

Notes

Excess molar volumes of binary mixed solvents containing tetraethylene glycol and benzene, toluene, acetone and acetonitrile at 308.15 K

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Received 24 July 1995; revised 30 January 1996

Excess molar volumes of binary mixed solvents containing tetraethylene glycol and benzene, toluene, acetone and acetonitrile have been measured as a function of composition at 308.15 K. The measurements have been carried out with a continuous-dilution dilatometer. The excess volumes are all negative over the entire range of composition. The results are discussed in terms of the interaction between components. The Flory model has been used to calculate the excess volumes, and are compared with experimental data for the four mixtures.

In continuation of our earlier works on the thermodynamic properties of amphiphiles in different solvents¹⁻³, we report here experimental excess molar volumes of binary solvent mixtures containing tetraethylene glycol and benzene, toluene, acetone and acetonitrile over the whole mole fraction range at 308.15 K. Interpretation of the results in terms of the theory of Flory^{4,5} is also given.

Experimental

Benzene (SD Fine Chemicals, spectroscopic grade, 99.5%) and toluene (SD Fine Chemicals, AR grade, 99.5%) were purified as described by Rastogi, Nath and Misra⁶. Acetone (SD Fine Chemicals, spectroscopic grade, 99.8%) and tetraethylene glycol (E Merck, FRG, 97%) were first dried over anhydrous calcium chloride for 24 h and then fractionally distilled from phosphorus pentoxide. The glycol was distilled under reduced pressure and the middle fraction was dried over anhydrous sodium sulphate for few days. It was then redistilled and stored over nitrogen. The final sample had a specific conductance less than $3 \times 10^{-6} \text{ S cm}^{-1}$. Acetonitrile (BDH, GR grade, GLC, 98%) was purified by fractional distillation as described elsewhere¹¹. Prior to actual measurements, all liquids were partially degassed under vacuum and dried over 4A molecular sieves to reduce water content. The densities of the purified samples of tetraethylene

glycol, benzene, toluene, acetone and acetonitrile at 308.15 K were found to be 1113.1, 863.0, 853.8, 772.7 and 767.2 kg m^{-3} , respectively which are in good agreement with the literature values⁷⁻¹².

Densities of pure liquids were measured by use of a bicapillary pycnometer having a total volume of about 15 cm^3 . The measurements at $(308.15 \pm 0.01) \text{ K}$ have an estimated reproducibility of 0.3 kg m^{-3} .

The measurements of excess molar volume were carried out in a continuous-dilution dilatometer similar to that described by Dickinsen *et al.*¹³. Calibrations and operational procedures have been described previously^{14,15}. All measurements were made in a thermostatically controlled, well-stirred water bath whose temperature was controlled to $\pm 0.01 \text{ K}$. The measured excess molar volumes were accurate to $\pm 0.003 \text{ cm}^3 \text{ mol}^{-1}$. The composition of each mixture was obtained from the mass of the components with an accuracy of $\pm 1 \times 10^{-4}$. Corrections were made for buoyancy.

Results and discussion

Our experimental results for the excess molar volume V_m^E of the four systems as a function of composition at 308.15 K are graphically shown in Fig. 1. The results for all the mixtures were fitted to a Redlich-Kister type Eq. (1):

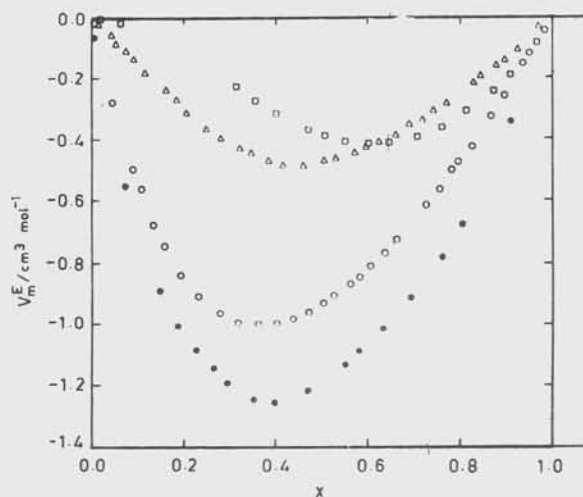


Fig. 1—Excess molar volumes V_m^E for Δ , $[x\text{CH}_2\text{OH}(\text{OC}_2\text{H}_4)_3\text{CH}_2\text{OH} + (1-x)\text{C}_6\text{H}_6]$; \square , $[x\text{CH}_2\text{OH}(\text{OC}_2\text{H}_4)_3\text{CH}_2\text{OH} + (1-x)\text{C}_7\text{H}_8]$; \bullet , $[x\text{CH}_2\text{OH}(\text{OC}_2\text{H}_4)_3\text{CH}_2\text{OH} + (1-x)\text{C}_3\text{H}_6\text{O}]$; \circ , $[x\text{CH}_2\text{OH}(\text{OC}_2\text{H}_4)_3\text{CH}_2\text{OH} + (1-x)\text{C}_2\text{H}_3\text{N}]$ at 308.15 K.

Table 1—Values of the parameters of Eq. (1) with standard deviation of the fit $\sigma(V_m^E)$ at 308.15 K

Mixture	a_1	a_2	a_3	a_4	a_5	a_6	$\sigma(V_m^E)$ ($\text{cm}^3 \text{mol}^{-1}$)
$x\text{CH}_2\text{OH}(\text{OC}_2\text{H}_4)_3\text{CH}_2\text{OH} +$ (1-x) C_6H_6	-1.9278	0.5403	0.6848	-0.9971	-0.3888	0.4936	0.0057
(1-x) C_7H_8	-1.5633	-1.1309	0.6426	0.6349	-0.6897	-1.1336	0.0021
(1-x) $\text{C}_3\text{H}_6\text{O}$	-4.7727	1.9577	-1.2804	-1.7723	-0.9706	3.2658	0.0054
(1-x) $\text{C}_2\text{H}_3\text{N}$	-3.7514	1.8078	-1.0698	0.4211	-	-	0.0058

Table 2—Parameters of the pure components

System	Temp/K	$\alpha \times 10^{+4}$ (K^{-1})	v	v_m ($\text{cm}^3 \text{mol}^{-1}$)	v^* ($\text{cm}^3 \text{mol}^{-3}$)	P^* (cal cm^{-3})	T^* (K)
$\text{CH}_2\text{OH}(\text{OC}_2\text{H}_4)_3\text{CH}_2\text{OH}$	308.15	7.01 ^a	1.1883	174.49 ^a	146.84	172.34 ^c	6552
C_6H_6	308.15	12.50 ^b	1.3049	90.44 ^b	69.32	144.55 ^b	4740
C_7H_8	308.15	10.85 ^b	1.2721	108.04 ^b	84.93	130.49 ^b	5085
$\text{C}_3\text{H}_6\text{O}$	308.15	13.87 ^a	1.3262	53.51 ^a	40.35	234.24 ^c	4550
$\text{C}_2\text{H}_3\text{N}$	308.15	15.14 ^a	1.3531	75.17 ^a	55.55	169.33 ^c	4348

^aValues computed from our measured values of densities.

^bValues obtained from the data tabulated in ref. 16.

^cValues estimated by using the relation given in ref. 17.

Table 3— V_m^E values computed from Flory's theory for various binary mixtures for equimolar compositions

Mixture	Temp/K	T	Flory parameters		$V_m^E/(\text{cm}^3 \text{mol}^{-1})(x=0.5)$	
			χ_{12}	$\theta_2 \times 10^2$	Flory	Exptl.
$[x\text{CH}_2\text{OH}(\text{OC}_2\text{H}_4)_3\text{CH}_2\text{OH} +$ (1-x) C_6H_6	308.15	0.052756	7.61	37.74	-0.484	-0.481
(1-x) C_7H_8	308.15	0.051946	9.18	40.97	-0.313	-0.390
(1-x) $\text{C}_3\text{H}_6\text{O}$	308.15	0.052931	-7.21	29.71	-1.163	-1.193
(1-x) $\text{C}_2\text{H}_3\text{N}$	308.15	0.050556	-33.06	34.34	-0.939	-0.931

$$V_m^E(\text{cm}^3 \text{mol}^{-1}) = x(1-x) \sum_{j=1}^n a_j (2x-1)^{j-1} \quad \dots (1)$$

where x is the mole fraction of tetraethylene glycol. The values of the coefficients, a_j , obtained by the least squares procedure with all points weighted equally are summarized in Table 1 along with the standard error of the estimate $\sigma(V_m^E)$ which is calculated using Eq. (2).

$$\sigma(V_m^E)(\text{cm}^3 \text{mol}^{-1}) = [\sum (V_{\text{expt}}^E - V_{\text{cal}}^E)^2 / (n-p)]^{1/2} \quad \dots (2)$$

where n is the total number of data points and p is the number of coefficients considered.

The study of alkoxyethanols is of interest because of investigating the effect of the simultaneous presence of etheric and alcoholic oxygen atoms in the

same molecule. The presence of the etheric oxygen enhances the ability of the $-\text{OH}$ group to form hydrogen bonds.

For all the mixtures studied V_m^E is negative over the whole mole fraction range and decreases in the sequence acetone > acetonitrile > benzene > toluene. Alkoxyethanols self-associate like alcohols. The hydrogen bond of the self-associated alkoxyethanol can be broken and new hydrogen bonds formed between acetone, acetonitrile, benzene and toluene. The hydrogen bond took place between the π -electron cloud of acetonitrile, benzene and toluene and the carbonyl group of acetone with the $-\text{OH}$ group of glycol. The strength of bonding is higher in acetone than in acetonitrile due to the electron-donating inductive effect of the two alkyl groups in acetone. On the other hand, for toluene which has a methyl group, V_m^E is less negative at lower values of x and were measured only for $0.07 > x > 0.30$ because

of the unfavourable interactions and the difficulty coming from the different miscibilities of the components.

The Flory theory has been very useful in predicting and correlating the thermodynamic properties of binary mixtures of non-polar molecules of different sizes and shapes. Here, even with these limitations, we have applied this approach to some mixtures involving ether molecule which has a moderate polarity. The values of the properties of the pure liquid components (molar volume V_m , thermal expansion coefficient α and characteristic pressure P^* etc.) required in the Flory formalism are presented in Table 2. The key quantity of the theory, the interaction parameters κ_{12} , is usually determined using H_m^E values. For these system, however, values of H_m^E are not available; thus the κ_{12} parameter was adjusted by fitting the experimental V_m^E data over the whole concentration range¹⁸. The resulting κ_{12} was used to calculate V_m^E . These are summarised in Table 3 where κ_{12} , the calculated and observed V_m^E for equimolar mixtures are given. It can be seen from Table 3 that the theory correctly predicts the sign of V_m^E . The calculated values of V_m^E are in excellent agreement with the experimental value.

Acknowledgement

One of the authors (YPS) is thankful to the

university authorities for awarding a University Research Fellowship.

References

- 1 Pal A & Singh W, *Indian J Chem*, 34A (1995) 389.
- 2 Pal A & Singh W, *J chem eng Data*, 40 (1995) 1130.
- 3 Pal A, Sharma H K & Singh W, *Indian J Chem*, 34A (1995) 987.
- 4 Flory P J, *J Am chem Soc*, 87 (1965) 1833.
- 5 Flory P J & Abe A, *J Am chem Soc*, 87 (1965) 1838.
- 6 Rastogi R P, Nath J & Misra R R, *J chem Thermodyn*, 3 (1971) 307.
- 7 Timmermans J, "Physico-chemical constants of pure organic compounds" (Elsevier), 1950.
- 8 Nath J & Tripathi A D, *J chem eng Data*, 28 (1983) 263.
- 9 Aralaguppi M I, Aminabhavi T M, Harogopad S B & Balundgi R H, *J chem eng Data*, 37 (1992) 298.
- 10 Aralaguppi M I, Aminabhavi T M & Balundgi R H, *Fluid phase equilibria*, 71 (1992) 99.
- 11 Riddick J A, Bunger W B & Sakano T K, *Techniques in chemistry*, Vol. II: *Organic solvent*, 4th edn (John Wiley, New York) 1986.
- 12 Pal A, Halder P N & Singh W, *Indian J Chem*, 33A (1994) 154.
- 13 Dickinson E, Hunt D C & McLure I A, *J chem Thermodyn*, 7 (1975) 731.
- 14 Pal A & Singh Y P, *J chem Thermodyn*, 26 (1994) 1063.
- 15 Pal A & Singh Y P, *J chem eng Data*, 40 (1995) 818.
- 16 Nigam R K & Singh P P, *J chem Soc Faraday Trans I*, 65 (1969) 950.
- 17 Jain D V S & Singh Surjit, *Chemical physics Letters*, 20 (1973) 374.
- 18 de Ruiz Halgado M E, de Schaefer C R, Arancibia E L & Katz M, *Fluid phase equilibria*, 95 (1994) 299.