

mortar resulted in desorption of water and the decomposition of this ternary compound into NaCl and solid solution. This indicates that the mechanochemical equilibrium in the open mortar grinder is determined by water exchange between the solids and the atmosphere.

The differences in the products of the two grinding techniques can be explained from the phase diagram. The ball mill is a closed system, and the adequate water partial pressure is maintained. In the open mortar grinder the adsorbed water comes from the atmosphere and its content is considered as the equilibrium water content. During grinding, H₂O partial pressure in the laboratory atmosphere was about 12 mbar. According to water determination and halide content of the mixtures, points II-V are located in the area BCY, where only two phases coexist, the solid solution and NaCl. It appears from the phase diagram that in open systems, due to the low water content of the atmosphere, the double salt is not stable. The solid solution, on the other hand, is stable.

The evaporites were also obtained in an open system, where the solid phase was in an equilibrium with the atmosphere and where water exchange between the solid and the atmosphere took place. Consequently, the double salt which was obtainable when the solid phase was in equilibrium with a saturated aqueous solution (2) was not detected among the evaporites.

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Registry No. NaCl, 7647-14-5; CsCl, 7647-17-8.

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Excess Volumes for the Systems Mesitylene + Dimethylformamide and Mesitylene + Hexamethylphosphortriamide at 298.15 K

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Excess volumes were measured for the systems mesitylene (1) + dimethylformamide (2) and mesitylene (1) + hexamethylphosphortriamide (3) at 298.15 K and atmospheric pressure. The excess volumes were negative for the mesitylene (1) + dimethylformamide (2) system with an excess volume minima at $x_1 = 0.332$. The excess volumes were positive for the mesitylene (1) + hexamethylphosphortriamide (3) system with an excess volume maxima at $x_1 = 0.248$. Data from both systems have been correlated by generalized equations.

This article reports the excess volume measurements for the systems mesitylene + dimethylformamide and mesitylene + hexamethylphosphortriamide at 298.15 K. The correlating equations relating excess volumes as a function of the mesitylene mole fraction are also reported for each system.

The systems were chosen in response to the unusual shape of the mesitylene + acetonitrile excess volume function as determined by Absood (1). The solvents, dimethylformamide and hexamethylphosphortriamide, are similar to acetonitrile in that all three are polar nonhydroxylic solvents.

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Table I. Comparison of Component Densities at 298.15 K

compound	$\rho / (\text{g cm}^{-3})$	
	lit. (4)	this work
dimethylformamide	0.9439	0.9420
hexamethylphosphortriamide	1.0202	1.0179
mesitylene	0.8611	0.8587

Experimental Method

The excess volumes were measured directly by a continuous dilution dilatometer, as described by Kumaran and McGlashan (2). A back-pressure device was used to compensate for pressure differentials within the dilatometer during the dilution run. The temperature of the water bath used to contain the dilatometer was maintained to ± 0.01 K with a Tamson TCV 70 bath and a Neslab Model PBC-2II bath cooler. The bath temperatures were measured with an NBS calibrated thermometer to within 0.05 K. A more detailed discussion of the experimental method has been described elsewhere (3).

The molar volume of each component was calculated via density values measured with a pycnometer. The measured values, along with values reported in the literature (4), are shown in Table I.

The test system benzene + cyclohexane at 298.15 K was studied in an effort to evaluate the accuracy of the experimental

Table II. Excess Molar Volumes for Mesitylene (1) + Dimethylformamide (2) and Mesitylene (1) + Hexamethylphosphortriamide (3)

x_1	$V^E / (\text{cm}^3 \text{mol}^{-1})$	$\delta(V^E) / (\text{cm}^3 \text{mol}^{-1})$	x_1	$V^E / (\text{cm}^3 \text{mol}^{-1})$	$\delta(V^E) / (\text{cm}^3 \text{mol}^{-1})$
Mesitylene (1) + Dimethylformamide (2)					
0.0182	0.0000	0.0009	0.2746	-0.0377	0.0060
0.0521	-0.0073	-0.0014	0.3012	-0.0382	0.0065
0.1009	-0.0202	-0.0037	0.3313	-0.0395	0.0056
0.1343	-0.0297	-0.0056	0.3618	-0.0484	-0.0036
0.1505	-0.0262	0.0013	0.3878	-0.0405	0.0037
0.1872	-0.0320	0.0024	0.3895	-0.0483	-0.0041
0.2095	-0.0400	-0.0023	0.4208	-0.0434	-0.0001
0.2442	-0.0375	0.0041			
Mesitylene (1) + Dimethylformamide (2)					
0.4591	-0.0478	-0.0056	0.7141	-0.0422	-0.0045
0.4946	-0.0477	-0.0063	0.8490	-0.0127	0.0077
0.5364	-0.0426	-0.0017	0.9156	-0.0099	-0.0027
0.6525	-0.0387	0.0013			
Mesitylene (1) + Hexamethylphosphortriamide (3)					
0.0359	0.0141	-0.0042	0.1984	0.0530	-0.0061
0.0534	0.0324	0.0067	0.2349	0.0704	0.0088
0.0692	0.0388	0.0071	0.2640	0.0639	0.0015
0.1325	0.0488	-0.0006			
Mesitylene (1) + Hexamethylphosphortriamide (3)					
0.2840	0.0647	0.0022	0.5749	0.0526	0.0010
0.3204	0.0731	0.0112	0.6039	0.0520	0.0008
0.3323	0.0731	0.0115	0.6092	0.0522	0.0011
0.3756	0.0446	-0.0152	0.6353	0.0555	0.0045
0.4144	0.0531	-0.0048	0.6613	0.0594	0.0085
0.4544	0.0608	0.0050	0.6908	0.0624	0.0115
0.4915	0.0535	-0.0006	0.7221	0.0430	-0.0078
0.5748	0.0533	0.0017			
Mesitylene (1) + Hexamethylphosphortriamide (3)					
0.7563	0.0394	-0.0109	0.9009	0.0321	-0.0041
0.7942	0.0416	-0.0074	0.9323	0.0267	-0.0014
0.8299	0.0290	-0.0176	0.9596	0.0107	-0.0080
0.8651	0.0314	-0.0112			

technique and the equipment used in this investigation. The test system parameters have been extensively documented by Handa and Benson (5). A comparison of the benzene + cyclohexane results obtained during this work with data from Handa and Benson indicates that the equipment and technique used throughout this work are acceptable.

The correlating equation used to relate the excess volume as a function of the mesitylene mole fraction is given by

$$V^E / (\text{cm}^3 \text{mol}^{-1}) = x_1 (1 - x_1) \sum_{k=0}^4 A_k (1 - 2x_1)^k \quad (1)$$

The number of parameters used was determined by sequentially fitting the data with larger numbers of parameters until either the optimum standard deviation was identified or five constants were used.

Results and Discussion

Table II lists the excess molar volumes, V^E , calculated from measurements made with the dilatometer on the system mesitylene (1) + dimethylformamide (2), along with the deviations, $\delta(V^E)$, of the measured values from the values determined by the correlating equation. The parameters, A_k , and the standard deviation, s , for this system are given in Table III.

The resulting excess volume function for the mesitylene (1) + dimethylformamide (2) system at 298.15 K was asymmetric and negative throughout the mesitylene concentration range. The excess volume minima of the correlated data occurred at $x_1 = 0.332$. The value of the excess volume at the minima was $-0.0451 \text{ cm}^3 \text{mol}^{-1}$.

Table II also lists the excess molar volumes, V^E , and the deviation values from the correlating equation for the mesitylene (1) + hexamethylphosphortriamide (3) system. The parameters,

Table III. Constants for Equation 1 for Mesitylene + Dimethylformamide (DMF) and Mesitylene + Hexamethylphosphortriamide (HMPPTA)

constants	mesitylene + DMF	mesitylene + HMPPTA
A_0	-0.1654	0.2152
A_1	-0.0350	0.0793
A_2	-0.2815	0.3399
A_3	-0.0108	0.0679
A_4	0.4843	0.0000
$s / (\text{cm}^3 \text{mol}^{-1})$	0.0042	0.0070

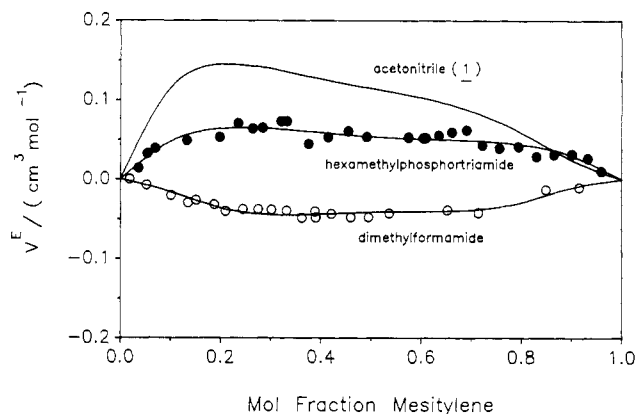


Figure 1. Comparison of excess volume functions.

A_k , and the standard deviation, s , for this system are given in Table III.

The resulting excess volume function for the mesitylene (1) + hexamethylphosphortriamide (3) system at 298.15 K was asymmetric and positive throughout the mesitylene concentration range. The excess volume maxima of the correlated data occurred at $x_1 = 0.248$. The value of the excess volume at the maxima was $0.0653 \text{ cm}^3 \text{mol}^{-1}$.

The molar excess volume function for mesitylene + acetonitrile at 303.15 K has been determined previously (1). These data, along with the data from the systems investigated in this work, have been plotted in Figure 1 for comparison purposes. It was assumed that the 5 K temperature differential between the mesitylene + acetonitrile system and the systems investigated during this work was insignificant for qualitative comparison. As indicated, the systems mesitylene + acetonitrile and mesitylene + hexamethylphosphortriamide exhibit similar shapes at low mesitylene concentrations. This infers that this region of the excess volume functions for these two systems is controlled by the mesitylene.

Glossary

A_k	curve-fitting parameter
V^E	excess volume
$\delta(V^E)$	deviation of measured excess volume from correlation
x_1	mesitylene mole fraction

Registry No. $\text{Me}_2\text{NC(O)H}$, 68-12-2; hexamethylphosphortriamide, 680-31-9; mesitylene, 108-67-8.

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