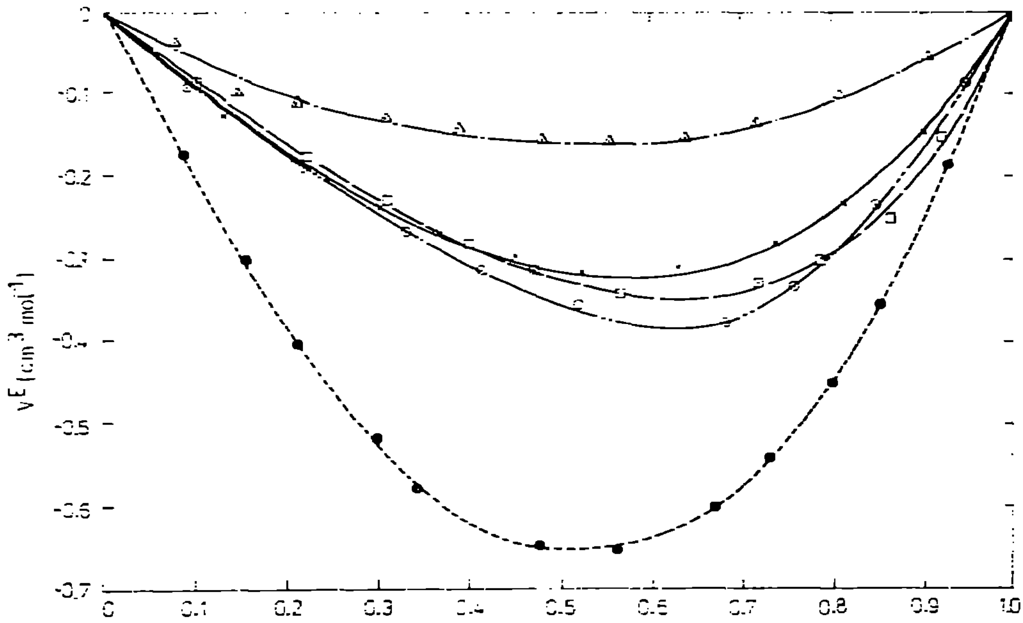

Fig. 1. Molar excess volumes at 298.15 K for the binary mixtures tetrahydrofuran (1) + formamide (2) (●), methylformamide (2) (×), dimethylformamide (2) (△), methylpropionamide (2) (○), butylacetamide (2) (□).

TABLE 1

Excess volumes of mixing, V^E (cm^3 mole^{-1}), for the binary mixtures at 298.15 K

X_1	V^E
Tetrahydrofuran(1) + formamide(2)	
0.0858	−0.175
0.1549	−0.301
0.2103	−0.405
0.2942	−0.521
0.3423	−0.581
0.4764	−0.651
0.5630	−0.656
0.6729	−0.603
0.7324	−0.543
0.8011	−0.448
0.8558	−0.355
0.9307	−0.186
Tetrahydrofuran(1) + methylformamide(2)	
0.1302	−0.128
0.2057	−0.181
0.3008	−0.237
0.3648	−0.268
0.4518	−0.294
0.5250	−0.314
0.6286	−0.307
0.7384	−0.277
0.8115	−0.235
0.9007	−0.146
Tetrahydrofuran(1) + dimethylformamide(2)	
0.0771	−0.038
0.1451	−0.101
0.2123	−0.112
0.3093	−0.131
0.3882	−0.143
0.4823	−0.155
0.5507	−0.155
0.6381	−0.152
0.7193	−0.136
0.8091	−0.101
0.9084	−0.055
Tetrahydrofuran(1) + methylpropionamide(2)	
0.0912	−0.095
0.2177	−0.192
0.3314	−0.266
0.4137	−0.313
0.5239	−0.357
0.6821	−0.376
0.7593	−0.332
0.8500	−0.234
0.9517	−0.085
Tetrahydrofuran(1) + butylacetamide(2)	
0.1023	−0.088
0.2216	−0.176
0.3117	−0.229
0.3974	−0.282
0.4738	−0.312
0.5675	−0.340
0.7211	−0.327
0.7886	−0.301
0.8657	−0.250
0.9187	−0.151

TABLE 2

Parameters of eqn. (1) at 298.15 K and standard deviation, $\sigma(V^E)$, of experimental values

	A	B	C	D	$\sigma(V^E)$ (cm^3 $mole^{-1}$)
Tetrahydrofuran (1) + formamide (2)	−2.6450	−0.235	0.097	−0.286	0.004
Tetrahydrofuran (1) + methylformamide (2)	−1.2249	−0.334	−0.246	0.019	0.002
Tetrahydrofuran (1) + dimethylformamide (2)	−0.6228	−0.073	−0.125	0.189	0.007
Tetrahydrofuran (1) + methylpropionamide (2)	−1.3953	−0.747	−0.255	0.468	0.006
Tetrahydrofuran (1) + butylacetamide (2)	−1.2816	−0.648	−0.393	−0.138	0.007

solutions follow the expected order: formamide < methylformamide < dimethylformamide. The influence of the size of the alkyl group substituted for the amidic hydrogen is insignificant and negligible, as is obvious from a comparison of V^E at equimolar concentrations for butylacetamide solutions, −0.320 cm^3 $mole^{-1}$, and that for methylacetamide solutions, −0.327 cm^3 $mole^{-1}$ (the average of the corresponding values for methylformamide solutions, −0.306 cm^3 $mole^{-1}$, and methyl propionamide solutions, −0.349 cm^3 $mole^{-1}$).

The difference between V^E at equimolar concentrations for methylformamide solutions, −0.306 cm^3 $mole^{-1}$, and for methylpropionamide solutions, −0.349 cm^3 $mole^{-1}$, suggests that the number of carbon atoms in the parent acid influences the amide—tetrahydrofuran interactions. The effect, though small, is significant. Further investigations on such mixtures are underway.

ACKNOWLEDGEMENT

The author wishes to record his gratitude to Prof. R.H. Wood, Chemistry Department, University of Delaware, Newark, DE, 19711 (U.S.A.), for providing laboratory facilities.

REFERENCES

1 S.K. Suri, R.C. Maheshwari and P.L. Yadav, Indian J. Chem., 12 (1974) 620.
2 Y.P. Rao and S.K. Suri, Thermochim. Acta, 36 (1980) 243.
3 Y.P. Rao and S.K. Suri, submitted to J. Chem. Eng. Data.
4 J.A. Riddick and W.B. Bunger (Eds.), Technique of Organic Chemistry, Vol. II, Organic Solvents, Wiley-Interscience, New York, 3rd edn., 1970.
5 J. Timmermans (Ed.), Physicochemical Constants, Elsevier, Amsterdam, 1965.
6 R.C. Maheshwari, S.K. Suri and U.S. Tewari, J. Chem. Eng. Data, 24 (1979) 237.
7 G.S. Kell, J. Chem. Eng. Data, 15 (1970) 119.